Book of abstracts

Plenary talks

P 01

Radiocarbon Dating of Historic Sites in the Age of Single-year Calibration

Bayliss A1, Marshall P1

¹Historic England, London, United Kingdom

IntCal20 marks the start of the next era of radiocarbon dating, as high-precision single-year calibration is extended across the radiocarbon timescale. Increasingly precise ¹⁴C measurements on single-entity samples produced by Accelerator Mass Spectrometry, combined with archaeological and historical prior information using Bayesian chronological modelling, means that this new high-resolution calibration can be used to construct accurate chronologies that are precise to within a decade or two for many kinds of sites.

Producing such chronologies demands much of laboratory accuracy, and much of the kinds of samples and prior information provided by archaeologists. We are at the start of a journey to discover how such chronologies can be produced in practice. What kinds of quality assurance data do laboratories need to provide to ensure the necessary measurement accuracy? What kinds of samples should archaeologists submit for dating, and how do they construct the sampling strategies needed to make the most of the opportunities provided by single-year calibration? What kinds of sites and problems will produce substantively more precise and reliable chronologies using single-year calibration, and what kinds of sites will not? How do we weave those sites that do not into our wider narratives?

This paper provides some initial thoughts on these issues illustrated by a range of recent case studies.

P_02

Radiocarbon calibration: from bane to blessing

Bronk Ramsey C1

¹University Of Oxford, United Kingdom

Temporal and spatial variation in radiocarbon in the atmosphere has been the subject of investigation from the first pioneering work of Libby and Arnold in the middle of last century. However, as the precision of measurements has improved, now by almost two orders of magnitude, what constitutes a significant variation has also changed. Furthermore, through the development of other dating techniques applied to global records, it is possible to test degrees of variation over much longer timescales and with ever wider geographic coverage. As knowledge has improved, the interpretation of radiocarbon measurements has had to be revised, often very significantly as with the first comprehensive calibration curves. These re-evaluations, and the loss of chronological precision that comes with accurate calibration, have often been seen as an unfortunate drawback in the radiocarbon dating method. However, 'necessity is the mother of invention' and these problems have stimulated extensive research in global radiocarbon records, in statistical methods for dealing with complex radiocarbon data, and in measurement methods. This research has both provided a wealth of information useful for other scientific challenges, most notably the quantification of the global carbon

cycle, but also enabled, in the right circumstances, measurement precision an order of magnitude better than if there had been no variation in atmospheric radiocarbon. Challenges remain in many areas but, taking a long perspective, the research undertaken for radiocarbon calibration has, through its ingenuity and innovation, provided rich scientific dividends in both chronology and broader geoscience.

P 03

Dating the spread of modern humans and the extiction of archaic hominins in Eurasia

Conard N¹

¹University of Tuebingen, Tübingen, Germany

By 300 ka BP anatomically modern humans evolved in Africa. This is also the time when early Neanderthals and, although the record is less well documented, early Denisovans evolved in Eurasia. Starting after 50 ka BP modern humans spread rapidly across Eurasia, and by 40 ka BP had marginalized and displaced many populations of archaic humans. Interbreeding between modern humans and both Neanderthals and Denisovans is well documented on the basis of studies of aDNA from from human fossils. At the same time the archaeological record shows a rich record of cultural innovations in both practical technologies and symbolic artifacts including personal ornaments, figurative art and musical instruments. This paper eximines the temporal patterns of these developments and addresses some of the challenges of obtaining high temporal resolution in reconstructing the extinction of Neanderthals and Denisovans and the spread of modern humans in a period near the limit of reliable radiocarbon dating.

P 04

Estimating the age of carbon respired from terrestrial ecosystems using radiocarbon

<u>Trumbore S</u>¹, Sierra C¹, Hilman B¹, Hoyt A^{1,2}

¹Max Planck Society, Jena, Germany, ²Stanford University, Stanford, USA

Tracing radiocarbon through land ecosystems provides important information on the timescales of land C cycling. The global 'bomb' radiocarbon tracer is particularly important for studying C sequestration and loss processes that can be altered by land management or climate change.

While many studies use radiocarbon to estimate the age of stored C, this talk will focus on estimating the age of carbon respired from ecosystems - the transit time of ecosystem carbon. In particular it will focus on the transit time distributions in different ecosystems with examples of CO_2 respired by plants and soils. The age of carbon respired from plants mixes very recently fixed photosynthetic products with C fixed years up to decades previously, depending on the ecosystem and the status of plant C balance. The age of C respired from soils is mostly younger than the C age of bulk soil organic matter, and reflects the age of 'labile' or microbially accessible C fractions. However, the age of respired C increases with soil depth, reinforcing the fact that C age is not a direct measure of decomposability. Globally extrapolated transit times will provide an important constraint for C cycle models predicting dynamics into the next century. Data used in this presentation are from ISRaD, the international soil radiocarbon data base (www.soilradiocarbon.com), that is a community effort to provide an open platform for the ever-increasing data on radiocarbon in soils. As the global capacity to measure radiocarbon increases, how we manage data has become a major challenge.

(R)evolutionary developments towards high precision radiocarbon analyses

Synal H1

¹ETH Zurich, Zurich, Switzerland

Since the discovery of accelerator mass spectrometry (AMS) measurement procedures have undergone a continuous evolution. Modern AMS instruments are still following design concepts of the pioneering experiments, but they do not have much in common with huge accelerator infrastructures. AMS is based on fundamental principles which made suppression of nuclear and molecular isobaric interferences possible. Violent charge exchange processes are exploited to remove binding electrons of light molecular ions to reach charge states of 3+ or higher where no molecular bound states exist. This elegant procedure was taken for granted as the "golden rule". Instability of molecular ions in charge states lower than 3+ had been realized early, but the potential to simplify AMS technology had not been realized. Measurement of the molecule dissociation cross sections made substantial improvements of AMS instrumentation possible. Groundbreaking progress was made by introducing vacuum insulated accelerations stages feed by solid state power supplies. To utilize the unique properties of helium as stripping gas some technical obstacles were solved and by introducing fixed field magnets for the momentum selecting filter stages, power consumption was minimized. With these improvements stateof-the-art AMS instruments are comparable in size and complexity to high end traditional mass spectrometers. Due to their compact layout and based on optimized ion optical designs they are capable to measure carbon isotopic ratios with sup permille precision. Thus, quality of radiocarbon analyses is more and more no longer limited by the instrumental capabilities but rather by the quality and reproducibility of the sample preparation procedures.

A01 Agriculture, migration, DNA

A01_01

Dating the Earliest Evidence of Farming and Animal Husbandry in the Dutch Wetlands

<u>Dreshaj M</u>¹, Raemaekers D¹, Peeters H¹, Dee M¹ ¹University Of Groningen, Groningen, Netherlands

The beginning of farming and animal husbandry in the Dutch wetlands has long been debated due to ambiguity in the domestication status of local species (Sus and Bos), a shortage of reliable chronologies for keystone sites, and a 300-year calibration plateau which spans the timeframe in which these developments likely occurred. As a result, the Netherlands remains a noticeably blank spot on the Neolithization map of northwestern Europe. In response, our team has conducted an extensive interdisciplinary project on the key sites, combining paleogenomics, stable isotope studies, zooarchaeology, and radiocarbon dating coupled with Bayesian modelling. Here, we report the results of a chronological study on the Swifterbant S3 and S4 sites, which contain the oldest known evidence of cereal cultivation and animal husbandry in the Dutch wetlands. Our findings draw upon the results of new paleodietary research, revealing the earliest dietary management of Sus and Bos, as well as ancient DNA confirming the presence of domestic haplotypes in cattle. To overcome the calibration plateau, we radiocarbon dated sequences of charred naked barley seeds from occupation layers across the sites and employed intricate Bayesian modelling. Our outputs significantly narrow down the temporal span achievable by individual dates and demonstrate that S3 and S4 were occupied for a remarkably short

period of time. Our results indicate that farming and animal husbandry began before 4000 BCE in the Dutch wetlands, predating similar patterns in Scandinavia and the British Isles, and represent an important contribution to the debate on this transition in northwestern Europe.

A01 02

Early Maize in Eastern North America: Results from Spatial Modeling of Directly Dated Maize Macrobotanical Remains

Druggan P1

¹Pennsylvania State University, University Park, United States

Maize agriculture was ubiquitous in the Eastern Woodlands of North American at contact; however, the nature of its dispersal from Mesoamerica is unclear. Previously reported accelerator mass spectrometry radiocarbon dates at a number of sites suggested that maize was introduced approximately 2000 years ago or earlier. Understandings of maize histories in North America have recently been challenged through reanalysis of curated macrobotanical remains, demonstrating that each example of early maize was either much younger than originally reported or the samples were not maize based upon $\delta^{13}C$ values inconsistent with maize. Paradoxically, while the macrobotanical record has been revised to suggest a later introduction of maize, analysis of pot sherd residues has indicated the presence of maize by 300 BC. These studies underscore the necessity of critically reevaluating our understanding of maize dispersal and the validity of legacy dates. I build upon this work by assembling a database of directly dated maize macrobotanical remains and performing regression analyses to estimate earliest maize arrival, utilizing Monte Carlo methods to incorporate chronometric uncertainty. Results support a later introduction of maize, and comparison to a database of human stable isotopic data support rapid adoption.

A01 03

Combined radiocarbon dating and stable isotope analyses on Neolithic cereal finds identifies turning points in crop dynamics (ca. 6000-3000 BC)

<u>Antolin F</u>¹, Martínez-Grau H², Soteras R¹, Guidobaldi G³, Jaggi M³, Wyss K³, Bernasconi S³, Hajdas I³ ¹German Archaeological Institute, Natural Sciences Unit, Berlin, Germany, ²IPNA, University of Basel, , Switzerland, ³ETH Zurich, , Switzerland

The SNF-Funded AgriChange project (www.agrichange.duw.unibas.ch) intends to reconstruct agricultural decision-making processes among early farmers. The identification of moments of agricultural changes and their correlation with environmental proxies was therefore a priority for the project. For this reason, a large number of radiocarbon dates (to date, ca. 250) and stable isotope analyses (ca. 1500) were obtained, thanks to the collaboration of several archaeologists and archaeobotanists with the project. Charred cereal grains of mostly barley, naked wheat, einkorn and emmer where used. The results indicate two important moments of change around 5300 BC and around 4000 BC/3700 BC. Carbon stable isotope analyses have been used to reconstruct water availability during crop growth (as an indicator of spring precipitation) and the relationship between crop changes and carbon stable isotope ratios have been explored at a regional level. Our results indicate that scarce water availability was sometimes a limiting factor affecting crop choice in the NW Mediterranean area, while excessive precipitation might have influenced crop choice in the Alpine Foreland ca. 3600 BC. Other changes (at ca. 4000 BC) observed in the Mediterranean Area and Southern Alps do not seem to have clear correlation with carbon stable isotope values and other factors (i.e. crop pests and cultural contacts) are argued.

Radiocarbon dating of human remains of first farming societies in the Western Alps. Tracking the evolution of Neolithic funerary customs.

Steuri N¹, Milella M², Lösch S², Szidat S^{3,4}, Hafner A^{1,4}

Neolithic cist graves – known in the Western Alpine region as Chamblandes type – are usually composed by four lateral stone slabs or more rarely wooden planks, and can contain single, as well as collective burials. Due to the lack of distinctive grave goods, insights about the chronology and evolution of these funerary custom depend on extensive series of precise radiocarbon dates. In the context of our research project, we radiocarbon dated the skeletal remains of 124 individuals from 15 sites, located in western Switzerland, eastern France, and northern Italy. Our data allow doubling the number of modern radiocarbon data available for this burial type. Results suggest an almost contemporaneous emergence of the use of cist burials in the 48th century BCE on the southern shore of Lake Geneva and several Inner-Alpine valleys. The adoption of cist graves seems to spread after 4500 BCE, to be then abandoned around 4000/3800 BCE.

By incorporating different burial features (e.g., treatment of human remains related to burial processes or used grave construction material) into this established chronology, we propose two distinct funerary customs within Western Alpine cist graves: first, alongside the northern Alpine foothills and, second, in the inner-Alpine valleys. In conclusion, our study provides new evidence about the evolution of Neolithic burial practices and intra-Alpine exchange networks based on a large series of radiocarbon dates.

A01 05

A Regional-Scale Bayesian Reevaluation of Radiocarbon Data from Early Formative Mesoamerica

Mejía Ramón A¹

¹Okinawa Institute Of Science And Technology, Onna-son, Japan

Early Formative Mesoamerica was witness to some of the most important transformations during the transition from hunter-gatherers to agricultural societies. Recently studies employing high-resolution AMS dating and Bayesian modeling have challenged long-held notions about the maize's synchronous appearance alongside sedentism and ceramics. Much less recent attention has been given to the settlement and ceramic chronologies themselves. This is unfortunate, since archaeologists largely rely on typologies dated decades ago before the widespread use of high-resolution AMS dating and Bayesian modeling. In this paper, I discuss a Bayesian re-analysis of 713+ published dates from 120+ sites (as of submission) spanning Panama through West Mexico, finding significant issues with the currently accepted narrative for the adoption of ceramics and transition to agriculture. I create cross-referenced stratigraphic models for every dated Early Formative site with published excavation information, nesting those within trapezium models for cultural phases unconstrained by a sequential assumption---in other words phases are allowed to overlap and are allowed to have a gap between them. I find that archaeologists have consistently discarded the earliest identified dates not for reasons of 'chronometric hygiene' but because they antecede the expected arrival of ceramics by hundreds of years despite a clear regional trend from at least the third millennium calBC. Furthermore, there is little evidence to support the hypothesis that Barra ceramics were necessarily the first ceramics in Mesoamerica or that they existed by themselves within the Soconusco. I suggest a moiety-like form of social organization expanding from Lower Central America to explain the observed record.

¹Department of Prehistoric Archaeology, Institute of Archaeological Sciences, University of Bern, Bern, Switzerland,

²Department of Physical Anthropology, Institute of Forensic Medicine, University of Bern, Bern, Switzerland,

³Department of Chemistry, Biochemistry and Pharmaceutical Sciences, University of Bern, Bern, Switzerland,

⁴Oeschger Centre for Climate Change Research (OCCR), University of Bern, Bern, Switzerland

North American Pleistocene Fiber, Hide, and Wood Technologies from the Paisley and Cougar Mountain Caves, Oregon, USA

Rosencrance R¹, Kallenbach E², Connolly T², Jazwa C¹, Jenkins D², McDonough K², Smith G¹, <u>Culleton B</u>³, Davis M³

¹University of Nevada, Reno, Reno, United States, ²University of Oregon, Eugene, United States, ³Penn State University, State College, United states

Archaeologists consider the development of structurally and functionally complex organic technologies during the Pleistocene as one of the catalysts that allowed Homo sapiens to disperse into new areas of the globe. The earliest people to settle in the Americas undoubtedly used fiber, wood, and hide-based tools, but preservation skews current discourse toward stone and bone technologies, limiting our understanding of early lifeways. In this paper, we present radiocarbon dates and technological analyses of nearly 40 organic artifacts from the Paisley and Cougar Mountain Caves in Oregon's (USA) northern Great Basin region. All specimens are directly dated to the late Pleistocene and constitute the majority of directly dated non-osseous organic tools of this age in the Americas. The fiber assemblage is dominated by 3-strand braided cordage and variously gauged rope, but also includes a basket weft, twined mat, and raw material bundle. Other directly dated items include wooden tools, hide strips, and a piece of hide stitched with fiber cordage. The raw materials and some of the construction techniques of these items continue to be used by local Indigenous peoples today, reaffirming the deep ties to their homelands. Though the materials from the Paisley and Cougar Mountain caves do not represent the earliest development of complex organic technologies such as sewn hide and fiber cordage, they are some of the oldest directly dated examples of such tools from the Western Hemisphere and thus offer new perspectives on Pleistocene lifeways.

A01 07

Dating the emergence and development of nomadism in the Altai

Svyatko S1, Reimer P1, Papin D2, Seregin N3

¹14CHRONO Centre for Climate, the Environment and Chronology, Belfast, United Kingdom, ²Institute of Archaeology and Ethnography, Siberian Branch of the Russian Academy of Sciences, Novosibirsk, Russia, ³Altai State University, Barnaul, Russia

We present the preliminary results of the first systematic investigation into the absolute chronology of the Early Iron Age in the Altai region, southern Siberia, specifically targeting the emergence and dynamics of local nomadism and its place in the Eurasian Steppe context, using AMS radiocarbon dating and multi stable isotope analysis. Altai, located at the ancient crossroads between Central and North Asia, was the principal region through which prehistoric Eurasian steppe populations and cultures passed into China. Being the center of intensive cultural genesis and development, this relatively small and isolated region strongly influenced the lifestyle of many societies. However, no reliable chronologies have ever been developed even for the key periods and sites. We present the ¹⁴C dates for the signature nomadic sites, as well as sites representing the transitional periods in the area – boundaries between the LBA and EIA, and EIA and the Medieval period – which is especially important for assessing the issues of cultural genesis in the region. The new series of dates provides the first approach to a generalized broad picture of the development of nomadism in Altai, allowing more accurate interpretations on the emergence and development of different cultures and economies in various geographical zones (steppe, forest-steppe, mountains), as well as verifying the general sequence of the cultures.

A Multi-scalar Approach to Mobility: interpreting sulfur isotope values within relative and radiocarbon dating frameworks

Hamilton D¹, Sayle K¹, Steinke K²

In the past 10 years sulfur isotope analysis has become increasingly employed to investigate the movement and mobility of pre-historic people and animals. While the questions can focus on the same type of 'one-off' movements often considered when using strontium and oxygen analyses to study human migrations or pastoral economies, the combination of sulfur analyses with different sampling approaches can yield novel insights into past movement of individuals and populations.

This paper aims to present some of the ways archaeologists can incorporate sulfur isotope analysis with radiocarbon chronologies, the relative dating associated with sampling skeletal elements that represent different times in an individual's life, and even sequential sampling within an individual skeletal element. These approaches will be illustrated using data from both human and animal populations from Middle Iron Age (~400–200 cal BC) sites in southern Britain.

A01 09

Where are the dead? Prehistoric and historic funerary and population dynamics in Belgium, the impact of radiocarbon dating cremated bones

<u>Capuzzo G</u>¹, De Mulder G², Sabaux C^{2,3,1}, Dalle S^{2,3}, Boudin M⁴, Annaert R⁵, Hlad M^{3,1}, Salesse K⁶, Sengeløv A^{1,2}, Stamataki E^{3,1}, Veselka B³, Warmenbol E¹, Vercauteren M¹, Snoeck C³

¹Université Libre De Bruxelles, Brussels, Belgium, ²Ghent University, Ghent, Belgium, ³Vrije Universiteit Brussel, Brussels, Belgium, ⁴Royal Institute for Cultural Heritage, Belgium, ⁵Flemish Heritage Agency, Brussels, Belgium, ⁶Masaryk University, Brno, Czech Republic

The radiocarbon dating lab at the Royal Institute for Cultural Heritage (KIK-IRPA) in Brussels, Belgium, has a long tradition in radiocarbon dating cremated bones since 2003, after it was demonstrated that calcined bone can be dated by using the carbon in the bioapatite of bone (Lanting et al. 2001). This discovery has led to an exponential increase in the amount of ¹⁴C dates associated with cremation burials. Additionally, in the last four years, 500 new samples of calcined bone have been dated at KIK-IRPA within the EOS-funded CRUMBEL project (Snoeck et al. 2019), which studies the collections of cremated bone found in Belgium dating from the Neolithic to the Early Medieval period using state of the art analytical and geochemical analyses. The aim of this presentation is to explore the outcomes of this large dating campaign - a unique case in the European panorama - to shed light on continuities and discontinuities in past funerary practices and population dynamics in Belgium. This has been possible by statistically modelling ¹⁴C dates from settlements and funerary contexts (both cremation deposits and inhumation burials) between Late Neolithic and Early Middle Ages. Results highlight a major episode of population decline in the Final Neolithic-Bronze Age transition in correspondence with the 4.2 ka cal BP climatic event and a repopulation of Belgium in the Middle Bronze Age from 1800 BC. A remarkable increase in the number of cremation deposits is observed in the 1st century AD as a consequence of the romanization of the area.

 $^{^1}$ University of Glasgow, East Kilbride, United Kingdom, 2 University of Edinburgh, Edinburgh, United Kingdom

Migrations and Cultural Evolution in the Light of Radiocarbon Dating of Bronze Age Sites in the Southern Urals

Epimakhov A¹, Zazovskaya E²

¹South Ural State University, Chelyabinsk, Russian Federation, ²Institute of Geography, Russian Academy of Sciences, Moscow, Russian Federation

The Southern Urals in the Bronze Age was the center of the formation of Andronovo family of cultures, as well as a zone of interaction of different traditions (Srubnaya, Seima-Turbino, etc.) Paleogenetic data confirm the heterogeneity of the population and diagnose two waves of migrations in the 3rd and early 2nd millennium BCE. These waves alternate with periods of stabilization and evolutionary change. The migration events are well provided with radiocarbon dating, but the periods of stability have turned out to be almost completely out of the focus of the interests of specialists in recent decades. 14C dates obtained in the 1970s - early 2000s are contradictory and insufficient for the reconstruction of processes. More than 30 samples were produced at the Institute of Geography RAS. Graphitization and pressing of the target for ¹⁴C AMS were conducted with the automated graphitization system AGE 3. ¹⁴C AMS measurement was performed at the Center for Applied Isotope Studies, University of Georgia (Athens, USA) using the CAIS 0.5 MeV accelerator mass spectrometer. Eight sites and seven cultural traditions have been dated. The new results were compared with dates obtained earlier. This allows us to solve problems of various scales: clarify the chronological position of some important complexes and objects; form (or significantly correct) the intervals of existence of a number of cultural traditions: improve the discussion of forms of their interaction; to simulate the duration of the functioning of sites and phases for some of them.

A01 P02

Secrets of the iron. A Case-study of iron-objects from Nowe Brzesko (Lesser Poland) deposit.

Bulas J¹, **Huels M**², Michał Kasiński M³, Okońska-Bulas M^{1,3}

¹Arch Foundation, Krakow, Poland, ²Leibniz-Laboratory for Radiometric Dating and Isotope Research, Kiel, Germany, ³Institute of Archaeology, Jagiellonian University, Krakow, Poland

A rarely found iron tool group deposit was recently discovered at what needs to be considered a multicultural and multiphase site of Nowe Brzesko (Lesser Poland) along the Vistula River. In the past the site was occupied by different populations, oldest traces discovered date back to the Neolithic (approx. 6 - 2 thousand yrs BC). More numerous finds originate from the La Tène and Roman periods (e.g., Celts and representatives of the Przeworsk culture), as well as from the Middle Ages.

A group of several dozen metal objects were found on the surface within 1.5 m² at the topsoil. The artefacts discovered consists mainly of agricultural tools and were preserved in whole or in fragments. Lacking additional contextual and chronological evidence and having unspecific features, their chronology was initially assigned broadly from the Roman Iron Age to the late Middle Ages. Radiocarbon measurements were conducted on four selected iron objects and allowed to relate the findings to the Late Roman period (i.e., 3rd – 4th century AD). Metallographic analyses on the metal objects were also carried out, indicating comparable production processes (i.e., the bloomary process), but may also indicate differences with respect to source material.

This study, one of the first examples of direct radiocarbon dating of Przeworsk culture iron objects, may open new research perspectives related to the economy of iron production within the late Przeworsk with respect to resources.

Contextualizing the presence of Late Bronze Age Millet at the Arnbjerg site - Investigating settlement dynamics in Jutland, Denmark

Kanstrup M¹, Sørensen C², Olsen J¹

¹Aarhus University, Aarhus C, Denmark, ²Viborg Museum, Viborg, Denmark

Situated near Viborg, just south of Lake Søndersø, large-scale archaeological excavations at Arnbjerg N revealed a great amount of Settlement evidence. A priority within the project was to Radiocarbon date a wide range of samples in order to investigate the duration of the different settlement features and the dynamics of the site compared with the Settlement History in the same region using Bayesian modelling. In total more than 220 samples were dated, giving ages mainly ranging from The Late Neolithic to the Early Iron Age with a relatively large concentration of dates situated on the Hallstatt Plateau. The overall distribution of the dates demonstrates site continuity with a few interesting exceptions. Here we focus on the settlement recovery and consolidation phase following a clear hiatus from 1200-800 BCE. This Hallstatt settlement phase is particular since we here see clear evidence of Late Bronze Age Millet farming in the archaeobotanical assemblages. Millet is not a common crop found to be cultivated in Denmark. The spread of millet to Northern Europe tend to give rise to considerations about linkages to pan-continental communicative networks, and the exchange of both goods, social mobility, and technology. Besides the obvious new and more exotic agrarian trait, the archaeology in the Hallstatt phase of Arnbjerg also reveal new features in the architectural lay out of the longhouses. Combined the different sources of evidence points out differences in the development in the Settlement structure compared to earlier phases.

A01_P04

Development of a new method to extract and date of carbonized material in pottery

<u>Kunikita D</u>¹, Obata H², Miyaji S³, Omori T⁴, Ozaki H⁴, Yoneda M⁴

¹Hokkaido University, Hokkaido, Japan, ²Kumamoto Unibersity, Kumamoto, Japan, ³Kyushu Historical Museum, Fukuoka, Japan, ⁴The University of Tokyo, Tokyo, Japan

The timing of the introduction of grains such as rice, foxtail and broomcorn millets originating from mainland China into the surrounding areas is an important issue in discussing agriculture throughout East Asia. However, data on carbonized grains are extremely rare in Japan at the beginning of early agriculture, there remains uncertainty in whether the grains coincided with the accompanying pottery type.

We proposed a new method that uses X-ray equipment to search for carbonized grains embedded within earthenware and directly date these grins in order to solve this problem. We applied this method to a key site, the Etsuji site, Kyushu Island, to examine the introduction of rice and millet agriculture to Japan (Obata and Kunikita, 2022).

In this presentation, we compare the ages of the newly obtained pottery-embedded carbonized materials at the Higashihataze site with the ages of the pottery-adhered carbonized materials. In the Japanese archipelago, marine organisms often affect the contents of boiled foods, and the age may be older than the actual age. This method could make a significant contribution to the study on the pottery typologies and the age of carbonized grains without being affected by the marine reservoir effect.

Obata, H., Kunikita, D., 2022. A new archaeological method to reveal the arrival of cereal farming: Development of a new method to extract and date of carbonized material in pottery and its application to Japanese archaeological context. Journal of Archaeological Science 143.

New evidence for early human activity in Shigatse, Southern Tibetan Plateau during Late MIS3 epoch.

<u>Li W</u> 1,2,4 , Zhou W 1,2,3 , Cheng P 1,2 , Shu P 1,2 , Du H 1,2

¹1 State Key Laboratory of Loess and Quaternary Geology, Institute of Earth Environment, Chinese Academy of Sciences, Xi'an, China, ²Shaanxi Key Laboratory of Accelerator Mass Spectrometry Technology and Application, Xi'an AMS Center of IEECAS and Xi'an Jiaotong University, Xi'an, China, ³CAS Center for Excellence in Quaternary Science and Global Change, Xi'an, China, ⁴ University of Chinese Academy of Sciences, Beijing, China

New evidence for early human activity in Shigatse, Southern Tibetan Plateau during Late MIS3 epoch

Tibetan Plateau (TP) is a hotspot for early human history research. However, there is limited evidence of prehistoric human activity on southern TP, and the validity of these dates requires additional investigation. Here, we present 21 AMS ¹⁴C dating results of bones collagen and charcoal remains from a newly discovered lithic site (including paleolithic and microlithic) in Shigatse, Yarlung Zangbo River Valley basin, southern TP. The dating results for collagen and charcoals show strong conformity. These two Our extensive chronological data reveal that people occupied in the Yarlung Tsangpo River basin from 960 to 680 cal yr B.P, 2730 to 2370 cal yr B.P, and 29110 to 23090 cal yr B.P. To the best of our knowledge, our new finds provide the first evidence for early human activity in the Southern TP during Late MIS3 epoch.

A01 P06

A Multidisciplinary approach to the comprehension of the peopling of Portus Romae Antemurale area

Rossi P^3 , De Angelis F^2 , Rickards O^2 , Di Cicco M^1 , Mantile N^1 , Altieri S^1 , Vetromile C^1 , Spagnuolo A^1 , Cocozza C^1 , Vaccaro S^3 , <u>Lubritto C^1 </u>

¹Università della Campania "Luigi Vanvitelli" - Dipartimento DiSTABiF - iCONa LAb & MAReA centre, Caserta, Italy, ²Centre of Molecular Anthropology for Ancient DNA studies, Department of Biology, University of Rome Tor Vergata, Roma, Italy, ³Servizio di Antropologia, Parco Archeologico di Ostia Antica, Ministero della Cultura, Roma, Italy

The Antemurale area of Portus Romae (Rome, Italy) returned several burials from the Late Antiquity/ early Medieval period. The site was ever investigated until the nineteenth century. In this paper a multidisciplinary approach, involving archaeological, bioanthropological, isotopic, and molecular analyses has been used to study people buried in that area. Radiocarbon dating, stable isotopes analysis, anthropological and DNA studies, has been performed on the 14 individuals from this area, and this sample represent now the first nucleus of investigation of a much broader research that aims to reconstruct the peopling and the change of human life style through the time in the ancient town so called Portus Romae.

Moreover, an explorative sample of 4 individuals was submitted to genomic analyses through a Whole Genome Sequencing to dissect their genetic ancestry to broaden our knowledge of the biological characteristics of people living in the area. Even though the DNA preservation was mined by chemical-physical diagenesis, we could detect reliable information about the European ancestry in Portus Romae, by comparing the data with roughly coeval and diachronic samples. Furthermore, we determined the genetic sex in children by mapping the reads to the sex chromosomes, starting to contribute to the demographic analysis of the area.

A02 Diet and reservoir effect

A02_01

Compound-specific radiocarbon dating of lipid residues in pottery vessels: a new approach for detecting the exploitation of marine resources

<u>Casanova E</u> ^{1,2}, Knowles T², Bayliss A³, Barclay A⁴, Walton-Doyle C², Evershed R ¹Museum national d'histoire naturelle, Paris, France, ²University of Bristol, Bristol, UK, ³Historic England, London, UK, ⁴Costwold Archaeology, Cirencester, UK

Over the last decades, organic residue analysis has been shown to be especially useful in ancient diet reconstruction; however, it is only recently that the direct radiocarbon dating of lipid residues has become a reliable method for dating pottery vessels and food procurement activities. We applied lipid residue analysis to late Bronze Age pottery vessels from the site of Cliffs End Farm (UK), previously dated by their visible charred residues and dated four of these vessels by compound-specific radiocarbon analysis (CSRA) of their absorbed lipids. Lipid biomarker detection was limited to only one class of aquatic biomarker in four vessels, which indicated that the diet relied mainly on terrestrial animals. Four vessels datable from their absorbed lipids produced ¹⁴C measurements significantly older than those on the charred residues, suggesting a reservoir effect affecting the dated lipids. Furthermore, the low abundance of pig remains (1-4%) at the site suggests that enriched δ^{13} C16:0 and δ^{13} C18:0 values recorded on the absorbed fatty acids were caused by marine contributions. The percentage of marine products in the CSRA dated vessels was quantified using the $\delta^{13}\text{C}$ values of individual fatty acids and from a modern reference database. These percentages were incorporated in mixed-source radiocarbon calibration using OxCal for the correction of a marine reservoir effect. Therefore, the combination of lipid compositions, radiocarbon dates and faunal analyses enabled the identification of marine product exploitation at the site. Finally, this allowed comparisons to be made with the dates of charred residues obtained from the same sherds.

A02 02

Efforts to remove ancient carbon from charred food crust: Successes and Failures

Varney R¹, Scott Cummings L¹

¹PaleoResearch Institute, Inc., Golden, United States

After radiocarbon dating reference foods, and long after some archaeologists had abandoned getting reliable dates from pottery, we conducted experimental pretreatments to remove ancient carbon from the archaeological contexts. We used a mixture of chemicals to mobilize both water-soluble and nonwater-soluble compounds in the food crusts — with many good results. We used a variety of chemical extraction methods including hydrolysis. We examined placement of the samples on the vessel — with good results. Rims generally yielded dates more congruent with dates on annuals from the same context. The key lay in viewing the cooking process as a proxy for chromatography. Carbohydrates, which are presumed to take in atmospheric carbon, burned or charred first and usually at or near the rim. Proteins charred to a lesser degree, and fats/lipids remained uncharred. Therefore, we sought to remove all of the fats/lipids and any uncharred proteins using these chemicals to be able to obtain more congruent dates, which we did. But some dates remained too old, suggesting the charred food crust had integrated proteins that contained ancient carbon. At this time we focused on a simplistic animals vs. plants model. We read about medical research that could "uncook" proteins, returning them to a mobile

rather than a fixed state. We participated in an experimental trial to test whether our charred food crust was a good candidate for this treatment. It was not. We present the multiple radiocarbon dates on these fractions for comparison and discussion.

A02 03

Examining carbon sources and radiocarbon dates on food plants and animals to understand offset dates on charred food crust

Scott Cummings L1, Varney R1

¹PaleoResearch Institute, Inc., Golden, United States

When ceramics, charred food crust, or even bone collagen yields ages older than expected, the Freshwater Reservoir Effect is suspected in several parts of Europe and North America, as well as elsewhere in the world. Research has examined whether or not regional offsets may be calculated or estimated and also whether or not some or all of the ancient carbon may be removed, particularly from ceramics or charred food crust. Although we expect that all carbon entering an organism is available for deposition into the cells of that organism, few studies have examined distribution of radiocarbon dates within single organisms by tissue type. In light of the fact that individual vessels may be used to cook or process multiple meals and foods, we have focused a portion of our research on radiocarbon dating several portions of that food prior to the time when it become food for human consumption. After radiocarbon dating bone collagen from four fish caught in 1939 and observing offsets varying from approximately 300 to 1200 radiocarbon years, we have broadened our research to include radiocarbon dating multiple samples (tissue and bone collagen) from reference animals, as well as stomach contents. For plants we examine seeds, stems, and leaves. Stomach contents of aquatic animals have yielded greater offsets than did either the flesh or bone collagen of those animals. We compare this information with radiocarbon dates on charred food crusts from various projects in the US.

A02_04

Permafrost melt as the driver of archaeological and modern freshwater reservoir effect

Hyland C¹, Schulting R¹, Weber A², Styring A¹

¹University Of Oxford, Oxford, United Kingdom, ²University of Alberta, Alberta, Canada

Freshwater reservoir effects (FRE) are extremely varied in their driving factors which makes them challenging to correct with both high accuracy and precision. Identifying the factor(s) that have driven the incorporation of "old carbon" into freshwater environments helps researchers to improve the precision and accuracy of dating archaeological remains from important freshwater resource contexts. New insights from the radiocarbon dating and stable carbon and nitrogen isotope analysis of modern freshwater fish from the rivers surrounding Lake Baikal, Russia provide insight into the driver of this region's modern FRE. The modern freshwater fish and previous paired dating of archaeological terrestrial faunal in direct association with human remains indicate a negative relationship exists between bulk δ^{13} C values and offsets in the ¹⁴C age caused by FRE. This research proposes that both the modern and archaeological FRE is driven primarily by the incorporation of permafrost melt into these freshwater ecosystems. The permafrost melt acts as both a source of "old carbon" and a driver of low bulk δ^{13} C values due to the C₃ vegetation that the permafrost contains. Additional research using stable sulfur and hydrogen isotope analysis will further examine the role of permafrost melt in the FRE of the Lake Baikal region.

Elite diet and its effects on the ¹⁴C dates of Estonian Bronze Age human remains

Tõrv M¹, Oras E¹, Meadows J², Lang V¹, Kriiska A¹

¹University of Tartu, Tartu, Estonia, ²Zentrum für Baltische und Skandinavische Archäologie, Schleswig, Germany

Human bone is a valuable material for dating ancient events, but these 14 C dates can be misleading if the ingested carbon derives from organisms outside of the atmospheric isotopic equilibrium. Dietary intake of freshwater and marine species may result in markedly older dates than the actual event. Thus, to interpret the 14 C dates obtained from human bone, we firstly need to identify the food sources and their proportions in the diet of the analysed individuals. We will present an exemplary case study about the Bronze Age stone cist grave populations – the first archaeologically visible elite buried into the monumental graves – in Estonia. Recently ca. 100 new radiocarbon dates have been obtained from these human skeletal remains to establish a new Bronze Age chronology in Estonia. To critically evaluate these dates, we revisited the published 14 C dates and present new stable isotope results – carbon (δ^{13} C) and nitrogen (δ^{15} N) – from these graves, focussing on the relationship of the 14 C dates to the individual dietary preferences.

We reconstructed the elite food habits of the Bronze Age populations in Estonia. We employed quantitative palaeodiet reconstruction and dietary reservoir effect estimation to indicate the complexities behind dating ancient human remains. Statistical modelling of calibrated dates further allowed reconstructing the chronology of specific burial practices. With this study we aim to exemplify how combined analytical approaches allow more refined interpretation of ¹⁴C dates and reconstruct both site-specific and wider chronology of Bronze Age elite burial customs in Estonia.

A02_06

Dietary reservoir effect correction for mid-Holocene human remains from Sakhtysh, Russia: a novel regression-based approach

Meadows J^{1,2}, Khramtsova A³, Kostyleva E⁴, Krause-Kyora B⁵, Piezonka H⁶

¹ZBSA (Centre for Baltic and Scandinavian Archaeology), Kiel, Germany, ²Christian-Albrechts-Universität zu Kiel, Leibniz-Labor für Altersbestimmung und Isotopenforschung, Kiel, Germany, ³Excellence Cluster ROOTS, Christian-Albrechts-University Kie, Kiel, Germany, ⁴State University Ivanovo, Ivanovo, Russian Federation, ⁵Institute of Clinical Molecular Biology (IKMB), Christian-Albrechts-University Kiel, Kiel, Germany, ⁶Institute for Pre- and Proto-History, Christian-Albrechts-University Kiel, Germany

Several small prehistoric cemeteries at Sakhtysh, Ivanovo Oblast, Russia, are attributed to the middle Neolithic Lyalovo and late Neolithic-Eneolithic Volosovo cultures (c.5000-4000 cal BC and c.4000-2500 cal BC respectively). Human bone $\delta^{13}C$ and $\delta^{15}N$ results confirm that these groups were hunter-gatherer-fishers, with sometimes large dietary differences between individuals (Engovatova et al. 2015). Accurate dating has been challenging, due to variable collagen preservation, uncertain association between human skeletal remains and osseous grave goods, and the unknown magnitude of mid-Holocene freshwater reservoir effects, which must have been much greater than those recorded in modern fish. We present a regression-based approach, which instead of comparing ^{14}C ages of human bones to those of associated grave goods, relies on ^{14}C -age differences between different skeletal elements of the same individual. The resulting dietary reservoir effect estimates for 53 samples from 39 individuals are compatible with estimates produced by a diet-reconstruction model based on realistic stable isotope and freshwater reservoir effect baseline values, and with a handful of ^{14}C dates of osseous grave goods (Macāne et al. 2019). Calibrated dates of individual burials remain imprecise, but we can still observe temporal trends in human diets, which parallel trends elsewhere in northeastern Europe over the same date range.

Direct and Indirect Attempts at Diachronic Quantification of the Marine Reservoir Effect

Niedospial J¹, Sevink J², Maurer A, Mazzini I⁴, Arienzo I⁵, Kuijper W⁶, van Hall R², <u>Dee M</u>¹

¹Centre for Isotope Research, University of Groningen, Groningen, Netherlands, ²Institute for Biodiversity and Ecosystem Dynamics, University of Amsterdam, Amsterdam, Netherlands, ³Groningen Institute of Archaeology, University of Groningen, Groningen, Netherlands, ⁴Institute of Environmental Geology and Geoengineering, National Research Council of Italy, Rome, Italy, ⁵National Institute of Geophysics and Volcanology, Naples, Italy, ⁶Faculty of Archaeology, Leiden University, Leiden, Netherlands

The marine reservoir effect (MRE) is fundamental to understanding the carbon cycle and for correction of radiocarbon dates on samples either partially or wholly derived from marine carbon. Estimates of the offset commonly make use of paired samples of contemporary marine and terrestrial material, with the resultant offset then applied to the time period of interest. Paradoxically, it is widely accepted that the MRE at any one location is likely to have fluctuated over time, calling into question the validity of such retrojections. In this

study, we set out to both calculate the MRE for a specific location and then to understand the dynamics behind its variation over time using an array of geochemical and palaeoecological proxies. Previous research at our study site of Puntone, on the Tyrrhenian Sea, revealed that the area had transitioned between open marine, lagoonal and terrestrial regimes, and hence the local MRE was likely to have altered over time. This expectation was confirmed by the new radiocarbon data we obtained on marine shells and terrestrial plant remains. First attempts at using metal ion and isotope ratios through the core to elucidate, and indeed model, the MRE fluctuations have shown signs of promise but additional research is required to develop these approaches.

A02 P02

Variability of Radiocarbon reservoir age effects in lakes and rivers of Eastern Anatolia and Lesser Caucasus

FONTUGNE $M^{1,2}$, <u>HATTÉ C^{2,3}</u>, TISNÉRAT-LABORDE N^2 , OLLIVIER V^1 , KUZUCUOGLU C^4 ¹LAMPEA, Aix-en-Provence, France, ²LSCE - CEA, Gif-sur-Yvette, France, ³Silesian University of Technology, Gliwice, Poland, ⁴Laboratory of Physical Geography, Meudon, France

Multiproxy sedimentary sequence analysis constitutes the basis for reconstructions of past paleoenvironments and climate evolution. These sequences are, for the most part, obtained by coring in lakes (maar or crater) whose waters can record volcanic activity or karstic contributions, especially in Eastern Anatolia and the Lesser Caucasus. The main consequence is to generate a reservoir age effect and to bias the radiocarbon dates of sedimentary records from these lakes. In the same way, the halieutic resources bordering these lakes also record this reservoir effect. And, as they constitute the food resources of the local populations, this reservoir effect is also reflected in the skeleton of the lake population. We present, here, some results obtained from eastern Anatolian lakes, Van and Sevan lakes and from archaeological sites along the Kura river and its tributaries from Lesser Caucasus.

Identification of marine reservoir effect in the Holocene sediments from the Nobi Plain, central Japan

Nakanishi T¹, Hori K², Nakashima R³, Hong W⁴

¹Museum of Natural and Environmental History, Shizuoka, Japan, ²Department of Earth Science, Tohoku University, Sendai, Japan, ³Geological Survey of Japan (GSJ), Advanced Industrial Science & Technology (AIST), Tsukuba, Japan, ⁴Korea Institute of Geoscience and Mineral Resources (KIGAM), Daejeon, Republic of Korea

To investigate the relationship between paleoenvironmental changes and marine reservoir effects, the radiocarbon ages of marine shells and terrestrial plants were measured from the same horizons of the Holocene sediments. Two sediment cores, HN1 and OG, were obtained from the western margin of the Nobi Plain, which faces the Kuroshio warm current. This plain is a fluvial-coastal lowland formed mainly by Kiso, Nagara, and Ibi rivers (Hori et al., 2019). These drilling sites are located in subsidence area associated with the Yoro fault (Kuwahara, 1968; Ishiyama et al., 2007). Based on analyses of lithology, molluscan assemblages, and radiocarbon dating, we interpreted five sedimentary units in order of older age: estuary, prodelta, delta front, delta plain, and artificial soil. These paleoenvironmental changes had been mainly associated with the sea-level rise during the deglacial period. Terrestrial accumulation curve was consistent with the Kikai-Akahoya volcanic ash (K-Ah: ca. 7,300 cal BP; Machida and Arai, 2003). The reservoir ages during the period from 9,300 to 2,800 cal BP of 13 pairs obtained from the estuary to delta front facies were evaluated. The average from 140 ± 70 to 900 ± 50 was 350 ± 180 years. The chronological change in the reservoir effect will be compared with the previous results from the other coastal area in Southwest Japan (Nakanishi et al., 2017ab, 2019). Drilling program of the sediment cores were supported by the Grants-in-Aid for Scientific Research, Kakenhi JP17K18526. Radiocarbon dating was funded by the JSPS Kakenhi grant number JP18H01310.

A02_P04

Time varying Local Marine Reservoir Effect in Coastal Systems

<u>Macario K</u>¹, Alves E¹, Oliveira F¹, Chanca I², Scheel-Ybert R³, Gaspar M³, Tenorio C³, Dias F¹, Aguilera O¹, Bianchini G³, Vitorino B¹, Cardoso R¹, Anjos R¹, Muniz M¹

¹Universidade Federal Fluminense, Niteroi, Brazil, ²Max Planck Institute, Jena, Germany, ³Universidade Federal do Rio de Janeiro, Rio de Janeiro, Brazil

The radiocarbon (14 C) Marine Reservoir Effect (MRE) is known to vary with time due to global environmental changes, now better represented by the Marine20 calibration curve. In coastal regions, however, the scenario is considerably more complex and the MRE is influenced by carbon sources that exhibit a wide range of isotopic signatures. Indeed, the complexity of the carbon cycle in coastal systems demands extensive research for an accurate quantification of the MRE and its variability, which has the effect of hindering accurate 14 C chronologies on the coast. The local MRE offset (Δ R) in estuaries, is subject of the interplay of the hydrography with factors such as the regional geology, upwelling and sealevel variations. Using paired archaeological samples from the Southeastern coast of Brazil, we show a highly variable MRE and a possible correlation with the sea level regression.

Freshwater reservoir effects in charred 'food crusts' on pottery: frequency, magnitude, risk factors and prospects for correction

Meadows J^{1,2}, Lucquin A³, Gonzalez Carretero L^{3,4}, Dolbunova K^{4,5}, Craig O³, Heron C⁵

¹ZBSA (Centre for Baltic and Scandinavian Archaeology), Kiel, Germany, ²Christian-Albrechts-Universität zu Kiel, Leibniz-Labor für Altersbestimmung und Isotopenforschung, Kiel, Germany, ³BioArCh, University of York, York, United Kingdom, ⁴Department of Scientific Research, The British Museum, London, United Kingdom, ⁵State Hermitage Museum, St Petersburg, Russia

The ERC-funded INDUCE project is concerned with the adoption of pottery by hunter-gatherer-fishers in northeastern Europe. In this region and period, it is often difficult to date pottery find contexts, but potsherds often have carbonised deposits ('food crusts', FCs). Thus ¹⁴C dating of FCs is desirable, but these FCs probably contain carbon from aquatic organisms with unknown ¹⁴C reservoir effects. The problem is more salient at inland sites, given the potential scale of freshwater reservoir effects (FREs). To investigate pottery function, INDUCE has acquired EA-IRMS data (%C, %N, δ^{13} C, δ^{15} N) on FCs on more than 400 sherds, from over 50 sites. In most cases we have also obtained biomarker (GC-MS) and compound-specific δ^{13} C (δ^{13} C16:0, δ^{13} C18:0) data on soluble lipids extracted from the same FC. Some FCs have also been examined by SEM-EDX microscopy. These analyses confirm that FCs are composed primarily of food remains, which are dominated by aquatic species.

We have dated more than 100 FCs, often when their context date, and/or local FRE, is well-constrained. We have tested whether any combination of isotopic, biomolecular and microscopic data predicts apparent ¹⁴C age offsets in FCs. Contrasting results from sites with >10 dated FCs illustrate the scope for using FC ¹⁴C to date hunter-gatherer-fisher pottery. Where FC ingredients are more varied, a multi-proxy approach appears to account for most of the variation in FC offsets, but at other sites, FC composition is too uniform, and FREs are too varied, to justify attempts at FC ¹⁴C-age 'correction'.

A02_P06

Estimating freshwater reservoir ages using Bayesian models for the Mesolithic to neolithic transition

Olsen J¹, Maaring R¹, Mannino M¹
¹Aarhus University, Aarhus, Denmark

The chronology of the Mesolithic to Neolithic transition is difficult to date accurately using radiocarbon analysis on human or animal bone remains. This is because that in particular the hunter-gather culture of the Mesolithic involves diets from multiple sources. When both marine and freshwater food webs are exploited, it becomes difficult to correct the radiocarbon ages for possible reservoir effects. In particular, the freshwater reservoir effect is unknown and expected to vary substantially. We have collected a large dataset of dog bones across the Mesolithic to Neolithic transition from which we have deduced the percentage of terrestrial, marine and freshwater diets using a FRUITS model. Further, we have included a dataset of domesticated cattle. All from multiple sites across Denmark. We have constructed a Bayesian model with phases based on the archaeological typology, i.e. belonging to either Mesolithic or Mesolithic. In the model we have allowed for estimating the total reservoir age using a wide uniform prior. If we assume that the marine reservoir age is known then the freshwater reservoir age can be estimated from the posterior total reservoir age probability distribution. The calculated freshwater reservoir age vary from a few hundred ¹⁴C years and up 1200 ¹⁴C years. Further, we have tested the robustness using different Bayesian model of the Mesolithic to Neolithic transition and found our freshwater reservoir estimates are similar and independent of model choice.

Reservoir Effect determination in marine shells from Mexico

Rodriguez-Ceja M^1 , Díaz-Castro M^2 , Solis C^1 , Álvarez-Lajonchere L^3 , Méndez-García $C^{1,4}$, Chávez-Lomelí E^1 1 Universidad Nacional Autónoma de México, Mexico City, Mexico, 2 2 Instituto Superior de Tecnologías y Ciencias Aplicadas. Universidad de La Habana, Cuba., La Habana, Cuba, 3 Museo de Historia Natural Felipe Poey. Universidad de la Habana, Cuba., LA Habana, Cuba, 4 Cátedras Conacyt. Instituto de Física. Universidad Nacional Autónoma de México., Mexico City, Mexico

When trying to establish the chronology of a site through radiocarbon dating, terrestrial samples are usually preferred. However, since they are not always available, an alternative is the use of malacological material from marine organisms as mollusks.

Given that radiocarbon activity in aquatic environments is usually different from that of the atmosphere, organisms that grow in both environments have different apparent ages, even though they are contemporary. This apparent age is known as "reservoir effect" and varies depending on latitude and other local factors.

Mexico is a country with a littoral of more than 11,000 Km, and a great interest in dating malacological samples from coastal contexts. However, reservoir effect studies are still scare. Must of the available data come from studies done in the 60s and 90s decades, of the XX century.

We present new reservoir effect data from coastal Mexican sites in the Pacific Ocean and the Caribbean Sea, obtained from a Collection of Mexican shells samples belonging to the Natural History Museum Felipe Poey, from the Universidad de La Habana, Cuba and to the Institute of Biology of the Universidad Nacional Autónoma de México.

A03 Archeological samples for accurate radiocarbon dating

A03_01

The Meryt Model: towards a new chronometric model for the Egyptian Old Kingdom

Quiles A¹, Aubourg E², Beck L³, Ciavatti A¹, Delqué-Kolic E³, Ferrant M^{1,4}, Muller S⁵, Salati P⁶

¹Institut français d'archéologie orientale (IFAO), Cairo, Egypt, ²Laboratoire AstroParticule et Cosmologie, Paris, France, ³Laboratoire de Mesure du Carbone 14/LSCE, Gif-Sur-Yvette, France, ⁴Laboratoire De la Molécule aux Nano-objets: Réactivité, Interactions et Spectroscopies, Sorbonne Université, Paris, France, ⁵Institut de Systématique, Évolution, Biodiversité (ISYEB), , France, ⁶Laboratoire d'Annecy-le-Vieux de Physique Théorique, Université de Savoie Mont Blanc & CNRS, Annecy, France

The MERYT project aims to build an accurate, high-resolution and multi-technical chronological model for the Egyptian Old Kingdom (~2900-2200 BCE), through an integrated approach bringing together all the analytical criteria of Egyptology, Archaeology and Archaeometry. It addresses two major issues: to develop a definitive chronological framework of the Old Kingdom, reign by reign, by building a statistical model reconciling Egyptological and analytical data; to explore the IntCal calibration curve considering the specific environmental conditions in Egypt, in particular due to the Nile flooding. In that respect, through a historical approach, we have re-evaluated textual sources owing chronometric

evidence to re-evaluate all reign certificates and assess their reliability to restore an updated succession of kings' list and the most accurate estimates of their reigns' duration. Through an archaeometric approach, we have carried out ¹⁴C dating's series almost all on samples collected directly on on-going

archaeological excavations in Egypt, which age is clearly associated with a single reign. Specifical improvements have been performed on textile samples' analysis protocol to ensure their dating when contaminated by funeral chemicals, and accurately model their result. We also have investigated possible regional offset to IntCal within the Egyptian land due to seasonal effect, by analyzing botanical samples from the Paris Herbarium. The whole is finally confronted together in a statistical Bayesian model whose formalism is fully developed for this project.

This talk will present first results of the Meryt Model and be completed by open perspectives, bringing new insights on the start of the Egyptian state.

A03 03

Dating the stylistic periods of Australian Aboriginal Rock Art

<u>Finch D</u>¹, Gleadow A¹, Hergt J¹, Heaney P³, Green H¹, Myers C⁴, Levchenko V²

¹University Of Melbourne, Parkville, Australia, ²Australian Nuclear Science and Technology Organisation, Sydney, Australia, ³Rock Art Australia, Melbourne, Australia, ⁴Dunkeld Pastoral Company, Dunkeld, Australia

The Kimberley region in north-western Australia is home to one of the world's richest rock art provinces. Field observations at almost 4000 rock art sites over the last 40 years led researchers to define five main styles of painted rock art, some of which were thought to date back to the Pleistocene. While there is general agreement regarding the relative sequence of stylistic phases, there has been very little geochronological evidence to support the proposed sequence or its antiquity. Only some of the rock art from the most recent period contains material that is suitable for radiometric dating. All recent attempts to date the art, therefore, focus on determining the age of material found overlying or underlying paintings to establish minimum or maximum age constraints for individual motifs.

Our research uses radiocarbon dating of mud wasp nests found in contact with rock art to constrain the age of individual paintings. Results to date have established that the stylistic sequence spans at least 17,000 years. Age constraints for multiple motifs, of the same stylistic period, are used to estimate when that particular style of painting was employed. Statistical analysis of the results then explores the level of uncertainty associated with the currently available data and is used to estimate what additional dating results are required to achieve higher levels of confidence.

A03 04

Wiggle-match dating on display: minimally destructive analysis of early American museum objects

Hadden C¹, Napora K²

¹Center For Applied Isotope Studies, Athens, United States, ²William S. Webb Museum of Anthropology, Lexington, United States

Wiggle-match dating of tree-ring sequences is particularly promising for achieving high-resolution dating across periods with reversals and plateaus in the calibration curve, such as the entire post-Columbian history of North America. Here we describe the process of wiggle-match dating two museum objects of significance to 18th–19th century United States history: (1) a cypress dugout logboat exhibiting a unique combination of European and Native American design elements; and (2) a tulippoplar wood trough utilized by an enslaved workforce in the production of saltpeter. Tree rings were counted and sampled for dating from exposed, rough cross-sections in the wood, with no or minimal surface preparation, to preserve these fragile objects. Both contained relatively long tree-ring sequences (>220 rings). Single-year samples were collected from the innermost ring and at approximately 10-year intervals from the outer ~50 rings, with practically no visible damage to the objects. The samples were radiocarbon dated by AMS, and the dates were modeled in OxCal using the Sequence and Interval functions to account for uncertainty in ring counts, rather than the D_Sequence and Gap functions that are more commonly

used in wiggle-match dating. By this method, the outermost tree ring of the logboat's hull dated to 1766–1796 cal AD, and the trough to 1778–1804 cal AD (95% highest posterior density ranges). Dendrochronological dating supports the radiocarbon wiggle-match dating for both objects. This study demonstrates that high-precision dating can be achieved for 18th–19th century objects through wiggle-match dating, with minimal damage to the objects of study.

A03 05

Sampling ritual complexity: the case study of the megalithic Panoría site (Granada, Spain).

<u>Milesi García L</u>¹, Aranda Jiménez G¹, Díaz-Zorita Bonilla M², Sánchez Romero M¹, Vilchez Suárez M¹, Robles Carrasco S¹

Late prehistoric south-eastern Iberia is considered a privileged setting for studying the development of important Megalithic sites as well as the emergence of complex societies during the Copper and Bronze Ages. Through several chronological projects and diverse sampling strategies, our research has increased the number of radiocarbon dates in more than 250, covering 12 sites from the coastline to the inland of the region.

We present here the analysis of one of them as it is an excellent case study to demonstrate how chronologically oriented fieldwork planning, remain recovery processes and anthropological study of potential radiocarbon dating samples have a critical effect on results and accurate chronologies, especially in contexts where depositions are highly commingled.

The megalithic cemetery of Panoría (Granada, Spain), with nine excavated tombs, counts on a well-known stratigraphy and seventy-three radiocarbon dates, also analysed within a Bayesian framework. Results allow us now to explore the tempo of ritual activities throughout time for each tomb. Also, they lead us to some refined chronological conclusions for the site where: 1) the second half of the 4th millennium BC was an intensive and brief period of funerary depositions in all tombs; 2) most of the dolmens were reused in the 25th and 21st centuries cal BC during even shorter periods; 3) the cemetery was still recognised as a ritual place and used in the Late Antiquity.

A03_07

Developing a chronology for pre-Columbian Amazonia through the HERCA project

Becerra-Valdivia L¹, Bronk Ramsey C¹

Pre-Columbian (pre CE 1492) Amazonia is typically believed to have been sparsely inhabited by huntergatherers largely constrained by their environment. Increased research, however, shows evidence for sedentarism, stratification, and a long history of landscape manipulation. This includes the construction of monumental structures in large (>100 ha), urban settlements (1); canal and causeway networks (2); and plant domestication dating to the early/mid Holocene (3). Aimed at better understanding these societies and their relationship with the environment, 'Human-Environment Relationships in pre-Columbian Amazonia' (HERCA) is an interdisciplinary project that integrates archaeological and paleoecological data through the lens of time. Chronometric research, based at the Oxford Radiocarbon Accelerator Unit, includes the creation of highly resolved human-occupation and paleoenvironmental sequences, the integration of chronometric and contextual information through Bayesian modelling, and data management. Here we present current research results and the newly built HERCA Database. The latter, currently holding >500 unique records, allows for the storage/management of multi-proxy data and associated materials. Investigations to be discussed include the development of key

¹Universidad De Granada, Granada, Spain, ²Universität Tübingen, Tübingen, Germany

¹Oxford Radiocarbon Acceleration Unit, Oxford, United Kingdom

archaeological and paleoecological chronologies in the region, and the commencement of monumental construction in Brazil and Bolivia.

- 1. Prümers et al., Lidar reveals pre-Hispanic low-density urbanism in the Bolivian Amazon. Nature (2022). doi:10.1038/s41586-022-04780-4.
- 2. Lombardo & Prümers, Pre-Columbian human occupation patterns in the eastern plains of the Llanos de Moxos, Bolivian Amazonia. J. Archaeol. Sci. 37, 1875–1885 (2010).
- 3. Watling, et al., Direct archaeological evidence for Southwestern Amazonia as an early plant domestication and food production centre. PLoS One 13, e0199868 (2018).

A03 08

Pre-Columbian occupation chronology of southern coast of Nayarit, Mexico.

Solis C²

¹Dirección de Salvamento Arqueológico, INAH, Mexico City, Mexico, ²Instituto de Física, Universidad Nacional Autónoma de México, Mexico City, México, ³Facultad de Ciencias, Universidad Nacional Autónoma de México., Mexico City, México, ⁴Instituto Superior De Tecnologías y Ciencias Aplicadas, Universidad de La Habana, La Habana, Cuba

The area of western Mexico has been little studied, mainly due to difficulties of access. Chronicles from the first half of the 16th century describe fertile plains and densely populated wetlands. The Directorate of Archaeological Salvage of INAH, conducts archaeological research when it comes to modern works, and undergoes studies of previously unknown Pre-Columbian occupation sites. The present work deals with the study of the material recovered from two sites in Costa Canuva (Pacific Ocean), in the South of the state of Nayarit: Becerros (site mainly used for burials) and Naranjos (used for residence and burials). The majority of the ¹⁴C dating of materials recovered at Becerros provided a chronological framework of absolute dates for the occupation of the site from 217 cal A.D. to 1025 cal A.D., corroborating the ceramic studies in the sense that human settlement activities date from the Tombs of Tyre Tradition (300 B.C. to 600 A.D.) to the Early Postclassic (900 to 1100 A.D.). The dated materials from the Naranjos site, yielded ages correlated with the Classic period (500-750 AD), however, material dating from 1670-1780 was also found, associated with glazed ceramics, a technique introduced by the Spaniards. This indicates that rituals in these regions may have continued for another 100 years after the conquest of the altiplano. Finally, dates of charcoal and associated shell samples from the Naranjos Unit were compared to complement the dating of the occupation of the site.

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A03 09

The dating of dolomitic mortars with uncertain chronology from Müstair Monastery: sample characterization and combined interpretation of results

Caroselli M¹, Hajdas I², Cassitti P³

¹SUPSI, Mendrisio, Switzerland, ²ETH, Ion Beam Physics Lab. , Zurich, Switzerland, ³Foundation Pro-Kloster St. Johann , Müstair, Switzerland

To obtain scientific data regarding the chronology of archaeological structures, lime mortar radiocarbon dating has often demonstrated to be a decisive method. However, it is well known that certain chemical-mineralogical characteristics of the mortars can greatly influence the results. Among other issues, the dating of magnesian mortars can be particularly difficult because of the combined slaking,

setting and hardening reactions of the calcium and magnesium phases, typical of these mortars. The formation of numerous mineralogical phases depending on reaction conditions adds further complexity to the dating method, which deserves to be studied with further detail. During the project "Mortar technology and construction history of Müstair Monastery" thanks to the presence of numerous mortar fragments belonging to different construction phases, the first experiments in this regard had yielded encouraging results. An additional 5 samples from buildings with controversial chronology, thought to belong approximately to the 9th, 12th and 15th centuries, were selected, prepared and radiocarbon dated. The data obtained were discussed by integrating preliminary petrographic and chemical characterization analyses of the mortars with archaeological information and excavation records. The results provided a better understanding of the potential and limitations of dating dolomitic mortars coming from archaeological context.

A03 10

Characterization and selection of mortar samples for radiocarbon dating in the framework of MODIS2 intercomparison: results of the Italian laboratories

<u>Maspero</u> **F**¹, Galli A¹, Panzeri L¹, Martini M¹, Ricci G², Secco M³, Artioli G², Fedi M⁴, Barone S⁴, Liccioli L⁴, Marzaioli F⁵, Passariello I⁵, Terrasi F⁵

¹Dipartimento di Scienza dei Materiali, Università degli Studi di Milano-Bicocca (Italy) and CUDAM (Centro Universitario Datazioni e Archeometria Milano-Bicocca), Milano, Italy, ²Dipartimento di Geoscienze, Università degli Studi di Padova, Padova, Italy, ³Dipartimento di Beni Culturali, Università degli Studi di Padova, Padova, Italy, ⁴INFN, Sezione di Firenze, Firenze, Italy, ⁵Dipartimento di Matematica e Fisica, Università degli Studi della Campania Luigi Vanvitelli, Napoli, Italy

Since several decades, many efforts have been devoted to improve the accuracy of mortar radiocarbon dating and to assess the reliability of the results in relation with the typology of the examined specimen. Several assumptions for the application of the method are in many cases not fulfilled, among which: a) complete primary limestone dissociation during calcination; b) efficient separation of geogenic carbon contained in calcareous aggregates; c) short carbonation time; d) absence of dissolved CO₂ in running water exchanging carbonate ions. Many laboratories all over the world have proposed different methods to select suitable fractions of mortar particles.

The first intercomparison attempt, involving eight international laboratories, was made in 2016 to reach a common characterization and pretreatment method of mortars to optimize the radiocarbon dating results. Following this first step, a new intercomparison experiment was proposed and set up in 2018 during the Mortar Dating International Meeting (Bordeaux, FR). A new set of three mortar samples was chosen, taking care about the selection of standardized materials (homogeneous, with defined mineral types, devoid of exogenous inclusions, of known ages).

This work describes the results of the Italian laboratories involved in the intercomparison. The samples were characterized, selected and dated depending on each laboratory strategy. The data are encouraging and shed light on future steps to be taken to standardize a method for prior characterization and selection of samples suitable for radiocarbon dating.

A03 11

Radiocarbon and OSL dating of Caesar's Forum in Rome

<u>Olsen J</u>¹, Schrøder T¹, Kinnard T, Kristiansen S, Kindbjerg J, Presicce C, Vitti M, Raja R ¹Aarhus University, Aarhus, Denmark

Here we present radiocarbon dating of 122 animal bone samples and OSL profiling to accurately date the stratigraphy of Caesar's Forum in Rome. The stratigraphy covered the period from the Recent Bronze Age (13th Century BCE) to the 1932s. Stable isotope analysis on the bone samples provided

data for a discussion of dietary baselines. The radiocarbon dates fell within the approximate range 400-3000 ¹⁴C years BP, as expected from the stratigraphy. Three Bayesian chronological models were made by assuming a sequence of overlying stratigraphic units, while the models used outlier modelling that allowed a sample to be redeposited in its associated stratigraphic unit. The OSL profiling aided the Bayesian modelling and sample selection by identifying phases with a high risk of re-deposition. Bayesian modelling was conducted on two excavation areas (A and C). In area A, the chronological model showed activity in late antiquity and early medieval era, from the 3rd century CE to the 8th century CE. In area C, the first chronology showed activity in the archaic era to antiquity, from 8th century BCE to the 4th century CE. In area C, the second chronology told of activity from the medieval era to the renaissance, 10th century CE to the 16th century CE. In area C's first chronology an interesting aspect was to look for the end of the archaic era and the floor of Caesar's forum. In area C's second model an interesting aspect was stratigraphic units with many outliers, which were signs of redisposition of soil.

A03 12

Effect Of Lime Production And Processing Methods On The Presence Of Geogenic Carbon In Historical Mortars

<u>Válek J</u>¹, Kozlovcev P¹, Fialová A¹, Kotková K¹, Frankeová D¹, Světlík I², Pachnerová Brabcová K²

¹Institute of Theoretical and Applied Mechanics of the Czech Academy of Sciences, Prague, Czech Republic, ²Nuclear Physics Institute of the Czech Academy of Sciences, Prague, Czech Republic

The presence of geogenic carbon makes the radiocarbon dating of historical mortars a challenging task. Part of the geogenic carbon in mortars is commonly present due to the production and processing of lime binder. Lime burnt with wood in a traditional kiln was assessed for the presence of residual CO₂. Quicklime samples were taken from various locations in the kiln and thermal analysis was used to quantify the CO₂ residual levels. The quicklime obtained was slaked in excess of water and the presence of unburnt particles was investigated after sedimentation of the lime putty at three depth levels: top, middle and bottom. An optical microscope with Cathode Luminescence probe was used to qualitatively evaluate the presence of unburnt particles. In addition, the three putty specimens per lime sample were left to carbonate at laboratory conditions. After carbonation, the content of stable isotopes ¹³C and ¹⁸O was determined. This experimental procedure allows for description and estimation of the presence of geogenic carbon in quicklime produced in a wood-fired single batch kilns. It also shows the effectiveness of sedimentation treatment to reduce under-burnt lime particles. The comparative study of stable isotopes studies the possibility of evaluating a carbonated lime binder prior to its ¹⁴C analysis. The results suggest that the historical treatment of lime to produce a fine binder could potentially lead to mortar samples that are more suitable for radiocarbon dating than mortars produced directly from quicklime or dry slaked lime to hydrate.

A03 14

Alpine archaeology and radiocarbon analysis: a match made in heaven!

Leuzinger U¹, Hajdas I², Guidobaldi G², Wyss K², Imhof W³

¹Amt für Archäologie Thurgau, Frauenfeld, Switzerland, ²Ion beam Physics ETH Zurich, Zurich, Switzerland, ³Staatsarchiv Schwyz, Schwyz, Switzerland

A team of researchers have been examining rock shelters and ruins in the municipality of Muotathal (Canton Schwyz, Switzerland) at the behest of the State Archive of Canton Schwyz since 2006. The study region is located in the pre-Alps and extends to altitudes of between 600 and 2400 m a.s.l. Many of the small archaeological test excavations yield charcoal fragments and faunal remains. Radiocarbon analyses carried out on the organic remains allow us to assess the potential of any newly discovered site. At this stage, the period covered by the finds stretches from cave bears dated to around 36,000 BP to

Mesolithic hunters' camps from around 9000 BP, to Neolithic, Bronze Age, Iron Age and Roman-period finds from between 5000 and 2000 BP as well as numerous medieval and post-medieval deserted Alpine huts and pens.

The Berglibalm and Flözerbändli rock shelters discovered in 2015 and 2020 respectively are of international significance. They yielded layers containing animal bones, stone artefacts and botanical remains from the Epipalaeolithic but mostly from the Early Mesolithic. While the microliths made of flint can be typologically dated to the Mesolithic, radiocarbon analysis of the hearths allows us to date the finds even more precisely.

One of the more remarkable objects discovered is a decorated piece of red deer antler from Muotathal-Flözerbändli, which was radiocarbon dated to the Azilian (ETH-109223, 10354±31 BP) at the Laboratory of Ion Beam Physics at ETH Zurich. It is the only decorated antler artefact from that period found in Switzerland so far.

A03 15

When the boundaries do not hold: alternative interpretation for archaeological transition, cultural changes and climate

Boaretto E1

¹D-REAMS Radiocarbon Lab, Weizmann Institute of Science, Rehovot, Israel

Chronology is at the base of archaeological and paleoclimate research and it is fundamental for synchronization of different events. The time frames need to be as precise as possible and to be determined independently from other stratigraphic and cultural sequences. The assumption of time contemporaneous boundaries between archaeological periods is often used for synchronization between sites, and to correlate the cultural periods without radiocarbon dating. I have documented several examples of misinterpretation of such correlations in the absence of radiocarbon dating, and in some cases sites are just a few kilometers apart and in the same environmental niche. Furthermore, when the assumption that "similar cultural remains reflect similar time periods" is applied, and when time boundaries contradict radiocarbon dates, the latter are often regarded as the source of the problem. The underlying inconsistencies are often revealed in the radiocarbon modelling. The study of the archaeological record and its stratigraphy both at the macroscopic level and most important at the microscopic level is of fundamental importance. Examples will be presented along the 50000 years of ¹⁴C range, such as the association of the Younger Dryas and the transition to the earliest settlements, the integration or replacement of the Byzantine culture by the Islamic conquest in the peripheral region of the Negev, and the decline of the City States in the Levant.

A03_16

A radiocarbon chronology for Iron Age Jerusalem: Hallstatt Plateau, known age events, and regional offsets

<u>Regev J</u>¹, Uziel J², Gadot Y³, Ben-Ami D², Mintz E¹, Regev L¹, Boaretto E¹

¹Weizmann Institute of Science, Rehovot, Israel, ²Israel Antiquities Authority, Jerusalem, Israel, ³Tel Aviv University, Tel Aviv, Israel

The Iron Age in Jerusalem, covering the 13th to 6th centuries BC, is one of the most excavated, studied, and debated topics in the southern Levant archaeology. Much of the interest has been sparked and fuelled by the ancient texts relating to Jerusalem and, in particular, the biblical narrative, also attracting wide public attention.

However, these events were never anchored with an absolute chronology based on independent radiocarbon dates. Only recently, we have integrated the microarchaeology-based radiocarbon sampling to Jerusalem, to build an absolute and accurate chronology.

We have studied three areas in the "City of David," covering the entire Iron Age period. One of the major challenges for chronology was the Halstatt plateau. Samples dating between the 8th-6th centuries BC all give similar calibrated ranges coinciding with the later part of the Judean kingdom. We exposed superimposed pottery-rich floors, from which in-situ contexts were characterized and dated. These measurements allowed for "short-lived wiggle matching" through stratigraphic modeling, consequently providing a high precision dating even during the Hallstatt plateau.

We high-precision dated a context relating to the earthquake mentioned in the book of Amos and several contexts from the time of destruction by the Babylonians in 586 BC. The stratigraphic sequences and events, considered historically well established, provided an opportunity to assess the existence of regional differences in past ¹⁴C concentrations. The dates measured from several structures occupied till the Iron IIC showed a discrepancy between the meager quantity of early pottery types vs. the significant presence of early dates.

A03 17

Untangling chronology at Tel Gezer: connecting radiocarbon, archaeology, Egyptology and the Bible

<u>Webster L</u>¹, Wolff S², Ortiz S³, Tsuk T⁴, Warner D⁵, Parker J⁵, Yannai E⁶, Dee M⁷, Hua Q⁸, Jacobsen G⁸, Höflmayer F¹

¹Austrian Academy Of Sciences, Vienna, Austria, ²W. F. Albright Institute for Archaeological Research, Jerusalem, Israel, ³Lipscomb University, Nashville, USA, ⁴Israel Nature and Parks Authority, Jerusalem, Israel, ⁵New Orleans Baptist Theological Seminary, New Orleans, USA, ⁶Israel Antiquities Authority, Jerusalem, Israel, ⁷University of Groningen, Groningen, Netherlands, ⁸Australian Nuclear Science and Technology Organisation, Sydney, Australia

Gezer is among the most prominent ancient city mounds in Israel, and exceptionally well-attested in historical sources. During the Bronze and Iron Ages, Egyptian, Biblical and Assyrian sources associate it with activities and conquests of specific local rulers and foreign invaders. Thus, Gezer provides a rich opportunity to test correlations between archaeology and text using a ¹⁴C-based local site chronology. Though Gezer has been the subject of intense excavation, minimal radiocarbon data was available until recently. Here we present more than 70 new dates from the Middle Bronze Age (MBA) through Iron Age levels, obtained via targeted sampling of previously exposed sections as well as active excavation. The new chronological model clarifies many aspects of the site history and contributes to region-wide debates. For example, we obtain early dates for the construction and destruction of the MBA city, and evidence countering low Philistine and Iron Age chronologies. In one part of the site, radiocarbon led to exceptionally large corrections of up to 300 years, helping to identify errors in stratigraphic interpretation and pottery-based dating, and modifying the site-wide correlation of remains; in the process, we revealed previously unrecognised and elusive evidence of resettlement during the early Late Bronze Age. By comparing the new site chronology with texts and the 14C-based Egyptian chronology, we can also present a fresh evaluation of possible associations of destruction layers and monumental architecture with historical figures.

A03_P01

Comparing Apatite and Collagen Radiocarbon dates from a 16th century Cemetery Context – El Japón, Xochimilco, Mexico City

<u>Alarcón Tinajero E</u>^{1,2}, Hadden C², Cherkinsky A², Villegas Camposeco B³, Gómez-Valdés J^{3,4}

¹Department of Anthropology, University of Georgia, Athens, United States, ²Center for Applied Isotope Studies, University of Georgia, Athens, United States, ³Escuela Nacional de Antropología e Historia, Posgrado en Antropología Física, Mexico City, Mexico, ⁴Instituto Nacional de Antropología e Historia, Mexico City, Mexico

El Japón is a sixteenth century hamlet site occupying the marshlands of the southern Basin of Mexico in central Mesoamerica. Radiocarbon dating and OxCal modelling of human bone collagen (n=11) identifies

a range of burials at El Japón cemetery from 1550-1650 cal. CE. The radiocarbon chronology identifies use of this rural settlement well after the onset of colonial government-sponsored relocation of Indigenous people to larger settlements – congregaciones. Radiocarbon dating in historic archaeology often takes a secondary role in comparison to artifact typologies and reliance on historical records – the Basin of Mexico is no exception. Historically documented information in this work refines chronological modelling beyond stand-alone calibration. Stable isotopic study of bone samples demonstrates similar sources of dietary protein and carbohydrates. Similarity of carbon sources for bone apatite and collagen offers security that both bone fractions are viable radiocarbon dating opportunities. Recent extension of this work examines apatite radiocarbon dates (n=6) from the same bone samples when restricted collagen quality parameters are met – atomic carbon-nitrogen ratios of 3.2-3.3 and collagen yield of 10-20%. No significant difference is found between paired collagen and apatite dates for five of six individuals. Radiocarbon dates from human bone samples in this primarily terrestrial dietary context can be successfully acquired from either collagen or apatite fractions.

A03_P02

Defining the chronology of Teotônio, a pre-Columbian archaeological site in Amazonia

<u>Bentley M</u>¹, Becerra-Valdivia L¹, Kater T², Pereira Furquim L², Linscott B¹, Chivall D¹, Bronk Ramsey C¹
¹Oxford Radiocarbon Accelerator Unit, School of Archaeology, University of Oxford, Oxford, United Kingdom, ²Museu de Arqueologia e Etnologia, Universidade de São Paulo, São Paulo, Brasil

Pre-Columbian Amazonia contains a rich archaeological record indicative of complex cultural activity starting at 12,000 cal BP. The site of Teotônio, Brazil, shows a long history of human occupation, containing the oldest anthropogenic black-earth soils in the Amazon (~4,500 BCE) and early evidence of plant domestication.¹ The presence of distinct pottery traditions at the site also mark the complexity and organisation of manufacturing among ancient indigenous communities.² As such, Teotônio offers an important opportunity to better understand the human landscape in SW Amazonia during the late Holocene. Current work by the 'Human-Environment Relationships in pre-Columbian Amazonia' project aims to disentangle human-environment dynamics in the region, but study at Teotônio is limited by poor chronological constraint. To resolve this, we present the results of a radiocarbon dating and Bayesian modelling programme that defines the chronology at the site, enabling the framing of Teotônio within regional archaeological and paleoecological evidence.³ With a chronology in place, we also present the results of organic residue analysis, which point to the function of ceramic traditions through time.

- 1. Watling, et al., 2018. Direct archaeological evidence for Southwestern Amazonia as an early plant domestication and food production centre. PloS one, 13.
- 2. Almeida and Moraes. 2016. A Cerâmica Polícroma do Rio Madeira, in: Barreto, C., Lima, H.P., Betancourt, C.J. (eds.), Cerâmicas Arqueológicas da Amazônia. Rumo a uma sintese. Iphan, Brazil.
- 3. Lombardo, et al., 2018. Alluvial plain dynamics and human occupation in SW Amazonia during the Holocene: A paleosol-based reconstruction. Quaternary science reviews, 180.

A03_P03

Tar Production in the Medieval Bohemia Tracked Through Gas Chromatography and Radiocarbon Dating

<u>Brychova V</u>¹, Krofta T², Svetlik I¹, Pachnerova Brabcova K¹, Petrova M¹

¹Czech Radiocarbon Laboratory, Department of Radiation Dosimetry, Nuclear Physics Institute CAS, Prague, Czech Republic, ²Department of Information Sources and Landscape Archaeology, Institute of Archaeology of the CAS Prague, Prague, Czech Republic

Accurate dating of tar kilns is crucial not only for understanding economic history but also for historical anthropology and environmental history. The historical production of tar in Bohemia is one of the neglected topics, although tar was an indispensable substance with a wide range of applications, and evidence of its production in Bohemia is dated back to the Neolithic. Dry distillation of coniferous wood leads to different types of products. A liquid organic phase, tar, is rich in diterpenic compounds, mostly retene, abietic acid and its derivatives. From the analysis of several archaeological pottery and soil samples, it is known these compounds can survive in a depositional environment over a long time scale. In this study, we sampled charcoal, pottery, and charred resinous residue from a supposedly medieval tar kiln in Brdy mountains (Central Bohemian region). Samples of pottery and resinous surface residues were subjected to solvent extraction and gas chromatography analysis to scan organic compounds preserved. Samples of charcoal and charred residue were radiocarbon dated. Pottery and charred residues solvent extracts differed in organic compound composition and concentration. Pottery extracts were dominated by long and very long fatty acids with a contribution of diterpenic residues - retene and abietic acid derivatives. Radiocarbon dates of charcoals fall into 12th century AD. Radiocarbon dating of pottery extract or surface residue through a more compound-specific approach is under further study.

A03 P04

¹⁴C preparation protocols for archaeological samples at the LMC14, Saclay, France.

Dumoulin J¹

¹CNRS, Saclay, France

The LMC14 (Laboratoire de Mesure du Carbone 14) and its AMS ARTEMIS is the national facility dedicated to high-precision radiocarbon measurement for five French institutions (CNRS, CEA, IRD, IRSN, Ministère de la Culture). Around 4000 samples of different types of organic matters and carbonates are prepared and measured every year (Dumoulin et al. 2017). Radiocarbon analysis of very small samples (below 0.2 mg of carbon) has also been explored (Delqué-Kolic et al. 2013) and modified graphitization procedures combined with a specific protocol of measurement are now used when the carbon content is low (Moreau et al. 2020). Samples like archaeological iron (Leroy et al. 2015) as well as water (Dumoulin et al. 2013) are also analyzed. Since 2017 and our last status report, we have developed new protocols to expand our range of datable samples and take into account the expectations of new archaeological projects. The specific protocols developed for dating cellulose (wood), oxalates (rock art) or lead white (cosmetics and paintings) will be detailed. The results obtained for artifacts containing various carbon contents as paint, leather, wax or pearl will also be presented.

A03 P05

OSL mortar dating inter-comparison study. The second round of MODIS, MOrtar Dating Inter-comparison Study

Panzeri L¹, Martini M¹, <u>Maspero F</u>¹, Galli A¹, Urbanova P², Guibert P², Sanjurjo Sánchez J³

¹Dipartimento di Scienza dei Materiali, Università degli Studi di Milano-Bicocca and CUDAM, Milano, Italy, ²(2)

Archéosciences-Bordeaux UMR 6034, CNRS-Université Bordeaux Montaigne, Bordeaux, France, ³(3)

Instituto Universitario de Geología, Universidade da Coruña, A Coruña, Spain

Two physical dating methods currently enable us to date binders: radiocarbon (¹⁴C) dating and optically stimulated luminescence (OSL). During the first MODIS (MOrtar Dating Inter-comparison Study), which was initiated by specialists in ¹⁴C dating in 2014, two laboratories with expertise in luminescence dating joined the group. They attempted to apply the OSL dating to mortar samples selected for the MODIS study.

Due to the lack of a detectable signal when using "the single grain" procedure on these samples, both OSL laboratories based the dating process on the analyses of coarse quartz fractions measured by the multigrain technique. The results obtained showed general agreement both between OSL laboratories and with ¹⁴C dating results. Following this first step, a new inter-comparison experiment was set up in 2018 during the Mortar Dating International Meeting (Bordeaux, FR).

When applying the OSL method, it is necessary to evaluate environmental dose rate received by each sample. The context in situ from which mortar samples are extracted thus needs to be known when OSL dating is used, contrary to the ¹⁴C method.

As the needs for the selection of samples convenient for an inter-comparison are not the same between ¹⁴C and OSL, it has been decided to choose two different sample sets, one to share between the radiocarbon labs and one for the OSL dating. As for the OSL samples the Bordeaux group proposed three samples that were available in a sufficient quantity to be divided between participants. The data obtained within this inter-comparison will be discussed.

A03_P06

Identification of high-status medieval individuals by Bayesian chronological modelling of precise ¹⁴C ages

Meadows J^{1,2}, Lemm T¹, Homann A³, Nösler D⁴, Krause-Kyora B⁵, Jungklaus B, Hamann C²

¹ZBSA (Centre for Baltic and Scandinavian Archaeology), Kiel, Germany, ²Leibniz-Laboratory for AMS Dating and Stable Isotope Research, Christian-Albrechts-University Kie, Kiel, Germany, ³Städtisches Museum Schloß Salde, Salzgitter, Germany, ⁴Archäologische Denkmalpflege des Landkreises Stade, , Germany, ⁵Institute of Clinical Molecular Biology (IKMB), Christian-Albrechts-University Kie, Kiel, Germany

Excavations in 1992-93 at the Harsefeld abbey, in Stade, northern Germany, recovered 26 skeletons from the burial ground of the Udonen family. Graves were unmarked, but the Udonens, also known as the Counts of Stade, are historically well-documented. The first count buried at Harsefeld was Heinrich (d.975/976). Count Udo was killed during a Viking raid on Stade in 994; his nephew Siegfried was injured in the same attack and died a few months later. Other documented burials include women born elsewhere, such as Mechtild of Swabia (died before 1016). The latest burials predate a destructive fire recorded in 1236.

We aim to identify each skeleton with a historically documented individual, through a combination of osteological, genetic, and isotopic analyses, including Bayesian chronological modelling to estimate the birth and death dates of each skeleton. After recording age-at-death, sex, height, pathologies and trauma, each individual was sampled for ancient DNA, 14 C, δ^{13} C, δ^{15} N, δ^{34} S and 87 Sr/ 86 Sr isotope analyses. Where possible, we dated both a rib and a petrous bone from each individual.

Our chronological model combines 47 ¹⁴C ages (with allowance, where indicated, for modest ¹⁴C reservoir effects) with collagen residence time estimates based on age-at-death and the skeletal element dated, stratigraphic constraints on the sequence of burials, and archaeogenetic kinship constraints on the maximum differences between birth dates. It produces a chronology with generational precision, permitting individual skeletons to be identified using complementary information such as their region of origin, injuries or illnesses.

¹⁴C dating of mortars from Monastery Hill in Tyniec, Poland

Michalska D¹, <u>Krapiec M</u>², Gronowski M^{3,4}, Łyczak M^{5,8}, Bojęś-Białasik A⁶, Kamińska M⁷

¹Institute of Geology, Faculty of Geographical and Geological Sciences, Adam Mickiewicz University, Poznań, Poland,
²AGH University of Science and Technology, Faculty of Geology, Geophysics and Environmental Protection,
Mickiewicza Av. 30, 30-059 Krakow, Poland,
³Benedictine Abbey, Tyniec, Poland,
⁴Institute of History, University of
Silesia, Katowice, Poland,
⁵Archaeological Company FRAMEA, ul. Na Kozłówce 4a/10, 31-664 Krakow, Poland,
⁶History of Architecture and Monument Preservation, Faculty of Architecture, Krakow University of Technology, ul.
Kanonicza1, 31-002 Kraków, Poland,
⁷Institute of Art History of the Jagiellonian University, ul. Grodzka 53, 31-001
Krakow, Poland,
⁸Institute of Archeology, Department of Historical Sciences, Cardinal Stefan Wyszyński University, ul.
Wóycickiego 1/3, 01-938 Warsaw, Poland

The Benedictine Abbey in Tyniec is the oldest existing monastery in Poland (11 cent. AD). The historic walls of the Monastery have survived to this day and crown the limestone hill on the Vistula River. The geological structure of the surrounding area is of great importance and is reflected in the composition of the mortars.

In vicinity of Tyniec one may observe outcrops of Upper Jurassic limestones represented by two facies: bedded limestones with cherts and massive limestones. Recently, it was discovered that the monks not only fortified the Tyniec hill but also partly built it up with loess. Additionally, a massive "stepped" stone platform was later built to strengthen the edge of the hill.

The mortars radiocarbon dating provides the first attempt to obtain the wide chronology of the extension of Tyniec walls. Petrographic analyzes were used to characterize the binder and aggregate from mortars, especially to identify the carbonaceous components like not totally burnt limestone fragments, lime lumps or secondary calcite. Mortars were analyzed using scanning electron microscope with electron dispersive spectrometer and polarizing light microscope. Different pretreatment and sample separation protocols were applied to illustrate the huge influence of mortar components and the local geological structure on the ¹⁴C measurement results.

In addition to the mortar analyzes, ¹⁴C measurements were also made for charcoal and wood samples from Tyniec Abbey. Radiocarbon dating was performed on the selected fractions using Accelerator Mass Spectrometry (AMS).

A03 P08

Modeling the actual age of mortars - experimental research

Michalska D¹, Pawlyta J²

¹Adam Mickiewicz University, Institute of Geology, Poznań, Poland, ²Department of General Geology and Geotourism, AGH University of Science and Technology Faculty of Geology, Geophysics and Environmental Protection, Kraków, Poland

An attempt to model the age of mortar were made on the basis on the results of the 14 C measurement for the bulk material together with the knowledge of the δ^{13} C of various mortar components. In order to assess the variability of isotopic fractionation during CO_2 absorption by mortar carbonates depending on the environmental conditions and the type of mortar, the δ^{13} C measurements were performed for the mortars from Kraków. Similar analyzes were also carried out for natural limestone and for the experimental mortars produced in the laboratory. Knowledge about the isotopic fractionation allows to make an age correction for mortars along with the verification of such correction based on the percentage estimation of the carbonate components. The obtained results were compared with earlier attempts to model the age of mortars from Sussita (Sea of Galilee).

Radiocarbon dating and Sr isotope analysis of cremated bones excavated from the Ishibotokedani site in Binmanji Temple, Shiga prefecture, Japan

Sawada R¹, **Minami M**¹, Wakaki S²

¹Nagoya University, Nagoya, Japan, ²KOCHI JAMSTEC, Nangoku, Japan

Numerous cremated bones have been excavated from the Ishibotokedani archaeological site located adjacent to Binmanji Temple, Shiga Prefecture, Japan. It is believed that people related to Binmanji, such as the priests of Binmanji and the surrounding residents, were buried here. Since Binmanji was burned down in the 16th century, few documents remain. Thus, in this study, ¹⁴C dating, Sr isotope analysis, and trace element analysis of approximately 30 cremated remains excavated from survey areas A, D, F, and G were conducted to investigate the age and residence of the buried people.

Radiocarbon dating of the cremated bones from the Ishibotokedani site indicate that the cremated bones from area A date from the 12th to 14th century, those from area D belong to the 13th century, those from area F date from the 12th and 13th centuries, and those from area G date back mainly to the 14th century. This is consistent with the period of activity of Binmanji (12th–16th centuries), as established by ancient documents.

The ⁸⁷Sr/⁸⁶Sr isotopic ratios of the cremated bones ranged from 0.70938 to 0.71079. Compared to the ⁸⁷Sr/⁸⁶Sr isotopic ratios of the geochemical samples of the surrounding areas, the cremated bones showed 87Sr/86Sr isotopic ratios similar to soil of the Ishibotokedani (0.70942–0.71040) and the adjacent Seri River water (0.70926–0.71002). This indicates that the people buried in the Ishibotokedani site mainly ate crops grown in the vicinity of Binmanji or the Seri River.

A03 P10

Extensive survey on radiocarbon dating of organic inclusions in historical mortars

<u>Pachnerova Brabcova K</u>¹, Kundrat P¹, Krofta T¹, Suchy V¹, Petrova M¹, John D^{1,2}, Kozlovcev P³, Kotkova K³, Fialova A³, Valek J³, Svetlik I¹

¹Nuclear Physics Institute of the CAS, Praha, Czech Republic, ²Faculty of Nuclear Sciences and Physical Engineering, Czech Technical University in Prague, Praha, Czech Republic, ³Institute of Theoretical and Applied Mechanics of the CAS, Praha, Czech Republic

Direct radiocarbon dating of historical mortars remains challenging due to complex processes during mortar maturation that can mislead the interpretation. Organic inclusions in the mortars, such as charcoals, seeds, microbiotas, wood, or bones, represent important alternative or complementary dating material providing the date as a terminus post quem.

This work adds to the determination of how reliable such organic inclusions can be for radiocarbon dating. For the analysis, we have collected 129 charcoals from five different early to late medieval castles and churches located throughout the Czech Republic. The architectural objects were chosen to meet the following criteria: i) known age documented in written sources and optimally also obtained through other dating method or complemented with radiocarbon dating of samples other than mortar-derived ones; ii) known history of repairs and maintenance; iii) age falling before 1650 AD to avoid issues related to inconclusive radiocarbon dating in the early modern period.

Most of the samples were measured on our new AMS MILEA. The results demonstrate that a notable fraction of inclusions corresponds to charcoals from old wood, often a few hundred years old when raising the object, presumably originating from timber cut-offs. For some sites we found several samples related to later repairs, despite trying to limit the sampling areas to original masonry only. Based on this comprehensive study, we recommend a rather high number of samples be collected per dated object, at

least 5 - 10 for sites with uncomplicated building history, so that radiocarbon dating provides reliable results.

A03 P11

¹⁴C dating for MODIS 2 carbonate mortars – do time and size matter?

Pawełczyk F¹, Gu Y^{2,3}, Piotrowska N¹, Ustrzycka A¹, Hajdas I²

¹Institute of Physics - CSE, Silesian University of Technology, Gliwice, Poland, ²Laboratory of Ion Beam Physics, ETHZ, Zurich, Switzerland, ³Laboratory of AMS Dating and the Environment, School of Geography and Ocean Science, Nanjing University, Nanjing, China

In our work we present a procedure applied for the ¹⁴C dating of three samples of mortars from the project MODIS 2, which is an international laboratory intercomparison. The samples selected for the exercise comprise three different mortars:

- 1) MODIS2.1: mortar from Finnish medieval church
- 2) MODIS2.2: mortar from Swedish medieval church
- 3) MODIS2.3: mortar from Spanish early Christian basilica

The material was sieved and three different size fractions were separated: <45 micrometers, 45-63 micrometers, and >63 micrometers. The composition of each fraction was analyzed under the binocular microscope.

The mortar carbonates were dissolved under vacuum conditions, using H_3PO_4 and the CO_2 coming from following time intervals was collected: 1-3sec, 4-6sec, 7-9sec, 10-12sec, and remaining CO_2 . Also, the bulk carbonate from each size fraction was dated. In general, a growing age trend was observed with older age for samples from later time intervals, and the oldest for remaining CO_2 fraction. The CO_2 was graphitized using AGE system at the ETH or Gliwice, or introduced to gas ion source of the MICADAS at the ETH. Moreover, the charcoal fragments were discovered in a sample MODIS2.2. The age of this charcoal was measured in ETH and Gliwice laboratories to 1090±30 BP and 950±30 BP, respectively. For comparison, the age of carbonate fractions for this mortar ranged from 600 to over 2000 BP.

In addition, the stable isotope IRMS measurements were performed for carbonates from different size fractions and bulk material using the CF-IRMS IsoPrime coupled to Multiflow device.

A03_P12

Radiocarbon dating of poorly preserved bones from church of St. Wenceslav in Plasy, Czech Republic

<u>Petrova M</u>¹, Sneberger J^{1,2,3,4}, Brychova V¹, Pachnerova Brabcova K¹, Svetlik I¹

¹Department of Radiation Dosimetry, Nuclear Physics Institute of the Czech Academy of Sciences, Prague, Czech Republic, ²Department of Genetics and Microbiology, Faculty of Science, Charles University in Prague, Prague, Czech Republic, ³Department of the History of the Middle Ages of Museum of West Bohemia, Pilsen, Czech Republic, ⁴Department of Natural Sciences and Archaeometry, Institute of Archaeology of the Czech Academy of Sciences, Prague, Czech Republic

Rescue archaeological research at the Church of St. Wenceslav in Plasy, Czech Republic, revealed a burial ground. Radiocarbon dating of the remains (teeth, bones) was used to explore the history of the premonastic settlement. Due to a low quality of the analysed samples, a standard acid-base-acid sequence was followed by ultrafiltration to purify gelatinized fraction. The yields, dates and stable isotope ratios of non-ultrafiltered and ultrafiltered samples are compared and the impact of the ultrafiltration on the data interpretation is discussed.

Stone-paved cellars in the Danish Stone Age? Research potential and strategies for radiocarbon dating at rescue excavations

Brinch M¹, Philippsen B¹, Groß D¹, Kanstrup M²

¹Museum Lolland-Falster, Nykøbing F, Denmark, ²Aarhus AMS Centre, Department of Physics and Astronomy, Aarhus University, Aarhus, Denmark

We present the excavation results from a Middle Neolithic site associated with the Funnel Beaker Culture. During a rescue excavation, a recessed area was recorded within two overlaying house features which was constructed using different sized pebbles. The arrangement and form of the feature clearly indicated anthropogenic origin and is understood as belonging to one of the house structures. Consequently, it is interpreted as a paved cellar – a feature yet unknown from Danish Stone Age archaeology. Additional features at the site were several pits and postholes that indicated the presence of a palisade or fence structure with up to seven different parallel lines. Indirect dating of the features through associated organic material has shown that the fence or palisade has existed contemporaneously with the houses and can, hence, be interpreted as belonging to the same settlement. We present the results from the excavation and integrate the site in its regional archaeological landscape.

Finally, we discuss the radiocarbon dating strategies for rescue excavations both on the scale of individual features as well as for entire development projects. We show how targeted sampling and analysis can preserve the research potential of those sites for future research.

A03 P14

Human occupation sequence in the context of an archaeological site of Salapunku (Cusco, Peru)

Sieczkowska D¹, <u>Rakowski A</u>², Pawlyta J⁴, Bastante J³,1 Ziółkowski M¹

¹ University of Warsaw, Warsaw, Poland, ²SUT, Gliwice, Poland, ³National Archaeological Park of Machupicchu, Cusco, Peru, ⁴AGH, Kraków, Poland

The Salapunku archaeological site is located within the Machupicchu National Archaeological Park in the Cusco area of Peru. Although Salapunku is located in the area of the Inca-related Machupicchu, within the archaeological site during the archaeological work it was possible to distinguish different moments of multicultural presence which allowed the creation of a sequence of human occupation in the study region. The Inca occupation phase is the most recent use of the site, but in earlier periods there were human settlements in this area associated with the Killke culture and even with human presence during the local formative period. Previous research on the chronology of the site was based on typological analyses of pottery and other artefacts found during excavations. With research extended by radiocarbon analyses, it has been possible to establish a chronology of settlement development in this part of the Park considered to be the gateway to the Cordillera of Vilcabamba. The purpose of this presentation is to show the recent findings of human presence in this area and its possible relation to climate/environment changes.

Radiocarbon dating of Herodium, the Mountain palace-fortress, and the monumental burial complex of Herod the Great

<u>Regev L</u>¹, Porat R², Botosh A², Leibner U², Regev J¹, Mintz E¹, Boaretto E¹

¹Weizmann Institute of Science, Rehovot, Israel, ²The Hebrew University of Jerusalem, Jerusalem, Israel

The site, situated between Jerusalem and the Judean Desert, comprises several palaces and complexes built mostly by Herod the Great, who ruled over the region during the first century BC under Roman rule. The main palace was built as a round fortress, five stories high (ca. 25 meters), with a tower reaching the estimated height of up to 40 meters. The fortress was later covered by earth, creating a volcano-like shape. The site was excavated for over 50 years, mainly under the late archaeologist prof. Ehud Netzer from the Hebrew University in Jerusalem.

Five main construction phases were identified at the fortress: (a) its construction; (b) modifications at the east wing of the complex; (c) its covering by earth, forming the artificial mount; (d) the Great Revolt (70 AD); and (e) a later phase of tunnel diggings during the Bar-Kokhba revolt (2nd century AD). Due to the region's dry climate, abundant wooden remains were found at the site. From which, in-situ construction beams from all construction phases were sampled and dated by cellulose extraction and radiocarbon dating. The results confirm that the first three phases are contemporaneous to Herod's reign, while the source of the beams used by the rebels during the Bar-Kokhba revolt is somewhat surprising.

A03 P16

Modelling temporality of a Late Neolithic-Early Iron Age cemetery at Mang de Bargen, Germany

Rose H¹, Schaefer-Di Maida S², Kneisel J²

¹Zentrum für Baltische und Skandinavische Archäologie (ZBSA), Schleswig, Germany, ²Institute of Pre- and Protohistoric Archaeology, CAU Kiel, Kiel, Germany

Round barrows dating to the Late Neolithic and Early Bronze Age form visible funerary monuments in today's landscape. They have revealed extraordinary oak-coffin graves that can be relatively dated using typo-chronology, but little is known about the temporal relationships between these and later, more inconspicuous, re-burials in the barrows. We present new results from the Late Neolithic-Early Iron Age cemetery at Mang de Bargen in Schleswig-Holstein, Germany. Here, a group of round barrows were first recorded in the 1970s and part of these were excavated over several field campaign in the last two decades. We returned to the site in 2016-2019 and conducted thorough investigations and revisions of 20 barrows and an urn cemetery. This also resulted in 106 new radiocarbon dates on 84 burials and related features, offering the first possibility to model the temporality of a dynamic funerary landscape in northern Germany. There is no direct stratigraphic link between the barrows at Mang de Bargen, but individual barrows are often constructed in more phases and using Bayesian chronological modelling we estimate their temporal relationships and if primary and secondary burials were interred within 'living memory' of the last internment. More changes of funerary practices can be detected at Mang de Bargen, such as the introduction of cremation and the transition from burials in barrows to burials in flat graves.

Variation of ¹⁴C results from different samples in an archaeological context

<u>Seiler M</u>¹, Svarva H¹, Rzadeczka-Juga I¹, Nadeau M¹

¹The National Laboratory for Age Determination, NTNU University Museum, Trondheim, Norway

Archaeological contexts contain different materials and pieces that can be selected for radiocarbon dating. While one tries to select short lived samples such as plant material, charred seeds, or charcoal from shorter lived tree species, the connection between the samples selected and the event to be dated might be uncertain. Financial considerations prevent the measurement of multiple samples to date single contexts such as a cooking pit or even a dwelling. The small amount of material needed by AMS often leads to the measurement of only one charcoal piece or hazelnut shell.

We analysed different pieces from large samples of mixed charcoal from archaeological excavations in Norway to assess how representative a single piece is for the sample as a whole. We found that the results for the same wood species do match well, while there is a discrepancy between different wood species, particularly older ages for longer-lived tree species, which could be explained by the 'old wood' effect. The magnitude of this effect varies between sites, and is more relevant for radiocarbon results with smaller uncertainties.

A03 P18

Archaeological sandals from the Balsas Basin, Mexico

Solis C¹, Martínez Carrillo M², <u>Rodríguez Ceja M</u>¹, Xelhuantzi López M³, Alvarado J³, Sánchez Martínez F⁴

¹Instituto de Física. Universidad Nacional Autónoma de México., Mexico City, Mexico, ²Facultad de Ciencias,
Universidad Nacional Autónoma de México., Mexico City, México, ³Subdirección de Laboratorios y Apoyo Académico,
INAH., Mexico City, México, ⁴Centro INAH Morelos, Cuernavaca, Mexico, ⁵Licenciatura en Ciencia Forense, Facultad
de Medicina, UNAM., Mexico City, México

The Balsas basin is a critical geographic region for studying the settlement and development of ancient human populations in Mexico. Located in the central region of Mesoamerica, the Balsas River basin offered numerous rock shelters that provided safe shelter, water, and stable climatic conditions to hunter-gatherer groups that, according to archaeological evidence, would have settled 4,000 years B.P. In the Balsas Basin caves, professional searchers of archaeological pieces collected various objects, including vegetable fiber sandals (huaraches). The exact place of origin and context from which the pieces were extracted are unknown.

In 1999 the collection of fifty huaraches was recovered by the National Institute of Anthropology and History (INAH), which constitutes one of the largest collections of pre-Hispanic huaraches recorded. The first study of the pieces consisted of the macroscopic analysis of each of the huaraches, considering the degree of conservation, structure, morphology, size, and particular characteristics. Then, the botanical identification of the vegetable fibers used to manufacture the pieces was carried out to determine the origin of the plants used for its manufacture. Because there are pieces of different sizes and in different conservation conditions, the possible use of the pieces was determined.

This work presents the radiocarbon-AMS dating of the vegetable fibers of several huaraches to provide information that allows them to be in time within the Balsas Basin area. In the complementary analyses, we sought to identify the plants by stable isotope analysis and to confirm it with genetic analysis.

Dating the concealment of the Library Cave at Mogao, Dunhuang

<u>Staff R</u>¹, Liu R², Pollard M³, Zhao Y⁴, Yu Z⁴, Zhang X⁴, Monteith F⁵, Guo Q⁴, Su B⁴

¹University Of Glasgow, Glasgow, United Kingdom, ²British Museum, London, United Kingdom, ³University of Oxford, Oxford, United Kingdom, ⁴Dunhuang Academy, Dunhuang, China, ⁵Northwest University, Xi'an, China

The Mogao Grottoes, located 25 km southeast of Dunhuang in Gansu province, China, contain 735 caves carved into the rock. Of these, the majority of the 492 caves in the south section contain Buddhist art, many of which are regarded as the finest extant early Buddhist paintings in China. As a UNESCO World Heritage Site situated at the eastern end of the Silk Road, the construction and development of the Dunhuang Grottoes vividly illustrates the arrival and transformation of Buddhism in China. However, the full potential of the site to inform the broader field of Buddhist studies is limited by a paucity of robust chronology.

Chief among the grottoes, the so-called 'Library Cave', accidentally rediscovered in 1900, housed >60,000 manuscripts and drawings dating from the first millennium CE. Among the myriad questions relating to the site, the date of the concealment of the Library Cave has been highly debated; it is directly linked to the nature of the manuscripts recovered from the Cave, and the broader historical context in which the concealment took place.

Here, we apply radiocarbon dating and Bayesian chronological modelling to narrow down the timing - and hence the likely circumstances - of the Library Cave's concealment.

A03 P20

AMS, Historical and Archaeological Dating in the Oponice Castle

<u>Styková B</u>^{1,3}, Styk M², Světlík I¹, Megisová N¹, Petrová M¹, Repka D²

¹Department Of Radiation Dosimetry, Nuclear Physics Institute CAS, Řež - Husinec, Czech Republic, ²Department of Archaeology Faculty of Arts, Constantine the Philosopher University in Nitra, Nitra, Slovakia, ³Regional centre Banská Bystrica, The Monument Board of the Slovak Republic, Banská Bystrica, Slovakia

The 5th season of Oponice castle excavation in 2022 was located in the lower castle's courtyard. There was discovered original clay floor strongly burned with charred plank and a rectangular stone-brick structure laying on it. This structure has collapsed upper part with a fallen low brick arc. In whole space were also documented numerous stove tiles fragments same as the discovery of one clay mould for the production of front heating walls of chamber tiles. Based on it this structure was identified as a pottery kiln dated to the second half of the 16th till the first half of the 17th century AD by the findings from excavated layer, which was probably related to kiln destruction. At the same time, the written sources mention big fire in 1645 caused the end of the castle. Different types of samples were collected for AMS dating to CRL (Czech Radiocarbon Laboratory) in Prague. This sampling was focused on site formation process determination of pottery kiln use and the way of its destruction. Applying of Bayesian analysis tent to improve overall dating and historical events recreating. The results and methodology of the radiocarbon dating will be presented in poster form.

Radiocarbon dating of multiple materials for clarifying of medieaval settlement formation in the outskirts of Prague Castle (CZ).

Tomanová P1

¹Nuclear Physics Institute CAS, Řež, Czech Republic, ²Insitute of Archaeology of the CAS Prague, Prague, Czech Republic

An archaeological excavation was conducted in the street U Kasáren in the Prague Castle area (Czech Republic) in 2020. The excavation revealed an intensive early mediaeval settlement of the 10th-13th centuries. The settlement features included different types of house constructions (sunken houses, masonry construction), pyrotechnical (possibly metallurgical) features and evidence of several fire events. Archaeobotanical analysis of selected samples proved the earliest evidence of viniculture in the outskirts of Prague Castle area, showed presence of some extinct species of weeds and contributed to the research of crops distribution in the early mediaeval central places.

However, the archaeological data allow only a rough dating of the researched settlement and it is hardly possible to date individual formation phases of the site. Only a limited number of datable pottery fragments was obtained. Furthermore, the research circumstances allowed us to document the area in separate sections, which makes it difficult to interconnect the data in a clear picture of the formation of the site.

This poster shows how radiocarbon dating of various materials (animal bones, archaeobotanical samples) can clarify the absolute chronology of the formation of the settlement in the outskirts of Prague Castle (e.g. the shift from log houses to masonry constructions, the beginnings of metallurgical activity and the viniculture in this area).

A03 P22

Pre-screening of lime mortars for ¹⁴C dating – Preliminary results

Wojcieszak M^{1,2}, Fontaine L¹, Hayen R¹, Elsen J³, <u>Van den Brande T</u>¹, Oostvogels A¹, Ligovich G¹, Rich M¹, Boudin M¹

¹Royal Institute for Cultural Heritage (KIK-IRPA), Brussels, Belgium, ²Evolutionary Studies Institute (ESI), University of the Witwatersrand, Johannesburg, South Africa, ³Department of Earth and Environmental Sciences, KU Leuven, Leuven, Belgium

The oldest known use of lime mortars dates from the Neolithic period. The production process incorporates atmospheric CO_2 and gives rise to the formation of calcium carbonate (CaCO₃). Radiocarbon dating of anthropogenic lime carbonates was first developed in the 60's. These first results were very promising and the French researchers Jacques Labeyrie et Georgette Délibrias already pointed out that microscopic observation should be performed to check out the eventual presence of foraminifera (microfossils) susceptible to false the date result, since they are made of very ancient carbonates. Other types of carbonates can be present in mortars because of the mortar formation process and possible subsequent weathering. These carbonate contaminations are unburnt or underburnt limestone used for lime production, fossil carbonates such as shell fragments in sands, reused limestone and mortars crushed and used as aggregate, or specific minerals containing carbonates. Their presence results in a lower ¹⁴C/¹²C ratio which generates an older date, as they are radiocarbon free. Another category of carbonates are secondary carbonate deposits, which can cause an increase of the ¹⁴C/¹²C ratio but can also incorporate older carbon. Using the stepwise acid hydrolysis method on the binder (and when possible pure lime inclusions dating), this project aims to develop a pre-screening method, by means of different analytical techniques such as polarized light microscopy, Fourier transformed Infrared spectroscopy, cathodoluminescence and thermal analyses (TGA-DSC) to verify the "mortar quality" in order to decide whether the radiocarbon date will be reliable or not.

AMS dating data on excavations at the citadel of Yaroslavl solve the dispute between archaeologists and dendrochronology specialists

Engovatova A¹, Cherkinsky A³, Matskovsky V², Karpukhin A¹, <u>Zazovskaya E</u>²

¹Institute of Archaeology RAS, Moscow, Russian Federation, ²Institute of Geography RAS, Moscow, Russian Federation, ³University of Georgia, CAIS, , Athens

During the excavations in 2004-2022 in the citadel of Yaroslavl (Central part of Russia) were found nine sanitary burials of the time of the defeat of the city in 1238. For a more accurate dating of the event, samples were taken from each of the nine burials. All 37 AMS dates (UGAM) obtained fit into a narrow data interval - when all the results were combined, a calibrated date of 1221–1259 was identified. In 2020, archaeologists unearthed another burial. Dendro dates obtained for this burial did not coincide with previous results. Ten oak samples have been successfully cross-dated, and a floating chronology 177 years long has been built. As there is no oak tree-ring chronology for Yaroslavl, this floating chronology has been cross-dated with the nearest Smolensk oak chronology (~600 km distance to South-West from the city of Yaroslavl). However, cross-dating statistics is not high enough to be sure in the acquired dating. For this reason, we additionally obtained AMS dates (IGAN) for 17 wooden samples. Some of the ¹⁴C dates overlap with the obtained tree-ring dates, others do not. We also failed to obtain convergence on wiggle-matching (D_Sequence, OxCal) for all the 17 AMS dates. Those seven dates that converge, however, show earlier period for the outermost rings of the floating oak chronology: AD 1214-1232 (95.4%). Despite some contradictions in the acquired AMS dating results, we found better correspondence of the seven converged dates to the archaeological context, than to

A04 Archaeology and radiocarbon dating at the limit of the method

A04_01

The challenge of dating archaeological sites beyond ~35,000 BP: Progress and future prospects in radiocarbon dating the Palaeolithic of Eurasia

Higham T¹

¹University of Vienna, Vienna, Austria

the obtained dendrochronological dates.

The Late Middle and Early Upper Palaeolithic (~35-60,000 years ago), is a key period in human evolution. It witnesses the transition between a Neanderthal (and Denisovan) dominated Eurasia, to one which was exclusively occupied by Homo sapiens. Recent discoveries in archaeology, genomics, isotope geochemistry, residue analysis, dating science and more, have revolutionised our understanding of the period. We now have some answers to what were seemingly intractable big questions; did Neanderthals and Homo sapiens meet? How long was their overlap, and where did they encounter one another? But

other answers remain elusive. At the heart of many of these uncertainties lies a robust chronology, so radiocarbon dating has been at the centre of many debates in the Palaeolithic.

There are many 'legacy' radiocarbon measurements from the Palaeolithic that are often erroneous. Over the last 10-15 years, however, there have been significant improvements in routine dating science. Three principal areas will be discussed. First, we have better measurement precision, lower backgrounds in accelerators and more accurate subtraction of laboratory derived ¹⁴C pretreatment backgrounds. Second, improvements in chemical pretreatment and sample decontamination of bone proteins and charcoal samples. Third, the application of Bayesian age modelling coupled with newer extended calibration curves, allowing the inclusion of dates from other methods and archaeological prior information.

Over the last few years >1,000 samples from more than 100 key European Palaeolithic sites have been obtained. I will discuss the results from some of these key sites across Eurasia in the wider context of the Palaeolithic.

A04 02

Investigating the co-occurrence of Neanderthals and Modern Humans in Belgium through direct compound-specific radiocarbon dating

<u>Devièse T</u>^{1,2}, Abrams G^{3,4}, Pirson S⁵, De Groote I^{6,7}, Flas D^{8,9}, Semal P¹⁰, Di Modica K^{3,11}, Higham T^{12,2}

¹Aix Marseille University, Aix en Provence, France, ²University of Oxford, Oxford, United Kingdom, ³Espace Muséal d'Andenne, Andenne, Belgium, ⁴Leiden University, Leiden, Netherlands, ⁵Agence wallonne du Patrimoine, Namur, Belgium, ⁶Ghent University, Gent, Belgium, ⁷Liverpool John Moores University, Liverpool, United Kingdom, ⁸University of Liège, Liège, Belgium, ⁹University Toulouse Jean-Jaurès, Toulouse, France, ¹⁰Royal Belgian Institute of Natural Sciences, Brussels, Belgium, ¹¹University of Namur, Namur, Belgium, ¹²University of Vienna, Vienna, Austria

Determining the timing of the transition between Neanderthals and anatomically modern humans (AMHs) is crucial in archaeology and paleoanthropology. While there is increasing evidence of admixture and co-existence of the two hominin species in Central and Eastern Europe, Belgium might show a different scenario. This key area sits at the crossroads between Palaeolithic cultural facies with influences from eastern, western, and southern Europe intermingling during the Late Middle Palaeolithic and the Middle to Upper Palaeolithic transition.

Recent DNA analyses seem to indicate a hiatus in the occupation of the Belgian territory. However, this interpretation is based on a limited number of hominin specimens because of their scarcity in the archaeological record. Mousterian and Aurignacian industries, associated with Neanderthals and AMHs respectively, are present in much larger quantities. They can also be used to define the timing of both occupations.

In this presentation, we report new compound specific radiocarbon dates obtained on Neanderthal specimens from Spy, Engis and Fond-de-Forêt. We also reevaluate the chronology of the latest Mousterian and earliest Aurignacian evidence. This new data tends to confirm that there may have been a hiatus implying that Neanderthals and Anatomically Modern Humans did not co-exist in this region. These results also show how much sample preparation can impact on the AMS measurements when specimens have been heavily preserved with conservation materials (which is often the case for human remains) and their age is approaching the limit of radiocarbon dating.

MIS-3 megafauna radiocarbon ages and blank control practices at ANSTO

<u>Levchenko V</u>¹, Bertuch F¹, Smith A¹, Jenkinson A¹, Hua Q¹, Williams A¹, Kumar S¹, Yang B¹
¹ANSTO, Kirrawee DC, Australia

Reliable radiocarbon age determinations close to the limit of the method are dependent on effective pre-treatment and correction for extraneous carbon added during processing. At ANSTO this is controlled by processing continuous stream of various representative blanks to characterise major pre-treatment protocols – ABA, cellulose purification, collagen extraction, also combustion-graphitisation and hydrolysis-graphitisation procedures.

Special collections of materials with ages beyond the radiocarbon limit are used – charcoal from a million-year-old tree, MIS-5 bones from permafrost, subfossil wood, IAEA-C1 marble, and Ceylonese and commercial graphite. For graphitisation blank, the cylinder with geological CO_2 is used. Blanks ranging from ten of μg to several mg of carbon are processed for every AMS radiocarbon run. For each material and procedure, a mass dependence function for blank pMC values is constructed on the subset including the most recent few-month determinations. This allows building a representative statistic for blank variability and flags any significant blank level increases prompting a review of relevant laboratory activity.

As an example, we present the dating of Diprotodon remains from Lake Callabonna in South Australia. Diprotodons became extinct around 70-50 ka BP, period also noted by the arrival of humans to Australia. To better understand the extinction causes, a reliable determination of the species extinction time is required. To date, all diprotodon remains returned infinite ages beyond the radiocarbon limit. Our studied specimen after a set of determinations produced a finite age of 51,900+/-1200 radiocarbon years, bringing the species survival time to the times of human presence in Australia.

A04_P01

"Here we go again": the inspection of collagen extraction protocols and why compound specific radiocarbon dating matters

Devièse T¹

¹Aix Marseille University, Aix en Provence, France

The radiocarbon dating of archaeological bones is widely used across various fields of research, most notably by palaeontologists, palaeoecologists, archaeologists and geneticists. The radiocarbon dates obtained on fossils allow scientists to reconstruct ancient ecosystems and the rates of faunal change in these communities as well as human occupations. Reliable and accurate dating is therefore hugely important. However, there are major challenges when radiocarbon dating bone specimens over 30,000 years old and there is considerable uncertainty over some of the published data.

The method currently used by most radiocarbon laboratories to date archaeological bones was developed in the 1970s and consists of a succession of chemical treatments designed to extract and purify collagen before measurement on the Accelerator Mass Spectrometer. However, for radiocarbon results to be reliable, samples must be totally free of contamination, and this is not always possible, particularly when the contaminants are cross-linked to the collagen. An alternative is to use the so-called "compound specific dating approach", focusing on a single amino acid, hydroxyproline (HYP) within the bone collagen. Extracting and dating HYP results in excellent levels of reliability that no other method can provide.

After a description of the method's principle, this presentation will show, with several case studies, that many dates published in the literature and obtained after less robust pretreatments can be highly inaccurate. Such errors can then lead to incorrect interpretations of dispersal and rates of change in the archaeological, climatic, and evolutionary records, as the dates are the foundation of all these models.

A04 P02

Comparison of radiocarbon dates of animal bones from Vindija and Mujina Pećina caves

<u>Krajcar Bronić I</u>¹, Karavanić I², Sironić A¹, Vukosavljević N², Banda M², Smith F³, Radović S⁴

¹Division of Experimental Physics, Ruđer Bošković Institute, Zagreb, Croatia, ²Department of Archaology, Faculty of Humanities and Social Sciences, Zagreb, Croatia, ³Department of Sociology and Anthropology, Illinois State University; Department of Anthropology, University of Colorado, Normal; Boulder, USA, ⁴Institute for Quaternary Paleontology and Geology of Croatian Academy of Sciences and Arts, Zagreb, Croatia

Bone samples from two caves, Vindija (Donja Voća, NW Croatia) and Mujina Pećina cave (Plano, near Kaštela, Dalmatia), were selected for radiocarbon AMS dating at the Ruđer Bošković Institute (RBI) laboratory. Collagen extraction yielded >1% of collagen for 10 samples. From six samples the collagen yield was lower than 0.5 % and those bones could have not been dated. The low collagen yield (<1%) may produce an underestimated radiocarbon age. For comparison, bone samples were sent to Oxford Radiocarbon Accelerator Unit (ORAU) for radiocarbon dating with an additional step of ultrafiltration (UF) to select collagen fraction having molecules larger than 30 kDa. Four of them could not have been dated due to low collagen yield, five were dated in spite of low yield, and only three of them were successfully dated.

The results of delta-¹³C values of bone samples showed the same range in both RBI and ORAU laboratories, between -18.3 ‰ and -21.8 ‰, which are typical values for bone collagen. Radiocarbon conventional ages of these limited number of bone samples were comparable.

The preliminary results presented here point to the possible obstacles in radiocarbon dating of late Middle Paleolithic samples: bones are not well preserved, yield of collagen is often low, and the age is close to the limit of the radiocarbon method.

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A04 P03

Chronology of the Barabinskaya culture (south of Western Siberia): Early Neolithic

Molodin V¹, Mylnikova L¹, Parkhomchuk E¹, Reinhold S², Nenakhov D¹

¹Institute of Archaeology And Ethnography SB RAS, Novosibirsk, Russian Federation, ²German Archaeological Institute, Berlin, Germany

In the southern part of Western Siberia Early Neolithic sites were discovered, which are characterized by flat-bottomed pottery. This allowed to distinguish the Barabinskaya culture. It is represented in settlements and ritual complexes, has a specific economic, as well as a certain set of stone and bone artifacts. The presentation offers an overview of the radiocarbon dates of the Barabinskaya culture, obtained at the Curt-Engelhorn-Centre of Archaeometry (Germany) and at the "Accelerator mass spectrometer" BIMP SB RAS (Russia). In total 32 samples were dated.

Dates obtained from the Vengerovo-2 site: (29409) 7510±26, (NSK-02843) 72014±139 BP. 19 samples have been dated from the Tartas-1 site. Six of dates origin from the dwellings: early – (NSK-1645) 7532±97, late – (29403) 7449±23 BP. Another 13 dates are related to fish conservation pits. The

sample from the pit No 991 provided an early date (26158) of 8034±36 BP. For the pit No 1229 a date (29407) of 7344±24 BP was obtained.

A sanctuary at the Ust-Tartas-1 site dates from (NSK-2392) 7610±82 to (NSK-2394) 6389±57. For the pits No 18 and No 27, that accompanying the sanctuary, the following dates were obtained: (NSK-2181) 6394±64 and (NSK-2179) 7246±190 BP respectively. "Fish pits" No 7 and No 65–66 were dated of (39313) 7936±23, (39314) 7726±24 BP, (NSK-2182) 8170±71 and (NSK-2207) 8023±96 BP.

Thus, the Barabinskaya culture dates to the 7th millennium BCE with some precursors dating back to the 8th and an aftermath in the 6th millennium BCE.

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Keywords: Western Siberia, Barabinskaya culture, chronology.

A04 P04

Finite ages from the Mesozoic era - is bone collagen an open system?

Taylor S¹, Thomas B¹

¹University Of Liverpool, Liverpool, United Kingdom

The first detectable pMC results from analysis of dinosaur collagen using AMS are presented and discussed. Over 40 pMC results taken from samples of known provenances showed expected decreases in measured ¹⁴C as expected for Medieval, Roman era, and ice age bone samples, but failed to show the expected step-downs to Cretaceous and Jurassic fossilised material. This raises the question as to whether bone collagen is an open system and if so, to what extent. A literature search revealed previously published radiocarbon in carboniferous material including fossils from Mesozoic and earlier deposits. This showed that although unexpected, the data presented here have precedents. Dinosaur bone samples were sent to 2 radiocarbon laboratories. Both managed to extract collagen and dated the collagen, apatite, and bulk samples, all to finite ages. A survey of six collagen versus apatite pMC differences suggested that some Mesozoic material has experienced a degree of isotopic alteration. Twenty one pMC values from nine Mesozoic bone samples sorted by three bone fractions (collagen, apatite, and bulk) showed a largely randomised distribution that does not confirm the expectation that isotopic alteration would affect one fraction more than another. A linear trendline intersects all Mesozoic bone material, but none of the three control materials at the resolution displayed. These results are most consistent with the hypothesis that ¹⁴C in Mesozoic and possibly older materials represent a combination of primary and secondary sources, with the caveat that no known cause of secondary sourcing stands out.

A05 Geoarchaeology: humans, landscapes, climate and ecology

A05_01

Humans in Siberia at the Last Glacial Maximum: desolate landscapes or suitable habitats?

Kuzmin Y¹,

¹Sobolev Institute of Geology and Mineralogy, SiberianBranch of the Russian Academy of Sciences, Novosibirsk 630090, Russian Federation

Recent progress in Paleolithic chronology of northern Eurasia with the help of radiocarbon dating has allowed us to sub-divide the Upper Paleolithic into stages. One of the most intriguing issues is the

possibility of humans to exist in Western/Central Europe north of the Alps, in Eastern Europe, and in Siberia during the coldest phase of the Upper Pleistocene, the Last Glacial Maximum (LGM), ca. 19,000–26,500 cal BP. Some scholars previously suggested that people retreated from South Siberia and Central/Eastern Europe at the peak of the LGM. However, according to the latest summaries there are about 35 sites in Southern/Central Siberia (south of 58° N) dated to ca. 22,600–27,700 cal BP. Some sites possibly associated with the LGM are found in more northern latitudes, up to 70° N. One of the recent examples of human adaptation to the cold and dry LGM environment is the Volchia Griva site in central Western Siberia (54.7° N) where several radiocarbon dates (run on animal bones and hearth charcoal) in the interval of ca. 22,200–23,600 cal BP were generated from a habitation layer. The high degree of adaptation (efficient hunting strategies, tailored fur clothes, and dwellings) allowed humans to colonize the vast swathes of southern and central Siberia at the height of the LGM. It is now clear that the concept of the "depopulation" of Siberia during the LGM is completely out of date. This research is funded by the Russian Science Foundation, grant 20-17-00033.

A05 02

Chuchuwaya: People and Nature in the Similkameen – Chronological modelling –

Quiles A¹, Delannoy J², Allison M³, Chalmin E², Clyburn A⁴, Gould B⁵, Jacquet J², Rowley S⁶, Geneste J⁷

¹Institut français d'archéologie orientale (IFAO), Cairo, Egypt, ²Université Savoie Mont-Blanc – Laboratoire EDYTEM, Le Bourget-du-lac, France, ³Upper Similkameen Indian Band, Hedley, Canada, ⁴independent researcher, Hedley, Canada, ⁵Similkameen Consulting, Hedley, Canada, ⁶Museum of Anthropology - University of British Columbia, Vancouver, Canada, ⁷UMR 5199 CNRS Pacea, Bordeaux, France

Chuchuwayha rockshelter (British Columbia, Canada) is a sacred place within the territories of the Upper Similkameen Indian Band, who initiated this project. Occupants have left evidence of their presence in archaeological deposits and through the over 70 pictographs. The project is developed in a multiscalar approach, both spatially and temporally, involving the fields of archaeology, geosciences, archaeometry and ethno-archaeology. It aims to restore the temporalities of the major events that have shaped the life of the site, whether natural or anthropogenic, and to frame the realization of the preserved rock art. Cosmogenic dating (10Be) is used to determine the age of the site as used by people. Its application is based on the morphogenic evolution of the site and the different identified collapses phases, using the 3D model of site evolution. 14C dates on organic materials collected during the excavation enable modeling the time depth of human occupation and the pictographs making. A homogeneous compact ash level marks the major ancient catastrophic event of Mt St Helens Yn that occurred more than 3000 years ago. The precise timing of this event and the time frame within which people could reoccupy the region is being modeled. Silico-calcic crusts are covering and fossilizing ancient decorated wall morphologies and sometimes pictographs. 14C/U-Th cross-dating of wall crusts will enable us to set termini for the art realisation.

The resulting multitechnical chronological model will restore the story of the life of the Chuchuwayha site, both from human, animals and natural points of views.

Chronology, Climate & Resilience: Using Multi-Proxy Bayesian Chronologies to Examine Pastoralist Responses to Dynamic Steppe Environments and Landscapes in Mongolia.

Green E1

¹University Of Aberdeen, Aberdeen, United Kingdom

This paper presents a novel approach for the examination of chronology alongside paleoclimatic proxies for specific localities, helping to bridge gaps in Mongolian paleoclimatic records, and focusing on understanding climatic and environmental change from the 'smaller picture' up. Presented here will be an extensive suite of new and published radiocarbon dates alongside stable isotope data for C/N, O, S isotopes from human and animal remains excavated from burial contexts across the Egiin Gol to construct a robust Bayesian chronology for north Mongolia that supplements current chronological frameworks, corroborates emerging narratives of increasing cultural complexity across Eurasian Prehistory and demonstrably questions traditional narratives of homogeneity. This multi-faceted study explores the application of stable isotopes as proxies for paleoclimate (alongside diet and foddering practices) and explores how nomadic pastoral communities adapted to the dynamic and changing environments of Eastern Eurasia during the Middle Holocene, and the Bronze and Iron Ages. This will enable a better understanding of the environments and climates of Eurasian landscapes, whilst contributing to Pan-Asian narratives of human adaptation and resilience throughout the Holocene.

A05 04

The unique early Holocene cetacean skeleton accumulation of the Forth Valley, Scotland

<u>Staff R</u>¹, McMaster P¹, Owen A¹, Persano C¹

¹University Of Glasgow, Glasgow, United Kingdom

Accumulations of cetacean (marine mammal) skeletons are rare in the geological record. One such accumulation, identified in early Holocene deposits of the valley of the River Forth, central Scotland, has been known since the early 1800s. However, the circumstances which permitted cetacean skeletons to accumulate there remain unclear. Association with Mesolithic inhabitants of Scotland (c.12,000-6000 cal BP) has been recognised, but their role as a causal agent of this accumulation has previously been dismissed. Using radiocarbon dating to provide robust chronology, we speculate here upon whether natural processes alone can explain the accumulation of this unique cetacean assemblage.

A05 05

Landscape transformations since first farmers to presence recorded in soil pauperization in Eastern Bohemia

<u>Lisa L</u>¹, Bajer A², Kočár P³, Petr L⁴, Štolc D⁵, Peška J⁶, Světlík I¹

¹Academy of Sciences, Institute of Nuclear Physics, Prague, Czech Republic, ²Mendel University, Brno, Czech Republic, ³University of Western Bohemia, Pilsen, Czech Republic, ⁴Masaryk University, Brno, Czech Republic, ⁵Archaia, Prague, Czech Republic, ⁶ACO, Olomouc, Czech Republic

The current, very gradually undulating morphology of the landscape in Eastern Bohemia is often attributed to the physical properties of the subsoil. However, a very important modeling factor, namely man, is often neglected. Thanks to rescue archaeological excavations during the construction of the highway, a number of buried paleo-valleys were discovered. The base of the valleys at a depth of more

than four meters is formed by a dark infill. The bases of profiles were dated to the time of the first farmers in the Neolithic. The original Neolithic landscape therefore had to look relatively different, furrowed by relatively deep valleys of streams that no longer exist today. These valleys had to be a source of water and vegetation, so their identification in the landscape is quite important. Due to the changes induced either climatically or anthropogenically, slope processes had to take place in the past, thanks to which the valleys were filled with slopes. It remains clear that the overburden of the buried soil is covered with soil originating from the immediate vicinity of the valley and contaminated (mixed) with the subsoil. In time, this obscuration is probably comparable to the medieval colonization of the landscape. However, the upper 70 cm of the filling is necessarily an anthropogenic matter, most likely associated with modern field consolidation. This corresponds to the general scheme that has been indicated so far in the interpretation of the formation processes of paleo Valley filling in this area.

A05 06

Data before the deluge: Prospects and limitations of summarising large radiocarbon datasets to investigate climate- and environmental impact on hunter-gatherers

<u>Hoebe P</u>¹, Peeters H¹, Arnoldussen S¹
¹University Of Groningen, Groningen, Netherlands

Radiocarbon 'dates as data' approaches (Summed Probability Distributions - SPDs) have become common in archaeological studies as instruments to investigate the impact of external events on societies. Such studies use radiocarbon dates as a proxy for the intensity of past human activity. Research- and preservation bias are inherent issues in such studies that have to be contended with. Do density fluctuations relate to changes in human activity, or to the intersection of site accessibility, differences in organic preservation, and the process of archaeological research and policy?

We collected a large radiocarbon dataset of Late Palaeolithic and Mesolithic Britain, Belgium, the Netherlands, Germany and Denmark, consisting of ca. 5500 radiocarbon dates. We investigated whether changes in the density of hunter-gatherer communities' activity correlates with the timing of Late Glacial climate fluctuations, Early Holocene climate events (11.4, 10.3, 9.3 and 8.2ka events), and the drowning of 'Doggerland' (i.e. the North Sea).

Our SPD model tests (conducted with the R package rcarbon) show several significant density fluctuations that may be correlated to climate and environmental events, and others that may relate to sociocultural changes or to bias. To deal with bias, we conducted permutation tests on subsets of the dataset that are potentially affected by different formation processes. This exploration highlights the impact of sample material choice, which is constrained by geographically and temporally differentiated preservation conditions and influenced by policy. Future steps involve expanding the analysis in relation to landscape dynamics as well as closer analysis of the timing of cultural changes.

Radiocarbon dating occupation of The Riverland region of the Murray River, South Australia.

<u>Jacobsen G</u>¹, Roberts A², Westell C², Jones R², Moffat I², Morrison M³, Rudd R⁴, River Murray and Mallee Aboriginal Corporation⁵

¹ANSTO, Lucas Heights, Australia, ²College of Humanities, Arts and Social Sciences, Flinders University, Adelaide, Australia, ³Department of Archaeology, University of New England, Armidale, Australia, ⁴School of Earth and Environmental Sciences, University of Queensland, St Lucia, Australia, ⁵River Murray and Mallee Aboriginal Corporation RNTBC, Adelaide, Australia

The Riverland region in South Australia is on the River Murry, Australia's longest river, which originates in the Australian Alps in New South Wales and is part of an extensive river system that encompasses one-seventh of Australia – The Murray-Darling Basin (MDB).

Until recently, there had been few radiocarbon determinations in the Riverland region, creating a large gap in understanding past occupation in the MDB. To address this gap in knowledge, the Flinders University is working with the indigenous landowners, represented by the River Murray and Mallee Aboriginal Corporation (RMMAC) to identify and investigate archaeological sites in the Riverland region to determine a chronology for occupation and learn how the RMMAC ancestors adapted to the changing environment.

An extensive research project is underway, here we present initial radiocarbon dating and findings, encompassing occupation since before the Last Glacial Maximum (LGM) to the time of the European invasion in the 19th Century. Dating of 48 shell and charcoal shell samples have provided the earliest date for occupation of this region to 29 ka, this is followed by a hiatus until around 15 ka with subsequent occupation continuing through the Holocene. At around 4 ka oven mounds appeared, indicating innovations to broadening food resources in response to changing environmental conditions.

A05_08

Reservoir effect of shells from Tell Abraq, Sharjah Emirate, UAE

Lindauer S¹, Händel M², Magee P³

¹Curt-Engelhorn-Centre Archaeometry, Mannheim, Germany, ²Austrian Academy of Sciences, Vienna, Austria, ³Zayed National Museum, Abu Dhabi, United Arab Emirates

We present reservoir effects on shells of species Terebralia palustris and Marcia sp. that have been recovered in the course of archaeological excavations at the multi-period site of Tell Abraq, Sharjah Emirate, UAE. The site was inhabited from the early Bronze Age, throughout the Iron Age, and into the pre-Islamic period. Situated in a lagoonal environment with former mangrove forests at the Arabian Gulf coast, Tell Abraq provides a well-defined and stratigraphically controlled archaeological context for investigations on the reservoir effect of the two species chosen. The data will be discussed in a wider context with respect to results obtained at other sites. This allows for a differentiation between environmental effects on a local scale in comparison to more global effects. Shells are not only indicators of palaeoenvironmental conditions but also represent an important tool to reconstruct the precise chronologies of both ocean circulation and human occupation on the Arabian Gulf coast of southeast Arabia in the mid to late Holocene.

Decisive Progress in the Absolute Chronology of Ancient Egypt

<u>Erdil P</u>¹, Kuitems M¹, Webster L², Knoblauch C³, Bestock L⁴, Höflmayer F², Beeckman H⁵, Fuller D⁶, Manning S⁷, Dee M¹

¹Centre for Isotope Research, ESRIG, University of Groningen, Groningen, the Netherlands, ²Austrian Academy of Sciences, Austrian Archaeological Institute, Vienna, Austria, ³Department of Heritage, History and Classics, Swansea University, Wales, UK, ⁴Joukowsky Institute for Archaeology and the Ancient World, Brown University, Providence, USA, ⁵Service of Wood Biology, Royal Museum for Central Africa, Tervuren, Belgium, ⁶Institute of Archaeology, University College London, London, UK, ⁷Cornell Tree Ring Laboratory, Department of Classics, Cornell University, Ithaca, USA

In recent decades, there have been numerous attempts to use radiocarbon dating to establish an absolute chronology for ancient Egypt; however, important discrepancies have remained unresolved, especially with regard to the Old and Middle Kingdom periods. As part of the ECHOES project at the University of Groningen, we have conducted a new study that builds on previous radiocarbon-based research. Here, we present close to 50 new radiocarbon dates obtained on samples from secure Old and Middle Kingdom contexts and, in conjunction with existing data, we provide an updated absolute chronology for the dynastic period. We discuss key modelling assumptions, such as the application of a regional offset to samples from the Nile Valley. We report two key findings: First, our new model much better secures the absolute position of the Old Kingdom and lends support to the hypothesis that this period of political unity ended around the time of the so-called 4.2 ka aridification event. Second, we address the placement of the reign of the king Senusret III, where different interpretations of a Sothic (Sirius) record have led to a long-running debate. Our Middle Kingdom model includes 38 high-precision radiocarbon dates from Uronarti, an Egyptian fortress in Nubia. With this data, we restrict the accession year of Senusret III to the early 19th century BCE. Accordingly, at 95% probability, our model supports only the High Chronology position for the Middle Kingdom, thereby resolving the long-running debate over the date of this king and the chronology of the whole Middle Kingdom.

A05 P01

Indigenous Dynamics and the Early North American Fur Trade: Results from AMS Dating Iroquoian Villages in southern Ontario, Canada

Conger M¹

¹University Of Georgia, Athens, United States

Formally established in the 1580s, the North American fur trade quickly became an important point of articulation between Indigenous and European societies and economies. While direct trade was mostly confined to the north Atlantic coast, increased demand for small mammal pelts prompted "down-the-line" changes in Indigenous landscape and resource use far inland. The Tionontate, an Iroquoian group living northwest of Lake Ontario, are thought to have formed in the 1580s in response to the fur trade. In this poster I present new date estimates, derived from AMS dating and Bayesian Chronological modeling, for Sidey-Mackay and McQueen-McConnell, two of the earliest (assumed ca. AD 1580-1600) Tionontate villages. I employ multiple sampling and modeling strategies which have been developed to overcome mid-sixteenth century calibration curve plateaus and wiggles, and to take advantage of the short-lived nature of Iroquoian village sites. This includes the use of unidentified wood charcoal as terminus post quem, and site Phase duration constraints. Results, while not entirely independent, indicate that the two sites were occupied up to 70 years prior to the formal inception of the fur trade, during a period of increased regional conflict and political consolidation. This suggests that Indigenous North Americans were involved with the down-the-line effects of seasonal and coastal European-Indigenous trade much earlier than previously thought, and situates that involvement within a dynamic

Indigenous sociopolitical landscape. Further, this research underscores the importance of absolute dating on Indigenous sites believed to date to the early colonial era in North America.

A05 P02

Pollen and bulk radiocarbon ages from a montane lake core – Yagour Plateau, High Atlas, Morocco

Cornelissen H¹, <u>Fink D</u>², Fletcher W¹, Hughes P¹, Bell B¹, Rhoujjati A³, Ewague A⁴

¹Department of Geography, University of Manchester, Manchester, United Kingdom, ²ANSTO, Sydney, Australia, ³Faculté des Sciences et Techniques, Université Cadi Ayyad, Marrakech, , Morocco, ⁴Université Chouaib Doukkali, El Jadida, , Morocco

The Yagour plateau in the Marrakech High Atlas, Morocco (31.31°N, 7.60°W, 2460 masl.) supports a montane (sub-alpine) wetland. It contains a rich collection of petroglyphs and pastoral usage on the plateau by surrounding villages is maintained by adherence to an historic cultural and community-based system called Agdal that regulates annual grazing access. We retrieved a 290 cm sediment core with excellent preservation from a marginal lake that spans 13 ka BP providing a high-resolution palaeoenvironmental Holocene record and insights into the archaeological and cultural heritage of the region. Our age-depth model rests on a 28-sample radiocarbon Bayesian analysis of common depth pollen concentrates, charcoal and bulk organic sediment. We find significant age differences between these Cbearing materials which are thought to be due to site-specific processes. We surmise that old-carbon from a variety of possible sources is likely driving the age differences throughout the Holocene period. The most likely two sources would be secondary carbonate accumulation in the porous and faulted Triassic sandstone and surface pedogenic carbonates produced during drier conditions. Increased groundwater pressure due to Holocene niche snowpack melt in the nearby mountains drove a larger input of spring water at Yagour. However, unknown factors drive a reversal in the chronological trend in the Late-Glacial period. The age-differences between sample-types highlight the importance of a cohesive understanding of lithostratigraphy and hydrology of previously undated sites in order to underpin robust chronologies used for environmental and cultural research.

A05 P03

Dating of the Kawela Mound, one of the earliest habitation sites in the Hawaiian Islands

Weisler M^{1,2}, <u>Hua Q</u>³, Rogers A⁴, Collins S⁵, Mendes W⁶

¹School of Social Science, University of Queensland, St Lucia, Australia, ²Archaeology Programme, School of Social Sciences, University of Otago, Dunedin, New Zealand, ³Australian Nuclear Science And Technology Organisation, Lucas Heights, Australia, ⁴ARC Centre of Excellence for Australian Biodiversity and Heritage, Monash Indigenous Studies Centre, Monash University, Clayton, Australia, ⁵Pacific Consulting Services, Honolulu, USA, ⁶P.O. Box 144, Ho'olehua, , USA

Chronometric dating of colonisation period sites is arguably amongst the most contentious issues in island and coastal archaeology worldwide, and it is certainly true for Polynesia. The human colonisation of East Polynesia has garnered most attention in Oceania as the earliest sites anchor foundational discussions of the timing, speed, and direction of colonisation of the last region settled on Earth. Recent reviews have critiqued and summarised the literature for the Hawaiian Islands, suggesting that the islands were colonised following the general model of initial colonisation in fertile, windward-valley environments, local population growth, and subsequent expansion to marginal, leeward locales. However, this observation was based on a limited sample of the oldest sites in windward settings, including three habitation sites and one agricultural complex.

In this paper, we discuss the leeward environmental context and dating of the Kawela Mound habitation site on Moloka'i island. A total of 21 samples from four cultural layers, including twigs, charred nuts and wood, and marine shell, from three excavated trenches were radiocarbon dated. The resulting dates and Bayesian phase modelling indicate that the earliest occupation of the Kawela Mound is 1124-1261 AD (95% CI), documenting it as the oldest on Moloka'i island and one of a handful of early habitation sites in the archipelago. Our results suggest that early coastal habitations can be found in leeward as well as windward sides of islands and can be used to provide a model for locating early sites along this leeward coastline that should be applicable elsewhere.

A05 P04

Holocene activity of the Tanna faults revealed by sediment core analyses and ground penetrating radar profiling, the Izu Peninsula, Japan

<u>Kimura H</u>¹, Nakanishi T², Yukawa M¹, Hosoya T³, Sung K⁴, Hong W⁵

¹Central Research Institute of Electric Power Industry, Abiko, Japan, ²Museum of Natural and Environmental History, Shizuoka, Shizuoka, Japan, ³Chuo Kaihatsu Corporation, Kawaguchi, Japan, ⁴Carbon Analysis Lab. Co., Ltd., Gyeryongsi, Republic of Korea, ⁵Korea Institute of Geoscience & Mineral Resources, Daejeon, Republic of Korea

The active left-lateral strike-slip Tanna fault is one of the major faults of the NS-trending Kita-Izu fault zone, which ruptured during the 1930 Kita-Izu earthquake (Mjma=7.3). The fault zone is located in the Izu Peninsula, northern tip of the Izu–Bonin–Mariana arc, at about 100 km southwest from Tokyo. In order to reveal the Holocene activity on the Tanna fault, we surveyed the near-surface structure of an offset valley across the fault by radiocarbon dating of sediments obtained from arrayed four drilling cores and ground penetrating radar (GPR) profiling. The drilling sites were located across the NS-trending secondary strand that runs parallel to the northern part of the main strand of the Tanna fault approximately 50 m to the west. The GPR surveys were conducted along the arrays of the drilling sites. We interpreted several dipping horizons showing sedimentary structure on the geological cross-sections. The horizons were dated by AMS radiocarbon ages of plant fragments and organic soil samples that were measured by Carbon Analysis Laboratory (CAL) and Korea Institute of Geoscience & Mineral Resources (KIGAM). The results explained the Holocene vertical offsets associated with the oblique slip of the Tanna fault. This work was started as a research project funded by the Izu Peninsula UNESCO Global Geopark, and supported by Grants-in-Aid for Scientific Research (KAKENHI) JP15K01255 and JP18K03768 from the Japan Society for the Promotion of Science (JSPS).

A05 P05

Absolute dating of the rampart of an Early Iron Age hillfort in Chotyniec (Poland) in the context of radiocarbon dating

<u>Krapiec M</u>¹, Czopek S², Tokarczyk T²

¹AGH University of Science and Technology, Krakow, Poland, ²University of Rzeszow, Rzeszow, Poland

The Early Iron Age hillfort in Chotyniec near Radymno (south-eastern Poland, 8 km west of the current Poland–Ukraine border) has been systematically excavated since 2017. It is the mostly north-west located hillfort of the Scythian cultural circle in its forest-steppe variant.

It has an earthen rampart within which no archaeological material allowing dating was found. At the bottom of the rampart there is a central trench, probably for a palisade, which was the oldest fortification. The radiocarbon method was used for dating of 20 samples of charcoal and fragments of wood. The duration of successive phases of the rampart was determined using a Bayesian model, allowing the calculation of probability distributions for the beginning, end and possible duration in calendar age.

The end of the functioning of the first phase (with the central pit) can be identified in the 2nd half of the 7th-1st half of the 6th century BC. The earthen rampart, like the previously dated zolnik, was functioning in the 6th century BC.

A05_P06

Absolute chronology of the pile-dwelling constructions at Seretya II site (Western Russia) and palaeoecological context

Krapiec M¹, Mazurkevich A², Kittel P³, Dolbunova E², Bernard V⁴, Maigrot Y⁵, Szychowska-Krąpiec E¹

¹AGH University of Science and Technology, Krakow, Poland, ²The State Hermitage Museum, St. Petersburg, Russia, ³University of Lodz, Lodz, Poland, ⁴Université de Rennes 1, Rennes, France, ⁵CNRS-Université Paris 1 Panthéon – Sorbonne, Nanterre, France

Results of several years archaeological research of the Serteya II site revealed the use of the area by hunter-fisher-gatherer socialites from the Mesolithic, through the Early Neolithic until the Mid- and Late Neolithic. Extremely important are the wooden constructions of Late Neolithic pile-dwellings of domestic structures, which are well-preserved within lacustrine sediment along with reach artefacts and ecofacts. The archaeological layer, at a depth from ca. 80 to ca 150 cm b.s.l. within coarse detritus gyttja, was excavated using underwater and wetland archaeological methods. Until now, six pile-dwellings, with floor remains made from large wooden bark placed on poles and wooden planks, as well as fireplaces with sand bases, were discovered. The accompanying artefacts were attributed to the Zhizhitsa Culture (ca. 2900–2000 BC). The archaeological layers are also rich in ecofacts, as: fish remains, shells of hazelnuts, water chestnuts, acorns, bones.

The radiocarbon date set shows that these constructions could have existed between 2900 and 2000 cal. BC, while the heydays of the pile-dwelling settlement took place ca. 2470–2270 cal. BC. The archaeological and palaeoenvironmental contexts suggest that they functioned in a palaeolake shore zone with seasonal(?) water table fluctuations. The disappearance (or at least a decrease in the importance) of the pile-dwelling settlement coincided with the 4.2 ka BP cooling event, resulted in an increase of palaeolake water table.

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A05 P07

Implications concerning the palaeoenvironment of a Late Pleistocene woolly rhinoceros specimen lived in the Pannonian Basin

<u>Major I</u>¹, Lisztes-Szabó Z¹, Gasparik M², Magyari E³, Szabó B³, Pandolfi L⁴, Borel A⁵, Futó I¹, Horváth A¹, Kiss G¹, Markó A⁶, Molnár M¹

¹Eötvös Loránd Research Network, Debrecen, Hungary, ²Hungarian Natural History Museum, Budapest, Hungary, ³Eötvös Loránd University, Budapest, Hungary, ⁴Università di Firenze, Florence, Italy, ⁵Histoire Naturelle de l'Homme Préhistorique , Paris, France, ⁶Hungarian National Museum, Budapest, Hungary

The excavations (2014-2017) at the Pécel-Kis hársas site (Hungary) yielded the remains of an old female woolly rhinoceros (Coelodonta antiquitatis) together with four chert and three obsidian artefacts. To gather more information on this species and the contemporary palaeoenvironment of the finding location, multi-isotopic analyses were performed. The specimen died ca. 20.5 ka, at the very end of the Last Glacial Maximum (LGM) of the Pleistocene, presumably due to Epigravettian hunters. In a European context, it is one of the latest occurrences of the species in the continent. Based on bone stable carbon and nitrogen isotope, dental wear and dental plant microfossil results, a lichen (possibly moss) dominant diet could be drawn. Such diet element was so far unknown concerning woolly rhinos. In accordance with the optimum environmental conditions of the foraging plants, the stable strontium and oxygen isotope results of bioapatite also suggest a relatively cold local climate with a calculated mean annual air

temperature of around 0.7 °C. Thus, a mosaic, pioneering vegetation and a tundra/steppe-like habitat can be assumed to have been dominated at the Pécel-Kis hársas site at the end of the LGM. Considering the longer turnover time of the ¹⁵N isotope in collagen, the harsh conditions could probably endure for a longer period, not just for a winter season.

A05_P08

Detection of tectonic movement and marine reservoir effect in the Holocene sediments from the Ukishima plain, Shizuoka, central Japan

Nakanishi T¹, Ishiyama T², Noguchi M³, Hong W⁴

¹Museum of Natural and Environmental History, Shizuoka, Shizuoka, Japan, ²the University of Tokyo, Tokyo, Japan, ³Geoanalysis Network of Tokyo capital region, Tokyo, Japan, ⁴Korea Institute of Geoscience & Mineral Resources, Daejeon, Republic of Korea

To investigate paleoenvironmental changes and tectonic activities, one Holocene sediment core with length of 30 meters was obtained from the Ukishima plain in the inner part of Suruga Bay, which corresponds on the boundary of the Eurasia and Philippine Sea Plates. This drilling site locates in a subsidence area associated with the subduction of the Philippine Sea Plate (Matsuda, 1978, Matsubara, 1984, Fujiwara et al., 2006, 2008, Komatsubara et al., 2007). Based on analyses of lithology, molluscan and diatom assemblages, and radiocarbon dating, we interpreted six sedimentary facies in order of older age: transgressive lag, estuary, estuary front, inner bay, lagoon, and artificial soil. These paleoenvironmental changes had been mainly associated with the sea-level rise during the deglacial period. To determine marine reservoir effects, the radiocarbon ages of marine shells and terrestrial plants were measured from same horizons of estuary to inner bay sediments. Reservoir ages of 6 pairs from these facies were recognized during the period from 7,900 to 6,800 cal BP. The average was 310 \pm 120 years within 150 ± 70 to 470 ± 60 . The chronological change in the reservoir effect will be correlated with the Holocene sediments from the coastal area in Southwest Japan under the Kuroshio warm current (Nakanishi et al., 2017ab, 2019). This core was obtained by the Headquarters for Earthquake Research Promotion at the Japanese Ministry of Education, Culture, Sports, Science and Technology. Radiocarbon dating was partially funded by the Japan Society for the Promotion of Science KAKENHI grant number JP18H01310.

A05 P09

Newly found settlement features from Nitra-Lupka

Nezvalová L^{1,2}, Fottová E², Milová B²

¹Czech Academy of Sciences, Praha 8 - Libeň, Czech Republic, ²Slovak Academy of Sciences, Nitra, Slovakia

Nitra-Lupka is the important site from the Great Moravian period in Slovakia. Fortified hillfort which was supposed to be from this period, battery of pottery kilns and Early Medieval cemetery were found there. It was researched from 1959 until 1975. Few small range excavations took place on the site at the beginning of the 21st century. At the same time the dating of hillfort into the Early Medieval period was questioned. There was also problem with localisation of settlement which would belong to the battery of pottery kilns. The settlement was discovered recently in 2021 during development-led excavations at Nitra-Šindolka. It was found during the construction of ecoduct. Two bread kilns and four other features were discovered. Numerous ceramics and other findings were discovered in them. In the feature 6, which was probably used for storage, numerous sherds and some animal bones were discovered. The two of the bones (phalanges of cattle) were dated by radiocarbon dating. These are the first ¹⁴C data which were obtained from this site and they are very important for precise dating of this site.

Chronology of Lake Lubińskie (W Poland) sediments

<u>Piotrowska N</u>¹, Bonk A², Żarczyński M², Tylmann W², Enters D^{3,4}, Makohonienko M⁵, Rzodkiewicz M⁵

¹Institute of Physics-CSE, Silesian University of Technology, Gliwice, Poland, ²Division of Geomorphology and Quaternary Geology, Faculty of Oceanography and Geography, University of Gdańsk, Gdańsk, Poland, ³Lower Saxony Institute for Historical Coastal Research, Wilhelmshaven, Germany, ⁴Institute of Geography, University of Bremen, Bremen, Germany, ⁵Institute of Geoecology and Geoinformation, Adam Mickiewicz University, Poznań, Poland

Landscape and ecosystem transformations depend on combined climatic forcing and human activity. The assessment of ecological baseline conditions and eutrophication trends requires, among others, the analysis of different proxies providing qualitative and quantitative results. Diatom and pollen preserved in lake sediments hold excellent potential for the reconstruction of lake trophic conditions. Combined with geochemical data and a robust chronology they allow a detailed reconstruction of long-term conditions for individual sites and precisely defining the timing of changes. Among them, lakes containing annually laminated (varved) sediments offer records with one of the highest time-resolution possible. We used a multiproxy combined dating techniques including varve microfacies analysis and varve counting, radiometric measurements (¹⁴C, ¹³⁷Cs, and ²¹⁰Pb), and Bayesian age-depth modelling. Due to some parts of poor varve preservation and possible hiatuses, the final chronology is based on combination of radiometric dating results analyzed statistically in OxCal and supported by varve counting. The composite 506-cm-long sediment core from Lake Lubińskie covers the time period from 2007 CE (year of coring) to 946 +113/-144 BCE.

A05_P11

Radiocarbon dating of the ancient canals in the lower Mekong delta, Vietnam

Quang Mien N¹, Nang Chung T²

¹Institute of Archaeology, Ha Noi, Vietnam, ²Association of Archaeology, Ha Noi, Vietnam

This study presents preliminary results of research on ancient canals near the ancient town of OcEo - BaThe in the lower Mekong delta of southern Vietnam. The canals have been mapped by aerial photograph interpretation and investigated in the field by hand auger drilling and trenching of one of these. The geophysical methods were used: electromagnetic profile and electric resisitivity tomography. The results indicates the base of the canal as well as revealing disturbance and mixing of the canal infill sediments. Radiocarbon dates of the canal bed identify excavation (or re-excavation) of the canal bed between the first millennium BC and the middle of the first millennium AD. This age is consistent with the time of initial occupation of OcEo-BaThe in the fourth century BC. Multiple charcoal samples with a pooled age of late sixth to early seventh century AD probably signal the onset of canal infilling. The apparent demise of the canals coincide with a major change in land-use signalled in pollen and diatom data from the regional plain. This tentative chronology will be refined when more canals are investigated and greater precision is achieved in radiocarbon dates as well as combining with other dates.

A radiocarbon chronology for "Grotte di Pertosa" in Campania, Southern Italy

Larocca F^{1,2}, Breglia F^{2,3}, Calcagnile L⁴, D'Elia M⁴, Quarta G⁴

¹University of Bari "Aldo Moro", Gruppo di ricerca speleo-archeologica, Bari, Italy, Bari, Italy, ²Centro di ricerca speleo-archeologica "Enzo dei Medici", Roseto Capo Spulico (CS), Italy, ³Department of Cultural Heritage, University of Salento, Lecce, Italy, ⁴CEDAD-University of Salento, Lecce, Italy

The Pertosa Caves, today also known as the Pertosa-Auletta Caves, constitute an important karst system in the Campania region (southern Italy). Crossed by the waters of a river that re-emerges on the surface, they have an overall development of about 3 km. Thanks to the width of the entrance, the excellent position, the general convenience and the natural availability of water directly on the site, the initial part of the cavity was frequented by humans, without interruption, from prehistoric times to the Middle Ages. During the protohistory, in particular, the moment of most marked human presence is recorded in the cave: in this phase an extensive pile-dwelling system was built on the waters of the underground river. The system was probably created to make the environment, subject to frequent flooding, suitable to settle. This structure today constitutes an archaeological unicum not only in Italy but throughout Europe. We briefly analyze its general characteristics providing a radiocarbon chronology which allowed to assess the occupation phases of the contexts and the life span of the wooden artefacts, which came to us to us in a very good state of preservation.

A05 P13

The open-air Middle Palaeolithic sites on the East European Plain: improved chronology and environmental context

Otcherednoy A¹, **Zaretskaya N**², Hein M³, Hoffecker J⁴, Panin A²

¹Institute for the History of Material Culture, Russian Academy Of Sciences, St-Petersburg, Russian Federation, ²Institute of Geography, Russian Academy of Sciences, Moscow, Russian Federation, ³Max Planck Institute for Evolutionary Anthropology, Leipzig, Germany, ⁴Institute of Arctic and Alpine Research, University of Colorado, Boulder, USA

One of the principal obstacles to further study of the Middle Palaeolithic of Northern Eurasia is the lack of an adequate understanding of the chronological position of the cultural layers of key open-air sites on the East European Plain. Until recently, radiocarbon dating was exclusively used to obtain chronometric data on Middle Palaeolithic sites. Accordingly, chronology of Middle Palaeolithic sites was largely based on radiocarbon dating. Renewed study of Khotylevo I and Betovo (Desna River valley, basin of Dnieper), has been pursued with radiocarbon dating as well as other serial chronometric methods (Otcherednoy et al. 2019; 2022; Hein et al. 2020). Conventional and AMS dating, including ultrafiltration and other methods of sample purification (XAD-2) were extensively used. The dates obtained were older than 40 000 or between 25 and 30 ka BP. The results can be divided into two groups: a series of dates with numerous inversions that are not consistent with the stratigraphy, as well as widely varying dates on the same cultural layer (Khotylevo I) or a series of dates that significantly antedate previously assumed age of the site (Betovo). Two series of OSL dates obtained for these sites fell in the MIS 5c-MIS 4 age range for the Khotylevo I cultural-bearing deposits, confirming the earlier stratigraphic and geomorphological conclusions, but showed the good agreement with 14C calibrated dates at Betovo. Thus, we conclude that the area was inhabited throughout the Pleniglacial, and the combined dating results on the stratigraphic "canvas" significantly increase the reliability of chronology.

Radiocarbon dating of Xiawangdu neolithic site at coastal plain in eastern China and its environmental settings

Zhang H¹, Lin P¹, Gu Y¹, Wu J¹, Lu H¹

¹School of Geography and Ocean Science, Nanjing University, Nanjing, China

The lower Yangtze region in China, with varied coastal environments and a flourishing Neolithic culture, was one of the major rice domestication centers in Asia. Sedentary societies occupied the Lower Yangtze in the eastern coastal regions of China at the beginning of the Holocene. In present day China, the region is highly developed, densely populated, and is commonly referred to as "the land of fish and rice." Environmental changes, such as climate, vegetation, and sea-level rise, play major roles in supporting sustainable development. A detailed radiocarbon dating of the Neolithic sites is critical to understand the relationship between the process of domestication and climate variability and sea-level rise. And, furthermore, help to accurate predict future climate change impacts, including recent global warming and on-going sea-level rise, thereby benefitting societies and their economies. Here we present the results of 36 radiocarbon datings(including TOC, pollen concentration, seeds and wood)and 24 grain-size analyses from Xiawangdu neolithic site in the Ningshao Plain, southern part of the lower Yangtze which in cluding both Hemudu and Liangzhu cultural stages. The results show that Xiawangdu site was fromed older than 6300 cal. yr BP when Hemudu culture was declining and the Lianghzu culture started developing at about 5200 cal. yr BP. Radiocarbon dating of TOC and pollen concentration are usually older than the actual stratigraphic age because participation of organic matter from source areas. The prosperity of Hemudu culture may be rising by the increasing of regional precipitation and suitable environment.

A06 Art and cultural heritage

A06_01

The relevance of carbon dating for the study of Oriental manuscripts and the history of the Qur'ān

Marx M¹

¹Berlin-Brandenburg Academy of Sciences, Potsdam, Germany

Since 2013 the research project "Corpus Coranicum" of Berlin-Brandenburg Academy of Sciences and Humanities has carried out — in close collaboration with ETH Zurich — carbon dating of Oriental manuscripts (Arabic, Ancient South Arabian, Georgian, Greek, Hebrew, Syriac) written on paper, papyrus, parchment and wooden palm sticks (Yemen) from collections in Europe and the Middle East. In the talk, an overview of this first systematic application of scientific measurements in the field of Oriental philology is presented. In the second part, the contribution of carbon dating results to the study of Oriental manuscripts and palaeography is discussed. We will describe also different positions of scholars in Arabic philology toward this established dating technique and its somewhat reluctant reception. In the third part, two recurrent types of problems encountered during our measurements campaign are presented: (1) divergent measurements from one and the same sample, (2) divergent measurements from different pages of one and the same manuscripts. In the fourth and final part, with regard to obtained measurements of manuscripts ms.or.fol. 4313 (Berlin), Cod. or. 14.545 a/b/c (Leiden), DAM 01-27.1 (Sanaa), DAM 01-29.1 (Sanaa) and Ma VI 165 (Tübingen), we will suggest an earlier chronology of Qur'ānic script styles (palaeography). Based on carbon dating, material evidence

for the history of the Qur'ān can be traced back to middle of the 7th century, chronologically close to the proclamation of the Qur'ān (between 610 and 632 CE according to Muslim scholarly tradition).

A06 02

The Common Thread: Authenticating a Nazca tunic using combined dye analysis by LCMS and radiocarbon dating on a single fiber

Hendriks L¹, Haghipour N^{3,4}, Chen V², Holden A², Smith G²

¹School Of Engineering And Architecture Of Fribourg, Switzerland, ²Conservation Science Laboratory, Indianapolis Museum of Art at Newfields,, Indianapolis, USA, ³Geological Institute, ETH-Zurich, Zurich, Switzerland, ⁴Laboratory of Ion Beam Physics, ETH-Zurich, Zurich, Switzerland

Accessioning historic textiles into museum collections often requires objective information regarding the object's appropriateness and authenticity before being accepted. In the case of dyed fibers, evidence of period appropriate dyestuffs builds confidence and reduces the chances of the object being a simple fake produced using modern materials. Increasingly, objective age estimates in the form of radiocarbon (14C) dating are needed to further prove that the naturally occurring materials match the purported date of the textile. Each of these techniques are destructive requiring a small sample of the object, and are typically conducted separately by different laboratories on individual samples. In 2020, the Indianapolis Museum of Art at Newfields sought to acquire a Nazca dyed camelid wool tunic dated to the period 100 BCE - 600 CE. Because of the supple feel and excellent condition of the artifact, concerns were raised over its purported age. Museum curators and conservators requested an investigation of the object's materials. This report demonstrates for the first time the sequential, combined analysis of dyes by liquid chromatography-diode array detection-mass spectrometry (LC-DAD-MS) and subsequent ¹⁴C dating of the same extracted fibers. Reusing the extracted fibers for radiocarbon dating reduced the risk of additional damage to the textile. The analysis confirmed that the wool fibers were dyed with common Peruvian dyestuff (indigo blue, purpurin red, quercetin yellow) and the ¹⁴C results placed the object between 550 and 650 CE. Based on these confirmatory findings, the Nazca tunic was accessioned into the collection in 2021.

A06 03

Carbon Dating versus Philology? Convergence of evidence for the dating of manuscripts of Central Library of the University of Tehran

Aghaei A¹

¹Paderborn University, Paderborn , Germany

This talk presents carbon dating results of manuscripts kept by the Central Library of the University of Tehran carried out in my project "Irankoran" in 2019. Analysed manuscripts include (1) the Arabic dictionary Muğmal al-Luġah of Ibn Fāris (d. 1004CE), (2) the Encyclopaedia of Medicine Daḫīra-ye Khwārazmšāhī of al-Ğurǧānī (d. 1137CE), (3) the epos Panǧ Ganǧ of Neẓāmī (d. 1209CE), (4) a collection of aphorisms, Ādāb al-Falāsifah, attributed to Ḥunayn b. Isḥāq (d. 873CE) and (5) one of the oldest extant copies of the (Zoroastrian) Avesta Wīdēwdād (dated to 1607CE). As dates of these documents are disputed among scholars, carbon dating provides evidence to understand their history from a new perspective, independent from philology. Carbon age results in the case of the five documents show that dates of scribal notes (colophons) present accurate dates for their production. In the case of Daḫīra-ye Khwārazmšāhī, samples were taken from two different pages with dramatically different results: 870,20BP (corresponding the scribal note) against 163,20BP. Triggered by these conflicting results, a study of script styles and linguistic features has found indicators that the text of the page in question is not authentic, confirming obtained carbon dating measurements. Probably, this page was produced and added during the 19th century to replace a damaged page of Daḫīra-ye Khwārazmšāhī. For all five cases

presented in the talk, the correlation of scientific evidence and philological features is discussed. In conclusion an outlook is given how this first mesuring campaign in Iranian collections can be developed.

A06 04

Unraveling the history of a Venetian antiphonary.

Rzadeczka - Juga I¹, Zurbach D¹, Juga P², Nadeau M¹, Løvstrand Svarva H¹, Seiler M¹, Grootes P¹

1The National Laboratory for Age Determination, NTNU University Museum, Trondheim, Norway, ²Ringve Music Museum, Trondheim, Norway

Complex objects such as old books contain many materials: paper, ink, cardboard, leather, parchment, strings, glues, and metal buckles. Each of which can provide clues to the origin and history of the object. We present the results of a multifaceted study of an antiphonary – a liturgical song book – presumed to be made in Venice in 1607, now in the Ringve Music Museum in Trondheim, Norway. The book is handsewn on raised cords, bound in full leather on cardboard covers originally with metal clamps. The paper block consists of printed pages in black and red ink that include both song texts and music scores. The antiphonary shows several signs of repair including the possibility of re-binding. Different analyses were carried out with emphasis on non-destructive methods. The aim of the project being to confirm the printing date, and possibly its origin, and to document repairs and modifications through the ages. Both classical and modern methods were used. The origin of the leather, threads and strings were determined by optical microscopy. The elemental compositions of the metal buckle and pigments were established using X-ray fluorescence (XRF). The glues used in the spine and for repairs were studied by Fourier Transform Infrared Spectroscopy (FTIR) and zooarchaeology by mass spectrometry (ZooMS) in the hope to identify the collagen source used. Finally, all organic materials were radiocarbon dated, some multiple times to assess the variability of the materials, leading to the reconstruction of the history of this beautiful object.

A06 05

An original contribution to document some Khmer bronze statues : analysis and radiocarbon dating of their iron backbone

<u>Delque-Kolic E</u>¹, LEROY S², VEGA E², VINCENT B³, McGILL F⁴, FENN M⁴, CREANGE S⁵

¹LMC14/LSCE/CNRS, Gif Sur Yvette, France, ²LAPA-IRAMAT/CNRS, Gif Sur Yvette, France, ³EFEO, Siem Reap, Cambodge, ⁴Asian Art Museum, San Francisco, United States, ⁵Rijksmuseum, Amsterdam, Netherlands

In 1964, a set of 53 Buddhist bronze statues were discovered at Prakhon Chai (Buriram province, Thailand) without any indication of the origin of the statues nor the reason of their presence. The stylistic study of some of them suggested that they could have different geographical origins within a chronology ranging from the seventh to the ninth century. Such a hoard constitutes an invaluable source of historical information that is worth investigating beyond the stylistic assessment. Yet all the statues were lost-wax cast in copper alloy and reinforced with internal iron armatures for the largest ones. As demonstrated for several years by the authors, a methodological approach combining metallographic observations, chemical analysis of slag inclusions and radiocarbon dating of the iron can deliver technological and chronological outcomes. As part of the IRANGKOR project, which focuses on the production and use of iron in the areas of Cambodia and northeastern Thailand, we then proposed to focus on the iron made armatures that are not used to be considered as a critical data for that kind of art object.

We will present the approach specifically developed for the ¹⁴C dating of such valuable objects and the decisive results obtained for four bronze statues from the Prakhon Chai hoard. Beyond the expected comparison with the chronology that has been suggested from stylistic indicators, the radiocarbon dates are also intended to be reinvested in a broader framework of comparison of data, by confronting them with the metallurgical observations previously obtained within the IRANGKOR project.

Geochronology ¹⁴C applied to organic coatings of musical instruments and other modern Heritage objects

Durier M¹, Hatté C^{2,3}, Vaiedelich S¹

¹Équipe Conservation-Recherche, Musée de la Musique – CNRS : UAR3224, Centre de recherche sur la conservation, Paris, France, ²Laboratoire des Sciences du Climat et de l'Environnement - CEA, CNRS, UVSQ, Université Paris-Saclay, Gif-sur-Yvette, France, ³Institute of Physics – CSE, Silesian University of Technology, Gliwice, Poland

Musical instruments present a complex materiality as an object of art and (musical) uses. Their constitutive parts underwent successive undocumented interventions for playing purposes, alterations and restorations. The varnish, traditionally preserved through time, is also a testimony of the material history of the instrument with undatable interventions using conventional museum techniques such as stylistic studies, dendrochronology, etc.

An innovative study based on advanced technology in ¹⁴C geochronology, combining historical documentation and material characterization analyses, has been applied to modern musical instruments and other modern Heritage objects (16th-19thc.). The organic coatings were micro-sampled (from 0.2 to 5.4 mg) layer by layer using micro-scalpels in order to separately date the original layers and later interventions.

Here, we present some case studies to illustrate the information highlighted on the making period, the making processes and the use(s) of the Heritage objects. For example, the case study of a qin (no. 276, CNAM, Paris) unraveled the storage of the wooden support, the presence of malachite in the underlaying black lacquer and the making period has been clarified thanks to the ¹⁴C dating of the upper red lacquer. The impact of restoration products from 20th-c. museum interventions has also been evaluated on early 18th-c. horse-drawn carriages (no. TR1868, RMAH, Brussels and CMV64.002, MNVT, Compiègne).

This study shows that the more curate historical and material descriptions, the more suitable the protocol adaptations and interpretation of the ¹⁴C results will be in order to build a 'history of use' of the musical instrument and other Heritage objects.

A06 07

The application of radiocarbon dating of lead white in the study of polychrome stone sculptures

Sá S¹, Hendriks L^{2,3}, Hajdas I³, Pombo Cardoso I¹

¹Department of Conservation and Restoration and LAQV—REQUIMTE, NOVA School of Science and Technology, 2829-516 Caparica, Portugal, ²School of Engineering and Architecture of Fribourg, HES-SO University of Applied Sciences and Arts Western Switzerland, Pérolles 80, CH-1700 Fribourg, Switzerland, ³Laboratory of Ion Beam Physics, ETH Zürich, Zurich, Switzerland

Polychrome sculpture was a foremost artistic expression in the Middle Ages proven by numbers and persistent production. However, studying the polychromy of these sculptures is extremely challenging as, frequently, these objects got their decoration periodically renovated, supposedly to hinder the poor preservation state of the previous polychromy or to answer to changes in artistic taste and style. Today, many polychrome sculptures present intricate surfaces as a result of the loss and degradation of paint material, of the consecutive reapplication of new paint layers over the centuries, and of the uneven removal of paint layers in past restoration interventions. Hence, the understanding and interpretation of these surfaces and the identification of the original polychromy is rather complex and requires assistance of different sources of information.

Unlike other cultural heritage objects, such as wooden sculptures or paintings on canvas, polychrome stone sculptures do not bear an organic substrate which may be radiocarbon dated. Providentially, lead white, which was recently put forward as novel proxy for artwork dating, is ubiquitous on the decoration

of these sculptures. The present study¹ discusses the pioneering application of ¹⁴C analysis on paint samples from polychrome limestone sculptures by specifically targeting the lead white pigment and organic binder. The radiocarbon dating survey conducted on 16 Portuguese sculptures confirmed that some polychromies were produced within the medieval period while others were revised, hereby demonstrating the potential of the radiocarbon dating technique in the transdisciplinary approach used to study the complex paint stratigraphies found in medieval sculptures.

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A06 08

Radiocarbon dating contents from a two-handled combed ware jar from a burial chamber from Giza.

<u>Jacobsen G</u>¹, Sowada K², Wetterstrom W³, Serpico M⁴, Bertuch F¹

¹ANSTO, Lucas Heights, Australia, ²Macquarie University, Sydney, Australia, ³Harvard University, Cambridge, USA, ⁴University College London, London, United Kingdom

The Museum of Fine Arts, Boston holds a collection of combed ware jars excavated from burial tombs from Giza by G.A. Reisner, over 1902 to 1942, for the Harvard University-MFA Egyptian Expedition. Two-handled combed jars were manufactured in Byblos in the Central Levant and used to transport liquids to Egypt. As part of a larger study of these jars, we present a case study of one jar – MFA 47.1662, found in a burial chamber dated to the Fifth Dynasty. Along with this jar is a plastic bag labelled as being the contents of MFA 47.1662, this bag (OP.1.47.1662) contains a mix of materials including resin fragments, plant matter and faunal remains. With no record of the contents of the bag, it is not known if all, or some, of the contents are indeed related to jar MFA 47.1662. Analysis of the contents found some of the material from the bag could not have been from the jar as it includes plant material not found in Egypt at that time. Results from the contents analysis and radiocarbon dating of four botanical and faunal specimens selected from the bag will be presented. The radiocarbon results demonstrate the likelihood of multiple modern interventions in the life-cycle of the jar, and concomitant difficulties in assessing legacy data from old excavations.

A06_09

Dating of wooden heritage objects in the Gliwice ¹⁴C and Mass Spectrometry Laboratory

<u>Piotrowska N</u>¹, Kłusek M¹, Boroń P², Imiołczyk E³, Budziakowski M⁴, Poloczek A⁵, Poloczek-Imielińska A⁵, Jaksik M⁵

¹Silesian University of Technology, Institute of Physics, Gliwice, Poland, ²University of Silesia, Faculty of Humanities, Institute of History, Katowice, Poland, ³Museum of Upper Silesia, Department of Archaeology, Bytom, Poland, ⁴Cracow University of Technology, Faculty of Architecture, Cracow, Poland, ⁵RECO Konserwacja Zabytków Sp. z o.o., Katowice, Poland

Radiocarbon and dendrochronology are powerful tools to determine the age of wooden objects. Hereafter we present the three objects of high importance for cultural heritage in Poland, where both methods supported each other to enhance the reliability and increase the precision of age determination.

1. Richly ornamented, ca. 60-cm-long wooden cane, was discovered in the 1990s during excavations on the market in Bytom, founded in 1254 under German law. The cane could have been used in court proceedings in the Germanic law circle (Rechtsstabe) and two cuts indicate the judge's practice to break the cane over the head of the accused at the time of the sentence. Archaeological context imply 13th century AD, and ¹⁴C result corresponds perfectly with this time.

- 2. A column, which supports the main altar in the St. Leonard Church in Lipnica Murowana (UNESCO World Heritage Site), was made of 4-m-tall oak trunk. Due to some carvings the local story said it was previously devoted to Światowid, a pagan idol. Our analysis excluded pre-Christian age, as the tree came from the middle of the 15th century or from a later period.
- 3. Saint Lawrence Church in Bobrowniki is a unique wooden church with a complicated renovation history, and up to 5 layers of polychromic paintings, including some of high artistic value. We dated 3 samples from one of the original wooden boards from the presbytery, and by adding the information about dendrochronological sequence the calibrated age interval was spectacularly narrowed from 1650-1950 AD to AD 1731-1754.

A06 10

A meta-analysis of available radiocarbon dates for the Early Iron Age in Italy

Oddo M¹

¹University Of Pavia, Pavia, Italy

Over the past thirty years, the traditional chronology of the Late Bronze Age - Early Iron Age transition in Italy has been the object of a complex debate. Dendrochronology dates of Swiss lake-dwellings, as well as radiocarbon dates from Central Europe and the Mediterranean area prompted a lively dispute which is yet to be resolved.

In this paper the author collects and compares a large number of radiocarbon dates produced in the latest 30 years. Besides providing a list of samples collected in Italian Early Iron Age archaeological sites, the author also analyzes samples taken in the Mediterranean region and in Central Europe, related to Italian Early Iron Age contexts by means of cross-dating or historical texts.

This research then focuses on the time-units associated to each date: the phase of a settlement, an archaeological period in the region, a specific ceramic class or type, etc.

After verifying the validity of the radiocarbon dates as indicators for the intended time-units, the author proceeds to test whether the above-mentioned units can be organized and used as Bayesian priors.

The results will provide a much needed overview of relevant radiocarbon dates for the Italian Iron Age, while clarifying their relation with archaeological and historical data in a schematic and interoperable manner.

A06 11

Results and findings from an international mortar dating intercomparison MODIS2

<u>Scott M</u>¹, Lindroos A², Barrett G³, Boudin M⁴, Hajdas I⁵, Olsen J⁶, Maspero F⁷, Marzaioli F⁸, Michaska D⁹, Moreau C¹⁰, Sironic A¹¹, Pawelczyk F¹²

¹University Of Glasgow, Glasgow, United Kingdom, ²Åbo Akademi University, Vaasa, Finland, ³Queens University Belfast, Belfast, United Kingdom, ⁴KIK-Irpa, Brussels, Belgium, ⁵ETH, Zurich, Switzerland, ⁶Aarhus University, Aarhus, Denmark, ⁷Università di Milano Bicocca, Milano, Italy, ⁸Università degli Studi della Campania Luigi Vanvitelli, Caserta, Italy, ⁹Adam Mickieiwcz University, Poznan, Poland, ¹⁰Université Paris-Saclay, Gif sur Yvette, France, ¹¹Rudjer Boškovic Institute, Zagreb, Croatia, ¹²Silesian University of Technology, Gliwice, Poland

Dating of mortars remains an undertaking which a relatively small number of laboratories are engaged in. At the same there have been developments of different pre-treatment methods, dating of different fractions etc, all of which have the potential to contribute to variability observed in dating results. It is in this context that a further mortar dating intercomparison has been undertaken.

Three samples from the "International mortar dating" (www.mortardating.com) projects' sample collection were selected for this inter-comparison study. The consensus was that the samples should represent different chronologies and typologies and come from geographically different regions and have known ages. Because of the large number of laboratories participating in the inter-comparison, the main sample selection criterion turned out to be the size of the samples available. The age of the youngest sample is well known and the age of the two others is known from earlier ¹⁴C dating of mortar, and their context.

Before distribution, the samples were split into pieces and each laboratory received one piece of each sample for characterization of the mortar. The remainder of each sample was crushed further with plastic covered pliers and sieved in a mechanically vibrated sieve series for 15 min whereafter the <150 micrometer (μ m) grain-size fraction was collected and homogenized by shaking. Each laboratory received approximately 1000 mg of the fraction in a small glass vial.

The results from the intercomparison and their analysis will be presented, focusing on the variations observed and their potential attribution.

A06 12

Grain fractions versus time intervals – mortars radiocarbon dating

Michalska D¹, Hajdas I²

¹Adam Mickiewicz University, Institute of Geology, Poznań, Poland, ²Laboratory of Ion Beam Physics, Dep. of Earth Sciences, ETHZ, Zurich, Switzerland

Pretreatment is very important issue in case of mortars dating. Depending on the composition of the mortar, various preparation techniques allow to obtain the actual age of mortar production and thus the erection of a given wall (Modis 1 and 2). Due to the methodical nature of the work, selected mortar samples from Royal Castle in Poznań were ¹⁴C measured in different time interval and different grain fractions.

The construction of the castle began in the north-west part of a small hill. Due to the unstable ground, a stone foundation was created in the first stage and poured over with lime mortar. Then the castle walls were built of brick.

Radiocarbon dating of mortars provide the first attempt to determine the age of castle buildings. In the case of these mortars, the results of the ¹⁴C measurement showed that the most important factor influencing the real age of the castle construction, was the time interval in which the gas portion was collected during the chemical decomposition of carbonates. It was connected with the composition and preservation state of those mortars. Selection of the appropriate time interval in which the gas is collected for measurement, as well as the method of preliminary preparation can be adapted to a specific type of mortars.

A06 13

Ramped Pyrolysis Radiocarbon Dating of Lime Lumps: Establishing the Earliest Mortar-Based Construction Phase of Turku Cathedral, Finland

<u>Barrett G</u>¹, Allen K¹, Reimer P¹, Ringbom Å², Lindroos A²

¹14Chrono, Queen's University Belfast, Belfast, United Kingdom, ²Åbo Akademi, Turku, Finland

Ramped pyrolysis radiocarbon dating was carried out on lime lumps from the oldest remains of Turku Cathedral, Finland, the first sacristy. Lime lumps from four sampling locations were analyzed. For each sample, 5-6 fractions of CO_2 from different temperature fractions were trapped, converted to graphite and radiocarbon dated.

One of the four samples exhibited contamination for its lowest temperature fractions. For the remaining samples, the age-temperature profiles were well-behaved, exhibiting a plateau of dates that were all in statistical agreement and indicative of a sample where only a single carbonate source (lime

binder from the construction phase) is contributing to the radiocarbon dates. For each of the four samples, the combined radiocarbon age resulted in a late 13th century calibrated age. Combining the radiocarbon dates from all four samples (19 in statistical agreement, χ 2-test: df=18, T = 4.5, 5% = 28.9) provided a calibrated age of 1271-1292 cal AD (95.4%).

This set of results strengthens previous mortar dating results (acid hydrolysis on bulk and lime lumps) and confirms that Turku Cathedral was first constructed from stone and mortar in the late 13th century. The results find remarkable convergence with written sources that suggest Bishop Magnus I may have been elected there in 1291 AD and that the building was inaugurated as a cathedral in 1300 AD. Ramped pyrolysis combined with suitably selected lime lumps is shown, in this instance, to be a robust approach for dating lime-based mortars.

A06 14

A case of mysterious identity: one of the earliest churches of medieval Trondheim, Norway

Nadeau M¹, Petersén A², Sæhle I², Svarva H¹, Seiler M¹

¹National Laboratory for Age Determination, NTNU University Museum, Trondheim, Norway, ²NIKU, Trondheim, Norway

Christianity was introduced in Norway during the 10th Century. King Olav Haraldsson built St Clement's Church in Trondheim in 1015 AD and played an important role in the transition from paganism to Christianity. According to the sagas "... after a while, the coffin miraculously rose out of the earth. It was then moved and buried anew at St. Clement's Church it looked as if Olav was simply sleeping ..." The saga of Olav Haraldsson and the legend surrounding his sainthood soon became central to the Norwegian national identity. The locality of this church has intrigued historians for centuries. In 2016-2017, an archaeological excavation conducted in the historical part of Trondheim revealed amazing features distributed over 15 phases from the 10th century onward. The earlier phases contain urban occupation and secular buildings, representing the late Viking Age/ early Medieval period, capped by a thick burnt layer. A sequence of five wooden churches were uncovered above this layer. The earliest church could be considered a candidate for the St. Clement's Church. Several methods were used to date this difficult site. Posts from secular buildings and churches were dated both by dendrochronology and radiocarbon wiggle matching. The posts that include the 994 AD Miyake event were dated separately using this event. In addition, single radiocarbon results were obtained on human, wood, and plant remains. We present here a model used to establish a chronology for the whole site and discuss whether it could contain the early 11th century St. Clement's Church.

A06 15

Progress towards a Byzantine-Medieval Historic Buildings Tree-Ring Chronology from Cyprus using dendrochronology and radiocarbon

<u>Manning S</u>^{1,2}, Lorentzen B¹, Bakirtzis N², Soyluoğlu M²
¹Cornell University, Ithaca, United States, ²The Cyprus Institute, Nicosia, Cyprus

The painted churches of the Troodos Mountains in Cyprus are monuments of global significance and form key references for Byzantine and Medieval art and architecture in the broader Eastern Mediterranean. However, exact timelines for their building biographies are only approximately known, based on subjective stylistic and typological criteria and a few inscriptions that are not always directly related to the building or the associated artwork. Wooden elements employed in the architecture, decoration and furnishing of these and other historic structures in Cyprus can offer both a key independent chronological resource and also inform on the associated processes of resource acquisition and use. We report on a research project using dendrochronological analysis combined with

radiocarbon to begin to date and source the wooden cultural heritage of Cyprus from the Byzantine, Medieval and Ottoman periods. The ultimate aim of the project is to create the first high-precision timeline for Byzantine and post-Byzantine art and architecture in Cyprus, and to better illuminate the building histories of these structures. Here we report on initial work from the project on a key group of Cypriot painted churches and other historic monuments. While we have been able to directly date some more recent timbers and wooden cultural heritage against forest tree-ring chronologies, new multicentury floating Byzantine tree-ring sequences from several monuments have been preliminarily anchored in calendar time within a few years via radiocarbon wiggle-matching. This work is beginning to create the basis of a high-resolution record linked with over 800 years of cultural heritage.

A06 P01

Project Radiocarbon: big data and cross-border histories

Griffiths S¹, <u>Bayliss A</u>², Brown L³, Carlin N⁴, Evans T⁵

¹Manchester Metropolitan University, Manchester, United Kingdom, ²Historic England, London, UK, ³Historic Environment Scotland, Edinburgh, UK, ⁴University College Dublin, Dublin, Ireland, ⁵University of York, York, UK

The development of radiocarbon dating revolutionised the practice and philosophy of archaeology internationally by providing independent time reckoning. Radiocarbon is the global scientific dating technique because suitable samples and high-precision calibration curves are available internationally. It could provide the potential for a truly internationalised research agenda. As relative processing costs have fallen and Accelerator Mass Spectrometry has reduced required sample sizes, the number of radiocarbon measurements produced annually has increased hugely.

However, the boom in the production of measurements has led to a fundamental problem. Structures for conserving and accessing these data are not matched by data production. International research is impoverished by the lack of interoperability. There are no international datasets that are supported inter-jurisdictionally by national historic environment agencies, with periodic updates to keep them dynamic and scalable. As a result, millions of euros worth of data are being lost, becoming inaccurate, corrupted, or inaccessible, damaging our collective inheritance understanding the archaeological record.

Project Radiocarbon is designed to assemble and validate radiocarbon results along with detailed metadata from across six national jurisdictions on the islands of Ireland and Britain We will produce an open-access digital repository for radiocarbon results and their associated archaeological information making them interoperable, with a commitment to support a live, dynamic resource, which we believe represents a first in radiocarbon big data projects. The project will make a significant contribution to understanding our shared European heritage, and to the management of heritage assets and the historic environment.

A06_P02

When corrosion is useful: the incorporation of ¹⁴C in lead white

<u>Beck L</u>¹, Messager C¹, Germain T¹, Hain S¹ ¹LMC14-ARTEMIS, Gif-sur-yvette, France

Recent studies have shown that radiocarbon dating can be applied to inorganic compounds such as synthetic lead carbonates, cerussite ($PbCO_3$) and hydrocerussite ($2PbCO_3Pb$ (OH)₂ (Beck et al. 2019; Messager et al. 2020). Known as lead white, lead carbonates were used as white pigment or cosmetics from the 4th century BC to the 20th century and were formed by the corrosion of metallic lead by vinegar and horse manure up to the 19th c. In order to better understand the incorporation of ^{14}C in cerussite and hydrocerussite, lead carbonates were produced in laboratory by the corrosion process under various monitored experimental conditions. Lead carbonates were obtained using two types of

acid (vinegar containing 14 C vs 14 C free acetic acid) and three types of CO_2 sources (air, horse manure containing 14 C and 14 C free fossil CO2 gas). Twelve different conditions were tested and 14 C was measured in all the corrosion products: lead acetates when CO_2 was absent and cerussite when CO_2 was present. The results show that cerussites carry the 14 C signature of CO_2 produced by the horse manure or from the fossil gas, indicating that vinegar/acetic acid acts as a precursor and horse manure as a reagent to produce carbonates. These experiments demonstrate that CO_2 produced by horse manure fermentation is incorporated into the corrosion products, meaning that the carbonate function of the lead carbonates carries a 14 C signature corresponding to the natural organic matter. This step is crucial for an absolute dating of lead carbonates by the radiocarbon method.

A06 P03

Integrated methodology for the investigation of paintings – The rediscovery of Jan Ruyscher

Fiorillo F¹, Hendriks L², Hajdas I³, Huysecom E⁴

¹The Fitzwilliam Museum, University of Cambridge, Cambridge, United Kingdom, ²School of Engineering and Architecture of Fribourg, HES-SO University of Applied Sciences and Arts Western Switzerland, Fribourg, Switzerland, ³Laboratory of Ion Beam Physics, ETH Zürich, Zurich, Switzerland, ⁴Faculty of Sciences, University of Geneva, Geneva, Switzerland

The challenging reconstruction of the history of a painting involves several questions: when the object was made being the easiest one to answer based on scientific evidence, while defining the authorship is more complex.

Within the context of heritage sciences, ¹⁴C analyses are gaining popularity owing to advances in microsamples. The integration of radiocarbon dating on the support, the natural organic binder and lead white pigment, with spectroscopic techniques used to investigate the paint layers, offers a complementary approach to characterise an artwork.

To illustrate its potential, this combined methodology was applied to a case study: a landscape painting bearing the signature of Jan Ruyscher, one of the 'Little Dutch Masters' of the 17th century. Radiocarbon analysis of the support dated the wooden panel to the mid-18th century; however, spectroscopic analyses identified titanium white in the paint layers, a pigment put into commerce only in the 1930s.

From an historical perspective, Jan Ruyscher vanished from art history after his death and was rediscovered in the 1930s. The combination of art historical information and scientific findings shed new light on the story of the object; a painting of a less-known painter was made in a specific timeframe, likely following an increased demand of its artworks. The deliberate re-use of an old panel revealed the forger's intent to deceive.

The methodology provides critical arguments for the identification of a period of creation of the painting, a possible reconstruction of its history, and its classification – in this case, a forgery.

A06_P04

Archaeological site of Vetricella: chronology and anthropic and natural landscapes

Di Cicco M¹, Mantile N¹, Marasco L², Bianchi G², Altieri S¹, Vetromile C¹, <u>Lubritto C</u>¹

¹University Of Campania, Caserta, Italy, ²University of Siena, Siena, Italy

In this paper we show results concerning the chronological and landscape reconstruction of Vetricella (Scarlino, GR) archaeological site, situated in the centre of the coastal plain crossed by the river Pecora, near Scarlino Castle. The research work is based on a multidisciplinary strategy: the high variety of material remains discovered, as numismatic, ceramics and vitreous finds; archeometallurgical, archeozoological and archaeobotanical studies, radiocarbon dating and stable isotope analyses

permitted to reconstruct the economic and productive activities, datable from at least the 7th to the 11th century. In particular radiocarbon dating of organic remains and mortar sample permitted to recognize the signs of 4 distinct periods of presence, which can be divided into a chronological period between the 7th - 8th century and the first half of the 11th century, due the type of the recovered finds. Moreover the multi-analytical study permitted to discover the reduced time frame within which the "birth" and the greater development of the site are allocated, corresponding to the end of the 9th and the end of the 10th century.

The project has been realized in the framework of the ERC (European Research Council) research project "nEU-Med: Origins of a new Economic Union (7th to 12th centuries): resources, landscapes and political strategies in a Mediterranean region".

A06 P05

Archeometric research of samples from Huelva La Joya (SW Iberia)

<u>Michalska D</u>¹, Krueger M², Mrozek-Wysocka M¹, Moreno Megías V³

¹Adam Mickiewicz University, Institute of Geology, Poznań, Poland, ²Faculty of Archeology, Adam Mickiewicz University, Poznań, Poland, ³Departamento de Prehistoria y Arqueologia, Universidad de Sevilla, Seville, Spain

Samples from the cemetery of Huelva La Joya (Spain) excavated in the sixties and seventies of the 20th century have been analyzed in order to refine the chronology of the grave archaeologically attributed to the early Iron Age. In the grave no. 9 a double burial, cremation and inhumation, accompanying by rich grave goods of local and foreign provenance were found. The radiocarbon dating of selected charcoal fragments was compared with the relative chronology. Samples from the cemetery were carefully analyzed. Selected fragments of charcoals were also identified.

Then, the results obtained for the Huelva La Joya site were compared with the results of ¹⁴C measurements for the archaeological material from the Setefilla site. These results showed that the biconic bowls are much older than originally thought, the oldest ones dating back to the last centuries of the Bronze Age.

A06_P06

Viking or hippie? A leather bag found in a bog in southern Norway

Nadeau M¹, Zurbach D¹, Rzadczka-Juga I¹, Opheim-Larsen K², Andersen Ø³, Svarva H¹, Seiler M¹
National Laboratory for Age Determination, NTNU University Museum., Trondheim, Norway, ²Olav Magnussonsveg 56, Saksvik, Norway, ³Innlandet fylkeskommune, seksjon for Kulturarv, Hamar, Norway

A treasure can be found anywhere, at any time. In 2021, while hiking in the Dovrefjell, Norway, an area which contains snow patches and is often frozen, a young man discovered a well preserved but relatively old, odd looking leather bag in a peat bog. The bag is made of rather thick but very soft leather in natural colour. It has been sewn with thin leather bands and decorated with stiches and metal studs. The good condition of the bag and the apparent lack of comparative objects from prehistoric times led the local authorities to conclude that it could be as new as the 1970s. The uniformity of the metal studs and the fact that they were not usual decorations support this conclusion. Nevertheless, the young man sent a sample for radiocarbon dating.

The leather sample was cleaned with a sequence of organic solvents before the standard acid-alkali-acid (AAA) treatment. The solvent sequence was applied three times, followed by AAA treatment and ¹⁴C measurement after each step to ensure that all contaminants were removed and that the results did not change. The leather and thread were also analysed by FTIR. Optical microscopy was used to identify the origin of the leather and thread.

We present here the results of the different analyses leading to our conclusion. Far from being from the seventies, radiocarbon results indicate that it might have been the prized possession of someone 800 years before that. However, one could buy it online...

New dating sequence for Andean oracle at Maucallacta; Arequipa, Peru

Sobczyk M¹, Huels M², <u>Rakowski A</u>³, Olaya Cotera C⁴, Kłaput J¹, Pawlyta J⁵, Sieczkowska D¹, Ziółkowski M¹ ¹University of Warsaw, Warsaw, Poland, ²Uni Kiel, Kiel, Germany, ³SUT, Gliwice, Poland, ⁴Independent researcher, Lima, Peru, ⁵AGH, Kraków, Poland

The acheological research related to the Maucallacta site is part of the project carried out since 1996 by the University of Warsaw, (Poland) and the Catholic University "Santa María" (Arequipa, Peru). The Project covers archaeological investigation in the vicinity of the snow-covered volcano Coropuna which was frequently mentioned by chroniclers of the 16th and 17th centuries as an oracle, worshiped since pre-Inca times. The archaeological site of Maucallacta is located approx. 170 kilometers north-west of the city of Arequipa in thesouthern highlands of Peru in District of Pampacolca, Province of Castilla, Department of Arequipa (LS; 3,750 m asl). The architectural complex of Maucallacta, composed of more than three hundred stone buildings, tombs and ceremonial structures. Maucallacta may be considered the principal administrative, pilgrimage and religious center related to the volcano and one of the most important Inca site discovered in Kuntisuyu, the Fourth Quarter of the Inca State. The ceremonies that took place there are evidenced by extensive deposits containing numerous organic remains, including fragments of camelids bones (lama, alpaca). They were discovered at the foot of the largest square, located on a huge stone platform. The dating of the material (bone fragments) from the individual layers of the stratigraphic deposits allows to obtain new data on the probable sequence of celebrations carried out in this complex.

A06 P08

Dating the Wilson's Arch complex, Jerusalem: methodological insights

Regev J¹, Uziel J², Mintz E¹, Regev L¹, Boaretto E¹

¹Weizmann Institute of Science, Rehovot, Israel, ²Israel Antiquities Authority, Jerusalem, Israel

Radiocarbon dating is rarely applied in Classical and Post-Classical periods in the Eastern Mediterranean, as it is not considered precise enough to solve specific chronological questions, often causing the attribution of historical monuments to be based on circumstantial evidence. This research, applied in Jerusalem, presents a novel approach to solve this problem. Integrating fieldwork, stratigraphy, and microarchaeology analyses with intense radiocarbon dating of charred remains in building materials beneath Wilson's Arch, we absolutely dated monumental structures to very narrow windows of time – even to specific rulers.

Most of the dated samples were organic remains extracted from the mortar between the building stones. As the site was filled and covered over the years, microarchaeological methods were used first to verify the identification of the original mortars. Furthermore, hard work was invested to find and identify sufficiently large single fragments of short-lived samples, confirming that each date represents a single point on the calibration curve.

Various construction technologies were used along the 1300 years time span over which the buildings were constructed. As we searched for, identified, extracted, and dated the organic aggregates within the plasters and mortars, very different stages of preservation were identified: in some cases even fresh straw was extracted, while in other materials, the organic remains were extremely fragile. Another aspect to consider is that different building material functions require different technology. The resulting chemical properties of the context affect the preservation state of the material for dating and allows secure dating by chemically definable original material.

Mortar dating of the Stari Most bridge at Otres, Croatia, using data extrapolation

<u>Sironić A</u>¹, Alajbeg A², Cherkinsky A³, Borković D¹, Barešić J¹, Krajcar Bronić I¹
¹Ruđer Bošković Institute, Zagreb, Croatia, ²Museum of Croatian Archaeological Monuments, Split, Croatia, ³Center for Applied Isotope Studies, University of Georgia, Athens, United States of AMerica

Many different approaches exist to radiocarbon dating of mortar, and there is still no universal recipe that would work in all cases. We experimented with data extrapolation from the dates of CO₂ fractions collected by sequential dissolution. The method was modelled after data obtained from two laboratory mortars. Here we use the same method for dating the archaeological site − the Stari Most (Old bridge) at Otres, Croatia.

The arch of the bridge is still partially preserved, making it possible to walk over the Otres creek even today. Based on cadastral and archive data it can be ruled out that the bridge was built after the beginning of the 19th century. A considerable number of stone bridges in the southern Croatian region Dalmatia were built during the Ottoman rule (16th-18th century), but the way of its construction reveals that the Stari Most bridge does not belong to this period either. Since Roman stone bridges were also built differently, the most probable possibility remains that the Stari Most at Otres is medieval. The preliminary dating of the bridge places it from the 9th to the 13th century. The preliminary dating correlates the bridge to the neighboring Otres-Crkvina archaeological site, where most of the activities took place between the 9th and 15th centuries. This is the first attempt to date this arch bridge.

A06 P10

Dating by U-Th and ¹⁴C of secondary carbonate deposits: search for validation criteria. Application to rock art at Nerja cave

Pons-Branchu E¹, Barbarand J², Caffy I³, Dapoigny A¹, Dumoulin J³, Medina-Alcaide M^{4,5}, Nouet J², Sanchidrian Torti J⁵, <u>Tisnerat-laborde N</u>¹, Valladas H¹

¹LSCE/IPSL, CEA-CNRS-UVSQ Univ. Paris Saclay, Gif-sur-Yvette, France, ²GEOPS, Univ. Paris Saclay, Orsay, France, ³LMC14, CEA-CNRS-UVSQ Univ. Paris Saclay, Gif-sur-Yvette, France, ⁴PACEA, Univ. de Bordeaux, Pessac, France, ⁵University of Cordoba, Geography and Territory Sciences, Cordoba, Spain, ⁶Instituto Andaluz de Ciencias de la Tierra, Granada, Spain

Accurate dating of cave carbonate parietal samples is a real scientific issue that would have a major impact in prehistory. Decorated Paleolithic caves are abundant and most of them contain wall decorations engraved or traced with metal oxides that cannot be directly dated by carbon 14; their chronology is therefore very uncertain. Many drawings are covered with carbonate deposits that can be dated by radionuclear methods making it possible to open a new field of investigation for research on Paleolithic art.

Since almost 10 years, researches conducted at Nerja cave on these carbonate layers permitted to establish validity criteria. To get meaningful chronological information on the carbonate formation above or below the parietal representation and define validation criteria for dating, we i) characterized the mineralogical structure of the samples to verify that they behaved as a close system and ii) combined ¹⁴C and ²³⁰Th/²³⁴U dating methods on the same sample in order to estimate the reliability of measured ages. We will present a review of previously obtained data and new ones.

¹⁴C Dating of historical Japanese musical instrument flute sack

YOKOYAMA M¹, SAKAMOTO M, Takaya H

¹Kyoto University, Kyoto, Japan

The radiocarbon dating method was applied to the study of Japanese traditional textiles. The Japanese traditional texture studied includes the traditional musical instrument flute sack which is possessed by Japanese Emperor Go-Daigo (1288-1339).

In our previous work, we studied and applied the radiocarbon dating method to one of the oldest Japanese flag Emperor Go-Daigo possessed. The ¹⁴C dating of this flag was 1463-1528 or 1553-1634. We launched a research project of Southern-Northern court at Yoshino of Nara, Japan and clarify blank history of Japan by applying radiocarbon dating method to Emperor's Imperial Treasure in Anou history and folklore museum.

A07 Radiocarbon & the protection of cultural heritage

A07 01

Radiocarbon Laboratories and the protection of Cultural Heritage—update and discussion

Jull A^{1,2}, Hajdas I³

¹University Of Arizona, Tucson, United States, ²Institute for Nuclear Research, Debrecen, Hungary, ³ETH-Zurich, Zurich, Switzerland

Some spectacular dating of famous antique objects such as the Shroud of Turin, the Dead Sea Scrolls, Vinland Map and Gospel of Judas demonstrate the power of the method for the detection of forgeries and verification of a heritage object's true age. The antiquities trade now relies heavily on ¹⁴C analysis when art works and cultural objects are offered for sale. The provenance of such objects is important to avoid misunderstanding, fraudulent or inaccurate representation of ownership of art works. Currently, forty-seven radiocarbon laboratories listed here http://radiocarbon.webhost.uits.arizona.edu/node/11 have agreed to follow a protocol that requires verification of information on origin of cultural samples and antique objects submitted for ¹⁴C analysis. This paper will summarize the development of this initiative for the protection of cultural heritage and open a discussion within the community.

A07 02

Last chance for carbon-14 chronology of Bolshoi Sintashta Kurgan: Mesopotamian ziggurat in the South Urals

Panyushkina I¹, Milyutina T², Jull A³, Molnar M³, Cherkinsky A⁴, Agafonov L⁵

¹University of Arizona, Tucson, United States, ²Chelyabinsk Pedagogical University, Chelyabinsk, Russia, ³Isotope Climatology and Environmental Research Centre, Debrecen, Hungary, ⁴Center for Applied Isotope Studies, University of Georgia, Athens, United States, ⁵Institute of Plant and Animal Ecology, Yekaterinburg, Russia

Research into the sociocultural complexity of the Eurasian steppe in the Bronze Age has been challenged by recent advances in the prehistorical calendar chronology derived from high-precision AMS carbon-14

measurements. The medley of archaeological cultures in the Southern Urals is well distinguished in space with the prominent typology of ancient ceramic traditions. For the past several decades, they have been thought to be disconnected chronologically. The recent chronological framework of the Bronze Age archeology has struggled with bewildering evidence of chronologically-overlapped and contemporaneous cultures that were previously viewed as a sequential series. New ¹⁴C dating results have uncovered a problem with past dating strategies and suggest a resampling of archaeological materials to address controversial interpretations of the Eurasian Steppe history. We resampled the crumbling ruins of Bolshoi Sintashta Kurgan (BSK) at Sintashta (Indo-Aryan outpost of Middle Bronze Age) and developed 18 new AMS dates from wood and slag. Sintashta as a prominent metallurgical, military and early urban center is dated to the interval 2100-1800 BCE. BSK can be described as is large worship structure built in the shape of terraced compound resemble a Mesopotamian ziggurat. A Bayesian approach to calibration and re-analysis of the new and historical ¹⁴C BSK datasets showed that the worship structure was built between 1500 and 1300 BCE above the deteriorated tholos covering the chamber burial. The tholos chamber is possibly 300-500 years older than the worship structure above. The revised chronology indicates the continuity of the Sintashta, Fedorovo and Alakul cultures on the site.

A07 03

Inquisitive or Nefarious: The Case of Non-Academic Radiocarbon Customers

Hundman B¹, M. Tate A¹
¹Directams, Bothell, United States

The people that seek the use of radiocarbon dating to gain information on objects of cultural heritage are as unique as the objects themselves. In addition to the traditional academic disciplines, "private" individuals, ranging from art dealers and auction houses to amateur scientists and average citizens, bring a myriad of intentions to their specific research questions. It is incumbent upon testing laboratories to assess the objects, and their owners, by identifying potentially vulnerable provenance locations, forgeries, and illicit acquisitions. In 2018, DirectAMS adopted the recommendations of the Radiocarbon community for the protection of objects of cultural heritage. By requiring inquirers to provide additional provenance and provenience for these items, we have been successful in facilitating genuine scientific exploration, while screening potentially objectionable materials from analysis. This presentation discusses the implementation of the ethical approach employed by DirectAMS to assess these core intentions and several case studies of material submitted for analysis.

A07_04

Scoop on Poop (or You Are What You Eat): Radiocarbon Examination of Linen and Fecal Material from a Coptic Textile

<u>Cox J</u>¹, Rowe M¹, Blinman E¹, Jones S¹, Welte C^{2,3}

¹Office Of Archaeological Studies, Center for New Mexico Archaeology, Santa Fe, United States, ²Laboratory of Ion Beam Physics, ETH Zűrich, HPK, H29, Otto-Stern-Weg 5, CH-8093, Zürich, Switzerland, ³Geological Institute, ETH Zürich, NO, Sonneggstrasse 5, CH-8092, Zürich, Switzerland

A textile was provided to the Office of Archaeological Studies Plasma Oxidation Laboratory to determine if it was possibly of Coptic age. In the process of examining the material, feces of insect larvae (likely clothes moths) were found between the acrylic sheets that were placed on either side of the textile for preservation and presentation purposes. The insect infestation was relatively modern (within the last 15-20 years). The excrement stood out as the insects weren't able to metabolize the dyes in the textile thus leaving blue and orange pellets.

A single linen fiber was chosen from the textile for dating purposes using an oxidizing plasma to collect enough CO_2 gas for dating before being sent to ETH-Zürich to be processed with a MICADAS AMS system. In addition, the fecal material was oxidized in an oxygen plasma. Multiple carbon samples were collected with no visible change of the fiber itself, but the pellets lost the surface dye color during the oxidation process, leaving the base linen color.

Regular cleaning procedures were followed with initial oxygen plasmas used to clean the chamber until <0.5 μ g of carbon were present. This was followed by argon plasmas until <0.5 μ g of carbon were present. Finally, oxygen plasmas were run to produce enough CO₂ for measurement purposes (20-100 μ g carbon) to be analyzed at ETH-Zürich.

The agreement between the radiocarbon dates from the linen and the fecal matter indicate that no apparent modern day contamination occurred during the metabolization process of the larvae.

A07 05

Carbon-14 chronology of the Golden Horde in Kazakhstan

<u>Panyushkina I</u>¹, Usmanova E², Uksenbay K³, Jull T^{1,4}, Molnar M⁴, Varga T⁴

¹University of Arizona, Tucson, United States, ²Buketov Karaganda University, Kraganda, Kazakhstan, ³ABDI Institute for Humanitarian Studies, Almaty, Kazakhstan, ⁴Isotope Climatology and Environmental Research Centre, Debrecene, Hungary

The historiography of the Golden Horde (1221–1438 CE), the successor of the Mongol World Empire ruled by the Chinggisids, is not well-defined and bears many contradictories. We located 34 burial complexes of Islamic tradition attributed to the Golden Horde with folk and legends in the Ulytau Mountains of Kazakhstan, which is translated from Turk languages as a "Grand Place of Ancestors". The burial rites of Mongol nobility remained the same throughout the Mongol Empire and were under the sacred rules of Tengri. The royal cemetery was forbidden ground with an undisclosed grave. The Chinggis funeral tradition excluded a mausoleum, although most of the known Mongol burials today are enclosed in the Islamic Mausoleums. Since Islam became the official religion of the Golden Horde after 1313 AD, we propose high-resolution carbon-14 measurements for the Golden Horde mausoleums to link historical evidence and the calendar chronology of medieval architecture in Kazakhstan. We present the results on ¹⁴C dating of two mausoleums: Joichi Khan, the oldest son of Chinggis Khan, died in 1225 CE and Alasha Khan lived in the early 15th century and was a highly acclaimed tribal leader of Kazakhs, Karakalpaks, Kirghiz, Bashkirs, Nogays, and Tatars. The dating argues that the Jochi Khan mausoleum was built about 100 years after the death of Jochi and renovated at least once in the mid-14th century. The Alasha-Khan Mausoleum is most likely built ca. 1315-1360 CE. Historical attribution of both mausoleums does not concur with the age of the building materials.

A07_P01

Dating the Egyptian mummies curated at the University of Tartu Art Museum collections

<u>Oras E</u>¹, Tõrv M¹, Rannamäe E¹, Anderson J²
¹University of Tartu, Tartu, Estonia, ²University of Tartu Museum, Tartu, Estonia

Two ancient child mummies accompanied by a bird and a dog mummy are exhibited at the University of Tartu Art Museum, Estonia. According to museum records the mummies were brought to Estonia from Egypt by a young Baltic-German scholar and voyager Otto Friedrich von Richter in the early 19th century. Yet, their exact provenance and date was unknown. An interdisciplinary team of experts was summoned to study these unique heritage objects using modern analytical methods, including radiocarbon dating. To establish the age of these objects and their temporal relation to each other, the total of eight samples were AMS dated: four from human and four from animal mummies. The AMS dates and further modelling allowed identifying the chronological sequence of the two boy mummies

showing that they were not contemporaneous. The animal mummies displayed as accompanying burial goods at the exhibition turned out to be earlier than the human specimens. Hence, we could conclude that there is no contemporaneous connection between the animal and human mummies. Furthermore, our multiple sampling approach enabled us to detect some considerable dating discrepancies between different sample types from the same object. Our study highlights the fruitfulness of combining thorough scientific expertise and multi-analytical research methods when it comes to disentangling curated heritage objects with intricate secondary history. We also exemplify the relevance of multi-proxy and multi-sample approaches for analysing complex heritage items, allowing to display a more truthful picture of the past for the research communities as well as the wider public.

A07 P02

Radiocarbon dating of the Church of St. Margaret of Antioch in Kopčany (Slovakia): International consortium results

Povinec P¹, Kontul' I¹, Cherkinsky A², Hajdas I³, Gu Y^{3,4}, Jull A^{5,6,7}, Lupták T⁸, Mihály M⁶, Steier P⁹, Svetlik I¹⁰

¹Comenius University, Faculty of Mathematics, Physics and Informatics, Bratislava, Slovakia, ²University of Georgia, Center for Applied Isotope Studies, Athens, USA, ³ETH Zürich, Zürich, Switzerland, ⁴Nanjing University, School of Geography and Ocean Science, Nanjing, China, ⁵University of Arizona, Accelerator Mass Spectrometry Laboratory, Tucson, USA, ⁶Institute for Nuclear Research, INTERACT Centre, Debrecen, Hungary, ⁷University of Arizona, Department of Geosciences, Tucson, USA, ⁸Restauro, s.r.o., Bratislava, Slovakia, ⁹University of Vienna, VERA Laboratory, Vienna, Austria, ¹⁰Czech Academy of Sciences, Nuclear Physics Institute, Prague, Czech Republic

An international consortium of radiocarbon laboratories was established to date the origin of the Church of St. Margaret of Antioch in Kopčany (Slovakia), because its age was not well established in previous investigations. Altogether, 19 samples of wood, charcoal, mortar and plaster were analyzed. The ¹⁴C results obtained from the different laboratories as well as between the different sample types were in reasonably agreement, resulting in a ¹⁴C calibrated age of 780–870 AD (94% probability) for the Church. Although the ¹⁴C results have very good precision, the specific plateau-shape of the calibration curve in this period caused the wide range of the calibrated age. The probability distribution from OxCal calibration shows, however, that about 80% of the probability distribution lies in the period before 863 AD, implying that the Church could have been constructed before the arrival of Constantine (St. Cyril) and St. Methodius to Great Moravia. The Church thus represents, together with the St. Georges's Rotunda in Nitrianska Blatnica, probably the oldest standing purpose-built Christian church in the eastern part of Central Europe.

C01 Climate and paleoclimate studies

C01_01

Prospects and limitations of marine radiocarbon simulations in (paleo) climate studies

Butzin M¹, Köhler P², Lohmann G^{1,2}

¹MARUM-Center for Marine Environmental Sciences, University of Bremen, Bremen, Germany, ²Alfred Wegener Institute, Helmholtz Centre for Polar and Marine Research, Bremerhaven, Germany

On the timescale of hundreds to thousands of years, the oceans play a key role in the climate system by exchanging momentum, energy, freshwater, and carbon dioxide with the atmosphere. The oceans are also the biggest sink of radiocarbon. Observations of recently dissolved marine radiocarbon have provided, and still are, a benchmark for assessing ocean circulation models, which are an essential ingredient of climate models nowadays. Marine radiocarbon records from older times have been used

not only as a dating tool, but also to infer past states of ocean overturning and ocean ventilation. However, these records are sparse, scattered and discontinuous, and their interpretation in terms of past climate change is not straightforward. Numerical simulations could help, but radiocarbon-equipped models often use simplified approaches or setups to keep the computational costs low. In our presentation, we will revisit some of these potential issues and discuss recent developments in ocean-climate-radiocarbon modeling.

CO1 02

A dual chronological approach for more robust paleoclimate reconstructions in semi-arid regions – a case study from Mongolian lake sediments

<u>Bliedtner M</u>¹, Strobel P¹, Struck J¹, Salazar G², Szidat S², Nowaczyk N³, Bazarradnaa E⁴, Lloren R^{5,6}, Dubois N^{5,6}, Haberzettl T⁷, Zech R¹

¹Institute of Geography, Friedrich Schiller University Jena, Jena, Germany, ²Department of Chemistry, Biochemistry and Pharmaceutical Sciences and Oeschger Centre for Climate Change Research, University of Bern, Bern, Switzerland, ³Section Climate Dynamics and Landscape Evolution, GFZ German Research Centre for Geosciences, Potsdam, Germany, ⁴Institute of Plant and Agricultural Sciences, Mongolian University of Life Sciences, Darkhan, Mongolia, ⁵Department of Surface Waters Research and Management, Eawag, Dübendorf, Switzerland, ⁶Department of Earth Sciences, ETH Zürich, Zürich, Switzerland, ⁷Physical Geography, Institute for Geography and Geology, University of Greifswald, Greifswald, Germany

Semi-arid Mongolia is a highly sensitive region to paleoclimate changes, but the region's paleoclimatic evolution and its underlying forcing mechanisms have been controversially discussed. In this context, chronological control of the region's existing paleoenvironmental reconstructions are often imprecise because chronologies are mostly derived from few ¹⁴C-dates on bulk organic material. Bulk organic carbon has often been used in semi-arid regions due to the absence of terrestrial macrofossils. Compared to terrestrial macrofossils, which are assumed to be rapidly deposited in lakes, bulk organic carbon can be "pre-aged" because organic material accumulates in the catchment over hundreds to thousands of years and possibly overestimates the "true" deposition age when ending up in the lake. Here we present the chronology of a 7.4 ka sediment record for paleoclimate reconstructions from the high-altitude Shireet Naiman Nuur (Nuur = lake) in the central Mongolian Khangai Mountains. We extensively ¹⁴C-dated bulk organic carbon and terrestrial macrofossils from the lake sediments and provide a robust and precise chronology for the past 7.4 ± 0.3 cal. ka BP, with mostly all ¹⁴C-ages in stratigraphic order. The ¹⁴C-based chronology is confirmed by paleomagnetic secular variations, which resemble the predictions of spherical harmonic geomagnetic field models. The very good chronological control makes paleomagnetic secular variation stratigraphy a powerful tool for evaluating and refining regional ¹⁴C chronologies when compared to our newly obtained record. Based on our good chronological control, we finally reconstructed variations in paleotemperature and paleohydrology based on established sedimentological proxies and innovative compound-specific δ^2 H analyzes of specific biomarkers.

C01 03

Combining radiocarbon and stable C isotopes of stalagmites to gain novel insights into geochemical processes at Spannagel Cave

Welte C¹, Fohlmeister J³, Wertnik M², Spötl C⁴

¹LIP, ETH Zurich, Zurich, Switzerland, ²Geological Institute, ETH Zurich, Zurich, Switzerland, ³Federal Office for Radiation Protection, Berlin, Germany, ⁴University of Innsbruck, Innsbruck, Austria

Stable carbon (C) isotope records from stalagmites are readily available as they are often measured alongside stable oxygen isotopes (δ^{18} O). Their interpretation, however, remains challenging due to

myriad processes contributing to changes in the C-isotope ratio. Spatially resolved radiocarbon (14 C) data can help to interpret 13 C signatures[1], but are rarely available due to expensive and time-consuming analysis. Rapid and continuous analysis of 14 C concentration in carbonate samples at spatial resolution down to 100 µm is now possible using LA-AMS (laser ablation accelerator mass spectrometry). Combined δ^{13} C and 14 C profiles (expressed as dead carbon fraction, dcf) allowed to hypothesize on the interplay of regional climate and contribution of an old organic C reservoir to stalagmite growth at Spannagel Cave, Austria, in a previous study[2]. Here, we present LA-AMS results from a second Holocene stalagmite from Spannagel Cave (SPA 128). Both stalagmites show large and fast variations in the dcf and δ^{13} C. SPA 128 has a generally higher dcf (\sim 50%) and a more negative δ^{13} C signal that point towards continuous contribution of an old organic C reservoir to the stalagmite C. Even though, the observed signals cannot be explained conclusively so far, it can be stated that the stable oxygen isotopes agree well in both stalagmites. This is an encouraging finding for future studies making use of δ^{18} O as climate proxy.

[1]D. Rudzka et al., (2011) GCA 75, 4321-4339.[2] C. Welte et al., (2021). Clim. Past 17, 2165–2177.

C01 04

Toward Reconciling Radiocarbon Production Rates WithCarbon Cycle Changes of the Last 55,000 Years

Köhler P¹, Adolphi F¹, Butzin M¹, Muscheler R²

¹Alfred Wegener Institute Helmholtz Centre For Polar And Marine Research, Bremerhaven, Germany, ²Department of Geology, Lund University, Lund, Sweden

Since it is currently not understood how changes in 14 C production rate (Q), and in the carbon cycle, can be combined to explain the reconstructed atmospheric Δ^{14} C record, we discuss possible reasons for this knowledge gap. When combining Q with carbon cycle changes, one needs to understand the changes in the atmospheric 14 C inventory, which are partially counterintuitive. For example, during the Last Glacial Maximum, Δ^{14} C was ~400% higher compared with preindustrial times, but the 14 C inventory was 10% smaller. Some pronounced changes in atmospheric Δ^{14} C do not correspond to any significant changes in the atmospheric 14 C inventory, since CO_2 was changing simultaneously. Using two conceptually different models (BICYCLE-SE and LSG-OGCM), we derive hypothetical Qs by forcing the models with identical atmospheric CO_2 and Δ^{14} C data. Results are compared with the most recent data-based estimates of Q derived from cosmogenic isotopes. Millennial-scale climate change connected to the bipolar seesaw is missing in the applied models, which might explain some, but probably not all, of the apparent model-data disagreement in Q. Furthermore, Q based on either data from marine sediments or ice cores contains offsets, suggesting an interpretation deficit in the current data-based approaches.

C01 06

Ultra-small AMS ¹⁴C sample analysis to reconstruct changes in the water availability of the Atacama Desert

<u>Gwozdz M</u>¹, Heinze S¹, Hackenberg G¹, Herb S¹, Stolz A¹, Dewald A¹, Jaeschke A², Rethemeyer J², Schiffer M¹

¹Institute for Nuclear Physics, University of Cologne, Cologne, Germany, ²Institute for Geology and Mineralog, University of Cologne, Cologne, Germany

Traces of plant and microbial life preserved in the hyper-arid soils of the Atacama Desert show a strong dependency on water availability, which is the main controlling factor determining the presence of life.

The ultra-small soil samples with 1-20 μ g carbon content will be used to reconstruct changes in the water availability. Ultra-small AMS ¹⁴C sample analysis will be applied for determining ages of organic compounds isolated from the desert soils.

The coupling of an isotope ratio mass spectrometer (irMS) to the AMS system will allow online-analysis of 14 C, δ^{13} C, and δ^{15} N of ultra-small samples. δ^{13} C values will be used for correction of fractionation in the AMS system, to increase the measurement accuracy and finally, to solve dating problems in different archives of the desert, e.g. sediments from clay pans, phytoliths and lipid bio markers like plant wax lipids.

For the analysis of ultra-small soil samples from the Atacama desert, gas ion source AMS 14 C analysis is applied, due to the achieved reliable results for samples with 2.5-50 µg carbon content and ages higher than 25,000 yr BP. The CO₂ from the sample combustion in an elemental analyzer (EA), which oxidizes solid samples under a constant Helium flow, is split and a small quota is directed towards the irMS, whereas the rest is directed to the AMS ion source by the gas injection system (GIS). While δ^{13} C, and δ^{15} N can be measured with the irMS, the 14 C content is simultaneously measured with the AMS system.

C01 P01

U/Th dating and radiocarbon measurement potentials using marine mollusks around Japanese archipelago

Hirabayashi S¹, <u>Aze T</u>¹, Miyairi Y¹, Kan H², Yokoyama Y¹

¹Atmosphere and Ocean Research Institute, The University of Tokyo, Kashiwa, Japan, ²Research Center for Coastal Seafloor, Kyushu University, Nishi-ku, Japan

Radiocarbon dating of mollusks are widely used in paleoclimatology and archeology, while Uraniumthorium (U/Th) dating is generally difficult to provide reliable age using mollusks. However, several recent studies suggested that the U/Th dating potential using marine bivalves in Mediterranean Sea, Caspian Seaand Korea. These studies have investigated using limited mollusks species and regions. In this study, we investigated the distribution of radiocarbon and uranium in mollusks, including the calcified opercula of Turbo sazae Fukuda, Turbo marmoratus and Tridacnina sp. collected from Ryukyu region and Chiba, Japan, to evaluate the possibility of U/Th dating potentials using marine mollusks around Japanese archipelago. We measured high-resolution radiocarbon and uranium concentration using single stage AMS (Yokoyama et al., 2019) and laser-ablation ICP-MS in Atmosphere and Ocean Research Institute, The University of Tokyo, respectively. Our results showed that uranium in opercula of modern Turbo sazae Fukuda and Tridacnina sp. were unevenly distributed and those concentration were 1000 times-less than that in coral skeletons, while radiocarbon in the shell samples were reflected the radiocarbon values in the ambient seawater as well as corals. The uranium in the calcified opercula of Holocene Turbo marmoratus was also unevenly distributed but concentrated area in the opercula was different from that of the modern samples, which suggested exchange uranium after they were deposited. Our results suggested that the uptake processes of radiocarbon and uranium isotopes into mollusks shell were different, and it is important to understand the criteria of choosing the mollusks species for U/Th dating around Japan.

Climatic signal in tree ring δ^{13} C and its temporal stability - case study for Suwałaki region

Pawełczyk S¹, **Benisiewicz B**²

¹Silesian University Of Technology, Gliwice, Poland, ²Silesian University Of Technology, Gliwice, Poland

Isotopic measurements in tree rings can be very useful in reconstructing past climate. However, such reconstructions may encounter some problems. One of these, especially at the present time, is an environmental change caused by anthropopression, which also affects the stable isotope ratios. Investigations of stable carbon isotope composition in α -cellulose extracted from tree rings of pines (Pinus sylvestris L.) growing in the ecologically clean Suwałki region, North Eastern part of Poland, are undertaken. Carbon isotopic composition of α -cellulose samples was determined using a mass spectrometer coupled to the elemental analyzer. Analyzed isotope record cover the period from 1932 to 2003. Values of δ^{13} C measured in the α -cellulose of tree rings were compared to meteorological data. Values of δ^{13} C in cellulose strongly respond to temperature, insolation, relative humidity, and precipitation of the current year. The relative August humidity values yield the best correlation between climate and carbon isotope data (r=-0.65). Relations between isotopic and meteorological data demonstrate that precipitation influences the stable carbon isotopic ratios to a lower extend than the humidity. Using a moving interval technique, the temporal stability of correlation between isotope chronology and climate was investigated. These studies showed no climate signal stability for the years of the maximum industrial human activities.

This work is a part of EU ISONET project No. EVK2-CT-2002-0014 (400 years of Annual Reconstructions of European Climate Variability using a High Resolution Isotopic Network).

C01 P03

Evidence of Holocene Hydroclimate Variability in Northern India and Links to the Indus Civilization

Cherkinsky A¹, Niederman E², Porinchu D¹, Kotlia B³

¹University Of Georgia, Athens, United States, ²Stetson University, Deland, United States, ³Kumaun University, Nainital, India

Multi-proxy analysis of a lake sediment core from Uttarakhand, India was undertaken to: characterize regional hydroclimate variability during the middle to late Holocene; and determine if evidence of Indus civilization characterized by well developed agriculture between 4200-3900 cal yr is present at the site. Deoria Tal is a small (2.7 ha), moderately deep (16.0 m), tectonically formed lake situated in a high-grade metamorphic terrain above the Main Central Thrust zone in the Garhwal Himalaya. Chronological control is based on ten AMS ¹⁴C dates obtained on Trapa seed cases. The age-depth model, developed using BACON, indicates that the core spans ~ 5300 years and that a notable increase in the sedimentation rate occurs at 2100 cal yr BP. The results of non-destructive, radiological analyses (XRF, CT scans) suggest that elevated detrital input, greater sediment density, decreased lake ventilation, and lower autochthonous productivity, reflecting a deepening of the lake, occurred between 4350 and 4200 cal yr BP. An abrupt shift in elemental concentrations and sediment density indicated the onset of lake drawdown at 4200 cal yr BP and a negative hydroclimate anomaly between 4200 and 4050 cal yr BP. At present, we cannot distinguish if the hydroclimate anomalies identified at Deoria Tal are due to variations in summer and/or winter precipitation; however, it is notable that the positive hydroclimate anomalies at Deoria Tal are associated with intervals of strengthened mid-latitude Westerlies.

Holocene fire recorded in dune footslope deposits at the Cooloola Sand Mass, Australia

Patton N^{1,2}, Shulmeister J^{1,2}, <u>Hua Q</u>³, Almond P⁴, Rittenour T⁵, Hanson J^{1,2}, Grealy A², Gilroy J², Ellerton D^{2,6}
¹School of Earth and Environment, University of Canterbury, Christchurch, New Zealand, ²School of Earth and
Environmental Sciences, The University of Queensland, Brisbane, Australia, ³Australian Nuclear Science And
Technology Organisation, Lucas Heights, Australia, ⁴Department of Soil and Physical Sciences, Lincoln University,
Christchurch, New Zealand, ⁵Department of Geology, Utah State Luminescence Laboratory, Utah State University,
Logan, USA, ⁶Department of Geological Sciences, Stockholm University, Stockholm, Sweden

Fire is one of the most dominant landscape disturbances on Earth. There are large and growing paleofire datasets, but they are strongly biased towards wetland areas (e.g., peat bogs, swamps and lakes). In this study, we investigate whether terrestrial depositions within the Cooloola Sand Mass coastal dune field, Australia, contain a reliable record of fire history. We excavated four profiles at the base of dune slipfaces (foot-slopes) and calculated charcoal concentrations for three size classes (180-250µm, 250-355µm and 355µm-2mm) at predetermined depth intervals. Bayesian age-depth models were constructed for these profiles using radiocarbon measurements on charcoal (n = 46) and basal OSL dates (n = 4). All records appeared intact with little evidence of post depositional mixing as demonstrated by minimal age-reversals and consistent trends in charcoal concentration and accumulation rates amongst size classes. Aggregating all four records, we generated a terrestrial fire history for the past ca. 7 ka that depicts five distinct peaks representing periods of increased local fire activity: ca. present-0.25, 0.4-1.2, 1.8-2.2, 2.6-3.6 and 5.2-6.7 ka. In general, the charcoal peaks increase in frequency after ca. 4 ka, possibly related to the onset of ENSO. Our findings parallel those recorded outside the dune field and highlight their utility as an ecological and geomorphological record that is abundant across the landscape. As dune fields are much more common than wetlands and lakes in semi-arid and arid areas, these deposits have the potential to increase the spatial resolution of fire records globally.

C01 P05

Sedimentary environment and depositional process of reworked materials in the subaqueous Yangtze Delta during the middle and late Holocene

Wang K^{1,2}, Saito K², Tada R^{2,3}, Irino T¹, Zheng H⁴, Sugisaki S⁵, <u>Uchida M</u>⁶

¹Hokkaido University, Sapporo, Japan, ²University of Tokyo, Hongo, Japan, ³Chiba Institute of Technology, Tsudanuma, Japan, ⁴Yunnan University, Kunming, China, ⁵National Institute of Advanced Science and Technology (AIST), Tsukuba, Japan, ⁶National Institute for Environmental Studies (NIES), Tsukuba, Japan

Origin and formation mechanism of the subaqueous Yangtze Delta is of primary importance owing to massive inputs of terrestrial materials from the Yangtze River. It is necessary to examine the transportation mechanism of Yangtze-derived sediment including sediment reworking / re-deposition by coastal current, tide and local input, the migration of shoreline and estuary of the Yangtze River, as well as changes of depocenter in the Yangtze Delta associated with the postglacial sea-level rise in order to interpret and further understand paleoclimatic information record in the Yangtze Delta. YD13 core recovered from the subaqueous Yangtze Delta at 37-m water depth was used to examine the depositional process through time. The age model of YD13 core was established on the basis of the AMS¹⁴C dates of shell fossil, which revealed that the top 10 m of YD13 core corresponds to the last 5.1 ka. The top 10 m of YD13 core sediments are mainly composed of gray silt with intercalations of many thin coarse silt to sand layers. Comparison among ages of shell fossil, benthic foraminifera, particulate organic carbon (POC) and optically stimulated luminescence (OSL) dating, we assumed that YD13 core sediments deposited during 5.1 to 2.3 ka were significantly affected by the reworked materials, which

were originally deposited during the transgression in the early to middle Holocene in addition to the riverine sediments discharged directly from the Yangtze estuary.

C01 P06

Updated radiocarbon age-depth model from Lake Baikal sediment: Implication for past hydrological changes for last glacial to the Holocene

Nara F^{1,2,3}, Watanabe T⁴, Lougheed B⁵, Obrochta S⁶

¹Nagoya University, Nagoya, Japan, ²Kanazawa University, Kanazawa, Japan, ³Chukyo University, Nagoya, Japan, ⁴Japan Atomic Energy Agency, Gifu, Japan, ⁵Uppsala University, Uppsala, Sweden, ⁶Akita University, Akita, Japan

We present an updated ¹⁴C age model using IntCal20 to calibrated new AMS data applied to a Lake Baikal sediment core (VER99G12) in south Siberia. ¹⁴C measurements showed that the core extends to 32 ka BP. To take into account uncertainties in ¹⁴C age and sedimentation depth in the core, a new age-depth modeling routine, undatable, was used in this study. Undatable revealed that the significant changes in the sedimentation rate correspond to global climate events, either warm or cold, which are the Meltwater pulses (MWP) at 19 and 14 ka BP and the Last glacial maximum (LGM) at 21 - 20 ka BP. Since the Selenga River accounts for 50 % of the total river inflow to Lake Baikal, we interpret that these changes in sedimentation rate could be signals of significant increase in Selenga River discharge to the lake, which is expected to be affected by global climate change. Total organic carbon content and mean grain size increase concurrent with sedimentation rate, suggesting river inflow increased available nutrients for biological activity. Our results indicate that hydrological changes corresponding to MWP events can be observed in continental area of the Northern hemisphere.

C01_P07

Paleoclimate study in the Indonesian throughflow region using carbon and beryllium isotopes

<u>Nemoto K</u>¹, Yokoyama Y¹, Horiike S¹, Obrochta S², Miyairi Y¹, Aze T¹

¹The University Of Tokyo, Kashiwa, Japan, ²Akita University, Akita, Japan

The Indonesian throughflow (ITF), the only pathway between the Pacific and Indian Oceans, transports relatively cool, less saline water from the Pacific to the Indian Ocean. Air-sea interactions change dynamically in correspondence with ITF variability, which in turn affects climate (Song & Gordon, 2004). It is also known that the strength of the ITF fluctuates with glacial cycles (Hendrizan et al., 2017; Fan et al., 2018) Thus, reconstruction of past changes in ITF strength is important to better understand global climate. Even though several previous studies address the reconstruction of past ITF variability, more spatially high-resolution data are needed considering the complex pathway of the ITF. In this study, two cosmogenic isotopes are measured to reconstruct past climate change around the Timor Sea, which is one of the ITF pathways. Radiocarbon dating was performed on planktonic foraminifera and total organic carbon. The offset between each age and carbon nitrogen ratio provides information on past changes in terrigenous material movement. In addition, beryllium 10, another cosmogenic nuclide, and its stable isotope beryllium 9, sourced from weathering, are measured. The effect of environmental components such as grain size can be removed by measuring these two isotopes (Simon et al., 2016). This is the first study to apply multiple cosmogenic nuclides (carbon 14 and beryllium 10) to reconstruct the paleoclimate of the ITF region.

A 900-Year Isotopic Proxy Rainfall Record from central Botswana

Patrut R¹, Woodborne S², <u>Patrut A</u>^{1,3}, Hall G⁴, Robertson I⁵, Winterbach C⁶, Rakosy L⁷

¹Babes-Bolyai University, , Faculty of Chemistry and Chemical Engineering, Cluj-Napoca, Romania, ²iThemba LABS, Johannesburg, South Africa, ³Babes-Bolyai University, Raluca Ripan Institute for Research in Chemistry, Cluj-Napoca, Romania, ⁴Mammal Research Institute, University of Pretoria, Pretoria, South Africa, ⁵Swansea University, Department of Geography, Swansea, UK, ⁶Tau Consultants (Pty) Ltd, Maun, Botswana, ⁷Babes-Bolyai University, Faculty of Biology and Geology, , Cluj-Napoca, Romani

High resolution climate archives for southern Africa are essential for designing and validating climate projections. For southern Africa and Botswana in particular, the interannual rainfall variability is associated with sea surface temperatures in the Agulhas Current Core region, which determine the eastwest displacement of tropical temperate troughs (TTTs). Stable carbon isotope analysis and radiocarbon dating of the African baobab (Adansonia digitata L.) can provide reliable reconstructions of rainfall variability in its distribution area. We obtained a proxy rainfall record for central Botswana based on the historic Chapman baobab, which collapsed in 2016 during an intense El Niño event. The two investigated samples of the oldest stems of the baobab, which exhibited an open ring-shaped structure composed of 6 stems, provide insight into the precipitation regime over the last millennium, showing centennial and decadal scale variability. The results indicate that the lowest rainfall occurred during the Little Ice Age (1300-1350), while the Warm Medieval Period was marked by relatively stable precipitation. Previous studies suggested positive sea surface temperature (SST) anomalies in the Mozambique Channel led to an eastward movement of the TTTs but our proxy record shows a westward displacement in the past, causing drought in north-eastern South Africa and wetter conditions in the central part of southern Africa. The positive rainfall correlation with SST anomalies and ENSO reversed after 1900, causing a gradual decrease in precipitation and confirming the current aridity trend for Botswana. The research was funded by the Romanian Ministry of Research CNCS-UEFISCDI under grant PN-III-P4-ID-PCE-201620-2567, No. 145/2021.

C01 P09

Improving radiocarbon based chronologies in semi-arid regions using paleomagnetic secular variations – a case study from Mongolian highaltitude lakes

 $\underline{\textbf{Strobel P}}^1$, Haberzettl T², Struck J¹, Salazar G³, Szidat S³, Nowaczyk N⁴, Bazarradnaa E⁵, Zech R¹, Bliedtner M¹

¹Institute of Geography, Friedrich Schiller University Jena, Jena, Germany, ²Physical Geography, Institute for Geography and Geology, University of Greifswald, Greifswald, Germany, ³Department of Chemistry, Biochemistry and Pharmaceutical Sciences and Oeschger Centre for Climate Change Research, University of Bern, Bern, Switzerland, ⁴Section Climate Dynamics and Landscape Evolution, GFZ German Research Centre for Geosciences, Potsdam, Germany, ⁵Institute of Plant and Agricultural Sciences, Mongolian University of Life Sciences, Darkhan, Mongolia

The paleoenvironmental evolution of semi-arid Mongolia is not well understood so far. To some degree, this is because chronologies in the region are often imprecise limiting the reliability of paleoenvironmental reconstructions. Most chronologies rely on a limited number of ¹⁴C-dates on bulk organic material, which comprises aquatic and terrestrial organic material potentially effected by "hard water" and "pre-ageing" effects. However, it is often impossible to disentangle both effects and resulting age-offsets lead to an overestimation of the true sedimentation age. To overcome these issues, paleomagnetic secular variations (PSV) can be a valuable independent chronological control tool to evaluate and refine ¹⁴C-based chronologies in semi-arid regions.

Here we present a chronological approach including ¹⁴C dating of different sediment compounds and PSV from Lake Khar Nuur, which is located in the Mongolian Altai Mountains. While ¹⁴C-ages of aquatic

macrofossils are stratigraphically consistent, ¹⁴C-ages of bulk organic material show partly age-offsets due to pre-aging and sediment relocation. However, we cannot exclude that both compounds are additionally affected by a hard water effect resulting in a general overestimation of the true depositional age. Therefore, analyses of PSV are currently in progress and will be compared to the recently established PSV record from the high-altitude Lake Shireet Naiman Nuur (Bliedtner et al., 2022), which is located in the Mongolian Khangai Mountains and has a very precise chronological control. Comparison of the two ¹⁴C independent PSV records will allow to evaluate and potentially refine our ¹⁴C-based chronology at Lake Khar Nuur.

C01 P10

Optically stimulated luminescence dating of marine sediments from the Bering Sea

Sugisaki S¹, Buylaert J, Murray A³, <u>Uchida M</u>⁴, Stephan R⁴, Mantoku K⁴, Sakai S⁵, Harada N⁶, Tada R⁷
¹Geological Survey of Japan, AIST, Tsukuba, Japan, ²Department of Physics, Technical University of Denmark,
Roskilde, Denmark, ³Nordic Laboratory for Luminescence Dating, Department of Earth Sciences, Aarhus University,
Roskilde, Denmark, ⁴Earth System Division, National Institute for Environmental Studies, Tsukuba, Japan,
⁵Biogeochemistry Research Center, Japan Agency for Marine-Earth Science and Technology, Yokosuka, Japan,
⁶Atmosphere and Ocean Research Institute, The University of Tokyo, Kashiwa, Japan, ⁷Institute for Geo-Cosmology,
Chiba Institute of Technology, Narashino, Japan

Marine sediments contain important archives of past ocean and climate changes, but at high latitudes, such as the polar regions, the absence of carbonate has prevented the construction of accurate chronological models. To establish an age model, a method which does not rely on carbonate is needed. Optically stimulated luminescence (OSL) dating makes use of the omnipresent quartz and feldspar grains in the sediment so there is no limitation in the presence of the dosimeter.

In this study, we have investigated the potential of fine-grained (4-11 μ m) quartz OSL dating to establish a chronology for deep sea sediment core (MR0604 PC23A, 60°09.52′N, 179°27.82′W, water depth of 1,002m) from the Bering Sea. In addition, we check the accuracy of OSL ages by comparison with AMS ¹⁴C dating on planktonic foraminifera and with marine oxygen isotope stratigraphy where possible.

The obtained OSL ages are in good agreement with AMS ¹⁴C ages during Younger Dryas (YD) and Heinrich Event H0, however, there is an offset between the OSL and AMS ¹⁴C ages during MIS 3. Our study confirms that OSL dating using fine-grained quartz that is distributed all over the ocean has great potential in the establishment of an absolute chronology for deep sea sediments.

C01_P11

Mid- to Late- Holocene sea level changes recorded in corals from Philippines

Yokoyama Y¹, Maeda Y², Siringan F³, Miyairi Y¹, Aze T¹, Sawada C¹

¹The University Of Tokyo, Kashiwa, Japan, ²University of Hyogo, Kobe, Japan, ³University of Philippines, Quezon City, Philippines

Sea level observations in the fields (relative sea level: RSL) can provide information on both climate and solid earth properties. Sites located far-away from former ice sheets (ie. far-fields) are useful to reconstruct polar ice sheets melting histories because they are relatively less sensitive to solid Earth properties (Yokoyama & Purcell, 2021). Since Antarctic ice sheets deglacial pathways are still not well understood, mid- to late- Holocene far-filed sea levels can constraint the ice sheets behavior in the past with respect to global climate changes (eg., Yokoyama et al., 2019). The Philippines is in a far-filed site, and coral reefs, which is a reliable RSL indicator (Yokoyama & Esat, 2015), can be found in widespread

areas of the country's coastline. We retrieved fossil micro atoll corals in different part of the Philippines and have conducted series of radiocarbon dating. In this presentation, we will discuss melting histories of Holocene Antarctic ice sheets and vertical tectonic movements of the Philippines coastline obtained from fossil coral data.

References:

Yokoyama, Y. and Purcell, A. (2021) On the geophysical processes impacting palaeo-sea-level observations. Geoscience Letters 8:13.

Yokoyama, Y., et al. (2019) Holocene Indian Ocean sea level, Antarctic melting history and past tsunami deposits inferred using sea level reconstructions from the Sri Lankan, Southeastern Indian and Maldivian coasts. Quaternary Science Reviews 206:150–161

Yokoyama, Y., Esat, T.M. (2015) Coral Reefs. In: Long A, Horton B, Shennan I (eds) Handbook of sea-level research. Wiley, Chichester, pp 104–124

C02 Anthropogenic impacts

C02_01

Radiocarbon measurements on soot particles preserved in sediments illustrate past fossil fuel usage history in China

Dusek U¹, Tang Y², N. Waters C⁴, Schneider T⁵, Yao P¹, Han Y^{2,3}

¹Centre for Isotope Reserach, University Of Groningen, Groningen, Netherlands, ²Institute of Earth Environment and Center for Excellence in Quaternary Science and Global Change, Chinese Academy of Sciences, Xi'an, China, ³Jiaotong University, Xi'an, China, ⁴University of Leicester, Leicester, United Kingdom, ⁵Columia University, New York, USA

Fossil fuel (FF) combustion accounts for a large, but uncertain, amount of elemental carbon (EC) in the atmosphere, where EC plays an important role in climate warming and adversely affects human health. However, historical estimates of FF contributions to air pollution are limited by uncertainties in fuel usage and emission factors. Here, we developed a novel radiocarbon method specifically applied to sedimentary soot, defined as the most refractory part of EC. The method was based on a two-step thermal protocol for isolating EC from atmospheric aerosol samples. Then, we constrained FF-soot emissions from southeastern China over the past 110 years using a sediment core from a maar lake. For this lake, exogenic material such as soot, originates almost entirely from atmospheric deposition.

The reconstructed soot accumulations reflect the integrated effects of increased fossil fuel use caused by economic development and reductions in emissions due to pollution controls. A sharp increase in FF-soot started at 1950 as southeastern China industrialized and developed economically, but both the percentage and the fluxes of FF-soot fraction decreased over the past decade, confirming the efficiency of pollution controls on the reduction of soot emissions. We compare FF-soot history to changes in CO₂ emissions, industrial and economic activities, and pollution controls and show that FF-soot fluxes are more readily controlled than atmospheric CO₂. Our independent FF-soot record provides insights into the effects of economic development and controls on air pollution and the environmental impacts from the changes in soot emissions.

Using radiocarbon in tree rings to track nuclear power plant emissions and fossil fuel contributions in Ontario, Canada

Martin D¹, Pisaric M², Crann C³, Vogel F⁴

¹Department of Biological Sciences, Brock University, St. Catharines, Canada, ²Department of Geography and Tourism Studies, Brock University, St. Catharines, Canada, ³AEL-AMS Laboratory, University of Ottawa, Ottawa, Canada, ⁴Climate and Research Division, Environment and Climate Change Canada, Toronto, Canada

The atmospheric radiocarbon (14C) signature can help inform atmospheric carbon inventories for environmental monitoring and observing anthropogenic atmospheric carbon-source impacts as it is influenced by global-scale inputs (e.g., natural ¹⁴C production, the industrial revolution, nuclear weapons testing) and local inputs (e.g., nuclear power plants, urban centres). In this study, we measure Δ^{14} C in tree rings to look at the history of anthropogenic carbon dioxide (CO₂) contributions from local emission sources in Southern Ontario that either contribute 14C (e.g., nuclear power) or 12, 13C (e.g., burning of fossil fuels). Ontario's energy portfolio includes 50% nuclear power produced using Canadian Deuterium (CANDU) reactors and includes the world's largest nuclear power station: Bruce Nuclear Generating Station (BNGS). Results from tree ring Δ^{14} C near Bruce show an enrichment in 14 C compared to background and a correlation with emissions data from Bruce Nuclear. Since the BNGS is 200 km upwind of the Greater Toronto Area (population > 6.3 million), it is important to consider the magnitude of the $^{14}\mathrm{C}$ signature across space and time when studying the $\Delta^{14}\mathrm{C}$ signature in the urban area of the Greater Toronto Area (GTA). Depleted Δ¹⁴C signatures (relative to clean air measurements at Jungfraujoch, CH, and Egbert, ON) in tree ring and atmospheric Δ^{14} C measurements in the GTA largely reflect urban sprawl over the past 30 years, but also tell the story of COVID-19 lockdowns in March 2020 when there was less population mobility and subsequent declines in ¹⁴C-depleted atmospheric CO₂ concentrations due to less fossil fuel consumption.

CO2 03

Radiocarbon Inventories of Switzerland: Spatial Radiocarbon Signatures of Carbon exported by Swiss Rivers

<u>Rhyner T</u>¹, Haghipour N¹, Bröder L¹, Eglinton T¹ *ETH, Zurich, Switzerland*

In the Anthropocene, there is the need to investigate changes in the nature of carbon within the biosphere, hydrosphere, atmosphere, geosphere and the connection between them. The RICH-project (Radiocarbon Inventories of Switzerland), is a world premiere in constructing a first national-scale census of carbon across aquatic, terrestrial, and atmospheric reservoirs. Within the global carbon cycle, inland waters play a crucial role, where rivers act as principal connectors between different carbon reservoirs. However, there is still limited understanding of the drivers that control carbon mobilization and mineralization in rivers. This project will establish radiocarbon inventories of dissolved and particulate carbon phases across major river systems of Switzerland. In many cases, the inputs of C to a reservoir can derive from multiple sources, where radiocarbon has been used in combination with 13C to disentangle a C mixture into its source components of modern, pre-aged, or fossil carbon. This can be used to estimate the relative contributions of individual sources with different ¹⁴C-signatures to a given system. Combining emergent ecosystem properties across the five ecoregions of Switzerland, there will be the notion of a radiocarbon compilation to develop an integrated perspective on carbon cycling on a national scale. A field sampling campaign in 2021 revealed spatial variability in radiocarbon content, where riverine Δ^{14} C ranged from -477 ‰ to 58 ‰. These data form the foundation for future in-depth investigations using ¹⁴C measurements on compound-specific biomarkers to constrain the temporal dynamics and transport pathways of biospheric carbon.

Carbon Isotope Changes Through the Recent Past: $F^{14}C$ and $\delta^{13}C$ values in single barley grain from 1852 to 2020

<u>Dunbar E</u>¹, Scott M², Tripney B¹, Addis H³

¹SUERC, University of Glasgow, Glasgow, UK, ²University of Glasgow, Glasgow, UK, ³Rothamsted Research, Hertfordshire, UK

Annual records are gaining increasing prominence, whether in the form of tree rings (with their growing importance in IntCal) and other reservoirs, or from the more recent past, such as grain with a single known year of growth. Such annual $F^{14}C$ and $\delta^{13}C$ data from the past 60 years has proven a useful tool in the study of both environmental processes and in forensic science, generating "bomb $F^{14}C$ curves". Presented here are $F^{14}C$ and ancillary $\delta^{13}C$ values on barley grain (Hordeum vulgare L. spring barley) covering the period 1852 to 2021, collected from the sample archive of the Long-Term Experiments (LTEs) Hoosfield Spring Barley at Rothamsted Research (Hertfordshire, UK) – the oldest agricultural research station in the world, founded in 1843.

The barley grain data is presented alongside data from barley mash samples which have formed a part of several intercomparison studies undertaken in the past 30 years. Together, these data add value to the post bomb F¹⁴C curves. Furthermore, it is now evident that recent F¹⁴C values for grain are approaching the nominal activity of an 1890 wood (F¹⁴C value of 1), raising the questions: When will the F¹⁴C value decrease below 1? Will this cause difficulties in establishing whether a sample derives from the pre- or post-nuclear era?

C02 P02

Radiocarbon Concentration Measurements in Tree Leaves near SOCOCIM (Rufisque, Senegal), A Cement Factory

NDFYF M1

¹Laboratoire Carbone 14, Dakar, Senegal

Radiocarbon content in biogenic samples is widely used to study the variation of atmospheric CO_2 due to anthropogenic activities. A total of 20 samples of several types of tree leaves, were analyzed for this study. Sampling was carried out at the end of the rainy season in 2017 from the surrounding of the SOCOCIM cement factory in Rufisque town. Rufisque is located on the peninsula of Cape Verde, 25 km east of Dakar, where it is the «south gate» of the agglomeration. Reference samples of five different species were collected during the same period (2017) from a clean zone. The 14 C method was used for the determination of Δ^{14} C values. The data show that the 14 C concentration in the studied sites was significantly lower than the clean area, due to the release of anthropogenic CO_2 . To estimate the Suess effect, the fossil fuel fraction was determined based on equations of mass balance for CO_2 concentration, stable isotopic composition of carbon, and 14 C concentration. The results show that selected locations are affected differently according to their distance from the factory and the wind direction.

Keywords: Radiocarbon Concentration, Fossil Fuel Fraction, Tree Leaves, Cement Factory

Influence of the human activity on the source of soil inorganic carbon in grassland from Tibet and Inner Mongolia

Ping D^{1,2}, Yiwei C^{1,2}, Sanyuan Z^{1,3}, Chengde S^{1,2}, Ning W^{1,2}

¹State Key Laboratory of Isotope Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou, China, ²CAS Center for Excellence in Deep Earth Science, Guangzhou, China, ³State Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou, China

Soil Inorganic carbon (SIC) in two Alpine Meadow soil profiles from Tibet (Nam Co, $30^{\circ}46'12''$ N, $90^{\circ}57'13''$ E, amsl. 4737 m & Dangxiong, $30^{\circ}22'40''$ N, $90^{\circ}55'45''$ E, amsl. 4294 m) and two grassland soil profiles from Inner Mongolia (DXC, $43^{\circ}00'25''$ N, $117^{\circ}29'43''$ E, amsl. 1352 m & GYC, $43^{\circ}34'32''$ N, $116^{\circ}40'16''$ E, amsl. 1225 m) were investigated. 14 C ages of soil organic carbon (SOC) and SIC in Tibet show a significant positive correlation (Nam Co, R2=0.95 & Dangxiong, R2=0.94) between each other, suggesting a stable contribution of SOC to the SIC since 4.0-5.0 ka. Shrink of Nam Co lake at 3.0-2.0 ka and weakening of summer monsoon precipitation likely played little influence on the source of SIC in Tibet since mid-Holocene. For comparison, 14 C ages of SOC and SIC in Inner Mongolia indicate an obviously positive correlation (DXC, R2=0.97 & GYC, R2=0.91) from 4.0-5.0 ka to 2.0 ka, and almost a stable 14 C age of SIC after 2.0 ka, reflecting a different source of soil IC after 2.0 ka in Inner Mongolia grassland. Variation of monsoon precipitation from 4.2 to 2.1 ka seems did not change the correlation obviously during that time in Inner Mongolia. Intensive human activities, such as farming and grazing since 2.0 ka in Inner Mongolia, likely led to the deterioration of the grassland and then the deflation of deeper soil layers, which finally changed the source of SIC in the shallow layers.

CO3 Radiocarbon production and cosmic events

C03_01

The ice core radionuclide perspective on past cosmic ray events

Muscheler R¹, Paleari C¹, Mekhaldi F^{1,2}, Nguyen L¹, Zheng M^{1,4}, Adolphi F³, Christl M⁴, Vockenhuber C⁴, Gautschi P⁴, Beer J⁵, Brehm N⁴, Erhardt T^{3,6}, Wacker L⁴, Nilsson A¹, Herbst K⁷

¹Lund University, Lund, Sweden, ²British Antarctic Survey, Cambridge, UK, ³Alfred-Wegener-Institut, Bremerhaven, Germany, ⁴ETH Zürich, Zürich, Switzerland, ⁵Swiss Federal Institute of Aquatic Science and Technology, Dübendorf, Switzerland, ⁶University of Bern, Bern, Switzerland, ⁷Christian-Albrechts-Universität zu Kiel, Kiel, Germany

The recent discovery of strong and rapid radionuclide production enhancements has opened up a whole new field of paleo space weather research. In this presentation we will give an overview of the present status of the ice-core based assessment of past cosmic ray events in comparison to radiocarbon records. We will review the present detection limit and show the comparison of the proposed radionuclide spikes in tree-ring radiocarbon with ice core ¹⁰Be and ³⁶Cl records. We will discuss unresolved issues in either the carbon cycle, ¹⁰Be and ³⁶Cl transport and deposition and/or their theoretical production rates. Furthermore, we will discuss the potential of these rapid production rate enhancements for climate research in general.

A Polar Bias in Ice Core ¹⁰Be-Data

Adolphi F¹, Herbst K², Nilsson A³, Panovska S⁴

¹Alfred Wegener Institute For Polar And Marine Research, Bremerhaven, Germany, ²Institut für Experimentelle und Angewandte Physik, Christian-Albrechts-Universität zu Kiel, Kiel, Germany, ³Department of Geology, Lund University, Lund, Sweden, ⁴GFZ German Research Centre for Geosciences, Helmholtz Centre Potsdam, Potsdam, Germany

Cosmogenic radionuclide records from polar ice cores provide unique insights into past cosmic ray flux variations. Besides allowing reconstructions of past solar activity, space weather, and geomagnetic field changes, they provide independent estimates of radiocarbon production rate changes in the past and are thus, an independent means to assess the radiocarbon calibration curve. However, all these applications rely on the proportionality of the ice core radionuclide records to the global mean production rate changes. This premise has been long debated from the model and data perspective. Here, we address this issue through atmospheric mixing model experiments and comparison to independent data. We find that all mixing scenarios that do not assume complete tropospheric mixing result in a polar bias. This bias is more prominent for geomagnetic field changes than solar modulation changes. Supported by independent geomagnetic field records and marine 10 Be, the most likely scenario results in a dampening of geomagnetic field-induced changes by 23-37% and an enhancement of solar-induced changes by 7-8%. We propose a correction function that allows deconvolving the ice core to restore proportionality to the global mean signal and discuss the relevance for understanding past variations in Δ^{14} C.

C03_03

Detection of solar events by using radiocarbon in tree-rings

<u>Brehm N</u>¹, Christl M¹, Adolphi F², Muscheler R³, Synal H¹, Mekhaldi F³, Paleari C³, Knowles T⁴, Bayliss A⁵, Nicolussi K⁶, Pearson C⁷, Fonti P⁸, Nievergelt D⁸, Hanterimov R⁹, Wacker L¹

¹Eth Zürich, Zürich, Switzerland, ²Alfred Wegener Institute for Polar and Marine Research, Bremerhaven, Germany,
³Lund University, Lund, Sweden, ⁴University of Bristol, Bristol, UK, ⁵Historic England, London, UK, ⁶Universität Innsbruck, Innsbruck, Austria, ⁷University of Arizona, Tucson, USA, ⁸Eidgenössische Forschungsanstalt WSL,
Birmensdorf, Switzerland, ⁹Laboratory of Dendrochronology, Institute of Plant and Animal Ecology, Ekaterinburg,
Russia

The Sun irregularly expels large amounts of highly energetic particles into the interplanetary space and towards Earth which can be observed as so-called solar energetic particle (SEP) events. SEP events can potentially cause major damage to satellites and can even disrupt sensitive electronic systems at ground level. While direct observations of SEP events are limited to the last few decades, cosmogenic radionuclides such as ¹⁴C can be used to detect and study them much further back in time. The production rate of cosmogenic nuclides, such as ¹⁴C, is primarily dependent on the incoming flux of highly energetic galactic cosmic rays. Normally solar particles expelled into the interplanetary space have not sufficient energy to cause radionuclide production in the Earth atmosphere, but SEP events may cause sudden increases in radionuclide production.

Analyzing 14 C concentrations in annual tree-rings from Switzerland, Germany, Ireland, Russia, and the USA, we recently discovered two new spikes in atmospheric 14 C in 7176 and 5259 BCE. The 2 % increases of atmospheric 14 C recorded for both events exceed all previously known 14 C peaks. Here we summarize and characterize all the found 14 C production events that are attributed to SEP events. We find that the two newly found events are comparable to the largest event of this type discovered so far at 775 CE.

Annual dating of Late Glacial trees from the French Alps. Implications of a spike at ca. 14.3 cal kyr BP

<u>Bard E</u>¹, Miramont C², Capano M¹, Guibal F², Marschal C², Rostek F¹, Tuna T¹, Fagault Y¹ ¹CEREGE, Aix-en-provence, France, ²IMBE, Aix-en-Provence, France

We present new ¹⁴C results measured on subfossil Scots pines recovered in the eroded banks of the Drouzet watercourse in the region of the middle course of Durance River in the Southern French Alps. Recent fieldwork enabled us to complement previous studies starting with Miramont et al. (2000 Radiocarbon). Dendro-matching of wood sequences allowed to construct 3 chronologies with durations ranging between 200 and 400 years, each including between 23 to 59 individual trees. Selected trees were sampled at annual resolution and every third ring was pretreated by using methods previously developed for trees from the nearby site of Barbiers (Capano et al. 2018, 2020 Radiocarbon included in IntCal20 Reimer al. 2020 Radiocarbon). So far, about 400 new ¹⁴C ages were measured on 15 trees, which allowed to construct a ≈ 700-yr long chronology. Preliminary matching with the Late Glacial German pine chronology shows that the Drouzet chronology reaches ca.14.4 cal kyr BP. The resulting Δ^{14} C record exhibits a century-long event between 14 and 13.9 cal kyr BP and a large and abrupt spike occurring in a single year around 14.3 cal kyr BP (evidenced in 2 dendro-matched trees). We will compare our record with that obtained in a floating tree from Northern Italy (Adolphi et al. 2017 QSR). The abrupt spike around 14.3 cal kyr BP, together with the length of the Drouzet record and its long overlap with the German pine chronology should be helpful to refine the comparison and tuning between the Greenland ice and IntCal chronologies.

C03 05

Toward detections of ¹⁴C spikes: regional differences in ¹⁴C data

<u>Miyake F</u>¹, Hakozaki M², Kimura K³, Tokanai F⁴, Nakamura T¹, Takeyama M⁴, Moriya T⁴, Panyushkina I⁵, Hantemirov R⁶, Helama S⁷, Jull A⁵

¹Nagoya University, Nagoya, Japan, ²National Museum of Japanese History, Sakura, Japan, ³Fukushima University, Fukushima, Japan, ⁴Yamagata University, Yamagata, Japan, ⁵University of Arizona, Tucson, USA, ⁶Institute of Plant and Animal Ecology, Ekaterinburg, Russia, ⁷Natural Resources Institute Finland, Rovaniemi, Finland

Annual ¹⁴C data in tree rings is a good proxy for past extreme solar energetic particle (SEP) events. As far, several signatures of extreme SEP events have been found in ¹⁴C data, such as 774 CE, 993 CE, 660 BCE, and 5259 BCE events. Although these events are characterized by a rapid ¹⁴C increase and a following decrease, ¹⁴C data recorded worldwide do not always show similar variations. Such regional differences in ¹⁴C data hinder a consistent understanding of the event and a detection of small 14C spikes, and affect a dating using ¹⁴C spikes. Here, we focus on a timing of rapid ¹⁴C increases and discuss a possible relationship with the atmospheric transport effect.

On Proposed New Single-Year Radiocarbon Production Events and the Limits of Event Detectability

<u>Scifo A</u>¹, Abi Nassif T¹, Zhang Q², Sharma U², Bayliss A⁴, Marshall P⁴, Pope B^{2,3}, Dee M¹

¹Centre For Isotope Research (CIO), University of Groningen, Groningen, the Netherlands, ²School of Mathematics and Physics, The University of Queensland, St Lucia, Australia, ³Centre for Astrophysics, University of Southern Queensland, Toowoomba, Australia, ⁴Historic England, London, United Kingdom

Over the last decade, the field of radiocarbon analysis has been revolutionised by the discovery of single-year production anomalies, sometimes called Miyake events, as they are both indicators of extreme space weather phenomena, and useful as anchors for exact-year dating. Brehm et al. (2021) proposed two new candidate events in the years 1052 and 1279 CE. Their data showed annual Δ^{14} C increases over these years of 5.9‰ and 6.5‰, respectively. We have also recently analysed dendrochronologically dated samples spanning these two periods of time, from Furness Abbey and Apethorpe Church, England. Our results, although statistically consistent (at 2σ) with those presented by Brehm et al. (2021), show much less obvious increases of around 4.5‰ and 3‰, respectively. Furthermore, we have also modelled our new datasets, as well as those of Brehm et al. (2021), in ticktack, the first open-source Python package that connects box models of the carbon cycle with modern Bayesian inference tools (Zhang et al., forthcoming). The radiocarbon production rates we obtain pose questions about the actuality of cosmic ray events at these times, and the limits of detectability of such phenomena more generally.

Brehm et al. (2021). Eleven-year solar cycles over the last millennium revealed by radiocarbon in tree rings. Nature Geoscience 14: 10–15.

Zhang et al. (forthcoming). Bayesian inference of radiocarbon production from tree-ring data.

C03 07

New records of ¹⁴C excursions at 664/62 BCE and 1279/81 CE from Inner Eurasia examine signal timing

Jull A^{1,2}, Panyushkina I³, Molnar M², Varga T², Livina V⁴, Sljusarenko I⁵, Myglan V⁶, Miyake F⁷

¹University Of Arizona, Tucson, United States, ²Institute for Nuclear Research, Debrecen, Hungary, ³Laboratory for Tree-Ring Research, Tucson, USA, ⁴National Physical Laboratory, Teddington, UK, ⁵Institute of Archaeology and Ethnography, Novosibirsk, Russia, ⁶Siberian Federal University, Krasnoyarsk, Russia, ⁷Institute for Space-Earth Environmental Research, Nagoya, Japan

Excursions in the annual ¹⁴C production rate in the atmosphere are manifest in an excess of up to 20 ‰ in tree rings, caused by transient increases in the ¹⁴C production rate. These signals rise rapidly over a period of 1-2 yr and has a decay time of about 15-20 yr. These events are generally explained as a rapid increase of incoming cosmic rays or gamma rays. Only a few have been reproduced in multiple tree-ring records from many locations around the globe, particularly at 7176BCE, 5259BCE, ~660BCE, 774-775CE and 993-994CE reported by different laboratories. These excursions are positively connected to the impact of strong Solar Energetic Particles (SEP) events and are also observed from ¹⁰Be and ³⁶Cl excursions in polar ice cores. Other proposed events show different structures and either coincide with Grand Solar Minima or other effects of a lesser magnitude. These include reported events at 815BCE, 5480BCE, 5410BCE, 1052/1054CE and 1279CE events. We focus on a new detailed record of the 664-662BCE event from the Altai Mountains. It appears that the intensity and structure of the ¹⁴C signal is multifaced in space and time, which complicates understanding of the forcing and attribution to the underlying astrophysical events. Timing of these events is important to register the recurrence intervals of these events for past and future ¹⁴C excursions. We investigated the time concordance of a number of these events and possible explanations.

Finding smaller solar particle events from tree-ring ¹⁴C time-series data

<u>Uusitalo J</u>^{1,2,3}, Hackman T^{1,3}, Oinonen M^{1,2}

¹University Of Helsinki, Helsinki, Finland, ²Finnish Museum of Natural History, Helsinki, Finland, ³Department of Physics, Helsinki, Finland

Tree-ring ¹⁴C measurements are an excellent way for studying past solar particle events (SPEs) and other anomalous astronomical phenomena. Following the discovery of the AD 774 solar storm by Miyake et al. in 2012, the number of annually resolved tree-ring ¹⁴C measurements have grown significantly. Since then, these annually resolved measurements have led to new discoveries that are similar in magnitude with the Miyake event. However, assuming a power-law distribution for SPEs, one would expect there to be many more less intense particle events causing smaller ¹⁴C spikes, yet only few such candidates have been found. One reason for this could be that it is hard to separate the signal from the statistical noise and short-term natural variability, caused mainly by the 11-year solar cycle, so many smaller events might end up being missed. However, it should be possible to spot new and so far unrecognized events using time-series methods specifically built for this purpose. In this work, we present one such new method that takes into account the respective ¹⁴C baseline, the sudden increase and the full shape of the event. Furthermore, we analyze and discuss how the longer-scale structures in ¹⁴C records, such as steep downslopes or uphill's affect the general detectability of such small events.

C03 P01

Cosmogenic radionuclides at Law Dome, East Antarctica, record the 774/5 AD and 993/4 AD Miyake Events.

Smith A¹, Curran M², Dee M⁴, Fink D¹, Kuitems M⁴, Levchenko V¹, Moy A², Scifo A⁴, Simon K¹, Wilcken K¹

¹ANSTO, Sydney, Australia, ²Australian Antarctic Division, Hobart, Australia, ³Institute for Marine and Antarctic Studies, University of Tasmania, Hobart, Australia, ⁴Centre for Isotope Research, University of Groningen, Gronigen, Netherlands

This project investigates increased atmospheric production of cosmogenic radionuclides in ice core records at Law Dome, East Antarctica, for three extreme events: the Carrington Event (CE) of 1859 AD and the Miyake Events (ME) of 774/5 AD and 993/4 AD. Ice samples for ¹⁰Be and ³⁶Cl analysis were taken from ice cores drilled near the summit of Law Dome, East Antarctica. This will be the first time these radionuclides have been measured at the same site for these events, allowing a direct comparison of ME774, ME993 and CE1859 under similar transport conditions.

A survey of 10 Be at annual resolution spanning 30 years allowed an exact location of the events in the ice cores. We clearly identified the expected ME774 and ME993 10 Be peaks, which were $^{\sim}$ 4 years earlier and $^{\sim}$ 2 years earlier, respectively, than the layer-counted ice core chronology, but within the margin of error. No discernible 10 Be peak or 36 Cl peak was found for CE1859 at annual resolution.

A further set of ¹⁰Be samples at bi-monthly resolution were taken over ME774 and ME993 to better define the fine structure and amplitude of the signal. These sub-annual results confirm the survey results, showing additional structure and higher ¹⁰Be concentrations. High resolution ¹⁴C analysis has already been undertaken at Groningen over all three events and will be reported at this meeting. Finally, we will be combining the mobile phases from the sub-annual and annual 10Be processing to yield sufficient sample for ³⁶Cl AMS analysis across these two Miyake Events.

The potential for using Δ^{14} C excursions to accurately date floating pine chronologies from the Hallstatt period

Damian W¹, <u>Rakowski A</u>², Krapiec M¹, Pawlyta J¹, Barniak J¹, Szychowska-Krąpiec E¹ AGH, Kraków, Poland, ²SUT, Gliwice, Poland

In Central Europe, the dendrochronological method in absolute dating is widely used, but a significant difficulty in its application is the lack of pine (Pinus sylvestris) chronologies reaching back more than tenth century CE. Recently, long floating pine chronologies covering the last thousand years of the BCE were compiled at the Dendrochronological Laboratory of AGH University of Science and Technology in Krakow. These are mean curves developed from hundreds of trunks of subfossil trees found in Polish peatlands. They were preliminarily dated using the wiggle-matching method. Later, rapid Δ^{14} C changes at 660 BCE and at 814-813 BCE were used for their precise dating with annual precision.

C03 P03

Variations in the radiocarbon calibration curves around known and suspected $\Delta^{14}\text{C}$ excursions

<u>Rakowski A</u>¹, Pawlyta J², Krąpiec M², Huels M³, Molnar M⁴

SUT, Gliwice, Poland, ²AGH, Kraków, Poland, ³Uni Kiel, Kiel, Germany, ⁴ATOMKI, Debrecen, Hungary

The search for and analysis of rapid $\Delta^{14}C$ changes in the past has received much attention in recent years. In this paper, we will present the results of searching for rapid $\Delta^{14}C$ changes in the raw data used to build radiocarbon calibration curves: IntCa20 and SHCal20 and attempts to identify them in rings of single trees from Poland. We collected information on the periods of occurrence of rapid changes identified by other authors and within our own review of $\Delta^{14}C$ variability in raw data of calibration curves. For some of the periods we found, we were able to find research material in the form of tree trunks from areas of Poland. We determined the concentration of ^{14}C in tree rings. In this paper we present a comparison of the obtained $\Delta^{14}C$ for our samples and raw data and the IntCal20 curve itself.

CO4 Dendrochronology and radiocarbon analysis

C04_01

Analysis of solar minima by using radiocarbon in tree-rings

<u>Brehm N</u>¹, Christl M¹, Synal H¹, Bayliss A², Nicolussi K³, Pearson C⁴, Bleicher N⁵, Brown D⁶, Wacker L¹

¹Eth Zürich, Zürich, Switzerland, ²Historic England, London, UK, ³Universität Innsbruck, Innsbruck, Austria, ⁴University of Arizona, Tucson, USA, ⁵Underwater archaeology and Dendroarchaeology, Zürich, Switzerland, ⁶ The Queen's University, Belfast, UK

The Sun provides virtually all the principal energy input to the Earth's climate system and solar variability is a significant external climate forcing. While direct observations of the sun's activity via sunspots only cover the last about 400 years, cosmogenic radionuclides such as ¹⁴C, 10Be and 36Cl stored in tree-rings and ice cores serve as solar activity proxies extending back thousands of years.

¹⁴C is produced continuously in the Earth's atmosphere by highly energetic cosmic rays. The rate of production depends on solar activity and geomagnetic field strength. Dendrochronologically dated trees represent the most reliable archive for reconstruction of the past atmospheric ¹⁴C concentration over the past 14 000 yr, because of the absolute dating of a tree ring and the tree's capability to record the atmospheric ¹⁴C concentrations at annual resolution.

Here we present two annually resolved records of atmospheric ¹⁴C covering two different solar minima and the following solar maxima. The new data, which covers the time periods from 5450-5000 and 1950-2400 years BP, is analyzed by using a carbon cycle box model to reconstruct past solar activity. The reconstructed high-resolution solar activity records are compared with the solar activity recontructed from the Spörer and Maunder minima which occurred during the last millennium. The data gives more high resolution insight on two of the most extreme solar minima during the past 6000 years.

C04 02

The effect of altitude and latitude on growing season and radiocarbon content in tree rings

Svarva H¹, Grootes P¹, Seiler M¹, Nadeau M¹

¹The National Laboratory for Age Determination, NTNU University Museum, Trondheim, Norway

The construction of high-precision, single-year calibration curves for radiocarbon dating needs to take into account the tree physiological, seasonal, and regional differences in the radiocarbon content of tree rings. ¹⁴C variations can be caused by e.g. carbon stored from previous years and by growing season differences.

Previous studies have shown that the stored photosynthate component is less important for evergreen conifers. However, the timing of growing season can have a significant impact on the radiocarbon content of tree rings, especially during periods of large atmospheric ¹⁴C fluctuations such as the 1960s bomb spike. The calibration of results from trees that grew during different periods of the year than the trees used for the calibration curve will also be impacted. Cellulose in sub-annual sections of tree rings can be used to trace changes in atmospheric radiocarbon content at a biweekly to monthly resolution. We present the sub-annual radiocarbon contents of three Scots pines from Norway from 1953 to 1965. One tree grew at a low elevation near Trondheim in central Norway. The others grew nearby at a high elevation and at a low elevation in northern Norway, thus having a generally shorter growing season. Analyses of the differences between the radiocarbon content in the trees through time and comparison with climate records allows us to untangle the differences caused by growing season from inaccuracies in the timing of each increment and potential latitudinal differences in atmospheric ¹⁴C content.

C04_03

Interfacing Radiocarbon Production Events from Cosmic-ray Bursts with Other Fields of Research

Kuitems M¹, Dee M¹

¹University Of Groningen, Groningen, Netherlands

Since Miyake et al. (2012) published the spike in radiocarbon production caused by a cosmic-ray strike in the year 774 CE, numerous other distinct yet ephemeral features in the radiocarbon record have been discovered. The cosmic-ray events that occurred in 774 and 993 CE have proven especially effective for dating wooden items, and their associated historical or geological contexts, to the exact year. As part of the ECHOES project, other avenues of research centring on the utilisation of these events are now being explored. The new applications vary in nature and scope. One aspect involves the use of high-precision radiocarbon measurements on individual tree-rings to overcome long-standing barriers in dendrochronology. In other applications, radiocarbon data from disparate periods and geographical

regions are being combined with new proxies, such as stable isotope records and even genetic data, to maximise the potential of these versatile time markers.

C04 04

European Glacial tree-ring chronologies - New high-resolution ¹⁴C-series

<u>Friedrich M</u>¹, Kromer B², Cercatillo S³, Wacker L⁴, Toniello V⁵, Bicho N⁶, Horta P⁶, Adolphi F⁷, Muscheler R⁸, Talamo S³

¹Hohenheim Gardens (772), University of Hohenheim, D-70599 Stuttgart, Germany, ²Institute of Environmental Physics, Heidelberg University, Heidelberg, Germany, ³Department of Chemistry G. Ciamician, Alma Mater Studiorum, University of Bologna, Bologna, Italy, ⁴Laboratory of Ion Beam Physics, ETH Zurich, Zurich, Switzerland, ⁵Gruppo Speleologico C.A.I. di Vittorio Veneto (TV), Vittorio Veneto, Italy, ⁶Interdisciplinary Centre for Archaeology and the Evolution of Human Behavior, University of Algarve, Faro, Portugal, ⁷Helmholtz Centre for Polar and Marine Research, Alfred Wegener Institute, Bremerhaven, Germany, ⁸Department of Geology, Quaternary Sciences, Lund University, Lund, Sweden

The ¹⁴C-calibration curve IntCal is a key-record in paleosciences that provides a chronological framework for a wide range of disciplines studying environmental and cultural changes during the late Pleistocene and the Holocene. Tree-rings directly record atmospheric ¹⁴C/¹²C relationship at their time of growth and are thus the ideal natural archive to construct a terrestrial calibration curve - if they can be well dated. However, they are continuously available only back to 14.226 years BP. Before this time, the resolution of the calibration curve drops substantially, or relies on ¹⁴C data that do not directly reflect atmospheric ¹⁴C.

In the Late Pleistocene, a number of floating tree-ring ¹⁴C-series from subfossil trees exist, that can provide snapshots of past ¹⁴C-variability and have a tremendous potential. The challenge here is to establish their absolute chronology by providing high-resolution ¹⁴C-dates with tight error ranges, because that is the prerequisite e.g. for successful comparisons of the solar induced decadal to subcentennial ¹⁴C-variability to the ¹⁰Be-record of the ice cores.

In this contribution, we present newly constructed Glacial tree-ring chronologies of subfossil trees from northern Italy and Portugal at 18ka resp. 32ka BP, and respective high precision, sub-decadal ¹⁴C-series achieved by the ERC-project 'RESOLUTION'. We discuss their absolute chronological dating by comparisons with terrestrial calibration series and the possibility to infer links to the Greenland ice core timescale.

The new tree-ring based ¹⁴C-series will contribute to characterize past atmospheric ¹⁴C variability and will improve the radiocarbon calibration towards achieving a precise high-resolution chronology of human evolution.

C04_05

Towards a continuous, annually resolved tree-ring record spanning the past 6000 years

<u>Wacker L</u>¹, Brehm N¹, Christl M¹, Synal H¹, Bayliss A², Nicolussi K³, Pearson C⁴, Bleicher N⁵, Brown D⁶, Bollhalder S¹, Alter M¹

¹Laboratory of Ion Beam Physics, ETH Zurich, Zürich, Switzerland, ²Historic England, London, Great Britain, ³Universität Innsbruck, Innsbruck, Austria, ⁴University of Arizona, Tucson, USA, ⁵Underwater archaeology and Dendroarchaeology Zurich, Zürich, Switzerland, ⁶The Queen's University, Belfast, Great Britain

As a consequence of the instrumental progresses combined with more efficient sample preparation, IntCal20 contains now 5 000 new AMS measurements in addition to 1 000 decay measurements on annually resolved tree-rings of the previous IntCal iteration (IntCal13). It is primarily this new annually resolved data, that nearly doubled the dataset, on which IntCal20 is based today. Still, the significantly increased resolution of IntCal20 can be considered just as the start for a more detailed (spatio-)

temporal mapping of past atmospheric radiocarbon concentrations. Only 20% of the last 14 000 years available at annual resolution are yet measured, while the rest is only available at decadal or lower resolution.

We will present an update on our efforts to measure the hole tree-ring based part of IntCal annual resolution. We present more than 3 000 new annually resolved ¹⁴C measurements performed on tree-ring samples covering the last 6 000 years. A thorough analysis of reproducibility will be presented and possible reginal offsets will be discussed. The new data represents a significant progress towards an enhanced high-resolution calibration curve.

C04 06

Establishing prehistoric tree-ring chronologies for the southern Balkans: first results from lakeshore settlements of the 6th to 1st millennium BC

Maczkowski A^{1,2}, Bolliger M^{1,2,3}, Francuz J¹, Reich J^{1,3}, Hostettler M^{1,2,5}, Szidat S^{4,2}, Hafner A^{1,2,6}

¹Institute of Archaeological Sciences, University of Bern, Bern, Switzerland, ²Oeschger Centre for Climate Change Research, University of Bern, Bern, Switzerland, ³Archaeological Service of the Canton of Bern, Bern, Switzerland, ⁴Department of Chemistry, Biochemistry and Pharmacy, University of Bern, Bern, Switzerland, ⁵Department of Archaeology and Ancient History, University of Uppsala, Uppsala, Sweden, ⁶MacMillan Center for International and Area Studies, Yale University, New Haven, USA

During several archaeological campaigns on wetland prehistoric sites in North Macedonia, Greece and Albania almost 2000 subfossil wood samples have been collected. The fieldwork campaigns were conducted within the framework of the ERC Synergy Project EXPLO. The wood has been sampled from building and structural remains on lakeside and underwater archaeological sites and is thus unambiguously linked to the human occupation of these sites. Through dendrochronological measurement of wood from various tree species, multicentennial floating tree-ring (TR) chronologies have been constructed. Radiocarbon dating was used to position the floating chronologies on the calendar age frame, but also to confirm dendrochronological findings. The new TR chronologies open the possibility for refining the cultural chronology in the region, during various periods in the 6th through 1st millennia BC. Possible off-sets between species on non-annual radiocarbon will also be discussed. Additionally, newly discovered Miyake events enable the absolute dating of floating prehistoric chronologies much sooner than it seemed possible only a decade ago.

C04_07

Tree species in Central Amazon basin show uniform levels of ¹⁴C bombpeak as well as fossil-CO₂ contributions from mining operations

<u>Santos G</u>¹, Albuquerque R², Barros C², Ancapichun S^{3,4}, Oelkers R⁵, Andreu-Hayles L⁵, de Faria S⁶, De Pol-Holz R³, Brandes A⁷

¹University of California, Irvine, Irvine,, United States, ²Escola Nacional de Botânica Tropical, Rio de Janeiro, , Brazil, ³Universidad de Magallanes, Punta Arenas, Chile, ⁴Universidad de Concepción, Concepción, Chile, ⁵Columbia University, Palisades, , USA, ⁶Empresa Brasileira de Pesquisa Agropecuária, Seropédica, , Brazil, ⁷Universidade Federal Fluminense, Niterói, , Brazil

Tree rings has been widely used for atmospheric radiocarbon (14C) calibration purposes, but such records have been limited along tropical latitudes. Here we report precisely measured 14C dates in tree rings (1937 to 2007) of the parenchyma-rich Hymenolobium petraeum tree species from the Central Brazilian Amazon (Porto Trombetas, 1°S, 56°W). Bomb-peak tree-ring 14C reconstruction coincides with the broader changes associated with reported values of the Southern Hemisphere 14C curve (Hua et al. 2021), suggesting that inter-hemispheric air-mass transport of excess-14C injected into the stratosphere during aboveground nuclear tests is relatively uniform across distinct longitudinal regions. From the early 1970s onwards, H. petraeum had lower 14C values than recently developed pantropical 14C records

(e.g., Camanducaia; Santos et al. 2015, and Altiplano; Ancapichún et al. 2021). Through ¹⁴C-based estimation, we found a strong influence of local fossil-fuel CO₂ contributions. While the Oriximiná district's population density (0.5/km²) cannot be considered as its main cause, mining operations and waterway shipping traffic are potentially responsible for the local dilution of atmospheric ¹⁴CO₂. In addition, air parcels reaching Porto Trombetas during the growing season follow the Amazon River path, which handles most of export shipments of country's ore, soybean and corn by transnational business giants. Our findings invite further ¹⁴C analyses using tree rings of tropical tree species as a potential tracer for a wide range of environmental sources of atmospheric ¹⁴C-variability.

Hua et al. 2021. Radiocarbon, 1-23. DOI: https://doi.org/10.1017/RDC.2021.95 Santos et al. 2015. QUAGEO 25, 96-103 Ancapichún et al. 2021. STOTEN 774, 145126

C04 08

Single-year radiocarbon dating applied to Viking Age towns and trade connections

Philippsen B^{1,2,3}, Feveile C⁴, Olsen J^{2,3}, Sindbæk S²

¹Museum Lolland-Falster, Nykøbing F, Denmark, ²Centre for Urban Network Evolutions, School of Culture and Society, Aarhus University, Højbjerg, Denmark, ³Aarhus AMS Centre, Department of Physics and Astronomy, Aarhus University, Aarhus, Denmark, ⁴Museum of Southwest Jutland, Ribe, Denmark

Radiocarbon calibration curves have improved significantly after the discovery of solar particle events and the addition of annual data to calibration datasets. In this study, we apply IntCal20 with additional annual measurements to 140 radiocarbon dates from the Viking Age emporium Ribe in Denmark. We combine the radiocarbon dates with dendrochronological dates and the site's detailed stratigraphy, built up of clay floors and activity layers, in a Bayesian age model. We show that maritime trade began already around AD 750, as evidenced by artefacts imported from Norway. The expansion of trade, especially towards the Middle East, and other aspects of the beginning of the Viking Age occur in layers dated here to AD 790 \pm 10. We also identify the clay floor that was in use when the AD 775 solar particle event took place.

Finally, we apply the same techniques to radiocarbon dates of other Viking Age sites from the literature. We explore the potential of re-calibrating and modelling legacy dates to improve the chronology of individual sites and their relations with other sites.

C04 09

A Simulation Approach to Quantify the Parameters and Limits of the Radiocarbon Wiggle Match Dating Technique

McDonald L1, Manning S1

¹Cornell Tree-ring Laboratory, Ithaca, United States

Worldwide, radiocarbon (¹⁴C) wiggle-match dating is increasingly used to produce high-resolution, 'near-absolute', chronologies in a range of different contexts, yet the exact properties and limitations of the technique are not well understood. Here we present the results of extensive and systematic simulations that allow the precision limits of wiggle-match dating to be quantified for different time periods. In this presentation we use the periods 4000-3600 BCE and 1000-1800 CE as case studies. We have also been able to quantify the effect of modeling decisions on precision possible in terms of how many measurements to make, how far apart to space them, and which calibration curve to employ. We find that while recent trends towards large numbers of annually spaced measurements can improve precision, the effect is generally small, except when the dated sequence falls on a plateau in the

calibration curve. Finally, we demonstrate that wiggle matching against an unsmoothed record of atmospheric ¹⁴C can provide better precision than wiggle matching against the smoothed IntCal20 or SHCal20 curves. We argue, however, that until intra-hemispheric variation in ¹⁴C is better understood, the hemispheric averages provided by IntCal20 and SHCal20 will be the more appropriate datasets for the majority of wiggle-match applications.

C04 P01

δ^{13} C and intrinsic water use efficiency (iWUE) for trees in various health conditions – case study for Świerklaniec Forest District

Benisiewicz B¹, Pawełczyk S², Kłusek M³

¹Silesian University Of Technology, Gliwice, Poland, ²Silesian University Of Technology, Gliwice, Poland, ³Silesian University Of Technology, Gliwice, Poland

The research was carried out for two pines growing side by side in the Świerklaniec Forest District. One tree was in good health condition, the other pine had damaged crown and was destined to be cut down. Tree cores were subjected to dendrochronological analysis. Based on these studies, cores were divided into annual increments and subjected to chemical preparation. Carbon isotopic composition of α -cellulose samples was determined using mass spectrometer coupled to the elemental analyzer. Additionally, based on the δ^{13} C values, the iWUE values were calculated, and trees sensitivity to change of temperature and sum of precipitation was checked. Isotopic studies covered the years 1967-2020.

Until the end of the 1990s, the record of $\,\delta^{13}$ C had significantly lower values for a healthy tree than for a damaged tree. The isotope record of a healthy tree since 1980 is characterized by a horizontal trend, in the case of a damaged tree there is a clear downward trend from 1985 to 2000. Correlation coefficients between isotopic and climatic data indicate different sensitivity of trees to climatic factors. Apart from climatic factors, pollutant emissions could have had an impact on tree growth and δ^{13} C values, especially since there is a zinc smelter near the sampling site. The characteristics of the trend can be justified by the number of pollutants emitted by industrial plants (especially SO_2), which were the highest in the 1970s and 1980s, and significantly decreased in the 1990s. Differences in iWUE, calculated from data sets, representing two trees are signifficant.

C04_P02

New high RESOLUTION project ¹⁴C data from a Glacial sub-fossil pine forest in Furadouro, Portugal

Cercatillo S¹, Friedrich M², Kromer B³, Palecek D¹, Wacker L⁴, Talamo S¹

¹Department of Chemistry G. Ciamician, Alma Mater Studiorum, University of Bologna, Via Selmi 2, 40126, Bologna, Italy, ²Hohenheim Gardens, University of Hohenheim, Ottilie-Zeller-Weg 8, D-70599, Stuttgart, Germany, ³Institute of Environmental Physics, Heidelberg University, D-69120, Heidelberg, Germany, ⁴Laboratory of Ion Beam Physics, ETH Zurich, 8093, Zurich, Switzerland

The year 14,226 BP marks an important border in the actual radiocarbon (¹⁴C) calibration curve: the high resolution and precision characterising the first part of the curve thanks to the potential of tree-rings, systematically decrease going back in time, where only a few floating tree-ring chronologies alternate to other low-resolution records.

The lack of resolution in the dating procedure before 14,200 years BP leads to significant issues in the interpretation and untangling of tricky facts of our past.

The research for sub-fossil trees, within the RESOLUTION project, which directly recorded atmospheric carbon (12 C, 13 C and 14 C), and the construction of new Glacial tree-ring chronologies can improve the radiocarbon dating and therefore, to resolve puzzles in the Human Evolution history.

The sub-fossil pine trees found in situ under the current coast sediments of Furadouro, Portugal, are remnants of a Glacial lagoonal forest and represent a significant example of the huge potential given by

the rare findings of trees grown during the Glacial in refugia areas, where the environmental conditions and climate allowed growth of pine trees.

Here we report of a new 220-year long pine tree-ring chronology, grown during GI 5: we describe the carefully sampling, the dendrochronological analysis and cross-dating of the trees, and the high resolution, highly reliable radiocarbon age-series with tight error ranges that we have achieved by applying the most suitable cellulose extraction protocol for sub-fossil Glacial trees, and the most advanced technologies of the MICADAS system at ETH-Zurich.

C04 P03

Radiocarbon ages of annual tree rings collected in Korea (AD 900 - 2021, 81 - 168, 131 - 211)

<u>Hong W</u>¹, Park Y¹, Sung K¹, Park G¹, Sakamoto M², Hakozaki M², Park J¹

¹Korea Institute of Geoscience and Mineral Resources (KIGAM), Daejeon, South Korea, ²National Museum of Japanese History, Sakura City, Japan

Radiocarbon ages of annual tree rings collected in Korean Peninsula were measured using KIGAM 1MV AMS. All samples were treated by alpha cellulose extraction methods at KIGAM and NMJH. Reduction process of CO₂ to graphite was done using 24-line automatic reduction system at KIGAM. The radiocarbon ages from AD 1250 to 1850 were reported in 2013 (Hong et al.1, 2013 and Hong et al.2, 2013) with dendrochronological ages. After the reports, radiocarbon ages of tree rings from AD 1093 to 1162, AD 1188 to 1249, and AD 1851 to 1950 have been measured. The calendric ages of these samples were determined by dendrochronology or oxygen isotope patters. And recently, additional tree rings from AD 81 to 168 and from AD 131 to 211 collected from an archaeological site, Gochon-ri, were measured. The calendric ages of the samples were determined by oxygen isotope dendrochronology. Modern tree rings after AD 1950 collected from a mountain called Sogri-san, which is located in the center of South Korea, were also measured up to 2021. Those ages will be reported in this presentation and compared with IntCal13 and IntCal20 curves. Chronological variation of regional offsets in the radiocarbon ages of tree rings grown in East Asia from IntCal13 and IntCal20 will be discussed.

C04_P04

A growth rate variability of Ziziphus spina christi in North-central Oman determined by a series of radiocarbon measurements

Kitagawa H¹, Miki T², Kuronuma T³, Kondo Y³

¹Institute for Space-Earth Environmental Research, Nagoya University, Nagoya, Japan, ²The University Museum, The University of Tokyo, Tokyo, Japan, ³Research Institute for Humanity and Nature, Kyoto, Japan

Ziziphus spina christi, known as Christ's Thorn Jujube, is a thermophilic tree grown in arid and semi-arid areas. It was already in use as a medical plant in Ancient Egypt and is currently used for multipurpose such as food, fodder, fodder fuel, drink, timber, and medicine. The ecological and chemical properties of the multipurpose plant have been intensively studied, but there is a missing knowledge about the growth rate of Ziziphus spin christi that the annual ring is unclear. We conducted a series of radiocarbon measurements of a 23 cm-long core of Ziziphus spina christi collected from Wādī Tanūf, Northcentral Oman. The secular change of growth rate was estimated by a wiggle matching method incorporating dynamic time wrapping (DTW) algorism for measuring similarity between two temporal sequences: radiocarbon calibration (IntCal20) and dataset from the Ziziphus spina christi (this study). Based on the growth rate estimated, we discussed the climatic influence on the growth rate. Our result supports the hypothesis that an increase in winter temperature may be beneficial for growth and the recent widespread of Ziziphus spina christi in the eastern Mediterranean is presumably related to a gradual increase in winter temperatures.

Single-year ¹⁴C dating of the lake-fortress at Āraiši, Latvia

Meadows J^{1,2}, Zunde M³, Lēģere L⁴, Dee M⁵, Hamann C²

¹ZBSA (Centre for Baltic and Scandinavian Archaeology), Schleswig, Germany, ²Leibniz-Laboratory for AMS Dating and Stable Isotope Research, Christian-Albrechts-University Ki, Kiel, Germany, ³Institute of Latvian History, University of Latvia, Riga, Latvia, ⁴Āraiši lake-fortress archaeological park, Cēsis, Latvia, ⁵Centre for Isotope Research, University of Groningen, Groningen, Netherlands

A timber lake-fortress on a flooded island in Lake Āraiši, central Latvia, was excavated in 1965-69 and 1975-79 by the pioneering underwater archaeologist Jānis Apals, who recognised five construction phases. Dendrochronological analysis originally produced a mixed-species conifer site chronology, which was tentatively cross-matched to a reference chronology from Novgorod, Russia, indicating a felling date of c.AD 930 for timbers from the earliest phase. A more rigorous analysis produced a 95-year floating chronology for the best-preserved Norway spruce (Picea abies (L.) Karst.) timbers from the earliest phase, which was dated by ¹⁴C wiggle-matching with the IntCal13 calibration curve, suggesting a felling date of cal AD 775-784 (Meadows and Zunde 2014, Geochronometria 41(3):223-33). If this range was accurate, it should have been possible to locate the AD 775 Miyake event (Miyake et al. 2012, Nature 486(7402):240-2) in single-year cellulose samples from the final decade of the Āraiši spruce chronology. However, repeated attempts, with replication of the final decade between the Kiel and Groningen laboratories, were unsuccessful. Additional sampling in 2020-21 unambiguously located the AD 775 event 60 years before the spruce felling date, dating the first phase of construction to AD 835. The new results raise questions both about the treatment of ¹⁴C outliers in the original (2014) wigglematch, and about the IntCal20 data set; like Philippsen et al. (2021, Nature 601(7893):392-6), we suspect that IntCal20 is too low in the 830s AD.

C04_P06

AMS radiocarbon investigation of the African baobabs from the semiarid cloud forest of Wadi Hinna, Dhofar, Oman

Patrut A^{1,2}, Molnar M³, Patrut R¹, Rakosy L⁴, Brown J⁵, Varga T⁶, Ratiu I^{1,2}

¹Babes-Bolyai University, Faculty of Chemistry and Chemical Engineering, Cluj-Napoca, Romania, ²Babes-Bolyai University, Raluca Ripan Institute for Research in Chemistry, Cluj-Napoca, Romania, ³Interact Centre,Institute for Nuclear Research, Debrecen, Hungary, ⁴Babes-Bolyai University, Faculty of Biology and Geology, , Cluj-Napoca, Romania, ⁵Qatar University, College of Arts and Sciences, Doha, Qatar, ⁶University of Debrecen, Doctoral School of Physics, , Debrecen, Hungary

Wadi Hinna is a small semi-arid valley (3 km2) at the edge of the Dhofar Mountains (17º03' N, 54º36' E, altitude 300-360 m) and at 20 km from the coastal plain, in southern Oman. Wadi Hinna hosts a unique water-limited cloud forest of African baobabs (Adansonia digitata).

The precipitation (annual rainfall 130 mm) falls during the rainy season (mid-June to mid-September), when moist air from the Indian Ocean, i.e., the southwest monsoon, encounters the mountains, leading to clouds and dense fog. The rainfall is significantly supplemented by horizontal precipitation, namely cloud water interception within the canopy of trees.

Over 120 baobabs grow on a slope among huge stones of sedimentary rocks. We dated by AMS radiocarbon wood samples from the largest baobabs. We found that they exhibit, with one exception, ages of several hundreds of years. The exception is the Big tree of Wadi Hinna, which is by far the biggest and oldest baobab. The oldest part of the Big tree started growing more than 1000 years ago. The African baobab typically exhibits well-defined growth rings, which correspond in many cases to one rainy season. Nevertheless, age modeling of baobab rings demonstrated that ring-growth anomalies occur more frequent than for other tree species. For the old baobabs of Wadi Hinna, we found that the

ring frequency varies between 0.43 and 0.78 rings/year. The large number of missing rings is due to the semi-arid climate.

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C04 P07

Improved calibration method for dating multiple tree-rings and its implication on the Santorini debate

Raj H¹, Regev L¹, Boaretto E¹

¹Dangoor Research Accelerator Mass Spectromerty (D-REAMS) Laboratory, Weizmann Institute of Science, Rehovot, Israel

The Minoan eruption of Santorini, Greece, is an important and probably most debated chronological marker in contexts of the Eastern Mediterranean region. Among various age estimates of this event, one based on wiggle-matching of ¹⁴C dates from an olive branch found in Santorini by Friedrich et al. (2006) has been widely discussed. Four ¹⁴C ages were reported from this olive branch, each corresponding to a group of rings identified by X-ray tomography. Calibrated age estimates based on wiggle-matching of these ¹⁴C ages have been changing with improvements in the radiocarbon calibration curve. Such changes are important as the debate on the timing of the Minoan eruption is still not settled. It is understood that the calibration curve plays a crucial role in defining the calendar age range corresponding to ¹⁴C age(s). Interannual ¹⁴C levels can change significantly in the calibration curve, and the average ¹⁴C age of multiple rings dated together cannot always be calibrated to the middle year. Therefore, a different approach should be taken to calibrate the average ¹⁴C age of the multiple tree rings. We propose that calibration using the moving average calibration curve is more appropriate in such a case. Here, we recalibrated the four ¹⁴C ages reported for the above olive section on the moving average calibration curves. Considering the ring counts of the above olive section accurate, the resulting calendar age for the last ring ranges between 1608-1589 BCE (68.3% confidence) and 1616-1576 BCE (95.4% confidence) with a peak at ca. 1600 BCE.

C04 P08

High precision dating of a Neolithic wooden trackway from Lower Saxony, Germany, using radiocarbon wiggle matching

Rose H¹, Brozio J², Shindo L³, Meadows J^{1,4}, Feeser I², Dörfler W², Heumüller M⁵

¹Zentrum für Baltische und Skandinavische Archäologie (ZBSA), Schleswig, Germany, ²Institute of Pre- and Protohistoric Archaeology, University of Kiel, Kiel, Germany, ³ROOTS Cluster of Excellence, University of Kiel, Kiel, Germany, ⁴Leibniz-Laboratory for Radiometric Dating and Stable Isotope Research, University of Kiel, Kiel, Germany, ⁵Lower Saxony State Office for Heritage, Hannover, Germany

Wooden trackways dating from the Neolithic to the medieval period are well-documented in Europe. The earliest finds date to the middle of the 5th millennium BC and are linked to the invention of wheeled wagons, which are known in northern Germany from 3400 BC. We present new results from a wooden trackway found east of Aschener Moor in Lower Saxony, Germany. It was discovered in the 1890s and a 100-meter-long section was excavated in the 1980s. We returned to the site in 2021 and excavated a smaller section left untouched by the earlier campaign. The trackway is wide enough to allow passage of a wagon, but it is unclear where it led; across the marshy area of the Aschener Moor would be an obvious possibility, but previous attempts to prove this have been unsuccessful. The trackway is constructed of wooden trunks placed diagonally in two layers, consisting primarily of alder (Alnus sp.), but with a smaller number of birch (Betula sp.). This excludes traditional dendrochronological dating, but using radiocarbon wiggle matching, we have dated the felling date of one alder trunk to a 20-year-window in the mid-25th century BC. Such a precise date is rare for the

Neolithic period, but it is supported by chronological modelling of dates on branch wood found between the trackway logs. On-site palaeoenvironmental analyses relate the trackway construction to its local environment and periods of increasing precipitation. We will also compare our findings to the chronology of other wooden trackways in northern Europe.

C04 P09

Origin and age of carbon in cellulose of mid-latitude tree rings

Kromer B¹, <u>Wacker L</u>², Friedrich M³, Lindauer S⁴, Friedrich R⁴, Treydte K⁵, Fonti P⁵, Martinez E⁵

¹Institute of Environmental Physics, Heidelberg, Germany, ²Laboratory of Ion Beam Physics, ETH Zurich, Zurich, Switzerland, ³University of Hohenheim, Stuttgart, Germany, ⁴Curt-Engelhorn-Centre Archaeometry, Mannheim, Germany, ⁵WSL Birmensdorf, Birmensdorf, Switzerland

Annual rings of most trees in the middle and high latitudes are composed of the earlywood (EW), formed at the beginning of the growing season, and the latewood (LW), formed from summer onwards. A substantial part of EW in ring-porous deciduous tree species is formed before budburst, i.e. before leaves or needles have unfolded, which is a prerequisite for uptake of atmospheric CO₂. Hence, an essential share of carbon for the construction of EW must come from non-structural, mobile carbon sources (NSC), i.e. from reserve materials formed in the previous year or years. This naturally raises the question to what extent the carbon of an annual ring reflects the atmospheric carbon of the current year.

Here, ¹⁴C measurements on EW and LW tree-ring cellulose from deciduous tree species as well as non-deciduous species in selected years around the ¹⁴C bomb spike in the 1960s are presented. The measured ¹⁴C concentrations of the EW and to a lesser extend of the LW show significant deviations from the atmospheric ¹⁴C values at the time xylem cell wall deposition. With a simple model the fraction of NSC from reserves in addition to carbohydrates photosynthesized in the year of formation is quantified.

CO4 P10

Using rapid atmospheric ¹⁴C changes to precise dating part of the floating chronology for pine tree from Józefowo (north Poland)

<u>Wiktorowski D</u>¹, Krąpiec M¹, Barniak J¹
¹AGH University of Science and Technology, Kraków, Poland

Miyake was the first to describe rapid and short-lasting increases of radiocarbon (14C) concentration in the annual tree rings between AD 774 and 775 and AD 993 and 994. This sudden increase of radiocarbon has been confirmed also by other scientists. Similar study has been conducted in Poland at the AGH University of Science and Technology. The results clearly show a rapid increase of ¹⁴C concentration in these years. Results of last studies confirmed that the abrupt increase in ¹⁴C concentration is also visible between 663 and 662 BC. In this period is also located the floating pine chronology for north Poland. Due to the characteristic of the sharp increase in radiocarbon concentration that occurs in this phenomena, and due to the global character of this effect, it is possible to use it for accurate dating of annual tree rings, using radiocarbon method. In practice, linking the relative dendrochronological dating and radiocarbon analysis of annual growth rings is possible to use "Wiggle matching" technique to precise determination of the calendar age. Samples from Grabie, a village near Krakow (south-easter Poland) were control series, of known calendar age and known changes of radiocarbon concentration around 660 BC. The values of these changes were compared with the values noted in samples of pine tree from Józefowo (floating pine chronology) to its precise dating (with an accuracy of up to one year). This allowed the absolute dating of tree rings from floating pine chronology, which has been so far unattainable using radiocarbon method.

C05 Radiocarbon calibration: data, tools and modelling

C05_01

Statistical challenges and opportunities when modelling multiple radiocarbon dates

Heaton T¹

¹University Of Sheffield, Sheffield, United Kingdom

The recent explosion in the availability of radiocarbon dates has been accompanied by an ever-increasing interest in the application of data science techniques within the archaeological and environmental science communities. Detailed modelling and computational analyses of large sets of dates have the potential to provide unprecedented inference on our past, on rates of change, and on population dynamics. It is essential however that the methods underpinning these "big-data" analyses are rigorous and robust. This concern is particularly relevant for radiocarbon dating since the need for calibration of the determinations introduces considerable, and complex, uncertainties in our dates that must be incorporated into any inference.

This talk will discuss some of the opportunities, and challenges, for the modelling of multiple radiocarbon dates. We will introduce statistically-rigorous alternatives to summed probability distributions (SPDs) that provide robust predictive calendar age summaries, with accompanying uncertainty bands that are essential to aid inference, as well as improved calibration accuracy. We will also discuss how radiocarbon users might obtain more from the IntCal20 radiocarbon calibration curve. Current approaches to calibration consider the calibration curves as normally-distributed around their published pointwise mean. This simplification results in some potentially crucial information about the calibration curve, such as on its covariance, being entirely lost to calibration users. The new IntCal20 methodology generates multiple possible calibration curve realisations, each representing an entire plausible ¹⁴C history from 55,000 – 0 cal yr BP. Using the collection of these realisations, rather than pointwise means, may provide improved inference for complex modelling.

C05 02

Development of the IntCal database

<u>Bronk Ramsey C</u>¹, Austin W², Bard E³, Bayliss A⁴, Cheng H⁵, Friedrich M⁶, Heaton T⁷, Hogg A⁸, Hughen K⁹, Manning S¹⁰, Muscheler R¹¹, Palmer J¹², Pearson C¹³, Reimer P¹⁴, Reimer R¹⁴, Turney C¹², Wacker L¹⁵, IntCal Working Group

¹University Of Oxford, , United Kingdom, ²University of St Andrews, , United Kingdom, ³Cerege, Aix-en-Provence, France, ⁴Historic England, , United Kingdom, ⁵Xi'an Jiaotong University, , China, ⁶University of Hohenheim, , Germany, ⁷University of Sheffield, , United Kingdom, ⁸University of Waikato, , New Zealand, ⁹Woods Hole Oceanographic Institute, , USA, ¹⁰Cornell University, , USA, ¹¹Lund University, , Sweden, ¹²University of New South Wales, , Australia, ¹³University of Arizona, , USA, ¹⁴Queen's University Belfast, , United Kingdom, ¹⁵ETH Zurich, , Switzerland

The IntCal family of internationally-agreed radiocarbon calibration curves is built upon data from research spanning several decades. Most of the data are presented within primary publications and includes meta-data. In addition to the curves themselves, the IntCal group have collated these data and (since 2010) made them available for other sorts of analysis through an open-access database portal and to ensure transparency in what has been used in the construction of the ratified calibration curves. As the database of associated data expands, work is underway to facilitate best practice for new data

submissions, make more of the associated metadata available in a structured form, and to help those wishing to work with the data using programming languages such as R, Python and MatLab. The data is complex because of the range of different types of archive, each with their specific requirements. A restructured interface will include visualisation that enable the data to be plotted and compared without needing to be exported. This development is building on a general open access data model 'IntChron' designed for the sharing of databases of this kind. The intention is to include complementary datasets which can be used with the main radiocarbon series to provide new insights into the global carbon cycle. As well as facilitation of access to (and use of) the data by other researchers, this work aims to streamline the generation of new calibration curves.

C05 03

In light of Marine20 – how old is the Greenland shark?

Olsen J¹, Nielsen J², Grønkjær P¹, Steffensen J³

¹Aarhus University, Aarhus, Denmark, ²Greenland Institute of Natural Resources, Nuuk, Greenland, ³University of Copenhangen, Copenhagen, Denmark

In 2016 the longevity of the Greenland shark (Somniosus microcephalus) was determined to 392 \pm 120 years using radiocarbon analysis of eye lenses of 28 specimens. The age of pre-bomb sharks was determined using the Marine13 radiocarbon calibration curve with the assumption that the carbon source of the eye lens nucleus reflects food webs of potentially different ΔR levels. The common wisdom is that because both the absolute reservoir age R and the regional reservoir ages ΔR are changed with Marine20, then the calibrated ages are more or less unchanged. Nonetheless, what happens when you a Bayesian model with greatly increased error margins? Here we present an updated age estimate of the longevity of the Greenland shark using Marine20 with updated ΔR values by employing a Bayesian model. Further constrains are added by radiocarbon dating of new specimens from the bomb curve era. To support the new post-bomb eye lens radiocarbon data, a marine reference dataset will be presented based on enamel radiocarbon dating of know-age 29 hooded seals (Cystophora cristata) from West Greenland.

C05_04

Current compilation of recent atmospheric radiocarbon

<u>Hua Q</u>¹, Turnbull J^{2,3}, Santos G⁴, Rakowski A⁵, Ancapichún S^{6,7}, De Pol-Holz R⁷, Hammer S⁸, Lehman S⁹, Levin I⁸, Miller J¹⁰, Palmer J^{11,12}, Turney C¹³

¹Australian Nuclear Science And Technology Organisation, Lucas Heights, Australia, ²Rafter Radiocarbon Laboratory, GNS Science, Lower Hutt, New Zealand, ³CIRES, University of Colorado, Boulder, USA, ⁴Earth System Science, University of California, Irvine, , USA, ⁵Institute of Physics, Center for Science and Education, Silesian University of Technology, Gliwice, Poland, ⁶Postgraduate School in Oceanography, Faculty of Natural and Oceanographic Sciences, Universidad de Concepción, Concepción, Chile, ⁷Centro de Investigación GAIA Antártica (CIGA) and Network for Extreme Environment Research (NEXER), Universidad de Magallanes, Punta Arenas, Chile, ⁸Institut für Umweltphysik, Heidelberg University, Heidelberg, Germany, ⁹INSTAAR, University of Colorado,, Boulder, USA, ¹⁰NOAA Global Monitoring Laboratory, Boulder, USA, ¹¹ARC Centre of Excellence for Australian Biodiversity and Heritage, School of Biological, Earth and Environmental Sciences, University of New South Wales, , Australia, ¹²Chronos 14Carbon-Cycle Facility and the Earth and Sustainability Science Research Centre, University of New South Wales, , Australia, ¹³Division of Research, University of Technology Sydney, , Australia

The last couple of centuries has seen substantial changes in atmospheric radiocarbon driven by the combustion of fossil fuels free of ¹⁴C since the mid-19th century and the injection of bomb-derived radiocarbon into the atmosphere, mostly in the late 1950s and early 1960s. The current compilation of recent atmospheric radiocarbon levels, covering the period from 1950 to 2019, was released late last year. It consists of zonal, hemispheric and global summer data sets for use in carbon-cycle studies and monthly data sets for five zones (Northern Hemisphere zones 1, 2, and 3, and Southern Hemisphere

zones 3 and 1-2) for more accurate radiocarbon dating of recent terrestrial samples. After describing the current compilation, the presentation will focus on new and future collections. This discussion includes new data sets such as atmospheric sampling from Alert and Neumayer (Levin et al., 2021), tree rings from Eastern Amazon Basin (Santos et al., in prep.) and southern Chile (De Pol-Holz et al., in prep.). The new data enables the extension to a more recent time period and the improved determination of zonal borders. Autumn and winter plant/seed data during the early bomb period (e.g., Hüls et al. 2021), where atmospheric sampling is not available, can allow an improved compilation of monthly zonal data. Finally, data quality considerations, such as applying dendrochronological methods, tree-ring pre-treatment and replicate radiocarbon analyses, will also be discussed.

Hüls, M. et al. 2021. Radiocarbon 63, 1387-1396. Levin, I. et al. 2021. Radiocarbon, doi:10.1017/RDC.2021.102

C05 05

Southern Levant calibration regional offsets identified by short-lived archaeological materials

Regev J^1 , <u>Regev L</u>¹, Uziel J^2 , Gadot Y^3 , Ben-Ami D², Mintz E¹, Boaretto E¹

¹Weizmann Institute of Science, Rehovot, Israel, ²Israel Antiquities Authority, Jerusalem, Israel, ³Tel Aviv University, Tel Aviv, Israel

The topic of regional offsets from the northern hemisphere calibration curve has been gaining attention in recent years as part of a community effort to increase the radiocarbon calibration resolution. Usually, the suggested offsets are identified by modern, known-age samples or tree rings, dendrochronologically dated. Our group has developed over the years microarchaeological tools, which enable radiocarbon-aimed field sampling for high-resolution dating and modeling using short-lived charred remains. These analyses can provide confidence in the archaeological context and stratigraphy in relation to such samples. Therefore, once those sequences are wiggle-matched, they follow the calibration curve with very few outliers.

We have encountered two instances, one in the 1st millennium BC and the other in the 3rd millennium BC, in which our modeled results extended beyond the calibration curve with an excess of ¹⁴C by a few permille. Furthermore, we have found the opposite effect of ¹⁴C depletion when dating the historically known-age destruction event of Jerusalem by the Babylonians in 586 BC. In those instances, wherever the calibration curve is not based on single tree rings, some Irish oak and/or bristlecone pine samples were additionally measured.

C05 06

Annual radiocarbon dating of tree rings of the beginning and the end of the Yayoi period, Japan.

<u>Sakamoto M</u>^{1,2}, Hakozaki M¹, Nakatsuka T³, Ozaki H⁴

¹National Museum of Japanese History, Sakura-shi, Japan, ²The Graduate University for Advanced Studies, Sakura-shi, Japan, ³Nagoya University, Nagoya-shi, Japan, ⁴The University of Tokyo, Bunkyo-ku, Japan

Paddy rice cultivation is thought to have been introduced to Kyushu Island of the Japanese archipelago from mainland China via the Korean Peninsula, but until now no dendrochronological dating of the trees which had been growing at that time on Kyushu Island has been achieved. However, the practical application of oxygen isotope dendrochronology has enabled to date a wide range of tree species and regions and has opened the possibility of developing calibration curves based on its results. In this report, we examine the behavior of radiocarbon ages of the annual rings of a buried chinaberry (Melia

azedarach) from 1025 to 927 B.C.E. excavated in Kagoshima, southern Kyushu Island, which is dated by oxygen isotope dendrochronology.

Two datasets of Japanese tree rings were introduced for IntCal20, which made a change in the shapes of the curve from the 1st to 3rd centuries C.E. However, the validity of the revision should be considered by accumulating radiocarbon dating of tree rings. We also measured radiocarbon dates of Japanese zelkova (Zelkova serrata) buried in Miyagi, northeastern prefecture of the Japanese archipelago, which was dated by oxygen isotope dendrochronology (41 B.C.E – 130 C.E.). Although this sample is older than expected age of the end of the Yayoi period, regional offset in radiocarbon age can be discussed by comparing with Korean tree rings (Hong et al., this conference).

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C05_07

A pollen ¹⁴C stratigraphy of Lake Suigetsu from 12 to 20 ka BP

Omori T¹, Yamada K², Kitaba I², Nakagawa T²

¹The University Museum, The Uiniversity of Tokyo, Tokyo, Japan, ²Research Centre for Palaeoclimatology, Ritsumeikan University, Shiga, Japan

A radiocarbon stratigraphy of terrestrial fossil pollen grains extracted from Lake Suigetsu's varved sediment has been established from 12 ka to 20 ka cal BP in multi-decadal resolution. The obtained curve showed i) an overall good agreement with that of terrestrial macro fossils (Bronk Ramsey et al. 2012), and ii) significantly smoother decadal trends than those of the terrestrial macro fossils. These results indicate that the fossil pollen grains are i) as good indicator of the atmospheric radiocarbon concentration as terrestrial leaf fossils, and ii) picking up decadal signals of the atmospheric radiocarbon variability, free from inter-annual scatters which are inevitable with terrestrial leaf fossils. Because pollen grains fix the contemporary atmospheric radiocarbon, the smoothness of the curve should be a good indication of the true radiocarbon variability, rather than the terrestrial radiocarbon reservoir effects. The fact that curve is relatively free from the influence of inter-annual variability, which has been proved to be more significant than was previously believed (Bronk Ramsey et al. 2020, Miyake et al. 2017), implies that the radiocarbon datasets of fossil pollen grains are likely to have stronger power to constrain ages, when used as a radiocarbon calibration model.

C05_08

Semi-millennial structure of the Suigetsu atmospheric 14C record

<u>Sarnthein M</u>¹, Grootes P¹
¹University of Kiel, Kiel, Germany

Centennial-to-millennial-scale fluctuations in atmospheric ¹⁴C concentration on time-scales from years to millennia have been documented by tree-rings for the last 15 kyr. Further back, terrestrial macrofossils from sediment cores of Lake Suigetsu extend this ¹⁴C record from ~10 ka to 50 ka. The significance of these features is under debate since the signal-to-noise ratio of the record is low. Yet, coherent semi-millennial-scale structures were identified by three different techniques, namely visual inspection, a first derivative of the ¹⁴C-age vs calendar age, and Bayesian spline inflections of ¹⁴C concentration vs calendar age. Accordingly, the semi-millennial features of the noisy Suigetsu ¹⁴C record may be objectively real. Being corroborated by the tree ring-based ¹⁴C master record ~10 to ~15 cal. ka, the features attain global significance and extend the fine-scale variability back to ~35 cal. ka. Carbonate-based ¹⁴C records from ocean sediments and speleothems appear far smoother. Together with data from Suigetsu and floating tree ring sections, these records form the backbone of the IntCal20 record that beyond 15 ka largely misses the Suigetsu fine structure. ¹⁴C decay reduces ¹⁴C-signal amplitudes over time, so Holocene ¹⁴C signals of solar modulation disappear below noise level during earlier times. Accordingly, most ¹⁴C structures visible >15 ka originally had larger signals, most likely,

connected to climate, ocean-atmosphere CO₂ exchange, and carbon cycle. During this time, the Suigetsu ¹⁴C fine structure may thus give valuable information about these forcings. Also, it may serve for valuable global stratigraphic correlation of pertinent ¹⁴C records of oceanic plankton sediments.

C05_P01

Radiocarbon analysis of annually published journals

<u>Gautschi</u> P¹, Brehm N¹, Wertnik M¹, Synal H¹, Wacker L¹ ¹ETH Zurich, Zurich, Switzerland

The paper of books or journals is typically produced from cellulose extracted from trees. This makes them potentially suitable for radiocarbon dating. However, precise calendar age determination of the measured radiocarbon ages is difficult. Paper production has a lot of unknown factors such as different tree ages, i.e. number of tree rings, which go into the production of cellulose. Additionally, storage time between harvest of a tree and final publication is usually unknown and may vary. Therefore, the atmospheric integration time of a paper product, is an unknown distribution.

A series of 52 annually published journals over the 14 C bomb pulse (1947 - 2021 AD) have been prepared for radiocarbon analysis to study the age assembly and the storage time of trees used for the paper. The measured 14 C concentrations were compared to modelled 14 C concentrations in paper, which are based on a simple tree-ring model and assuming the cellulose was formed from atmospheric CO_2 at the year of formation. Best agreements were obtained assuming a mean age of trees of 40 to 80 years and a relatively short storage time of two years between the harvest of trees and the final publication. Although the measured journals follow the model qualitatively, some significant deviations were observed between individual years of publication.

C05 P02

Barley Mash its history in the Radiocarbon Inter-comparison studies and its role as a modern carbon standard.

Naysmith P1, Scott M2, Dunbar E1

¹SUERC, East Kilbride, United Kingdom, ²School of Mathematics and Statistics, University of Glasgow,

Over the past 30 years, the format of the radiocarbon (¹⁴C) inter-comparison studies has changed due to the change and development in measurement techniques. The selection of sample types used in these studies has remained constant—namely, natural and routinely dated materials that could subsequently be used as in-house laboratory standard material. Barley Mash, a by-product from the manufacture of malt whisky, is a good example of one of the widely used material from the Intercomparison studies. Barley from a single year's growing season is used in the production of whisky, often coming from a single geographical location and is available is large quantities, thus making it a suitable modern carbon reference material. Barley Mash samples have been used ten times in inter-comparison starting with TIRI, in 1992 through to GIRI, in 2021, with the same batch of barley mash being used in multiple intercomparison studies. In this paper, the barley mash results from all the intercomparisons will be collated and reanalysed.

During the last 19 years, the Barley Mash TIRI A has been used in the SUERC ¹⁴C laboratory as an inhouse laboratory standard material resulting in a dataset of several thousand of measurements. Such a rich data set is mined to illustrate some of the benefits arising from the inter-comparison program.

Determination of the influence of air parcels in the Northern and Southern Hemisphere on radiocarbon calibration in Southern America

Ancapichun S¹, Pawlyta J², <u>Rakowski A</u>³, Sieczkowska D⁴

¹Universidad de Concepción, Concepción, Chile, ²AGH, Kraków, Poland, ³SUT, Gliwice, Poland, ⁴University of Warsaw, Warsaw, Poland

The chronology of Machu Picchu was traditionally associated with the period attributed to the reign of Pachacuti Inca Yupanqui. Within the scheme of the so-called historical chronology, proposed by John H. Rowe in 1945, the ascension to power of Pachacuti Inca took place around 1438 CE and the construction of Machu Picchu began by 1450 -1460 CE. Several radiocarbon-dated samples may help to understand the chronology of the construction of llagta of Machu Picchu, Chachabamba, and Chogesuysuy. However, there is a lack of consensus between different radiocarbon-based Inca chronologies, because of the lack of information of which calibration curves to use: Northern Hemisphere (NH), Southern Hemisphere (SH), or a mixed calibration curve? Thus, the main goal of the present investigation is to develop a new methodological approach to reconstruct a consistent radiocarbon-based Incan chronology, an approach based on the determination, through modeling, of the proportion of NH and SH air parcels arriving at three relevant Inca settlements. We found air parcels contributions from the NH and SH for: Machu Picchu (50% NH and 50% SH), Chamical (29% NH and 71% SH), and Tiquischullpa (41% NH and 59% SH). Thereby, our investigation brings three proportions to mix NH and SH 14C curves, based on an empirical method, for Inca's radiocarbon dating studies. Our study emphasizes that great attention should be paid when applying radiocarbon calibration to radiocarbon measurements of samples originating in regions under the influence of the atmospheric circulation-boundary between hemispheres.

C05 P04

Comprehensive update of marine reservoir values for New Zealand coastal waters to inform coastal hazard research

Turnbull J^{1,2}, Clark K¹, Ferrick T¹, Marshall B³, Howarth J⁴

¹GNS Science, Lower Hut, New Zealand, ²CIRES, University of Colorado, Boulder, USA, ³Te Papa Tongarewa Museum of New Zealand, Wellington, New Zealand, ⁴Victoria University of Wellington, Wellington, New Zealand

Accurate dating of coastal hazard events such as earthquakes and tsunamis typically hinges upon marine radiocarbon ages, and a well-constrained marine reservoir correction is vital to evaluating the size and frequency of large to great subduction earthquakes and tsunamis. Yet in New Zealand, we have relied on only 31 Δ R values from four locations to estimate Δ R for the entire coastline. Here we add 170 new measurements to the marine reservoir correction dataset for the mainland New Zealand and evaluated the influence of location, feeding method, living depth, environmental preference and species on the variance in Δ R values. We find there are no significant differences between Δ R values from suspension-feeding organisms compared to browsing/scavenger/carnivore-feeding organisms, and we find little variability between species that prefer estuarine environments to open coastal environments. This means that when dating shells from geological records, we do not need to take particular care to avoid certain species that may have anomalies of carbon precipitation in their shells. Importantly, location is the dominant control on Δ R variability and we recommend the subdivision of New Zealand into five large regions, each with a different Δ R value.

G01 Atmospheric radiocarbon

G01 01

Atmospheric ¹⁴CO₂ time series from Point Barrow, Alaska: ending of the "Bomb Radiocarbon Period" in the Northern Hemisphere

Xu X¹, Walker J², Newman S^{3,5}, Trumbore S^{1,4}

¹Keck Carbon Cycle AMS Lab, Department of Earth System Science, University of California, Irvine, Irvine, United States, ²André E. Lalonde AMS Laboratory, University of Ottawa, Ottawa, Canada, ³Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, USA, ⁴Department Biogeochemical Processes, Max-Planck-Institute for Biogeochemistry, Jena, Germany, ⁵Bay Area Air Quality Management District, San Francisco, USA

The distribution rate and pattern of 14 C produced by nuclear weapons testing during late 1950s – early 1960s has provided a unique opportunity for tracing global carbon cycles, and also for studying atmospheric mixing. The atmospheric 14 CO₂ peaked around 1964, and since then has decreased as excess 14 C cycled between atmospheric, oceanic and terrestrial carbon reservoirs and was diluted by fossil fuel CO₂ addition to the atmosphere. In this century, fossil fuel dilution has become the major factor controlling the rate of decrease in the atmospheric 14 CO₂.

We report a continuous, high precision and high temporal resolution $\Delta^{14}\text{CO}_2$ record from Barrow, Alaska (71°N, 157°W) from 2003 to 2022. Sample collection was through the NOAA/ESRL flask sampling network program, which enables comparison of radiocarbon data with other trace gases and isotopes, including CO and CO₂ mixing ratios and $\delta^{13}\text{C}$ and $\delta 180$ of CO₂. There are distinct $\Delta^{14}\text{CO}_2$ seasonal cycles in this record, with a broad minimum around Mar-Apr and a maximum in Sep-Oct with an amplitude of ~7%. From 2003 to the end of 2019, $\Delta^{14}\text{CO}_2$ decreased linearly by ~4.3%/year, although it slowed during 2020 which may likely have resulted from reduced fossil fuel CO₂ emission during the global lockdown imposed by the COVID-19 pandemic. By the end of 2021, $\Delta^{14}\text{CO}_2$ at Barrow declined to below 0%, ending the "Bomb Radiocarbon Period" in the Northern Hemisphere. This iconic event is of global significance because the artificial "aging" of the atmosphere has the potential to affect many radiocarbon applications in the future.

G01 02

Tracking changes in fossil fuel CO₂ emissions using citizen science supported radiocarbon observations

Turnbull J^{1,2}, Domingues L¹, Turton N¹

¹GNS Science, Lower Hut, New Zealand, ²CIRES, University of Colorado, Boulder, USA

Emissions from on road transportation are one of the largest sources of fossil fuel CO_2 globally. For many cities, they are the largest single emission source, and hence are a primary target for mitigation actions not only to reduce fossil fuel CO_2 emissions, but adding the co-benefits of reduced traffic, reduced reliance on fuel imports and cleaner air.

Mitigation strategies include improved vehicle efficiency, transition to electric vehicles, and traffic reduction strategies.

The travel and work restrictions imposed by COVID-19 lockdowns resulted in dramatic changes in fossil fuel CO_2 emissions around the world, most prominently in the transportation sector. This provided an ideal opportunity to test our ability to observe and quantify local changes in fossil fuel CO_2 emissions. We used a novel citizen science campaign to collect grass samples from around New Zealand and use radiocarbon measurements to quantify the recently added, local, fossil fuel CO_2 mole fraction at the local and time period that the grass grew.

Our results from 17 sites in five cities around New Zealand demonstrate dramatic reductions in traffic emissions of 75 ± 3 % during the most severe lockdown restriction period. The less restrictive 2021 lockdown resulted in spatially variable transportation emission reductions, apparently due to local traffic patterns and traffic flow. Overall, the grass sampling methodology gives surprisingly robust results, engages the community and policy makers, and provides a straightforward method for evaluating the impact of local-scale emission mitigation strategies.

G01 03

Investigating the variability in the CO:CO₂ff emission ratio at different site types and times of day in Auckland, New Zealand

<u>Young H</u>¹, Turnbull J^{1,2}, Keller E^{1,3}, Domingues L¹, Parry-Thompson J¹, Hilton T¹
¹GNS Science, Wellington, New Zealand, ²University of Colorado, Boulder,, USA, ³Antarctic Research Centre, Wellington, New Zealand

Cities occupy just 3% of Earth's surface area yet contribute ~70% of the world's fossil fuel CO_2 (CO_2 ff) emissions resulting in them becoming focal points for observing emissions. While it is difficult to determine CO_2 ff emissions from CO_2 measurements alone, radiocarbon in CO_2 ($^{14}CO_2$) is an excellent tracer for CO_2 ff. Carbon monoxide (CO) is produced as a by-product of combustion, with each emission source producing a varying amount of CO and CO_2 ff, reported as the $CO:CO_2$ ff emission ratio. By combining CO and CO_2 measurements, it is possible to evaluate local source types as each has its own unique signature.

As part of the CarbonWatch-NZ research programme, air samples were collected in flasks around Auckland and measured to determine CO:CO₂ff at 28 sites over four years. Samples were grouped by location to provide overall emission ratios for each site type (motorway, urban, suburban, and industrial). The emission ratios were then used to identify and compare local CO₂ff sources at each site type. Since vehicles are major contributors to city emissions, CO:CO₂ff for traffic is especially useful. Flasks collected at motorway sites showed emission ratios consistent with expectations for traffic. Suburban and light industrial locations showed ratios consistent with traffic as the dominant CO₂ff source. Urban areas showed a smaller ratio, reflecting a larger CO₂ff contribution from other sources. This observed distribution of sources provides an independent validation of the expected CO₂ff emission sources determined from the Mahuika high-resolution CO₂ff inventory for Auckland.

G01_04

Fifty-five years of radiocarbon studies in Bratislava: From the atmosphere to tree rings and wines

<u>Povinec P</u>¹, Kontuľ I¹, Šivo A¹, Ješkovský M¹, Kaizer J¹, Kvasniak J¹, Richtáriková M¹, Zeman J¹ Comenius University, Department s of Nuclear Physics and Biophysics, Bratislava, Slovakia

Radiocarbon investigations in Bratislava started in 1966 with the aim to develop techniques for sampling and measurement of C-14 levels in the air around a nuclear power plant (NPP) which was under construction in Jaslovské Bohunice, about 60 km NE from Bratislava. Simultaneously, a background monitoring station was established in Bratislava to identify contributions from combustion of fossil fuels and possible emissions from the Jaslovské Bohunice NPP. A correlation has been found between atmospheric radiocarbon data measured at both stations when there was a favorable transport of air masses from Jaslovské Bohunice to Bratislava. The radiocarbon concentrations in the heavily polluted atmosphere of Bratislava were during eighties by about 100‰ and at Jaslovské Bohunice by about 50‰ lower than the European clean air represented by the Jungfraujoch radiocarbon data. After 1994, when the industrial activities in the region decreased, the radiocarbon concentrations were similar at both

sites, and from 2000 they were close to the European clean air levels. Annual tree rings have been used later as archives of past radiocarbon levels in the biosphere either for solar activity studies or for investigations of fossil fuel and NPP emissions. Atmospheric and tree ring data from the Jaslovské Bohunice NPP were compared with those measured in the polluted Bratislava, as well as with two background monitoring stations. Wine samples have also been found as good archives of past radiocarbon levels in the atmosphere. Their ability to record and preserve past radiocarbon levels has also been utilized for dating of old wines.

G01 05

Atmospheric ¹⁴CO₂ observations in megacity Delhi: Inferences for fossil fuel CO₂ (CO₂ff) emissions

<u>Sharma R</u>¹, Kumar Kunchala R¹, Ojha S², Kumar P², Gargari S², Chopra S²

¹Indian Institute of Technology Delhi, New Delhi, India, ²Inter University Accelerator Centre, New Delhi, India

Radiocarbon is an ideal tracer for fossil fuel CO_2 estimations in the atmosphere because of its absence in the fossil fuels. It is formed in the atmosphere by the interaction of cosmic rays with ¹⁴N atoms and distributed in the different reservoirs of earth systems in the form of ¹⁴CO₂. In present study, we have presented the analysis on the fossil fuel CO_2 emissions in megacity Delhi using ¹⁴CO₂ observations for the period from 2017 to 2022. Weekly and sub-weekly integrated atmospheric CO_2 samples are collected in the form of carbonates by absorbing CO_2 over sodium hydroxide at accelerator mass spectrometry (AMS) facility building in Inter University Accelerator Centre (IUAC), New Delhi. These carbonate samples are acid hydrolyzed using carbonate handling system (CHS) and graphitized using automated graphitization equipment (AGE). Radiocarbon in the form of ¹⁴C/¹²C ratio is measured using a 500 kV ion accelerator at IUAC – AMS facility with the precision between 2 to 3 ‰ and measured ¹⁴C/¹²C ratios are converted into Δ ¹⁴C values and CO_2 ff values are calculated using Δ ¹⁴C values. Results of this study in terms of annual and seasonal variations of Δ ¹⁴C and CO_2 ff will be presented for the study period over Delhi. Correlations of Δ ¹⁴C and CO_2 ff with other pollutant concentrations (PM2.5, CO, NO₂, SO₂ etc.) from the nearest air quality monitoring stations and available bottom up CO_2 ff inventories will also be discussed.

G01 06

Radiocarbon Inventories of Switzerland (RICH): Source apportionment of atmospheric CO₂, sampling strategy and first results

<u>Geissbühler D</u>^{1,2}, Laemmel T^{1,2}, Gautschi P³, Wacker L³, Szidat S^{1,2}

¹Department of Chemistry, Biochemistry and Pharmaceutical Sciences, University of Bern, Bern, Switzerland, ²Oeschger Centre for Climate Change Research, University of Bern, Bern, Switzerland, ³Laboratory of Ion Beam Physics, Institute for Particle Physics and Astrophysics, Federal Institute of Technology Zurich (ETHZ), Zurich, Switzerland

Anthropogenically-induced climate change is strongly linked with perturbations of the carbon cycle causing the emission of greenhouse gases into the atmosphere, especially carbon dioxide (CO₂). Radiocarbon (¹⁴C) measurements of atmospheric CO₂ are unique in their capabilities to provide information on carbon source apportionment and transport, especially of fossil-fuel derived CO₂ which is ¹⁴C-free.

The Radiocarbon Inventories of Switzerland (RICH) project aims to build a comprehensive database and model of the distribution and cycling of radiocarbon in Switzerland across the atmosphere, soils, rivers and lakes. The project presented here will serve to specifically construct an inventory of atmospheric ¹⁴CO₂ in this larger scope. This will be achieved by sampling air in strategic ways, and measuring its ¹⁴CO₂ content, as well as CO₂ concentration. This will bring information on the radiocarbon signature of concentrated anthropogenic emissions in air masses, the spatial representation of diffuse natural

emissions in multiple ecosystems, as well as their subsequent atmospheric transport. One of the main challenge in this work is to develop a robust sampling method allowing us to effectively capture $^{14}\text{CO}_2$ signatures. Graphitization of air samples will be done by using the Air Loading Facility developed at ETHZ (Gautschi, 2017). Measurements from leaf biomass are also planned, which will allow an insight into the integration of $^{14}\text{CO}_2$ to the vegetation, and ultimately to soils.

Presented here are the current status of the sampling methods and strategy development, as well as results from the first campaigns.

G01 07

Atmospheric ¹⁴CH₄ measurements over Switzerland: first data and modeling results

<u>Laemmel T</u>^{1,2}, Geissbühler D^{1,2}, Espic C^{1,2}, Bantle M¹, Leuenberger M^{2,3}, Henne S⁴, Brunner D⁴, Szidat S^{1,2}
¹Department of Chemistry, Biochemistry and Pharmaceutical Sciences, University of Bern, Bern, Switzerland,
²Oeschger Centre for Climate Change Research, University of Bern, Bern, Switzerland, ³Climate and Environmental Physics, Physics Institute, University of Bern, Bern, Switzerland, ⁴Empa, Laboratory for Air Pollution/Environmental Technology, Dübendorf, Switzerland

Methane (CH₄) is the second most important anthropogenic greenhouse gas after carbon dioxide (CO₂). While biogenic emissions of CH₄ contain present-day radiocarbon (¹⁴C) levels, CH₄ derived from fossil sources is ¹⁴C-free so that ¹⁴CH₄ measurements can be used as a source apportionment proxy to distinguish anthropogenic from biogenic CH₄ sources. Recently, a new methane preconcentration and purification setup (MPPS) was developed at the Laboratory for the Analysis of Radiocarbon with AMS, University of Bern (Espic et al., 2019). Typical samples are 60L of atmospheric air collected in bags, resulting after extraction in about 60 µg carbon in CH₄-derived CO₂ form, enough for a ¹⁴C gas measurement on a MICADAS (Mini Carbon Dating System) accelerator mass spectrometer. This contribution presents the new MPPS, its performance and ¹⁴CH₄ measurements of biweekly air samplings at four sites in Switzerland, for most of them continuously since 2019: the high altitude research station Jungfraujoch considered as a European continental background station, two tall towers in Beromünster and Sottens and an urban site in Bern. The CH₄ source apportionment at these sites is challenged by sporadic transport of ¹⁴CH₄ emitted from pressurized water reactors of nuclear power plants in Switzerland and neighboring countries. To identify and filter out these situations, forward simulations of atmospheric ¹⁴CH₄ transport using the model FLEXPART-COSMO, including nuclear power plants emissions, are applied.

This sampling strategy is part of the ongoing project RICH (Radiocarbon Inventories of Switzerland) aiming to develop a national radiocarbon inventory in the atmospheric, terrestrial and aquatic carbon pools.

Quantitative evaluation of OC aerosol sources and aging processes: insights from a comprehensive method of dual-carbon isotopes and tracers

 $\underline{\text{Jiang }}\mathbf{F}^{1,6}$, Liu J¹, Cheng Z^{2,7}, Ding P^{3,7}, Zhu S^{2,7}, Yuan X¹, Zhang Z⁴, Zong Z⁵, Tian C⁵, Hu W^{2,7}, Zheng J¹, Szidat S⁶, Li J^{2,7}, Zhang G^{2,7}

¹Institute for Environmental and Climate Research, Jinan University, Guangzhou, China, ²State Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou, China, ³State Key Laboratory of Isotope Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou, China, ⁴South China Institute of Environmental Sciences, Ministry of Environmental Protection, Guangzhou, China, ⁵Key Laboratory of Coastal Environmental Processes and Ecological Remediation, Yantai Institute of Coastal Zone Research, Chinese Academy of Sciences, Yantai, China, ⁶Department of Chemistry, Biochemistry and Pharmaceutical Sciences and Oeschger Centre for Climate Change Research, University of Bern, Bern, Switzerland, ⁷CAS Center for Excellence in Deep Earth Science, Guangzhou, China

Organic carbon aerosol (OC) is a pivotal component of $PM_{2.5}$ in the atmospheric environment, yet its emission sources and atmospheric behaviors remain poorly constrained. In this study, a comprehensive method based on the combination of dual-carbon isotopes (^{13}C and ^{14}C) and macro tracers was employed in the PRDAIO campaign performed in the megacity Guangzhou, China. The ^{14}C analysis showed that 60 % of OC during the sampling campaign was associated with non-fossil sources such as biomass burning activities and biogenic emissions. It should be noted that this non-fossil contribution in OC would significantly decrease when the air masses came from the eastern cities. Overall, non-fossil secondary OC was the largest contributor (89 %) to OC, followed by fossil secondary OC (26 %), non-fossil primary OC (21 %), and fossil primary OC (14 %). Also, we established the dynamic variation of 13 C as a function of aged OC and VOCs oxidized OC to explore the aging processes of OC. Our pilot results showed that a large fraction (average: 53 %) of OC was not from the gaseous oxidation but the aging formation. This study confirmed that non-fossil sources played an important role in the loading of organic aerosol in this megacity and the aging processes were probably highly involved in the formation of organic aerosol.

G01 P01

Changes in fossil CO₂ emissions in Mexico City during the Covid-19 lockdown deduced from atmospheric radiocarbon concentrations

<u>Beramendi-Orosco</u> $L^{1,3}$, González-Hernández $G^{2,3}$, Cienfuegos $E^{1,3}$, Otero $F^{1,3}$, Santos-Arévalo F^4 , Gómez-Martínez I^4

¹Instituto de Geología, UNAM, Ciudad De México, Mexico, ²Instituto de Geofísica, UNAM, Ciudad de México, Mexico, ³Laboratorio Nacional de Geoquímica y Mineralogía, UNAM, Ciudad de México, Mexico, ⁴Centro Nacional de Aceleradores, Sevilla, Spain

The Mexico City Metropolitan Area is a complex megacity with a mixture of CO₂ emission sources, where atmospheric ¹⁴C variability is influenced mainly by changes in fossil fuels burning and wildfires in the mountains surrounding the valley, common during the hot-dry spring season. In this contribution we present atmospheric radiocarbon concentrations from CO₂ monthly-integrated samples taken between January 2019 – June 2021 at the southern area of the Mexico City Basin and explain the changes in terms of the Covid-19 lockdown and restrictions imposed form March 2020. To stop the spread of the Covid-19 epidemy, the Mexican government imposed a partial lockdown closing schools and universities on 20th of March 2020, extending the lockdown to all non-essential activities with a significant reduction in public transport services on 30th of March, and further restrictions with a complete lockdown imposed on 21st of April when the country started the phase of higher risk of Covid-19 transmission. This complete lockdown lasted up to 13th of May, and from 1st of July some non-essential

activities were gradually opened with some restrictions in place up to 2021, and schools and universities remaining closed up to September 2021. Atmospheric radiocarbon concentrations clearly followed the different phases of the Covid-19 restrictions, with significantly higher values (p<0.001) during March – May 2020, indicating, as expected, an important reduction of fossil CO_2 emissions. Furthermore, the post-March 2020 values are higher with lower variability, ranging between 0.9906–1.0108, as compared to the pre-Covid-19 pandemic values, ranging between 0.9639–0.9951.

G01 P02

Evolution of fossil and non-fossil emission sources of carbonaceous aerosol in the Swiss Plateau from 2012 to 2020

Crova F^{1,2}, Strähl J², Szidat S²

¹Department of Physics, Università degli Studi di Milano, and INFN-Milano, Milan, Italy, ²Department of Chemistry, Biochemistry and Pharmaceutical Sciences, and Oeschger Centre for Climate Change Research, Bern, Switzerland

Carbonaceous aerosols are a major component of the fine fraction of atmospheric aerosol; moreover, they can influence Earth's climate and are related to adverse health effects. Therefore, the identification and quantification of their emission sources are crucial.

In Switzerland, like in many other European countries, control strategies for ambient air pollution have focused mostly on emissions deriving from fossil fuel combustion (e.g., road traffic), but non-fossil contributions can be the predominant sources of carbonaceous aerosols in different periods of the year (e.g., biomass burning during winter) [Zotter et al., 2014]. Consequently, studying the evolution over long periods of the relative contributions of fossil and non-fossil sources of carbon is mandatory to understand the variation of their impact.

In this work, a source apportionment study of carbonaceous aerosol sources in the Swiss Plateau region from 2012 to 2020 was carried out by performing radiocarbon measurements on separated carbon fractions. Indeed, such measurements have been proved to be very effective to separate the contribution of different carbon emission sources in the atmosphere [Szidat et al., 2006]. Aerosol samples in the size fraction PM2.5 collected daily by Empa (Swiss Federal Laboratories for Material Science and Technology) in three different monitoring stations (Bern, Zurich, and Payerne) were exploited for this purpose. Radiocarbon measurements were performed by accelerator mass spectrometry (AMS) at the Laboratory for the Analysis of Radiocarbon with AMS (LARA) at the University of Bern on the total and elemental carbon fractions. Preliminary results concerning the site of Bern will be presented.

G01_P03

Radiocarbon concentration of wheat (Triticum aestivum L.) and soybean seeds (Glycine max (L.) Merr.) grown during the bomb spike.

<u>Huels M</u>¹, Hamann C¹, Börner A²

¹Christian-albrechts-university, Kiel, Germany, Kiel, Germany, ²2) Leibniz Institute of Plant Genetics and Crop Plant Research (IPK), Seeland, OT Gatersleben, Germany

Here we report radiocarbon measurements made on soybean seeds (Glycine max (L.) Merr.), grown and harvested on the experimental fields of the IPK in Gatersleben, Saxony-Anhalt, Germany, between 2000-2021, complementing the 14 C measurements from wheat seeds over the bomb-spike (Hüls et al 2021). Soy is sown around mid May and harvested by the end of September / beginning of October, forming its main bean tissue between July and October. The results give an overview of 14 C in agricultural grown plant tissue during the growth-period between April to September. The combined wheat and soybean seed radiocarbon record is compared to known pre- and post-bomb radiocarbon records (e.g. atmospheric Jungfraujoch, Schauinsland, and NH $_1$ datasets).

The Gatersleben plant tissue radiocarbon concentration indicates incorporation of fossil carbon of about 1% with respect to the high alpine, clean-air CO_2 of the Jungfraujoch station between 1987 and 2019. As shown previously with wheat seed (Hüls et al 2021), recent (i.e. 2021) grown plant-tissue give apparent ^{14}C concentrations slightly below the 1950 reference level (i.e., -5.3±2 % for wheat, -6.9±3% for soybean, respectively).

We suggest to use the pre- and post-bomb radiocarbon record of Gatersleben seeds as a reference in forensic investigations, such as the age estimation of paper by analyzing starch used in paper manufacture. A further advantage of the dataset reported here lies in its comparably simple extensibility by adding new analyses from future harvests.

G01 P04

Vertical dynamics of particulate carbon sources during a haze pollution episode using the measurements of dual-carbon isotopes

<u>Jiang F</u>^{1,2}, Liu J¹, Strähl J², Szidat S², Wang Y¹, Cheng Z^{3,7}, Zhu S^{3,7}, Ding P^{4,7}, Cao F⁵, Zhang Y⁵, Zhou S⁶, Zheng J¹, Li J^{3,7}, Zhang G^{3,7}

¹Institute for Environmental and Climate Research, Jinan University, Guangzhou, China, ²Department of Chemistry, Biochemistry and Pharmaceutical Sciences and Oeschger Centre for Climate Change Research, University of Bern, Bern, Switzerland, ³State Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou, China, ⁴State Key Laboratory of Isotope Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou, China, ⁵Yale-NUIST Center on Atmospheric Environment, International Joint Laboratory on Climate and Environment Change, Nanjing University of Information Science and Technology, Nanjing, China, ⁶School of Atmospheric Sciences, Sun Yat-sen University, Guangzhou, China, ⁷CAS Center for Excellence in Deep Earth Science, Guangzhou, China

Carbonaceous aerosols, an important component of PM_{2.5}, have been identified as the critical trigger influencing the formation and evolution of severe atmospheric haze pollution in many regions around the world. Stable carbon isotope (¹³C) and radiocarbon (¹⁴C) measurements are powerful tools for identifying and quantifying the relative contributions of key sources to haze pollution. In this study, we investigated the dynamic changes of the signals of ¹³C and ¹⁴C in PM_{2.5} samples collected at different heights of the Canton Tower in Guangzhou in South China in the 2020/2021 winter season, during which a severe haze episode occurred. The ¹⁴C measurements showed that there is an obvious difference in the sources of total carbon aerosol among different heights. In addition, we found that the ¹⁴C signals varied dramatically during this haze episode, suggesting that the sources of particulate carbon were constantly changing during the formation and evolution of the atmospheric haze pollution. To further investigate the sources and formation mechanisms of this haze event, we will 1) refine the source information based on the measurements of ¹³C and ¹⁴C in subfractions of total carbon; 2) find out the key source and mechanism that triggered this haze pollution.

G01_P05

Source apportionment of atmospheric and sedimentary PAHs from Kolkata, India by using compound-class-specific radiocarbon analysis (CCSRA)

Kumata H¹, Uchida M², SAHA M^{3,4}, Mantoku K², Kobayashi T², Okuda T⁵, Shibata Y^{2,6}, Takada H³
¹Tokyo University of Pharmacy and Life Sciences, Hachioji, Japan, ²National Institute for Environmental Studies, Tsukuba, Japan, ³Tokyo University of Agriculture and Technology, Fuchu, Japan, ⁴Now at National Institute for Oceanography , , India, ⁵Keio University, Yokohama, Japan, ⁶Tokyo University of Science, Tokyo, Japan

Asia is one of the most important source regions for short-lived climate pollutant (SLCP), to the atmosphere. For polycyclic aromatic hydrocarbons (PAHs), known as major mutagens in atmospheric aerosols, Asian megacities have the highest levels across the globe.

We conducted compound-class-specific radiocarbon analyses (CCSRA) for surface sediments and aerosols collected in city center of Kolkata. Surface sediments were collected from city canals using a grab sampler. The study site was chosen because the preliminary survey showed it has extremely high-level contamination. Collected sediments were roughly sectioned on-site and approximately upper half (0-7 cm, depth from the surface of the sediment) was used. The fC values of sedimentary PAHs in Kolkata city canal sediments ranged 0.056 to 1.0 in the north canal and 0.078 to 0.080 in the south canal, indicating strong influences (i.e., >90%) from fossil fuel combustions. Combined with molecular fingerprinting study, relative contribution from coal combustion in brickyards to sedimentary PAHs was estimated to be >50%. As monsoon driven runoff events flush canals every year, this may portray the input of particle-borne pollution over the last few years. Based on the results obtained, we discuss the importance of contemporary sources of combustion-derived PAHs in Indian Mega city.

G01 P06

Characterization of Carbonaceous Components and Fossil and Non-Fossil Carbon Contents in Fine Aerosols in the Eastern Mediterranean Troposphere

Pavuluri C^{1,2}, Mihalopoulos N³, <u>Uchida M</u>⁴, Mantoku K⁴, Fu P^{1,2}, Kawamura K^{1,5}

¹Institute of Low Temperature Science, Hokkaido University, Sapporo, Japan, ²Institute of Surface-Earth System Science, School of Earth System Science, Tianjin University, Tianjin, China, ³ECPL, Department of Chemistry, University of Crete, Heraklion, Greece, ⁴AMS Facility (NIES-TERRA), National Institute for Environmental Studies, Tsukuba, Japan, ⁵Chubu Institute for Advanced Studies, Chubu University, Kasuqai, Japan

Atmospheric fine (PM₁) aerosols are mainly produced by secondary processes and contain a major fraction of organic compounds, which have serious impacts on the Earth's climate system directly by scattering and absorbing solar radiation and indirectly by acting as cloud condensation nuclei. They also cause adverse effects on human health and play an important role in atmospheric chemistry. It is well recognized that summertime ozone is enhanced in the Mediterranean troposphere and the aerosol radiative forcing is among the highest in the world over this region in summer. Although carbonaceous components have been studied well, their origins and atmospheric processing are not yet fully understood in the Mediterranean. We collected PM₁ samples at a remote marine background site, the Finokalia research station, in the Eastern Mediterranean troposphere on a weekly basis for two consecutive days each during a one-year period: October 2009 to October 2010. We measured the carbonaceous components: elemental carbon (EC) organic carbon (OC) and water-soluble OC (WSOC) and stable carbon (δ^{13} C) and radiocarbon (Δ^{14} C), a unique tracer for distinct fossil and non-fossil carbon, isotope ratios of total carbon (TC) in the PM1.0. Here we report (i) the characteristics of carbonaceous components and (ii) percent of modern carbon (pMC) in TC. Based on the results obtained together with their comparison with molecular marker species, we explore the origins and the extent of secondary formation of carbonaceous aerosols as well as their seasonality in the Eastern Mediterranean.

G01 P07

Abundance of Non-Fossil Carbon Content in the Tropical Indian Carbonaceous Aerosols

Pavuluri C^{1,2}, **Uchida M**³, Mantoku K³, Fu P^{1,2}, Kawamura K^{1,4}

¹Institute of Low Temperature Science, Hokkaido University, Sapporo, Japan, ²Institute of Surface-Earth System Science, School of Earth System Science, Tianjin University, Tianjin, China, ³AMS Facility (NIES-TERRA), National Institute for Environmental Studies, Tsukuba, Japan, ⁴Chubu Institute for Advanced Studies, Chubu University, Kasuqai, Japan

Carbonaceous aerosols that represent a large fraction of fine aerosol mass have serious impacts on the Earth's climate system directly by scattering and absorbing solar radiation and indirectly by acting as cloud condensation nuclei. They also cause adverse effects on human health and play an important role in atmospheric chemistry. Although carbonaceous components have been studied well, their origins and atmospheric processing are not yet fully understood in the tropical Indian aerosols. To apportion the fossil and contemporary carbon content in the tropical carbonaceous aerosols from the Indian region, we collected atmospheric aerosols (PM₁₀) on day- (approximately 6:00–18:00 LT) and nighttime (18:00– 6:00 LT) bases in winter (January 23 to February 6, n = 29) and summer (May 22–31, n = 20) 2007 from a mega-city, Chennai (13.04°N; 80.17°E) located on the southeast coast of India. We measured the carbonaceous components, molecular composition and distributions of various organic classes of compounds and their stable carbon isotopic composition (δ^{13} C), and radiocarbon (Δ^{14} C), a unique tracer for distinct fossil and non-fossil carbon, isotope ratios of total carbon (TC) in the PM₁₀. Here we report the characteristics of Δ^{14} C as percent of modern carbon (pMC) in TC, together with the comparison with the carbonaceous components and molecular marker species in PM₁₀. Based on the results obtained, we discuss the importance of contemporary sources and aging of the tropical carbonaceous aerosols, including their diurnal and seasonal changes, in the Indian region.

G01 P08

Atmospheric CO₂ carbon isotope composition in urban and clean areas of costal Northern Croatia

<u>Sironić A</u>¹, Hess E², Borković D¹, Kanduč T³, Barešić J¹, Krajcar Bronić I¹

¹Ruđer Bošković Institute, Zagreb, Croatia, ²Department of Physics, University of Rijeka, Rijeka, Croatia, ³Department of Environmental Sciences, Jožef Stefan Institute, Ljubljana, Slovenia

Fossil fuel combustion decrease ¹⁴C activity and ¹³C composition of atmospheric CO₂, which is also known as the Suess effect. For one year (2021), we have been monitoring carbon isotope composition of atmospheric CO₂ at locations under maritime influence of the Adriatic Sea: coastal city of Rijeka and at two clean air sites in vicinity, Gornje Jelenje and Parg with mountain climate. Carbon isotope composition at all sites shows seasonal variation, with the lowest ¹⁴C activities and δ^{13} C in winter-spring, and the highest in summer, ranging from -41.3 to 25.2 % for Δ^{14} C and -13.1 to -11.3 % for δ^{13} C, respectively. Rijeka has systematically the lowest and Parg the highest Δ^{14} C, however δ^{13} C at the sites are not statistically different one from another. Leaves of deciduous trees were also collected. Their Δ^{14} C reflect the trend of atmospheric Δ^{14} C, being the lowest at Rijeka and highest at Parg.

G01_P09

Variation of fossil CO₂ in Mexico City during the month of December before and after the COVID-19 partial lockdown.

Solis C

¹Universidad Nacional Autónoma de México, Mexico City, Mexico, ²Instituto Tecnológico de Estudios Superiores de Monterrey, CDMX, México, Mexico City, Mexico, ³Universidad Autónoma Metropolitana Azcapotzalco, Mexico City, Mexico

Mexico City (CDMX), the largest urban center in Mexico, has a population dynamics, industrial development, orography, and climate that make it a major source of pollution and health problems. Mexico City has 5.9 million vehicles and intense industrial activity. Fossil fuel consumption is responsible for 95% of CO₂ emissions. Due to the COVID 19 pandemic, the government imposed a partial shutdown of all non-essential activities since March 2020 in the public and private sector, schools and universities as part of containment measures. Vehicular traffic decreased by 62% relative to 2019. Because of the important decrease in vehicular traffic and other activities, CO₂ emissions decreased from 487,570 megatons in 2019 to 407,695 megatons in 2020. In this work, we applied the AMS detection of ¹⁴CO₂ to

infer the reductions in the fossil fraction caused by the decrease in activities by COVID-19 pandemic. The ¹⁴CO₂ measurement was conducted in December (winter) 2020 and compared to the activity in the same month of 2019. The ¹⁴CO₂ measurement has been used to assess the emissions of the modern and fossil fractions.

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G01 P10

Atmospheric radiocarbon analysis of grass samples; weekly resolution comparison and fossil fuel reconstruction of high traffic and background sites.

Usher E¹, Wood R², Esmay R¹, Fallon S¹

 1 ANU Radiocarbon Dating Laboratory, Canberra, Australia, 2 Oxford Radiocarbon Dating Laboratory , Oxford, UK

The atmosphere's composition and dynamics, and particularly the role which carbon dioxide has within these, have become topics of increasing scientific importance in a world of anthropogenic climate change. The radioisotope composition of atmospheric CO₂ is an integral component for these topics as it can allow for anthropogenic influence to be identified and even quantified due to the Suess effect. Biotic assimilation proxies present an avenue to investigate atmospheric ¹⁴C at varying temporal and spatial scales. Grass as a biotic proxy has successfully been used to reconstruct fossil fuel contribution to atmospheric CO₂ in a point source analysis by Turnbull et al. (2016). In this work grass samples from three locations, two background and one sample site, will be analysed for F¹⁴C values in order to reconstruct the fossil fuel contribution (CO₂ff) from traffic next to one of Canberra's busiest roads, Parkes Way Road. Grass is sampled weekly from these sites and cryogenically frozen until pretreatment, then measured with an AMS. This work uses a relatively novel biotic proxy to identify emissions contributions from motor vehicles in Canberra. The early results from this study show that there is a measurable difference in F¹⁴C values between the background sites and the road site consistent with an average of ~4ppm contribution from CO₂ff.

Turnbull, J, Keller, E, Norris, M, Wiltshire, R. (2016). Independent evaluation of point source fossil fuel CO_2 emissions to better than 10%. Proceedings of the National Academy of Sciences. 113. 201602824. 10.1073/pnas.1602824113.

G01 P11

Using ¹⁴CO₂ to derive fossile fule CO₂ in the UK.

<u>Wenger A</u>¹, Knowles T¹, Chawner H¹, Rlgby M¹, O'Doherty S¹ ¹University Of Bristol, Bristol, United Kingdom

Estimating the anthropogenic component of carbon dioxide emissions from direct measurements is difficult, due to the large natural carbon dioxide fluxes. One way of determining the fossil fuel component of atmospheric carbon dioxide is the use of radiocarbon measurements, as carbon from fossil fuel is completely devoid of radiocarbon due to its age.

The DARE-UK project is attempting to use high frequency ¹⁴CO₂ observations at atmospheric observation sites to infer UK fossil fuel emissions.

We will present the first year of atmospheric $^{14}\text{CO}_2$ data from 2 UK sites and a background site in Ireland. To cope with the large sample volume, we partially automated the $^{14}\text{CO}_2$ sample preparation by developing an automated CO_2 extraction system, that interlinks with a commercially available graphitization system.

A sampling system for ¹⁴C analysis of atmospheric methane: from a laboratory prototype to an automated system.

Zazzeri G¹, Gautschi P¹, Graven H², Wacker L¹

¹ETH, Zürich, Switzerland, ²Imperial College London, London, United Kingdom

Measurements of radiocarbon (¹⁴C) in atmospheric methane (CH₄) provide a powerful tool to distinguish fossil from biogenic methane emissions, because fossil methane is completely devoid of ¹⁴C. However, these measurements are particularly challenging as CH₄ is at low concentration in the atmosphere and large volumes of air must be sampled.

At Imperial College London we developed a unique sampling system for ¹⁴C analysis of atmospheric CH₄ that addresses the sampling challenge, enabling extraction of carbon while sampling and collection of the air sample onto a small trap of molecular sieve (Zazzeri et al. 2021). This system is currently a laboratory prototype and technical developments are needed to make it portable and flexible to user need. The technical changes are being implemented at the Laboratory of Ion Beam Physics at ETH and include: 1) reducing the size of the system components to make the system fully portable, 2) making the sampling procedure fully automated, 3) interfacing the system with the gas ion source of the AMS system Micadas.

Here we present an overview of such developments, with a focus on the testing of a new molecular sieve sample trap. The new sample trap, with a smaller size than the one employed in the original system, will facilitate extraction of the collected carbon for ¹⁴C analysis and will enable direct interfacing with the gas ion source of the AMS system, making ¹⁴CH₄ measurements easier to perform.

Zazzeri, G., Xu, X., & Graven, H. (2021). Environmental Science & Technology, 55(13), 8535-8541.

G02 Oceanic carbon cycling

G02_01

Recent changes in ocean DI14C and implications for ocean circulation

<u>Lester J</u>¹, Graven H¹, Khatiwala S², Key R³, McNichol A⁴

¹Imperial College London, London, United Kingdom, ²University of Oxford, Oxford, United Kingdom, ³Princeton University, , USA, ⁴Woods Hole Oceanographic Institution, , USA

Anthropogenic perturbations from fossil fuel burning and nuclear bomb testing have created a useful transient tracer of ocean circulation from measurements and modelling of dissolved ^{14}C . The atmospheric $^{14}\text{C/C}$ ratio ($\Delta^{14}\text{C}$) peaked in the early 1960s and has decreased now to nearly pre-bomb levels. We present the first analysis of a new decade of observations from 2007 to 2016 which gives a comprehensive overview of the changes in ocean $\Delta^{14}\text{C}$ since the 1990s. Surface ocean $\Delta^{14}\text{C}$ decreased from the 2000s to 2010s at a similar rate as from the 1990s to 2000s (20%/decade). In contrast to the period from the 1990s to the 2000s when denser waters gained ^{14}C from the continued downward ventilation of bomb ^{14}C , the extent of positive $\Delta^{14}\text{C}$ between the 2000s to 2010s is much reduced. Comparison to two ocean models, the Community Earth System Model v2 (CESM2) and the Estimating the Climate and Circulation of the Ocean v4 (ECCOv4), shows evidence from $\Delta^{14}\text{C}$ of decadal variability in the ventilation of Southern Ocean intermediate waters. The decrease in surface tracers from the 2000s to the 2010s is consistently stronger in observations than in these models, which may result from a reduction in vertical transport and mixing due to stratification.

Evolution of radiocarbon in the North Atlantic during 1990s-2020 inferred from in-situ observations and model simulations

<u>Castrillejo M</u>^{1,2}, Wacker L², Lester J¹, Graven H¹

¹Department of Physics, Imperial College London, London, United Kingdom, ²Laboratory of Ion Beam Physics, ETH-Zurich, Zurich, Switzerland

Radiocarbon in dissolved inorganic carbon (Dl14C) is an important tracer of the carbon cycle and of the processes involved in its uptake and redistribution such as the ocean circulation. In this work, we assess the spatial and temporal evolution of Dl14C in the North Atlantic to better understand the processes driving its distribution in the water column. To that end, we use new Δ^{14} C observations and model simulations obtained from the 'Nucleus for European Modelling of the Ocean' model, as well as other model outputs from the Coupled Model Intercomparison Project Phase 6. We focus on GO-SHIP A25 and A05 lines that cover the subpolar gates to the Arctic Sea and subtropical latitudes, respectively. The region between the two oceanic sections hosts major water mass transformation processes involved in the shallow to deep sequestration of climate properties. We collected 400 seawater samples in 2018-2020 to determine D1 14 C using the new ETH-LIP analytical method. The new Δ^{14} C data are used to infer the water masses involved in major radiocarbon changes since the 1990s by comparison to previously reported data available in GLODAPv2 and CCHDO. Then Δ^{14} C observations are compared to model outputs sampled at nearby geographical locations to identify the strengths and weaknesses of the various models in simulating Δ14C. Some model simulations were conducted using different wind forcing and atmospheric Δ^{14} C and CO₂ boundary conditions, therefore allowing us to evaluate the role of ocean circulation (stationary vs time variable) and bomb-14C in shaping the water column distribution of DI14C.

G02 04

Climate induced thermocline aging and ventilation south of the Azores front over the last 32,000 years

<u>Beisel E</u>¹, Frank N¹, Lausecker M¹, Friedrich R², Therre S¹, Schröder-Ritzrau A¹, Butzin M³

¹Institute of Environmental Physics, Heidelberg University, Heidelberg, Germany, ²Curt-Engelhorn-Center Archaeometry, Mannheim, Germany, ³MARUM-Center for Marine Environmental Sciences, University of Bremen, Bremen, Germany

The radiocarbon analysis of uranium-thorium-dated cold-water corals (CWC) provides an excellent opportunity for qualitative reconstruction of past ocean circulation and water mass aging. While middepth water mass aging has been studied in the Atlantic Ocean, the evolution of the thermocline, tightly coupled to the atmosphere, remains largely unknown. Here we present a high-resolution dataset of combined ¹⁴C and U/Th data obtained from thermocline-dwelling CWCs at various sites in the Atlantic Ocean, directly compared to simulation results of the ¹⁴C-equipped Large Scale Geostrophic ocean general circulation model for the last 32 ka. CWCs off Angola provide the link between previous records from the equatorial Atlantic and Southern Ocean at greater depths, opening the possibility of a unified southern ¹⁴C signal in the Last Glacial Maximum (LGM). In contrast to the South Atlantic and to modeling results, North Atlantic CWCs show strong variations of a well-ventilated water mass near the Azores Front. Our results confirm previous observations of enhanced ventilation during the Bølling-Allerød interstadial (B/A), both shallower and deeper water layers exhibit the same radiocarbon signal. We conclude that the North and South Atlantic must be considered as separately acting reservoirs during the LGM, subsequent deglaciation and B/A. Respired carbon is stored in the dynamic mid-depth to deep Atlantic south of the Azores Front, while the subpolar North Atlantic waters remain a persistent wellventilated ocean. Consequently, CWC-14C records from the South Atlantic and Southern Ocean provide

the opportunity to determine a high-precision calibration curve for the radiocarbon content of the thermocline.

G02 05

Dissolved inorganic radiocarbon (DI¹⁴C) constraints on the biogeochemistry of marine dissolved organic matter (DOM)

Beaupre S¹, Walker B², Druffel E³

¹School of Marine and Atmospheric Sciences, Stony Brook University, Stony Brook, United States, ²Department of Earth and Environmental Science, University of Ottawa, Ottawa, Canada, ³Department of Earth System Science, University of California Irvine, Irvine, United States

Marine dissolved organic matter (DOM) comprises all organic substances smaller than ~1 µm in seawater, with myriad physical properties, chemical reactivities, and biogeochemical lifetimes ranging from seconds to millennia. Yet, global DOM concentrations and Δ^{14} C values have remarkably predictable vertical distributions. This may be due, in part, to DOM's shared propensity for transport predominantly as solutes in moving currents. Dissolved inorganic carbon (DIC) is both a tracer of ocean circulation and the ultimate source of most DOM carbon atoms (DOC). In this way, DIC Δ^{14} C can also be used as a tool to constrain the biogeochemistry of DOM. Analyses of the concentrations and fractionation-corrected ¹⁴C atom abundances (¹⁴C*) of DOC and DIC in contemporaneous profiles show consistency with the simple two-component mixing model and yet, simultaneously, reveal readily distinguishable depths exerting unique biogeochemical controls on DOM. Variability in DOM concentrations and Δ^{14} C values are dominated by net imbalances of in situ production and loss processes in the upper ocean, and by transport in the deeper ocean. In addition, profiles of Z-scores of DOC and DIC concentrations and ¹⁴C abundances are identical throughout the deeper ocean at Station M in the eastern North Pacific, demonstrating that their biogeochemical sources and sinks are tightly coupled. Collectively, DIC and conservation of mass may be useful tools for constraining the net reactivity of DOC in the deep sea, and for predicting and interpreting the global distribution of DOC Δ^{14} C values.

G02 06

From the Southern Ocean to the Bering Sea: using radiocarbon to investigate dissolved organic carbon aging in the Pacific

Schlagenhauff S¹, Bercovici S³, Grotheer H¹, Niggemann J³, Dittmar T³, Mollenhauer G^{1,2}

¹Alfred Wegener Institute, Bremerhaven, Germany, ²Marum Center for Marine Environmental Research and Department of Geosciences, Bremen, Germany, ³Institute for Chemistry and Biology of the Marine Environment, Oldenburg, Germany

Although marine dissolved organic matter (DOM) mainly forms from primary production at the surface, from sources with young Δ^{14} C values, DOM from deep water samples is significantly older (4000-6300 years) and is either supplemented by an older source or persists on millennial timescales. Understanding how DOM endures in the ocean is key to predicting future DOM fluctuations. This project presents the Δ^{14} C values of marine DOM from a Pacific transect collected on the RV Sonne in 2016 and 2017. The transect runs from 58.9°N along the 180°E longitudinal meridian to 52.1°S and provides an unprecedented dataset of Δ^{14} C values of Pacific DOM. The samples were solid phase extracted and then isotopically analyzed on the MICADAS mini-carbon dating system. At the surface (upper 100 m), Δ^{14} C values ranged from -302 % in the subtropics to a more depleted value of -466 % in the Southern Ocean, likely influenced by upwelling deep waters via the Antarctic Circumpolar Current. In deeper waters across the transect (3000 – 6000 m) the average Δ^{14} C value was -548 ± 25 % with a minimum value of -603 % in the Bering Sea. The northern stations also revealed local areas of old DOM input to the ocean, likely from the Bering Sea. The Δ^{14} C values generally align well with known water mass

gradients across the Pacific and decrease with depth. These findings provide evidence for (1) a stable pool of aged DOM in the deep ocean and (2) localized processes adding autochthonous DOM to the system.

G02 07

Seawater dissolved organic carbon is rapidly removed in ultramafic hydrothermal systems and replaced by ¹⁴C-free labile organics

<u>Lang S</u>^{1,2}, Benitez-Nelson B², Vincent M², Mau A², Simpson A³, Kock F³, Lysak D³, Soong R³
¹Woods Hole Oceanographic Institution, Woods Hole, United States, ²University of South Carolina, Columbia, United States, ³University of Toronto, Tronto, Canada

Large volumes of water have passed through the hot, rocky subseafloor throughout Earth's history. This circulation of fluids through oceanic rocks is sufficiently large to impact the cycling of marine dissolved organic carbon (DOC) and to sequester oceanic carbon in the subseafloor over geologic timescales. While the fate of DOC in numerous mafic systems has been examined, there have been no previous reports on the less studied but still abundant ultramafic systems. We analyzed the concentration and composition of DOC from two systems hosted on ultramafic rocks, the Lost City hydrothermal field (30°N, Mid-Atlantic Ridge) and the Von Damm hydrothermal system (Mid-Cayman Rise). We show that per liter of seawater, more DOC is removed and at an >700 time faster rate than in mafic ridge flank systems. Simultaneously, labile ¹⁴C-free organics are exported from the system in concentrations up to 20 times higher than deep seawater. Early in Earth's history, similar sequestration could have served to concentrate organic molecules for further prebiotic geochemical reactions, in the lead up to early life.

G02 08

Bridging marine biosphere and geosphere using compound-specific radiocarbon analysis of amino acids in fish muscle

<u>Ishikawa N</u>^{1,2}, Blattmann T^{1,2}, Haghipour N², Ogawa N¹, Eglinton T², Ohkouchi N¹ ¹Biogeochemistry Research Center, Yokosuka, Japan, ²Geological Institute, Zürich, Switzerland

The Earth surface is a dynamic environment of carbon exchange among different pools. Of these, the linkage between biosphere and geosphere is of key importance for understanding the global carbon cycle. In this presentation, we test a hypothesis that amino acid-specific radiocarbon signatures reflect the exchange of carbon between the marine biosphere and geosphere. To this end, we employed compound-specific radiocarbon analysis of amino acids in fish muscle using High-Performance Liquid Chromatography followed by Elemental-Analyzer Accelerator Mass Spectrometry, which allows us to downsize the final target compounds of > 20 μ gC (Ishikawa et al. 2018; Haghipour et al. 2019). Most amino acids did not show Δ^{14} C values significantly different from those of their expected carbon source (i.e., seawater dissolved inorganic carbon: DIC). However, some amino acids exhibited remarkably low Δ^{14} C values, suggesting that their carbon skeleton is derived from other carbon sources with signatures different from seawater DIC. The results will not only revise the current picture of carbon cycling in connection with the biosphere, but also open up a new frontier of amino acid biogeochemistry.

References:

Ishikawa, N. F., Itahashi, Y., Blattmann, T. M., Takano, Y., Ogawa, N. O., Yamane, M., Yokoyama, Y., Nagata, T., Yoneda, M., Haghipour, N., Eglinton, T. I., & Ohkouchi, N. (2018). Analytical Chemistry, 90(20), 12035-12041.

Haghipour, N., Ausín, B., Usman, M. O., Ishikawa, N., Wacker, L., Welte, C., Ueda, K., & Eglinton, T. I. (2018). Analytical Chemistry, 91(3), 2042-2049.

G02 09

Sedimentary organic carbon ¹⁴C age and D¹⁴CTOC variations in a 200-yr core from Santa Barbara Basin: Anthropogenic and climatic influences

Li H¹, Chang H¹, Shen T¹

We have done 210Pb dating, varve counting, AMS 14C dating and scanning XRF and acid (0.5N HCl) leachate elemental (ALE) contents on a 51-cm core from the depo-center of Santa Barbara Basin (SBB). The core contains a depositional history during 1815-2011 CE. A total of 89 AMS ¹⁴C measurements on samples from 66 horizons show apparent ¹⁴C ages between 500 and 4000 yr BP. Among these AMS dates, 78 TOC ¹⁴C dates from 62 horizons provide high-resolution D¹⁴C variations ranging from -64.3% to -383.8%. The ¹⁴CTOC is influenced by the input of terrigenous sediments, changes in ocean circulation, biological input and carbon remineralization as well as anthropogenic impacts. Three strong old ¹⁴CTOC excursions at 1964~69, 1884~87 and 1819~21 CE caused by some unusual events (e.g., oil spill and extraction, flood event and earthquake). The D14CTOC shifts in three zones were mainly caused by changes in fossil carbon emission from the seafloor and the atmospheric nuclear bomb ¹⁴C input. On interannual scales, variations of D14CTOC correspond to ENSO and PDO effects. During the La Niña period (and cold PDO phase), stronger upwelling and northerly California Current bring nutrientenriched water into SBB and lead to higher productivity. The organic carbon and carbonate enriched sediment layers contain lower scanning XRF K and Ti but higher ALE with higher D14CTOC during La Niña period. During the El Niño period, the phenomena are opposite. Spectrum analyses of the SOI and the D¹⁴CTOC and their comparison support our scenarios.

G02_P01

Radiocarbon geochemistry of amino acids in marine sediments

<u>Blattmann T</u>^{1,2}, Ishikawa N², Keil R³, Yokoyama Y⁴, Ogawa N², Haghipour N^{1,5}, Sun Y^{2,4,6}, Neibauer J³, Duffy M³, Suga H², Miyairi Y⁴, Eglinton T¹, Takano Y², Ohkouchi N²

¹ETH Zurich, Zurich, Switzerland, ²Biogeochemistry Research Center, JAMSTEC, Yokosuka, Japan, ³School of Oceanography, Seattle, USA, ⁴Atmosphere and Ocean Research Institute, The University of Tokyo, Kashiwa, Japan, ⁵Laboratory of Ion Beam Physics, ETH Zurich, Zurich, Switzerland, ⁶Department of Earth and Planetary Science, The University of Tokyo, Tokyo, Japan

The "building blocks of life" occur ubiquitously on Earth's surface in the form of proteins, peptides, and single amino acids. To shed light on amino acid sources, cycling, and preservation, we have conducted amino acid-specific radiocarbon analysis on surficial marine sediment from the North American west coast. As the main goal for these investigations, we test a hypothesis that amino acid-specific radiocarbon signatures reflect the interactions of organic matter with mineral surfaces on a molecular level. This hypothesis was inspired by laboratory-based sorption experiments showing strong differences in the partitioning of different amino acids between dissolved and clay mineral adsorbed states (Blattmann & Ishikawa, 2020). We employed high-performance liquid chromatography described in Blattmann et al. (2020) to isolate individual amino acids extracted from marine sediment which were vetted for their purity via chromatography and elemental composition. Isolated amino acids were measured on accelerator mass spectrometers as gas and graphite samples at ETH Zurich and the University of Tokyo, respectively. Amino acids showed multiple centuries age difference demonstrating differential turnover within this compound class in marine surface sediments. The results highlight the role of clay minerals in modulating the preservation of amino acids in the sedimentary record.

¹Department of geosciences, National Taiwan University, Taipei, Taiwan

References:

Blattmann, T.M. & Ishikawa, N.F. (2020) Theoretical amino acid-specific radiocarbon content in the environment: Hypotheses to be tested and opportunities to be taken. Frontiers in Marine Science 7. Blattmann, T.M. et al. (2020) Liquid chromatographic isolation of individual amino acids extracted from sediments for radiocarbon analysis. Frontiers in Marine Science 7.

G02 P02

Ensuring comparability of radiocarbon measurements in dissolved inorganic carbon of seawater between ETH-Zurich and NOSAMS

Castrillejo M^{1,2}, Hansman R³, Wacker L², Lester J¹, Graven H¹

¹Department of Physics, Imperial College London, London, United Kingdom, ²Laboratory of Ion Beam Physics, ETH-Zurich, Switzerland, ³Woods Hole Oceanographic Institution - National Ocean Sciences Accelerator Mass Spectrometry Facility, Woods Hole, USA

Radiocarbon observations provide useful information about carbon cycling and ocean circulation of the real ocean and of model simulations. In an effort to provide high-quality radiocarbon observations, the Laboratory of Ion Beam Physics (LIP) developed the ETH-LIP analytical method allowing the rapid and precise analysis of radiocarbon in small seawater samples. The performance of this method is continuously assessed by following several internal quality controls. Yet, further steps have been taken to ensure the comparability of the data produced at ETH to previously existing observations.

In the absence of standards or reference materials of seawater, comparability can be assessed through inter-laboratory comparisons. To that end, an inter-comparison exercise was conducted in 2021 between ETH and the National Ocean Sciences Accelerator Mass Spectrometry (NOSAMS) Facility at Woods Hole Oceanographic Institution. In February 2020, duplicate seawater samples were collected from 14 depths and geographical locations distributed along the GO-SHIP A05 line in the subtropical North Atlantic (~ 24.5° N). This work presents the results reported from the two laboratories, which overall showed a very good agreement. We further discuss important aspects related to the different sample collection, preservations and storage techniques used to collect the seawater for NOSAMS and ETH.

G02 P03

AMS ¹⁴C dating and stable isotope analysis on an 8-kyr oyster shell from Taipei Basin: Sea level and SST changes

Chou C¹, Kang S¹, Liu T¹, Li H¹

¹Department Of Geosciences, NTU, Taipei, Taiwan

A giant oyster shell (42 cm long), Crassostrea gigas, was uncovered from an oyster reef on the ancient shore of eastern Taipei Basin in 2002. The oyster reef was 14.9 m below the ground surface which has an elevation of 10 m a.s.l. Eight AMS 14 C dates along the growth axis of the shell are from 8130±200 yr BP to 8435±155 yr BP, indicating that the shell was formed and deposited about 8300 years ago during the high sea level stand of middle Holocene. A plancenta shell collected 5 m above the oyster reef shows a 14 C age of 7640±60 yr BP, indicating that Taipei Basin was covered by ocean water during 7640±60 $^{\sim}$ 8435±155 yr BP. A total of 79 stable isotope samples were collected in a 5.5-cm section from the oldest part of the shell, giving δ^{18} O range of -6.03% $^{\sim}$ -1.33% and δ^{13} C range of -2.21% $^{\sim}$ -0.31% (VPDB). These δ^{18} O and δ^{13} C values illustrate that the oyster grew in a saline environment. Compared with the

 δ^{18} O profiles of modern oyster shells in Taiwan, the ancient oyster grew in a much warmer shoreline water environment. According to the studying section, the oyster reef had an elevation of 0 m at 8300 yr BP, and the Plancenta shell had 3-5 m a.s.l. at 7600 yr BP.

Key words: Taipei Basin, early-Mid Holocene, oyster shell, ¹⁴C dating, stable isotopes

G02 P04

Tracking the ¹⁴C bomb peak recorded in Arctica Islandica across the North Sea and Northeast Atlantic Ocean

Christiane Y¹, Christl M¹, Witbaard R², Wacker L¹, Hattendorf B³, Welte C^{1,4}, Synal H¹
¹ETH Zurich, Laboratory of Ion Beam Physics, Zurich, Switzerland, ²Royal Netherlands Institute for Sea Research, Texel, Netherlands, ³ETH Zurich, Trace Element and Microanalysis, Zurich, Switzerland, ⁴ETH Zurich, Biogeosciences, Zurich, Switzerland

Spatially resolved radiocarbon profiles were recorded using Laser Ablation AMS (LA-AMS) from six Arctica Islandica shells collected at different locations in the North Sea and Northern Norway. The profiles were combined with independently derived chronologies from counting the growth bands of the bivalves to reconstruct spatial and temporal differences in the marine 14 C bomb pulse. Shells were sampled from a range of water depths, i.e., 15 to 150 m, with growth rates varying between 3 and <0.1 mm/yr. For 14 C sampling, the shells were moved under the laser with a speed of 10-25 μ m/s with an integration time of 10 s. The recorded 14 C profiles were further integrated to reduce noise and scatter of the data resulting in a final sampling resolution between 1 and 10 yrs. Comparison of the LA-AMS derived data with graphite measurements from earlier studies was very good.

The ¹⁴C bomb peak was identified in all samples, but with different timing and amplitude compared to the modeled marine mixed layer (MMML) calibration curve. The maximum of the ¹⁴C signal in the shells correlates inversely with water depth, while the delay of the peak increases with greater water depth. Both observations consistently indicate a dampening of the atmospheric signal with water depth due to the increased influence of Atlantic deep waters. The presented profiles show the potential of LA-AMS to map the spatiotemporal variation of the marine bomb pulse, providing valuable information on local deviations from the MMML and constraining simulations of the marine bomb peak.

G02 P05

Radiocarbon in the ocean: ensuring high quality results

Hansman R¹, Key R², McNichol A¹, Sonnerup R³

¹Woods Hole Oceanographic Institution, Woods Hole, United States, ²Princeton University, Princeton, United States, ³University of Washington, Seattle, United States

Repeat open ocean radiocarbon measurements of dissolved inorganic carbon (DIC) have led to a better understanding of key ocean processes such as mixing, ventilation rates, air-sea gas exchange, and ocean biogeochemistry. Until recently, only a few laboratories had the ability to make the precise ¹⁴C analyses necessary to document ocean circulation and the oceanic uptake of anthropogenic CO₂, but technological advances have reduced sample size requirements, brought new methods online, and made it easier for more laboratories to collect and analyze DI¹⁴C in the ocean. However, as there are presently no recognized standards or reference materials for radiocarbon in seawater, it is critical to ensure the quality and data comparability of these measurements across laboratories and over time. To this end, a three-day virtual workshop sponsored by the Ocean Carbon & Biogeochemistry program was held in November 2021 to discuss best practices for the measurement, data handling, and reporting of carbon isotopes in the ocean. While the workshop included the analysis of both DI¹³C and DI¹⁴C, an immediate need for an inter-laboratory comparison exercise of radiocarbon in seawater DIC was determined. We will present a summary of the workshop discussion and outcomes, including imminent

plans for this DI¹⁴C inter-comparison, as well as work towards establishing reference materials for the community.

G02 P06

Long Term Time Series of Surface Water Dissolved Inorganic Carbon Isotopes from the Southern California Bight

<u>Hauksson N</u>¹, Griffin S¹, Xu X¹, Martinez H¹, Pedron S¹, Druffel E¹ *¹University Of California, Irvine, Irvine, United States*

The Southern California Bight is an oceanographically complex region in a Mediterranean climate, strong upwelling, and limited rainfall. The health of kelp forests and marine protected areas in these waters depend on the balance of waters from wind-driven upwelling, the California current, and the California counter-current. Water mass tracers, such as carbon isotopes, inform the movement of water masses in this region. We report dissolved inorganic carbon (DIC) Δ^{14} C and δ^{13} C values in seawater collected from the Newport Beach Pier in Orange County, California from 2011 to 2022. The Δ^{14} C values decrease over this period, consistent with depletion of the 14 C generated by thermonuclear weapons testing and dilution of 14 C-free CO₂ from fossil fuel combustion. We analyze the relationship of these isotopes with the environmental conditions during this time series.

G02 P07

The chronology of the sedimentation in the Danube abyssal fan records the major episodes of the late-Holocene Black Sea evolution

<u>Ilie M</u>^{1,2}, Sava T¹, Vespremeanu-Stroe A³, Duliu O², Cristea G⁴, Ion G⁵, Olteanu D^{1,3}, Haliuc A⁶, Manailescu C¹, Sava G¹

¹RoAMS Laboratory, Horia Hulubei National Institute For R&D In Physics And Nuclear Engineering (IFIN-HH), Magurele, Ilfov, Romania, ²University of Bucharest, Faculty of Physics, Magurele, Romania, ³GEODAR Research Center for Geomorphology, Geoarchaeology and Paleo-environments, Faculty of Geography, University of Bucharest, Bucharest, Romania, ⁴Department of Mass Spectrometry, Chromatography and Applied Physics, National Institute for Research and Development of Isotopic and Molecular Technologies, Cluj-Napoca, Romania, ⁵National Institute of Marine Geology and Geo-Ecology (GeoEcoMar), Bucharest, Romania, ⁶Romanian Academy, Institute of Speleology, Cluj-Napoca, Romania

The construction for the high-resolution Bayesian sedimentation model spanning the last 5500 years based on 25 AMS radiocarbon dated sediments of bulk organic matter (OM) sampled from the NW Black Sea anoxic waters of the continental slope is presented in this paperwork. The corrections for the ¹⁴C ages due to marine reservoir effect (MRE) and detritus organic carbon are correlated with exogenous information such as 210Pb dating, metallurgy pollution and human-induced soil erosion, highlighting the Danube influence on the geochemistry and chronology of the NW Black Sea sediments through the input of terrigenous organic matter.

The results show excellent agreement with some of the previous studies, supporting a total age offset for the bulk OM of 60 years as MRE and 580 years as detritus organic carbon influence. The revisited chronology pinpoints the first and second invasion of the coccolitho-phores Emiliania huxleyi at 2524 \pm 87 and 625 \pm 65 years cal. BP. The sedimentation rate shows an increase of about three times with the starting of the late Medieval, which corresponds to the highest observed sediment discharge of the Danube as are considered the last 500-300 years.

This type of high-resolution sedimentation model is an important step for constructing the carbon budget in bottom waters of variable oxygen concentration.

Organic carbon cycling in the deep ocean: Implications from radiocarbon

Kim M^{1,2,3}, Hwang J², Haghipour N^{3,4}, Eglinton T³

¹Kyungpook National University, Daegu, South Korea, ²School of Earth and Environmental Sciences/Research Institute of Oceanography, Seoul National University, Seoul, South Korea, ³Geological Institute, Swiss Federal Institute of Technology in Zürich (ETHZ), Zurich, Switzerland, ⁴Laboratory of Ion Beam Physics, ETH Zürich, Zurich, Switzerland

The transport of carbon from surface waters to the deep ocean via primary production and subsequent export of POC, known as the biological carbon pump, is a crucial process for sequestration of atmospheric CO₂. Large-scale sediment trap studies have advanced our understanding of material fluxes during vertical transit from surface to deep waters. However, despite the potential importance in the oceanic carbon cycle, the global feature of lateral supply of aged organic matter hosted on lithogenic particles derived from sediment resuspension has not been systematically examined. Here I summarize the results of previous studies that have insights on the lateral transport of aged organic matter: Amundsen Sea, East/Japan Sea, deep abyssal Pacific, and the Northwest Atlantic. Especially in Kim et al. (2020), we compiled concentrations and fluxes of lithogenic material in the ocean on a global-scale by using literature data of sediment trap studies to understand the contribution of resuspended sediment to sinking particulate matter. Examination of Δ^{14} C values of sinking POC revealed strong relationships with parameters that represent contribution of resuspended sediment. We then derive estimates for the contribution of aged POC from sediment resuspension to sinking POC based on these relationships and global lithogenic material flux data. Based on this relationship, and the global mean of lithogenic content of sinking particulate matter, we calculate that aged POC from sediment resuspension comprises 3~5 % of sinking POC intercepted by sediment traps.

G02_P09

Tracing bomb radiocarbon in sinking particulate organic carbon in the deep Sargasso Sea

<u>Schnepper C</u>¹, Pedrosa-Pamies R², Conte M², Gruber N¹, Haghipour N¹, Eglinton T¹

¹Geological Institute, ETH, Zürich, Switzerland, Marine Biological Laboratory, WHOI, Woods Hole, USA

The imprint of bomb radiocarbon on sinking particulate organic carbon (PO14C) intercepted by sediment traps, together with flux and compositional data, provides information about the origin and dynamics of oceanic particles (Hwang et al., 2010). Of particular interest is the question of whether the intercepted POC in the deep ocean stems from overlying primary production, i.e., as part of the "extrinsic" biological pump, or whether the POC additionally originates from advection and subsequent aggregation of resuspended sedimentary carbon originating from continental margins and other far-away sources ("intrinsic" flux). Measurements by Kim et al. (2020) revealed significant variability in PO14C, however the processes driving this variability remain poorly understood. To quantify the intra- and inter-annual variability in PO14C, an in-depth study was initiated at the Ocean Flux Program site in the Sargasso Sea. This sediment trap time-series has generated (bi-)weekly samples and resulting information on particle fluxes and flux compositions at three water depths (500, 1500, 3200 m) since 1978. Preliminary data reveal intra-annual variations in PO 14 C with an amplitude of ca. 100 \infty. Seasonal Δ^{14} C variations are paralleled by shifts in the POC/Lithogenic ratio. This supports the notion that POC with high Δ^{14} C values, high POC/Lithogenic ratio and POC flux reflects supply of particles that originate via the "extrinsic" biological pump, while lower Δ^{14} C values and POC/Lithogenic ratios may reflect the "intrinsic" flux including resuspended sediments with higher lithogenic content emanating from continental margins. A nascent global PO14C database will allow to assess the broader relevance of our findings.

Age offsets between marine-derived lipid biomarkers, TOC, and foraminifera during cross shelf-slope lateral transport revealed by compound-specific radiocarbon dating

 $\underline{\text{Uchida M}}^1$, Eglinton T², Coppola L³, Gustafsson Ö⁴, Mollenhauer G⁵, Hayes J^{6,8}, Ahagon N⁷, Harada N⁷ ¹Earth System Division, National Institute For Environmental Studies, Tsukuba, Japan, ²Geological Institute, ETH, Zurich, Switzerland, ³Villefranche-sur-mer, Alpes Maritimes, France, ⁴Institute of Applied Environmental Research, Stockholm University, Stockholm, Sweden, ⁵Alfred Wegener Institute for Polar and Marine Research, Bremerhaven, Germany, ⁶National Ocean Sciences Accelerator Mass Spectrometry facility, Woods Hole Oceanographic Institution, Woods Hole, U.S.A., ⁷Japan Agency for Marine-Earth Science and Technology, Yokosuka, Japan, ⁸Deceased 3 February 2017,

Compound-specific radiocarbon analysis was performed on bulk sediments and different grain-size fractions (>250μm, 150-250μm, 63-150μm,38-63μm, <38μm) of shelf-slope surface sediments (0-2cm, outer shelf of 150m water depth and upper slope of 600m water depth) from Washington Margin to examine their relationships between hydrodynamic sorting of sediments and timescales and preservation of organic carbon. Here we obtained datasets of radiocarbon ages of alkenone, low molecular weight fatty acids (LMW-FAs, C₁₄, C₁₆, and C₁₈), high molecular weight fatty acids (HMW-FAs, C24, C26, and C28), total organic carbon and planktic foraminifera. These results were also discussed with previous reported lateral transport times of organic carbon (Bao et al., 2019). Age offsets between planktonic foraminifera, LMW-FAs, and alkenone in bulk phase sediments were significantly large in shelf compared with slope. On the other hand, age offsets between size fractions were not likely observed between LMW-FAs and alkenone except for large fractions(>250µm). Ages of LMW-FAs for both shelf and slope were younger than those of alkenone in all fractions including bulk-phase sediments. Moreover, we obtained radiocarbon ages of marine-derived compounds (alkenone, LMW-FAs), plant wax-derived compounds(HMW-FAs), planktic foraminifera, and total organic carbon from the last deglaciation- Holocene covered-marginal sediments from western North Pacific (1366m water depth, N41°) and Okhotsk Sea (1225m water depth, N44°). We discuss with palaeoceanographic interpretation on sedimentary records such as alkenone temperatures and ventilation.

G02_P11

Carbon isotopic constraints on the sources and preservation of organic compounds in sediment of the South China Sea

Wang $F^{1,2}$, Fu W^1 , Ren P^2 , Zhang H^1 , Luo C^1 , <u>Wang $X^{1,2}$ </u>
¹Ocean University Of China, Qingdao, China, ²Qingdao National Laboratory of Marine Science and Technology, Qingdao, China

Organic matter (OM) preservation in marine sediments is an important sink of carbon cycle and provides useful information on the sources, biodegradation and transformation of organic carbon during early diagenesis. The South China Sea (SCS), as one of the largest semi-enclosed marginal sea in the western North Pacific Ocean, receives large amount of organic carbon fluxes from river input and land erosion, especially in its northern shelf and slope regions. The burial of organic compounds in sediment of the SCS, however, has not been well studied. Here, we present the first data set of radiocarbon combined with stable carbon isotope measurements of total organic carbon (TOC), hydrolysable amino acids (THAA), total lipids, humic acids (HA), and acid-base insoluble OM in four sediment cores collected from the northern slope of the SCS. Distinct differences in both 13 C and 14 C values were found among these compound classes. The δ^{13} C values are more depleted for total lipids and HA (-23.1% to -30.2%) than the THAA and the acid-base insoluble OM (-15.3% to -20.6%). The D 14 C values ranged from -632% to -194% in TOC, -331% to -66% in THAA, -574% to -253% in total lipids, -569% to -168% in HA, and -

848‰ to -458‰ in acid-base insoluble OM, respectively. The acid-base insoluble OM has the oldest ¹⁴C ages (mean 7800 years) among the compound classes in the sediments. These distinct isotopic signatures provide new insight and reveal the selective decomposition, transformation and preservation mechanisms of OM derived from different sources in marine sediment.

G02 P12

Bomb-pulse radiocarbon record for a well-dated Caribbean coral core

Winkler S^{1,2}, Steier P², Carilli J³

¹Helmholtz-zentrum Dresden-Rossendorf, Dresden, Germany, ²Universität Wien, Wien, Austria, ³ University of California San Diego, La Jolla , USA

The radiocarbon bomb-pulse created by nuclear weapons testing in the 1950s and 1960s has created a massive spike of atmospheric 14 C, which has been used in the study of the global carbon cycle in many subsystems including the marine environment. Coral records of bomb-pulse era 14 C have been studied over the past decades to gain insight into the uptake and mixing of atmospheric CO₂ in the ocean. The 14 C level seen in surface waters is specific to the origin of the water masses and ocean-atmosphere exchange of CO₂.

We present results for radiocarbon levels in coral aragonite with yearly resolution for a coral core from Belize. The core has a well-established stratigraphy, stretching from the onset of atmospheric testing of thermonuclear devices to 2007. The core has previously been analyzed for and trace metal content in relation to environmental impacts and the bomb-pulse of ²³⁶U. We compare the results with existing results and model expectations for the Caribbean Sea. We further discuss the close agreement for the prior results in terms of feasibility and the achievable accuracy of cross-dating of cores using the rise of radiocarbon by the atmospheric bomb-pulse.

G03 Freshwater aquatic continuum

G03 01

Rock-leached organic carbon drives subsurface microbiomes

<u>Heinze B</u>^{1,2}, Schwab V², Trumbore S^{2,3}, Xu X³, Schroeter S², Chaudhari N^{1,4}, Küsel K^{1,4}

¹Aquatic Geomicrobiology, Institute of Biodiversity, Friedrich Schiller University, Jena, Germany, ²Department Biogeochemical Processes, Max-Planck-Institute for Biogeochemistry, Jena, Germany, ³Department of Earth System Science, University of California, Irvine, USA, ⁴German Center for Integrative Biodiversity Research (iDiv), Halle-Jena-Leipzig, Germany

More than 99% of global carbon is stored in sedimentary rocks, with an estimated 0.1 Gt CO $_2$ released every year due to weathering of rock organic carbon. However, little is known about the role of sedimentary rocks as source of energy and carbon in subsurface microbiomes. To study the extent to which rock-derived organic carbon is driving microbial activities in aquifers, we incubated crushed carbonate rocks rich in alkanes or aromatics with groundwaters under oxic and anoxic conditions. Rocks immediately leached aromatic and aliphatic substances into the groundwater, leading to a 50% increase in dissolved organic carbon (DOC). Interestingly, the Δ^{14} C-signature of the DOC was in the range of -322 to -447% – 'young' compared to the ¹⁴C-dead rock-kerogen, suggesting the addition of younger, fresher organic materials along surfaces on rock fractures exposed to groundwater. The ¹⁴C-content of membrane lipids extracted from the POC of the incubations indicated that most of their C (96-100% in anoxic and 44-77% in oxic groundwaters) were derived from the younger rock leachate (i.e. DOC) rather than ¹⁴C-free sedimentary organic matter. Replicate incubations amended with ¹³C-labelled inorganic C

showed little to no autotrophic C fixation over the time of incubation, excluding DIC as an important C source. Metagenomics identified potential bacterial degraders of rock-derived hydrocarbons within Desulfosporosinus and Dechloromonas (anoxic), and Rhodoferax, and Methyloversatilis (oxic). Our findings show that besides surface-derived or primarily produced C, organic C leached from sedimentary rocks can drive subsurface ecosystem metabolism, underlining the importance of microorganisms in geogenic C turnover.

G03_02

Time-series measurements of dissolved organic and inorganic radiocarbon from Switzerland's two largest lakes

<u>White M</u>¹, Mittelbach B¹, Rhyner T¹, Haghipour N¹, Blattmann T¹, Jacquin C², Schubert C³, Wessels M⁴, Dubois N^{1,3}, Eglinton T¹

¹Department of Earth Sciences, ETH Zürich, Zürich, Switzerland, ²Department of Process Engineering, Eawag, Dübendorf, Switzerland, ³Department Surface Waters Research & Management, Eawag, , Switzerland, ⁴Institut für Seenforschung der LUBW, Langenargen, Germany

The Radiocarbon Inventories of Switzerland (RICH) project aims to construct the first national-scale census of carbon across aquatic, terrestrial, and atmospheric reservoirs. Within the Swiss carbon cycle, inland waters play a crucial role with lakes integrating carbon from various sources within their catchment in addition to that fixed by local primary productivity. Here we present measurements of dissolved organic and inorganic radiocarbon from monthly water column samplings of Switzerland's two largest lakes: Lake Constance and Lake Geneva. Such high-resolution temporal measurements can uncover the nature and drivers of seasonal carbon dynamics in these well-studied lake ecosystems. Comparison of water column profiles from river proximal and river distal sites within each lake will constrain fluvial influence. In addition to isotope data, measurements of the optical properties of dissolved organic matter will aid in untangling sources and cycling of lake water DOC. Preliminary results show that the average radiocarbon signature of DIC in both lakes is depleted relative to atmospheric CO₂, suggesting a ca. 15% contribution from weathering of petrogenic (rock-derived) carbon.

G03 03

Sedimentary radiocarbon signatures reveal persistent input of soil organic matter into Lake Constance

<u>Mittelbach</u> B^1 , White M^1 , Rhyner T^1 , Blattmann T^1 , Haghipour N^1 , Wessels M^3 , Dubois N^2 , Eglinton T^1 ¹ETH Zurich, Zürich, Switzerland, ²Eawag, Dübendorf, Switzerland, ³Institut für Seenforschung der LUBW, Langenargen, Germany

Inland waters play a crucial role in the global carbon cycle, as the sequestration of organic carbon (OC) in lake sediments constitutes a sink of atmospheric CO_2 . Notably, the source of this sequestered OC has important implications for carbon cycling and climate. The burial of recently synthesized terrestrial and aquatic biospheric OC and of aged, soil-derived OC represents a drawdown of atmospheric CO_2 . In contrast, erosion, transport, and reburial of rock-derived OC exert no net effect on atmospheric CO_2 levels.

Radiocarbon can be used to differentiate between these different sources of OC and constrain proportions of recent, pre-aged, and fossil carbon. Moreover, the 20th-Century radiocarbon "bomb spike" offers the possibility to resolve organic matter turnover and transport on decadal timescales. We combine ^{14}C and stable $\delta^{13}\text{C}$ isotope signatures of bulk OC from sediment cores retrieved from perialpine Lake Constance to assess the nature and dynamics of OC accumulation over the last century. Information about OC source isotope signatures was gathered from soil and bedrock profiles in the catchment as well as sediment traps in the lake.

Our results show a muted, but distinct, bomb spike with $\Delta^{14}C$ values of bulk OC increasing from -250‰ to -100‰ in the early 1960s. A linear mixing model reveals that soil-derived, pre-aged carbon comprises the largest contributor to the bulk sedimentary OC pool. We attribute the presence of the bomb spike signal to inputs of aquatic biomass, arguing for a rapid incorporation of bomb carbon into the lake DIC pool.

G03 P01

Source apportionment of fugitive methane emissions using radiocarbon in a Scottish river.

Gulliver P1, Ascough P1, Murray C1, Taylor C1, Waldron S2

There is a long history of underground and open cast mining in Scotland. Closure of these mines results in local water table rebound as the mines slowly fill with water. This affects a number of Scottish river catchments and the escape of rebounding mine water provides a simple explanation for the presence of high methane concentrations in spring waters in such a catchment.

However, radiocarbon analysis of the dissolved methane in multiple springs of a Scottish catchment underlain by abandoned mine workings gave results of approximate 70 % modern, clearly showing that the methane is not solely geologically derived.

Radiocarbon analysis of the dissolved inorganic and organic carbon (DIC and DOC respectively) pools at the same sites showed that despite having lower % modern values then the dissolved methane, neither pool had a solely geological signature.

The source organic matter contributing to the majority of the dissolved methane and a significant proportion of the DIC and DOC comes from a much younger source and is biologically produced.

G03_P02

Bulk Organic Carbon Isotopes From the Santa Clara River During Rain Events

<u>Thomas K</u>¹, Hauksson N¹, Druffel E¹ ¹UC Irvine, Irvine, United States

Small mountainous rivers leading into the ocean, such as the Santa Clara River in Southern California, export considerable amounts of organic carbon to the ocean, and the magnitude and composition of which reaches the ocean is widely studied. With rainfall events in California mostly during winter, the composition and ^{14}C age of the organic carbon deposited by rivers is likely dependent on the magnitude of these events. In this study, we measured $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$ values of sedimentary organic carbon (SOC) and particulate organic carbon (POC) after rain events near the Santa Clara River. We present these analyses that show high variability of ^{14}C age and composition of organic material moved downstream with the amount of precipitation and runoff entering the river. This study contributes to our knowledge of organic carbon cycling from small mountainous rivers.

 $^{^1}$ University Of Glasgow, East Kilbride, United Kingdom, 2 University of Glasgow , Glasgow, United Kingdom

Anthropogenic perturbations change the quality and quantity of terrestrial carbon flux to the coastal ocean

<u>Wei B</u>^{1,2}, Mollenhauer G^{1,3,4}, Kusch S⁴, Hefter J¹, Grotheer H¹, Schefuß E⁴, Geibert W¹, Ransby D¹, Jia G^{1,6}

¹Alfred Wegener Institute, Helmholtz Centre for Polar and Marine Research, Bremerhaven, Germany, ²State Key
Laboratory of Marine Geology, Tongji University, Shanghai, China, ³Department of Geosciences, University of
Bremen, Bremen, Germany, ⁴MARUM-Center for Marine Environmental Sciences, University of Bremen, Bremen,
Germany, ⁵University of Cologne-Centre for Accelerator Mass Spectrometry, University of Cologne, Cologne,
Germany, ⁶Southern Marine Science and Engineering Guangdong Laboratory (Zhuhai), Zhuhai, China

Rivers export organic carbon (OC) sourced from their watersheds, offering an opportunity to assess impacts of climatic change and anthropogenic perturbations on the transfer of terrestrial OC to the ocean. Using ¹³C and ¹⁴C compositions of OC exported by the Pearl River during the Industrial Age, we show that anthropogenic activities primarily control the quantity and quality of terrestrial OC fluxes to the coastal ocean. Damming the river and accelerating coal consumption have led to increasing burial flux of petrogenic OC, a rather stable carbon fraction. Man-made ecosystem changes including deforestation, cropland extension, urbanization, and river management increased fresh terrestrial biospheric OC burial, additionally contributing to the long-term carbon sink. Our data help identifying the drivers of sustained change in terrestrial OC export and reveal that human activities substantially enhance the transfer of petrogenic OC and fresh biospheric OC to the coastal ocean, acting as an important sink for anthropogenic CO₂.

G04 The polar carbon cycle – radiocarbon in the cryosphere

G04 03

Quantifying fossil carbon utilization and release from eroding permafrost coastlines – results from an incubation experiment

Ruben M^{1,2}, Marchant H^{3,4}, Wietz M^{1,4}, Genz T¹, Mollenhauer G^{1,2,3}

¹Alfred-Wegener-Institut, Helmholtz-Zentrum für Polar- und Meeresforschung, Bremerhaven, Germany, ²Universität Bremen, Bremen, Germany, ³MARUM - Zentrum für Marine Umweltwissenschaften der Universität Bremen, Bremen, Germany, ⁴Max-Planck/Institute for Marine Microbiology, Bremen, Germany

The carbon-rich permafrost bounded coastlines of the Arctic represent around a third of the total global coastline. Rising sea-level and temperatures are increasing erosion of these coastlines by tens of meters annually. Coastal erosion results in the mobilization of large quantities of previously freeze-locked fossil organic carbon, which then may become degraded, potentially causing a positive feedback loop. Despite the tremendous impact the mobilized permafrost organic carbon may have on atmospheric greenhouse gas levels, the extent to which eroded fossil permafrost organic matter can be utilized by microbes in the Arctic Ocean is poorly constrained. Hence, previous studies, models, and eventually decisions of policy makers have relied largely on assumptions on the strength of this permafrost carbon feedback. To tackle this issue, we incubated permafrost soil from the Lena delta in natural coastal sea water collected in the Arctic Ocean in the eastern Kara Sea. Using a multi-disciplinary approach combining biogeochemical analyses (C, N, & P), DNA sequencing of bacterial communities and radiocarbon dating, we are now for the first time able to prove and quantify fossil carbon utilization and establish tentative links to microbial communities. Our data clearly indicate that fossil permafrost organic carbon is highly

bio-available to water column microorganisms, indicating that coastal permafrost erosion is a source of fossil carbon emissions, thus constituting a self-enhancing positive feedback loop of Arctic climate change.

G04_04

Radiocarbon age of organic matter of supraglacial systems of mountain glaciers using the example of the Garabashi Glacier (Northern Caucasus)

<u>Zazovskaya</u> E^1 , Mergelov N^1 , Dolgikh A^1 , Shishkov V^1 , Turchinskaya S^1 , Dobryanskiy A^1 , Goryachkin S^1 Institute of geography RAS, Moscow, Russian Federation

In modern terms, glaciers constitute a large terrestrial biome, unique in that they integrate autotrophicheterotrophic ecosystems with the most significant contribution from abiotic processes. This view of glacial systems makes it particularly interesting to consider how old carbon can accumulate in glaciers, what its sources are, and what contribution this carbon makes to the formation of ecosystems, including soils, during modern glacial melt. The object of our study is the Garabashi mountain-valley glacier (430 18' N, 42o 28'E, North Caucasus). Between 1997 and 2020 the glacier decreased by 27%. The content of organic carbon, nitrogen, their isotopic composition, and radiocarbon age (AMS) were determined in the cryoconite, moraines and soils. The resulting radiocarbon ages of the cryoconites range from 850 to 7500 ¹⁴C years BP. It is important to note that we didn't obtain a modern date for any sample of cryoconite. The age of soil organic matter on the 40 years old moraine is about 1000 ¹⁴C years BP, indicating an inherited carbon character. The age of organic matter from nearby moraines also varies widely, ranging from 1000 to 4000 ¹⁴C years BP. The obtained data on the age of cryoconites correlate with the results obtained earlier by different researchers for Arctic and Antarctic cryoconites. However, in general there is still no explanation for such an ancient age of cryoconite material. The main problem in the dating and interpretation of radiocarbon data obtained from the cryoconite material is the inability to confidently interpret the source of OM.

G04_05

Insight in high alpine soil carbon dynamics from compound-specific and soil fraction radiocarbon analysis on a glacier forefield chronosequence

Smittenberg R^{1,2}, Schwab V³, Gierga M², Bernasconi S², Hajdas I⁴, Wacker L⁴, Trumbore S^{3,5}, Xu X⁵

¹Department of Geological Sciences, Stockholm University, Stockholm, Sweden, ²ETH Zurich, Geological Inst., Zurich, Switzerland, ³Department Biogeochemical Processes, Max-Planck-Institute for Biogeochemistry, Jena, Germany, ⁴Laboratory of Ion Beam Physics, ETH Zurich, Zurich, Switzerland, ⁵Department of Earth System Science, University of California, Irvine, USA

The ecosystem carbon balance of high latitude and high altitude ecosystems are particularly sensitive to climate change, where increasing temperatures generally lead to a rise of the ecosystem carbon balance, but also increasing carbon turnover times. In this study, we investigated the carbon dynamics of the 150 year-long Damma Glacier forefield chronosequence, Switzerland. Specifically, we performed radiocarbon analysis of total soil carbon, supposedly 'stable' carbon pools (fine mineral-bound, and peroxide-resistant carbon), respired CO₂, dissolved soil organic carbon (DOC), hydrophobic leaf wax-derived alkanes, and microbial-derived fatty acids. Comparison of our results with the penetration of the radiocarbon bomb spike and the increase of soil and ecosystem carbon over the chronosequence allowed us to make the following inferences: (i) A small but persistent contribution of ancient carbon is present in forefield, which is particularly visible in the hydrophobic leaf wax ¹⁴C data. From this we conclude that this old carbon pool is at least in part a remnant of ancient soil carbon from a previous

warm and glacier-free period, besides a potential contribution of fossil-fuel derived black carbon deposition. (ii) There is a significant portion of soil carbon with a decadal-scale carbon turnover rate, and (iii) mineral-bound carbon clearly has a lower turnover time. (iv) Microbial lipids, soil CO₂ and DOC ¹⁴C content reflect different carbon sources: in younger soils, relatively low ¹⁴C contents indicate a higher relative contribution of ancient carbon decomposition, while in older soils this signal is swamped by decomposition freshly photosynthesized organic matter.

G04₀₆

Export of pre-aged carbon to the Bay of Biscay at the end of the LGM

<u>Queiroz Alves E</u>¹, Wang Y², Hefter J¹, Grotheer H¹, Zonneveld K³, Mollenhauer G^{1,3}

¹Alfred Wegener Institute (AWI), Bremerhaven, Germany, ²NORCE Norwegian Research Centre, Bergen, Norway,
³MARUM-Center for Marine Environmental Sciences, University of Bremen, Bremen, Germany

The last deglaciation was the most recent relatively well-documented period of pronounced and fast climate warming. As such, it holds important information for our understanding of the climate system. Notably, the mechanisms leading to rapid atmospheric CO₂ changes during this period are incompletely defined. While research into terrestrial organic carbon reservoirs has been instrumental in exploring the possible sources of atmospheric CO₂ during these periods of rapid change, the underlying processes are not yet fully understood. Here we investigate the mobilization of organic carbon to the Bay of Biscay at the mouth of the English Channel, where an enhanced terrigenous input has been reported for the last glacial-interglacial transition. We have established an accurate and robust chronological framework for this deposition, showing enhanced rates of sediment accumulation from approximately 20.2 to 15.8 cal ky BP. The compound-specific radiocarbon dating of n-alkanoic acids isolated from the sedimentary archive disclosed the deposition of pre-aged carbon with pre-deposition ages of up to ca. 30,000 yr, constituting the first direct evidence for the presence of ancient organic matter at the core location. In the light of what has been reported for other regions with present or past permafrost conditions on land, this result points to the possibility of permafrost and/or petrogenic carbon export to the ocean, caused by processes that likely furthered the observed changes in atmospheric CO₂.

G04 P01

Exploiting radiocarbon to investigate the fate of permafrost organic matter supply to the Canadian Beaufort Sea

<u>Bröder L</u>^{1,2}, Lattaud J¹, Juhls B³, Eulenburg A³, Priest T⁴, Fritz M³, Matsuoka A⁵, Pellerin A⁶, Bossé-Demers T⁷, Rudbäck D⁸, O'Regan M⁸, Whalen D⁹, Haghipour N¹, Eglinton T¹, Overduin P³, Vonk J²

¹Swiss Federal Institute of Technology, Zürich, Switzerland, ²Vrije Universiteit, Amsterdam, The Netherlands, ³Alfred Wegener Institute Helmholtz Centre for Polar and Marine Research, Potsdam, Germany, ⁴Max-Planck-Institute for Marine Microbiology, Bremen, Germany, ⁵University of New Hampshire, Durham, USA, ⁶Université du Québec à Rimouski, Rimouski, Canada, ⁷Université Laval, Québec City, Canada, ⁸Stockholm University, Stockholm, Sweden, ⁹Natural Resources Canada, Halifax, Canada

The Canadian Beaufort Sea receives large quantities of sediment, organic carbon and nutrients from rapid coastal erosion and permafrost thaw. In addition, the Mackenzie River, the largest North American Arctic river, discharges great amounts of freshwater, dissolved solids and suspended sediments to the Beaufort Sea. Current changes in these fluxes in response to the warming climate have uncertain consequences for the carbon budget on the shelf and in the deep ocean. To investigate the movement and transformation of organic matter along the land-ocean continuum, we collected water and surface sediment samples across the Beaufort Sea during fall 2021. Sampling locations span from shallow, coastal, sites with water depths ≤ 20 m, to shelf-break and deep-water settings on the continental slope (water depths of ≥1000 m). For this study, we use radiocarbon analyses of dissolved inorganic (DIC),

dissolved organic (DOC) and particulate organic carbon (POC) for surface and bottom waters, as well as surface sediments, in order to compare, contrast and constrain the relative source contributions and ages of these different forms of carbon. Our results will help to better understand the fate of permafrost organic matter in the marine environment and to ultimately improve assessments of the Canadian Beaufort Sea shelf as a carbon source or sink and its potential trajectory with ongoing environmental changes.

G04 P02

Radiocarbon age of plant remains in massive ground ice of the Barrow Permafrost Tunnel, Alaska

Iwahana G¹, Uchida M², Mantoku K², Kobayashi T²

¹University Of Alaska Fairbanks, Fairbanks, United States, ²National Institute for Environmental Studies, Tsukuba, Japan

Permafrost provides paleoenvironmental information from organic matter, gas, water, and sediment contents captured in the perennially frozen ground. Syngenetic ice wedges that grow laterally in frost cracks of the permafrost sediments are expected to be an alternative paleoenvironmental proxy where information from nearby glacier/ice sheet core or lake sediments is unavailable. Massive ground ice found in the Barrow Permafrost Tunnel at the depth range between 3 and 7 m from the surface has been interpreted as ice-wedge and used to reconstruct environmental changes in the early Holocene. To better understand the development of the massive ground ice, we conducted Radiocarbon dating of plant remains and stable isotope analysis of the ice along with two profiles. Combining with previous results, we mapped the radiocarbon age distribution within the massive ground ice. The age distribution from our dense sampling showed two ice regions with similar ages centering 11,200 and 10,200 yBP divided by a relatively narrow region of intermediate age along with the 5-m profile parallel to the tunnel long-axis. From the other sampling profile that is perpendicular to the tunnel, the youngest age (8,451 yBP) was found from the NW end of the profile. The water stable isotopes from the profile perpendicular to the tunnel showed the lowest anomaly at the SE end, which contradicts the ice-wedge origin assumption. Our results indicate the existence of unknown processes in the massive ice growth or large randomness of cracking locations during ice-wedge development.

G04_P03

Multiple radiocarbon dating of POC, DOC, DIC, and plant remains in ground ice of Siberian permafrost

Minami M¹. Sato R¹. Iwahana G². Hiyama T¹

¹Nagoya University, Nagoya, Japan, ²University of Alaska Fairbanks, Fairbanks, USA

For understanding paleoclimate changes and hydrological environmental changes preserved in ground ice, it is important to determine the chronology of the ice formation. To examine which carbon fraction in ground ice shows the most true formation age, we performed multiple ^{14}C dating of some carbon fractions in ground ice: particulate organic carbon (POC), dissolved organic carbon (DOC), dissolved inorganic carbon (DIC), and plant remains. The ground ice samples used are permafrost outcrops collected at Syrdakh and Churapcha, near the city of Yakutsk, Russia. The thawing samples were filtered through a 0.7-µm quartz filter, and the filtrate was ultrafiltered through a 10,000 MWCO (Molecular Weight Cut-Off) followed by a 3,000 MWCO (Vivaspin Turbo, Sartorius). The ^{14}C ages of POC in the ground ice samples were 40–27 kyr BP, which is about 10,000 years older than the plant age of 24–22 kyr BP, while the ^{14}C ages of DOC varied with molecular size: 28–19 kyr BP for the 0.7 µm–10,000 MW and 10,000–3,000 MW fractions, and a younger age of 18–12 kyr BP for the <3000 MW, which is similar to ^{14}C ages for DIC.

We will discuss the result of the multiple ¹⁴C dating to determine which carbon fraction in the ground ice is most suitable for accurate dating of the ice formation.

G05 Terrestrial carbon dynamics

G05 02

Mean transit time of carbon estimated through ¹⁴CO₂ measurements in a vertical profile in the central Amazon.

<u>Chanca I</u>^{1,2}, Levin I³, Sierra C^{1,4}, Hammer S³, Trumbore S¹, Macario K², Lavric J^{1,5}, Araújo A⁶

¹Max Planck Institute for Biogeochemistry, Jena, Germany, ²Radiocarbon Laboratory - Universidade Federal Fluminense, Niterói, Brazil, ³Institut für Umweltphysik - Universität Heidelberg, Heidelberg, Germany, ⁴Swedish University of Agricultural Sciences, Uppsala, Sweden, ⁵Acoem Australasia, Jena, Germany, ⁶Empresa Brasileira de Pesquisa Agropecuária (Embrapa), Belém, Brazil

The Amazon rainforest is important in the global carbon balance, but there is still a lack of information regarding the time scales of carbon cycling in these forests. One useful timescale metric is the transit time of carbon, defined as the age of carbon exiting the ecosystem, mostly as respiration. To estimate the mean transit time (TT) of ecosystem respiration (ER), we took advantage of the large variations in CO_2 in the atmosphere below the forest canopy to estimate the radiocarbon signature of mean ER (Δ^{14} C{ER}) using the Miller-Tans model. We collected samples of air in a vertical profile in 2019 during the dry season at the ATTO (Amazon Tall Tower Observatory) site, in the central Amazon, ca. 150km NE of Manaus, Brazil. Air samples were collected in a diurnal cycle from two heights below the canopy (4m and 24m) and, for the background, above the canopy at 79m. The Miller-Tans model estimated Δ^{14} C{ER} = (32.0 ± 7.4)‰. An estimate of the mean TT is derived from comparing this value with the atmospheric Δ^{14} CO₂ records that show values of 32-34‰ in the years 2012-2013. Therefore, the mean TT for the ATTO site is estimated in 6 to 7 years with an uncertainty of 2 years. This result is consistent with other TT estimations obtained through simulations and compartmental models of tropical rainforest.

G05_03

Global warming mitigation capacity of plant lines assessed by ¹³C and ¹⁴C. The case of rhizodeposition efficiency of pearl millet.

HATTÉ C^{1,2}, SITOR NDOUR P^{3,4}, ACHOUAK W⁵, HEULIN T⁵, COURNAC L³

¹LSCE - CEA, Gif-sur-Yvette, France, ²Silesian University of Technology, Gliwice, Poland, ³Eco&Sols, Montpellier, France, ⁴Mohammed VI Polytechnic University, Ben Guerir, Morocco, ⁵LEMIRE BIAM, 13115 Saint-Paul-Lez-Durance, France

In the context of climate change, a new challenge for agriculture is to sequester more carbon in the soil to mitigate CO_2 increase in the atmosphere. Then, plant breeding for root traits (architecture and root exudation) could be an original strategy to enhance SOC sequestration.

In order to evaluate how it may contribute to the carbon sequestration objective, the carbon input into the soil should be determined. However, due to the heterogeneous nature of the soil and particularly infield conditions, conventional carbon measurement methods could not answer this question in short-term experiments such as those used for screening plant genotypes. The change in carbon concentration would remain below the natural variability. Furthermore, the so-called priming effect that contributes to extra mineralization of molecules derived from soil old carbon, has also to be evaluated. As an alternative method, we've measured carbon deposition in the pearl millet (Pennisetum glaucum) rhizosphere using carbon isotopes (13 C and 14 C) that are much less sensitive to soil heterogeneity. This is furthermore indicative of the age of the primed carbon. Four pearl millet lines were tested and

associated soil was analyzed after only one month of growth. Using a conceptual model, we evidenced a priming effect for all pearl millet lines. Importantly, the priming effect amplitude was higher for the small rhizosheath (low-aggregation) line than for the large rhizosheath (high-aggregation) ones, indicating a better carbon sequestration potential of the latter.

G05 04

Evaluating the new generation of soil organic carbon models using radiocarbon

Brunmayr A¹, Graven H¹, Moreno Duborgel M^{2,3}

¹Imperial College London, London, United Kingdom, ²Eidg. Forschungsanstalt WSL, Birmensdorf, Switzerland, ³ETH Zurich, Zurich, Switzerland

In recent decades, soil carbon models have moved away from using ill-defined conceptual carbon pools and instead started using operationally defined pools which can be individually extracted from soil samples and measured for their carbon and ¹⁴C content. One major advantage of simulating measurable pools is the ability of directly assimilating not only bulk soil data but also pool-specific carbon and ¹⁴C measurements, which greatly aids with model calibration and validation. However, only a handful of these new-generation models with measurable pools has been tested with ¹⁴C data from field samples. As the dataset of ¹⁴C measurements for bulk soil and individual soil pools is expanding ever more rapidly, we should utilize the power of ¹⁴C as a carbon cycle tracer and take full advantage of pool-specific ¹⁴C data when calibrating new-generation models. In this study, we evaluate various new-generation models (including Millennial, MEND, SOMic, ...) with ¹⁴C measurements for individual soil pools across diverse geoclimatic regions. While some models with measurable pools perform rather well, a few seem to strongly underestimate the time scales of carbon storage in soils and thus produce unrealistic ¹⁴C values which miss the datapoints by large margins. These results raise questions about the validity of these models' carbon turnover predictions and demonstrate the importance of verifying the consistency of model output with measured ¹⁴C data.

G05_05

Capturing Radiocarbon Distributions in Soil Organic Matter Using a Thermal Fractionation Approach

Stoner S^{1,2}, Sierra C^{1,3}, Doetterl S², Trumbore S¹

¹Max Planck Insitute For Biogeochemistry, Jena, Germany, ²ETH Zürich USYS, Zürich, Switzerland, ³Swedish University of Agricultural Sciences, , Sweden

Understanding soil organic matter (SOM) dynamics requires knowledge and quantification of diverse soil processes and characteristics of SOM. Radiocarbon in SOM aggregates into a single metric a large variety soil carbon (C) processes, resulting in a C pool with a range of ages reflecting the drivers of C turnover. However, a mean bulk soil radiocarbon value often lacks crucial details. Here, we present techniques for predicting and measuring radiocarbon distributions in soils. Compartmental models constrained by radiocarbon can predict the distribution of ¹⁴C at any point in time as a model output, highlighting the controls of fast and slow cycling C, and the effect of the "bomb spike" on mean soil ¹⁴C. In addition, new research on thermal fractionation of SOM, through heating soil at a constant rate and using temperature of decomposition as a proxy for activation energy, allows for the rapid collection of multiple C fractions along a meaningful gradient of stability. The resulting profile of CO₂ release and ¹⁴C concentration as a function of temperature can be transformed into a mass-weighted distribution of radiocarbon within a soil sample. We present these novel methods, compare their ability to estimate ¹⁴C distribution, and present case studies of their application. Applying radiocarbon through a combination

of simple but powerful models and high-throughput laboratory techniques will better constrain our ability to detect and understand diverse controls of carbon stabilization in complex systems.

G05 06

The inbuilt age of charcoal fragments in a sand-bed stream, Macdonald River, NSW, Australia

<u>Wood R</u>¹, King F³, Chen Q⁴, Esmany R¹, Schneider L¹, Dotte-Sarout E⁵, Fryirs K⁶, Fallon S¹, Gillespie R¹, Blong R⁷

¹University Of Oxford, Oxford, United Kingdom, ²Australian National University, Canberra, Australia, ³La Trobe University, Melbourne, Australia, ⁴Independent scholar, Independent scholar, Independent scholar, Independent scholar, ⁵University of Western Australia, Perth, Australia, ⁶Macquarie University, Sydney, Australia, ⁷Risk Frontiers, Sydney, Australia

Charcoal in fluvial and lacustrine environments can have a considerable inbuilt age, confounding efforts to approximate sedimentation age with radiocarbon dating. Carbon is sequestered in tree rings during growth, and may be hundreds of years older than the charring event ('old wood effect'). Charcoal is then transported and stored at various positions along hillslopes before reaching the valley floor where it may be stored in floodplains and other riverine landforms.

To examine the extent of the inbuilt age, we redated charcoal that was first dated using conventional methods by Blong and Gillespie (1978) in the Macdonald River, NSW, Australia. In that study, charcoal was sieved and four size fractions of bulk charcoal dated. The smaller fragments had a greater age than the larger fragments.

Here, 31 individual charcoal fragments from the 2-3 mm size fraction, (SUA-618, 1050-670 calBP) were dated. Only two date to the time of collection, and the oldest was 1700-1590 calBP. It is clear that large numbers of individual charcoal fragments need to be dated to obtain the correct age of deposition when radiocarbon dating charcoal from fluvial and lacustrine environments. To assess whether it is possible to select charcoal with the least inbuilt age prior to dating, we characterized the taphonomic and dendrological features of the dated charcoal fragments. The impact of inbuilt age on Bayesian modeling in OxCal was assessed, and a revised Charcoal Outlier model is proposed for dating charcoal from lacustrine and fluvial settings.

Blong and Gillespie, 1978, Nature, 271, 739-741

G05 P01

What are soil microbes eating? Novel methods for determining the age of microbially utilized soil carbon

<u>Finstad K</u>¹, Nuccio E¹, Grant K¹, Broek T², Pett-Ridge J¹, McFarlane K¹

¹Lawrence Livermore National Laboratory, Livermore, United States, ²Woods Hole Oceanographic Institution, Falmouth, 02543

Soils represent a large component of the global C cycle, storing more C than plants and the atmosphere combined. Microbial processing of organic matter in soil is a main driver of soil C cycling, yet we lack robust methods for accurately identifying the age of C respired by microbial communities, hindering our ability to predict how disturbance or climate change affects soil C persistence. The most common method for identifying the age of microbially respired C is through laboratory incubations where homogenized soils are incubated in sealed jars until sufficient CO_2 has accumulated for ^{14}C measurement. However, comparison of lab incubation $^{14}CO_2$ to in situ field collections suggests that soil sampling and processing can cause incubated microbes to respire older C than they would under natural conditions. We therefore seek to develop a method to determine the age of microbially utilized C more accurately, such as the extraction and dating of microbial biomass. We find that in general, the $\Delta^{14}C$ of CO_2 from lab incubations in surface soils is indistinguishable from the $\Delta^{14}C$ of chloroform extracted microbial biomass, but the values diverge at depth, with the lab incubations often producing depleted

values relative to the extracted biomass. These findings corroborate previous suspicions that laboratory incubations may bias the results and falsely suggest the consumption of older soil C than occurs under natural conditions. Future work is being conducted to refine this method and investigate the utility of ¹⁴C measurements on nucleic acids extracted from soil.

G05 P02

Divergence of compound class persistence in a California grassland soil

Grant K¹, Repasch M^{1,2}, Finstad K¹, Broek T^{1,3}, McFarlane K¹

¹Lawrence Livermore National Laboratory, Livermore, United States, ²Institute of Arctic and Alpine Research, University of Colorado, Boulder, Boulder, United States, ³National Ocean Sciences Accelerator Mass Spectrometry (NOSAMS) Facility, Woods Hole Oceanographic Institution, Woods Hole, United States

Soils store more carbon than the atmosphere and vegetation combined. Soil organic carbon (SOC) is composed of a complex mixture of plant and microbial derived organic compounds with distinct cycling timescales. The residence time of individual SOC components depends on a combination of factors, including compound reactivity, mineral association, and climate conditions, making it difficult to accurately quantify. However, radiocarbon analysis of specific compound classes can disentangle the mixture of SOC ages within a single sample. We modified methods to measure the Δ^{14} C of distinct compound classes (lipids, amino acids, and carbohydrates) from bulk and physically fractionated grassland soils. Additionally, we measured the Δ^{14} C of the water-extractable fraction (WEOC) and the residual acid-insoluble fraction. Samples were collected from a grassland meadow in Hopland, CA which receives 940 mm yr-1 of rainfall and is dominated by Avena barbata. We sampled a 1m soil pit at depth intervals (0-10, 10-20, 20-50, 50-100 m) to study changes in SOC persistence with depth. We used solid state 13 C-NMR to measure the relative abundance of the target compound classes in soil. The $\Delta 14$ C of bulk soil decreased from +28±6‰ at 0-10cm to -495±23‰ at the 50-100cm depth interval. The clay fraction ($<63\mu$ m) had higher Δ^{14} C values than both the bulk (<2mm) and sand (<2mm to $>63\mu$ m) fractions. WEOC Δ^{14} C values ranged from modern to about -45.6%. Δ^{14} C values of total extracted lipids ranged from 36±4‰ at the surface to -215±3‰ at depth. Quantifying the age distribution of distinct compound classes gives insight into SOC persistence.

G05 P03

Towards a comprehensive understanding of the drivers of the reservoir effect (dead carbon fraction) in stalagmites - a modelling approach

Lechleitner F¹, Day C², Welte C³, Fohlmeister J⁴, Stoll H⁵

¹Department of Chemistry, Biochemistry and Pharmaceutical Sciences and Oeschger Centre for Climate Change Research, University of Bern, Bern, Switzerland, ²Department of Earth Sciences, University of Oxford, Oxford, UK, ³Department of Earth Sciences and Laboratory of Ion Beam Physics, ETH Zürich, Zürich, Switzerland, ⁴Federal Office for Radiation Protection, Berlin, Germany, ⁵Department of Earth Sciences, ETH Zürich, Zürich, Switzerland

A growing number of stalagmite ¹⁴C records have been generated over the past decades, from multiple climatic states, ecosystem types and lithologies. A number of processes have been identified that influence speleothem ¹⁴C activities, leading to deviations from the atmospheric value (the reservoir effect). However, it has so far been difficult to extract globally relevant relationships that describe the connection between environmental conditions and stalagmite ¹⁴C values.

Using numerical forward modelling and published datasets, we present a suite of sensitivity analyses that test the relative importance of different processes and carbon pools on the stalagmite reservoir effect. To evaluate model performance, we compare the model output of key chemical parameters in dripwaters relating to stalagmite 14 C (δ^{13} C, pH, Ca²+) from two independent geochemical models:

PHREEQC-based CaveCalc (Owen et al., 2018) and a simpler calcite dissolution model (Fohlmeister et al., 2011).

Subsequenly, we test the sensitivity of the stalagmite reservoir effect to processes that depend on climate, ecosystem and lithological parameters above the cave. In particular we focus on the impacts of: i) a large pre-aged soil OM reservoir, ii) host rock dissolution under a suite of conditions from open to closed system, iii) pyrite oxidation. These processes have been suggested to play a significant role, particularly in stalagmites that have very high reservoir effect values (> 50%). Our results help to identify whether observed variations in stalagmite reservoir effect can be realistically explained by such processes, and contribute to a global understanding of the factors influencing the stalagmite reservoir effect.

G05 P04

Old-growth forest and adjacent prairie show contrasting soil carbon properties not linked to above ground litter input and chemistry

McFarlane K¹, Mambelli S², Porras R³, Wiedemeier D⁴, Schmidt M⁴, Dawson T², Torn M^{2,3}

¹Lawrence Livermore National Laboratory, Livermore, United States, ²University of California - Berkeley, Berkeley, United States, ³Lawrence Berkeley National Laboratory, Berkeley, United States, ⁴University of Zurich, Zurich, Switzerland

Old-growth coast redwood (Seguoia sempervirens) forests store more carbon in aboveground biomass per area than any ecosystem, in trees that are among the oldest, largest, and most productive plant species on earth. Moreover, redwood litter contains high levels of aromatic compounds and is relatively resistant to decay. However, little is known about belowground carbon storage or turnover time in these forests. We compared soil carbon storage, distribution, chemical composition, and age in an oldgrowth redwood forest and adjacent prairie with comparatively lower productivity and more decomposable litter. Contrary to what the relative litter quality would suggest, total soil carbon stocks to 110 cm depth were higher in prairie (350 Mg C ha-1) than in redwood (277 Mg C ha-1) even with the forest O-horizon included, although differences were limited to the top 50 cm. In addition, radiocarbon values reflected shorter turnover times for bulk soil and light density fractions in redwood than prairie throughout the sampled profile. Higher amounts of pyrogenic carbon and a higher degree of SOM stabilization, as indicated by light density fraction carbon molecular characterization with ¹³C-NMR spectroscopy, appear to be instrumental in explaining the larger soil carbon stocks and longer turnover times in prairie, while differences in fine-root carbon inputs likely contribute to comparatively shorter turnover times in redwood. We conclude that at these sites fire residues, root inputs, and soil properties influence soil carbon dynamics to a greater degree than the properties of aboveground litter.

G05_P05

Species-definite AMS ¹⁴C dating, ²¹⁰Pb and ¹³⁷Cs dating on a peat core from Jinchuan Mire, NE China

<u>Misra S</u>¹, Kashyap S¹, Chou C¹, Chang T¹, Li H¹
¹National Taiwan University, Taipei, Taiwan

AMS ¹⁴C, ²¹⁰Pb and ¹³⁷Cs dating have been done on a 92-cm peat core from Jinchuan Mire in NE China, showing sedimentation rates ranging from 0.066 to 0.54 cm/year over the last 1050 years. Carex lehmanii (a plant of the genus Sedge in the Cyperaceae family) has been chosen for AMS ¹⁴C dating. A total of 110 AMS ¹⁴C dates on Carex from 85 horizons were yielded, in which 16 samples were treated by ABA treatment. The high resolution ¹⁴C dates show significantly variations throughout the core, indicating serious old carbon influence. The comparisons among the ¹⁴C, ²¹⁰Pb and ¹³⁷Cs dating results show mobilization problem of ²¹⁰Pb and ¹³⁷Cs. The detailed dating results exhibit that peat accumulation

was 0.102, 0.54 (human impact) and 0.066 cm/yr during periods of 2018~1964, 1964~1950 and 1950~900 CE, respectively. Furthermore, the ABA treated Carex is generally older than the non-ABA treated Carex in the same depth, except samples below 85 cm depth, implying that old carbon influence between 85 and 92 cm was negligible. The decomposition of the peat plants in deeper layers which is related to plant species and climatic conditions and groundwater table which is related to climatic conditions and drilling sites may cause the variation of old carbon (in the dissolved CO₂ uptaken by Carex) influence on the Carex ¹⁴C ages. The Carex AMS ¹⁴C dates will help us not only to refine the previous age model of JCA but also to understand hydro-climatic information recorded by JCA core sediments.

G05 P06

Multi-Pool Monitoring of Organic and Inorganic Carbon at Milandre Cave, Switzerland – Implications for Future Paleoecosystem Proxies.

<u>Rowan S</u>¹, Luetscher M², Szidat S¹, Laemmel T¹, Kost O³, Lechleitner F¹

¹University Of Bern, Bern, Switzerland, ²Swiss Institute for Speleology and Karst Studies, La Chaux-de-Fonds, Switzerland, ³ETH Zurich, Zurich, Switzerland

The organic matter (OM) fraction of speleothems, typically comprising 0.01-0.3% of the total carbon (Blyth et al., 2016), has the potential to offer information about past ecosystems. The provenances of speleothem OM are not well understood, though are speculated to be dominated by contributions from overlying vegetation and soil. Other potential sources include microbial activity within the karst system, cave fauna, and fossil carbon sourced from the carbonate (Blyth et al., 2016). The isotopic characterisation (δ^{13} C and 14 C) of stalagmite OM may give information about past ecological and climatic state of the surrounding region (Blyth et al., 2016).

Here we present the first results of a monitoring study of the organic and inorganic carbon fluxes in Milandre cave (Switzerland), whereby the main carbon source reservoirs will be monitored for two years. Our preliminary data includes 1) atmospheric, cave, soil, and well CO^2 $\delta^{13}C$ and ^{14}C , and 2) cave drip water dissolved inorganic carbon (DIC) $\delta^{13}C$, collected before significant degassing could take place. The cave gas samples are more depleted in ^{14}C than soil and well gas samples. This suggests either an additional fossil reservoir of CO^2 contributing to the cave air or substantial influence from degassing of carbonate-derived CO_2 from drips in the cave. The DIC $\delta^{13}C$ is isotopically light, implying that the cave is an open system with a substantial contribution of biologically respired CO_2 feeding carbonate growth. This information will be used to constrain the source of speleothem OC and its suitability as a proxy.

Isotopic signatures of fine organic aerosol in the deciduous forest and photosynthetic isotopic discrimination: Insights from compound-specific radiocarbon analysis

<u>Uchida M</u>¹, Kumata H, Kondo M^{3,4}, Chikaraishi Y⁵, Murayama S⁶, Mantoku K¹, Kobayashi T¹, Kawamura K⁵, Saigusa N¹, Koizumi H^{3,8}, Shibata Y⁹

¹Earth System Division, National Institute For Environmental Studies, Tsukuba, Japan, ²Faculty of Life Science, Tokyo University of Pharmacy and Life Science, , Japan, ³River Basin Research Center, Gifu University, , Japan, ⁴Now at Health and Environmental Risk Division, National Institute For Environmental Studies, Tsukuba, Japan, ⁵ Institute of Low Temperature Science, Hokkaido University, Sapporo, Japan, ⁶National Institute of Advanced Industrial Science and Technology, Tsukuba, Japan, ⁷River Basin Research Center, Gifu University, , Japan, ⁸Now at Waseda University, , Japan, ⁹Tokyo University of Science, , Japan

Organic aerosols including secondary organic aerosols have serious impacts on the Earth's climate system directly by scattering and absorbing solar radiation and indirectly by acting as cloud condensation nuclei. Forests release large amounts of volatile organic compounds into the atmosphere. However, the sources and fate of organic compounds of biogenic origin in a forest ecosystem are not yet well understood. This knowledge is also of importance to well understanding accurate carbon isotopic discrimination (Δ) by photosynthesis at the ecosystem scale for modeling terrestrial uptake of carbon dioxide. To understand the origin and fate of biogenic organic compounds in forest aerosol, we measured stable carbon isotopic ratios (δ^{13} C) and radiocarbon (14 C) contents of n-fatty acids, n-alkanes, and total organic carbon in forest aerosols, soil, and plant material as well as atmospheric CO₂. Fine aerosol samples (PM₁₀) were collected at few-week intervals from August 2003 to November 2004 during the growing season at Takayama Experimental site ($36^{\circ}80'$ N, $137^{\circ}26'$ E, 1420m a.s.l.) in a cooltemperate deciduous forest in Japan. Based on the results obtained, we discuss the sources and turnover time, and temporal variations of forest organic molecules as well as estimated plant wax-based photosynthetic isotopic discrimination(Δ).

G05_P08

Peatland initiation and carbon accumulation history during the Holocene in Xinjiang, China

Zhao H^{1,2,3}, Zhou W^{1,2,4,5,6,7}, Cheng P^{1,2,5,6}, Du H^{1,2}, Xian F^{1,2,4}, Shu P^{1,2}

¹The State Key Laboratory of Loess and Quaternary Geology, Institute of Earth Environment, Chinese Academy of Sciences, Xi'an 710061, China, Xi'an, China, ²Shaanxi Key Laboratory of Accelerator Mass Spectrometry Technology and Application, Xi'an, 710061, China, Xi'an, China, ³Xi'an Institute for Innovative Earth Environment Research, Xi'an, China, ⁴CAS Center for Excellence in Quaternary Science and Global Change, , China, ⁵Xi'an Jiaotong University, Xi'an, China, ⁶Open Studio for Oceanic-Continental Climate and Environment Changes, Pilot National Laboratory for Marine Science and Technology (Qingdao), Qingdao, China, ⁷Beijing Normal University, interdisciplinary Research Center of Earth Sciences, Beijing, China

Peatland ecosystems are important terrestrial carbon reservoirs, understanding the responses of carbon dynamics to climate change will provide useful insights into projecting the fate of peatland carbon in the future. Most studies about the carbon dynamics of peatlands were focused on boreal and tropical peatlands now. However, there are rare data about carbon dynamics in the Xinjiang region, which is sensitive to climate change. Here, we studied the carbon accumulation histories during the Holocene by measuring the radiocarbon ages, total organic carbon(TOC), and bulk dry density(BDD) at Halashazi(ALT, 48°06′58.2″N, 88°21′50.8″E, 2456.7 msl) and Tielishahan peatlands(KNS, 48°48′87.4″N, 86°54′60.0″E, 1766.5 msl) in the Altay mountains. The result indicates a rapid carbon accumulation (averages are 98.4

and 107.2 g C/m²/yr in ALT and KNS profile, respectively) happened in the early Holocene(10.5-8.4ka), then carbon accumulation deposition flux decreased (59.9 and 60.4 g C/m²/yr) during the mid-Holocene(8.4-4.2ka), after that, it significantly elevated(58.1 and 69.9 g C/m²/yr) during the early late-Holocene(4.2-2.0ka), followed by a rapid decline(only recorded in KNS profile with the average of 71.9 g C/m²/yr) at the end of late Holocene(after 2.0ka). Systematic analysis with 51 basal ages of peatlands in Xinjiang also suggested the fast peat initiation during the early Holocene and late Holocene. The peatland initiation and accumulation histories in Xinjiang are linked with the temperature records, suggesting the possible causal connection between peatland dynamics and local temperature. Furthermore, the fast initiation and accumulation of peat during the late Holocene might have contributed to high atmospheric carbon dioxide concentrations.

G05_P09

Why do tree tissues have older radiocarbon ages than chronological ages?

<u>Hilman B</u>¹, Solly E², Hagedorn F³, Kuhlman I¹, Herrera-Ramírez D¹, Trumbore S¹

¹Max-planck society, Jena, Germany, ²ETH Zurich, Zurich, Switzerland, ³Swiss Federal Institute for Forest, Snow and Landscape Research WSL, Birmensdorf, Switzerland

Tree tissues and especially fine roots (≤ 2mm) often have older ¹⁴C ages than chronological ages (¹⁴C excess). The common explanation is that stored and old non-structural carbon (NSC) contributes to new tissue growth. Accordingly, the ¹⁴C excess increases with the proportion of stored vs. recently fixed NSC in the growth substrate. Here we suggest that rather than this proportion, what determines the ¹⁴C excess is the turnover of the NSC pool. We demonstrate this using measurements of needles, branches, and fine roots of two coniferous trees in a treeline ecotone in Stillberg, Switzerland. In such ecotones the non-structural carbohydrates (NSCarb) stocks increase with elevation, probably due to the fact that low temperatures suppress growth more strongly than photosynthesis. In addition, we did not expect large variations in the proportion of stored NSC in the growth substrate. We expected initially that increasing NSCarb stocks with elevation is a proxy for slower turnover rates and therefore greater ¹⁴C excess. However, we observed the opposite trend in the fine roots with turnover intensification and smaller excess ¹⁴C towards the treeline, while ¹⁴C excess in aboveground tissues did not vary with elevation. Based on current and previous results we conclude that the greater surplus of photoassimilates in the treeline increases fluxes to both NSCarb and to belowground. The greater flux belowground speeds the turnover rate of the roots NSC and lowers its ¹⁴C excess.

O01 In-situ radiocarbon and other cosmogenic nuclides

001_01

Holocene glacier chronologies from various cosmogenic nuclides combined with radiocarbon dating

<u>Schimmelpfennig I</u>¹, Charton J¹, Jomelli V¹, Schaefer J², Lamp J², Godard V¹, Bard E¹

¹Aix Marseille Univ, CNRS, IRD, INRAE, CEREGE, Aix En Provence, France, ²LDEO, Columbia University, Palisades, USA

This presentation deals with the reconstruction of Holocene glacier advances and retreats using cosmogenic nuclide dating of glacial landforms in combination with radiocarbon-dates in various glacier

forefields. One site is Steingletscher (Central European Alps, Northern mid-latitudes), where we applied the emerging approach of paired ¹⁰Be-¹⁴C dating of recently deglaciated bedrock to constrain the duration of Holocene glacier recession. Combining the results with the ¹⁰Be moraine chronology and existing radiocarbon dates of organic material from the same site allowed reconstructing the glacier's Holocene retreat and advance history (Schimmelpfennig et al., Clim. Past 18, 23-44, 2022). Large glacier extents prevailed in the Earliest and the Late Holocene, while in between significant retreat occurred during several millennia, which is in agreement with existing glacier chronologies in the Alps and other parts of the North-Atlantic region as well as in the Tropics (Jomelli et al., Nat. Comm. 13, 1419, 2022). Another site is Ampere glacier on the basaltic Kerguelen archipelago in the Southern mid-latitudes. We reconstructed the Holocene behavior of this glacier, using ³⁶Cl dating of moraines and paired bedrock and erratic boulder surfaces (Charton et al., QSR 283, 107461, 2022). The results, combined with earlier published radiocarbon-dates of peat, imply that glaciers had significantly retracted extents throughout the Holocene, while Holocene maximum extents occurred only in the last millennium. This pattern is quasi-unique and highlights the non-uniformity of Holocene glacier behavior throughout southern mid-latitudes.

001 02

Ion-Laser InterAction Mass Spectrometry for long-lived cosmogenic radionuclides in stony meteorites

Martschini M¹, Merchel S¹, Marchhart O¹, Wieser A¹, Golser R¹

¹University of Vienna - Faculty of Physics, Isotope Physics - VERA, Vienna, Austria

Accelerator mass spectrometry (AMS) is usually the method-of-choice for the detection of long-lived cosmogenic nuclides such as ¹⁰Be, ¹⁴C, ²⁶Al, ³⁶Cl, ⁴¹Ca, ⁵³Mn and 60Fe with half-lifes between 6 ka and 4 Ma. Until recently however, tedious radiochemical separation to deplete matrices and isobars was a prerequisite for AMS hindering fast analysis.

Now, the world-wide unique Ion-Laser InterAction Mass Spectrometry (ILIAMS) system developed at the Vienna Environmental Research Accelerator (VERA) [1] can eliminate the need for chemistry in selected cases, i.e. presently for samples with stable isotope abundance of $\geq 1\%$ and isotopic ratios above 10^{-11} .

Laser photodetachment and ion-molecule-reactions of anions provide unprecedented isobar suppression for many AMS-isotopes by up to eleven orders of magnitude. Hence, ILIAMS-assisted AMS enables the direct detection of e.g., 26 Al/ 27 Al ($^{\sim}10^{-10}$, extraction of AlO $^{-}$) and 41 Ca/ 40 Ca ($^{\sim}10^{-11}$, extraction of CaF3 $^{-}$) in simply-crushed stony meteorites containing intrinsic $^{\sim}1\%$ Al and Ca. The presence of isobars originating from the natively-abundant elements (15% Mg, 1‰ K) does not cause any analysis problem making radiochemical separation redundant.

This newly-established instrumental AMS (IAMS) is opening routes to high-sample throughput analysis, reasonable and fast provenance checks for (extra-)terrestrial origin and identification of frauds. Additionally, first 26 Al/ 27 Al ($^{\sim}10^{-11}$) tests on terrestrial quartz samples from high altitudes used for exposure dating look promising to instantly set-up IAMS as a pre-screening and sample selection method for in-situ dating applications before starting tedious chemistry for more accurate results.

[1] M. Martschini et al. Radiocarbon 2021, first view, doi.org/10.1017/RDC.2021.73.

Soil dynamics revealed by cosmogenic nuclides

HATTÉ C^{1,2}, CORNU S³

¹Laboratoire des Sciences du Climat et de l'Environnement, Gif-sur-Yvette, France, ²Silesian University of Technology, Gliwice, Poland, ³CEREGE, Aix-en-Provence, France

Over the last few years, considerable attention has been devoted in the scientific literature and in the media to the concept of "ecosystem" services of soils. The monetary valuation of these services is often depicted as a necessary condition for the preservation of the natural capital that soils represent. Amongst the eleven recognized services of soil, at least eight are associated to soil carbon dynamics and to particles displacement: carbon sequestration, climate regulation, provision of food, nutrient cycling, habitat for organisms, flood regulation and foundation for human infrastructure.

Assessing the capacity of soils to provide these services is an immediate societal priority. Conventional solutions such as measuring carbon content, bulk density, particle size distribution... don't always allow to reach the dynamics notion and/or to answer questions quickly enough for a process reversal to take place. As an alternative method, measuring cosmogenic nuclides can be used to determine the timing of events and the dynamics of major pedological processes. They can provide clues to soil carbon dynamics and particle movement within the profiles themselves. Their use is thus beyond determining rates of erosion, denudation and uplift by analyzing the upper layers of soil profiles as typically done with such isotopes.

In this presentation, we will outline key elements delivered by cosmogenic nuclides to the soil sciences. They have been used alone or in combination with others isotopes. ¹⁴C, ¹⁰Be, ¹³⁷Cs, ²¹⁰Pb will be discussed for the modeling of carbon dynamics in soils and for the transfer of fine particles in profiles.

001 04

What we still need to learn: lessons from five years operation of the ANSTO in-situ ¹⁴C laboratory

Fulop R¹, SMITH A¹, Yang B¹, White D², Stutz J³, Codilean A⁴, Fink D¹

¹Australia's Nuclear Science and Technology Organisation, Sydney, Australia, ²University of Canberra, Canberra, Australia, ³Victoria University of Wellington, Wellington, New Zealand, ⁴University of Wollongong, Wollongong, Australia

In-situ ¹⁴C is slowly but steadily gaining its place in the cosmogenic nuclide toolkit. The isotope's relatively short half-life of 5730 years, when compared to the longer-lived and more routinely analysed cosmogenic nuclides, means that it is substantially more sensitive to short term variations in process rates or more suitable at investigating recent exposure events. The above property has proven very valuable in studying deglaciation histories in Antarctica, where the low erosion rates and cold-based glaciation produce widespread inheritance in erratics or bedrock surfaces making it difficult to quantify ice sheet retreat solely with ¹⁰Be. Furthermore, in-situ ¹⁴C used in combination with ²⁶Al and ¹⁰Be is also particularly well suited to studying the relatively short timescales that characterize fluvial sediment transfer and storage, once more illustrated well by recent work.

Despite the above, the extraction of in-situ ¹⁴C from geological samples is still problematic, with recent laboratory intercomparison studies showing considerable overdispersion in both intra and inter laboratory comparisons of standard materials. The discrepancies between laboratories have been attributed to several factors, including the quality of some intercomparison materials, however, clear consensus on the matter is yet to be reached.

We will discuss issues of in-situ ¹⁴C systematics related to phase transformation and micro graphitisation. We will also showcase examples where sample type and quartz impurity have large

bearing on success of sample extraction and obtained ¹⁴C results. Lastly, we revisit aspects of in-situ ¹⁴C systematics that still carry considerable uncertainty.

001 05

Reconstructing the timing of Pleistocene glacier advances in the Swiss northern Alpine Foreland

<u>Dieleman C</u>¹, Christl M², Vockenhuber C², Gautschi P², Akçar N¹

¹University of Bern, Bern, Switzerland, ²ETH Zurich, Zurich, Switzerland

During the last decade, isochron-burial dating was successfully used in constraining the timing of fluvial sediment deposition. Though, its application to glacial and glaciofluvial deposits is challenging because these deposits are generally characterized by low cosmogenic nuclide concentrations due to repeated glacial erosion. The Swiss northern Alpine Foreland witnessed repeated glacier advances during the Quaternary; thirteen advances were identified yet. The records of these advances are found in, from the oldest to the youngest, Höhere Deckenschotter (HDS; Higher Cover Gravels), Tiefere Deckenschotter (TDS; Lower Cover Gravels), Hochterrasse (HT; Higher Terrace) and Niederterrasse (NT; Lower Terrace). The Deckenschotter are characterized by a succession of glaciofluvial gravel beds intercalated with glacial and/or overbank deposits and considered to be the oldest Quaternary deposits, however their chronology is still under debate, because the first cosmogenic nuclide chronology, recently established at few sites, contradicts the existing morphostratigraphy. In this study, we present a solid cosmogenic nuclide chronology for the Swiss Deckenschotter reconstructed at eighteen sites during the last decade. Based on this chronology, we revealed the timing of five Pleistocene glaciations between ca. 2.5 Ma and ca. 250 ka, whereof three occurred during the Early Pleistocene prior to the Mid-Pleistocene Revolution (MPR) and two during the Middle Pleistocene. Based on this new chronostratigraphy, we conclude that the Swiss Deckenschotter are cut-and-fill sequences. Furthermore, these ages indicate a rather constant local base level between 2.5 Ma and 1 Ma, which has likely been lowered afterwards probably induced by the MPR.

001_06

Developing an in-situ ¹⁴C chronology for North Greenland

Søndergaard A¹, Steineman O¹, Haghipour N¹, Wacker L¹, Ivy-Ochs S¹, Larsen N²

¹Laboratory for Ion Beam Physics, Eth Zürich, Zürich, Switzerland, ²Centre for GeoGenetics, GLOBE Institute, University of Copenhagen, Copenhagen, Denmark

Determining the sensitivity of the Greenland Ice Sheet during the Holocene is a key prerequisite for understanding the future response of the ice sheet to global warming. It has proven difficult to constrain the glacial history of particularly North Greenland using 10Be exposure dating, an area predicted to be a key component in future mass loss from the ice sheet. This project will use cosmogenic in-situ 14C exposure dating to constrain Holocene ice sheet fluctuations in North Greenland. Cosmogenic nuclides are produced in rocks when cosmic rays hit the surface of the Earth. The cosmogenic nuclide inventory of a rock surfaces is therefore a key tool for chronicling the waxing and waning of ice. The most commonly analyzed nuclide is ¹⁰Be, which has a half-life of 1.4 Myr. However, a particular challenge arises in regions where the ice sheet base is cold and slow-moving. In these regions, erosion rates are low and 10Be inventories produced during earlier exposure periods accumulate instead of being removed, which result in exposure ages older than the last period of exposure. To circumvent this problem, we use in-situ produced cosmogenic ¹⁴C. Due to the shorter half-life (5730 yr), in-situ ¹⁴C inventories will, contrary ¹⁰Be, decrease not only because of rock surface erosion but also due to shielding from ice cover. Measurements of in-situ ¹⁴C, carried out at the in-situ ¹⁴C line at Laboratory of Ion Beam Physics, ETH Zürich, can therefore help to obtain more reliable ice reconstructions for North Greenland.

Studying LiBO₂ fluxes and low-temperature combustion systematics with a fully automated in situ cosmogenic ¹⁴C processing system at PRIME Lab

Lifton N¹, Koester A¹

¹Purdue University, West Lafayette, United States

Extraction procedures for in situ cosmogenic ¹⁴C (in situ ¹⁴C) from quartz require quantitative isotopic yields while maintaining scrupulous isolation from ubiquitous atmospheric/organic ¹⁴C. These time- and labor-intensive procedures are ripe for automation; unfortunately, our original automated in situ ¹⁴C extraction and purification systems, reconfigured and retrofitted from our original systems at the University of Arizona, proved less reliable than hoped. We therefore installed a fully automated stainless-steel system (except for specific glass or fused-quartz components) incorporating more reliable valves and improved actuator designs, along with a more robust liquid nitrogen distribution system. As with earlier versions, the new system uses a degassed LiBO₂ flux to dissolve the quartz sample in an ultra-high-purity oxygen atmosphere, after a lower-temperature combustion step to remove atmospheric/organic ¹⁴C.

We first compared single-use high-purity Al_2O_3 vs. reusable Pt/10%Rh sample combustion boats. The Pt/10%Rh boats heat more evenly than the Al_2O_3 , reducing procedural blank levels and variability for a given LiBO₂ flux. This lower blank variability also allowed us to trace progressively increasing blanks to the fluxes from our original manufacturer. Switching to a new manufacturer returned our blanks to consistently low levels.

We also analyzed the CRONUS-A intercomparison material to investigate sensitivity of extracted ¹⁴C concentrations to the temperature and duration of the combustion step. Results indicate that 1-hr combustion steps at either 500 or 600°C yield results consistent with the original intercomparison value of Jull et al. (2015), while 2 hr at 600°C results in loss of ca. 10% of the high-temperature ¹⁴C inventory.

001_08

Calculating catchmentwide erosion rates using an existing online calculator

Stübner K¹, Balco G²

¹Helmholtz-Zentrum Dresden-Rossendorf, Dresden, Germany, ²Berkeley Geochronology Center, Berkeley, USA

The calculation of exposure ages and erosion rates from ¹⁰Be and ²⁶Al concentrations in quartz is widely used in geomorphological and Quaternary geological applications. Existing calculators provide a simple means to compute age or erosion rate in a consistent and reproducible way and without the need to delve deeply into production scaling schemes and palaeomagnetic field models. Catchmentwide erosion rates reflect the production rates of the entire basin, and their calculation requires knowledge of the complete production rate model. A "basin production rate" may be approximated from the basin mean geographic coordinates and mean elevation, but because production varies (approximately) exponentially with elevation this approach generally underestimates the true production. Dedicated programs calculate production rates on the scale of a river catchment and explore, for example, the impact of different scaling schemes, muogenic production models, palaeomagnetic models, or the spatial resolution of topographic data. While these programs compute catchmentwide erosion rates the calculation is independent from the commonly used exposure age and erosion rate calculators, and the results are not directly comparable. Here we introduce a new python-based tool that uses the popular online calculator by G. Balco [http://hess.ess.washington.edu/] to compute the complete production rate model of a river catchment and to determine catchmentwide erosion rates from cosmogenic nuclide data. Our goal is to provide an easy-to-use catchmentwide erosion rate calculator, which is fully

integrated with existing exposure age and (in situ) erosion rate calculators for consistent and reproducible evaluation of cosmogenic nuclide data in Quaternary geology.

001 09

A software framework for calculating compositionally dependent in situ ¹⁴C production rates

Koester A1, Lifton N1

¹Purdue University, West Lafayette, United States

In situ cosmogenic nuclides have revolutionized surficial process and Quaternary geologic studies, yet in situ cosmogenic ¹⁴C (in situ ¹⁴C) is unique among commonly measured nuclides in that its 5.7 ky half-life enables constraints on complex exposure/burial histories during the last ~25 ka. However, measurements are currently limited to common, but not ubiquitous, coarse-grained quartz-bearing rocks. The ability to extract in situ ¹⁴C from quartz-poor and fine-grained rocks would expand applications to a broader array of landscapes. As a first step toward this goal, a robust means of interpreting in situ 14C concentrations derived from rocks and minerals spanning wider compositional ranges is crucial. We have developed a MATLAB®-based software framework to quantify spallogenic production of in situ 14C from a wide range of silicate rock and mineral compositions, based on measured and modelled excitation functions. As expected from prior work, production from oxygen dominates the overall in situ 14C signal, accounting for >90% of production at sea-level and high latitudes. This work confirms that Si, Al, and Mg are important targets, but predicts greater production from Na than previously recognized. The compositionally dependent production rates predicted for rock and mineral compositions considered are typically lower than that for quartz, dropping as compositions become more mafic (particularly Fe-rich). Production rates predicted for quartz and albite are comparable, however, reflecting the significance of production from Na. This framework should thus be a useful tool in efforts to broaden the utility of in situ ¹⁴C, but would benefit from improved excitation functions.

O01_P01

Isochron-burial dating of the oldest glaciofluvial sediments in the northern Alpine Foreland

<u>Broś E</u>¹, Ivy-Ochs S¹, Grischott R², Kober F³, Vockenhuber C¹, Christl M¹, Maden C⁴, Synal H¹

¹Laboratory of Ion Beam Physics, ETH Zurich, Zurich, Switzerland, ²BTG Büro für Technische Geologie AG, Sargans, Switzerland, ³NAGRA, Wettingen, Switzerland, ⁴Geochemistry and Petrology, ETH Zurich, Zurich, Switzerland

During the Middle and Early Pleistocene, the northern Alpine Foreland was glaciated several times and witnessed numerous phases of alternating incision and deposition, shaping the landscape that can be seen today. High elevated plateaus separated by deeply incised valleys, create a topography with relief of several hundreds of meters. On top of these plateaus can be found the oldest Quaternary glaciofluvial sediments in the northern Alpine Foreland. They have traditionally been divided into two gravel units: older Höhere (Higher, HDS) and younger Tiefere (Lower, TDS) Deckenschotter. The HDS is located topographically higher by ~100-150 m than the TDS. The Deckenschotter consist mainly of glaciofluvial sediments intercalated with glacial and/or overbank deposits and form gravel terraces located up to about 250 m above the modern valley bottom. Their exact time of deposition is an important source of information for establishing erosion and incision scenarios and quantification of landscape evolution in the northern Alpine Foreland during the Middle and Early Pleistocene. Our focus is placed on similar and complementary Deckenschotter deposits outcropping in several sites across the northern Alpine Foreland. In selected six sites, we implement isochron-burial dating technique with a pair of cosmogenic nuclides ²⁶Al and ¹⁰Be, to further examine and refine the question of the age of the Deckenschotter. The

first preliminary age estimates point to deposition in the latter part of the Early Pleistocene. With the aim to determine the age of these sediments, the results will also complement our understanding of landscape change during and after Deckenschotter times.

O01_P02

New evidence for the persistence of the Ilanzersee (Flims rockslide)

Grischott R^{1,2}, Wacker L², von Poschinger A³, Gilli A⁴

¹Büro Für Technische Geologie, Sargans, Switzerland, ²Laboratory for Ion Beam Physics, Zurich, Switzerland, ³Private adress, Kempfenhausen, Germany, ⁴Department of Earth Sciences, Zurich, Switzerland

The Flims rockslide is one of the largest known rockslide in the Alps and had a strong influence on the landscape evolution in the Vorderrhein-Valley. The Flims rockslide (volume 9–12 km³) has been dated to 9400 cal yr BP with the radiocarbon method [2]. The Vorderrhein was completely blocked by a more than 600 m-thick landslide dam and a lake, Ilanzersee, formed upstream [1]. Its maximum level obviously did not reach higher up than 930 m a.s.l. After the breach of the dam, an important sediment transport down the Rhine valley had occurred. Nevertheless, a relict lake existed for a longer time, probably for centuries. A level of about 820 m a.s.l that was held for fairly long time. The duration of this second lake level, until the lake was finally emptied, has not been clear so far. Drill cores retrieved along a transect of 4 km on top of the former delta plain of Ilanzersee revealed the continuous presence of typical fine-grained delta sediments overlain by recent fluvial sediments. A wood fragment embedded in delta sediment was dated to 8900-9000 cal yr BP and supports geological evidence found elsewhere, that the lake persisted during quite a long time. More samples from other drillings will be analysed to underline this first evidence.

[1]: Von Poschinger 2005

[2]: Deplazes et al., 2007

O01_P03

Comparison of two ¹⁰Be purification methods for AMS measurement

Loftfield J¹, Lachner J², Malter M¹, Stübner K², Adolphi F¹

¹Alfred Wegener Institute, Bremerhaven, Germany, ²Helmholtz-Zentrum Dresden-Rossendorf, Dresden, Germany

The cosmogenic radionuclide ¹⁰Be is a powerful tool in paleosciences. Its applications include the dating of rocks and sediments, reconstruction of past changes in solar activity and the geomagnetic field strength, and the synchronization of climate archives.

However, sample preparation and especially purification of Beryllium from environmental samples can be time consuming and expensive. Typically, purification of sediment samples is achieved by a combination of hydroxide precipitations and ion exchange chromatography. Here, we test a method of successive hydroxide precipitations at different pH-values in combination with precipitation in NaHCO₃, to purify samples of marine sediments from the Norwegian Sea and the Lomonosov Ridge for ¹⁰Beanalysis. We compare the performance of this method to an ion chromatography-based method (Simon et al., 2016) with respect to the Beryllium yield, purity of the resulting Be(OH)₂, blank, and performance in the AMS for both protocols. We discuss the advantages and challenges of the protocols, their applicability, and their capacity in terms of sample throughput.

Simon, Q., Thouveny, N., Bourlès, D. L., Nuttin, L., Hillaire-Marcel, C., & St-Onge, G. (2016). Authigenic ¹⁰Be/⁹Be ratios and ¹⁰Be-fluxes (230Thxs-normalized) in central Baffin Bay sediments during the last glacial cycle: Paleoenvironmental implications. Quaternary Science Reviews, 140, 142–162. https://doi.org/10.1016/j.quascirev.2016.03.027

Status report of the in-situ ¹⁴C extraction line at HEKAL AMS laboratory

Buró B¹, Fülöp R², Jull A^{1,3}, <u>Molnar M</u>¹

¹INTERACT AMS Laboratory, Debrecen, Hungary, ²Australian Nuclear Science and Technology Organisation, Lucas Heights, Australia, ³Department of Geosciences, University of Arizona, Tucson, USA

In this study we presented a new cosmogenic in-situ 14 C extraction line at the ICER laboratory, which is similar as the one published by Fülöp et al.(2019). These extraction system used the phase transformation of quartz to cristobalite on high temperature in order to quantitatively extract the carbon as CO_2 . The system consists of three independent components. 1: used for remove the atmospheric and meteoric 14 C, 2: offline high-temperature (1650 °C) oven for extract and trapped the cosmogenic in-situ 14 C from quartz, 3: CO_2 gas purification and mass measurement line. After the extraction and cleaning, the purified CO_2 sapmles are measured with compact 14 C AMS system (Environ MICADAS) and the gas ion source interface. The extraction line allows for rapid sample throughput of about 6 samples per week. The sample masses ranging between 4 and 7 g of clean quartz. Purified quartz samples were sieved and used for analyse the fraction of $250 - 500 \,\mu\text{m}$. The carbon yield from quartz samples are good and we have the expected values.

Our first tests were on the borehole CO₂ blank gas and Cronus-R standards. The blank level of the whole line is quite low. We get similar experiences and results as Fülöp et al. (2019).

O01 P05

32Si – An alternative radionuclide for dating the recent past?

Schlomberg M¹, Vockenhuber C¹, Synal H¹

¹Laboratory of Ion Beam Physics, ETH Zurich, Zurich, Switzerland

Dating the last few hundred years is challenging with currently used radionuclides: To date with 14 C (half-life of 5700 a) is difficult due to ambiguities in the calibration curve in the last $^{\sim}400$ years, although the last 80 years can be again well dated due to the bomb peak of the 14 C concentration and its subsequent dilution. Dating methods based on shorter-lived nuclides like 3 H (12.3 a) and 210 Pb (22.3 a) can only be used in the last $^{\sim}100$ a. A promising candidate for filling this dating gap is cosmogenic 32 Si with a half-life of $^{\sim}150$ a.

However, the application of ³²Si has so far been limited by the imprecisely known half-life. As part of the SINCHRON collaboration which aims at a redetermination of the half-life of ³²Si, the Laboratory of Ion Beam Physics (LIP) at ETH Zurich will perform the AMS measurements for the determination of the absolute number of ³²Si atoms in samples used for activity measurements.

In this poster, the potential of ³²Si as dating tool is discussed and an overview of the previous half life measurements is given. First results concerning the AMS measurement technique are presented and an outlook for potential ³²Si measurements in environmental samples is given.

Studying ¹⁴C production in meteorites using the Bernese ¹⁴C extraction line and the MICADAS system at LARA, University of Bern

Tauseef M¹, Leya I¹, Szidat S², Gattacceca J³

¹Space Research and Planetary Sciences, University of Bern, , Switzerland, ²Department of Chemistry, Biochemistry and Pharmaceutical Sciences, University of Bern, , Switzerland, ³CNRS, Aix Marseille University, CEREGE, Aix-en-Provence, France

Carbon-14 dating is the most robust technique for determining the terrestrial ages of meteorites. With our updated 14 C extraction system, we can measure up to 15 samples without breaking the vacuum, thereby achieving low blanks and a high sample throughput (Sliz et al. 2018, 2020). Briefly, we are able to quantitatively and reproducibly extract CO_2 gas from pre-cleaned meteorite samples (typical masses 50 mg). Preheating the samples at 500 °C in a continuous flow of pure oxygen reduces the remaining atmospheric contamination. Gas extraction is at $^{\sim}1600$ °C under an O_2 partial pressure of 30 ± 5 mbar for 10 min. Evolved gases are first purified at 500 °C -1000 °C using CuO, quartz spherules, and silver wool. Next, gases are cleaned and separated using a water trap at -78 °C and cold fingers ($^{\sim}100$ °C). The purified CO_2 gas is then collected in a glass capillary and is subsequently introduced into the gas ion source of the MICADAS AMS system (University of Bern). We finally give our results as specific activity concentrations (dpm/kg), which are then used to determine the terrestrial ages of meteorites. Here we will present new data for ^{14}C and ^{10}Be activity concentrations in freshly fallen meteorites to better constrain the ^{14}C and ^{10}Be production rates and consequently determine more accurate and more precise terrestrial ages of meteorites.

References

Sliz M.U. et al. 2018. 81st Annual Meeting of The Meteoritical Society 2018 (LPI Contrib. No. 2067) Sliz M.U. et al. 2020. Radiocarbon Vol 62, Nr 5, p 1371–1388

T01 Developments in measurement techniques

T01 01

Real-world ¹⁴C quantification by Saturated-absorption CAvity Ringdown (SCAR) spectroscopy

Carcione $F^{1,3}$, Delli Santi M^7 , Insero $G^{2,5}$, Cancio $P^{2,6}$, Galli $I^{2,6}$, Giusfredi G^6 , De Natale $P^{2,8}$, Mazzotti $D^{2,6}$, Defeo G^4 , Bartalini $S^{1,2,6}$

¹ppqSense Srl., Sesto Fiorentino, Italia, ²European Laboratory for Nonlinear Spectroscopy (LENS), Sesto Fiorentino, Italy, ³Università di Firenze, Dipartimento di Ingegneria, Firenze, Italy, ⁴Ars Tinctoria Srl., Santa Croce sull'Arno, Italy, ⁵Istituto Nazionale di Ricerca Metrologica (INRiM), Torino, Italy, ⁶Istituto Nazionale di Ottica (INO-CNR), Sesto Fiorentino, Italy, ⁷Istituto Nazionale di Ottica (INO-CNR), Firenze, Italy

Saturated-absorption cavity ring-down (SCAR) spectroscopy has pushed molecular detection to an unprecedented sensitivity of a few parts-per-quadrillion (ppq), thus allowing precise quantification of ¹⁴CO₂. Technology has been progressing since its first demonstration in 2011 and has taken to a portable instrument which is being deployed worldwide. Recently, our instrument has been applied for addressing specific problems in very different areas of science and humanities. Results will be shown for SCAR application to: discrimination of biogenic vs. fossil content in materials and fuels; radiological

assessment of waste coming from decommissioning of a nuclear power plant; dating of archeological samples from a 4500 years old Sumerian site.

Next applications aim to 14 C precise measurements in atmospheric samples, since distinguishing and measuring fossil vs. biogenic CO_2 in the atmosphere is the key to quantify the anthropogenic contribution to climate change. Aspects of the above applications, and many others that will come in the future, are in line with the European Green Deal, aiming to adopt a set of proposals to make the EU's climate, energy, transport and taxation policies fit for reducing net greenhouse gas emissions by at least 55% within 2030. In this perspective a cheap, compact, fast and clean technique for biogenic carbon analysis, like SCAR, will provide a crucial tool for implementing many of the European Green Deal strategies. We will also touch upon progress towards a biological SCAR instrument where dynamic range, throughput, and sample size are of the utmost importance.

T01 02

NIR-imaging and Radiocarbon dating together for making the invisible visible. A non-destructive visualization of collagen before attempting a radiocarbon date

<u>Catelli E</u>¹, Malegori C², Sciutto G¹, Oliveri P², Prati S¹, Benazzi S³, Cercatillo S⁴, Paleček D⁴, Mazzeo R¹, Talamo S^{4,5}

¹University of Bologna, Department of Chemistry "G. Ciamician", Ravenna Campus, Via Guaccimanni, 42, 48121, Ravenna, Italy, ²University of Genova, Department of Pharmacy, Viale Cembrano 4, I-16148, Genova, Italy, ³University of Bologna, Department of Cultural Heritage, Ravenna Campus, Via Degli Ariani, 1, 48121, Ravenna, Italy, ⁴University of Bologna, Department of Chemistry "G. Ciamician", Via Selmi, 2, 40126, Bologna, Italy, ⁵Department of Human Evolution, Max Planck Institute for Evolutionary Anthropology, Leipzig, Germany

Many archaeological rarest bones (human remains and precious bone objects) from Prehistory are enormously precious and are considered a cultural and historical patrimony. Radiocarbon dating is a well-established technique that estimates the age of bones by analyzing the collagen content. However, it is a destructive method and must be limited. In this study, we use imaging technology to visualize the presence of collagen on bone samples in a non-destructive way, hence minimizing the destruction of precious samples submitted to radiocarbon dating. The technique is near-infrared hyperspectral imaging (NIR-HSI).

NIR-HSI was used with a chemometric model to create chemical images of collagen distribution in ancient bones. The model also quantifies the collagen at every pixel and thus answering the questions: what, how much, and where.

Sixty archaeological samples (from the modern age to >50,000 years ago) have been used for developing the predictive model for quantifying collagen, based on partial least squares (PLS) regression. The amount of collagen in the selected bones was previously determined through the pretreatment of bone for the extraction of collagen for radiocarbon analysis. The model was validated using Cross-Validation (CV) and an independent test set of NIR-HSI bone images. The method represents a sustainable prescreening approach for identifying sampling points for subsequent specific analyses, such as ¹⁴C dating. Since the cultural heritage represents the testimony of past civilizations, our result will provide a significant advance not only for the study of human evolution but also for protecting and enhancing European cultural heritage.

Radiocarbon AMS below 100 keV

<u>Maxeiner S</u>¹, Synal H², De Maria D², Wacker L², Müller A², Fahrni S¹, Suter M² ¹Ionplus AG, Dietikon, Switzerland, ²Labora-tory of Ion Beam Phys-ics, ETH Zurich, Zurich, Switzerland

New technologies such as He-stripping have enabled the miniaturization and simplification of compact accelerator mass spectrometry (AMS) systems over the last two decades. As one of the most compact AMS systems, the MICADAS was optimized for stripping energies of around 240 keV and provides precise and efficient radiocarbon measurements for more than 15 years. In a collaboration between ETH Zurich and Ionplus AG, a new ultra-compact radiocarbon AMS system has been developed. It is based on many of the principles of MICADAS and operates near or at the physical limits of efficient radiocarbon AMS with stripping energies of around 100 keV. Measurements performed with an early prototype system showed that, despite the much lower beam energies, highly efficient, sensitive, and precise measurements comparable to MICADAS are possible. The technical challenges at such low voltages and the measurement results with different prototype configurations will be discussed and a new commercial product will be presented: the Low Energy Accelerator ("LEA"). With a footprint of 2.6 m x 1.8 m and with a tandem acceleration voltage of 50 kV, LEA is expected to perform similarly to the MICADAS at less than half its energy.

T01 04

Testing the measurement of small (<50 ug C) graphite samples on the ORAU MICADAS

<u>Becerra-Valdivia L</u>¹, Cameron J¹, Spindler L¹, Gianni M¹, Chivall D¹, Bronk Ramsey C¹, Wood R¹ ¹Oxford Radiocarbon Acceleration Unit, Oxford, United Kingdom

The Oxford Radiocarbon Accelerator Unit (ORAU) has processed about 5,000 samples for research and commercial purposes since the installation of a Mini Carbon Dating System AMS (MICADAS; Ionplus AG, CH) in 2019. Very few of the measurements produced, however, have been on graphite samples of less than 100 ug C. Given the need to reduce sample size in order to adequately address research questions across disciplines, a study was aimed at testing our ability to reliably measure very small graphite samples (<50 ug C) as an alternative to gas measurement by reassessing our current graphitisation (ironcatalysed hydrogen reduction), combustion and cleaning procedures. This included decreasing reaction vessel volume, increasing the mass of iron powder used, and decreasing graphitisation temperature to assess isotopic fractionation and AMS current behaviour. Throughout these experiments, efforts were made to efficiently and minimally adjust our current equipment set-up for simplicity. Here we present the preliminary results of this study and discuss archaeological and paleoecological applications.

T01_05

Rapid DIC extraction-to-graphite hybrid system at NOSAMS

<u>Gospodinova K</u>¹, Gagnon A¹, Wilson J², Hansman R¹, Elder K¹, Burton J¹, Lang S¹, Kurz M¹

¹Woods Hole Oceanographic Institution, Woods Hole, United States, ²AEON Laboratories, Tucson, United States

The Rapid Extraction of Dissolved Inorganic Carbon System (REDICS) is used to provide precise stable isotope and radiocarbon measurements of dissolved inorganic carbon (DIC) at the National Ocean Sciences Accelerator Mass Spectrometry (NOSAMS) facility. For the past year REDICS has primarily been used to provide oceanic radiocarbon measurements for the GO-SHIP program. REDICS automatically extracts sample DIC in the form of CO₂ using a membrane contactor and stores the extracted gas into a glass manifold for subsequent analysis on one of NOSAMS graphitization systems.

NOSAMS recently purchased a carbon extraction and graphitization system (CEGS) from AEON Laboratories, which was customized to automatically process and graphitize ten samples while obtaining sample splits for stable isotope δ^{13} C analysis. The system is compact, easily transportable, and, unlike other graphitization systems at NOSAMS, the sample graphitization begins immediately post-sample transfer to the reactor. These characteristics make it ideal for connecting to other CO₂ extraction systems.

Here we present our work on linking the REDICS and CEGS systems to create a hybrid system for rapidly processing DIC from seawater and groundwater samples. The analysis time from extraction to beginning of graphitization is on the order of 35 min, with current output designed for ten samples each day. Linking the two systems not only streamlines the process but shortens it from a two-day analysis to one, further increasing overall sample throughput at the facility.

T01 06

Simultaneous ¹⁴C and ¹³C measurements for any source of CO²

<u>Wertnik M</u>¹, Wacker L¹, Haghipour N¹, Bernasconi S¹, Synal H¹, Eglinton T¹, Welte C¹

IETH Zurich, Zürich, Switzerland

Carbon isotopes are an important source of information for a broad range of research fields related to carbon cycle studies and beyond. In this context, radiocarbon can be used to study temporal and partitioning effects, while the stable isotope (13 C) gives information about the source of the carbon (e.g. terrestrial or marine). Recently, an approach enabling the simultaneous analysis of all naturally occurring carbon isotopes in organic combustible materials has been introduced[1]. Here, we present a novel and very flexible method for simultaneous 14 C and 13 C measurements that can be combined with any CO_2 -feeding interface. The CO_2 from the sample is captured on a zeolite trap and subsequently transferred into a syringe, where it is diluted with Helium to a concentration of around 4%. The syringe allows constant feeding of the gas for simultaneous measurement with a split of 85% of gas to the accelerator mass spectrometer (AMS) and 15% to the isotope ratio mass spectrometer (IRMS). For carbonate samples, we can measure samples from 8 – 200 µg of Carbon to a precision of 0.1‰.

[1] C. P. McIntyre et al., 'Online 13 C and 14 C Gas Measurements by EA-IRMS-AMS at ETH Zürich', Radiocarbon, vol. 59, no. 3, pp. 893–903, Oct. 2016

T01_07

An automated processing line for the extraction of dissolved inorganic carbon from water for radiocarbon dating

<u>Yang B</u>¹, Williams A², Nguyen T¹, Freeman P¹, Jacobsen G¹, Smith A¹

¹Australian Nuclear Science & Technology Organization (ansto), Lucas Heights, Australia, ²Deceased.,,

At ANSTO, radiocarbon analyses of dissolved inorganic carbon (DIC) in groundwaters are in high demand for water resource sustainability research. A grant from the NSW Research Attraction and Acceleration Program enabled the development of an automated DIC extraction line for unattended processing of 10 samples. This line operates at ambient pressure with helium (He) gas as carrier. CO₂ gas is extracted from 50 mL of water in a 250 mL reaction vessel by adding 5 mL of phosphoric acid. The He gas is sparged through the water sample and then passed through two water traps at -100°C to remove water; and two CO₂ traps at -165°C to collect CO₂ gas. Complete recovery of CO₂ is determined by passing the He flow through a CO₂ analyser before releasing to waste to verify the absence of any residual CO₂. The CO₂ gas is then cryogenically transferred into one of 10 storage vessels until all queued samples on the system are processed. Between samples, the water traps and CO₂ traps are cleaned by evacuation to a

pressure $<5/10^3$ mbar. The water loop is flushed by He gas, followed by Milli-Q® water and a portion of the next sample, so eliminating sample memory. The line is controlled by a Python program running on a PC through serial connections, and several important parameters are logged to check that the system is working properly. After processing 10 samples, CO₂ sample is manually transferred to glass break seals for purification and conversion to graphite for AMS measurement.

T01 08

Direct Radiocarbon Analysis of Methane by Positive Ion Mass Spectrometry

<u>Mcintyre C</u>¹, Shanks R¹, Gulliver P¹, Dolan M², Freeman S¹ SUERC, East Kilbride, UK, ²GENeco, Avonmouth, UK

After carbon dioxide (CO_2), methane is the second most abundant anthropogenic atmospheric green house gas and it has a warming potential 25 times that of CO_2 . Radiocarbon (^{14}C) is useful for tracking the source, fate and quantity of methane within the atmosphere however, current techniques for its analysis are lengthy and use multiple preparative steps for concentration, combustion and purification.

Positive ion mass spectrometry (PIMS) can directly analyse the 14 C content of gases without the need for graphitization. It uses a plasma-based ion source to produce a positively charged carbon beam and a simple reaction cell to supress 14 C interferences. This plasma-based ion source typically operates on carbon dioxide but initial experiments have shown that methane analysis is also possible. Initial data from analysis of contemporary and fossil methane using PIMS will be presented and the performance compared with CO_2 PIMS and conventional AMS will be discussed. This new method opens up new areas of application, such as rapid biogas analysis.

In addition, the current status of the integration of automatic sample introduction to the PIMS system and its performance will be presented.

T01_P01

Double Trap Interface: A novel gas handling system for high throughput AMS analysis

<u>De Maria D</u>¹, Fahrni S², Wacker L¹, Synal H¹
¹ETH Zurich, Zurich, Switzerland, ²Ionplus AG, Dietikon, Switzerland

Over the last decade, the interest in a combustion based AMS technology has increased due to significant progresses made towards compact AMS systems and the development of hybrid ion sources, allowing the analysis of samples in gaseous form.

To address the requirements of higher samples throughput and level of automation, a novel gas handling system, the Double Trap Interface (DTI), was developed. The instrument couples an elemental analyzer (EA) to the ion source of a MICADAS (Micro Carbon Dating System) AMS system. The DTI features two external traps filled with a zeolite molecular sieve, which collect the sample material in form of CO_2 after combustion with EA. Subsequently, the gaseous sample is released by thermal desorption and injected into the ion source. The alternating use of the traps allows a quasi continuous analysis, as the loading and measurement procedures are now decoupled and run in parallel on the two traps. The analysis of a sample requires less than 5 minutes, corresponding to a throughput of 12 to 13 samples per hour. To speed up further the measurement routine, we implemented an option allowing multiple analyses on a single cathode.

The main target are biomedical companies conducting metabolism and pharmacokinetic studies using radiocarbon as tracer during the validation of new pharmaceutical compounds. However, the EA-DTI system is not limited to biomedical studies only. The methodology has a huge potential for all applications requiring an increased throughput but less precision, as for example environmental tracer studies or the analysis of organic sediments.

T01 P02

The progress of AMS ¹⁴C analysis for small samples down to ultramicroscale size (µg level) at Xi'an AMS Center

<u>Du H</u>^{1,2}, Fu Y^{1,2}, Yang B³, Zhou W^{1,2}

¹ State Key Laboratory of Loess and Quaternary Geology, Institute of Earth Environment, Chinese Academy of Sciences, Xi'an, China, ² Shaanxi Key Laboratory of Accelerator Mass Spectrometry Technology and Application, Xi'an AMS Center, Xi'an, China, ³Australian Nuclear Science and Technology Organisation, Sydney, Australia

As the urgent requirement at Xi'an AMS Center for Chronological Research and Tracer applications to radiocarbon (14C) analyze samples smaller than 0.1 mg carbon (mgC), a compact microgram carbon sample graphitization system has been applied. The system include two small-volume graphitization reaction units connected quartz manifold and a stainless steel cold finger which can be used as a transfer line for measuring carbon mass and effective trapping of water vapour during the reaction. In a 1.2 mL graphitization reactors we can prepare samples containing 10-600µgC using an iron catalyst with an excess of hydrogen, and even a few micrograms graphite (<10µg) can be obtained. We detailed the effect of the chemical reaction rates with different brand iron catalysts and the morphology analysis of microscale graphite, compared the conventional closed-tube combustion method with the combustion and purification system based on an elemental analyzer (EA) connected to cryogenic traps, especially for the preparation performance of microscale sample. Futhermore, we made some case studies of chronological research on several foraminiferal samples from marine sediment core, and got a series of microgram graphites which have been performed well by our upgrade 3MV Xi'an AMS facility. This is mainly a report of our current capability with the preparation and measurement of micro-sample ¹⁴C-AMS and in the future we will expand the application of microgram carbon sample ¹⁴C-AMS analysis to archaeological bone samples, the microgram carbon graphitisation system will provide the technological opportunities to develop some challenging research.

T01_P04

Radiocarbon analysis of methane

<u>Gentz T</u>¹, Höhn M¹, Grotheer H¹, Kattein L¹, Mollenhauer G¹
¹AWI-Bremerhaven, Bremerhaven, Germany

Methane (CH₄) is the most abundant organic compound in the atmosphere and its influence on the global climate is subject to widespread and ongoing scientific discussion. Two sources of atmospheric methane are the release of methane from the ocean seafloor, as well as from thawing permafrost. In recent years the origin, sediment and water column processes and subsequent pathways of methane have received growing interest in the scientific community. ^{13C}/¹²C ratio measurements can be used to determine the methane source (biogenic or thermogenic), but potential formation/alteration processes by microbes are not yet fully understood.

Radiocarbon analysis can help to understand these carbon cycling processes. The presented method is a novel approach for the radiocarbon age determination of methane. A modified PreConn is used to separate methane from other gases such as CO_2 in a gaseous sample. Afterwards, the purified methane is transferred to a furnace and oxidized to CO_2 . Subsequently, produced CO_2 is concentrated on a

custom-made zeolite trap, which can be connected to a novel sampling unit implemented into the GIS system (by Ionplus AG) for direct CO_2 measurements on a MICADAS. The zeolite trap has $\frac{1}{4}$ " quick-fit connectors (Swagelok) that allow to detach the trap from the oxidation unit and to re-attach it in the GIS. Initial testing showed minimal blank carbon incorporation associated with sample storage, transfer and handling of the custom-build zeolite trap.

Here we will present the setup of the method, first results of the blank determination as well as precision of common standard gases.

T01 P05

Determination of Carbon-14 specific activity in soil and sediments by tube combustion and liquid scintillation counting method

Krishnan K A¹, S B¹, N K¹

 1 Centre for Advanced Research in Environmental radioactivity (CARER), Mangalore, India

Carbon-14 (¹⁴C) is a pure beta emitter and occurs naturally in the environment due to cosmic ray induced production in the atmosphere. ¹⁴C is also released into the atmosphere by nuclear fuel cycle facilities and gaseous discharges from all types of nuclear power plants (NPPs). Oxidation of the samples in a combustion system, trapping the produced CO₂ in an amine-based absorber, and subsequent liquid scintillation analysis (LSA) is a proven method for samples with high carbon content, such as terrestrial plants. However, for soil and sediment matrices, which are considered poor carbon pools, improved methods are to be adopted for combustion since a large mass of these samples is to be combusted to produce sufficient CO₂ for saturation of the absorber.

This paper reports an improved method in which the conventional tube furnace system is used for combusting soil and sediment samples collected from the clean air region and from the vicinity of a NPP. The produced CO_2 was absorbed in NaOH, precipitated as $BaCO_3$, and CO_2 was regenerated by acid hydrolysis of $BaCO_3$ in a specially designed regeneration setup and trapped in an amine-based absorber, mixed with a liquid scintillator, and subjected to LSA. Validation of the method was performed by combusting IAEA C3 reference material. The method is capable of yielding accurate results with a deviation of <2.2 % from the target value. Upon validation, the suitability of the method for the determination of small excess ^{14}C activity in the vicinity of a nuclear power plant was demonstrated.

T01 P06

Absolute dating with ¹⁴C and ⁴¹Ca - is it feasible?

Kutschera W¹, Paul M²

¹University of Vienna, Vienna, Austria, ²The Hebrew University of Jerusalem, Jerusalem, Israel

It is well-known that 'wiggles' and 'plateaus' of the 14 C calibration curve often limit the precision of age determinations. In principle this problem could be avoided by absolute dating [1]. This requires to measure the 'mother/daughter' abundance ratio 14 C/ 14 N* which is independent of the initial 14 C abundance and only depends on the half-life and the age. Whereas 14 C dating in the 'classical' way is well established – although with the limitations mentioned above – dating with 41 Ca (half-life = 100,000 years) would require absolute dating because a global calibration curve for 41 Ca does not exist. In this case, the abundance ratio of 41 Ca/ 41 K* has to be measured. In both cases the ubiquitous existence of stable nitrogen or potassium on Earth makes the detection of the feeble radiogenic signals of 14 N* and 41 K* extremely challenging.

It was noted by Szabo et al. [1] that the kinematics of the ¹⁴C beta decay leads to ¹⁴N* recoil energies < 6.9 eV comparable to binding energies of atoms in molecules. Due to the pure electron-capture decay of

⁴¹Ca, the recoil energy of ⁴¹K* is even lower: <2.2 eV: Thus, there exist a certain retention probability for the decay products to stay in the original molecule or change their chemical character. Possible detection methods of ¹⁴N* and ⁴¹K* and their potential applications in archaeology will be discussed.

[1] J. Szabo, I. Carmi, D. Segal, E. Mintz, "An attempt at absolute ¹⁴C dating," Radiocarbon 40/1 (1998) 77-83.

T01_P07

A new setup for CH₄ analysis at CologneAMS

Melchert J¹, Rethemeyer J¹, Gierga M¹, **Gwozdz M**²,

¹University Of Cologne - Institute for Geology and Mineralogy, Cologne, Germany, ²University Of Cologne - Institute for Nuclear Physics, Cologne, Germany

The radiocarbon analysis of CH₄ required the development of a new sample handling routine and the establishment of a new vacuum system that converts CH₄ to CO₂ for direct measurement with the gas injection system of the AMS at the CologneAMS facility. First tests with multiple series of $_{14}$ C-free and modern standards, as well with a biogas mixture with sample sizes ranging from 20 to 50 μ g C resulted in a CH₄ to CO₂ conversion efficiency of 94 – 97%. Processed standards were further evaluated for contamination with extraneous carbon. With this new set up blank values achieved 0.006 \pm 0.003 F¹⁴C, which is comparable to blank values achieved with our routinely used CO2 vacuum system. With the processed standard series, we were able to quantify a low contribution of 0.26 \pm 0.13 μ g modern and 0.33 \pm 0.12 μ g dead exogenous carbon, respectively, for the new system. Both sources of contamination resulted in 0.58 \pm 0.18 μ g of extraneous C, introduced during sample handling and pre-treatment, with a corresponding F14C of 0.447 \pm 0.245. First tests with a near modern CH₄:CO₂ biogas mixture delivered reproducible results with a 14 C content of 0.978 – 1.010 F¹⁴C, after applying the correction for extraneously introduced carbon.

T01 P08

LEA – A novel Low Energy Accelerator for Radiocarbon Dating under a long-term Performance Test

<u>Ramsperger U</u>¹, De Maria D¹, Gautschi P¹, Maxeiner S², Müller A¹, Synal H¹, Wacker L¹ ¹ETH Zurich, Zurich, Switzerland, ²ionplus, Dietikon, Switzerland

Based on MICADAS (Mini Carbon Dating System) technology the acceleration voltage at the gas stripper unit, where charge exchange of the negative ions takes place and interfering isobar molecules are dissociated, is further reduced from 200 kV for MICADAS to 50 kV for LEA (Low Energy Accelerator) system. By using He stripper gas at a local areal density of ≈ 0.5 μg/cm² molecular interferences can be destroyed at a particle energy of less than 100 keV without excessive beam losses that would impede reproducible measurements conditions. Detailed optimization of the acceleration stage hosting the stripper gas volume where necessary to balance molecule dissociation power and optical beam losses to enable measurement conditions suitable for routine high performance radiocarbon dating measurements. Basic elements such as the ion source, injection magnet, and the fast beam bouncing system are copies of the MICADAS design, whereas the mass spectrometer following the acceleration stage had been modified according to the reduced ion energy. After an initial testing phase of the LEA system it has been installed at ETHZ in a configuration suitable for routine radiocarbon dating measurements. Here, we present data of long-term measurements over several days with the LEA system and compare the results with data of the well-established MICADAS system, with an emphasis on stability and accuracy.

Assessing radiocarbon blanks associated with solid phase extraction of dissolved organic carbon from sea water

Schlagenhauff S¹, Grotheer H¹, Niggemann J², Dittmar T², Mollenhauer G^{1,3}

¹Alfred Wegener Institute, Bremerhaven, Germany, ²Institute for Chemistry and Biology of the Marine Environment, Oldenburg, Germany, ³Marum Center for Marine Environmental Research and Department of Geosciences, Bremen, Germany

Radiocarbon analysis of marine dissolved organic carbon (DOC) gives insight into mixing timescales and C-storage, but technical challenges make obtaining samples for radiocarbon analysis costly and time consuming. Solid phase extraction (SPE) is a common technique to access not only the radiocarbon age of the SPE-DOC pool but also its molecular composition. The combination of SPE and low mass radiocarbon analysis using the MICADAS is a promising path to increase sample resolution but care must be taken to ensure confidence in the results. The aim of this work is to determine the amount and F14C value of extraneous carbon (Cex) in solid phase extracted samples to be analyzed on the MICADAS. The Cex of modified styrene divinyl benzene polymer (PPL) cartridges was investigated indirectly by measuring a ¹⁴C free fossil standard, a modern standard (F¹⁴C =1), as well as fresh water (Suwannee River 2R101N) and marine (NELHA) DOC reference materials. These standards were compared systematically across PPL cartridge sizes and lots. The Cex mass contribution from the SPE ranged from 5.5-17µgC while the F¹⁴C value of the blank was unique to each cartridge lot. Interestingly, no correlation was found between the size of the cartridge used and the amount of Cex introduced into the samples. Since it is not possible to predict or influence the F¹⁴C of blanks in each cartridge lot, when working with low mass SPE samples, it is necessary to incorporate thorough blank assessment procedure.

T01_P10

HVE design of a gas interface for routine ¹⁴C sample AMS measurement

Scognamiglio G¹, Klein M¹, Stolz A², Mous D¹

¹High Voltage Engineering Europa B.V., Amersfoort, Netherlands, ²Institute of Nuclear Physics, University of Cologne, Cologne, Germany

The 14 C AMS measurement of CO₂ gas samples has two main advantages compared to solid: (i) the time-consuming graphitization process is not required and (ii) small sample masses are sufficient for the measurement (below 150 µg carbon), while graphitized samples need few mg carbon. These advantages make the AMS measurement of gas samples a recognized tool in both biomedical and dating applications.

The gas measurement requires a gas interface between the CO_2 source and the AMS system that collects, dilutes with helium and transfers the sample gas with a specific flow and timing. In this contribution, we present the HVE design of a gas interface for the measurement of carbon samples combusted in an elemental analyzer. The CO_2 resulting from the combustion is collected in a zeolite trap and then transferred to a motor-driven syringe, which ensures the gas transfer to the AMS ion source in a controlled manner. The dead time is minimized by the implementation of two syringes and two zeolite traps. The gas interface is fully automated and can handle sample masses down to a few μ g carbon. In combination with the elemental analyzer and the AMS, it supports a throughput of more than 10 samples per hour.

Experimental study on charge exchange cross sections of low energy Carbon ions in helium at GXNU

Zhang G¹, Zhao Z¹, Shi S¹, Tang J¹, Wang L¹, Chen D¹, Qi L¹, Shen H¹,2

¹Guangxi Normal University, Guilin, China, ²Guangxi key laboratory of nuclear physics and nuclear technology, Guilin, China

Compared with nitrogen and argon, helium is lighter and can better reduce the beam loss caused by angular scattering during beam transmission, and the molecular dissociation cross-section in helium at low energy is high and stable, which makes the helium the prevalent stripping gas at low energy AMS. For the further study of the stripping behavior of ¹⁴C ions in helium at low energy, the charge state distributions of ion beams of carbon ions with -1, +1, +2, +3, and +4 charge states were measured at the energies of 40-220 keV with a compact 14C-AMS at Guangxi Normal University(GXNU). Based on the experimental data, the stripping characteristics of C-He in the energy range of 40-220keV were analyzed, and the new charge state yields and exchange cross-sections in C-He at the energies of 40-220keV were obtained.

Keywords: AMS; state yield; cross section;

T01 P12

Results of MODIS2 mortar dating intercomparison for the Zagreb Radiocarbon Laboratory, Croatia

Sironić A¹, Cherkinsky A², Borković D¹, Barešić J¹, Krajcar Bronić I¹

¹Ruđer Bošković Institute, Zagreb, Croatia, ²Center for Applied Isotope Studies, University of Georgia, Athens, United States of America

The second international Mortar Dating Intercomparison Study (MODIS2) conducted in 2020. Three mortar samples have been distributed among interested radiocarbon laboratories in form of 1 g particle size fraction smaller than 150 μ m and 2-5 g bulk mortar.

Our approach to dating MODIS2 mortars at the Zagreb Radiocarbon Laboratory, Croatia, was to separate $32-63~\mu m$ particle size fraction and to collect CO_2 by sequential dissolution with 85 % H3PO4 after 3 s, 15 s and until the end of reaction. The first fraction was regarded as date of the mortar, while the following fractions pointed to increase in dead carbon amount. The reported dates were: for sample #1 $640 \pm 20~BP$, for sample #2 $665 \pm 20~BP$ and for sample #3 $1750 \pm 20~BP$. In general, all the samples fit the expected ages, but bordering on upper limit age, implying still incomplete dead carbon removal. Here we will also present dates obtained by data extrapolation, which we found can eliminate dead carbon contamination, and we will discuss the differences between the two approaches.

Source Term Analysis and Experimental Measurement Design of Carbon-14 in High-Temperature Gas-Cooled Reactor Pebble-Bed Module

<u>Wang Y</u>¹, Guo J¹, Cao J¹, Xie F¹, Tong J¹, Dong Y¹, Zhang Z¹ 1 Tsinghua University, Beijing, China

As carbon-14 (14 C) plays an important role in the public radiation dose, increasing attention has been paid to the environmental impact assessment of nuclear power plants. Based on the experience and technology of the 10 MW high temperature gas-cooled reactor (HTR-10) and Arbeitsgemeinschaft Versuchsreaktor (AVR), the high-temperature gas-cooled reactor pebble-bed module (HTR-PM) has been designed and is currently under construction in China. In this article, the source terms of 14 C in the reactor core and primary loop of HTR-PM are presented along with a complete theoretical model. The production mechanism, distribution characteristics, reduction route, and release type of 14 C are illustrated. The average activity amount of 14 C per year in the core of HTR-PM was computed as 2.22 × 10^{12} Bq, and the activity concentration of 14 C in the primary loop at operating equilibrium was calculated as 2.51 × 10^4 Bq/m³ (STP). The calculation results indicated the dominant source of 14 C in both the reactor core and the primary coolant is the activation reaction of 14 N in the fuel elements. The 14 C sampling system in the helium purification system (HPS) of HTR-PM has been designed and illustrated, which can generate reliable activity concentration values of 14 C in the primary loop.

T02 Developments in classical sample pretreatment

T02 01

On the Prospects for Compound-specific Radiocarbon Analysis of Carbohydrates

Dee M¹, van der Wal K¹, Ghislain T², Jurak E³, Kuitems M¹

¹Centre for Isotope Research, University of Groningen, Groningen, Netherlands, ²Biomass Technology laboratory, University of Sherbrooke, Sherbrooke, Canada, ³Bioproduct Engineering, University of Groningen, Groningen, Netherlands

Compound-specific analysis of proteins and lipids lies at the forefront of current radiocarbon research. At the same time, interest has also been growing in radiocarbon measurements on carbohydrates, especially cellulose extracted from wood. Cellulose provides the most reliable record of fluctuations in the atmospheric concentration of ¹⁴CO₂ prior to the Modern Era. As well as information on the carbon cycle, such analyses have become increasingly important to palaeosolar investigations. Hydrolysing cellulose to glucose may appear redundant, given the fact the former is comprised wholly of the latter, but there are several potential advantages. Firstly, raw cellulosic extracts are more likely to retain chemically or physically bound exogenous carbon than a spectroscopically characterised monomer. Secondly, glucose is the primary product of photosynthesis – the most immediate manifestation of local ¹⁴CO₂ values. Thirdly, for cosmic-ray and carbon cycle analysis, radioisotope measurement need not be curtailed for calibration purposes. Such studies are only limited the purity of the extract obtained and the reproducibility of the associated measurements. Thus, compound-specific carbohydrate analysis may allow new levels of detail to be obtained on the past concentration of radiocarbon in the

atmosphere. Despite all this potential, previous attempts at glucose preparation for radiocarbon analysis have proven unsuccessful. Here, we discuss some recent investigations into this matter we have been conducting at the University of Groningen.

T02 02

ZooMS identified chimeras – removing collagen-based cow glue contamination from Palaeolithic whale bone objects prior to radiocarbon dating

van der Sluis L^{1,2}, McGrath K³, Cersoy S⁴, Thil F⁵, Pétillon J⁶, Zazzo A¹

¹Archéozoologie, Archéobotanique, Sociétés, Pratiques et Environnements (AASPE), UMR 7209, Muséum national d'Histoire naturelle, CNRS, Paris, France, ²Department of Evolutionary Anthropology, University of Vienna, Vienna, Austria, ³Department of Prehistory and Institute of Environmental Science and Technology (ICTA), Uni-versidad Autonoma de Barcelona, Barcelona, Spain, ⁴Centre de Recherche sur la Conservation (CRC), UAR 3224, Muséum national d'Histoire naturelle, CNRS, Paris, France, ⁵Laboratoire des Sciences du Climat et de l'Environnement, LSCE/IPSL UMR 8212, CEA-CNRS-UVSQ, Université Paris Saclay, F-91198, Gif-sur-Yvette, France, ⁶Travaux et Recherche Archéologiques sur les Cultures, les Espaces et les Sociétés (TRACES) UMR 5608, Toulouse, France

Eliminating contamination from exogenous carbon is essential prior to radiocarbon dating. Contamination can be derived from the burial environment or post-excavation treatments involving consolidation substances, which can be synthetic as well as organic in origin. Proteomic analysis (ZooMS) of Palaeolithic bone objects from France produced markers characteristic for both whale and cow. A modified extraction resulted in diminished cow peaks and enhanced whale peaks, suggesting these were originally whale bone objects that had been consolidated with collagen-based cow glue. Before subjecting these samples to radiocarbon dating, two cleaning protocols were tested to remove this type of contamination. Bone blank samples were consolidated with one type of collagen-based glue (bone glue, hide/skin glue or old bone glue from the museum), after which samples were either cured in the laboratory or artificially aged in a climate chamber for a month. While both cleaning methods produced excellent blank radiocarbon ages, the ages obtained from the archaeological material were still much too young considering their contextual age, suggesting that the collagen-based glue contamination had most likely cross-linked to the authentic collagen molecule. While compound-specific (hydroxyproline) radiocarbon dating and XAD resin are solutions to deal with cross-linked synthetic contamination, these are unlikely to help in the case of a collagen-based contaminant. Differential scanning calorimetry showed that the denaturation temperatures of both collagens (authentic and exogenous) were very close together. More research is needed to gain a deeper understanding of the occurrence and elimination of cross-linked collagen-based glues, as well as their prevalence in museum collections.

About the issue of restorations and possible contaminations: a new radiocarbon-friendly protocol for the preservation of archaeological bones

<u>Barone S</u>^{1,2}, Caramelli D⁵, Carretti E^{3,4}, Dei L^{3,4}, Fedi M¹, Lari M⁵, Liccioli L¹, Marradi G^{3,4}, Meoli A^{3,4}, Modi A⁵, Porpora F^{3,4}, Vai S⁵, Zaro V⁵

¹INFN - Sezione di Firenze, Sesto Fiorentino (FI), Italy, ²Università degli Studi di Firenze, Department of Physics and Astronomy, Sesto Fiorentino (FI), Italy, ³Università degli Studi di Firenze, Department Of Chemistry "Ugo Schiff", Sesto Fiorentino (Fi), Italy, ⁴Università di Firenze, CSGI Consortium, Sesto Fiorentino (Fi), Italy, ⁵Università degli Studi di Firenze, Department of Biology, Firenze, Italy

In archaeological contexts, skeletal remains represent an important source of information: for instance, palaeogenetic analyses and radiocarbon dating allows us to study the evolution of ancient populations, their adaptation mechanisms, migratory flows and their lifestyle.

Archaeological skeletal remains can have lain in direct contact with the soil for a very long time. This situation may lead to diagenesis and the loss of important information for our studies. To prevent further degradation, since the half of the XX century, synthetic organic polymers have been widely used for the consolidation of bones. However, these polymers have so far shown to cause additional problems to the preservation of bones over time, due to the poor compatibility between the polymers themselves and the bone matrix and to possible loss of solubility of those materials. Such issues can also affect the possibility to date those restored samples by radiocarbon.

In this work, we discuss the application of an innovative protocol for the consolidation of ancient bone remains not based on the use of organic substances but of nanometric HydroxyAPatite (HAP). The new consolidation method has been set-up through a multidisciplinary approach and tested to evaluate the possible effects on the palaeogenetic analysis and radiocarbon dating of the treated bones. We observed that HAP consolidation treatment does not introduce any contamination that could alter the results for both genetic characterization of the skeletal remains and radiocarbon dating. This consolidation procedure represents thus a more compatible conservation tool with respect to "old" procedures.

T02 04

GIRI-results from the global intercomparison

Scott M¹, Naysmith P², Cook G²

¹University Of Glasgow, Glasgow, United Kingdom, ²SUERC, East Kilbride, United Kingdom

GIRI (Glasgow International Radiocarbon Intercomparison) was designed to meet a number of objectives, including the most fundamental one, to provide an independent assessment of the analytical quality of the laboratory/measurement and an opportunity for a laboratory to participate and improve (if needed). The principles that we followed in the design of GIRI were to provide. A) A series of unrelated individual samples, spanning the dating age range, B) Some linked samples to earlier intercomparisons to allow traceability, C) Some known age samples, to allow independent accuracy checks, D) A small number of duplicates, to allow independent estimation of laboratory uncertainty and E) Two categories of samples - bulk and individual, to support laboratory investigation of variability. All of the GIRI samples are natural (wood, peat and grain), some are known age, and overall their age spans approx. >40,000 years BP to modern. The complete list of sample materials includes: humic acid, whalebone, grain, a number of single ring dendro-dated samples, a number of dendro-dated wood samples spanning a number of rings (e.g. 10 rings), background and near background samples of bone and wood, as well some samples connect to previous inter-comparisons allowing traceability of results.

We present an overview of the results received and preliminary consensus values for the samples supporting a more in-depth evaluation of laboratory performance and variability.

T02 05

Experimental Observations on Processing Leather, Skin and Parchment for Radiocarbon Dating

Davis M¹, <u>Culleton B</u>¹, Rosencrance R², Jazwa C²

¹PSUAMS Radiocarbon Lab, Pennsylvania State University, University Park, United States, ²Department of Anthropology, University of Nevada, Reno, Reno, United States

Leather, skin, and parchment in archaeological, historic and museum settings are among the most challenging materials to radiocarbon date in terms of removing exogenous carbon sources -- comparable to bone collagen in many respects but with much less empirical study to guide pretreatment approaches. In the case of leather, the radiocarbon content of materials used in manufacturing the leather can vary greatly, their initial presence before pretreatment and absence afterward is difficult to demonstrate, and the accuracy of dates depends upon isolating the original animal proteins and removing exogenous carbon. Parchments differ in production technique from leather, but offer similar unknowns, and it is not clear that lessons learned in the treatment of one are always salient for treating the other.

We measured the radiocarbon content of variously pretreated leather, parchment, skin samples, and extracts, producing apparent ages that varied by hundreds or occasionally thousands of years depending upon sample pretreatment. We learned that physical precleaning and solvent washes were essential, bleach washes systematically destroyed samples, and pretreating leather, skin or parchment with ABA resulted in contaminated samples with low yields. A Longin style bone demineralization and gelatinization followed by XAD purification of the hydrolyzed amino acids most consistently resulted in radiocarbon ratios that were statistically indistinguishable from known ages of the samples. Fourier Transform Infrared Spectroscopy (FT IR) provided insight into the chemical composition of carbon reservoirs contributing to age differences between different pretreatments of the same sample, and mass mixing models were used to quantify various carbon reservoirs.

T02_06

Is TiH₂ really necessary for Zn reduction? Discussion on graphitization at Circe Laboratory

<u>Capone B</u>¹, Passariello I¹, Terrasi F¹, Porzio G¹, Di Palma A¹, Rubino M¹, Marzaioli F¹

¹Università Degli Studi Della Campania "Luigi Vanvitelli", Caserta, Italy

The sample preparation procedure in use at CIRCE laboratory involves 3 main steps: chemical pretreatment of the sample in order to extract the carbon fraction of interest, oxidation of carbon to CO_2 by combustion with CuO or H_3PO_4 digestion for carbonaceous materials, and graphitization. The graphitization reaction leads to the formation of solid graphite targets and takes place in the presence of TiH₂ and Zn reagents and Fe as catalyst. Over more than a decade of using the procedure with a sample measurament rate of c.a. 1000/year, we observed a sharp increase in graphitization yield variabilty.

In order to verify the quality of the procedure, test measurements were performed on the IAEA C3 (cellulose) standard for combustion and graphitization reactions only. A fixed amount of about 1 mg of C was combusted by varying the amount of CuO and then graphitized by varying the amount of reagents. At the end of each step, samples were measured by IRMS in order to estimate the C isotopic fractionation, which is used as an indicator of reaction efficiency (i.e., the lower fractionation, the higher

the reaction efficiency). Preliminary results show that the presence of TiH₂ appears to reduce the graphitization efficiency suggesting that it is preferable to remove it from the reaction in agreement with the methods proposed for the ultra-small samples. AMS ¹⁴C measurements were also carried out in order to determine background induced, accuracy and precision of the procedure to be compared with data previously acquired in the same laboratory.

T02 07

Achieving low backgrounds during compound-specific hydroxyproline dating: HPLC column effects

<u>Linscott B</u>¹, Spindler L¹, Chivall D¹, Zelechonok Y², Wood R¹

¹University of Oxford, Oxford, United Kingdom, ²SIELC Technologies, Wheeling, United States of America

AMS radiocarbon dating is central to the development of robust chronologies in archaeological and paleoenvironmental contexts spanning the last 50,000 years. For dates to be accurate, samples must be free of exogenous carbon contamination. At the Oxford Radiocarbon Accelerator Unit (ORAU), considerable advancements in the dating of bone collagen have been made through the development of a high performance liquid chromatography (HPLC) method for the dating of the amino acid hydroxyproline (HYP), which can mitigate the effects of exogenous carbon contamination (1). However, recent changes in ligand manufacturing methods for the reverse-phase mixed-mode HPLC column (Primesep A, SIELC Technologies; IL, USA) used in the ORAU HYP protocol have resulted in unacceptably high analytical backgrounds. Prior to the manufacturing change, backgrounds (measured on background-age hydroxyproline isolated from Pleistocene bison bones) of 50k BP were achievable. Since the manufacturing change, due to column bleed, a mean background of 32.8k BP using hydroxyproline isolated from the same bones has been measured. The Primesep A column is no longer suitable for compound-specific amino acid radiocarbon measurements of older material. Here, we present background data and the chromatography conditions used to isolate hydroxyproline using an alternative column from the same manufacturer, which shows promising potential as an alternative for the routine isolation and AMS dating of hydroxyproline - especially approaching the limits of the method.

1. Deviese, T., Comeskey, D., McCullagh, J., Bronk Ramsey, C. and Higham, T., 2018. New protocol for compound-specific radiocarbon analysis of archaeological bones. Rapid Communications in Mass Spectrometry, 32(5), pp.373-379.

T02 09

Dating the "C" in Crown: Developing a method to extract protein in tooth enamel for radiocarbon dating.

<u>Raymond C</u>¹, Samper Carro S¹, Muhammad R², Wood R^{1,3}
¹Australian National University, Canberra, Australia, ²University of Malaya, Kuala Lumpur, Malaysia, ³University of Oxford, Oxford, United Kingdom

The rapid degradation of protein in bone in tropical environments represents a key barrier to the development of high quality radiocarbon chronologies for many archaeological and palaeontological sites across vast swathes of the world. Tooth enamel presents an alternative source of protein that could potentially be radiocarbon dated if an appropriate method to extract and purify endogenous peptides is developed. Although protein plays an important role in the formation of tooth enamel, most is removed during this process, and protein comprises only around 1wt% of fully mineralised enamel. However, enamel is far more resistant to diagenetic processes than bone due to its large apatite crystal size and low porosity, and protein is known to survive in enamel for 2 million years in tropical regions

(Welker et al. 2019). Successful extraction and radiocarbon dating of protein from tooth enamel presents an exciting alternative for dating non-collagenous skeletal remains.

At present, there is very little published research exploring the possibility of radiocarbon dating tooth enamel proteins. The aim of this project is to develop a method to extract and purify the protein found between the crystallites in enamel. Proteomic analysis of these proteins will be conducted to observe whether protein survivorship changes over time and help understand the impact of sample preparation methods.

Welker et al. Nature 576, 262-265 (2019)

T02_P01

Research on mortar radiocarbon dating in florence: state of the art and future perspectives

<u>Barone S</u>^{1,2}, Fedi M¹, Liccioli L¹, Calandra S³, Cantisani E⁴, Salvadori B⁴, Garzonio C⁵

¹INFN - Sezione di Firenze, Sesto Fiorentino (FI), Italy, ²Università degli Studi di Firenze, Department of Physics and Astronomy, Sesto Fiorentino (FI), Italy, ³Università degli Studi di Firenze, Department Of Chemistry "Ugo Schiff", Sesto Fiorentino (Fi), Italy, ⁴ISPC - CNR, Sesto Fiorentino (Fi), Italy, ⁵Università degli Studi di Firenze, Department of Earth Science, Firenze, Italy

As many studies have so far pointed out, despite the easiness of the principle, radiocarbon dating of mortars may present many issues in its application. Such issues are ascribable to the vast heterogeneity of mortars: anthropogenic calcite, which is the carbon fraction to be isolated for dating, is typically mixed with aggregates of several different compositions, even carbonaceous, and of different grain sizes; rest of geogenic calcite, as well as areas of uncomplete carbonation may be present; recrystallization phenomena may alter the original carbon content. The research during these years has highlighted that characterization of the mortar prior to dating is mandatory to identify the most efficient procedure to remove the possible contaminations in our mortar samples.

In the last few years, thanks to the multidisciplinary collaboration between INFN and ISPC-CNR in Florence, a procedure for the selection and treatment of mortars to be dated by radiocarbon was developed. The procedure includes a preliminary in-depth characterization of mortars, by means of different analyses such as XRD and FTIR-ATR, and the extraction of CO₂ from the datable isolated fraction through acidification, thanks to a new set-up that allows us to select different aliquots of CO₂ while the acidification reaction takes place. This set-up is coupled with the graphitization line specifically optimized for microsamples, allowing us to analyze small amounts of mortar calcite or one lump at a time.

In this poster we describe our procedure, the new experimental set-up installed at our laboratories and the results of the first tests.

T02_P02

Preliminary studies on tracing the source of carbon in organic matter and carbonate in coral and aquatic snail by ¹⁴C

<u>Cheng P</u>¹, Du H¹, Lu X¹

¹Institute of Earth Environment, CAS, Xi'an, China

The variation of ¹⁴C concentrations in organic matter and inorganic carbonates in coral and aquatic snail shells may reflect how carbon is used by these organisms. However, there are few studies on the source of organic matter in coral and snail shells. The main reasons are as follows:1) there is less organic matter

in shells and coral; 2) there are few reliable methods for extracting organic matter. In order to verify the reliability of our extracted method, four water-soluble substances with known ¹⁴C ages (50,000 to modern) were oxidized by sodium persulfate oxidation method. The results show there is no obvious old or young carbon contamination during the oxidation process. Further analysis of the samples showed that the ¹⁴C age of the organic matter of the coral was older than the ¹⁴C age of the carbonate, to a maximum of 670 years and to a minimum of 80 years, the organic matter of the snails in the lake had a ¹⁴C age 90 years older than the carbonates. The differences of ¹⁴C ages of organic matter and carbonate indicate that corals and aquatic snail have different carbon utilization and carbon source during growth. The change of carbon source is reasonable to trace the changes of water environment.

T02 P03

Optimisation of phosphoric acid digestion for cremated bones: ultrasonication and extension of collection time

Giannì M¹, Chivall D¹, Griffiths S²

¹Oxford Radiocarbon Accelerator Unit (ORAU), School of Archaeology, University of Oxford, Oxford, OX1 3QY, United Kingdom, ²Department of History, Politics and Philosophy, Manchester Metropolitan University, Manchester, M15 6LL, United Kingdom

Cremated bone pretreatment for radiocarbon dating at ORAU consists of acetic acid predigestion, to remove residual organic carbon, followed by phosphoric acid digestion to liberate endogenous carbonates as carbon dioxide. The phosphoric acid digestion follows a general protocol common to other materials including shells, foraminifera and other calcified material.

The phosphoric acid digestion is currently performed at 50° C for 2 to 3 hours. Afterwards, CO_2 is transferred, via a -65°C water trap (for 45 seconds), into vials using liquid nitrogen (for 15 seconds). The transfer is repeated three times taking a total of 3 minutes per sample.

Unlike shells and foraminifera, cremated bone takes 3.5 to 4.5 hours to turn in a dense liquid opaque mixture. Bubbles of trapped gas are clearly visible on the surface even after 3 minutes of CO_2 collection. The ability of ultrasonication to provide higher yield by releasing trapped gas was tested on cremated bone fragments by comparing non-ultrasonicated samples with duplicates that were ultrasonicated. Separately, another round of 3-minute collection was performed for which the yield and radiocarbon age were determined. Finally, dates were compared for consistency between all duplicates. Both ultrasonication and double-time collection increase the yield with minimal impact on date consistency, allowing for small samples (less than 500mg) to be accurately dated.

We therefore suggest a protocol modification that introduces a 5-minute ultrasonication step following digestion, before CO₂ collection, and an extension of the collection time from 3 to up to 6 minutes.

T02_P04

The impact of leaching on foraminifera radiocarbon ages

Grotheer H^{1,2}, Mollenhauer G^{1,2}

¹Alfred Wegener Institute Helmholtz Centre for Polar and Marine Research, Bremerhaven, Germany, ²University Bremen, MARUM, Bremen, Germany

Reliable radiocarbon ages of foraminifera are a prerequisite to generate robust high-resolution age-depth models or to obtain precise understanding of past carbon cycle dynamics. With the advance of small-scale radiocarbon measurements instrumental precision and levels of contamination become increasingly important to consider as with decreasing sample size the precision becomes progressively poorer, and the effect of contamination increases proportionally. To reduce the effect of carbon contamination, an attempt can be made to remove it by chemical pretreatment. An alternative might be mathematical corrections based on processing blanks of the same sample material and assuming constant contamination.

Here we report on radiocarbon analyses of monospecific foraminifera samples compared between different blank corrections and sample treatments I) to examine whether chemical pre-treatment and mathematical blank correction are comparable, and II) to determine limitations hindering reliable radiocarbon dating with ever smaller sample sizes. The data show that chemical pre-treatment does remove surface contamination and that the same effect on data reliability can be achieved by mathematically correcting for blank values determined from sample size-matched blank foraminifera. Theoretical considerations show that chemical pretreatment only has a beneficial effect where the isotopic difference between chemically untreated and pre-treated samples exceed the analytical precision

T02 P05

Radiocarbon dating of small snail shells in loess-paleosol sequence at Mangshan, central China

Gu Y^{1,2}, Lu H¹, Hajdas I², Haghipour N², Zhang H¹, Wu J¹, Shao K¹
¹Laboratory of AMS Dating and the Environment, School of Geography and Ocean Science, Nanjing University, Nanjing, China, ²Laboratory of Ion Beam Physics, ETH Zurich, Zurich, Switzerland

Radiocarbon age obtained on small snail shells show that the limestone effect is smaller than for the large shells, providing great potential to constrain accurate ages of late Quaternary loess deposits. In the Chinese Loess Plateau (CLP), snail shells are often the only radiocarbon dating material available for building chronology. However, the reliability of different small snail shells for radiocarbon dating remains an open question. Here, we collected different small snail shells from a loess-paleosol sequence located at south-east CLP to test their availability. Both solid graphite target AMS measurement and gas AMS measurement were performed to evaluate the reliability and possible contamination of different sizes of small shells for radiocarbon dating. 14C ages of graphitized samples are generally consistent with corresponding OSL ages, indicating the reliability of small snails ¹⁴C dating at CLP. Ages of the surface fraction of small snails are close to the ages of the interior part and the contamination after chemical treatment is limited, indicating fossil snail shells behave as a close system during burial. In addition, gas measurement results further demonstrate the different degrees of reliability among various snail species. For minute taxa, such as Vallonia and Pupilla, their shells can mainly reveal reliable ¹⁴C ages. While for larger taxa, such as Cathaica and Metodontia, much attention should be paid to selecting the appropriate shells. Large individuals and snail hatchlings may contain considerable old carbon and only small shells larger than newly incubation (<10 mm and > 2 mg) can provide reliable ¹⁴C ages.

T02_P06

Testing Protocols for Removing a Commercial Wood Stabilizer from Dry Wood for Radiocarbon Dating

<u>Hadden C</u>¹, Sheng H¹, Carmody D¹, Cherkinsky A¹ ¹Center For Applied Isotope Studies, Athens, United States

Conservation treatments such as wood stabilizers pose challenges for radiocarbon dating because they contain carbon of a different age than the object of study and must be removed completely in order to achieve an accurate radiocarbon age. Wood Juice© is a commercially available wood stabilizer with a proprietary formula that includes petroleum-based ingredients. It has been used recently by museum conservators in the United States to stabilize Native American dugout canoes and other logboats. The purpose of this study was to test whether Wood Juice can be effectively removed from dry wood to achieve reliable radiocarbon dates. For the experiment we intentionally contaminated with Wood Juice (25% by dry weight) a sample of a single-year tree ring from a pre-Columbian dugout canoe with a

radiocarbon age of 459 \pm 10 14 C yr. We tested the effectiveness of several common chemical pretreatment protocols for removing the Wood Juice, including a standard acid/base/acid (ABA) protocol, α -cellulose extraction, and a variety of organic solvents. We determined that ABA and α -cellulose protocols easily and effectively removed 100% of the contaminating carbon, without the need for an organic solvent. The results of this study will be of interest to radiocarbon researchers, archaeologists, and museum conservators working with canoes, logboats, and other wooden artifacts.

T02_P07

Samples screening and treatment for accurate radiocarbon dating

Hajdas I¹, Guidobaldi G¹, Haghipour N^{1,2}, Wyss K¹

¹Laboratory of Ion Beam Physics, ETH Zurich, Zurich, Switzerland, ²Earth Sciences Department, ETH Zurich, Zurich, Switzerland

Only carbon inherent to the material in quest of dating contains the original ¹⁴C signal from the time of formation or deposition. Apart from reservoir effects and calibration issues that must be considered, the major challenge in radiocarbon dating is the extraction of autogenic carbon. Various prescreening and purity checkups of sample material are vital to the choice of sample treatment. At the ¹⁴C prep laboratory ETH Zurich, the FTIR analysis supports the binocular investigations, which provides information on the sample's composition. Significantly, any anthropogenic conservation substances can be detected and identified, allowing for proper choice of treatment steps. Bulk sediments are cross-checked for carbonates or dolomite. Also, the treated samples are checked for purity before the final combustion. Occasionally, contaminated fractions are analyzed using a gas ion source to support evaluation.

Preservation of sample material is a crucial factor and assessing it helps choose an appropriate laboratory procedure. Currently, we estimate the N% and C/N ratio of the original bone sample to predict the success of collagen separation, although the use of FTIR analysis would simplify this step as the sample does not require weighing. On the other hand, the N% and C% of the original samples can be directly stored in the database after combustion in the elemental analyzer. Evaluation of procedures and their modifications is vital for an efficiently working laboratory. This paper will present an overview of methods applied to evaluate and treat various materials and samples.

T02_P08

Tree-ring-radiocarbon dating paraffin conserved charcoal: An experimental and archaeological case study

Kessler N¹

¹University Of Arizona, Tucson, United States

For wood and charcoal in museum collections, past conservation practices can be a challenge for high precision ¹⁴C-based chronometry. For example, in the United States, the treatment of archaeological charcoal with paraffin consolidant was a widespread practice. This complicates ¹⁴C dating of tree-ring segments in wiggle-matches as trace amounts of dead carbon can induce significant offsets. This poster presents experimental evidence for the efficacy of a solvent pretreatment protocol for known age and archaeological charcoal conserved with paraffin. FTIR and ¹⁴C analysis confirm that a chloroform pretreatment is very effective at removing paraffin from laboratory contaminated known-age charcoal as well as historically contaminated archaeological charcoal. Using the pretreatment protocol, new wiggle-matched dates were obtained from a large platform mound (Mound 10) at the Kincaid Site, a Mississippian center in southern Illinois U.S.A. Wiggle-matched cutting dates from the final construction episodes on Mound 10 at Kincaid, indicate that the mound was used in the late 1300s with the construction of a unique building on the apex occurring in the 1390s, just one or two generations prior to the depopulation of the site. This study demonstrates the potential for museum collections of

archaeological charcoal to contribute high resolution chronological information through wiggle-matching despite past conservation practices that complicate ¹⁴C dating.

T02 P09

Squeaky clean cellulose for different applications

Khumalo W¹, Svarva H¹, Zurbach D¹, Nadeau M¹

This project aims to determine the most time effective method of extracting cellulose "clean" enough for applications in 14 C dating and stable isotope analysis, namely δ^{18} O, for both young and old wood samples. We compare classic, commonly used, methods for the extraction of cellulose to more recent, simpler approaches.

 α -Cellulose is considered the best component to extract for high precision 14 C dating of younger wood samples. However, these methods are often too destructive on old wood samples resulting in sample yields too small for 14 C dating. Vigorous cellulose extraction methods needed for 14 C dating may not be necessary to produce accurate δ^{18} O results. Therefore, we also consider more crude cleaning methods. Specifically, the use of di-glyme and other organic compounds to pretreat wood samples in a much shorter time.

We analyse the purity of cellulose, determined by Fourier Transform Infrared Spectroscopy (FTIR), in relation to the 14 C and δ^{18} O results as well as pretreatment yields for modern and old samples. The goal of this being to determine how "clean" a sample must be to produce accurate results while avoiding unnecessary cleaning steps while producing a high enough yield for analysis. This project investigates if different approaches for wood pretreatment are needed depending on application and the preservation of the wood.

T02_P10

System for graphitization of CO₂ samples - development status.

<u>Kłosok K</u>^{1,2}, Rakowski A¹, Kolarczyk A², Miłosz S², Tudyka K¹
¹Silesian University Of Technology, Gliwice, Poland, ²miDose Solutions, Zabrze, Poland

The accelerator mass spectrometry (AMS) technique is widely used in radiocarbon dating and biocomponent determination due to the possible measurement of small samples with a carbon content of about 1 mg.

The design of a line for graphitisation of carbon dioxide samples for radiocarbon dating, along with the results of acceptance tests, have been presented in scientific articles (Krąpiec et al. 2018, Wiktorowski et al. 2020). Currently, within the Innovation Incubator 4.0 project, a prototype of an automatic line for graphitisation of samples, is being developed, which will allow to significantly reduce the time needed to prepare samples for measurement. The result of this project is expected to be a commercial device for automatic graphitisation of samples.

¹The National Laboratory for Age Determination, Trondheim, Norway

The Development of an Organic Solvent Pretreatment Based on Thermodynamic Insights for the Accurate Radiocarbon Dating of Conserved Samples

Lacey T¹, Tate A¹

¹DirectAMS, Bothell, United States

Conserved archaeological samples, while the subject of high academic interest, are challenging for radiocarbon dating laboratories because the conservation substance is usually unknown and may be chemically complex. Furthermore, the samples are typically poorly preserved, available in limited quantity, and require additional pretreatment with organic solvents to remove the applied carbon. To date, such solvent protocols have been presented with limited discussion of the underlying science of dissolution required to efficiently target the widest possible chemistries of conservation chemicals. A novel organic solvent protocol informed by the by Hansen Solubility Parameter model is discussed and its efficacy is assessed against a diverse set of polymeric conservation chemicals.

T02_P12

Funny and tricky sample wrappings – Challenging your radiocarbon laboratory

<u>Lindauer S</u>¹, Friedrich R¹

¹Curt-Engelhorn-Centre Archaeometry, Mannheim, Germany

Radiocarbon samples can be wrapped in all sorts of bag and materials to make sure the samples arrive safe and sound. Over the years variety of possible and impossible samples arrived at our lab, causing problems occassionally but often being the highlight of the day cheering up the people involved. When someone is in the field, sometimes an important samples needs to be taken when the person is totally unprepared. Then things like cigarette packets, or former office packets can become important to help out. But sometimes samples are taken, wrapped in aluminium foil and forgotten in the desks. See on our poster what happened to these.

This poster is meant to cheer you up, not to blame anybody. But also with a little warning here and there.

T02 P13

A short note on temperature influence of the acid step in bone sample preparation

Lindauer S¹, Friedrich R¹

¹Curt-Engelhorn-Centre Archaeometry, Mannheim, Germany

Several sample preparation protocols are known which deal with the trial to extract as much collagen of a bone sample in reliable quality as possible. In addition, care must be taken to conserve the isotope ratio if further investigations such as stable isotopes are planned. Often these protocols are compared by modifying several parameters at once so that the real effects of the different components cannot be compared very well. We concentrated our test on the temperature influence of the first acid step. This step serves to demineralize the sample. We compare sample preparation at room temperature with two acid strength concentrations and at 4°C with the same acid concentrations. Our results imply that the acid concentration is not the key influence on the collagen yield, but the temperature is.

An Approach to Dating Poorly Preserved Bones

<u>Eugenia M</u>¹, Regev L¹, Boaretto E¹

¹Weizmann Institute of Science, Rehovot, Israel

When analyzing bones found in arid regions such as Near East for radiocarbon dating, we are very often faced with low insoluble collagen contents (<1%) or the absence of insoluble collagen. We therefore try to find alternative solutions. We tested the suitability of dating the acid soluble fraction (ASF) recovered during the standard procedure of hydroxyapatite demineralization. This fraction is normally discarded during the extraction of collagen. For such samples, we propose a tailored approach that involves the separation of biological materials present in the ASF. This includes reassembled collagen and non-collagenous protein (NCP). Based on recent studies in the field of proteomic analysis, this fraction (NCP) is rich in biomolecular material. The problem of using ASF for radiocarbon dating, lies in the difficulty of removing exogenous carbon from the mixed material. In this study, we attempt to characterize the ASF from fossil bones, followed by isolation and dating of BGP (bone Gla protein) from the NCP.

T02 P15

Novel sample preparation approach to investigate

¹⁴C from iron material

<u>Baráth B</u>¹, Jull A¹, Molnar M¹

¹INTERACT Laboratory, Debrecen, Hungary

In this study, we present a novel approach for ¹⁴C analyses of iron material. Artefacts made from wrought iron, could incorporate some C content from the applied heating material (charcoal, wood), which deliver a measurable ¹⁴C content into the iron. This C and ¹⁴C might allow the ¹⁴C based dating of the production of the iron tool. Neutron flux could also produce significant amount of ¹⁴C atoms inside the iron based construction elements (vessel wall, tubes, etc) of nuclear reactors.

For all the above listed applications, we need a good sample preparation method, to extract the C from the iron. As the typical concentration is maximum a few percent C in the iron (m/m%), a complete combustion/oxidation of 0.1 - 1 g iron for this purpose is necessary. We present an elegant way of this preparation, using a LECO C744 type iron – C analyser. The exhaust gas of this automatized oxidizer is applied for trapping the produced CO2, for further isotope analyses. About 1g of iron is completely oxidized within 1 minute by the C744 unit, and the exhaust gas is collected. C yield, and reproducibility of this preparation method is investigated by AMS ¹⁴C analyses of known age iron artefacts, and several ¹⁴C reference materials.

This method could play an important role, when nuclear power plants are decommissioned and significant amount of iron waste has to be classified according their ¹⁴C isotope content.

T02_P16

A semi-automated graphitization system

Olsen J¹

¹Aarhus University, Aarhus, Denmark

Presented here is a semi-automated graphitization system. The design of the system is inspired by semi-automated graphitization system in use at the A.E. Lalonde Accelerator Mass Spectrometry (AMS) Laboratory. The system is made from stainless steel with VCR fittings and orbital welded joints and consists of 20 graphitization units connected to a common vacuum system. The graphitization ovens are

made with quick-fit joint to ease operation. Further the ovens are well insolated having an outer surface temperature of c. 30 °C when operated at core temperature of 550 °C. The system is controlled by a National Instruments real-time computer. This ensures continues monitoring of the system as well as ensuring a high degree of safety in terms on oven and vacuum interlocks. A gas inlet system with three channels for H_2 , Ar and O_2 enables the introduction of H_2 for CO_2 reduction and Ar for venting tube-crackers and reactors. O_2 is at present not installed on system but will enable pre-combustion of reactors for improved ¹⁴C backgrounds. The real-time FPGA unit ensures fast (ns) measurements of gas inlet flow rates and pressure to ensure quick shutdown of gasses in case of malfunctioning. The user interface (UI) is made using LabView and runs on a separate PC which can lock-on to the real-time system. The UI is build with database access and with a user friendly look to ensure safe and easy operation.

T02 P17

Predicting the collagen yield of unknown samples

<u>Olsen J</u>¹, Schrøder T¹, Philippsen B¹, Kanstrup M¹ ¹Aarhus University, Aarhus, Denmark

Bone samples for radiocarbon analysis are difficult and time consuming. Often the bone preservation is unknown and frequently the bone collagen yield is underestimated resulting in small samples. If the collagen can be predicting some of these problems can avoided. At Aarhus AMS Centre we have collected FTIR spectra, %C and %N of raw bone samples of more than 200 samples. Further, we extracted collagen and conducted FTIR analysis as well as elemental and stable isotope analysis. Presented here are modelling results from which the collagen yield is predicted from measurements of raw bones. Different types of models (correlation models, neural networks, machine learning) and their performance will be presented and discussed.

T02_P18

Radiocarbon dating of fossil wood - verification of the effectiveness of various preparation methods

Michczyńska D¹, Jędrzejowski M¹, Kłusek M¹, <u>Michczyński A</u>¹, Pawełczyk F¹, Piotrowska N¹, Wyss K², Hajdas I²

¹Institute of Physics - CSE, Silesian University of Technology, Gliwice, Poland, ²Laboratory of Ion Beam Physics, ETHZ, Zurich, Switzerland

A comparison of a few various preparation methods was carried out on sub-samples of fossil wood from Szczerców near Bełchatów (Central Poland). The tests were performed for both large and small samples - for LSC and AMS dating, respectively, and all preparation methods were performed two ways: with and without solvent washes in the Soxhlet apparatus. We compared the usefulness and effectiveness of individual methods based on the results of FTIR analysis and ¹⁴C measurements. Our aim was also to check whether the long, multi-stage preparation of large samples, with ¹⁴C concentration value close to the range of radiocarbon method, leads to significant absorption of CO₂. The conducted research and multi-criteria analysis, considering: cost, efficiency, repeatability and work- and time consumption, allowed to select the most effective method of fossil wood preparation.

Collagen extraction and amino acid purification for radiocarbon dating of a Late Neolithic mass grave

Philippsen B^{1,2}, Olsen J², Nørkjær Johannsen N³

¹Museum Lolland-Falster, Nykøbing F, Denmark, ²Aarhus AMS Centre, Department of Physics and Astronomy, Aarhus University, Aarhus, Denmark, ³School of Culture and Society - Department of Archeology and Heritage Studies, Aarhus University, Højbjerg, Denmark

The purpose of this paper is to improve the preparation of bone samples for radiocarbon dating. As a test case, we use the Late Neolithic mass grave of Koszyce, Poland.

DNA analysis of the individuals from the mass grave has demonstrated that they had been a large extended family. This supports the archaeological observation that the individuals were buried there in one single event. The mass grave thus contains bone samples of the same age and can be used to test radiocarbon sample preparation methods.

For an earlier study, we have extracted and radiocarbon dated bone collagen of fifteen human individuals and one sheep bone from the mass grave. With the traditional collagen extraction methods usually utilized at the Aarhus AMS Centre, only the sheep and three human bones yielded sufficient collagen for radiocarbon dating. We therefore modified the pretreatment procedure by using weaker reagents at lower temperatures. This enabled us to extract sufficient collagen from the remaining twelve human bone samples. However, the radiocarbon ages showed considerable spread, and several outliers had to be removed from the dataset. We therefore suspected that we had not been successful in removing all contaminants from the bone collagen and tested an alternative approach, purification of the collagen hydrolysate with an ion exchange resin.

T02 P20

Implementation of Fe/Zn graphitization method in Dendrochronological laboratory at AGH University of Science and Technology, Krakow, Poland

Krąpiec M¹, <u>Rakowski A</u>², Molnar M³, Pawlyta J¹, Huels M⁴

¹AGH, Kraków, Poland, ²SUT, Gliwice, Poland, ³ATOMKI, Debrecen, Hungary, ⁴Uni Kiel, Kiel, Germany

Accelerator mass spectrometry (AMS) is the most common measuring technique used in the radiocarbon dating. The procedure of age determination with this technique is divided into two parts: sample preparation and measurement. Sample preparation includes mechanical and chemical processes of cleaning, combustion, graphitization and pressing into sample holder to form a perfect cathode. Fe/Zn method for preparation of graphite targets for AMS measurements of radiocarbon concentration has been tested in the Dendrochronological Laboratory at AGH University of Science and Technology, Kraków. Performance of the method was tested with samples of NIST Ox-II, IAEA standards (IAEA C3, C5, C6, and C8), and blank samples. The test confirms good reproducibility of results obtained for the samples prepared using this method.

¹⁴C ramp-pyrolysis and FTIR analysis of Trondheim CaCO₃ precipitates of atmospheric CO₂ samples: further investigations and insights

<u>Santos G</u>¹, Leong C¹, Seiler M², Grootes P², Svarva H², Nadeau M²

¹University of California, Irvine, Irvine,, United States, ²The National Laboratory for Age Determination, NTNU University Museum, Trondheim, Norway

An archive of atmospheric CO₂ samples collected by the Trondheim Radiocarbon Laboratory (NTNU) since early 1960s, and precipitated as CaCO₃, has been evaluated by radiocarbon (14C) analysis for its reliability (Seiler et al. 2022). Results indicated the presence of a contaminant that was not removed by different chemical cleansing procedures. Here, we present a follow up investigation using a subset of the samples shown in Seiler et al. (2022). The selected CaCO₃ samples and several reference materials of carbonate and mixed matrix origins were subjected to ramp-pyrolysis at < 285°C. Upon 24 hours, CaCO₃ samples as well as reference materials were transferred still hot to the vacuum line, flame torch sealed, combusted, and then brought through graphitization using standard protocols. Radiocarbon measurements of CaCO₃ samples performed at Keck Carbon Cycle Accelerator Mass Spectrometer match with those recently attained by NTNU. To determine the performance of heat treatment, Fouriertransform infrared (FTIR) spectroscopy were performed on ramp-pyrolysis treated and untreated CaCO3 samples. While FTIR confirmed that water and chains of carbohydrates have been removed upon heating, their absence did not improve the ¹⁴C results of CaCO₃ powders. Maximum ¹⁴C depletion was still 11%. This may indicate that the elusive contaminant is of carbonate origin, possibly due to reactivation of carbonation by moisture and changes in temperature during decades of poor storage conditions. These findings will be discussed.

Seiler et al. 2022. Radiocarbon. Accepted.

T02 P22

Assessing a one-for-all alpha-cellulose procedure for ¹⁴C analysis of fossil to post-bomb ages

<u>Santos G</u>¹, Komatsu A¹, Renteria J¹, Brandes A², Leong C¹, Collado S³, De Pol-Holz R³
¹University of California, Irvine, Irvine, United States, ²Universidade Federal Fluminense, Niterói,, Brazil, ³Universidad de Magallanes, Punta Arenas, Chile

Cellulose is an important component in plants' cell walls and is often separated from other compounds, such as hemicelluloses, lignin and extractives by chemical steps in order to be utilized in isotopic studies. In 14 C analysis, reliable ages are fundamental, including those at the extremes of the 14 C age array, i.e., post-bomb 1950 AD and 14 C limit (beyond 50 kyrs). Finding a one-for-all procedure that can accurately provide results that satisfy the large 14 C age spectrum can be challenging. Therefore, any procedure and/or procedures that whereby can make wood cleaning or cellulose-rich residual fraction extractions easier, faster and reliable for the full 14 C age spectrum are preferable. Here, we describe a simple and fast manual procedure that can be easily scaled up or down as desired, as well as modified on demand (depending on samples requirements). Same-day or three-days are needed to extract chipped wood to alpha-cellulose homogenized fibers from batches of ≤ 10 to 40 samples, respectively. Procedure setup (e.g., reagents, laboratory instrumentation and consumables) are relatively simple, as they are all off-the-shelf items that are commercially available. High levels of precision and accuracy was attained from replicates ranging from post-bomb 1950 AD to 14 C limit by using woody reference materials as well as samples from pantropical regions (post-bomb, subfossil and fossil). Results were in the order of 0.3% or better, regardless of the age group studied. Details about this protocol will be shared and discussed.

Experimental Conditions for ¹⁴C graphite preparation at GXNU lab, China

<u>Shen H</u>^{1,2}, Wang L¹, Tang J¹, Li Z¹, Shi S¹, Zhang G¹, Chen D¹, Qi L, Wang N^{1,2}
¹Guangxi Normal University, Guilin, China, ²Guangxi key laboratory of nuclear physics and nuclear technology, Guilin, China

As a vital sample preparation method for ¹⁴C graphite, the Zn-Fe reduction method has been widely used in various laboratories. However, there are still few studies on the experimental conditions for the preparation of ¹⁴C graphite with this method. In this work, ¹⁴C graphite samples were prepared based on the Zn-Fe method, and the experimented key parameters such as the reduction reaction temperature, reaction time, reagent dosage, Fe powder activation, and other factors were investigated and determined. The results provide important instructions for the preparation line of ¹⁴C graphite at GXNU lab.

T02 P24

Preparation method of foraminifera radiocarbon sample and its age determination at GXNU-AMS

Qi L¹, Tang J¹, Shi S¹, Wang L¹, Zhang G¹, Chen D¹, <u>Shen H</u>^{1,2} 1 Guangxi Normal University, Guilin, China, 2 Guangxi key laboratory of nuclear physics and nuclear technology, Guilin, China

Foraminifera radiocarbon (¹⁴C) measurements allow absolute geological dating with high accuracy. However, the reliable and accurate measurement of foraminiferal radiocarbon is challenging due to the small sample size and the sample preparation procedure. A series of foraminifera and shell samples from the Pearl River Estuary of China were prepared and performed radiocarbon measurements with a campact accelerator mass spectrometer (GXNU-AMS) at Guangxi Normal University. The results showed that the recovery rate of the samples was more than 80%, and the formation time of foraminifera was between 525 yrBP and 37500yrBP.

Keywords: Foraminifera; GXNU-AMS; 14C

T02 P25

New developments in the radiocarbon-based source apportionment for the water-soluble organic carbon fraction of airborne particulate matter

<u>Strähl J</u>¹, Lechleitner F¹, Laemmel T¹, Geissbühler D¹, Salazar G¹, Szidat S¹

¹Department of Chemistry, Biochemistry and Pharmaceutical Sciences and Oeschger Centre for Climate Change Research, University of Bern, Bern, Switzerland

Air pollution is known for its adverse effects on human health (Burnett et al., 2014) and causes annually more than 6 million premature deaths (Gakidou et al., 2017). This demonstrates the exigency for effective mitigation strategies. Water-soluble organic carbon (WSOC) poses a large fraction of airborne particulate matter (Pöschl, 2005), and its source apportionment is crucial to understand the origin of pollution. The analysis of ¹⁴C is a powerful tool for source apportionment as it allows to discriminate between fossil and non-fossil emissions (Szidat, 2009). WSOC is extracted from samples using a wet

oxidation procedure, with the advantage of low blank contamination and rapid sample processing times (Rauber et al., in prep.). The CO₂ generated from the wet oxidation can be analysed for its ¹⁴C content using an accelerator mass spectrometer equipped with a gas ion source (Ruff et al., 2007). Here we present an optimized setup for the preparation and treatment of WSOC samples for ¹⁴C analysis that addresses concerns regarding sample recovery and blank contamination. A newly developed sintered needle minimizes losses of CO₂ during the sampling from the headspace of closed vials, while circumventing issues arising from the use of carbon-based glues. This allows the measurement of smaller sample amounts and simplifies the previous setup as no high-capacity water traps are needed anymore. A recently incorporated non-dispersive infrared CO₂ detector increases the accuracy of sample amount quantification. Finally, a detailed blank assessment on the new setup enables to detect possible remaining contamination sources and minimize their contribution.

T02 P26

Using XAD resin to remove synthetic contamination from archaeological bone prior to radiocarbon dating

van der Sluis L^{1,2}, Zazzo A¹, Thil F³, Pétillon J⁴

¹Archéozoologie, Archéobotanique, Sociétés, Pratiques et Environnements (AASPE) UMR 7209, Muséum national d'Histoire naturelle, CNRS, Paris, France, ²Department Of Evolutionary Anthrpology, University of Vienna, Vienna, Austria, ³Laboratoire des Sciences du Climat et de l'Environnement, LSCE/IPSL UMR 8212, CEA-CNRS-UVSQ, Université Paris Saclay, F-91198, Gif-sur-Yvette, France, ⁴Travaux et Recherche Archéologiques sur les Cultures, les Espaces et les Sociétés (TRACES) UMR 5608, Toulouse, France

Extraction protocols for radiocarbon dating bone collagen samples are continuously being tested and improved. Contamination can originate from the burial environment as well as post-excavation treatments, involving conservation treatments using synthetic consolidants. While most contamination can be removed using the ABA method, this is not the case for cross-linked contamination. The most suitable method to remove contamination from especially small bone samples seems to be the XAD method.

The XAD protocol was implemented at the MNHN radiocarbon laboratory and tested using known age bone samples and a Palaeolithic bone sample that had been consolidated and produced an anomalous peak in the FTIR-ATR spectra at 1725 cm⁻¹.

To test the functionality of the XAD resin, samples of known age were consolidated with shellac or Paraloid and artificially aged in a climate chamber for a month. Samples were then treated with or without the XAD resin and radiocarbon dated. The Hollis bone blank showed that XAD resin was able to remove young carbon from shellac, which was not the case for the ABA-only method. Results from VIRI I were more variable and VIRI F was possibly too young to show the effects of the consolidants. Four radiocarbon dates on the Palaeolithic bone after XAD treatment are statistically the same, while a sample without XAD treatment was significantly older, suggesting that the contaminant was not fully removed by the classical ABA treatment. This study demonstrates the interest of the XAD treatment to clean heritage bone samples stored in museums prior to geochemical analyses.

Preliminary study to reduce the amount of sampling for ¹⁴C dating of non-buried ivory

Wojcieszak M¹, <u>Ligovich G</u>, Van den Brande T, Boudin M ¹Royal Institute for Cultural Heritage (KIK/IRPA), Brussels, Belgium

According to European law and the Convention on International Trade in Endangered Species of Wild Fauna and Flora (CITES), worked ivory and raw tusks acquired before 1947 can be traded in the EU. Radiocarbon dating is an effective method to recognise ivory formed after 1947 since during 1950s and 1960s atomic bomb testing created a large increase in atmospheric radiocarbon content. Prior to dating the ivory, the common pre-treatment method is the same as the one used for bone and consists of extracting the collagen. Depending on the age and state of the ivory sample, the collagen content varies between ~10 and 20 % by weight. To obtain enough collagen for dating, around 100 mg of sample is needed and around 3.5 mg of collagen is combusted and graphitised. In this study we compared the ¹⁴C dates of samples prepared with the traditional collagen extraction, and samples directly combusted without any treatment. The preliminary tests show almost no differences between the dates obtained with the two methods. Around 10 mg of sample were used for the direct combustion method, which reduces the amount of sample needed by 10 times. This would be significant in the case of small ivory objects. However, this procedure can only be performed with non-buried materials since a pretreatment is necessary in the case of buried ones.

T02 P28

The impact of micro-CT scanning on radiocarbon dating of fossil material: a cautionary note

Wood R¹, Martín-Francés L², Duval M³

¹University Of Oxford, Oxford, United Kingdom, ²Centro de Evolución y Comportamiento Humanos (UCM-ISCIII), Madrid, Spain, ³Centro Nacional de Investigación sobre la Evolución Humana, Burgos, Spain

It is imperative that damage to rare and valuable remains is minimised in palaeoanthropological research. Micro-computerized tomography (mCT) scanning of fossils is now routinely used to record a high resolution three-dimensional reconstruction of samples prior to destructive analyses such as radiocarbon dating. It is therefore crucial to establish whether the method has a negative impact on the associated analysis, and to determine how this impact can be reduced. We examine whether a range of mCT acquisition parameters could influence collagen yield of a well preserved woolly rhino bone. Whilst mCT had no significant impact on the radiocarbon age obtained, we find that collagen yield is reduced from around 7% to 4.5%, suggesting protein is damaged during the scanning process. This does not seem to be strongly correlated to the x-ray intensity. In this bone, collagen yield remained well above the minimum cut-offs of 0.5 or 1% typically used in radiocarbon laboratories. However, it does imply that a larger sample may be required from bones that have undergone previous scanning. This might become an issue for highly valuable fossils like in palaeoanthropology. Additionally, samples with low collagen yield might also result unsuitable for ¹⁴C dating after mCT. This is the second study showing that mCT scanning of fossils may have a non-negligible impact on dating results, after a similar work focused on Electron Spin Resonance (ESR) dating. It might be worth reconsidering the systematic and unlimited use of mCT scanning in palaeoanthropology in the light of these results.

T03 Novel methods and applications for radiocarbon analysis of natural matrices

T03_01

A compact laser ablation system with a diode laser for AMS ¹⁴C measurement

Minamitani F¹, Omori T², Yoneda M², Ozaki H², Yamazaki K²

¹Graduate School of Frontier Sciences, The University of Tokyo, Kashiwa, Japan, ²The University Museum, The University of Tokyo, Bunkyo, Japan

We constructed a laser ablation (LA) system using a diode laser of organic materials for AMS 14 C measurement. The LA system can extract CO₂ in amounts of $^{\sim}$ 0.4 mg of carbon, using a 5.5W diode laser from a maximum of 0.6 mm diameter spot area. The LA system was assessed using standard materials (IAEA-C1, IAEA-C2, and IAEA-C3) and applied to natural samples such as tree-ring and bone. For LA sampling of organic samples, which often results in incomplete combustion, tungsten (VI) oxide was used as an oxidant to enhance complete burning. Results from the measurement of standard materials showed that the value of δ^{13} C agrees with book values. A low 14 C background of 0.0004±0.003 F^{14} C was obtained, and 14 C values were well reproduced within errors. This system was applied to 14 C mapping in organic tissues; for example, the detection of cosmic-ray events in annual rings and 14 C uptake during bone growth.

T03 02

New absorption-catalytic setup for graphitization of C-containing gases from water sources

<u>Parkhomchuk E</u>^{1,2,3}, Petrozhitskiy A^{1,2,3}, Ignatov M^{1,3}, Kuleshov D^{1,3}, Kalinkin P⁴, Novikov D⁵, Sabrekov A⁶, Parkhomchuk V^{1,2}

¹Novosibirsk State University, Novosibirsk, Russian Federation, ²Budker Institute of Nuclear Physics Siberian Branch Russian Academy of Sciences, Novosibirsk, Russian Federation, ³Institute of Archaeology and Ethnography Siberian Branch Russian Academy of Sciences, Novosibirsk, Russian Federation, ⁴Boreskov Institute of Catalysis Siberian Branch Russian Academy of Sciences, Novosibirsk, Russian Federation, ⁵Trofimuk Institute of Petroleum Geology and Geophysics Siberian Branch Russian Academy of Sciences, Novosibirsk, Russian Federation, ⁶Severtsov Institute of Ecology and Evolution Russian Academy of Sciences, Moscow, Russian Federation

The AMS Golden Valley laboratory is equipped with two accelerator mass spectrometers: BINP AMS facility and MICADAS-28, and two graphitization systems: AGE-3 and Absorption-catalytic setup, developed in Boreskov Institute of Catalysis (ACS BIC). The last one is designed for graphitization of labeled biomedical samples, dissolved organics and dissolved or gaseous carbon dioxide. Detailed description and characteristics of ACS BIC will be presented compared with that one's of AGE-3 on the samples from Glasgow International Radiocarbon Inter-comparison (GIRI). A comparison of the results from two series of experiments with GIRI samples: AGE-3 + MICADAS-28 and ACS BIC + MICADAS-28 will be given. Some results on dating of methane seeps – cm-sized holes and craters with an active release of gas bubbles and water, found in Western Siberia, and dating of carbon dissolved in springs in Novosibirsk region, will be also presented. Novel technique for graphitization of CH₄ and CO₂, dissolved in water, was provided by ACS BIC.

Radiocarbon dating correlated microlayers in engraved, oxalate-rich accretions: new archives of paleoenvironments and human activity from Australian rock art shelters

<u>Green H</u>¹, Gleadow A¹, Finch D¹, Myers C², McGovern J³, Levchencko V⁴, Heaney P⁵, Pickering R⁶, Balanggarra Aboriginal Corporation⁷

¹The University of Melbourne, Melbourne, Australia, ²Dunkeld Pastoral Company, Kununurra, Australia, ³The University of Queensland, Brisbane, Australia, ⁴Australian Nuclear Science and Technology Organisation, Lucas Heights, Australia, ⁵Lettuce Create, Brisbane, Australia, ⁶The University of Cape Town, Cape Town, South Africa, ⁷Balanggarra Aboriginal Corporation, Kununurra, Australia

Distinctive, dark coloured, glaze-like mineral accretions, often found in rock shelters around the world, offer important opportunities for radiocarbon dating of associated rock art. The mineralogy of these accretions is dominated by well-crystallised calcium oxalate and sulphate minerals, most commonly whewellite and gypsum, with significant occurrences of phosphates in some samples. The accretions are typically several millimetres thick and characterised by distinctive internal laminations and other apparently microbial features that support a microbiological origin for the oxalate component. Risks surrounding contamination and open system behaviour, previously limiting the application of radiocarbon dating to these accretions, are addressed by the well-crystallised nature of the oxalates and the preservation of fine laminar features within their internal stratigraphies. In a case study from the north Kimberley region of north-western Australia, we demonstrate the use of sample characterisation and chemical pre-treatment techniques to pre-screen for evidence of open system behaviour and address potential contamination. The results provide stratigraphically consistent sequences of radiocarbon dates in mm-scale laminated accretions, with correlations between distinctive patterns in the layer sequences visible in rock shelters up to 90 km apart. This demonstrates that pre-screened samples offer opportunities to reliably date rock art, particularly symbolic markings commonly engraved into these relatively soft deposits and suggests their synchronised formation is not entirely shelter specific but broadly controlled by variations in regional environmental conditions. Consequently, these accretions also offer potential as paleoenvironmental archives, with radiocarbon dating of layers in nine accretions indicating four, approximately synchronous growth intervals covering the last 43 ka.

T03_04

Refining the Bulk: Utilizing Complementary Pyrolysis-Gas Chromatography-Mass Spectrometry to Focus and Inform Ramped Pyrolysis Radiocarbon Analyses

<u>Ginnane</u> C^1 , Turnbull $J^{1,2}$, Phillips A^1 , Zondervan A^1 , Naeher S^1 1GNS Science, Lower Hutt, New Zealand, 2CIRES , University of Colorado at Boulder, Boulder, USA

Ramped pyrolysis oxidation-accelerator mass spectrometry (RPO-AMS) has been established at Rafter Radiocarbon Laboratory at GNS Science, NZ. RPO-AMS has a niche in Antarctic sediment chronology where traditional radiocarbon analyses are unsuitable. In this depositional environment, carbonates are not well-preserved, and autochthonous carbon is commingled with detrital carbon. RPO-AMS improves on bulk radiocarbon measurements for these challenging environments by partitioning the sedimentary organic carbon pool according to thermochemical stability. More labile, predominantly younger depositional carbon can be separated from older, refractory detrital carbon that skews the bulk radiocarbon measurement.

RPO-AMS presents a step change in radiocarbon measurement, providing an intermediate technique between bulk and compound-specific radiocarbon analysis (CSRA). More accurate information is obtained relative to bulk sediment dating without the cost and major technical challenges associated

with CSRA. By combining pyrolysis-gas chromatography-mass spectrometry (Py-GC-MS) with RPO-AMS, a chemical fingerprint is determined for each RPO split partitioned along the thermal gradient, informing the composition of the carbon source. Aliquots containing carbon compounds indicative of deposition can be identified prior to selecting samples for radiocarbon analysis. Focused analyses shorten run times and reduce measurement costs to achieve more accurate and comprehensive chronologies. In addition to targeted sample selection, the Py-GC-MS fingerprints can be used to interpret detrital depositional environments and sedimentary processes in tandem with RPO-AMS data.

T03 05

Microsublimation as final purification step for ¹⁴C analysis of specific compounds after chromatographic separation

<u>Heusser C</u>¹, Wacker L¹, Eglinton T¹, Welte C¹
¹ETH Zürich, Zürich, Switzerland

With the decrease in sample size requirements for radiocarbon (14C) analysis by accelerator mass spectrometry (AMS) down to 10 micrograms of carbon or less, measurement of individual source- or process-diagnostic compounds has become feasible. Many key target compounds are amenable to isolation using preparative chromatographic methods such as high-performance liquid chromatography (HPLC) and gas chromatography (GC). However, during compound isolation and other sample pretreatment steps, carbon from external sources can be introduced, which poses a major limitation to precise ¹⁴C dating at very small sample sizes. Here we test the potential of micro-sublimation as an approach for purification of selected compounds after chromatographic separation prior to ¹⁴C analysis. While sublimation is a well-established approach for purification of semi-volatile organic compounds in synthetic and analytical chemistry, commercial sublimation equipment is not designed for the purification of organic compounds in the sub-milligram range, a custom-built micro-sublimation apparatus has been developed, refined and tested. The sublimation characteristics, such as sublimation time, temperature and recoveries will be presented for a range of compound classes (amino acids, nalkanes, lignin phenols). We will critically discuss the benefits and limitations of using microsublimation as a final cleaning step for compound specific ¹⁴C analysis with special regards to counteract the risk of introducing external carbon.

T03 06

Radiocarbon in dissolved organic carbon by UV oxidation: an update of procedures and blank characterization at NOSAMS

<u>Xu L</u>¹, Roberts M¹, Elder K¹, Hansman R¹, Gagnon A¹, Kurz M¹ ¹Woods Hole Oceanographic Institution, Woods Hole, United States

Radiocarbon measurements of dissolved organic carbon (DOC) in aquatic systems provide key insights into the age and biogeochemical cycling of this large and reactive carbon reservoir. At the National Ocean Sciences Accelerator Mass Spectrometry (NOSAMS) facility, we have worked extensively to reduce the procedural blank of $DO^{14}C$ to $3.3 \pm 0.8 \, \mu g$ C with Fm of 0.35 ± 0.15 , down from $22.0 \pm 6.0 \, \mu g$ C in 2018. This was achieved through modifications of sample processing that included elimination of higher blank organic carbon reagents and improved sample and reactor handling intended to reduce exposure to laboratory air (which may contribute to the DOC blank via volatile organic compounds). Sample throughput has been improved three-fold to three samples per day by increasing the size of the UV oxidation chamber to allow for three reactors.

Eruption History of Mt. Fuji Further Constrained Through Radiocarbon Dating of Fossil Pollen Automatically Extracted from Lake Motosu Sediments

<u>Ota K</u>^{1,2}, Yokoyama Y^{1,2,3,4,5}, Miyairi Y², Obrochta S⁶, Yamamoto S⁷, Aurelia H⁸, V.M.A. H^{9,10}, M. De B¹⁰, Fujiwara O¹¹

¹University of Tokyo, Kashiwa, Japan, ²Atmosphere and Ocean Research Institute, University of Tokyo, Kashiwa, Japan, ³Graduate Program on Environmental Sciences, Graduate School of Arts and Sciences, The University of Tokyo, Bunkyoku, Japan, ⁴Biogeochemistry Program, Japan Agency for Marine-Earth Science and Technology, Yokohama, Japan, ⁵Research School of Physics, The Australian National University, Canberra, Australia, ⁶Graduate School of International Resource Science, Akita University, Akita, Japan, ⁷Yamanashi Prefectural Government Mount Fuji Research Institute, Yamanashi, Japan, ⁸niversity of Liege Department of Geography, Belgium, Belgium, ⁹Geological Survey of Belgium, Royal Belgian Institute of Natural Sciences, Belgium, Belgium, ¹⁰Ghent University Department of Geology, Belgium, Belgium, ¹¹Geological Survey of Japan, AIST, Tsukuba, Japan

Lake sediments continuously record paleoenvironmental changes and/or the history of volcanic eruptions, and the construction of highly accurate age models is important for paleoclimatic studies. Organic fossils such as leaves, which have been widely used for dating, are useful because they directly record atmospheric radiocarbon(¹⁴C) and are deposited quickly, but they are only rarely found in sediments, limiting high time-resolution studies. Pollen fossils, on the other hand, not only directly reflect atmospheric ¹⁴C, but also are not easily degraded and are commonly contained within sediments, making them valuable for high temporal resolution and high precision dating of any desired layer. However, manually collecting the requisite number of grains is prohibitively time consuming. Therefore, in this study, we applied flow cytometry to separate pollen grains for radiocarbon measurement of the sediments of Lake Motosu, at the northern part of Mt. Fuji, Japan. The ¹⁴C measurements were made using single-stage accelerator mass spectrometer (AMS) at the Atmosphere and Ocean Research Institute, University of Tokyo.

As a result, multiple age values were obtained from the sediments of Motosu Lake. The pollen ¹⁴C age agrees leaf fossils within the analytical uncertainty. Compared to the ¹⁴C age of bulk sediments, ¹⁴C age of pollen fossils are 300 to 350 years younger. Since several thin tephra layers in the sediments of Lake Motosu have been reported possibly to record small-scale eruptions of Mt. Fuji, pollen ¹⁴C dating will be applied above and below each tephra layer to further constrain the timing of Mt. Fuji eruptions.

T03_08

Lifespan of fishes and LA-AMS – Investigations of maximum age for grouper and alligator gar

Andrews A¹, Welte C^{2,3}, Wertnik M^{2,3}, Sanchez P⁴, Rooker J⁴, Daugherty D⁵, Smith N⁵

¹Age and Longevity Research Lab, Honolulu, United States, ²Laboratory of Ion Beam Physics, ETH Zürich, Zürich, Switzerland, ³Geological Institute, ETH Zürich, Zürich, Switzerland, ⁴Texas A&M University at Galveston, Department of Marine Biology, Galveston, USA, ⁵Texas Parks and Wildlife Department, Heart of the Hills Fisheries Science Center, Mountain Home, USA

The longevity of fishes is an important consideration for a proper understanding of population dynamics, survivorship strategies, and consequently management policy. Bomb radiocarbon dating of otoliths (ear stones) has validated lifespans that exceed 50-60 years for long-lived alligator gar and deep-water grouper in North America and the Gulf of Mexico (GoM). However, low variability in radiocarbon concentrations prior to the bomb-produced rise sets a limit for this technique to carbonates deposited after the mid-1950s.

Laser ablation accelerator mass spectrometry (LA-AMS) provides a novel approach through a high-resolution analysis that can locate the rise of bomb-produced radiocarbon within the growth zone

structure, away from the otolith core or nucleus (birth year material) typically sampled with a micromilling machine. In this study, we expand on previous results from red snapper in the GoM (Andrews et al. 2019) by applying the technique to three large-bodied grouper species of the GoM and to three specimens of large and likely very old alligator gar from tributaries to the GoM. Eight otolith thin sections were analyzed with scanning velocities between 5 and 10 μ m/s. Each laser scan was approximately 10 minutes and was unique with regard to the radiocarbon signal. The rise of the bomb peak was identified for each specimen and linked to a location on the sample allowing assignment of a calendar year to that growth zone layer. Overall, ages for each species were validated as being older than a single core extraction could resolve, thus extending longevity estimates for each species.

T03 09

Going with the flow: rapid pollen sorting for radiocarbon analysis

<u>Nakajima K</u>^{1,2}, Heusser C^{1,2}, Welte C^{1,2}, Wacker L², Eglinton T¹ 1 Geological Institute, ETH Zürich, Zürich, Switzerland, 2 Laboratory of Ion Beam Physics, ETH Zürich, Zürich, Switzerland

Pollen grains have long been suggested ideal targets for radiocarbon (14C) dating of terrestrial sediment records. They are ubiquitously abundant in lacustrine sediments and represent atmospheric 14C concentrations as they form each year. Because pollen are established markers for terrestrial ecosystem variability, pollen-based ¹⁴C data provide the ideal, proxy-specific chronology for palynological research. Traditional approaches for pollen separation from sedimentary matrices have proven difficult due to a trade-off between purity, processing time, and yield. In recent years, a growing number of studies have demonstrated the suitability of flow cytometry cell sorters, in combination with physical and chemical processing, for the rapid separation of pollen grains from terrestrial sediments at high purity, e.g., [1]. With a dedicated flow cytometer (BD Influx Cell Sorter, BD Biosciences, US), we examine the robustness of this novel approach to isolate pollen grains for ¹⁴C analysis. We will provide the relevant parameters for reliable sorting and a detailed assessment of sorting efficiencies. First ¹⁴C results with elementalanalyzer-accelerator-mass-spectrometry of blank assessments at different preparation stages of the pollen separation and finally of natural sediment samples show that our protocol is suitable for microscale (< 20 μg C) pollen-¹⁴C dating. This will enable the dating of sediments previously limited by the lack of suitable material. With an established protocol and a dedicated instrument paving the way for routine application, pollen-14C dating will provide a versatile alternative to traditional dating approaches for terrestrial records.

[1] R. K. Tennant et al. (2013), JQS 28(3), 229-236.

T03 10

Data Reduction for Rapid, Continuous Radiocarbon Measurements by Laser Ablation

<u>Wertnik M</u>¹, Wacker L¹, Christl M¹, Synal H¹, Welte C¹ *ETH Zurich, Zurich, Switzerland*

The unique Laser Ablation (LA) setup coupled to a MICADAS Accelerator Mass Spectrometer (AMS) at ETH allows for the rapid measurement of continuous radiocarbon records on carbonate archives (e.g. speleothems, corals, otoliths). Using LA-AMS, 14 C/ 12 C ratios in such archives have been successfully analysed at spatial resolutions of up to 100 μ m.

To ensure stable measurement conditions in the AMS, a continuous carbon flow of approximately 2.5 $\mu g/min$ needs to be produced by the laser. Accordingly, CaCO₃ is ablated at comparably high repetition

rates of 200 Hz, which in turn requires a continuous movement of the sample relative to the laser beam through a positioning system (typical velocities: $5 - 20 \,\mu\text{m/s}$). Single data points are produced at 10 sec intervals resulting in a dense dataset with well localised relative coordinates.

As LA-AMS provides a transient signal, special care needs to be taken in basic data processing and the proper assignment of the measured signal to the sampling location. Important to consider are especially signal extraction and noise reduction as well as mixing and washout effects. Here, we show the current status of data processing and report on improvements in data processing.

T03 11

Radiocarbon dating and differentiation of tsunami deposits from the Isumi River lowland, Eastern Boso Peninsula, Japan

<u>Soichiro O</u>¹, Obrochta S¹, Fujiwara O², Yokoyama Y³, Miyairi Y³, Hatakeyama Y¹
¹Akita University, Akita, Japan, ²National Institute of Advanced Industrial Science and Technology, Tsukuba, Japan, ³University of Tokyo, Kashiwa, Japan

We use high-density radiocarbon dating to assess the age of – and duration between – coarse overwash deposits that punctuate lagoonal to lacustrine sediments in a core recovered from the Eastern Boso Peninsula, Japan. The region has experienced seismic uplift, is now located several meters above sea level, and is prone to both tsunami and typhoon inundation. Several of the overwash beds appear stacked with a fining and thinning upward structure, which is characteristic of deposition by a tsunami "wave train" resulting from a single seismic event. However, without evidence of co-seismic uplift or run-up immediately followed by backwash, it is difficult to rule out a storm origin. We use the age modeling routine undatable to account for radiocarbon age uncertainty, sediment sample thickness, and dating material quality. Age model results indicate that the apparent groups of overwash beds lower in the core are separated by up to decades and therefore represent multiple washover events, and are therefore inconsistent with a tsunami "wave train". The sediment accumulation rate then increased drastically, exceeding 1000 cm/ky at ~2500 cal. BP, after which, many of the grouped overwash beds appear to have accumulated geologically instantaneously, which is consistent with a seismic origin, though further study is needed to identify whether uplift events occured simultaneously to overwash bed deposition. Carbon, nitrogen, and sulfur concentrations further provide information on environmental changes caused by the washover events.

T03_12

The comparison of four ¹⁴C pretreatment methods applied to archaeological shells from Vale Boi (Portugal).

<u>Paleček D</u>¹, Falini G¹, Wacker L², Bicho N³, Talamo S¹

¹Department of Chemistry G. Ciamician, Alma Mater Studiorum University of Bologna, Bologna, Italy, ²Laboratory of Ion Beam Physics, ETH, Zürich, Switzerland, ³Interdisciplinary Centre for Archaeology and the Evolution of Human Behavior, University of Algarve, Faro, Portugal

Mollusc shells are often found in archaeological sites, given their great preservation potential and high value as a multipurpose resource. Vale Boi (Algarve, Portugal) is a well-known Upper Paleolithic archaeological site representing the earliest recorded modern human occupation in southwestern Iberia, as attested by the Early Gravettian remains dated to c. 32 ka Cal BP. The continued use and importance of mollusc shells at this site is attested by their presence throughout the long stratigraphic sequence. Thus, it is especially important to determine their age and purpose at the site. Radiocarbon (¹⁴C) dating is a field in constant improvement; sample pretreatment chemistry is addressed by laboratories across the world, with the continuous development of new and improved protocols. Nevertheless, the pretreatment method for mollusc shells has not changed since the first

application and is still used in many laboratories, although a new protocol was introduced in 2010. In our new ¹⁴C lab (BRAVHO) at Bologna University, we tested and applied these two methods in order to compare them. Furthermore, we introduced two alternative methods to extract the organic matrix from the shell, as it is protected from the environment and should reveal the true age of the shell. Here, we compare the ¹⁴C dates obtained to determine the most reliable pretreatment method for mollusc shells. The results of this study will give us the possibility to construct precise chronologies for sites such as Vale Boi, where shells are abundant throughout the stratigraphic sequence.

T03 P01

Monitoring of biogenic carbon fraction of disposable packaging

Aziz Gill K¹, Michczyńska D¹, Michczyński A¹

¹Silesian University of Technology (Politechnika Śląska), Gliwice, Poland

Disposable packaging materials are typically single use items and commonly used for enclosing or protecting food products during storage, sale, delivery and for the regular use mainly at restaurants. Annually more than 18 million tonnes of waste can be collected in Europe by adopting the best strategies, resulting in 13% reduction in greenhouse gas emitted by packaging wastes. Europe intends to increase the recovered and recycled packaging waste which is 73 million tonnes (Tallentire and Steubing 2020). Disposable packaging prepared from sugarcane or paper can be a source of valuable resources and can overcome the plastic problem. Sugarcane plates are made from renewable sugarcane pulp so the compositing takeaway packaging minimizes the greenhouse gas emissions and improves the soil quality (APSnet). New paper production from waste paper requires less energy and emits less emissions than producing the same amount of paper from virgin materials, thus the recycling of waste paper could be beneficial to the environment (Merrild et al. 2008).

Our research aims to examine the ¹⁴C isotope concentration in disposable waste materials to make sure if indeed the materials contain some concentration of biogenic carbon to cause green effect in recycling. We examine the disposable paper plates, cups, straws, baking paper, sugar cane and wheat materials. The results of the measurements of bio carbon made by LSC and AMS techniques at Radiocarbon Laboratory in Gliwice (Pazdur et al. 2003; Piotrowska 2013) will be presented.

T03_P02

A new online ramped oxidation (ORO) system for improved coupled thermal and radiocarbon dissection of complex natural organic matter

<u>Bolandini M</u>¹, Bröder L¹, De Maria D², Eglinton T¹, Wacker L²

¹D-ERDW - Biogeoscience Group, ETH, Zürich, Switzerland, ²D-PHYS - Laboratory for Ion Beam Physics (LIP), ETH, Zürich, Switzerland

The coupling of serial or ramped pyrolysis and oxidation to carbon isotope measurements provides insights into the relationships between thermal activation energies and age distributions of natural organic materials. It therefore helps to elucidate controls on organic matter reactivity. The conventional approach involves heating of a bulk sample with a defined temperature ramp, simultaneous oxidation of thermal decomposition products, and collection of the resulting to CO_2 for subsequent ¹⁴C analysis.

The newly developed online ramped oxidation (ORO) system has been designed to sequentially trap and release evolved CO_2 via a customized interface to a gas-accepting source of an accelerator mass spectrometer (AMS), facilitating higher thermal and isotopic resolution of organic constituents. This is achieved via a two-stage oven that regulates the decomposition and subsequent oxidation of carbonaceous compounds to CO_2 in a mixture of He and O_2 . This is coupled with a double zeolite trap interface (DTI, De Maria et al. 2021) that modulates the collection and transfer of evolved CO_2 to the AMS system for ¹⁴C measurement.

A functioning prototype of the ORO system has been developed to perform initial combustion tests. To this end, blanks, standard material, and samples from complex matrices such as soils, river, lake, and marine sediments are being measured and results compared with reference data.

T03 P03

¹⁴C blank determination for compound-specific radiocarbon analysis of lignin phenols

Cao M¹, Hefter J¹, Grotheer H¹, Mollenhauer G^{1,2}

¹Alfred Wegener Institute For Polar And Marine Research, Bremerhaven, Germany, ²MARUM-Center for Marine Environmental Sciences, University of Bremen, Bremen, Germany

Compound-specific radiocarbon analysis (CSRA) is one technique commonly used to constrain the cycling of biomarkers, such as lignin, between reservoirs. However, purification procedures of lignin for CSRA are prone to introduce extraneous (blank) carbon into the samples. These blanks will potentially lead to erroneous interpretation of lignin CRSA results, making the assessment of procedural blanks an important prerequisite. We describe a revised method for purification of lignin from sediment and evaluate F¹⁴C and the mass of the associated procedural blank following the method of Sun et al. (2020). We used two commercially available lignin phenol standards with known age and validated the procedure with lignin extracted from a standard sediment using the method of Goñi and Montgomery (2000). We isolated lignin phenols by HLB SPE cartridges (Waters Oasis, 200 mg, 6 ml) followed by single compound collection using high pressure liquid chromatography. Ten lignin-derived compounds were purified with a Phenomenex Synergi Polar-RP column and three compounds were isolated by a ZORBAX Eclipse XDB-C18 column. Radiocarbon analyses of several different sized aliquots of the standard compounds were performed on the miniaturized radiocarbon dating system at Alfred Wegener Institute, Germany (Mollenhauer et al., 2021). Samples were transferred into tin cups and combusted using an elementar analyser coupled with the gas interface system. We report the current status of carbon blanks associated with our preparation protocol for radiocarbon analysis of lignin phenols.

T03 P04

Update of radiocarbon analyses on dissolved inorganic carbon of seawater at ETH-Zurich

<u>Castrillejo M</u>^{1,2}, Wacker L², Bollhalder S², Casacuberta N^{2,3}, Kündig K^{2,3}, Leist L³, Scacco G², Synal H², Wefing $A^{2,3}$

¹Department of Physics, Imperial College London, London, United Kingdom, ²Laboratory of Ion Beam Physics, ETH-Zurich, Switzerland, ³Department of Environmental Systems Science, ETH-Zurich, Zurich, Switzerland

In recent years, the Laboratory of Ion Beam Physics (LIP) has been actively involved in oceanographic expeditions to collect samples and measure radiocarbon on dissolved inorganic carbon of seawater. This work has been possible thanks to a new analytical method developed through the collaboration between oceanographers and experts in radiocarbon analysis at LIP. The fully automated method coupling the CO₂ extraction and graphitisation steps in a single line allows for rapid and precise determination of the radiocarbon content using only 50 ml of seawater. The method performs simultaneously on 7 samples and allows the processing of 21 samples a day.

Over the past two years, we have gained experience in sample collection, storage and processing allowing us to provide a substantial update on the ETH-LIP method that was first published by Casacuberta et al., (2020). We have compiled data on blanks, coral sample used as reference material, seawater replicates and data from a first interlaboratory exercise. Based on these new data, we discuss aspects related to sample collection and storage, background correction, accuracy, reproducibility and data comparability.

Casacuberta N., Castrillejo M., Wefing A.M., Bollhalder S., Wacker L. 2020. High precision ¹⁴C analysis in small seawater samples. Radiocarbon 62(1):13–24.

T03 P05

Direct graphitization of CO₂ from atmospheric air

<u>Gautschi</u> P¹, Wacker L¹, Synal H¹
¹ETH Zurich, Zurich, Switzerland

The atmospheric concentration of carbon dioxide (CO_2) is increasing rapidly since the industrialization. Emission of ¹⁴C free CO_2 from the combustion of fossil fuels, such as coal, oil or gas, reduces the ¹⁴ CO_2 to ¹² CO_2 ratio in the atmosphere. When the background ¹⁴ CO_2 level is known, the local surplus of fossil CO_2 in ppm can be calculated using the measured CO_2 concentration and the ¹⁴ CO_2 abundance at a given sampling site.

A simple and fast method to prepare whole-air samples for radiocarbon analysis of atmospheric CO_2 has been developed and tested at ETH Zurich. Atmospheric air is collected in sampling bags (5 L) and then transported back to the laboratory, where CO_2 is isolated using the molecular sieve trap implemented in the automated graphitization line AGE3. The trapped CO_2 is then graphitized and measured by accelerator mass spectrometry (AMS).

A programmable air loading box to automatically collect and graphitize up to seven air samples at a time was constructed for reliable and repeatable results. A major benefit of the presented method is the reduced labour needed for sampling and graphitization. In a pilot study, twelve air samples were automatically collected within 1.5 days near the city of Zurich and later graphitized within another day.

T03 P06

DOC radiocarbon measurements at the AWI-MICADAS facility, current method developments and improvements

<u>Grotheer H</u>^{1,2}, Gentz T¹, Höhn M¹, Kattein L¹, Schlagenhauff S¹, Hefter J¹, Mollenhauer G^{1,2}

¹Alfred Wegener Institute Helmholtz Centre for Polar and Marine Research, Bremerhaven, Germany, ²University Bremen, Dept. of Geosciences and MARUM, Bremen, Germany

Reliable radiocarbon ages of dissolved organic carbon (DOC) are a perquisite to obtain improved understanding of current carbon cycle dynamics. Dissolved organic matter (DOM) is an extremely complex natural organic mixture consisting of tens of thousands of individual compounds with a large variety of chemical and physical properties. Because of this complexity and the presence of sea salt, radiocarbon sample preparation for marine DOC is very challenging as available methods for extraction and purification (SPE, or ultra-filtration) depend on either physical or chemical properties and thus only consider a fraction of the DOC pool amenable to the preparation method. Consequently, the sample preparation selectivity hampers our wholistic understanding of the DOC pool, its cycling and reactivity. Today the only method available considered to reliably report bulk DOC radiocarbon composition is ultraviolet oxidation (UVox), where irrespectively of chemical or physical properties DOC molecules are quantitatively oxidized to CO₂. However, UVox is only available at a few very specialized laboratories, is very time consuming and tedious.

We will report on ongoing method developments for processing marine DOC by utilizing a modified, commercially available Gräntzel thin-film flow-through reactor enabling fast sample processing. The offline UVox system is coupled via a custom-built zeolite trap to the existing GIS infrastructure of the MICADAS system. Technical details, reproducibility tests and current blank levels will be reported.

DIC radiocarbon measurements at the AWI-MICADAS facility, current method developments and improvements

Grotheer H^{1,2}, Gentz T¹, Hammes J³, Hefter J¹, Mollenhauer G^{1,2}

¹Alfred Wegener Institute Helmholtz Centre for Polar and Marine Research, Bremerhaven, Germany, ²University Bremen, Dept. of Geosciences and MARUM, Bremen, Germany, ³University Bonn, Dept. of Geosciences, Bonn, Germany

Reliable radiocarbon ages of dissolved inorganic carbon (DIC) are a perquisite to obtain improved understanding of current carbon cycle dynamics. With the advance of small-scale radiocarbon measurements, it became possible to analyze samples in unprecedented spatial resolution and increasing precision obtained by replicate analysis. Small sample requirements allow reliable dating of DIC samples from even the most remote places on Earth, where access is challenging, and available material limited in quantities. Reliable high precision methodologies for these precious sample sizes are required, and due to the lack of accepted Δ^{14} C DIC standard material a sample processing consensus must be developed within the community.

We will report on ongoing method improvements for processing marine dissolved inorganic carbon samples. Our developments utilize the standard MICADAS peripheral carbonate handling system (CHS) coupled via the gas interface system (GIS) to the AWI-MICADAS. We report on reproducible ¹⁴C dates measured on DIC samples as small as 2 mL sea water. We describe our method improvement pathway including testing of different acids for DIC outgassing, sampling duration and volume dependency on ¹⁴C replicability.

T03_P08

A new UV-Oxidation set up for AMS radiocarbon analysis for small dissolved organic carbon in marine and fresh water samples

Haghipour N^{1,2}, Lupker M¹, Wacker L², Eglinton T¹

¹Geological Institute, ETH Zurich, Zurich, Switzerland, ²Laboratory of Ion Beam Physics, ETH Zurich, Zurich, Switzerland

Radiocarbon measurements of dissolved organic carbon (DOC) can give us valuable information about origin and age of DOC, a major, yet little understood component in the global carbon cycle. One way to measure DOC in water is to remove dissolved inorganic carbon first, oxidize organic carbon with UV irradiation and ultimately analyses the formed inorganic CO₂ for ¹⁴C. The main challenge of UV-Oxidation (UVox) methods is to extract the typically low concentrations of DOC with low blanks required for relatively high precision ¹⁴C measurements. A disadvantage of currently used UVox methods is that only one sample can be oxidized in a laborious process at the same time. Here we present a UV-Oxidation system where up to 12 water samples can be oxidized simultaneously in 12 separate quartz reactors arranged around a single UV lamp in a compact setup. The simple setup further uses helium instead of vacuum typically used by conventional extraction lines to speed up the extraction of the formed CO2 after oxidation. The key improvements of the new UVox setup are: 1) Reduced amount of water needed (30- 60 ml) as samples are measured for ¹⁴C with the Micadas gas ion source, 2) UV oxidation efficiency for standards is high (96%), 3) No KI trap is needed,4) Required time for sample preparation of up to 12 samples is 4-6 h. To test the oxidation efficiency, reproducibility and blank assessment we used different reference materials. Here we discuss the preliminary results from the performance of UVox extraction line.

One-pot processing of tree-ring samples for ¹⁴C analysis on cellulose

<u>PHOUYBANHDYT B</u>^{1,4}, DU BOISGUEHENEUC D^{1,2,4}, DAUX V¹, NOURY C¹, PIERRE M¹, STIEVENARD M¹, THIL F¹, HATTÉ C^{1,3}

¹Laboratoire des Sciences du Climat et de l'Environnement, Gif-sur-Yvette, France, ²Archéozoologie, Archéobotanique : Sociétés, Pratiques et Environnements, Paris, France, ³Silesian University of Technology, Gliwice, Poland, ⁴These authors contributed equally to this work, ,

Analyzing the radiocarbon fraction in tree rings is fundamental to the radiocarbon method in order to calibrate ¹⁴C years into calendar years. The increasing interest in measuring ¹⁴C at annual resolution implies an even larger number of tree-ring samples to be pretreated. And this, focusing on latewood cellulose to ensure that the carbon originates from only one year and has not been exchanged since formation.

To put ourselves on a battle footing for several projects we are involved in and that require large series of measurements, we confronted our protocol to others available in literature. We finally settled on an adaptation of the protocol used for stable isotopes measurements at LSCE that derives from the original protocol of Leavitt and Danzer (1993). We also considered some advice of Southon and Magana (2010) and added our own "touch".

The chemistry is done in a 1.5 L Erlenmeyer flask in which the samples and standards are pooled, packed in an individual Teflon bag. The protocol is divided into three main steps: removal of water-soluble compounds, removal of lignin by a two-step oxidative delignification and removal of hemicellulose by alkaline extraction.

Our protocol allows the preparation of up to fifteen samples and five standards at the same time, without cross-contamination, saving thus time in handling and reducing chemical consumption. We present here the results we obtained on blanks and reference materials of different ages. They clearly indicate that this protocol allows to obtain results as accurate as with individual treatments.

T03 P10

Application of ¹⁴C dating of earthworm biospheroids to investigate paleosol formation

Kertész T^{1,2}, Gergely V¹, Buró B¹, Molnár M¹

¹Institute for Nuclear Research, Debrecen, Hungary, ²Doctoral School of Earth Sciences, University of Debrecen, Debrecen, Hungary

¹⁴C dating of paleosols is a challenging task as ordinary soil organic matter (SOM) does not give a realistic ¹⁴C age of a soil layer. If one could not find some macrofossil remains in the discovered soil horizon then the age determination is always a matter of debate. In this study we have investigated the earthworms produced biospheroids as a possible material for soil ¹⁴C dating. Recent studies suggested that earthworms consume preferably fresh organic matter during their life in the soil, which means the products of their digestion would contain rather recent organic carbon instead of the aged carbon from the SOM fraction.

Although biospheroids are rather small (diameter < 2 mm and mass < 5 mg) pure calcite granules, AMS technique gives the possibility of their radiocarbon dating.

We have investigated 8 different recent topsoil samples collected at 5 different localities in the Hajdúság area (Hungary). Results confirmed that contemporary biospheroids mostly contain young (max age 30 years) carbon, which gives realistic (zero) age. The method was applied on buried paleobiospheroids from the 10-50 krys old paleosol profile at Süttő (Hungary). ¹⁴C ages were compared with previous OSL data too. The ¹⁴C results (29), cover a 6.1 m long section, with 10 cm resolution, and show an very consistent picture with the previous OSL results and also some with ¹⁴C ages of conventional macrofossil

from the same profile. Multiple repeated measurements were performed for reproducibility. Control samples may be present in the paleoenvironmental study of later Quaternary paleosols.

T03 P11

Simple method for analyses of total radiocarbon in water samples using wet chemical oxidation at HEKAL AMS Laboratory

Molnár A^{1,2}, Molnár M^{1,3}, Veres M², Czébely A², Rinyu L^{2,3}, Rozmanitz P⁴, Janovics R^{2,3}
¹University of Debrecen, Doctoral School of Physics, Debrecen, Hungary, ²Isotoptech Zrt., Debrecen, Hungary,
³INTERACT Centre, Institute for Nuclear Research, Debrecen, Hungary, ⁴Paks Nuclear Power Plant, Paks, Hungary

The ¹⁴C is the one of the most important radionuclides released from the nuclear facilities to the environment. Currently, the inorganic ¹⁴C is checked during regular environmental monitoring as part of the groundwater monitoring programme of the Paks Nuclear Power Plant.

One of disadvantages of the only inorganic carbon determination is that the DIC concentration has a significant dilution effect by the natural radiocarbon content of the groundwater on any discharged pollution surrounding the power plant.

For this reason, a wet oxidation method was developed for AMS ¹⁴C measurement technique to determine the ¹⁴C activity concentration of the total dissolved carbon content of water samples, coming from environmental monitoring wells. The typical ¹⁴C background is (1-2 pMC) obtained by preparation of blank samples, which allows a detection level of around 5·10-5 Bq L-1. The activity of the organic fraction can be calculated using the formula presented in the study. The method was applied for water samples deriving from environmental monitoring wells around Paks Nuclear Power Plant (pressurized-water reactors (PWR)). The results of our investigations over the 14 different water samples around the Paks NPP show that DO¹⁴C contribution to the total ¹⁴C activity concentration was between 5-25%. The elaborated method may be useful mostly upon the environmental monitoring analyses of nuclear facilities and radioactive waste disposal facilities, as with the help of this method, the total radiocarbon activity of groundwater can be determined as easily, as the commonly applied DI¹⁴C analyses.

T03_P12

First attempt of carbon extration for radiocarbon dating of ancient iron

PERRON M¹, Farcage D², Delqué-Kolic E¹, Semerok A², Leroy S³

¹Laboratoire des Sciences du Climat et de l'Environnement (LSCE - LMC14), Gif Sur Yvette, France, ²Service d'Études Analytiques et de Réactivité des Surfaces (SEARS), Gif Sur Yvette, France, ³Laboratoire Archéomatériaux et Prévision de l'Altération (LAPA), Gif Sur Yvette, France

The dating of steels by carbon 14 is a complex process involving the preliminary analysis of the material in order to identify the most carburized areas. Indeed, in archaeological steels, the low level of carbon and its heterogeneous distribution in the ferrous matrix lead to targeted sampling in areas rich in cementite (iron carbide). Currently, the sampling is carried out using a drill equipped with high-speed steel forests coated with titanium nitride of 2 to 3 mm in diameter. Finding that the precision of the samples was not optimal, we tested the extraction of carbon using a laser beam (Ytterbium 1064 nm fiber laser). In our device, the sample is placed in an enclosure in the presence of oxygen and then scanned by the laser beam that follows the sampling area defined by the metallographic observation. Another advantage of laser beam extraction is the direct formation of CO_2 in the cell, thus combining sampling and combustion in one step.

After some reminders on the dating of steels by carbon 14, we will present the installation developed for the extraction of carbon by laser beam and the conditions of handling. We will explain the first dating result obtained.

Radiocarbon dating putative homonin coprolites

Roberts M¹, Trowbridge N¹, Lardie Gaylord¹, Sistiaga A^{2,3}, Haws J⁴, Mojarro A³, Summons R³

¹Woods Hole Oceanographic Institution, Woods Hole, United States of America, ²Center for Evolutionary Hologenomics, University of Copenhagen, Copenhagen, Denmark, ³Department of Earth, Atmospheric and Planetary Sciences, Massachusetts Institute of Technology, Cambridge, United States of America, ⁴Dept. of Anthropology, University of Louisville, Louisville, United States of America

Several coprolites from a homonin habitation site on the Iberian Peninsula were recently submitted for radiocarbon analysis. Coprolites are proxies of the presence and diet of ancient animal populations. Based on chronostratigraphy, an average age of at least 40 kyr BC was expected. Bulk analysis of the organic fraction of the individual coprolites returned an average calibrated age of 28,000 (+/- 1000) (calBC). To better understand the conflict between the expected and measured ages, and to accommodate the very low total organic carbon of the samples, the organic fraction of a composite coprolite sample was further analyzed using the ramped pyrolysis and oxidation (RPO) system at Woods Hole. The sample was sequentially oxidized from room temperature to 1000 C at 5 °C/min and the evolved carbon dioxide was collected from five different temperature ranges or fractions. The first four temperature fractions returned calibrated ages all less than 31,000 (calBC). However, the highest temperature fraction (525-705 °C) returned a calibrated age of 39,900 (+/- 8,800) (calBC) in agreement with the chronostratigraphy. Analysis of the fractions using pyrolysis-GC-MS showed that only the high temperature faction released steroid biomarkers consistent with fecal matter. Phytosterols were detected in addition to trace amounts of coprostanol. Furthermore, a high temperature fraction between 525-600 °C pyrolyzed in the presence of a silylating reagent (MTBSTFA/DMF) enabled the identification of cholesterol and cholestanol. Utilizing the RPO system for coprolite radiocarbon analysis may provide a more representative age than bulk organic analysis. Sample preparation and measurement procedures will be presented.

T03_P14

Palynological samples in marine cores: pollen extraction, dating, comparison with foraminiferal shells: a methodological challenge to investigate past reservoir ages

<u>Tisnerat-laborde</u> N^2 , Coussin V^2 , Thil F^1 , Combrieu-Nebout N^3 , Fersi W^2 , Eynaud F^4 , Toucanne S^5 , Babonneau N^2 , Cattaneo A^5 , Penaud A^2

¹LSCE/IPSL , Gif-sur-Yvette, France, ²LGO Univ Brest IUEM, Plouzané, France, ³HNHP/CNRS-MNHN-UPVD, Paris, France, ⁴EPOC-OASU, Univ.Bordeaux, Pessac, France, ⁵IFREMER, Geosciences Marines, Plouzané, France

The reconstruction of changes in marine reservoir age is a particularly challenging task but essential in paleo-oceanography to improve the chrono-stratigraphy of marine cores. In this work we have investigated the possibility of using continental material as monospecific pollen grains (Pinus) as well as palynological treatment residues (bulk or additionally treated with KOH to dissolve amorphous organic matter) and foraminifera collected in the same levels to study reservoir age variations over time (INSU EC2CO-LEFE project "DATAPOL").

In a first step, we describe the methodology developed to extract pollen grains on cores MD04-2801 (Algerian Margin, Holocene) and MD13-3438 (northern Bay of Biscay, Heinrich Stadial 1) and the physico-chemical treatments of pollen carried out before ECHoMICADAS dating. The ¹⁴C results obtained between foraminifera, pollen, and palynological residues are here presented for the first time, highlighting a great variability of ages according to the nature of dated samples (organic matter vs. calcite). These first results raise questions about the effects reservoir ages of bottom water masses and potential diagenetic impacts on palynomorph membranes during organic matter fossilization. We also preliminary show that the use of palynological residues cannot be used to date marine cores. However,

new methodological investigation is necessary to find solutions to sort pollen more efficiently to advance the ¹⁴C dating of monospecific pollen samples.

T03 P15

Radiocarbon based fossil component analysis of food products

Varga T1, Molnár M1

¹ELKH - Institute for Nuclear Research - INTERACT, Debrecen, Hungary

The accelerator mass spectrometry and radiocarbon based bio and fossil component ratio analysis is widely used for plastic and fuel materials, but it is not frequently used for food products. Several materials, what are generally used in the food industry, can contain fossil carbon like the food coloring, flavouring and sweetener materials, due to the cost effective production. In general, the molecular composition of these materials are the same compared to the biol-based ones. In this case, the radiocarbon based analysis is one of the best way to distinguish the biological and fossil sources in these products. In this study, we present our ¹⁴C based fossil component analysis results on commercial food products and raw materials. The results show that several food and drink can contain more than a few percent fossil carbon, but generally, most of the food products are 100 % bio-based. The highest fossil component ratio was determined in the food coloring materials.

T03 P16

Inorganic radiocarbon dating of a moraine profile – a case study in a LGM moraine in Tianshan Mountains

Yi C^{1,4}, Liu X², Liu K³, Yi R^{1,3}

¹Beijing Niandai(dating) Company, Beijing, China, ²Institute of Heavey Ion Physics, Peking University, Beijing, China, ³Zhijiudiance (Nuclide-electron dating) company at Suzhou, Suzhou, China, ⁴Institute of Tibetan Plateau Research, Chine Academy of Sciences, Beijing, China

Organic matter in glacial moraines in humid areas is used to date the burial ages of glaciations using radiocarbon. However, biomass is rare in glacial sediments in arid and semi-arid areas. Our results show that a moraine in the source area of the Urumqi River valley, Tianshan Mountains was dated to 20790+140 yr cal using carbonate in fine, very similar to 10 Be exposure dating age. The ages of the upper part of the profile were younger than the middle part and then younger than the lower part. The ages in coarse size fraction (250-125 μ m) were younger than medium size fraction (125-63 μ m) and then younger than fine size fraction (< 63 μ m). The carbonate deposits on a roche moutonnee in front of Glacier 1 and in the matrix of a modern till were dated to modern carbon. We suggest that inorganic carbon decomposed from calcium minerals dissolving in subglacial meltwater was exchanged sufficiently with atmospheric carbon. When a glacier melted, pressure in sediment decreased and carbonate precipitated on the surface of the particles. Vertical movement of ground water dominates in arid and semi-arid areas. The carbon in the upper part of the sediment was most likely exchanged with atmospheric carbon after post deposition. The fraction with large grain size has large voids which were easily let water pass through for carbon exchange and 14 C age become younger. At a depth, exchange of carbon in fine matrix with atmosphere was weak and 14 C can be used for dating glacial moraine.

T04 New and updated facilities, Lab management, status reports

T04 P01

¹⁴C Measurement of Samples for Environmental Applications at the National Environmental Isotope Facility (NEIF) Radiocarbon Laboratory, SUERC, UK.

<u>Ascough P</u>¹, Bompard N¹, Garnett M¹, Gulliver P¹, Murray C¹, Newton J¹, Taylor C¹

**ISUERC, University Of Glasgow, East Kilbride, United Kingdom

The National Environmental Isotope Facility (NEIF) Radiocarbon Laboratory at the Scottish Universities Environmental Research Centre (SUERC) performs radiocarbon measurement of a wide range of sample matrices for applications in environmental research. The laboratory is funded by the UK's National Environment Research Council (NERC), as part of NERC's Scientific Services and Facilities portfolio. Radiocarbon is applied to palaeoenvironmental, palaeoceanographic, and palaeoclimatic investigations, as well as work to understand the source, fate, turnover, and age of the carbon in the modern carbon cycle. The NEIF Radiocarbon laboratory supports users in the development and deployment of novel sampling techniques and laboratory approaches. Here, we give an overview of methods and procedures used by the laboratory to support the field collection of samples and to perform the physical and chemical pretreatment of samples. This includes in-house development of novel and/or specialised methods and approaches, such as field collection of CO₂ and CH₄, hydropyrolysis, and ramped oxidation. The sample types covered include organic remains (e.g. plant material, peat, wood, charcoal, proteins), carbonates (e.g. speleothems, foraminifera, mollusc shell, travertine), waters (dissolved organic and inorganic carbon), gases (CO₂ and CH₄), soils and sediments (including sub-fractions).

T04_P02

New Installations at ¹⁴CHRONO, Queen's University Belfast: Ionplus MICADAS (Mini Carbon Dating System) and AGE (Automated Graphitisation Equipment) system upgrades

<u>Barrett G</u>¹, Allen K¹, Blaauw M¹, Reimer R¹, Reimer P¹

14Chrono, Queen's University Belfast, Belfast, United Kingdom

A laboratory upgrade, carried out in 2021, featured the installation of an Ionplus MICADAS, replacing a National Electrostatics Corporation 0.5MeV compact AMS system that had been in operation since 2007, and an Ionplus AGE, enhancing our existing graphitization capabilities. Post-installation validation tests for a range of intercomparison samples, secondary standards and backgrounds are presented and demonstrate agreement with consensus values and/or long-term measurements on our previous machine. A series of replicate measurements on 15 unknowns (bone and sediment) with well-distributed radiocarbon ages spanning approx. 170-12000 yr BP, previously measured with our NEC AMS on graphite from our zinc reduction line, is also presented; again, there is excellent agreement between both sets of measurements.

MAG-C63: a tree-ring standard for AD 1586

<u>Bayliss A</u>¹, Canti M¹, Dee M², Howard R³, Miles D⁴, Tyers C¹, Wacker L⁵

¹Historic England, London, United Kingdom, ²Rijksuniversiteit Groningen, Groningen, The Netherlands, ³Nottingham Tree-ring Dating Laboratory, Nottingham, UK, ⁴Oxford Dendrochronology Laboratory, Mapledurham, UK, ⁵ETH Zürich, Zürich, Switzerland

Standard materials are fundamental for accurate radiocarbon dating, but must be available in sufficient quantities for all AMS facilities worldwide to use as required. MAG-C63 is a beam removed from the Great Tower at St Mary Magdalen College, Oxford (51.75°N, 1.24°W) during repair works in the 1960s. It is 6.1m long, by 0.3m square and weighs over a metric tonne. It has been securely dated by ring-width dendrochronology as spanning AD 1487-1629, and has been purchased in its entirety by Historic England.

The ring selected for use as a tree-ring standard is that for AD 1586. It is 2.76mm wide, and sufficiently close to the outside of the timber that dissection in quantity is feasible, yet far enough from the outside of the timber to minimise the potential for contamination. Whole rings (earlywood and latewood) have been dissected by professional dendrochronologists, each sample being split across the ring so that it contains roughly equal amounts of earlywood and latewood. Each sample weighs approximately 50mg. We estimate that MAG-C63 will supply 40,000 such samples.

T04 P04

20 years of radiocarbon dating using the ARTEMIS facility at the LMC14 National Laboratory: review of service and research activities

<u>Beck L</u>¹, Caffy I¹, Delqué-Količ E¹, Dumoulin J¹, Goulas C¹, Hain S¹, Moreau C¹, Perron M¹, Setti V¹, Sieudat M¹, Thellier B¹

¹LMC14, Gif-sur-Yvette, France

In 2001, five French public organizations (CNRS, CEA, IRD, IRSN and Ministère de la Culture) signed an agreement to purchase a new Accelerator Mass Spectrometer for providing radiocarbon dating services at the national level. The Laboratoire de Mesure du ¹⁴C (LMC14) was set up in Saclay (France) around ARTEMIS, an AMS system based on a 3MV Pelletron from National Electrostatics Corporation (NEC; Middleton, Wisconsin, USA) and installed early 2003 (Cottereau et al. 2007). In 2015, the LMC14 joined the Laboratoire des Sciences du Climat et de l'Environnement, which allows to develop research projects in addition of the service activity. Since 2021, the LMC14 is a member of the IAEA Collaborating Centre "Atoms for Heritage" at the Université Paris-Saclay.

70 000 samples have been measured since then. Two-thirds of the samples have been prepared on site (wood, charcoal, carbonates, iron,...) and one-third in associated laboratories in Paris and Lyon (wood, charcoal, bones, ivory, hair,...). Over the past years, the LMC14 has participated to several international inter-comparisons (SIRI and GIRI) and has continuously improved its capabilities by developing new protocols for preparation and measurement (Dumoulin et al. 2017; Moreau et al. 2020). In this presentation, radiocarbon dating services of the last 20 years for research laboratories, museums and environmental monitoring will be reviewed and recent results from research programs on environmental and archaeological studies will be highlighted.

Facility Report: NOSAMS operations and the new MICADAS

<u>Broek T</u>¹, Roberts M¹, Longworth B¹, Burton J¹, Crossen A¹, Cruz A¹, Elder K¹, Gagnon A¹, Gospodinova K¹, Handwork S¹, Hansman R¹, Kurz M¹, Lardie Gaylord M¹, Trowbridge N¹, Xu L¹, Lang S¹

¹National Ocean Sciences Accelerator Mass Spectrometry Facility, Woods Hole, United States

The National Ocean Sciences Accelerator Mass Spectrometry (NOSAMS) facility at Woods Hole Oceanographic Institution provides ¹⁴C-AMS analyses and expertise in support of the US oceanographic and earth science communities. NOSAMS measures on average 7,300 unknowns per year on two unique AMS instruments. The CFAMS system, commissioned in 2006, is based around a 500 kV NEC Pelletron tandem accelerator and a modified 134 position NEC MC-SNICS ion source and currently serves as the primary instrument for client samples. In late 2021, the original NOSAMS 3 MV USAMS Tandetron instrument, in operation since 1992, was decommissioned and replaced in 2022 with an IonPlus 200 kV MICADAS with gas interface and associated sample introduction peripherals (elemental analyzer and carbonate handling system). Here, we provide an update on the NOSAMS facility AMS systems and present results from the initial implementation and operation of the MICADAS, including quantification of system accuracy and precision with both solid and gaseous samples, comparison of data from materials measured as both graphite and CO₂ gas, performance of small (<100 μg C) solid samples, and modifications to solid sample targets. We also discuss integration of the new system into our laboratory workflows, data reduction software, and database system.

T04 P06

Performance and inter-comparison tests of the MICADAS at the radiocarbon laboratory of Lanzhou University, China

Cao H¹, Zhou A¹, Wang Z¹

¹College of Earth and Environmental Sciences, Lanzhou University, Lanzhou, China

Radiocarbon laboratory of Lanzhou University was primitively organized in 1987, experienced long-term complement and development, and introduced a compact accelerator mass spectrometer (AMS)—a 200-KV mini carbon dating system (MICADAS) from lonplus AG in 2018, together with an auto graphitization equipment (AGE III). The laboratory has for a long time prepared graphite targets for radiocarbon dating of organic materials including charcoal, bone, plant remains, sediments. Herein, we give an overview of the operating status and performance of the dating facility. Fifteen sets of organic materials collected from archaeological sites in northwest China were selected for an inter-comparison study involving the participation of four specialist laboratories, the pretreatment, graphite preparation, and AMS testing of the samples were performed, respectively. The ¹⁴C dating results showed a high degree of consensus for the homogenized samples. The long-term measurement of the standard and blank samples indicated the that the results for MICADAS in Lanzhou University were accurate and stable and of high sensitivity, the mean background is about 47,000 years. The radiocarbon laboratory of Lanzhou University could provide stable and accurate ¹⁴C dating results, and has provided a large number of ¹⁴C dates for archaeological/environmental samples.

Recent Results from the Office of Archaeological Studies Plasma Oxidation Laboratory, Santa Fe, New Mexico

<u>Cox J</u>¹, Rowe M¹, Blinman E¹, Jones S¹, Welte C^{2,3}

¹Office Of Archaeological Studies, Center for New Mexico Archaeology, Santa Fe, United States, ²Laboratory of Ion Beam Physics, ETH Zűrich, HPK, H29, Otto-Stern-Weg 5, CH-8093, Zűrich, Switzerland, ³Geological Institute, ETH Zürich, NO, Sonneggstrasse 5, CH-8092, Zűrich, Switzerland

The plasma technique was originally developed in conjunction with dating rock art by Marvin Rowe at Texas A&M University. After retiring, Dr. Rowe moved to Santa Fe, NM where he helped establish our current plasma oxidation laboratory in 2013. Advantages of the plasma technique include the ability to produce very small samples for processing (20-100 µg carbon), no necessity for removal of carbonates or oxalates due to operational temperatures usually below 50°C, virtually non-destructive sampling, removing minute amounts of surface carbon and the ability to collect multiple dates from a single sample. In recent years, the Plasma Oxidation Laboratory has processed a wide variety of materials. In addition to using the plasma with standards, other materials include an alleged Picasso painting, multilayered extractions of soot, a probable Lewis and Clark iron axe head, Egyptian and Pecos River mummies and of course, rock art.

T04_P08

A new automatic sample preparation line for radiocarbon measurements on the carbonaceous fractions of atmospheric aerosol

<u>Crova F</u>¹, Barone S^{2,3}, Calzolai G², Chiari M², Fedi M², Forello A^{1,3}, Liccioli L², Lucarelli F^{2,3}, Massabò D⁴, Nava S^{2,3}, Prati P⁴, Valentini S¹, Valli G¹, Vecchi R¹, Bernardoni V¹

¹Department of Physics, Università degli Studi di Milano, and INFN-Milano, Milan, Italy, ²INFN-Firenze, Sesto Fiorentino, Italy, ³Department of Physics and Astronomy, Università degli Studi di Firenze, Sesto Fiorentino, Italy, ⁴Department of Physics, Università degli Studi di Genova, and INFN-Genova, Genoa, Italy

Radiocarbon measurements on organic and elemental carbon fractions are a powerful tool for separating the contribution due to fossil fuel combustion, biomass burning and natural sources to the emission of carbonaceous aerosols in the atmosphere [Szidat et al., 2006].

At INFN-LABEC in Florence, radiocarbon measurements on separated carbon fractions have been so far performed exploiting proper thermal protocols and a dedicated sample preparation line, which however is entirely manually operated and suitable for samples of about 200 μ gC [Bernardoni et al., 2013; Calzolai et al., 2011].

Recent developments at LABEC now allow the 14 C-AMS measurements of significantly smaller samples (about 50 µgC) mainly thanks to a new graphitization line [Fedi et al., 2020]. Following this experience, a new sample preparation line dedicated to atmospheric aerosol samples was designed and realised as part of the INFN-ISPIRA experiment (Integration of experimental methodologies for carbonaceous aerosol research) in Milan. The line scheme remains unchanged, but innovative elements allow the preparation of small-size samples in a partially automatic way, thanks to the automatic switch of combustion gas (He/Oxygen) and temperature ramps control in the different combustion phases, and the automatic maintenance of the temperature inside the cold traps for the CO_2 purification and collection. Thanks to these upgrades a higher number of samples will be prepared, and smaller samples (e.g., collected with higher temporal resolution or at remote sites) will be analysable, thus allowing to obtain more representative data.

The poster will present the features of the new experimental setup and the first tests.

Capabilities, Procedures, and Summary Statistics of the MICADAS and GIS at ACE Isotope Laboratory, Northern Arizona University

<u>Ebert C</u>¹, Schuur E¹, Kaufman D¹, Brown J¹, Propster J¹, Kelley A¹, Bright J¹, Carbone M¹, McKay N¹, Koch G¹

*Northern Arizona University, Flagstaff, United States

The Arizona Climate and Ecosystems (ACE) Isotope Laboratory at Northern Arizona University brought a MICADAS online on June 1, 2021. Our lab includes a Gas Ion Source (GIS) with a Carbonate Handling System (CHS2) and Automated Graphitization Equipment (AGE3), as well as manual graphitization equipment and a wet lab for sample pretreatment. In one year since measurement of unknown samples began, we have analyzed 1,553 graphite samples (including 967 unknown graphite samples) and 1098 gas samples (including 647 unknown gas samples). These unknowns include a variety of sample types: plant materials, atmosphere, ecosystem respiration samples, carbonates, megafauna coprolites, organic and inorganic soils, and dissolved organic carbon.

Our facility supports specific research projects of the coauthors and other NAU researchers, with a particular focus on Arctic carbon and its potential as a feedback to climate change. Other research includes: geochronology of sediment and lake cores, tree physiology, and ecosystem science.

Our MICADAS laboratory has performed similar to other AMS laboratories. During 202 graphite replications of SRM 4990C (Oxalic Acid II), the standard deviation is 2.3 permil. After running 107 OX-II replicates with the GIS, the standard deviation is 7.8 permil. Other SRMs demonstrate similar precision. Across 112 graphite radiocarbon blank repetitions, the average age is 50,200 years. 154 GIS blank replicates had an average age of 38,900 years.

T04_P12

A database of NERC Radiocarbon age measurements determined by accelerator mass spectrometry

Garnett M1, Gulliver P1,2, Ascough P1

¹NEIF Radiocarbon Laboratory, East Kilbride, United Kingdom, ²SUERC Accelerator Mass Spectrometry Laboratory, East Kilbride, United Kingdom

Radiocarbon measurements undertaken by the NERC Radiocarbon Laboratory using accelerator mass spectrometry are now freely available on a new database hosted on the World Wide Web. The measurements cover a wide range of sample types undertaken for Earth and environmental science research projects supported by the United Kingdom's Natural Environment Research Council (NERC). Sample types include but are not restricted to, organic remains, soils, sediments, carbonates, dissolved organic and inorganic carbon, and carbon dioxide. Currently, the online database contains radiocarbon ages for approximately 2000 individual samples reported between 2006 and 2010, but it is envisaged that this will expand considerably as more data are made available. Contextual information such as sampling location and associated publications are provided where available, and searches can be performed on sample location, type, project number and publication code. This new database compliments an existing, publicly available database of measurements performed using radiometric methods by the laboratory which has recently been expanded to present over 2000 measurements. It is hoped that this archive will prove useful to workers in the community who would benefit from greater availability of measurements for the purposes of performing meta-analyses, and/or synthesis of larger datasets.

First status report on ¹⁰Be and ²⁶Al sample preparation techniques at the IHEG, CAGS AMS laboratory (Xiamen, China)

Hui Z¹

¹Chinese Academy Of Geological Sciences, Shijiazhuang, China

The Institute of Hydrology and Environmental Geology (IHEG), Chinese Academy of Geological Sciences(CAGS) organized a research group engaged in radionuclides analysis and dating by AMS in 2015, then purchased its first multi-element AMS facility (1MV, HVEE) in 2017. Unfortunately, this facility has not been installed yet. The 10Be and 26Al sample preparation laboratory spent the better part of 2020 establishing pretreatment protocols, and streamlining sample processing, included optimizing extraction and purification of quartz, ion exchange chromatography methods, minimizing backgrounds. Here, we present an overview of sample processing protocols and results from measured standards, reference, and blank materials.

T04_P14

Development of the PATRIC14 project on the ARTEMIS AMS facility for the dating of low-carbon content cultural heritage materials.

<u>Moreau C</u>¹, Thellier B¹, Hain S¹, Beck L¹, Caffy I¹, Delque-Kolic E¹, Dumoulin J¹, Goulas C¹, Perron M¹, Setti V¹, Sieudat M¹

¹Laboratoire de Mesure du Carbone 14 (LMC14), LSCE/IPSL, CEA-CNRS-UVSQ, Université Paris-Saclay, Gif-sur-Yvette, France

The development of Accelerator Mass Spectrometry (AMS) dating technique has made it possible to considerably reduce the quantity of material necessary to carry out a dating. However, for archaeological works or objects low in carbon, the quantities of material to be sampled often remain too voluminous for dating to be considered. This is particularly the case for certain old ferrous objects for which previous studies have revealed very low carbon contents. This is also the case with other materials such as plaster and stucco, materials for sculptural and architectural creation, widely used since the ancient periods of Archeology and Art History. Currently, their dating is based solely on stylistic criteria, which sometimes leads to debate. The objective of the PATRIC14 project is therefore to develop a new instrumental device which will be installed on the ARTEMIS facility, in order to date low carbon content material. The aim is to add a gas ion source to the ARTEMIS facility and to develop a specific gas transfer module - compatible with the LMC14 sample preparation benches - allowing the injection in the AMS of samples directly in gaseous form, avoiding the transformation into solid graphite as at present. This solution will thus make it possible to considerably reduce the quantity of carbon necessary to carry out dating by AMS. The first applications using the new equipment will be carried out in collaboration with the partners of the project in different fields: archaeometry (LAPA), research and restoration (C2RMF) and museum (Louvre).

T04_P15

Aarhus AMS Centre – Status report

Olsen J1

¹Aarhus University, Aarhus, Denmark

A status report of the installation and use of the newly installed high intensity sputter ion source SO 110C is presented. The source produced a pre-acceleration 12 C beam of above 200 μ A during

demonstration . Here performance data of different source settings is shown together with machine performance for charge state +1 of a pre-acceleration 12 C beam between 80 - 100 μ A.

T04 P16

Comparative features of BINP AMS and MICADAS facilities, working at AMS Golden Valley, Russia.

<u>Petrozhitskiy A</u>^{1,2,3}, Parkhomchuk E^{2,3,4}, Ignatov M^{2,3}, Kuleshov D^{2,3}, Kutnyakova L³, Konstantinov E¹, Parkhomchuk V^{1,2}

¹Budker Institute Of Nuclear Physics Siberian Branch Russian Academy Of Sciences, Novosibirsk, Russian Federation, ²Novosibirsk State University, AMS Golden Valley, Novosibirsk, Russian Federation, ³Institute of Archaeology and Ethnography Siberian Branch Russian Academy Of Sciences, Novosibirsk, Russian Federation, ⁴Boreskov Institute of Catalysis Siberian Branch Russian Academy Of Sciences, Novosibirsk, Russian Federation

The AMS Golden Valley radiocarbon analysis laboratory is equipped with two accelerator mass spectrometers: BINP (Budker Institute of Nuclear Physics) AMS facility and MICADAS-28, and two graphitization systems: AGE-3 and Absorption-catalytic setup, developed in Boreskov Institute of Catalysis (ACS BIC). The laboratory provides routine ¹⁴C analyses of various samples: collagen, cellulose, humic acids, carbonates from sediments etc. The main focus of the laboratory is to determine the age of archaeological artifacts by radiocarbon dating.

Detailed description and characteristics of BINP AMS facility will be presented compared with that one's of MICADAS. In 2022 the AMS Golden Valley laboratory took part in the Glasgow International Radiocarbon Inter-comparison (GIRI). The samples were graphitized on the AGE-3 (4 targets from each sample, 8 targets from bone sample K) and subsequently measured on both AMS facilities. A comparison of the results from two series of experiments: AGE-3 + MICADAS-28 and AGE-3 + BINP AMS will be given.

T04_P17

CEDAD at the University of Salento: twenty years of operations and new perspectives

<u>Calcagnile L</u>¹, D'Elia M¹, Maruccio L¹, Scrimieri L¹, Quarta G ¹CEDAD-University Of Salento, Lecce, Italy

The Centre for Applied Physics, Dating and Diagnostics (CEDAD) was established in 2001 at the University of Salento in Lecce to be a National Centre in Italy for radiocarbon dating by Accelerator Mass Spectrometry. The Centre is based on a 3 MV TandetronTM accelerator manufactured by High Voltage Engineering Europa B.V.. The system initially equipped only with the ¹⁴C dating AMS beamline, has been significantly updated over the years and in the frame of different projects with the installation of other five beamlines dedicated to IBA (Ion Beam Analysis) both in vacuum and in air, ion irradiation and nuclear microprobe. A dedicated, multipurpose beamline has been also designed and built in-house for the AMS detection of rare nuclides from 10B to actinides. From the instrumental point of view the last upgrade consisted in the installation of a hybrid (solid and gas) ion-source coupled with the AMS system and a IRMS spectrometer (Thermo Fischer Delta V Plus). Samples with masses in the microgram range are routinely measured for applications spanning from archaeological to environmental sciences. Recently the set-up has been further improved by the installation of a gas-bench interface allowing the analysis of DIC from water samples and carbonates. Application fields spanning from archaeology, forensics, Earth and marine sciences to the analysis of sample of industrial interest (such as bio-fuels and biopolymers) are also reviewed.

Carbonus, the new carbon AMS facility devoted to paleoclimate studies at the University of Salamanca

<u>Quintana Arnés B</u>¹, Rodríguez Álvarez A¹, Ausín B¹, Borrego D¹, Flores J¹

¹Universidad De Salamanca, Salamanca, Spain

Carbonus is the new ¹⁴C facility at the University of Salamanca (Spain). It is made up of a MICADAS accelerator mass spectrometer and a clean chemical laboratory devoted specifically to prepare carbon samples and equipped with an AGE3, made by lonplus, which is coupled to an Elemental Analyser (EA). Additionally, ultra low-level LSC counting preceded by a benzene synthesis procedure is available to determine absolute ¹⁴C in large samples. The main purpose of this accelerator facility is to date samples of interest in paleoclimate studies. Being set in before the COVID pandemic and once several severe issues due to the building electrical current were solved, Carbonus is ready to start operation. In this work, the background study aimed to characterize the facility performance as well as the first results on Holocene marine sediments from the Powell 2020 Antarctic campaign will be presented. Previously, the facility will be described and the lessons learnt from the different issues that affected the Micadas operation will be given.

T04 P19

Fifteen years of the Centro Nacional de Aceleradores (CNA) radiocarbon facility.

<u>Santos Arévalo F</u>¹, Gutiérrez J¹, Gómez Martínez I¹, Galván Moreno J¹, Díaz Francés I¹, García León J¹, Peruchena Fernández J¹

¹Centro Nacional de Aceleradores (University of Seville, CSIC, Junta de Andalucía), Seville, Spain

The radiocarbon dating laboratory at CNA was the first one in Spain based on AMS measurements and started operation in 2007 based on a 1MV HVEE multielemental AMS system and a completely manual graphitization line for five samples. Fifteen years later, the facility has experimented changes both in the AMS system and the sample preparation lab. The most significant one was the installation of a Micadas system in 2012, which since then has been routinely used for the AMS measurements. Besides, the sample preparation lab has upgraded significantly, and it is now equipped with two automatic graphitization lines (AGE2 and AGE3) for seven samples each, coupled to an Elemental Analyzer and a Carbonate Handling System, as the most relevant elements. Sample pretreatments have also evolved in time. In this paper we will give an overview of the current situation of the radiocarbon facility, briefly discussing the sample preparation procedures. Some significant research and application projects will also be covered.

T04_P20

A Brief History of Sulfur Isotope Analysis in Archaeological Bone Collagen at the SUERC Radiocarbon Laboratory.

Savle K¹, Dunbar E², Hamilton D³

¹University of Glasgow, SUERC, East Kilbride, Scotland, ²University of Glasgow, SUERC, East Kilbride, Scotland, ³University of Glasgow, SUERC, East Kilbride, Scotland

The use of multi-isotopic analysis (δ^{15} N, δ^{13} C and δ^{34} S) of archaeological bone collagen to assist in the interpretation of diet, movement and mobility of prehistoric populations has been gradually increasing. Sulfur analysis has proven to be an extremely valuable additional tool for distinguishing between

individuals who have obtained their food from terrestrial, marine and/or freshwater resources, which in turn can affect their radiocarbon ages.

Sulfur concentrations in bone collagen are generally very low (ca. 0.2–0.3%) compared to nitrogen and carbon concentrations (ca. 15% and 40%, respectively). This has presented an analytical challenge for simultaneous δ^{15} N, δ^{13} C and δ^{34} S analysis and resulted in the need to analyse one sample for δ^{15} N and δ^{13} C and a second, larger sample, for δ^{34} S to obtain sufficient signals and data precision. Consequently, this led to longer analytical times and higher costs.

Recent advances in Elemental Analysis Isotope Ratio Mass Spectrometry (EA-IRMS) have opened up the potential for rapid, accurate and precise analysis at concentrations less than 10 μ g of sulfur, whilst simultaneously acquiring data for and $\delta^{15}N$ and $\delta^{13}C$, meaning samples can be analysed more rapidly and at a lower cost. Furthermore, depending on preservation, significantly smaller amounts of bone is required for analysis, and hence, less archaeological material is destroyed.

This poster will chart the development of sulfur isotope analysis in archaeological bone collagen at the SUERC Radiocarbon Laboratory over the past decade.

T04 P21

A home-made semiautomatic graphitization device for AMS ¹⁴C dating at NTUAMS Lab

Shen T¹, Chang H¹, Li H¹

¹Department of Geosciences, National Taiwan University, Taipei, Taiwan

We have built up a semiautomatic graphitization system with 6 units. The system can be connected with EA and IRMS or run alone with gas inlet. Once the CO_2 is transferred into the reactor and measured its pressure, pure H_2 is added into the reactor with 2.2 times of PCO_2 . The CO_2 will be reduced to graphite at 550°C. This 6-unit reaction system costs < US\$30K. Up to date, four background CO_2 gas input samples show that the $^{14}C/^{12}C$ values of the graphite samples made by the reaction system range from $1.56\cdot 10^{-15}$ to $3.06E^{-15}$, indicating very low background of the system. In the first batch test, six coal background (BKG) samples through the EA to the graphitization reactors yielded the $^{14}C/^{12}C$ values of the produced graphite samples ranging from 6.9E-15 to $4.13\cdot 10^{-14}$. The higher $^{14}C/^{12}C$ values are mainly attributed to weak ^{12}C current due to poor quality of the graphite. The second batch test contained 3 OXII, 2 BKG and 3 FIRI-M (4th inter-comparison sample with consensus age of 11139 yr BP). The measured ^{14}C ages of the three FIRI-M are ^{11}C (^{12}C current = ^{12}C), ^{11}C 0.3 ^{12}C 0.

T04_P22

The Radiocarbon and Tritum measurments at GXNU-AMS facility

<u>Shen H</u>^{1,2}, Tang J^{1,2}, Shi S¹, Zhang G¹, Wang L¹, Chen D¹, Qi L¹, He M³, Sasa K⁴, Jiang S⁴ ¹Guangxi Normal University, Guilin, China, ² Guangxi key laboratory of nuclear physics and nuclear technology, Guilin, China, ³China Institute of Atomic Energy, Beijing, China, ⁴ University of Tsukuba, Tsukuba, Japan

A single-stage accelerator mass spectrometer (GXNU-AMS) developed for Radiocarbon and Tritium measurements was installed and commissioned at Guangxi Normal University in 2017. During several years of operation, its performance has been continuously improved and applied in multidisciplinary fields. Currently, the measurement sensitivity for radiocarbon and tritium is 14 C/ 12 C \sim (2.23±0.045) \times 10-15 and 3 H/ 1 H \sim (1.23±0.17) \times 10-16, respectively, and the measurement accuracy is \sim 0.6%, which can meet the measurement requirements in the fields of life sciences and archaeology applications. This

study presents the performance characteristics of GXNU-AMS and several interesting application studies.

T04 P23

Safe delivery of graphite targets to AMS facilities, to minimize contamination. The final step of BRAVHO laboratory at Bologna University

<u>Tassoni L</u>¹, Kromer B², Friedrich R³, Wacker L⁴, Friedrich M⁵, Paleček D¹, Pelloni E¹, Talamo S¹

¹University of Bologna, Bologna, Italy, ²Heidelberg University, Heidelberg, Germany, ³Curt-Engelhorn-Centre Archaeometry, Mannheim, Germany, ⁴Laboratory of Ion Beam Physics, ETH, Zurich, Switzerland, ⁵University of Hohenheim, Stuttgart, Germany

Nowadays, most laboratories can reliably remove contamination during the pretreatment of organic samples (e.g. bones, charcoal or trees) thanks to several methods commonly used by the radiocarbon community. However, what about the final step, the storage of graphite? Rarely do the laboratories produce their own graphite and ship them as pressed targets to AMS facilities for measurement. Pressed graphite in aluminium targets is vulnerable to contamination and during the shipment or storage there can be an introduction of exogenous carbon.

Here we report a test on some archaeological samples materials (i.e. charcoal, bones and trees) from different environments and different time periods (from the Modern Age to the Middle Paleolithic period) which were transformed into graphite, with the AGE III (Automated Graphitization Equipment, IonPlusAG, Switzerland), pressed into targets at the BRAVHO lab (Bologna Radiocarbon laboratory devoted to Human Evolution) and sent to two different AMS laboratories to be dated. The two AMS labs chosen for this experiment are the Curt-Engelhorn-Centre Archaeometry, Mannheim, Germany and the Laboratory of Ion Beam Physics, ETH, Zurich, Switzerland. The experiment shows that it is possible to produce graphite in a sample preparation laboratory and send it safely to an AMS laboratory for measurement in a short time without significant contamination. Close cooperation and coordination between our chemical laboratory and AMS facilities, high standards in contamination removal and efficient measurement planning enabled us to obtain reliable outcomes within short times.

T04 P24

Status report on small sample measurements with ECHoMICADAS AMS facility: 6 years of data processing and statistical results.

Thil F¹, Tisnérat-Laborde N¹, Hatté C^{1,2}, Noury C¹, Phouybanhdyt B¹

¹Laboratoire des Sciences du Climat et de l'Environnement, LSCE/IPSL, CEA-CNRS-UVSQ, Université Paris Saclay, F91198, Gif Sur Yvette, France, ²Division of Geochronology and Environmental Sciences, Institute of Physics, Silesian
University of Technology, 44-100 Gliwice, Poland

In 2015, a new AMS facility, the ECHoMICADAS was installed in the Laboratoire des Sciences du Climat et de l'Environnement (LSCE) at Gif-sur-Yvette, France. Equipped with a hybrid source, it allows the analysis of solid or gas samples for 14 C measurement. This equipment is completed with several peripheral instruments. For solid measurement, 2 graphitisation systems are used: the homemade Graphitisation line (GéGé) to graphitize CO_2 and an Automated Graphitization Equipment (AGE3) for most of organic samples. For CO_2 gas measurement, the Gas Interface System (GIS) injects a mix of CO_2 and He into the source and allows to couple an elemental analyzer (EA) for organic sample, a tube cracking system for pure CO_2 , and more recently a Carbonate Handling System (CHS2) for carbonates or dissolved inorganic carbon.

This presentation focuses on measurement of small samples and how to process raw data. It is based on both CHS2-GIS and EA-GIS examples. We will describe how the data are processed, using a combination

of the calculation made in Bats software [a] and of the models which were chosen to consider the constant and the cross contamination [b]. Since 2016, measurements on blanks and standards allow to yield enough statistics to estimate, even before its measurement what will be the age uncertainty, based on several expected parameters: the weight (or quantity of carbon), the current, the sample age, the measurement duration, and the chemical protocol which can induce different contaminations.

[a] Lukas Wacker et al, NIMPR 2010

[b] Salazar et al, NIMPR 2015

T04 P25

A summary of quality assurance samples at the SUERC Radiocarbon Laboratory

Tripney B¹, Dunbar E¹, Naysmith P¹

¹Scottish Universities Environmental Research Centre, East Kilbride, United Kingdom

The SUERC Radiocarbon Laboratory reports approximately 3000 unknown samples per year with an additional 1200 samples processed for quality assurance (QA) purposes. In addition to the primary OXII standard (SRM-4990C) required for AMS batch normalisation, secondary known-age standards (TIRI A and SIRI N) have been used to evaluate batch quality over many years, while interglacial wood (VIRI K), geological-age carbonate (TIRI F) and mammoth bone are employed as 'background' standards for age calculation.

Further 'in-house' tertiary standards are used to monitor specific processes. Measurements on a 2007 new make spirit are used to promote confidence in the preparation of whisky samples, with kerosine providing a background check for the method. Starting in 2003 a series of known-age bones have been used to monitor collagen extraction, while repeat preparations of a cremated bone sample are a more recent addition.

Summary results for these samples are given, setting them within the context of the laboratory QA system.

T04_P26

Production of radiocarbon micro-samples at ANSTO

Hua Q¹, Levchenko V¹, Smith A¹, Varley S¹, Williams A², <u>Yang B</u>¹, Zoppi U³
¹Australian Nuclear Science & Technology Organization (ansto), Lucas Heights, Australia, ²Deceased, 9th February 2021., , , ³Deceased, 27the March 2016., ,

ANSTO's Centre for Accelerator Science has been providing radiocarbon analyses for nearly three decades using our solid sample ion sources. From the beginning, there was a need to refine capability for ever smaller samples. This paper summarises the various approaches we have developed to deal with samples containing just a few micrograms of carbon (μ gC). Initially we began optimising our 'conventional' graphitisation furnaces. We decreased the reaction volume to ~ 3.5 mL and investigated various catalysts and means of activating them. Today, we operate a bank of 24 conventional furnaces for samples containing >10 μ gC. In 2003 we developed novel, Laser Heated Furnaces using a focused infrared laser to directly heat the Fe catalyst in a quartz crucible, with temperature measured indirectly by infrared thermometry. These units have a reaction volume of ~0.25 mL. Smaller volumes allow a higher initial pressure for small amounts of CO₂, improving the graphite yield. Efficient trapping of byproduct H₂O and careful selection of the catalyst are also key to optimising graphitisation of microsamples. By localising the heated region within the reaction volume, the addition of extraneous carbon is minimised and samples containing just 1-2 μ gC are routinely prepared.

The fabrication approach developed for the LHF was adapted to a new type of miniaturised furnace, namely micro-conventional furnaces (MCF). These furnaces have a minimum reaction volume of 0.9 mL

with a small tube furnace for catalyst heating. Variable temperature cold traps have been developed to optimise sample processing with samples containing 5 µgC routinely prepared.

T04 P27

Status of the AMS-dating at Radiocarbon laboratory of the Institute of geography RAS

<u>**Zazovskaya E**</u>¹, Shishkov V¹, Turchinskaya S, Cherkinsky A²

¹Institute of geography RAS, Moscow, Russian Federation, ²University of Georgia, CAIS, Athens, USA

The Radiocarbon Dating Laboratory (Lab code IGAN) was founded at the Institute of Geography of the Russian Academy of Sciences in the 1970s and has since continuously dated different carbon-containing materials using the liquid scintillation counting method. In 2015, our Laboratory has acquired the Ionplus automated graphitization system – AGE 3, together with a Vario Isotope Cube CHNS elemental analyzer. In early 2018 (with the help of lonplus specialists), an isotope ratio mass spectrometer was coupled to the AGE 3 and our Laboratory staff members attended a brief training. Graphite 14C/13C ratios were measured using the CAIS 0.5 MeV Accelerator Mass Spectrometer at the Center for Applied Isotope Studies (CAIS), University of Georgia. Anthracite and phthalic anhydride were used as BG for graphitization. The BG results consistently give ages between 44,000 and 49,000 BP for anthracite and 46,000 and 52,000 BP for phthalic anhydride. OXII and OX1 are used as the modern standard for graphitization. An inter-laboratory comparison between IGAN and CAIS was conducted in respect to graphitization and dating of materials of known ages, with the results obtained being highly comparable. During the work of AGE-3 system more than 5000 graphites of high quality were obtained from such carbon-bearing materials as coal, wood (cellulose), human and animal bones, soils, sediments of different genesis, peats, fouling from ceramic material, fabric. Samples for graphitization are prepared according to accepted protocols. The methods modified in the IGRAN laboratory are also used when dating the organic matter of soils.

T04_P28

C-14 AMS data quality assessment: How it's done at the Rafter Radiocarbon Laboratory

Zondervan A¹, Turnbull J¹, <u>Ginnane C</u>¹, Norris M, Dahl J¹, Lewis C¹ ¹GNS Science, Lower Hutt, New Zealand

The Rafter Radiocarbon Laboratory, in operation since 1951, transitioned from decay counting to AMS in the 2nd half of the 1980s. In the decades since, numerous improvements were made to sample preparation lines and protocols and to AMS system hard- and software. The most recent of these were the development of high-precision measurement of 14 C in atmospheric CO₂, high throughput capacity for modern tree ring samples via accelerated solvent extraction, selective combustion of organics through ramped pyrolysis, and establishment of a custom protocol for tiny macrofossil samples. Presently, a new graphitisation system is under construction for reliable preparation for 0.05—0.15 mg C samples. It has been our longstanding practice to aim to report each 14 C analysis with an error value that captures all sources of uncertainty, not just the Poisson counting error.

We tune XCAMS, our present AMS system, on a graphitisation blank and IAEA-C6 sucrose. Oxalic-acid-I (Ox-I) remains our primary standard and every batch measurement on \leq 40 cathodes contains at least 6 of those. Raw AMS data are normalized to Ox-I per batch, while the blank correction for the samples in that batch is evaluated from blanks during the most recent 6—12 months. Lastly, repeated analysis of a few key radiocarbon inter-comparison materials allows us to estimate the residual, i.e. non-Poisson

uncertainty, specific to each sample type and size (range). We will present results for all control materials, to highlight dependencies on date of preparation, preparation method, and sample size.

Ta1 Tracer applications: Forensics, environment, biomedicine

Ta1 01

Changing the current drug development paradigm by unlocking the power of accelerator mass spectrometry

<u>Lozac'h F</u>¹, De Maria D², Fahrni S³, Marvalin C¹, Walles M¹, Camenisch G¹, Wacker L², Synal H²

¹Novartis Pharma AG, Basel, Switzerland, ²ETH Zurich, Zurich, Switzerland, ³Ionplus AG, Dietikon, Switzerland

Human metabolism ADME studies are pivotal in the clinical development of a pharmaceutical compound and usually mandatory to support acceptance by regulatory authorities. Conventionally, a radioactive therapeutic dose of ¹⁴C (manufactured according to GMP) is administered to healthy subjects or patients. However, to enable dosing of radioactivity to humans, dosimetry assessments need to be conducted by performing ADME studies in animals to determine and extrapolate relevant organ exposures to humans. Thus, due to high costs of these assessments and the attrition rate in early development, the human ADME study is usually conducted in a later phase.

Our idea is to change this current paradigm to a human first and human only paradigm, thanks to a microtracer approach in which trace amounts of radioactivity (ca. 1/1000 of conventional dose for ¹⁴C) can be dosed. The sensitivity of accelerator mass spectrometry (AMS) allows detecting these trace amounts of ¹⁴C. However, previous AMS instruments were big, expensive and run only with low throughput, which hampered a cost effective implementation for the profiling of biomedical samples.

Over the past 6 years, we have collaborated with ETH Zurich and the spin-off company lonplus to miniaturize this AMS technology and increase both samples throughput and level of automation. Finally, we will internalize an instrument by end of 2022 to try to push and frontload human ADME studies earlier in the drug development process. Moreover, we hope that the availability of this technology will trigger discussions about sophisticated clinical and preclinical study designs using microtracer studies.

Ta1 02

Why the radiolabelling approach is the gold standard for ecotoxicological investigation of nanoplastics?

AL SID CHEIKH M¹, De Maria D², Kaegi R³, Wacker L²

¹University Of Surrey, Guildford, United Kingdom, ²Swiss Federal Institute of Technology (ETH), Laboratory of Ion Beam Physics (LIP), Zurich, Switzerland, ³Swiss Federal Institute of Aquatic Science and Technology (EAWAG), Dubendorf, Switzerland

Studies investigating the effects of nanoplastics (NPs) on aquatic organisms used concentrations 2 to 7 order-of-magnitudes higher than those predicted in the open ocean to detect NPs. These studies divided the community into those who sounded the alarm based on observed ecotoxicological effects, and those who predicted that concentrations of NPs in the environment were well below any threshold-effect. In reality, most experiments were inadequately designed, and the results were therefore

unsatisfactory. Fit-to-purpose experimental designs have been hindered by a lack of appropriate NP models, tracking methods, and monitoring strategies for environmentally realistic concentrations. Using 14 C-labelled NPs and conventional nuclear techniques, I recently modelled that scallops chronically exposed (over a year) to environmentally realistic NP concentrations (15 μ g/L) could accumulate NPs and reach concentrations in body tissues at which effects were observed by those who raised sounded the alarm. Surprisingly, this suggests that NPs in organisms have already exceeded threshold levels and could be damaging the marine biota.

Here, I present an innovative approach to overcome the analytical limitations for the detection and quantification of NPs under realistic environmental conditions. By combining ¹⁴C-labelling of NPs with the ultimate sensitivity of Accelerator Mass Spectrometry (AMS), we will be able to conduct exposure experiments under realistic conditions. The ¹⁴C-labelling coupled with the AMS will provide an unprecedented level of sensitivity, allowing us for the first time, to account for any ¹⁴C when performing long-term experiments, closing the gap on many critical environmental questions about plastics.

Ta1 03

Application of ¹⁴C dating in the routine forensic practice: outcome of the IAEA Coordinated Research Project

<u>Calcagnile L</u>¹, Hajdas l², Molnar M³, Varga T^{3,4,5}, Major l³, D'Elia M¹, Jull A^{3,6}, Simon A⁷, Quarta G¹

¹CEDAD-Centre of Applied Physics, Dating and Diagnostics, University Of Salento, Lecce, Italy, ²Laboratory for Ion Beam Physics, ETHZ, Zürich, Switzerland, ³International Radiocarbon AMS Competence and Training (INTERACT) Center, Institute for Nuclear Research, Debrecen, Hungary, ⁴University of Debrecen, Doctoral School of Physics, Debrecen, Hungary, ⁵Isotoptech Ltd, Debrecen, Hungary, ⁶Dept. of Geosciences, University of Arizona, Tucson, USA, ⁷Division of Physical and Chemical Sciences, Department of Nuclear Sciences and Applications, International Atomic Energy Agency, Wien, Austria

Since 2017 the IAEA (International Atomic Energy Agency) has undertaken a Coordinated Research Project (CRP F11021) entitled "Enhancing Nuclear Analytical Techniques to meet the Needs of Forensics Sciences". The scope of the program is to develop and utilize the capabilities of nuclear and acceleratorbased analytical techniques towards recognized needs of forensic sciences that could not be efficiently addressed by other methods. Indeed, despite the relevant advantages of accelerator-based techniques, their application in the routine forensics practice appears to be still limited. Aim of the CRP was to support long term collaborations and networking between experts in nuclear analytical techniques and forensic science stakeholders such as law enforcement agencies, police corps and international organizations. We report on the outcomes of one of the WPs (WP4) which was entirely dedicated to the applications of ¹⁴C. Within this WP, in order to cope with the factors limiting the impact of AMS dating in forensics, a detailed research program was defined on the basis of discussions with forensic stakeholders and experts of other analytical techniques. The need to define common guidelines and quality assurance protocols for the application of ¹⁴C was established, also considering possible ethical issues, interpretation of data and the assessment of the achievable chronological resolution on classes of samples relevant in forensics. Different intercomparison exercises were then organized and run among three AMS facilities: CEDAD (Italy), ETHZ (Switzerland) and Isotoptech-ATOMKI (Hungary) aimed at addressing these issues on different sample materials such as ivory, bones, paper, textiles and foodstuff (wine and coffees).

The role of ¹⁴C dating in the identification of Missing Persons in Cyprus

<u>Quarta G</u>¹, Eleftheriou T², Engin I², Maruccio L¹, D'Elia M¹, Calcagnile L¹
¹CEDAD-University Of Salento, Lecce, Italy, ²Committee on Missing Persons in Cyprus, Cyprus

The Committee on Missing Persons in Cyprus (CMP) is a bicommunal committee with the mandate to locate and identify the skeletal remains of 2002 missing persons from the inter-communal fighting of 1963-1964, as well as the events of July 1974.

During the periods of conflict, several archaeological sites and old cemeteries were used as primary burial sites, as they were easily accessed by the persons involved in the interment and little effort was needed to conceal the bodies. The relatively large post-mortem interval and the generally poor post-mortem preservation of the skeletal remains poses an additional challenge in the forensic examination process, particularly in the absence of a context or artefacts/evidence.

Between 2016 to 2020, the CMP has been collaborating with CEDAD-Centre of Applied Physics, Dating and Diagnostics at the University of Salento to clarify the relevancy of several cases by using radiocarbon dating. The CMP submitted 139 unresolved cases to CEDAD, out of which 112 cases were determined to be archaeological in date and irrelevant to the CMP project. For the remaining samples bomb ¹⁴C was detected in bone collagen and the bomb peak dating technique was then used or further investigation of the cases.

The obtained results show that ¹⁴C dating on human remains recovered in archaeological sites and old cemeteries is an effective method to determine the year of death of the remains and then to identify the forensic significance of the cases recovered by the CMP.

Ta1 05

Radiocarbon analysis of human remains in forensic cases

Cherkinsky A¹, Bengtson J², Prasad G¹

¹University Of Georgia, Athens, United States, ²Southeast Missouri State University, Cape Girardeau, United States

Estimation of the date of birth and death of deceased individuals, whose remains make identification impossible, represents an important task for forensic science. The dramatic spike of ¹⁴C concentration in atmosphere in 1955 - 1963 due to above ground nuclear testing and its subsequent decline is documented by high resolution records which could help to solve this problem. We analyzed the proportion of bomb radiocarbon in the bioapatite of enamel and collagen of dentine to solve these problems. We analyzed seven cases of remains of unidentified victims recovered by law enforcement and submitted to Southeast Missouri State University for anthropological analyses. Some of them were recovered decades ago, while some were recovered more recently. All remains were analyzed on collagen fraction of the dentine and bioapatite fraction of the enamel. In two of sevens cases collagen was formed before 1950 AD collagen and these cases were excluded from determination. In the third case, enamel was formed before 1950 AD but death occurred after the bomb spike in 1962-1964 AD according of ¹⁴C concentration in collagen and the age of the victim. The other four cases were fitted in the bomb curve and allowed quite precise determination of dates of birth and death.

The δ^{13} C and δ^{15} N values for dentine collagen were higher than it would be expected for pure terrestrial diet, implying some consumption of marine food that could lead to reduced 14 C concentration. Taking into account the potential marine reservoir effect could slightly reduce the ages of those persons.

Modelling corrections of bomb-pulse radiocarbon dating in forensic cases

Sveinbjörnsdóttir A¹, Olsen J², Heinemeier J²

¹Institute of Earth Sciences, University of Iceland, Reykjavík, Iceland, ²Department of Physics and Astronomy, Aarhus University, Aarhus, Denmark

Identification of human remains by radiocarbon dating and stable isotope approach can be of extreme importance in forensic cases. However, radiocarbon dating has to rely on modelled corrections due to radiocarbon changes in the atmosphere, collagen turnover rate and marine reservoir effect that are often difficult to estimate and verify. In this presentation, we will ascertain how close the modelled corrections are to reality by comparing radiocarbon ages of human individuals with the known actual time of death (and birth).

Two bone samples from unidentified individuals were radiocarbon dated by request of the Icelandic police, to determine whether the human remains were recent and of forensic relevance. In both cases the bones were well preserved and the extracted collagen of good quality. The dates were performed in 2017 and 2019 respectively, and both individuals turned out to be modern, falling within the bomb-pulse period. Isotope data showed no or limited indication of marine diet. To provide a quick forensic result, we took the naïve approach of a standard ten-year correction for bone collagen turnover and no marine correction.

After our report, the police applied DNA testing and managed to identify both individuals. Accordingly, we now know their time of birth as well as their death dates. In both cases, we had estimated their time of death too early by 10 and 20 years respectively. We have initiated attempts of better modelling of bone turnover and marine reservoir corrections in connection with bomb-pulse dating.

Ta1 07

The Scale of the Trade: Determining a Pangolin's Date-of-Death Using F¹⁴C

<u>Barr E</u>¹, Wood R^{1,2}, Meagher P³, Fallon S¹

¹The Australian National University, Canberra, Australia, ²University of Oxford, Oxford, England, ³Taronga Conservation Society, Sydney, Australia

In wildlife forensics, it is important to know when an animal was killed to aid in the prosecution of traders and to gain a deeper understanding of the mechanisms of the trade. Such is the case for the pangolin (Manidae), a scaly mammal considered to be the most highly trafficked animal in the world. Pangolins are often poached for their hard, cornified scales that are used commonly in traditional medicines. Our study attempts to analyse F¹⁴C of keratin across a scale using accelerator mass spectrometry to determine an animal's date of death. We have developed an improved understanding of how the scale grows and propose the most effective method for producing a chronology is to take a series of samples proximal-distally down the scale. This assumes the proximal apex of the scale is the oldest tissue and that the distal attachment point to the epidermis is the most recent tissue and will provide the closest value to a date of death. We investigate whether results could be skewed by a reservoir effect created by the termites in a pangolin's diet, if the termites are feeding on old-carbon within decaying wood. By developing an effective method to determine the date of death of an animal from their scales alone, we may be able to better prosecute illegal traders and interrupt the current momentum driving pangolins towards extinction.

Taste it or date it: authentication of 10-yr and 20-yr fortified wines

Palstra S¹, Meijer H¹

¹University of Groningen, Groningen, Netherlands

Consumers of several fortified wines tend to believe that these wines have matured on casks for a specific period of time, e.g. 10, 20 of 30 years, because this is stated on the labels of the bottles. These statements give the idea of additional value and quality of the product to the consumer. EU-regulations request that claims about the content of food and beverages on product labels are correct and not misleading. In the production of fortified wines it is common practice to blend wines with different maturation ages to obtain wines that fulfil the defined and verified requirements regarding taste, smell, looks and several other aspects of matured fortified wines with a certain age. The real (average) maturation age is however not verified. For one of our customers we have verified the (average) maturation ages for a set of 20 different fortified wines by measuring radiocarbon in the ethanol and sugar fractions of these wines. In this presentation we will show the applied method and its verification. We will discuss the results, which indicate that part of the investigated fortified wines might have younger maturation ages than stated on the bottle.

Ta1 09

Sweet bomb-peak in the historical Tokaji Aszú wines

Molnar M¹, László E¹, Molnár A^{1,2,3}, Varga T^{1,2,3}

¹INTERACT AMS Laboratory, Debrecen, Hungary, ²University of Debrecen, Doctoral School of Physics, Debrecen, Hungary, ³Isotoptech Zrt., Debrecen, Hungary

Tokaji Aszú is one of the most important and traditional wines in the world, produced since the XVI. Century. It is a special wine produced in the Tokaj wine region (Hungary); it is the nectar of individually hand-picked "aszú" berries botrytised on the wine stock. It is made by bathing the dough in high quality must or wine of the same year from the Tokaj wine region. Following fermentation, it is maturing and refining in oak casks placed in a constant-temperature cellar. Besides the unique quality, this also explains the high price of Tokaji Aszu wines, as it is an extremely labour-intensive process. Thanks to its high sugar and acid content it is already highly enjoyable at the age of 150 years, which is why Tokaji Aszu is very popular among wine collectors. In this study we have investigated sets of several decades collection of Tokaji Aszu wine from different wine yards. Aszú samples were analyzed by AMS ¹⁴C technique to prove the power of high resolution dating/age determination by AMS technique on prestigious old wines. Atmopsheric ¹⁴C bomb-peak (1963-2020) allows one-year resolution wine "dating". Besides the wine ¹⁴C analyses, we have investigated their ³H signal too, to have an independent proxy regarding the bomb-signal. On the other hand, we compared the Aszú-bomb-curve to the local (Hungarian) atmospheric ¹⁴C records from tree rings and direct air sample observations.

Radiocarbon dating of forensic human bone to estimate the postmortem interval (PMI)

Indra L¹, Hamann C², Szidat S³, Kanz F⁴, Lösch S¹, Lehn C⁵

¹Department of Physical Anthropology, Institute of Forensic Medicine, University of Bern, Bern, Switzerland, ²Leibniz-Laboratory for Radiometric Dating and Stable Isotope Research, Christian-Albrechts-Universität zu Kiel, Kiel, Germany, ³Department of Chemistry, Biochemistry and Pharmaceutical Sciences & Oeschger Centre for Climate Change Research, University of Bern, Bern, Switzerland, ⁴Center for Forensic Medicine, Medical University of Vienna, Vienna, Austria, ⁵Institute of Legal Medicine, Ludwig-Maximilians-University of Munich, Munich, Germany

Estimating the postmortem interval (PMI) of human remains is important in forensic anthropology, e.g. to aid the identification process. For this, a frequently employed method is radiocarbon dating, using the bomb-peak-model after 1950. Because of the bone remodeling, there is a lag time between the calibrated skeletal radiocarbon data and the actual year of death of an individual. The remodeling rate depends on the physiological state of the bone and may be different for each skeletal element. Quantifying these factors is challenging. By adding more data to this research field, our study aims to enhance the accuracy of radiocarbon-based PMI estimations of skeletal remains.

We radiocarbon-dated bone collagen from 25 forensic cases in Switzerland, Germany and Austria, of individuals that had died between 19 and 98 years of age. We sampled skull (occipital, parietal and temporal bone) and femur and combined the calibrated F¹⁴C values with the known individual data of the deceased to calculate collagen remodeling rates.

Our results show that petrous bone remodeling rates are low and lag times increasing roughly proportionate with age-at-death. The petrous bone is therefore less suitable for PMI estimation because its radiocarbon value refers to the period of the (early) childhood. Femur and skull remodeling rates are comparable. However, the inter-individual variability is pronounced, especially in the elderly. To create a universal model for year-of-death estimation based on the radiocarbon data, we need to better understand factors such as physiological status of the individual and its influence on skeletal turnover rates.

Ta1 P02

Chronological records in animal tissues

<u>Pachnerova Brabcova K</u>¹, Kufnerova J¹, Valasek V¹, John D^{1,2}, Petrova M¹, Brychova V¹, Svetlik I¹

¹Nuclear Physics Institute of the CAS, Praha, Czech Republic, ²Czech Technical University in Prague, Praha, Czech Republic

Radiocarbon dating of recent and near-future samples faces an inability to distinguish these from the pre-bomb peak ones. It is caused by radiocarbon levels decline to pre-bomb activities.

If the samples in question are of the animal tissues, such as protected species being dated for legal purposes, possible mitigation of this unfavourable trend lies in exploitation of the tissue chronological record. In the best case, the known chronology can anchor the sequence on radiocarbon calibration curve, and thus reduce the ambiguity of the dating results.

Our research aims on tissues of several endangered species, such as ivory of elephants (Loxodonta africana), scales of pangolins (Smutsia gigantea, Manis tricuspis), or tortoise shells (Testuda hermanni, Testudo graeca, Testudo marginata). Radiocarbon dating of incremental lines was accompanied with other analysis, optical and scanning electron microscopy and X-ray fluorescence.

Absorption and Distribution of Ultra-Trace Exogenous ¹⁴C Urea in Rats

Wang L, Tang J^{1,2}, Zhang G¹, Shi S¹, Chen D¹, Qi L¹, Yang P³, Zhang X³, Xia C³, **Shen H**^{1,2}

¹Guangxi Normal University, Guilin, China, ²Guangxi key laboratory of nuclear physics and nuclear technology, Guilin, China, ³Guilin Medical University, Guilin, China

A study on absorption and distribution of radiocarbon labeled urea in rats was carried out at the ultra-trace level with AMS. The drug concentrations in plasma and tissues of rats after an oral administration of an ultra-trace dose of [14C] urea were measured. The drug concentration vs time curves in plasma and tissues were obtained. The results show that the drug distribution of ultra-trace dose is different from that of conventional-dose, and the [14C] urea is excreted mainly through urine and respiratory. This study provides information on the pharmacokinetics and tissue distribution of exogenous urea in rats at the ultra-trace level and verifies the feasibility of using AMS for ultra-trace dose drug research beyond the traditional measurement range.

Keywords: AMS, ultra-trace dose, [14C]urea, pharmacokinetics, distribution

Ta1_P04

Bomb pulse dating of human calculi

Wang 1,2,3 , Ding $P^{1,2,3}$, Shen $C^{1,2}$, Zhu $S^{2,4}$

¹State Key Laboratory of Isotope Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, , Guangzhou, China, ²CAS Center for Excellence in Deep Earth Science, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzho, China, ³Southern Marine Science and Engineering Guangdong Laboratory(Guangzhou), Guangzhou, China, ⁴State Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou, China

The onset ages of various human calculus diseases are usually later than the emergence ages of calculi in the body because the patients seek medical attention after the symptoms and complications are perceptible. Knowing the emergence ages of calculi will help doctors figure out the causes and benefit public health. In this study, we collected three kinds of calculi, including sialoliths (S), gallstone (GS), and bladder stones (BS) from 8 donors in Guizhou, Southwest China. Five of these samples are big and have multiple layers. We separated them into the inner core and outer crust parts and studied their ¹⁴C ages and ¹³C signatures. The results show the bomb pulse dating ages of BS and GS (c. 0 - 6 yrs) are much younger than those of sialoliths (c. 9 - 44 yrs). The difference between the ages of the outer crusts and inner cores indicates the growth period of calculi, ranging from 0.4 to 6.9 yrs. The growth rates of GS and BS are between 2.8 to 4.1 mm/yr. The δ^{13} C values of sialoliths, GS, and BS range from -23.9 to -21.5 %, -22.6 to -22.2 %, and -20.5 to -19.5 %, respectively. Distinguish ages and stable isotope distribution patterns likely exist among different kinds of calculi, but further studies are needed to give a statistical conclusion.