MOONMILK IN POSTOJNA CAVE PRECIPITATES UNDER ISOTOPIC EQUILIBRIUM CONDITIONS

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Summary

A part of a comprehensive multidisciplinary study of Postojna Cave, Slovenia, **(Figure 1)** related to modern speleothem formation conditions (Mandić, 2013) is presented. One year monitoring was conducted at nine locations within Postojna Cave in order to determine environmental conditions of carbonate deposition.

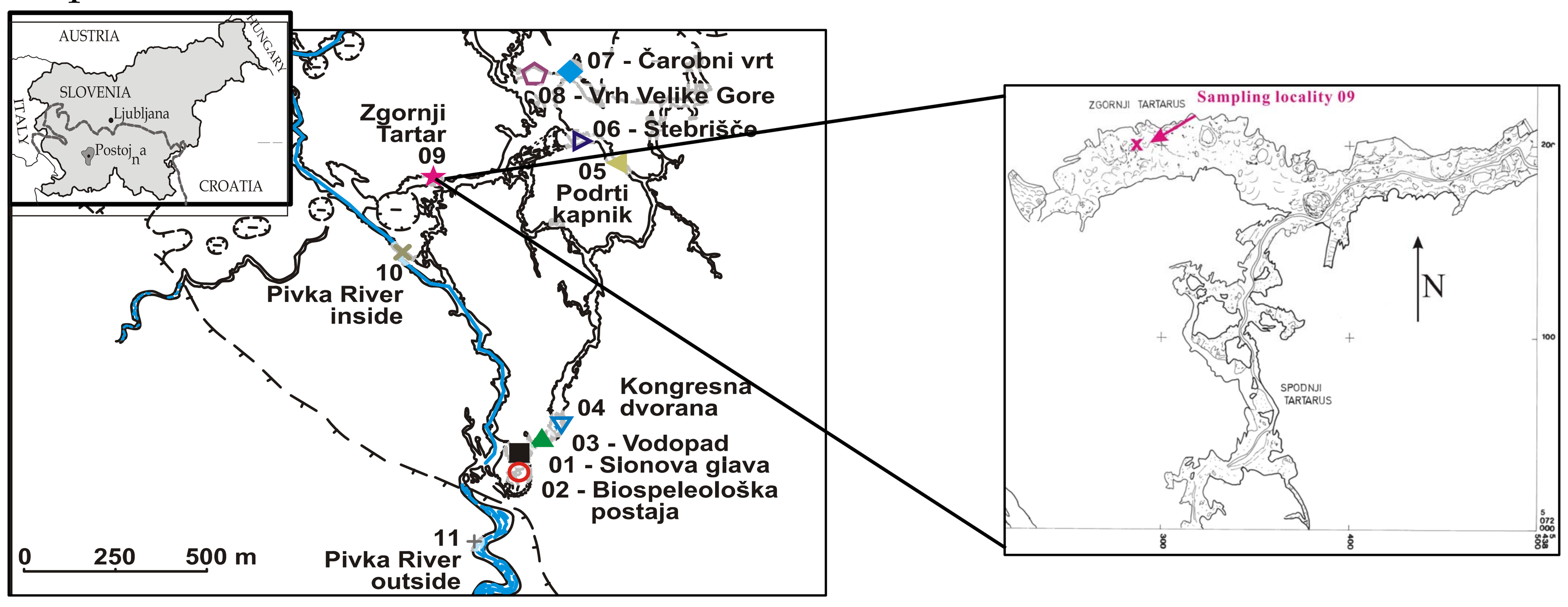


Figure 1. *Monitored locations within Postojna Cave, Slovenia with a detailed plot of micro location Zgornji Tartar*

Modern carbonates, mostly soda-straw samples, were collected and their stable isotope composition ($\delta^{13}C_c$ and $\delta^{18}O_c$) was determined. The assessment of process (equilibrium or kinetic) of precipitation for modern carbonates was done by comparing these values with isotopic composition of water ($\delta^{18}O_w$) and of dissolved inorganic carbon (DIC, $\delta^{13}C_{DIC}$): measured difference between $\delta^{13}C_{DIC}$ and $\delta^{13}C_c$ was compared with the theoretical fractionation ε value; fractionation factor (α) calculated from the measured $\delta^{18}O_w$ and $\delta^{18}O_c$ values was compared with the equilibrium fractionation factor α_{eq} for the measured temperature; temperature of carbonate precipitation was calculated from the isotopic ^{18}O composition of carbonate and water and compared with the measured temperature. Even thou the temperatures of calcite precipitation calculated by using different equations generally do not agree with the measured temperatures at given locations, research has resulted in finding locations and samples which are promising candidates for paleoclimate investigations.

First description of moonmilk in Postojna Cave

Because this is the first time that moonmilk is described in Postojna Cave, the investigation of its origin has started.

Petrographicaly, the moonmilk is composed of calcite needles approximately 100 µm long, and 10 µm wide (**Figure 2**).

SEM micrographs of moonmilk show evidence of microbial biomediation or bioprecipitation (**Figure 3**).

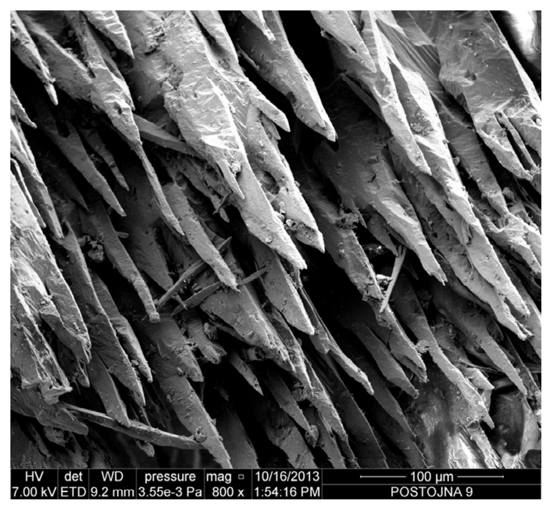


Figure 2. *Calcite needles*

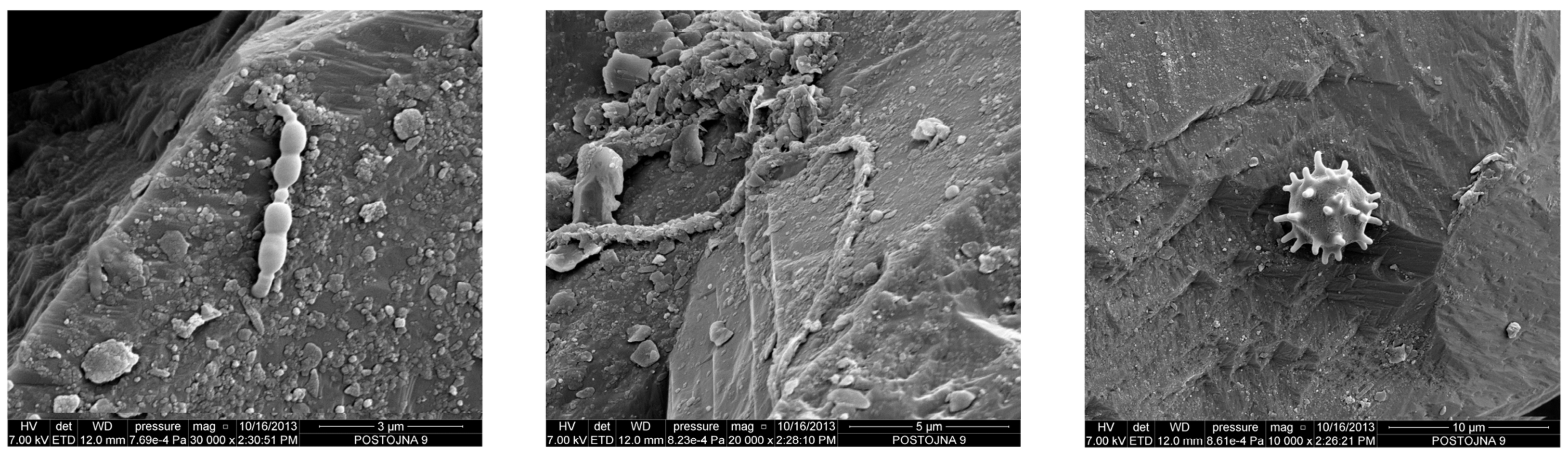


Figure 3. *According to shape and size (1 µm) there is evidence of bacterial existence*

ATR-FTIR* analysis (**Figure 4**) pertains to presence of organic compounds (Bullen et al., 2008, Appl. and Env. Microbiology, 74, 4553-4559). It has to be distinguished whether the organic compounds found in a moonmilk sample are a result of cave micro-organisms (native) or of allochthonous species. To rule out one of the two possibilities, a sample is given for RNA sequencing.

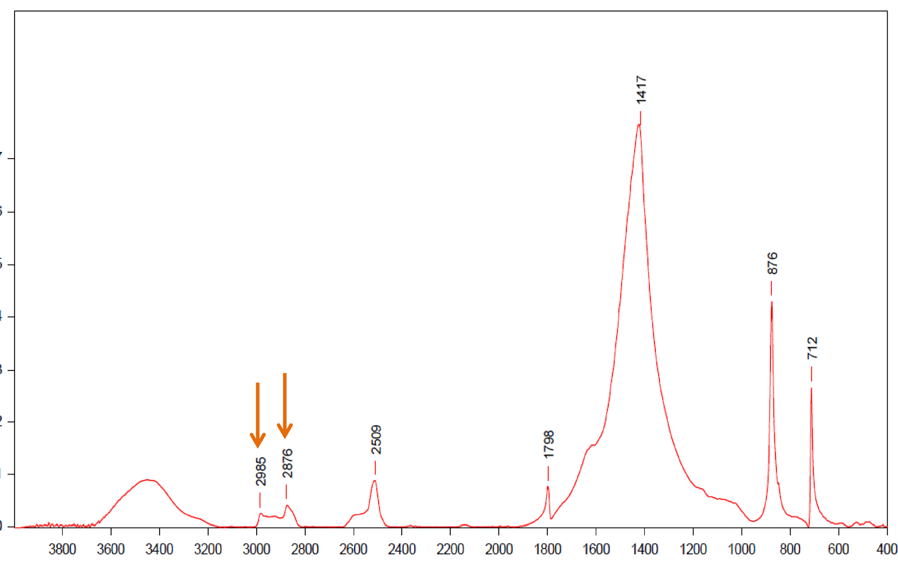


Figure 4. *Wavenumbers 2876 and 2985 cm^{-1} indicate the presence of organic matter in a sample*

*ATR-FTIR: Attenuated total reflectance Fourier transform infrared

Monitoring results at location Zgornji Tartar

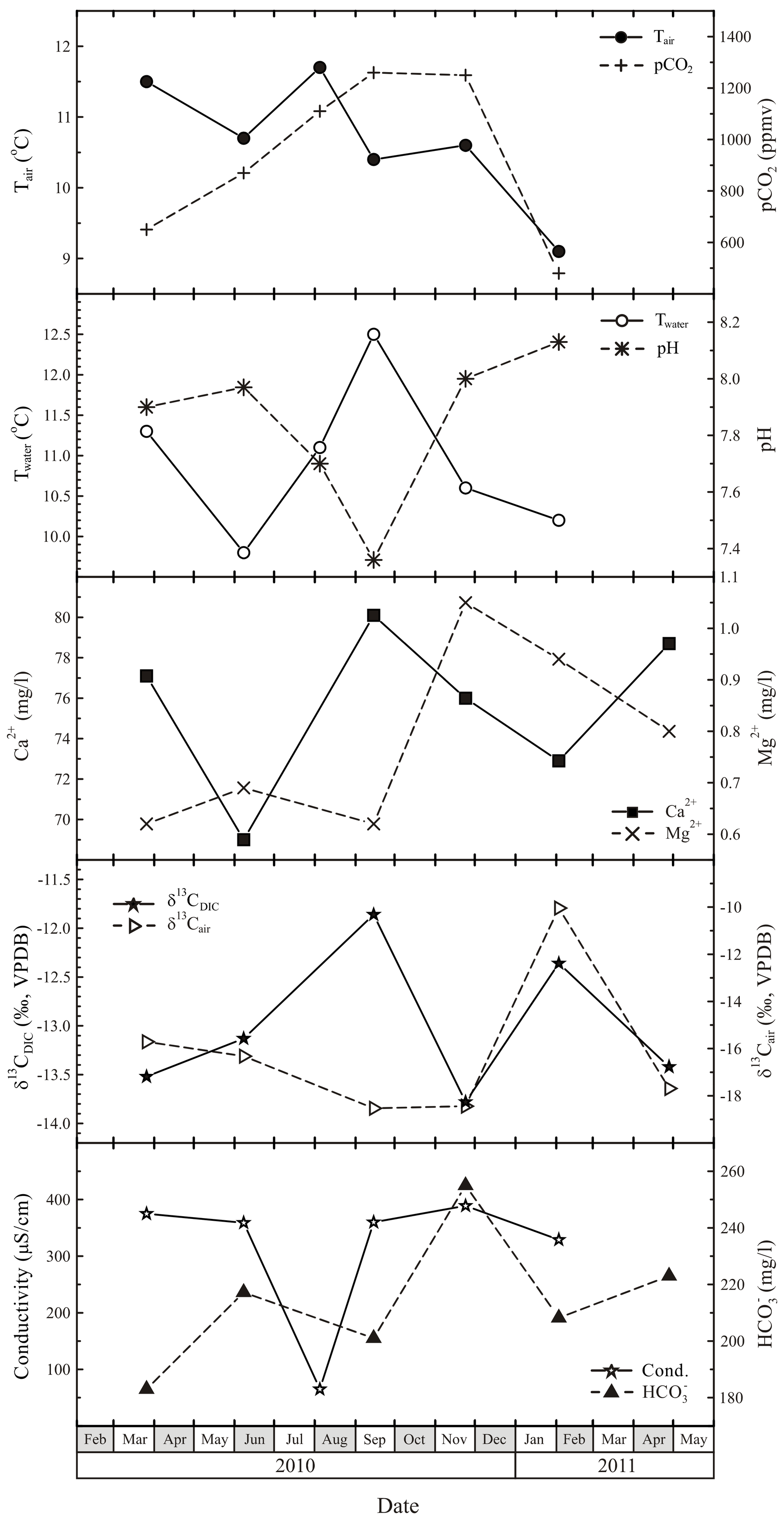


Figure 5. Monitoring results on location Zgornji Tartar

Location 09 – Zgornji Tartar ("Upper Tartar" or Tartarus) is situated in the part of the Postojna Cave which is isolated from tourist visit. The sampling location (**Figure 1**) is in a vicinity of Stara apnenca collapse doline. Location was in previous times under climatic influence of an opening which is nowadays closed by sediment (Gospodarič, 1976, Acta Carsologica 7, 5-135). Distance from this entrance is 110 m and from the main entrance to Postojna Cave is 1970 m.

Mean air temperature (**Figure 5**) at location 09 – Zgornji Tartar is 10.7 ± 0.9 ºC. The mean water temperature is 10.9 ± 1.0 ºC. The drip rate 80 ± 103 min^{-1} varies from 19 to 300 min^{-1}. Mean pCO_2 is 937 ± 325 ppmv. Mean values of conductivity, pH, and pCO_2 are 313 ± 123 µS/cm, 7.8 ± 0.3, and 937 ± 325 ppmv, respectively. Mean values of magnesium, calcium and bicarbonate concentrations are 0.8 ± 0.2 mg/L, 76 ± 4 mg/L, and 215 ± 24 mg/L, respectively. The mean $\delta^{13}C$ value in DIC is -13.01 ± 0.75 ‰. The mean $\delta^{13}C$ in air is (-16.1 ± 3.2 ‰).

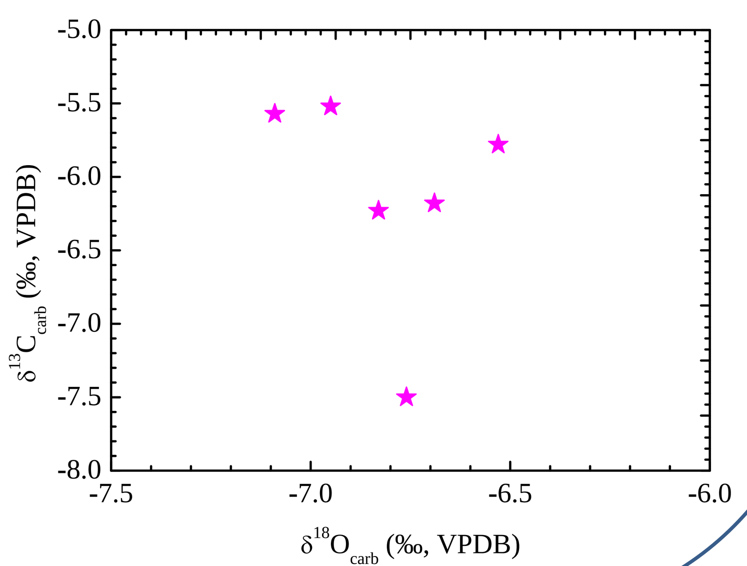


Figure 6. $\delta^{13}C$ and $\delta^{18}O$ composition of moonmilk from location 09

Mandić M., 2013. Determination of equilibrium conditions of carbonate precipitation in Postojna Cave with possible application to paleoclimatology. Ph.D. Thesis, Zagreb, University of Zagreb, 205 p.

Temperature calculation

Table 1. The α values calculated from measured $\delta^{18}O$ values of drip water and recent carbonates in Postrojna Cave and comparison with the equilibrium α_{eq} values.

		Equilibrium α values, α_{eq} $1000\ln\alpha = \frac{M\cdot10^6}{T(K)^2} + \frac{N\cdot10^3}{T(K)} - P$						α values for recent carbonates	
Location	t_{air} (ºC)	O'Neil et al., 1969; $1000\ln\alpha = \frac{2.78\times10^6}{T(K)^2} - 3.4$	Friedman and O'Neil, 1977 $1000\ln\alpha = \frac{2.78\times10^6}{T(K)^2} - 2.89$	Kim et al., 2007 $1000\ln\alpha = \frac{18.03\times10^3}{T(K)} - 31.17$	Coplen, 2007 $1000\ln\alpha = \frac{17.4\times10^3}{T(K)} - 28.6$	Chacko and Deines, 2008 $1000\ln\alpha = \frac{2.5735\times10^6}{T(K)^2} - 0.869$	Tremaine et al., 2011 $1000\ln\alpha = \frac{16.1\times10^3}{T(K)} - 24.6$	"Soda straw"	Peculiar growth types
01	9.8	1.0318	1.0323	1.0331	1.0334	1.0318	1.0328	1.0345	1.0360
02	9.9	1.0318	1.0323	1.0331	1.0334	1.0317	1.0328	1.0341	-
03	9.7	1.0318	1.0324	1.0331	1.0335	1.0318	1.0328	1.0347	-
06	11.3	1.0314	1.0320	1.0327	1.0331	1.0314	1.0325	1.0326	-
07	10.7	1.0316	1.0321	1.0329	1.0332	1.0316	1.0326	1.0337	-
08	11.6	1.0314	1.0319	1.0327	1.0330	1.0313	1.0325	1.0337	-
09	10.7	1.0316	1.0321	1.0329	1.0332	1.0316	1.0326	1.0341	1.0332

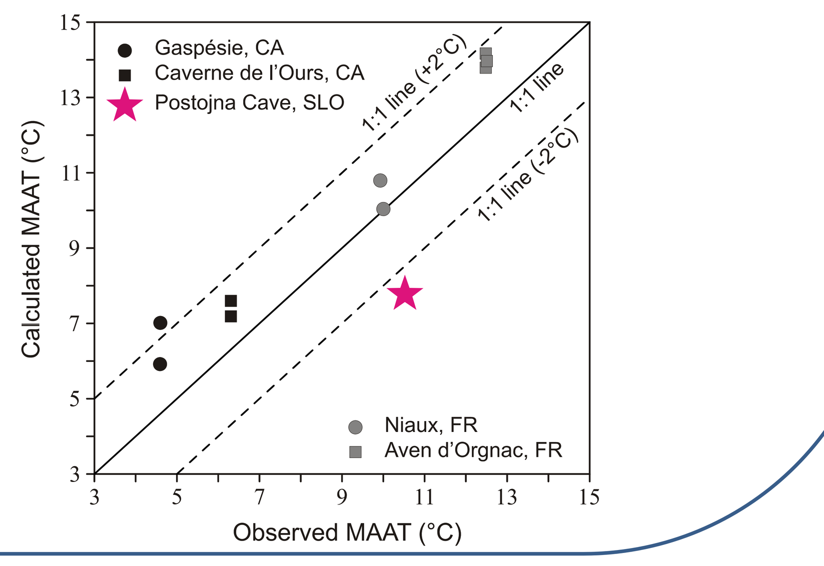
The α values (**Table 1**) are higher than the equilibrium fractionation factors α_{eq} given by various approaches. Only at locations 06 – Stebrišče and 09 – Zgornji Tartar the two values are comparable.

Table 2. Comparison of measured temperatures and temperatures determined from $\delta^{18}O$ of water and carbonates under assumption of precipitation under isotopic equilibrium conditions

Location	Measured temperature (°C)	Calculated temp. Range, (°C)	
		Soda straw	„Peculiar" types
01	9.8	-1.0 - 3.5	-2.1 -1.0
02	9.9	0.7 - 5.0	
03	9.7	-1.8 - 2.8	
06	11.3	5.7 - 10.3	
07	10.7	2.0 - 6.0	
08	11.6	0.5 - 4.7	
09	10.7	1.0 - 5.1	Moonmilk 7.4 - 7.8

Type	Reference	Equation	Source
$t(^oC) = a - bD + cD^2$; $D = \delta^{18}O_{carb} - \delta^{18}O_{water}$; $\delta^{18}O_{carb}$ in VPDB, $\delta^{18}O_{water}$ in VSMOW	Epstein and Mayeda, 1953	$t(^oC) = 16.5 - 4.3\,D + 0.14\,D^2$	Organic
	Craig, 1965	$t(^oC) = 16.9 - 4.2\,D + 0.13\,D^2$	Organic
	Shackleton, 1974	$t(^oC) = 16.9 - 4.38\,D + 0.10\,D^2$	Organic
	Grossman, 1982	$t(^oC) = 16.4 - 4.2\,D + 0.13\,D^2$	Inorganic
	Mulitza et al., 2003	$t(^oC) = 14.32 - 4.28\,D + 0.07\,D^2$	Organic
	Leng and Marshall, 2004	$t(^oC) = 13.8 - 4.58\,D + 0.08\,D^2$	Inorganic
	Andrews, 1994, 1997	$t(^oC) = 15.7 - 4.36 \times D + 0.12 \times D^2$	Inorganic

Figure 7. Observed mean annual air temperature in caves (Lacelle et al., 2004; Can. J. Earth Sci. 41: 1411-1423) versus calculated mean annual air temperature derived from the $\delta^{18}O$ values of moonmilk



SINA, 12th Austrian Stable Isotope Network Meeting, 15th & 16th November, 2013, Graz .