Available online at www.ij.s.speleo.it

International Journal of Speleology

Official Journal of Union Internationale de Spéléologie

Modern C, O, and H isotope composition of speleothem and dripwater from Modrič Cave, eastern Adriatic coast (Croatia)

Maša Surić¹, Zvezdana Roller-Lutz², Magda Mandić², Ines Krajcar Bronić³, Mladen Juračić⁴

Abstract:

Surić M., Roller-Lutz Z., Mandić M., Krajcar Bronić I., Juračić M. 2010. Modern C, O, and H isotope composition of speleothem and dripwater from Modrič Cave, eastern Adriatic coast (Croatia). *International Journal of Speleology*, 39 (2), 91-97. Bologna (Italy). ISSN 0392-6672.

Modrič Cave is a shallow horizontal cave situated in the middle of the eastern Adriatic coast (Croatia). The cave entrance is located 120 m from the coast at an altitude of 32 m above sea level, and due to its position on the SW slope of the Dinaridic mountain range, a Mediterranean climatic influence is dominant. Due to the stable environmental conditions [15.6 ± 0.1 °C] Modrič Cave was recognized as a potential site for detailed palaeoclimatic studies. Isotope analyses of modern carbonate speleothems, rain and dripwater were conducted in order to evaluate the isotopic equilibrium conditions. The $\delta^{18}\text{O}$ composition of rain and cave seepage waters shows an absence of kinetic isotopic fractionation within the epikarst zone, whereas the relation between $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ in modern carbonate samples and dripwater suggests the isotopic equilibrium conditions during the carbonate deposition. These results contribute to a better understanding of the present-day isotopic composition and provide a basis for interpretation of speleothem-derived palaeoclimatic records.

Keywords: carbonate speleothems, dripwater, stable isotopes, isotopic fractionation, Eastern Adriatic, Croatia

Received 14 April 2010; Revised 30 April 2010; Accepted 17 May 2010

INTRODUCTION

The Croatian coast, as a part of *Classical karst* with thousands of caves, offers an excellent potential for palaeoenvironmental studies based on speleothem records (eg. Horvatinčić et al., 2003; Surić et al., 2007; 2009; 2010; Surić & Juračić, 2010), but until now no comprehensive research has been conducted. Some studies on speleothems from the eastern Adriatic coast (Surić et al., 2005a, 2005b) demonstrated favourable conditions for speleothem deposition during the Last Glacial Maximum (LGM), unlike in the northern part of Europe, and similarly to the other Mediterranean regions, e.g. on Tyrrhenian coast of Italy (Alessio et al., 1992), and in Soreq Cave, Israel (Bar-Mathews et al., 1999). In order to conduct a broader study on past climate changes and to reveal possible teleconnections between neighbouring regions, the first step was to investigate the modern system including rain, dripwater, and cave deposits. Thus, the emphasis in this study is to characterize the environmental setting and possible fractionation

effects in Modrič Cave chosen for future palaeoclimate research.

Speleothems have been recognized as reliable archives of palaeoenvironmental change (palaeoprecipitation, palaeotemperature, palaeovegetation) since they offer important advantages over other continental and marine proxy records, e.g. they can be precisely dated and their occurrence is geographically widespread (McDermott, 2004). Furthermore, deposited in a sheltered stable cave environment with nearly constant cave-air temperature equal (or within ± 1 °C) to the mean annual surface temperature, they record climate conditions during their deposition, i.e. they reflect long-term temperature fluctuations (McDermott, 2004; Mickler et al., 2004; McDermott et al., 2005; White, 2007). The most valuable information derives from stable isotopic composition (O, C, H), and their climate-driven variability over the time, although some methodical difficulties still exist specially with respect to H isotopes analyses from speleothem fluid inclusions.

At slow degassing rates and no evaporation speleothem carbonate is deposited in isotopic equilibrium with dripwater, i.e. the relation between the isotope composition of the speleothem carbonate and the ambient water is a function of temperature (Lauritzen & Lundberg, 1999). Fast precipitation and/or evaporation due to the low cave humidity cause kinetic fractionation. Since kinetic fractionation complicates or even eradicates the climate signal in speleothems, an assessment of the degree of

1 Department of Geography, University of Zadar, Tuđmanova 24 i, 23000 Zadar, Croatia, msuric@unizd.hr

2 Stable Isotope Laboratory, Physics Department, School of Medicine, University of Rijeka, Braće Brannetetta 20, 51000 Rijeka, Croatia

3 Radiocarbon and Tritium Laboratory, Ruđer Bošković Institute, Bijenička 54, 10000 Zagreb, Croatia

4 Department of Geology, Faculty of Science, University of Zagreb, Horvatovac 102 a, 10000 Zagreb, Croatia

isotopic equilibrium is essential to correctly interpret speleothem $\delta^{18}\text{O}$ as a palaeoclimate record (Lachniet, 2009). Modern fractionation effects can be a pointer to similar conditions in the past (Mickler et al., 2004).

Variations of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ in precipitation are routinely used to track air-mass trajectories and to trace groundwater. In the cave environment, $\delta^{18}\text{O}$ and $\delta^2\text{H}$ dripwater composition, i.e. its comparison with the rainwater, indirectly offers insight into the residence time of the water in the epikarst zone, and possible fractionation along that pathway.

The carbon stable isotope ratio ($^{13}\text{C}/^{12}\text{C}$) in cave precipitates is related to the vegetative cover on the surface, and in principle, variations in $\delta^{13}\text{C}$ can record changes in the vegetation type. However, other factors (e.g. biological activity, bedrock proportion, rainfall, and drip rate), can also affect $\delta^{13}\text{C}$ variations (Lauritzen & Lundberg, 1999).

STUDY AREA AND ENVIRONMENTAL SETTINGS

Modrič Cave (44°15' N, 15°32' E) is located on the eastern Adriatic coast on the SW slope of the central part of the Dinaridic mountain range. It is a shallow, mostly horizontal cave (Fig. 1) with an entrance 32 m above sea level (a.s.l.) some 120 m off the coastline, and a total length of 829 m (Kuhta et al., 1999). The cave formed in well-bedded Cenomanian-Turonian limestone dipping 20–40° to the NW (Miko et al., 2002), within the 2.5 km wide fault zone on the contact of Adriaticum and Dinaricum structural units (*sensu* Herak, 1986). Intensive karstification resulted in the absence of surface runoff and fast direct infiltration into the underground (Miko et al., 2002). Seven other caves and two submarine springs (vruljas) located near Modrič Cave point to a larger cave system. Speleothems are common throughout Modrič Cave, and presently active stalactites and stalagmites occur in all its parts. The cave consists of two main passages, but due to the preservation of the right passage where bones of *Ursus spelaeus* and archaeological remains were found (Malez, 1987), the sampling and measurements were undertaken only along the left passage. The thickness of the heavily fractured bedrock above the cave gradually increases from 1 m near the entrance to 30 m towards the end of the left passage (Kuhta et al., 1999). Only the very last part (the end of Red chamber, Fig. 1) rises toward the surface. The rock thickness from site 3 to site 7 is 18–30 m, and above the sampling site 6 (under the hill peak) it is ~27 m. Vegetation cover above the cave is maquis - sparsely bush and grass vegetation (C3 plants) typical of the Mediterranean area with thin sporadic terra-rossa soil.

The region is under Mediterranean climatic influence, and according to Köppen's classification (Köppen, 1936), the regional climate is of the Cfa type, characterized by a temperate humid climate with hot summers (Fig. 2). Data from the climatological station Starigrad (8 km from the cave) for the 1992–2008 period show a mean annual temperature of 16.0 °C with mean monthly values ranging from 7.4 °C in January to 25.8 °C in July and August. The

mean annual total precipitation is 1187 mm with a maximum in December and a minimum in July (Meteorological and Hydrological Service, 2009). The impact of Velebit Mt. on the orographic precipitation in this region is evident from the difference in mean annual precipitation between the cave region and the adjacent meteorological station (Zadar, 30 km to the SW, Fig. 2), which is 879 mm for the 1971–2000 period (Zaninović, 2008).

Environmental conditions are stable almost throughout the whole cave, reflecting the mean annual temperature on the surface. After the entrance (1 m wide, 2 m high) and first 10 meters (2.5 m wide, 3.5 m high), along the next 30 meters of the cave there is a narrow zig-zag channel with several very tight and low passages that protect the rest of the cave from the outside influence, including the air flow. Three sets of measurements under different weather conditions along the left passage (with the presence of the researchers) recorded an average temperature of (15.9 ± 0.3) °C for sites 4–8. Deviations were observed only in the entrance part and near the end of the left passage (site 7) which is close to the surface (Fig. 3). A continuous measurement in the middle of the left passage (site 5 on Fig. 1) over a period of one year recorded an average temperature of (15.6 ± 0.1) °C.

SAMPLING AND ANALYTICAL METHODS

Sampling

In order to assess current isotopic equilibrium conditions within the cave, analyses of dripwater, rainwater and modern calcite samples were essential. Three types of dripwater samples were collected in narrow neck 50 ml HDPE bottles within the same chamber (arrow in Fig. 1): water infiltrated during the warmer part of the year in three sampling containers (July – November 2007; MODW 1, 2 and 3), during the colder period in two containers (November 2007 – May 2008; MODW 10 and 11) and water collected year around (July 2007 – May 2008; MODW 4). Also, the stable isotope data for the dripwater from a previous study were considered (Miko et al., 2002). For the rainwater composition we used data from the Zadar GNIP station (monthly mean values from the period 2001–2003) (IAEA/WMO, 2006; Horvatinčić et al., 2005; Vreča et al., 2006), and own data, i.e. three precipitation events collected in Zadar (removed from the rain collector soon after the rain). Samples of modern calcite for $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ measurements were taken from the tips of active stalactites (MOD 2, 6, and 7), from an active soda straw (MOD 3), and two samples of the calcite precipitated on a nylon sheet between 1999 and 2007 (MOD 8 and 9).

Stable isotope measurements

The stable isotope composition of the samples was analyzed at SILab Rijeka (Stable Isotope Laboratory at the Physics Department, School of Medicine, University of Rijeka). All measurements were done on the Delta^{Plus}XP (Thermo Finnigan) mass spectrometer (Mandić et al., 2008).

To obtain the $^{13}\text{C}/^{12}\text{C}$ and $^{18}\text{O}/^{16}\text{O}$ ratios of the

Fig. 1. Location, cross sections and plan of Modrič Cave with dripwater and modern calcite sampling site (arrow), and temperature measurement sites (dots 1-8)

powdered carbonate samples concentrated phosphoric acid was added to the sample vials containing approximately 250 µg each at a temperature of 70 °C, and GasBench (Thermo Finnigan) was used for carbonate samples measurements.

The oxygen and hydrogen stable isotope composition of water samples was analyzed in a HDO Equilibration Unit (ISO Cal) attached to a dual inlet port of the mass spectrometer. The $^{18}\text{O}/^{16}\text{O}$ and the $^2\text{H}/^1\text{H}$ ratios were obtained from CO_2 and H_2 gas, respectively, after equilibration with a 4 ml water sample.

Results are expressed in delta units as obtained

from the measured respective isotope ratios R by

$$\delta (\text{‰}) = [(R_{\text{sample}}/R_{\text{standard}}) - 1] \times 10^3 \quad (1)$$

relative to the international standards V-SMOW for oxygen and hydrogen in water, and V-PDB for carbon and oxygen stable isotopes in carbonate samples. Analytical reproducibility in dual inlet measurements is better than 1‰ for hydrogen and 0.1‰ for oxygen. For carbonate samples analytical reproducibility is better than 0.1‰. Data analysis was performed in Laboratory Information Management System (LIMS)

Fig. 2. Geographical distribution of Köppen's climate types in Croatia (adapted from Šegota & Filipčić, 2003). Note the abrupt transition toward the zone with humid boreal climate (Df). (Csa - Mediterranean climate with hot summer; Csb - Mediterranean climate with warm summer; Cfa - temperate humid climate with hot summer; Cfb - temperate humid climate with warm summer; Df - humid boreal climate)

Fig. 3. Cave air temperatures along the left passage: summer (black), winter event with cold and dry NE bora wind (grey) and with warm and wet SE sirocco wind (dotted line). Measurement points are marked on Figure 1. The value of site 1 relates to the outside temperature measured in front of the entrance, but sheltered from the cave air influence.

software for light stable isotopes (with permission of Mr. Tyler Coplen, USGS). SILab in-house standards calibration is given in detail in Mandić et al. (2008).

RESULTS AND DISCUSSION

Measured $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of speleothem carbonate (MOD 2, 3, 6, 7, 8 and 9) are given in Table 1, and $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values of dripwater (MODW 1, 2, 3, 4, 10 and 11) and rainwater (ZADW 1, 2 and 3) are presented in Table 2.

$\delta^2\text{H}$ and $\delta^{18}\text{O}$ in dripwater

The Global Meteoric Water Line (GMWL) represents a linear correlation of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values in global precipitation and is expressed by $\delta^2\text{H} = 8 \times \delta^{18}\text{O} + 10$ (Craig, 1961) or more precisely as $\delta^2\text{H}$

$= (8.20 \pm 0.07) \times \delta^{18}\text{O} + (11.27 \pm 0.65)$ (Rozanski et al., 1993). It is actually an average of a series of local meteoric water lines (LMWL) which differ from the GMWL both by slope and intercept as a result of different climate settings and geographical positions. Accordingly, local meteoric water values could reflect the source region of the air masses, while the similarity of LMWL with the water line of the dripwater in the cave can suggest a relatively short transit time of the water from the surface to the cave and no kinetic fractionation in epikarst (Lachniet, 2009).

Figure 4 shows the comparison of Modrić Cave $\delta^{18}\text{O}$ and $\delta^2\text{H}$ dripwater values with the isotope composition of precipitation at nearby Zadar. The monthly precipitation samples were collected at Zadar in the period 2001–2003, and the mean air temperatures and amount of precipitation were also recorded. Numerical values and detailed analyses of all recorded data are given in Horvatinčić et al. (2005) and Vreča et al. (2006). The GMWL, the LMWL of the Zadar region ($\delta^2\text{H} = (6.9 \pm 0.4) \times \delta^{18}\text{O} + (5.2 \pm 2.4)$; Vreča et al., 2006), and the Mediterranean meteoric water line (MMWL) ($\delta^2\text{H} = 8 \times \delta^{18}\text{O} + 22$; McGarry et al., 2004) are shown for comparison. The dripwater values tend to cluster along the LMWL, suggesting fast infiltration of the meteoric water into underground without significant kinetic (evaporative) fractionation. However, the lower slope of the LMWL in comparison with the GMWL slope indicates slight evaporative enrichment as recorded in the southern Adriatic region (Vreča et al., 2006). The mean annual deuterium excess in precipitation from period 2001 – 2003 varied from 8.8‰ to 12.6‰, with small seasonal variations - lower deuterium excess values are observed in spring-summer and higher in autumn-winter. The 3-year mean deuterium excess of 10.9‰ is close to the typical values of Atlantic air masses (10‰) showing the Atlantic air masses as the main source of precipitation. The mean deuterium-excess in dripwater of 11.5‰ corroborates this finding. Therefore, the observed deuterium excess is much lower than that associated with moisture derived from Mediterranean region (about 20‰, Ayalon et al., 1998; Rozanski et al., 1993), due to its lower relative humidity.

Weighted mean $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values for the 3-year period of precipitation in Zadar are -34‰ and -5.6‰, respectively (Vreča et al., 2006). Mean yearly values can vary between -33‰ and -35‰ and between -5.5‰ and -5.7‰, respectively. The mean values in the dripwater (Tab. 2) are $(-35 \pm 2) \text{‰}$ and $(-5.8 \pm 0.2) \text{‰}$, i.e., they are slightly more negative than the corresponding values in precipitation at Zadar. The difference in stable isotope composition can be caused by different mean annual temperatures at the two sites. However, from the mean temperatures (16.0 °C in Starigrad, 15.5 °C in Zadar) and by using the temperature coefficient of $\delta^{18}\text{O}$ equal to $0.25 \text{‰} \text{°C}^{-1}$ (Vreča et al., 2006) the expected difference in $\delta^{18}\text{O}$ is 0.12‰ more positive in Starigrad. Therefore, the observed difference toward more negative $\delta^{18}\text{O}$ values likely indicates more infiltration of water in the colder period of the year.

Table 1 $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ composition of modern speleothem carbonate

Sample	Description	$\delta^{18}\text{O}$ (‰ V-PDB)	$\delta^{13}\text{C}$ (‰ V-PDB)
MOD 2	tip of the active stalactite	-4.95	-6.07
MOD 3	tip of the active soda straw	-5.66	-8.19
MOD 6	tip of the active spaghetti stalactite	-3.58	-4.01
MOD 7	tip of the active spaghetti stalactite	-5.53	-4.76
MOD 8	modern calcite collected on a nylon sheet (1999-2007)	-5.48	-8.17
MOD 9	modern calcite collected on a nylon sheet (1999-2007)	-5.26	-9.77

Table 2 $\delta^{18}\text{O}$ and $\delta^2\text{H}$ composition of dripwater (MODW #) and rainwater (ZADW #) and calculated deuterium excess

Sample	Collection period	$\delta^{18}\text{O}$ (‰ V-SMOW)	$\delta^2\text{H}$ (‰ V-SMOW)	d-excess (‰)
MODW 1	July 2007 – November 2007	-5.86	-36.4	10.5
MODW 2		-5.69	-35.9	9.7
MODW 3		-5.82	-35.6	10.9
MODW 4	July 2007 – May 2008	-5.69	-31.6	14.0
MODW 10	November 2007 – May 2008	-6.04	-35.9	12.5
MODW 11		-5.50	-32.5	11.5
ZADW 1	3 August 2008	-4.10	-26.5	6.4
ZADW 2	9 August 2008	-2.38	-8.6	10.4
ZADW 3	10 August 2008	-2.64	-9.1	12.0

Isotopic fractionation

Deposition of modern calcite under isotopic equilibrium can be a good indicator that equilibrium conditions were fulfilled also in the past. Knowing the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ composition of the modern water and calcite and the cave temperature the fractionation conditions of modern precipitates can be evaluated. For the following calculations we used $\delta^{18}\text{O}_\text{C}$ from the most reliable carbonate samples, i.e. those that are surely most recently deposited: MOD 3 – soda straw in very initial phase, MOD 8 and 9 which precipitated on a nylon sheet from 1999 to 2007. Their $\delta^{18}\text{O}_\text{C}$ values are -5.66‰, -5.48‰ and -5.26‰ V-PDB, respectively (Tab. 1). For the dripwater samples we used data from the left passage from Miko et al. (2002) and from MODW 4 (collected year around) which have the same value of -5.69‰ V-SMOW. The fractionation effects can be checked by two expressions for temperature and $\delta^{18}\text{O}$ relation:

From known $\delta^{18}\text{O}_\text{C}$ and $\delta^{18}\text{O}_\text{w}$ values the temperature of calcite formation at isotopic equilibrium can be computed according to Craig's (1961) expression

$$T\ (^{\circ}\text{C}) = 16.1 - 4.15 \times (\delta^{18}\text{O}_\text{C} - \delta^{18}\text{O}_\text{w}) + 0.13 \times (\delta^{18}\text{O}_\text{C} - \delta^{18}\text{O}_\text{w})^2 \quad (2)$$

Using modern values of $\delta^{18}\text{O}_\text{C}$ and $\delta^{18}\text{O}_\text{w}$, temperatures for MOD 3, 8 and 9 of 16.0 °C, 15.2 °C and 14.3 °C are obtained with an average T_calc of 15.2 °C, which is in good accordance with the measured cave temperature T_meas of (15.6 ± 0.1) °C.

If we calculate the temperature-dependent equilibrium fractionation factor ($\alpha_{\text{c-w}}$) at $T_\text{meas} = (15.6 \pm 0.1) ^{\circ}\text{C}$ (288.8 K) using the equation of Friedman & O'Neil (1977)

$$1000 \ln \alpha_{\text{c-w}} = 2.78 \times (10^6 \times T^{-2}) - 2.89 \quad (3)$$

we get $\alpha_{\text{c-w}} = 1.0309$. This is in good agreement with the mean MOD 3, 8, and 9 value of $\alpha_{\text{c-w}} = 1.0312 \pm 0.0002$ which is obtained from:

$$\alpha_{\text{c-w}} = \frac{\delta^{18}\text{O}_{18\text{c}} + 1000}{\delta^{18}\text{O}_\text{w} + 1000} \quad (4)$$

Note that for the equation (2) $\delta^{18}\text{O}_\text{C}$ was given in V-PDB and $\delta^{18}\text{O}_\text{w}$ in V-SMOW, while in equation (4) $\delta^{18}\text{O}_\text{C}$ value was converted from V-PDB to V-SMOW, as required, using the expression of Coplen et al. (1983)

$$\delta^{18}\text{O}_{\text{V-SMOW}} = 1.03091 \times \delta^{18}\text{O}_{\text{V-PDB}} + 30.91 \quad (5)$$

Both calibrations support the assumption that modern speleothem carbonate precipitated at or close to isotope equilibrium with corresponding cave dripwater.

CONCLUSIONS

Modrič Cave is a well preserved protected site, rich in active and old speleothems, and it appears to be a suitable location for a wide spectrum of palaeoenvironmental studies using speleothems. Given its environmental settings with a stable temperature essentially

Fig. 4. $\delta^2\text{H}$ - $\delta^{18}\text{O}$ values of the precipitation and Modrić Cave dripwater in relation to the global meteoric water line (GMWL, solid line) and local meteoric water line (LMWL, dashed line) (Vreća et al., 2006). The Mediterranean meteoric water line (MMWL, dotted line) (McGarry et al., 2004) is shown for comparison.

equal to the average surface temperature, and a fast response to the surface precipitation, we addressed the question if the isotopic signal in cave deposits and seepage water could be affected by kinetic fractionation. The $\delta^{18}\text{O}$ and $\delta^2\text{H}$ in dripwater showed very good correspondence with the local meteoric water, i.e. the residence time of the infiltrating water is short enough to avoid kinetic fractionation due to evaporation in the epikarst.

The agreement of the measured cave temperature (15.6 ± 0.1) °C with the value calculated from the dripwater and modern calcite $\delta^{18}\text{O}$, i.e. the similarity of the equilibrium fractionation factor ($\alpha_{\text{c-w}}$) calculated for the measured cave temperature (1.0309) with the one (1.0312) obtained from the dripwater $\delta^{18}\text{O}_{\text{w}}$ and associated calcite $\delta^{18}\text{O}_{\text{c}}$, suggests the absence of significant kinetic fractionation during calcite precipitation.

According to these observations we hypothesise that modern carbonate deposition in the Modrić Cave occurs at or close to isotopic equilibrium. Assuming that similar conditions prevailed also in the past, we suggest that fractionation in the past was mainly affected by temperature. Hence, the isotopic signal of speleothem calcite can be regarded as a proxy of

palaeoenvironmental change, but forthcoming studies should be supported by additional analyses on sufficient number of samples. Also, further studies are planned to encompass not only Croatian coastal caves but also the inland sites on the other side of the orographic barrier of the Dinarides (Velebit Mt), and a comparison with other adjacent European and Mediterranean sites.

ACKNOWLEDGEMENTS

This study was supported by the Ministry of Science, Education and Sports of the Republic of Croatia through the scientific projects 119-1191152-1169, 269-2693084-1177, 098-0982709-2741, 062-0982709-0510. We thank M. Buzov (concessionaire of Modrić Cave), R. Lončarić and A. Lončar for the field assistance, and Prof F. McDermott for valuable suggestions. We are grateful to the reviewers and the editor for detailed reviews and constructive comments which improved the manuscript.

REFERENCES

- Alessio M., Allegri L., Antonioli F., Belluomini G., Ferranti L., Importa S., Manfra L. & Proposito A., 1992 - *Risultati preliminari relativi alla datazione di speleotemi sommersi nelle fasce costiere del Tirreno centrale*. *Giornale di Geologia*, ser. 3., **54/2**: 165-193.

- Ayalon A., Bar-Matthews M. & Sass E., 1998 - *Rainfall-recharge relationships within a karstic terrain in the eastern Mediterranean semi-arid region, Israel: $\delta^{18}\text{O}$ and δD characteristics*. Journal of Hydrology, **207**: 18–31.
- Bar-Matthews M., Ayalon A., Kaufman A. & Wasserburg G., 1999 - *The Eastern Mediterranean paleoclimate as a reflection of regional events: Soreq Cave, Israel*. Earth and Planetary Science Letters, **166**: 85–95.
- Coplen T.B., Kendall C. & Hopple J., 1983 - *Comparison of stable isotope reference samples*, Nature, **302**: 236–238.
- Craig H., 1961 - *Isotopic variations in meteoric waters*. Science, **133**: 1702–1703.
- Friedman I. & O'Neil J.R., 1977 - *Compilation of stable isotope fractionation factors of geochemical interest*. In: Fleischer M. (Ed.) - *Data of Geochemistry*. Washington, 14 p.
- Herak M., 1986 - *A new concept of geotectonics of the Dinarides*. Acta Geologica, **16**: 1–42.
- Horvatinčić N., Krajcar Bronić I. & Obelić, B., 2003 - *Differences in the ^{14}C age, $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ of Holocene tufa and speleothem in the Dinaric Karst*. Palaeogeography, Palaeoclimatology, Palaeoecology, **193**: 139–157.
- Horvatinčić N., Krajcar Bronić I., Barešić J., Obelić B. & Vidić S., 2005 - *Tritium and stable isotope distribution in the atmosphere at the coastal region of Croatia. Isotopic Composition of Precipitation in the Mediterranean Basin in Relation to Air Circulation Patterns and Climate*. TECDOC Series No. **1453**, IAEA, Vienna: 37–50.
- IAEA/WMO, 2006 - *Global Network of Isotopes in Precipitation. The GNIP Database*. Accessible at: <http://isohis.iaea.org>
- Köppen, W., 1936 - *Das geographische System der Klimate*. Handbuch der Klimatologie, Bd. 1, Teil C, Berlin.
- Kuhta M., Božičević S., Kapelj S. & Miko S., 1999 - *Studija zaštite i korištenja vrijednih prirodnih cjelina Modrič špilje i njene okoline (The protection and utilization study of the natural environment of the Modrič Cave and its surroundings)*. Croatian Geological Survey, 68 p.
- Lachniet M.S., 2009 - *Climatic and environmental controls on speleothem oxygen-isotope values*, Quaternary Science Reviews, **28** (5–6): 412–432.
- Lauritzen S.-E. & Lundberg J., 1999 - *Speleothems and climate: a special issue of The Holocene*. The Holocene, **9**: 643–647.
- Malez M., 1987 - *Kvartarna fauna vertebrate iz Modriča pećine kod Rovanijske (Hrvatska) (Quaternary vertebrate fauna from Modrič Cave (Croatia) near Rovanijska)*. Rad JAZU, **431**: 141–154.
- Mandić M., Bojić D., Roller-Lutz Z., Lutz H.O. & Krajcar Bronić I., 2008 - *Note on the spring region of Gacka River (Croatia)*. Isotopes in Environmental and Health Studies, **44** (2): 201–208.
- McDermott F., 2004 - *Paleo-climate reconstruction from stable isotope variations in speleothems: a review*, Quaternary Science Reviews, **23**: 901–918.
- McDermott F., Schwarcz H. & Rowe P.J., 2005 - *Isotopes in speleothems*. In: Leng M.J. (Ed.) - *Isotopes in Palaeoenvironmental Research*. Springer, Dordrecht, Netherland: 185–224.
- McGarry S., Bar-Matthews M., Matthews A., Vaks A., Schilman B. & Ayalon A., 2004 - *Constraints on hydrological and paleotemperature variations in the Eastern Mediterranean region in the last 140 ka given by the δD values of speleothem fluid inclusions*. Quaternary Science Reviews, **23** (7–8): 919–934.
- Meteorological and Hydrological Service of Croatia (2009) – official data obtained on request
- Mickler P.J., Banner J.L., Stern L., Asmerom Y., Edwards R.L. & Ito E., 2004 - *Stable isotope variations in modern tropical speleothems: Evaluating equilibrium vs. kinetic isotope effects*. Geochimica et Cosmochimica Acta, **68** (21): 4381–4393.
- Miko S., Kuhta M. & Kapelj S., 2002 - *Environmental baseline geochemistry of sediments and percolating waters in the Modrič Cave, Croatia*. Acta Carsologica, **31** (1): 135–149.
- Rozanski K., Araguas-Araguas L. & Gonfiantini R., 1993 - *Isotopic patterns in modern global precipitation*. In: Swart P.K., Lohmann K.L., McKenzie J. & Savin, S. (Eds.) - *Climate Change in Continental Isotopic Records*. American Geophysical Union, Washington DC: 1–37.
- Surić M. & Juračić M., (2010) - *Late Pleistocene – Holocene environmental changes – records from submerged speleothems along the Eastern Adriatic coast (Croatia)*. Geologia Croatica, **63/2**, doi: 10.1514/gc.2010.13.
- Surić M., Juračić M., Horvatinčić N. & Krajcar Bronić I., 2005a - *Late Pleistocene – Holocene sea-level rise and the pattern of coastal karst inundation: records from submerged speleothems along the Eastern Adriatic Coast (Croatia)*. Marine Geology, **214** (1–3): 163–175.
- Surić M., Horvatinčić N., Suckow A., Juračić M. & Barešić J., 2005b - *Isotope records in submarine speleothems from the Adriatic coast, Croatia*. Bulletin de la Société Géologique de France, **176** (4): 363–373.
- Surić M., Jalžić B. & Petricoli D., 2007 - *Submerged speleothems – expect the unexpected. Examples from the Eastern Adriatic coast*. Acta carsologica, **36** (3): 389–396.
- Surić M., Richards D.A., Hoffmann D.L., Tibljaš D. & Juračić M., 2009 - *Sea level change during MIS 5a based on submerged speleothems from the eastern Adriatic Sea (Croatia)*. Marine Geology, **262**: 62–67, doi: 10.1016/j.margeo.2009.03.005
- Surić M., Lončarić R. & Lončar N., 2010 - *Submerged caves of Croatia – distribution, classification and origin*. Environmental Earth Sciences, in press, doi: 10.1007/s12665-010-0463-0
- Šegota T. & Filipčić A., 2003 - *Köppenova podjela klima i hrvatsko nazivlje, (Köppen's classification of climates and the problem of corresponding Croatian terminology)*, Geoadria, **8** (1): 17–37.
- Vreča P., Krajcar Bronić I., Horvatinčić N. & Barešić J., 2006 - *Isotopic characteristics of precipitation in Slovenia and Croatia: Comparison of continental and maritime stations*, Journal of Hydrology, **330**: 457–469.
- White W.B., 2007 - *Paleoclimate records from speleothems in limestone caves*. In: Sasowsky I.D. & Mylroie J. (Eds.) - *Studies of Cave Sediments – Physical and Chemical Records of Paleoclimate*. Springer, New York: 135–175.
- Zaninović, K. (Ed.), 2008 - *Climate Atlas of Croatia 1961–1990, 1971–2000*, Meteorological and Hydrological Service of Croatia, Zagreb, 200 p.