COMPARISON OF TUFAS AS GEOCHEMICAL ENVIRONMENTAL PROXIES IN CONTINENTAL AND MEDITERRANEAN DINARIC KARST

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Tufas are increasingly gaining attention as potential environmental indicators, since their morphological, geochemical and isotopic characteristics reflect climatic conditions in the period of their growth, as well as discharge, precipitation, insulation, nutrient balance, anthropogenic influences etc. Their stable oxygen isotope composition ($\delta^{18}O$), distribution of trace cations such as Mg, Sr and Ba, as well as changes in concentration and molecular composition of organic substances reflect relative temperature changes in the period of their formation, whereas the stable carbon isotope composition ($\delta^{13}C$) reflects environmental changes, such as discharge, supply from biogenic CO_2 from the soil zone, precipitation and hydrological conditions in river systems.

Different types of tufa from Mediterranean and continental parts of the Dinaric karstic area were compared: bulk river tufa from two large groundwater-fed river systems (Krka, Croatia, discharging into the Central Adriatic, and Krka, Slovenia, belonging to the Danube river catchment) and two annually laminated crusts, one formed in a pipe diverting river water to the power plant on the Mediterranean river Krka, Croatia, and an incrustation formed on a wooden pillar in Plitvice Lakes (Continental Croatia). Isotopic ($\delta^{18}O$) and Mg thermometers were used to estimate the temperature of carbonate precipitation; these estimates were compared to the measured water temperatures, available from regular national hydrometeorological observation networks or measured in-situ during the course of the research. The uncertainties in the Mg temperature estimates were calculated from the first-order perturbation as the square-root of the sum of the squares of the contributing terms, namely the products of the derivatives with respect to individual parameters and their uncertainties. The parameters were the coefficients of the linear expressions for the temperature dependence of the Mg/Ca ratios of water and tufas, and Mg distribution coefficient.

It was found that the precipitation temperatures for bulk tufas calculated using the oxygen isotope thermometry overestimated the absolute temperature and the temperature range, compared to the measured water temperatures, although they generally reproduce the overall trend of temperature changes. Geochemical thermometry gave satisfactory results only where the [Mg/Ca] ratios of water were reasonably well correlated to the water temperature, which was not always the case. For bulk river tufas, hydrological parameters (discharge, recharge mode) critically influence the chemistry and isotopic composition of water, which makes them highly unreliable temperature proxies irrespective of the climate zone. Both isotopic and geochemical thermometers of laminar crusts reproduced the carbonate precipitation temperatures better than bulk tufas. However, beside the above-mentioned limitation, geochemical thermometry was shown to be extremely sensitive to anthropogenic pollution of water with metals since any contamination of water is reflected in the chemical composition of precipitates, leading to errors in temperature estimates.

For both river systems, the calibration uncertainties (weak or unclear relationship between proxy record and climate parameters) and process uncertainties (mathematical models translating proxy variables to a climate signal) were very large, at some sites even exceeding 10°C, which makes analysed tufas highly unreliable as palaeotemperature archives.