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Differences in the ^{14}C age, $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ of Holocene tufa and speleothem in the Dinaric Karst

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Abstract

We studied Holocene speleothems and tufa samples collected in numerous caves and rivers in the Dinaric Karst of Croatia, Slovenia, Bosnia and Herzegovina, as well as Serbia and Montenegro. Differences in the formation process of tufa and speleothems are discussed in the context of their isotopic composition (^{14}C , ^{13}C and ^{18}O), as well as the chemistry of surface water (rivers, lakes) and drip water (in caves). The physical and chemical parameters monitored in the surface water (tufa precipitation) and drip water (speleothem precipitation) show that more stable conditions accompany speleothem rather than tufa formation. This is particularly obvious in the water temperature variations (2–22°C in surface water and 7–12°C in drip water) and in saturation index variation (3–11 in surface water and 1–6 in drip water). The range of ^{14}C ages recorded by Holocene speleothems ($\sim 12\,000$ yr) is wider by several thousands years than that of Holocene tufa samples (~ 6000 yr). $\delta^{13}\text{C}$ values for tufa samples range from -12‰ to -6‰ and for speleothem samples from -12‰ to $+3\text{‰}$ reflecting higher soil carbon and/or vegetation impact on the process of tufa than on speleothem formation. The differences in $\delta^{18}\text{O}$ values of tufa and speleothem samples from different areas reflect different temperature conditions and differing isotopic composition in the water. The study shows that speleothems from the Dinaric Karst can be used as global palaeoclimatic records, whereas tufa records changes in the local palaeoenvironment.

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1. Introduction

Tufa is a product of calcium carbonate precipitation at near ambient temperature and typically it contains the remains of micro- and macrophytes and bacteria. Speleothems (stalactites and stalag-

mites) are carbonate deposits common in caves and are produced at ambient temperatures from waters dripping from the walls of the cave.

In the first step of tufa and speleothem formation rain water dissolves CO_2 produced by the decomposition of organic matter and by root respiration in the topsoil. The partial pressure of soil CO_2 exceeds atmospheric concentrations by two orders of magnitude. Percolating water rich in CO_2 dissolves carbonate rocks and forms bicarbonate. When water containing calcium and bi-

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carbonate ions emerges in the form of a karst spring or as drip water in the cave, precipitation of calcium carbonate occurs either due to the degassing of CO_2 from solution or by evaporation which leads to calcium carbonate supersaturation.

Tufa and speleothem formations are therefore the results of the same chemical process, but there is a significant difference in the prevailing environmental conditions. Tufa is deposited in the surface water by a combination of physico-chemical and biological precipitation processes. The carbonate is precipitated in association with a biofilm which is a by-product of the microbial metabolic activity of diatoms, bacteria and/or cyanobacteria (Chafetz and Lawrence, 1994; Chafetz et al., 1994; Pentecost, 1998; Pedley, 2000). Tufa formation is favoured where well-developed plants exist in streams and waterfalls and this results in different morphological forms (Pentecost, 1995; Ford and Pedley, 1996; Pedley et al., 1996). This process is very sensitive to physico-chemical or biological changes in the water and also to seasonal fluctuation, e.g. temperature change (Srdoč et al., 1985a; Herman and Lorah, 1988). Speleothems, on the other hand, are deposits common in caves overlain by soil cover and are produced by the outgassing of CO_2 under stable microclimatic conditions from water dripping from the cave walls (Ford and Williams, 1989; Vokal, 1999).

The theoretical geochemistry of CaCO_3 precipitation based on carbon and oxygen isotopic characterisation is well established for speleothem formation but this is not so for tufa precipitation. Hendy (1971) used a kinetic approach to explain isotopic exchange in the reaction chain $\text{CO}_2(\text{g})\text{--CO}_2(\text{w})\text{--HCO}_3^-$. He defined the physical and chemical conditions that had to be fulfilled for equilibrium fractionation of the carbon and oxygen isotopes during speleothem formation processes and in relation to both open and closed geochemical systems. He also discussed the isotopic evidence for non-equilibrium formation processes. A model to explain the ^{13}C content of precipitated carbonate (Salomons and Mook, 1986; Dulinski and Rožanski, 1990) predicts the carbon isotope composition of speleothem by simulating time variations in the chemical and isotopic composition of both the solution and the

deposited calcite. Carbon and oxygen isotope studies of the active water-carbonate system in a Mediterranean karstic cave have been discussed by Bar-Matthews et al. (1996) in terms of their implications for palaeoclimate research. Comprehensive studies of the ^{14}C exchange process in speleothem formation were undertaken by Geyh (1972), Mook (1976) and Fontes and Garnier (1979) to determine the initial ^{14}C activity (^{14}C reservoir effect). Genty et al. (1999, 2001) calculated the past dead carbon proportion in several stalagmites from different areas and showed that it slightly changed during speleothem formation in the Holocene. Investigation of the carbon transfer dynamics of recent laminated stalagmite showed that the ^{14}C activity of speleothem is sensitive to atmospheric ^{14}C bomb input (Genty et al., 1998; Genty and Massault, 1999). A study of the environmental conditions associated with speleothem formation in Postojna Cave based on chemical and isotopic measurements is described by Vokal (1999).

The process of tufa precipitation involves additional isotopic exchange processes compared with speleothem formation. This additional complexity reflects the very dynamic surface flow and strong exchange process between dissolved inorganic carbon (DIC) and atmospheric CO_2 and by the decisive role of biota. An increase in ^{14}C activity of DIC was observed in the downstream flow of the Plitvice Lakes (Srdoč et al., 1986a) and in some other karst rivers where tufa precipitates (Horvatinčić et al., 1989). Changes in $\delta^{13}\text{C}$ of the DIC and precipitated carbonates were also observed along the flow of the Plitvice Lakes. A systematic study to determine the initial ^{14}C activity of karst springs and tufa at Plitvice Lakes has been described by Krajcar Bronić et al. (1986, 1992).

Assuming isotopic equilibrium during calcite precipitation, then terrestrial carbonates such as speleothem, tufa or lacustrine sediment can provide a record of environmental and climatic information (Gascoyne, 1992). These palaeoclimatic and palaeoenvironmental data are especially important in the lower latitude regions with temperate climate, where most tufa and speleothem deposits are formed and the excellent records afforded by ice deposits do not exist. Variations

in growth frequency of speleothem and tufa deposits based on ^{14}C and $^{230}\text{Th}/^{234}\text{U}$ dating (Hennig et al., 1983; Baker et al., 1993) demonstrate that the formation of secondary calcite deposits was stimulated by changing climate, e.g. during interglacial periods with warm and humid conditions. The climate of the Eastern Mediterranean region during the last 60 kyr has been reconstructed via a high resolution study of the oxygen and carbon isotopic composition of speleothem in Israel (Bar-Matthews et al., 1997, 1999). Isotopic studies of tufa and speleothem in Europe have been used for palaeoclimatic and palaeoenvironmental interpretation in the karst regions of Poland (Pazdur et al., 1988, 1995, 1999), England (Andrews et al., 1994; Pentecost, 1995), Germany (Geyh and Hennig, 1986), France (Falgüeres et al., 1992) and Norway (Lauritzen et al., 1990; Lauritzen, 1995). Tufa, lake sediments and speleothems from the Dinaric Karst were also studied using isotope methods and the results were applied in studies of palaeoclimate (Srdoč et al., 1986b, 1994; Horvatinčić et al., 2000) and palaeoenvironment (Srdoč et al., 1992a; Genty et al., 1998).

The aim of this study is to compare tufa and speleothem deposits from the Dinaric Karst in terms of the conditions of formation, using physical and chemical parameters in conjunction with isotopic measurements ($\Delta^{14}\text{C}$, $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$). We also correlate the environmental conditions of present-day precipitation of calcite with its isotopic content in order to improve the value of carbonate deposits as palaeoenvironmental records.

2. Site description and sampling

Karst features are widespread in Croatia, covering approximately fifty percent of the country (Fig. 1). The main belt runs from the northwest on the Slovenian border and strikes to the southeast along the Dinaric Mountains towards Montenegro. This belt is called the Dinaric Karst and is recognised as the geological 'type region' for the definition of such deposits worldwide. The area has been and continues to be subject to consider-

able research interest and has good potential for future studies of palaeoclimate. Numerous caves are located in Slovenia (more than 7000) and Croatia (more than 6000) and many of them are very rich in speleothem. There are also several regions of lakes and rivers in the Dinaric Karst area where tufa is forming at present, but deposits of ancient tufa are also found.

The climatic and environmental characteristics of the main locations studied in this paper are presented in Table 1. The greater part of the Dinaric Karst area, including Plitvice Lakes and Postojna Cave, has a typically continental climate. In other areas like the Krka, Zrmanja and Krupa rivers as well as the Podstenjšek area, which are close to the Adriatic Sea, the influence of the Mediterranean climate is significant, and the mean annual temperature is higher while the amount of rainfall is lower (Table 1).

Tufa samples were collected in Croatia (Plitvice Lakes, Krka River, Zrmanja River, Krupa River) and in Slovenia (Podstenjšek Creek) (Fig. 1). Tufa samples for ^{14}C dating were collected at random, mostly from the surface of tufa barriers and sometimes from different stratigraphic layers. We collected preferentially hard, compact tufa from outcrops of old tufa deposits that are located outside the present watercourses and also from tufa barriers that are still active. Detailed descriptions of the tufa sampling sites around the Plitvice Lakes are published in the Radiocarbon Data Lists (Srdoč et al., 1982, 1987). Likewise, tufa samples from the Krka River are described in the Radiocarbon Data Lists (Srdoč et al., 1987, 1992b; Horvatinčić et al., 1999).

A detailed investigation of the physical and chemical parameters important for tufa formation in the Plitvice Lakes area has been published by Srdoč et al. (1985a). This involved systematic monthly measurements during the period 1980–1985 of surface water at 16 sampling points, from springs that feed the lakes to the mouth of the Korana River. For the present study we selected five sampling points in the stream water of the Plitvice Lakes: one at the spring where tufa does not precipitate and four at different distances from the spring, where intensive tufa precipitation is ongoing.

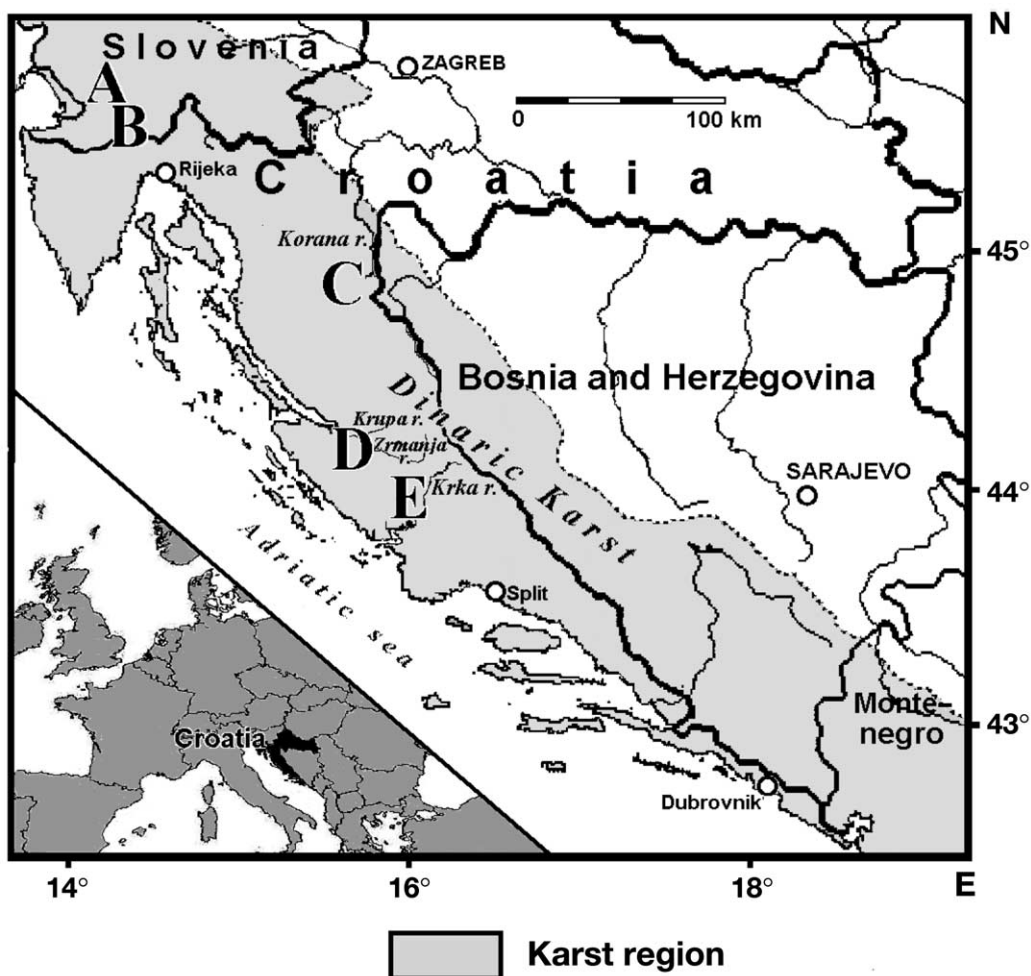


Fig. 1. The karst region where the tufa and speleothem samples were collected. Key: A, Postojna Cave; B, Podstenjšek Creek; C, Plitvice Lakes; D, Zrmanja and Krupa rivers; E, Krka River.

Speleothems were collected from 45 caves situated throughout the Dinaric Karst, but mostly in Croatia with some in Slovenia, Bosnia and Herzegovina, as well as Serbia and Montenegro. Descriptions of the speleothem sampling sites and the ^{14}C ages of speleothem were taken from the Radiocarbon Data Lists (Srdoč et al., 1973, 1975, 1977, 1981; Horvatinčić et al., 1999). Some new ^{14}C ages, measured in our laboratory and not yet published elsewhere, are also used.

An investigation of the parameters responsible for speleothem formation in Postojna Cave in Slovenia (Fig. 1) was carried out during 1996–1997 (Vokal, 1999; Vokal et al., 1999). For our

study we used data measured in drip water collected at three different locations (four sampling points) within the cave. These samples represent all types of cave water (slow-drip and fast-drip water) and positions with different thickness of rock ceiling: the cave's Entrance, Colourful Gallery and Brilliant, with thicknesses of the cave roof of about 10 m, 35–40 m and 120 m, respectively (Vokal et al., 1999).

3. Methods

Standard methods in aquatic chemistry were

applied for physical and chemical measurements on water samples. Temperature and pH were measured in situ with accuracies of $\pm 0.1^\circ\text{C}$ and ± 0.05 , respectively. Alkalinity was determined by the titration method with HCl with an estimated analytical error of $\pm 2\%$. Measurements of Ca^{2+} concentration were performed on the HACH spectrophotometer (surface water) and on a flame atomic absorption spectrometer VARIAN AA5 (drip water) with an analytical error of $\pm 4\%$ (Vokal, 1999). The I_{sat} was calculated according to the equation $I_{\text{sat}} = \text{IAP}/K_{\text{CaCO}_3}$, where IAP is an ionic activity product of Ca^{2+} and CO_3^{2-} and K_{CaCO_3} is the solubility constant of calcite.

Tufa and speleothem samples for ^{14}C analysis were treated with dilute HCl to obtain CO_2 , which was subsequently converted to methane. The ^{14}C activity of methane was measured by the gas proportional counter technique described elsewhere (Srdoč et al., 1971, 1979). For calculation of the ^{14}C values we followed the conventional protocol (Obelić, 1989; Mook and van der Plicht, 1999). ^{14}C activity is expressed as $\Delta^{14}\text{C}$, the relative content to modern standard ($\Delta^{14}\text{C} = 0\%$ for modern standard) normalised for isotope fractionation. The accuracy of $\Delta^{14}\text{C}$ is within the range of $\pm 3\%$ and $\pm 14\%$, depending on the activity of the sample. When appropriate, the ^{14}C age is expressed in conventional ^{14}C years BP, adjusted to initial ^{14}C activity, A_0 .

Mass spectrometry measurements of stable isotopes were performed at the Geowissenschaftliche Gemeinschaftsaufgaben, Hannover, Germany, and at the Jožef Stefan Institute, Ljubljana, Slovenia.

The stable isotope content is expressed in ‰ deviations from international standards: $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ in carbonate are expressed relative to the Pee Dee Belemnite (PDB) standard and $\delta^{18}\text{O}$ in water relative to the Standard Mean Ocean Water (SMOW) standard. The analytical error ranges from $\pm 0.05\%$ to $\pm 0.2\%$ depending on the type of samples.

4. Results and discussion

4.1. Physical and chemical measurements of water

We compare the following physical and chemical parameters important for calcium carbonate precipitation: water temperature, pH, concentration of bicarbonate and calcium ions, and saturation index of CaCO_3 (I_{sat}). The results are presented in Fig. 2. They represent mean values of monthly measurements for a 5-yr period at Plitvice Lakes and a 1-yr period for Postojna Cave and record maximum and minimum values in these periods.

The mean temperature of the water from which tufa precipitates is, on average, 2°C higher than that of the water from which speleothem precipitates: for tufa ranging from 10.2 to 12.2°C and for speleothem from 8.2 to 10.4°C . The variation of temperature for each sampling point is much larger in surface water because of the influence of seasonal changes. Drip water temperatures are more or less stable throughout the year indicating stable microclimate conditions within the cave.

Table 1
Climatic and environmental characteristics of the main studied locations

Site	Coordinates	Height above sea level (m)	Climate	Mean annual temperature ($^\circ\text{C}$)	Mean annual rainfall (mm)	Vegetation
Postojna Cave	45°46'N, 14°129E	529	Continental with Mediterranean influence	8	1500	Pine tree forest and grass
Plitvice Lakes	44°53'N, 15°37'E	636–505	Continental	8.7	1473 (5 yr)	Pine and beech forest, karst fields
Zrmanja and Krupa rivers	44°11'N, 16°03'E	385–0	Mediterranean	13	890 (5 yr)	Low vegetation, grass, bushes
Krka River	43°52'N, 16°00'E	216–0	Mediterranean	13	890 (5 yr)	Low vegetation, grass, bushes

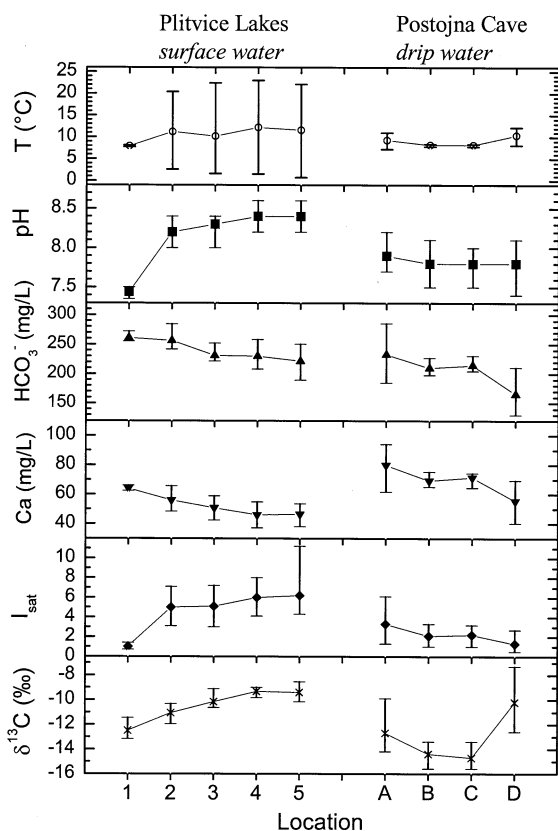


Fig. 2. Temperature, pH, concentration of bicarbonate and calcium ions, saturation index of CaCO_3 (I_{sat}) and $\delta^{13}\text{C}$ values of DIC in surface water at the Plitvice Lakes and in drip water in Postojna Cave. Mean values for a 5-yr period at Plitvice Lakes and a 1-yr period at Postojna Cave were used, with maximum and minimum values in these periods. Sampling points at the Plitvice Lakes with distance from the spring: 1, Crna Rijeka spring; 2, Labudovac, ~5 km; 3, Burget, ~7 km; 4, Novakovića Brod, ~10 km; 5, Korana bridge, ~15 km (Srdoč et al., 1985a). Sampling points in the Postojna Cave with cave roof thickness: A, Entrance, ~10 m; B, Colourful Gallery, 35–40 m; C, Colourful Gallery, 35–40 m; D, Brilliant, ~120 m (Vokal et al., 1999).

We noted that the water temperature of the three karst springs that feed the Plitvice Lakes is fairly constant throughout the year (7.3–7.9°C, with maximal variations <1°C) (Srdoč et al., 1985a).

The pH values are higher in surface waters (mean values from 8.2 to 8.4) than in drip water (mean values from 7.8 to 7.9) as a consequence of the higher concentration of dissolved CO_2 in drip water that originated mostly from topsoil organic

matter. Our systematic measurements of pH values at the karst springs that feed Plitvice Lakes showed that the pH values range between 7.6 and 7.8 and are similar to the pH of drip water. The pH values increase rapidly in the surface flow due to the degassing of CO_2 , and few hundred metres after the spring reach values of pH > 8 (Srdoč et al., 1985a; Horvatinčić et al., 1989).

Concentrations of bicarbonate and calcium ions steadily decrease downstream in the surface water at Plitvice Lakes due to tufa and lake sediment precipitation. Concentrations of these ions in drip water depend on the thickness of the cave roof, particularly on the overburden of humus. Soil organic matter in humus is the main source for the CO_2 reservoir in the topsoil and determines the carbon isotope composition of the solution that later dissolves carbonate rock (Hendy, 1971; Genty et al., 2001). It is noticeable that the highest concentrations, but also largest variations, of bicarbonate and calcium are in drip water at the Entrance point (Fig. 2, A) with thin cave roof. The concentrations of ions decrease with increasing of thickness of the cave roof. The possible explanation for this effect is that the process of carbonate (limestone) dissolution occurred in the soil zone caused by the high concentration of soil CO_2 and the higher temperature in the topsoil. Water becomes strongly saturated with calcite and enters into the cave as drip water. In the case with higher thickness of the cave roof some carbonate deposition may occur in the vadose zone when downward-percolating water becomes saturated with calcite, but before it reaches a cave.

The I_{sat} values show that tufa at the Plitvice Lakes precipitates in highly calcite supersaturated water (Fig. 2). The mean I_{sat} for surface water is between 5.0 and 6.2 and for drip water it ranges from 1.3 to 2.1. The fluctuation of the saturation index is larger in surface water and depends on season with higher values in summer (Srdoč et al., 1985a). At the karst springs of Plitvice Lakes the I_{sat} values range between 1.0 and 1.3 (Fig. 2, 1), but tufa precipitation does not occur.

Fluctuations in the measured parameters, particularly the temperature and I_{sat} values (Fig. 2), are most significant in surface water and correlate with seasonal change. Changes in the chemical

composition of water along the stream observed at Plitvice Lakes are similar to those observed in Westerhof stream, Germany (Uzdowski et al., 1979), and in Falling Spring Creek, Virginia (Lorah and Herman, 1988). The tufa growth rate at Plitvice Lakes follows closely the temperature of the stream water, with maximum deposition in August–September and minimum deposition in the winter months (Srdoč et al., 1985a). At some locations, e.g. at waterfalls, the tufa growth rate exceeds 10 mm/yr. The sedimentation rates of sediments in the two biggest lakes in the Plitvice Lakes area are as follows: in Kozjak Lake 0.8 mm/yr for the last 2000 years, and 1.1 mm/yr for the period 2000–6000 BP, and in Prošće Lake a uniform 1.4 mm/yr throughout the last 7000 years (Srdoč et al., 1986b). On the other hand, the process of speleothem formation is much slower than that of tufa formation, e.g. the sedimentation rate for speleothem in Postojna Cave is 0.1–1 mm/yr, i.e. one to two orders of magnitude lower than that for tufa at the Plitvice Lakes. Our previous studies of the process of tufa formation at the Plitvice Lakes, Krka River and in some other karst rivers (Srdoč et al., 1985a; Horvatinčić et al., 1989) showed that the conditions required for tufa precipitation in the water occurred only if the pH values were > 8.2 , the I_{sat} values > 3 and the water was very clean with respect to concentrations of dissolved organic carbon. At the same time tufa formation at the investigated areas is always associated with biota, predominantly microscopic algae and cyanobacteria, abundant moss growth and higher plant taxa (Golubić, 1973; Marčenko et al., 1989; Chafetz et al., 1994). Most studies of tufa formation recognise biological processes, which are considered to be responsible for the precipitation of freshwater carbonate within the tufa system (Ford and Pedley, 1996; Pedley et al., 1996; Pentecost, 1998; Pedley, 2000).

In drip water the physical and chemical conditions are more stable than in surface waters. The highest fluctuations of all measured values in drip water occurred at the Entrance site where the cave roof is relatively thin, ~ 10 m, and the surface water percolation is faster. It should be emphasised that tufa at Plitvice Lakes precipitates only

if water is highly supersaturated with calcite ($I_{\text{sat}} > 3$) (Srdoč et al., 1985a; Horvatinčić et al., 1989) while speleothem formation in Postojna Cave occurs with only slightly supersaturated drip water ($I_{\text{sat}} > 1$) (Vokal et al., 1999).

4.2. Isotope data from the depositional environments

In our study of tufa and speleothem formation we compared environmental isotopes that are involved in the carbon cycle (^{14}C , ^{13}C): ^{14}C activity and $\delta^{13}\text{C}$ values in DIC of surface and drip water, in atmospheric CO_2 as well as in the surface soil and vegetation of the investigated areas.

The bottom diagram of Fig. 2 records the $\delta^{13}\text{C}$ values of DIC in water. The mean values of $\delta^{13}\text{C}$ for DIC in the surface water increase from -11‰ to -9‰ along the surface flow of the Plitvice Lakes system. The mean values of $\delta^{13}\text{C}$ for DIC in all three springs are lower (between -12.5‰ and -12.7‰) than those in the lake area (Krajcar Bronić et al., 1986). The increase in $\delta^{13}\text{C}$ for DIC along the water flow is the combined result of CO_2 degassing and carbon isotope exchange between atmospheric CO_2 and DIC in the water (Deines et al., 1974; Srdoč et al., 1986a). The mean values of $\delta^{13}\text{C}$ for DIC in drip water at various locations within the Postojna Cave range from -14.1‰ to -10.2‰ .

The ^{14}C activity of the soil organic matter (SOM) within soil profiles in the Plitvice Lakes area was measured in 1974 and 1985, and showed that only ~ 10 – 15 cm of topsoil had been influenced by the higher atmospheric ^{14}C activity due to nuclear weapons testing. $\Delta^{14}\text{C}$ ranged from 20 to 194‰, depending on depth and location (Srdoč et al., 1985a; Krajcar Bronić et al., 1986). At 50–70 cm depth the ^{14}C content is much lower (-200‰ in 1974) than the contemporaneous atmospheric ^{14}C content (400‰). $\Delta^{14}\text{C}$ values from soil profiles above the Postojna Cave measured in 1997 gave an enriched value, $(176 \pm 17)\text{‰}$, at the surface, but this decreased to about -8‰ at 30 cm depth, showing that the influence of bomb ^{14}C was still predominantly in the topsoil (Vokal, 1999). The $\delta^{13}\text{C}$ of SOM at Plitvice ranges from -26‰ to -29‰ (Krajcar

Bronić et al., 1986), and from -27.4‰ to -26.2‰ in the Postojna region (Vokal, 1999).

The ^{14}C activity and $\delta^{13}\text{C}$ of atmospheric CO_2 were measured monthly during an 1-yr period both outside and inside the Postojna Cave. The mean annual $\Delta^{14}\text{C}$ from outside the cave was $(92 \pm 13)\text{‰}$ and from inside $(22 \pm 15)\text{‰}$, while the respective $\delta^{13}\text{C}$ values for CO_2 were $(-8.0 \pm 0.7)\text{‰}$ and $(-9.3 \pm 0.3)\text{‰}$. These $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$ values of the atmospheric CO_2 outside and inside the Cave show that CO_2 in the cave is mostly of atmospheric origin but with a small fraction of CO_2 originating from the SOM decomposition that comes into the cave through microfissures and pores in the overlying rock.

The anthropogenic influence on the ^{14}C activity of tufa and speleothem is well demonstrated by ^{14}C activity measured in the recent speleothem Pos-stm4 in Postojna Cave (Genty et al., 1998) and in surface lake sediment (Srdoč et al., 1992a). The peak of excess ^{14}C activity in the atmosphere produced by nuclear bomb tests (recorded in 1963) was recorded also in speleothem and in lake sediment but with a damped response and a delay of several years.

4.3. ^{13}C and ^{18}O in tufa, lake sediments and speleothems

The stable isotope compositions of tufa, lake sediments and speleothems are presented in Fig. 3 as $\delta^{13}\text{C}$ vs. $\delta^{18}\text{O}$ diagrams. The mean isotopic compositions at various locations, from which at least three samples were measured, are given in Table 2. Some data for speleothems from Slovenian caves (Škocjan, Dimnica, Divača, Kamniška, Predjama, Planinska, Mačkovca, and a few Postojna data) were taken from Urbanc et al. (1985), and data for the Postojna speleothem (Pos-stm4) from Genty et al. (1998).

The ranges of the $\delta^{13}\text{C}$ values for Holocene (full symbols) and Pleistocene (open symbols) (Fig. 3a) tufa samples from Krka and Plitvice are the same, from -10‰ to -6‰ . We compared the isotopic composition of old and Holocene tufa samples from the Plitvice and Krka areas by applying Student's *t*-test. The results are shown in Table 3. There is no statistical difference between the

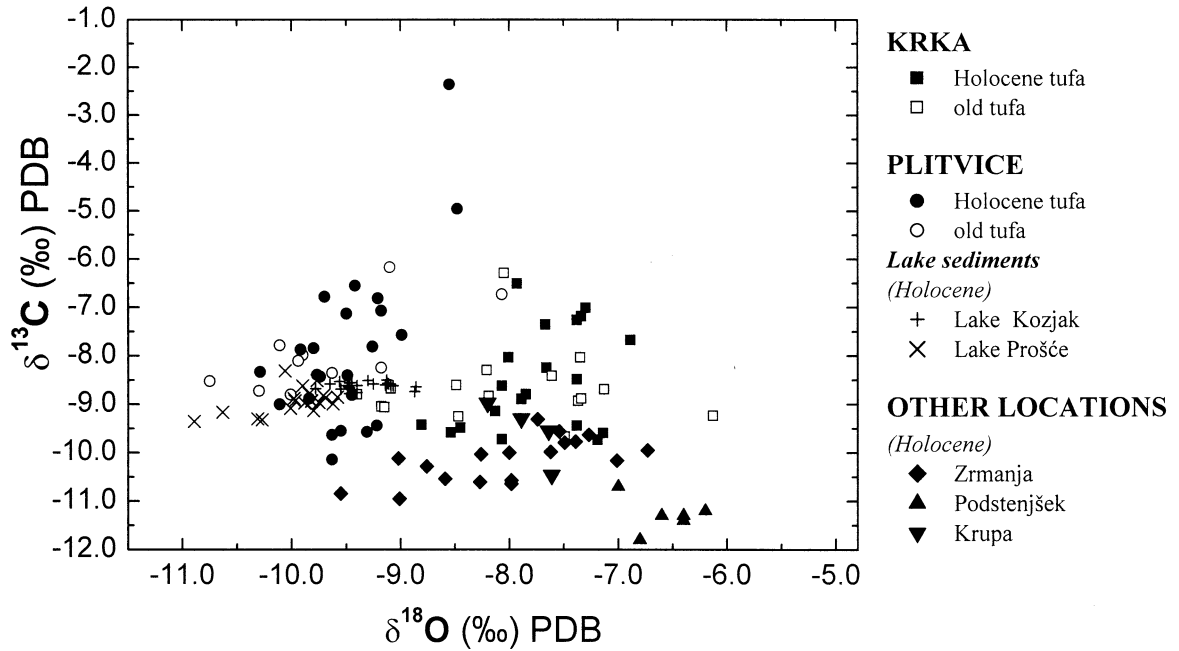
$\delta^{13}\text{C}$ values either between the tufa from the same location but different time periods or between the tufa from different locations and the same period. This indicates that conditions for tufa precipitation were similar during each period and for both areas.

Holocene tufa from the Zrmanja and Krupa River areas have somewhat lower $\delta^{13}\text{C}$ values (Table 2). $\delta^{13}\text{C}$ values for Podstenjšek tufa lie between -11‰ and -12‰ . In this area tufa precipitates 0.5–1.5 km from the spring which is much closer to the spring than tufa at the Plitvice Lakes (Fig. 2) and Krka River area. The lower $\delta^{13}\text{C}$ values for Podstenjšek tufa indicate less influence of the carbon isotope exchange process between atmospheric CO_2 and DIC in water.

The mean $\delta^{13}\text{C}$ values for the lake sediments taken from the 12-m-long sediment cores from two lakes in the Plitvice Lakes area, $(-8.6 \pm 0.1)\text{‰}$ and $(-8.9 \pm 0.2)\text{‰}$ for Lake Kozjak and Lake Prošće, respectively (Table 2), are similar to the mean $\delta^{13}\text{C}$ for tufa from Plitvice Lakes, $(-8.3 \pm 1.0)\text{‰}$, but show much smaller fluctuations. The narrow range of lake sediment $\delta^{13}\text{C}$ indicates more stable conditions during sediment precipitation than are associated with tufa precipitation.

Under the conditions of isotopic equilibrium the solid carbonate phase (calcite) is enriched in ^{13}C relative to DIC in the water (Turner, 1982; Emrich et al., 1970). At a temperature of 10°C the equilibrium fractionation factor ϵ between carbonate and bicarbonate is $\sim 1.5\text{‰}$. We can compare the $\delta^{13}\text{C}$ of DIC in water and the $\delta^{13}\text{C}$ of lake sediments in two lakes at Plitvice. The $\delta^{13}\text{C}$ of DIC in Lake Prošće is $\sim (-11)\text{‰}$, and that of DIC in Lake Kozjak $\sim (-10)\text{‰}$. The mean annual temperatures are 10.9 and 10.6°C , respectively. Thus, the difference $\epsilon = \delta_{\text{sedim}} - \delta_{\text{DIC}}$, which is 2‰ and 1.4‰ for Lakes Prošće and Kozjak, respectively, is in accordance with the equilibrium fractionation factor, and we can conclude therefore that sediment precipitation occurs under carbon isotope equilibrium. Similarly, calculated ϵ values for tufa from different locations at the Plitvice lakes range from 1.6‰ to 2.8‰ and for the Postojna speleothems ϵ is $\sim 3\text{‰}$. For tufa precipitation we may assume the attainment of only

a) Tufa and lake sediments



b) Speleothems

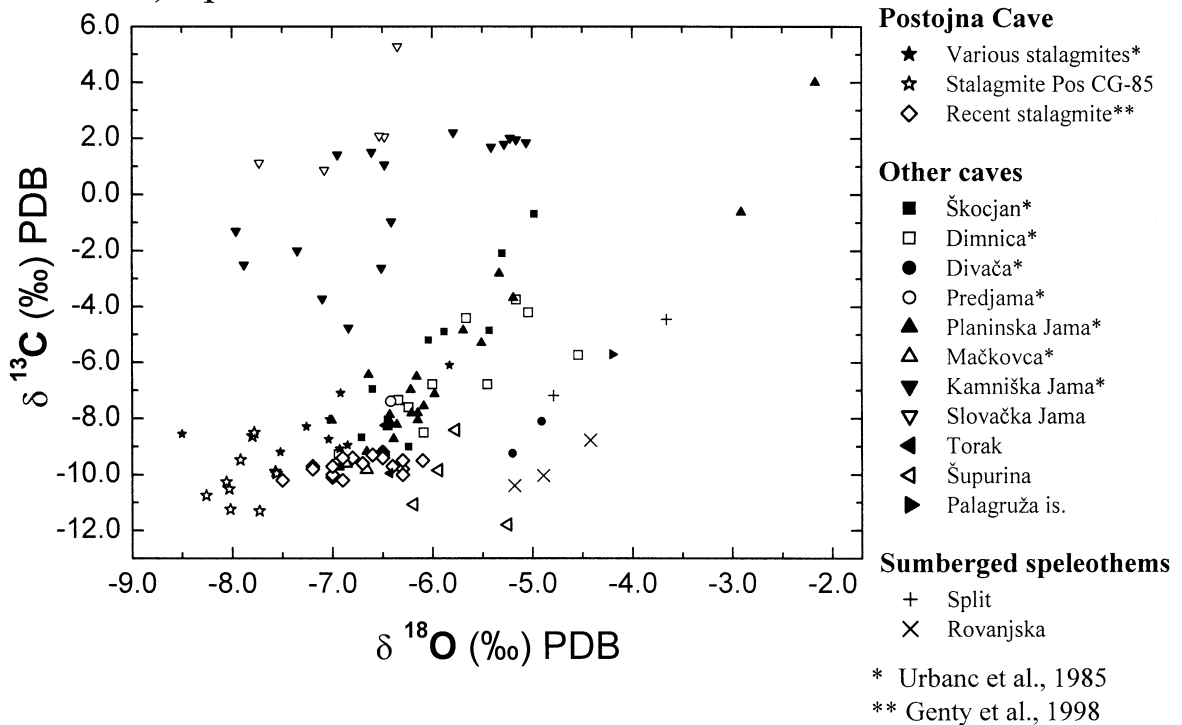


Fig. 3. $\delta^{13}\text{C}$ vs. $\delta^{18}\text{O}$ values for tufa and lake sediments (a) and speleothems from different caves (b).

approximate isotope equilibrium conditions, whereas for sediment precipitation the isotopic equilibrium holds more exactly.

$\delta^{13}\text{C}$ values for speleothem samples (Fig. 3, lower diagram) range from -12‰ to $+3\text{‰}$ (with two exceptions at $+5\text{‰}$). This is a good correlation with the theoretically predicted $\delta^{13}\text{C}$ values in speleothems (Dulinski and Rožanski, 1990). Their model predicts $\delta^{13}\text{C}$ values of deposited calcite (speleothems) within the range ca. -16‰ to $+3\text{‰}$ depending on temperature, chemical and isotope parameters of the initial solution and the actual degree of the precipitation process. The difference in $\delta^{13}\text{C}$ range of tufa (from -12‰ to -6‰) and speleothem reflects higher soil carbon and/or vegetation impact on the process of tufa production in the freshwater tufa system. Pedley et al. (1996) showed that during tufa formation inorganic precipitation is dominant under turbulent flow regimes, whereas bio-

mediation occurs in situations of sluggish flow or static water.

Most of the $\delta^{13}\text{C}$ values from speleothem samples range between -12‰ and -5‰ . Samples from different caves group together and the mean $\delta^{13}\text{C}$ values for different caves are compared in Table 2. Higher $\delta^{13}\text{C}$ values indicate proportionally more influence of carbon supplied by limestone or dolomite dissolution with a $\delta^{13}\text{C}$ at $\sim 0\text{‰}$. This is particularly noticeable for speleothem samples from the caves Kamniška jama (mean $\delta^{13}\text{C}$: $(-0.1 \pm 2.3)\text{‰}$) at an altitude of ~ 1400 m (Urbanc et al., 1985), and Slovačka jama at Velebit Mountain (mean $\delta^{13}\text{C}$: $(2.3 \pm 1.7)\text{‰}$) at an altitude of ~ 1300 m, where soil cover is very poor. Andrews et al. (1997) explained higher $\delta^{13}\text{C}$ values obtained for carbonate crusts from high Alpine sites as opposed to those from lowland sites as being a consequence of a smaller soil zone carbon component in the moun-

Table 2
Mean values of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ of tufa, lake sediments and speleothems from various locations in the Dinaric Karst

Location	Comment	$\delta^{13}\text{C}$ (‰ PDB)	$\delta^{18}\text{O}$ (‰ PDB)	Number of samples
<i>Tufa</i>				
Plitvice Lakes	Holocene	-8.3 ± 1.0	-9.6 ± 0.3	24
	Pleistocene	-8.0 ± 0.8	-9.7 ± 0.7	11
Krka	Holocene	-8.5 ± 1.0	-7.7 ± 0.5	20
	Pleistocene	-8.7 ± 0.7	-8.0 ± 0.9	16
Krupa	Holocene	-9.6 ± 0.6	-7.8 ± 0.3	5
Zrmanja	Holocene	-10.1 ± 0.5	-8.0 ± 0.8	18
Podstenjšek	Holocene	-11.3 ± 0.3	-6.6 ± 0.3	6
<i>Lake sediment</i>				
Lake Prošće	Holocene	-8.9 ± 0.3	-10.0 ± 0.3	20
Lake Kozjak	Holocene	-8.6 ± 0.1	-9.3 ± 0.2	22
<i>Speleothems</i>				
Postojna, Pos-CG-85	Holocene	-10.1 ± 1.0	-7.9 ± 0.2	10
Postojna, Pos-stm4	Recent	-9.7 ± 0.3	-6.7 ± 0.4	20
Postojna ^a	Holocene	-8.2 ± 1.0	-7.1 ± 0.2	9
Dimnica ^a	Holocene	-6.4 ± 1.9	-5.7 ± 0.7	10
Škocjan ^a	Holocene	-5.6 ± 2.9	-6.0 ± 0.6	9
Planinska jama ^{a,b}	Holocene	-6.3 ± 3.2	-5.9 ± 1.2	23
		-7.6 ± 1.2	-6.3 ± 0.4	18
Kamniška jama ^a	Holocene, 1400 m asl	-0.1 ± 2.3	$\sim (-6.5)$	16
Slovačka jama	1300 m asl	2.3 ± 1.7	$\sim (-6.5)$	5
Rovanjska	Submerged, Holocene	-9.7 ± 0.8	-4.8	3

^a Data from Urbanc et al. (1985).

^b The first value represents an average of all stable isotope measurements; for the second value five data pairs for non-equilibrium speleothem formation have been excluded (see text).

Table 3
Results of the Student's *t*-test of difference between two means with total degree of freedom being $n = n_1 + n_2 - 2$

$\delta^{18}\text{O}$	Plitvice - Holocene	Plitvice - Pleistocene	Krka - Holocene	Krka - Pleistocene
Plitvice - Holocene		$n=33$ ++	$n=42$ ++	
Plitvice - Pleistocene	$n=33$ ++			$n=25$ - +
Krka - Holocene	$n=42$ - -			$n=34$ ++
Krka - Pleistocene		$n=25$ - -	$n=34$ ++	

Key: +, data belong to the same distribution; -, data do not belong to the same distribution. Calculations were made for confidence intervals 95% (the first sign) and 99% (the second sign). Data above and to the right of the diagonal are for $\delta^{13}\text{C}$ values, and those below and to the left of the diagonal for $\delta^{18}\text{O}$ values.

tain sites where soils are thin, poorly vegetated, or even absent.

A large number of measurements is available for speleothems from Postojna Cave (Fig. 4). The $\delta^{13}\text{C}$ values range from -11.5‰ to -6‰ . In the case of a single recent speleothem, Pos-stm4, formed during the last 50 years, the $\delta^{13}\text{C}$ values range from -10.2‰ to -9.0‰ with a mean of $(-9.7 \pm 0.3)\text{‰}$ (Genty et al., 1998). This result reflects the $\delta^{13}\text{C}$ values prevailing under stable environmental conditions for this location. The distribution of $\delta^{13}\text{C}$ with distance from the top of the speleothem Pos-CG85 (stalagmite 85 cm long with a ^{14}C age of approximately 14000 yr BP), collected from the Colourful Gallery of Postojna Cave, is presented in Fig. 4b. The $\delta^{13}\text{C}$ value increases with distance from the top (linear correlation coefficient $R=0.95$) from -11.3‰ for recent (at the surface) to -8.5‰ for the oldest part of the formation. The $\delta^{13}\text{C}$ of speleothem represents the response of speleothem to the actual vegetation change (Dorale et al., 1998), therefore, this correlation would indicate an increase in the influence of biogenic CO_2 , i.e. increase in the vegetation density, for speleothem formation from the past to the present in this area. The difference in $\delta^{13}\text{C}$ values between two recent speleothems, -11.3‰ for the surface of Pos-CG85 and -9.7‰ for Pos-stm4 (Genty et al., 1998) follows the difference in $\delta^{13}\text{C}$ of DIC in drip water for these two locations, -14.4‰ and -12.7‰ , respectively (Fig. 2). This difference in

$\delta^{13}\text{C}$ for both speleothem and drip water for two locations in Postojna Cave can be a consequence of several factors such as variations in the type of dissolution (open/closed system), mixing ratio of soil and atmospheric CO_2 , localised geologic settings, and kinetic effects during calcite precipitation (Genty et al., 2001). The different thicknesses of the cave roofs, ~ 40 m and ~ 10 m for Pos-CG85 and Pos-stm4, respectively, is an additional factor that contributes to the variations of the $\delta^{13}\text{C}$ values.

The $\delta^{18}\text{O}$ values of tufa samples (Fig. 3a) range from -11‰ to -6‰ , and some grouping is again noticeable. Comparison of $\delta^{18}\text{O}$ of tufa shows that the Holocene and Pleistocene data sets from the Plitvice and Krka areas (Table 3) are similar only for the same location, while they are not similar for the same period and different locations, because of different types of climate (compare Table 1). There is practically no difference in the $\delta^{18}\text{O}$ values between tufa, $(-9.6 \pm 0.3)\text{‰}$, and lake sediments taken from 12-m-long sediment cores from two lakes in the Plitvice region (Table 2): $(-9.9 \pm 0.3)\text{‰}$ in Lake Prošće and $(-9.3 \pm 0.2)\text{‰}$ in Lake Kozjak. All of these values indicate stable climatic conditions for the region during the last 6000–7000 years, which is the ^{14}C age of Holocene tufa and lake sediments in this region (Srdoč et al., 1983, 1986b).

The $\delta^{18}\text{O}$ signature of tufa from Krka River (Fig. 3a; Table 2) is on average 1.7‰ (old tufa) and 1.8‰ (Holocene) higher than the $\delta^{18}\text{O}$ of tufa from the Plitvice Lakes. Tufa from Zrmanja, $(-8.0 \pm 0.7)\text{‰}$, and from Krupa River, $(-7.8 \pm 0.3)\text{‰}$, have $\delta^{18}\text{O}$ values similar to those from the Krka River area, $(-7.8 \pm 0.5)\text{‰}$. The difference between the Holocene tufa from Plitvice Lakes and other areas may be explained by a different $\delta^{18}\text{O}$ composition in waters from which tufa is formed and/or different mean yearly temperatures (Table 1). Both of these factors are indicative for the different climate of the regions and both give rise to more negative $\delta^{18}\text{O}$ values at Plitvice Lakes. The rivers Krka, Zrmanja and Krupa are close to the Adriatic Sea with higher average temperature and situated at lower altitudes than the Plitvice Lakes area. The higher altitude of Plitvice Lakes (500 m average differ-

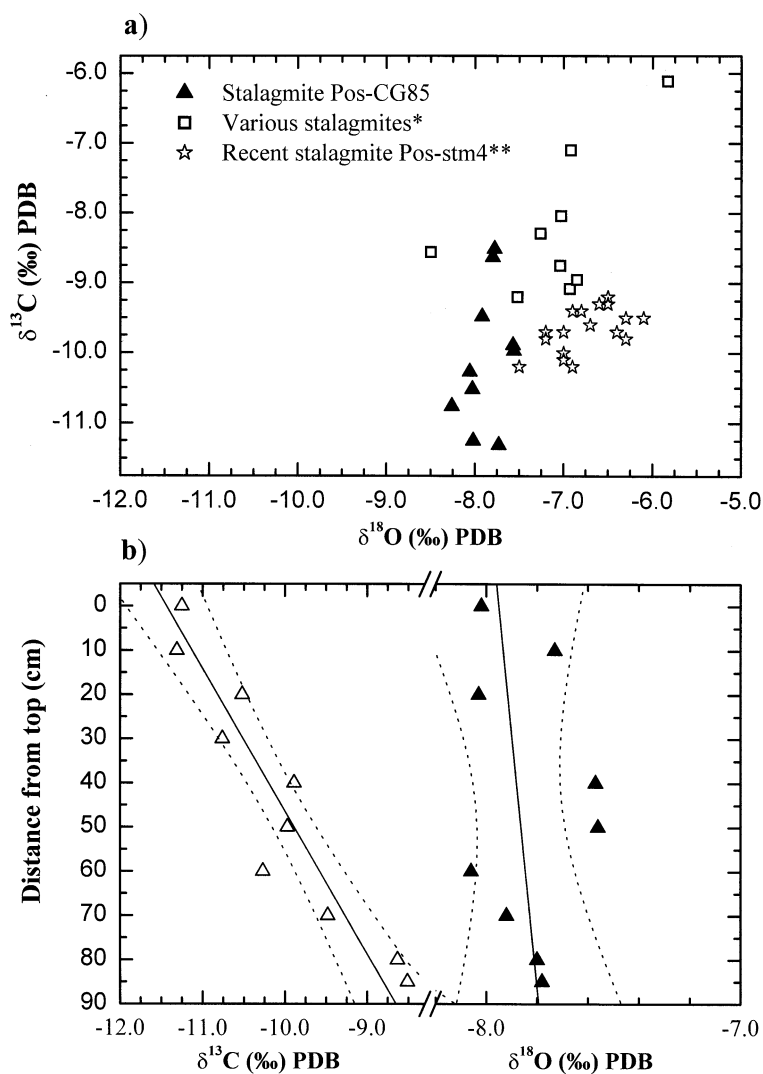


Fig. 4. (a) $\delta^{13}\text{C}$ vs. $\delta^{18}\text{O}$ values for speleothem samples from Postojna Cave (*after Urbanc et al., 1985; **after Genty et al., 1998). (b) $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values vs. distance from top of speleothem, Pos-CG85. Full lines represent linear fits, $R=0.95$ and $R=0.12$ for $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$, respectively. The dashed lines represent the 95% confidence limits of the correlation.

ence) can explain about 1‰ in the $\delta^{18}\text{O}$ difference between Plitvice and Krka (about 0.2‰ decrease in $\delta^{18}\text{O}$ for 100 m increase in altitude; Krajcar Bronić et al., 1998). The residual 0.7–0.8‰ can be explained by the mean annual temperature difference of 3°C (0.3‰/°C; Krajcar Bronić et al., 1998). The influence of the Mediterranean climate is even more evident in the high $\delta^{18}\text{O}$ values of tufa from the Podstenjšek area, which is very close to Adriatic coast.

The $\delta^{18}\text{O}$ values recorded by speleothem samples range from -8.5 to -3.5 ‰ (Fig. 3b). Most speleothems from areas with a prevailing continental climate have $\delta^{18}\text{O}$ values in the range -8 ‰ to -5 ‰, and those from areas influenced by the Mediterranean climate (Šupurina, Palagruža, Divača) and submerged speleothems (Split, Rovanjaska) range from -6 ‰ to -3.5 ‰. The entire range of $\delta^{18}\text{O}$ in speleothems is less negative than that for tufa owing to the different iso-

topic composition of water from which the calcite was precipitated. For example, tufa at Plitvice Lakes is precipitated from water with mean annual $\delta^{18}\text{O}$ values of -10.7‰ , while speleothems are formed from water with a mean annual $\delta^{18}\text{O}$ of -8.6‰ (Mačkovca, Planina, Postojna, Predjama), -7.2‰ (Divača) (Urbanc et al., 1987) and -8.3 to -8.9‰ (Postojna) (Vokal, 1999).

In Postojna Cave the $\delta^{18}\text{O}$ values range from -8.5‰ to -6‰ (Fig. 4a). The $\delta^{18}\text{O}$ values of speleothem Pos-CG85 (Fig. 4b) are rather constant along the growth profile ranging between -8.5‰ and -7.5‰ (mean value -7.9‰), indicating that no significant climatic change has occurred in this area during the last 14 000 years while changes in vegetation are possible, as discussed earlier.

It is possible to calculate the temperature of calcite formation assuming that the process occurs under equilibrium conditions, i.e. that kinetic effects are not significant. By the analysis of the carbon isotope data, we showed that tufa and speleothems, as well as lake sediments, are formed under, at least approximate, equilibrium conditions. Several samples that indicate a non-equilibrium calcite formation mechanism are discussed below. If the oxygen isotopic enrichments of calcite ($\delta^{18}\text{O}_c$) and water ($\delta^{18}\text{O}_w$) from which the calcite precipitates are known, then, according to Craig (1965), the temperature of calcite formation is given by the relationship:

$$T(^{\circ}\text{C}) = 16.1 - 4.15 \times (\delta^{18}\text{O}_c - \delta^{18}\text{O}_w) + 0.13 \times (\delta^{18}\text{O}_c - \delta^{18}\text{O}_w)^2 \quad (1)$$

To apply this calculation we used isotopic values measured from several recent speleothems found at places where stable equilibrium conditions can be assumed, i.e. where air circulation is minimal, and humidity and CO_2 partial pressure are effectively stable throughout the year. Several tufa samples found in conditions of steady state water flow, and lake sediments from the Lakes Kozjak and Prošće were also used to provide data for temperature calculation. We compared calculated temperatures of calcite formation with the measured mean annual temperature values (Fig. 5). The calculated temperatures for all

speleothem samples are in reasonable agreement with the actual mean yearly temperatures, so that the assumption of calcite precipitation under isotopic equilibrium is justified. Where slightly lower calculated temperatures than the measured ones are encountered these indicate that the speleothems were formed mainly in a colder period of the year (the wet season). The temperature calculated for tufa and lake sediment formation is higher than the measured average annual temperature and this is due to more intensive precipitation during the warmer period of the year. The seasonal dependence of tufa growth at Plitvice Lakes was also checked experimentally by Srdoč et al. (1985a) who showed that the tufa growth rate is up to 10 times higher in summer than in winter.

According to Hendy (1971), exceptionally high and simultaneously increased $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values may indicate non-equilibrium isotopic conditions of carbonate precipitation. Such examples are provided by two tufa samples from the Špiljski vrt location at Plitvice Lakes (Fig. 3a). These were taken from waterfalls, where the exchange of DIC with atmospheric CO_2 is very high. Two speleothem samples from a dry and windy area near the entrance to Planinska Jama Cave have higher $\delta^{18}\text{O}$ values (-2‰ and -3‰ , respectively) accompanied also by positive $\delta^{13}\text{C}$ ($+4\text{‰}$ and -0.5‰ , respectively) signatures indicating speleothem formation under non-equilibrium conditions, i.e. under enhanced evaporation or exchange with atmospheric CO_2 (Fig. 3b) (Urbanc et al., 1985). Many of the speleothem samples from Planinska Jama Cave lie in between the most negative values, reflecting isotopic equilibrium conditions, and the two outliers. In addition, data from Škocjanska Jama Cave show a simultaneous increase in both $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$. Such a correlation indicates the interplay of precipitation under isotopic equilibrium and non-equilibrium precipitation (Gonfiantini et al., 1968; Hendy, 1971). For each cave studied, the data having the lowest stable isotope content indicate speleothem formation under isotopic equilibrium conditions and these sets can be used for palaeotemperature estimation. Speleothem found close to the entrance of caves, where windy and dry environ-

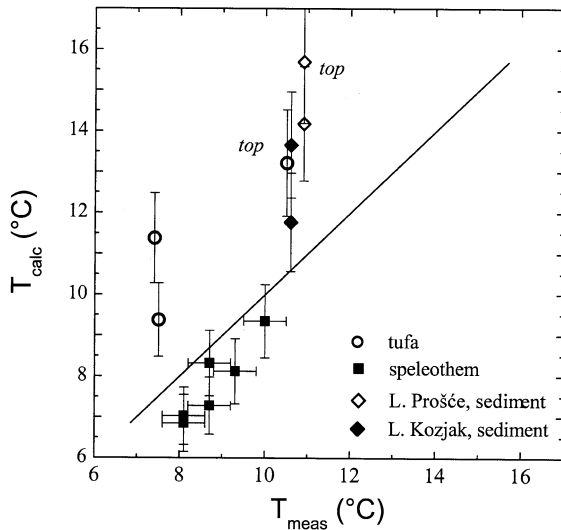


Fig. 5. Correlation between calculated temperature, T_{calc} , of calcite formation (Eq. 1) and measured mean yearly water temperature values, T_{meas} , for few speleothem, tufa and lake sediment samples. Line represents ideal agreement, $T_{\text{calc}} = T_{\text{meas}}$. Temperatures calculated for shallow lake sediment cores of ~ 30 cm depth, are marked by 'top'. 1σ errors in measured temperatures are shown only for speleothem samples. 1σ errors in calculated temperatures are obtained by the error propagation formula, taking errors in $\delta^{18}\text{O}$ from the measured data sets.

mental conditions prevail, and tufa grown at waterfalls where faster degassing and exchange with atmospheric CO_2 can occur, are not reliable palaeoclimatic indicators. If such $\delta^{18}\text{O}$ values from speleothems or from tufa formed under isotopic non-equilibrium conditions are used for temperature calculations, then the resultant temperatures are too low by as much as 5°C .

4.4. ^{14}C age of Holocene tufa and speleothem

The temporal distribution of the ^{14}C ages measured for tufa samples collected at various locations in the Dinaric Karst, including the Plitvice (160 samples), Krka (30 samples), Zrmanja (13 samples) and Krupa (5 samples) sites, together with the ^{14}C age distribution of 65 speleothem samples collected in 45 caves, also in the Dinaric Karst, are presented in Fig. 6. The histograms are constructed using 500-yr class intervals, and relative errors of ages are not considered. The initial

^{14}C activities (A_0) for Plitvice tufa were determined experimentally and ranged from 70 to 90% modern (2400–800 years equivalent) depending on the location (Srdoč et al., 1986b; Krajcar Bronić et al., 1992). A_0 for tufa from the Plitvice Lakes area was determined by: (1) measuring the ^{14}C activity of recent pre-bomb test calcareous deposits, (2) calculating the ratio of the ^{14}C activity of the calcareous sediment to that of the adjacent coeval wood, and (3) extrapolating ^{14}C activity of the deep lacustrine sediment layers to the surface, assuming a constant sedimentation rate. For tufa samples from other locations and for all speleothem samples we assumed an A_0 of 85%. This average value was determined earlier (Geyh, 1972; Vogel, 1983) and justified in more recent studies using pre-bomb ^{14}C values from annually laminated modern stalagmites (Genty and Massault, 1997, 1999; Genty et al., 1998, 1999). The possible variations of A_0 for different locations (Genty et al., 1999) could not influence significantly the ^{14}C age distribution of Holocene tufa and speleothem presented in Fig. 6 because they would cause the same shift of ^{14}C age distribution for both, tufa and speleothem.

The ^{14}C ages of Holocene tufa from all locations range up to ca. 6000 yr BP. The ^{14}C age distribution shows a maximum for young samples, up to 1000 yr BP, and then the number of tufa samples decreases with only a few samples with ^{14}C ages approaching 6000 yr BP. Younger samples dominate because the tufa samples were collected at random on dry tufa barriers and most of them were taken from or near the surface. Furthermore, the preservation of tufa deposits decreases with age.

The ^{14}C ages of Holocene speleothem samples again collected at random from different caves in the Dinaric Karst range up to ca. 12000 yr BP. This time period extends beyond that of the Holocene tufa samples by several thousand years. Consequently, direct comparison of Holocene tufa and speleothem from the Dinaric Karst shows that the process of tufa growth in interglacial conditions started several thousand years later than that of speleothem. Our previous investigations showed that the ^{14}C ages of Holocene tufa samples also coincide well with the ^{14}C ages of up

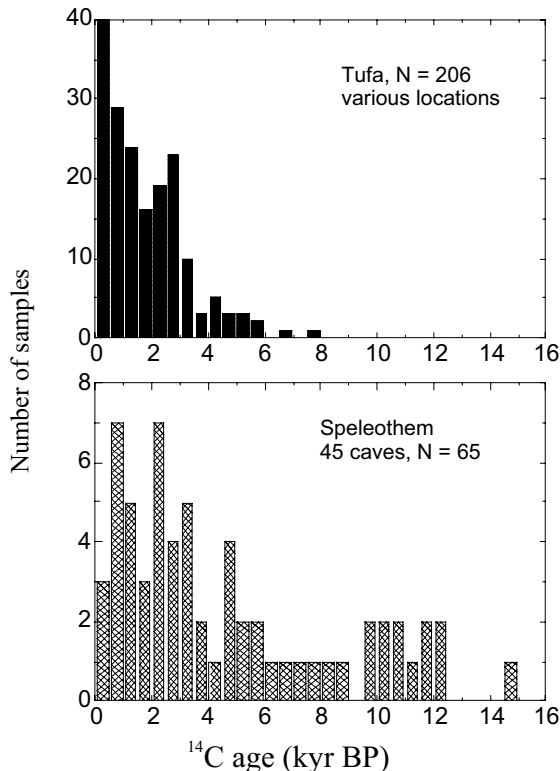


Fig. 6. Histograms of ¹⁴C dates of Holocene tufa and speleothems from the Dinaric Karst.

to 6000 and 7000 yr BP measured for lake sediment collected in the Lake Prošće and Lake Kozjak, Plitvice Lakes area, respectively (Srdoč et al., 1986b). In addition, the ¹⁴C ages of peat deposits collected in the same area coincide well with the Holocene tufa ages (Srdoč et al., 1985b). All of these dates support the hypothesis that the climatic conditions in this area during the last ~7000 years have been favourable for tufa growth and also for peat and lake sediment formation. This is also demonstrated by the constant $\delta^{18}\text{O}$ values throughout the sediment profile (depth of ~12 m) of lake sediments (Srdoč et al., 1986b).

The ¹⁴C age distribution of postglacial (Holocene) tufa in Europe indicates that deposition reached a maximum in the period 5000–10 000 yr BP (not corrected for reservoir effect) (Pentecost, 1995). In south Poland the ¹⁴C age of Holocene tufa is up to approximately 8000 years

(Pazdur et al., 1988) and at different sites in England ¹⁴C dates suggest that tufa production was most active ca. 5000–2000 yr BP, ca. 9000–4000 yr BP, and ca. 7000–2000 yr BP (Pentecost et al., 1990). Most of the Quaternary tufa deposits in Europe are located in karst areas with a mean annual air temperature of 5–15°C and a rainfall exceeding 500 mm yr⁻¹ (Pentecost, 1995).

On the other hand, speleothem formation in central Europe during the Holocene and Late Glacial coincides with a time period up to ca. 13 000–15 000 yr BP (Geyh and Hennig, 1986; Gascoyne, 1992; Pazdur et al., 1995; Goslar et al., 2000). The high-resolution records of stable isotopes in stalagmites from Soreq Cave, Israel (East Mediterranean region), indicate that all speleothems older than 7000 yr were formed under conditions that differ from those of today, and that about 7000 yr ago the general climatic conditions became similar to those of the present day (Bar-Matthews et al., 1996). Furthermore, radiocarbon-dated deposits of glacial drift indicate that alpine glaciers expanded in Early Holocene time in many areas of the world. This feature is worldwide and includes locations in both the Northern and Southern Hemisphere, in Europe and North America, in temperate high latitudes, and in areas of both maritime and continental climate (Beget, 1983). These data are strong evidence for a worldwide episode of cooler climate at ca. 8500–7500 yr BP.

According to the discussion presented above, we may conclude that climatic change during the Holocene influenced tufa formation, i.e. that tufa growth started several thousand years later than speleothem formation.

In Fig. 6 we present the ¹⁴C age distribution of Holocene tufa and speleothems only. However, in most of the locations we also found some old tufa deposits as well as old speleothems the ages of which were beyond the ¹⁴C detection limit of our dating system (> 37 000 yr BP). The ages of old tufa deposits at the Krka and Plitvice area and of a few speleothems were determined by the ²³⁰Th/²³⁴U dating method (Srdoč et al., 1994; Horvatinčić et al., 2000). The results, when compared with the marine palaeoclimatic $\delta^{18}\text{O}$ record, showed that the growth periods of

these old deposits coincided with oxygen isotope stage 5. There were a few tufa samples from stages 7 and 9.

5. Conclusions

By considering the physico-chemical conditions of tufa and speleothem formation in the Dinaric Karst, in conjunction with their stable isotope compositions and ^{14}C ages, we conclude that these discrete calcareous deposits have been formed under different environmental conditions.

(1) The physical and chemical parameters monitored in surface water (tufa precipitation) and in drip water (speleothem precipitation) show that more stable conditions accompany speleothem formation than tufa formation. This is particularly obvious in the water temperature variation (2–22°C in surface water and 7–12°C in drip water) and in saturation index variations (3–11 in surface water and 1–6 in drip water). The saturation index must exceed 3 for tufa precipitation while speleothem precipitates from drip water with $I_{\text{sat}} > 1$.

(2) The $\delta^{13}\text{C}$ values for tufa samples range from –12‰ to –6‰ and for speleothem samples from –12 to +3‰ in the Dinaric Karst, indicating that the influence of biogenic carbon is more significant for tufa than for speleothem formation. The wide range of $\delta^{13}\text{C}$ values obtained from speleothems together with the clearly different $\delta^{13}\text{C}$ values for different locations show that speleothem formation is also possible from water poor in biogenic carbon (e.g. at high altitudes), while the $\delta^{13}\text{C}$ values for tufa from the investigated areas show that biogenic carbon is more crucial in tufa formation.

(3) The $\delta^{18}\text{O}$ values for tufa samples range from –11‰ to –6‰ and for speleothem (mainly) from –8‰ to –4‰. The difference here is a consequence of the different stable isotope composition and temperature of waters from which the calcite precipitates. The calculated temperature for calcite that precipitated under isotopic equilibrium conditions showed a slightly lower temperature for speleothem than the measured one indicating that speleothem was mainly formed

in a colder period of the year (wet season). The estimated temperature of tufa and lake sediment formation is higher than the measured average annual temperature due to more intensive precipitation during the warmer period of the year.

(4) The ^{14}C dating of Holocene tufa and speleothem calcite from the Dinaric Karst shows that speleothem growth started several thousand years earlier than tufa growth. Most tufa sites in Europe show that the Holocene tufa growth has been at its most intensive in the last ca. 7000 yr. This is in good correlation with the ages of tufa in the Dinaric Karst. A possible explanation for the delay of tufa as opposed to speleothem growth in the Holocene is the importance of the biological component in the process of tufa precipitation from surface water, e.g. the presence of macrophytes (moss) and microphytes (algae, bacteria), is very important. The process of tufa formation will occur only if well-developed plants exist in the streams. It means that these conditions were not fulfilled in the Early Holocene. In contrast, the process of speleothem formation in caves was more readily initiated by temperature change and/or other climatic conditions at the beginning of the Holocene.

(5) Isotope analyses, including $\delta^{13}\text{C}$, $\delta^{18}\text{O}$ and ^{14}C age values, of tufa, lake sediments and speleothems in the Dinaric Karst confirm that these deposits record environmental and climatic information. While speleothem is a good indicator of global climate and palaeoclimatic changes, tufa is a more sensitive indicator of palaeoenvironmental changes.

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References

- Andrews, J.E., Pedley, H.M., Dennis, P.F., 1994. Stable isotope record of palaeoclimatic change in a British Holocene tufa. *Holocene* 4, 349–355.
- Andrews, J.E., Riding, R., Dennis, P.F., 1997. The stable isotope record of environmental and climatic signals in modern terrestrial microbial carbonates from Europe. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 129, 171–189.
- Baker, A., Smart, P.L., Ford, D.C., 1993. Northwest European palaeoclimate as indicated by growth frequency variations of secondary calcite deposits. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 100, 291–301.
- Bar-Matthews, M., Ayalon, A., Matthews, A., Sass, E., Halicz, L., 1996. Carbon and oxygen isotope study of the active water–carbonate system in the karstic Mediterranean cave: Implications for paleoclimate research in semiarid regions. *Geochim. Cosmochim. Acta* 60, 337–347.
- Bar-Matthews, M., Ayalon, A., Kaufman, A., 1997. Late Quaternary paleoclimate in the Eastern Mediterranean region from stable isotope analysis of speleothems at Soreq Cave, Israel. *Quat. Res.* 47, 155–168.
- Bar-Matthews, M., Ayalon, A., Kaufman, A., Wassergurg, G., 1999. The Eastern Mediterranean paleoclimate as a reflection of regional events: Soreq Cave, Israel. *Earth Planet. Sci. Lett.* 166, 85–95.
- Beget, J.E., 1983. Radiocarbon-dated evidence of worldwide early Holocene climate change. *Geology* 11, 389–393.
- Chafetz, H., Lawrence, R., 1994. Stable isotopic variability within modern travertines. *Geogr. phys. Quat.* 48, 257–273.
- Chafetz, H., Srdoč, D., Horvatinčić, N., 1994. Early diagenesis of Plitvice Lakes waterfall and barrier travertine deposits. *Geogr. phys. Quat.* 48, 245–255.
- Craig, H., 1965. The measurement of oxygen isotope paleotemperatures. In: Tongiorgi, E. (Ed.), *Stable Isotopes in Oceanographic Studies and Paleotemperatures*. Consiglio Nazionale delle Ricerche, Laboratorio di Geologia Nucleare, Pisa, p. 161.
- Deines, P., Langmuir, D., Harmon, R.S., 1974. Stable carbon isotope ratios and the existence of a gas phase in the evolution of carbonate ground waters. *Geochim. Cosmochim. Acta* 38, 1147–1164.
- Dorale, J.A., Edwards, R.L., Ito, Emi, González, L.A., 1998. Climate and vegetation history of the Midcontinent from 75 to 25 ka: A speleothem record from Crevice Cave, Missouri, USA. *Science* 282, 1871–1874.
- Dulinski, M., Rożanski, K., 1990. Formation of $^{13}\text{C}/^{12}\text{C}$ isotope ratios in speleothems: a semi-dynamic model. *Radiocarbon* 32, 7–16.
- Emrich, K., Ehhalt, D.H., Vogel, J.C., 1970. Carbon isotope fractionation during the precipitation of calcium carbonate. *Earth Planet. Sci. Lett.* 8, 363–371.
- Falguères, C., Lumley, D., Bischoff, J.L., 1992. U-series dates for stalagmitic flowstone E (Riss/Würm Interglaciation) at Grotte du Lazaret, Nice, France. *Quat. Res.* 38, 227–233.
- Fontes, J.Ch., Garnier, J.M., 1979. Determination of the initial ^{14}C activity of the total dissolved carbon; a review of the existing models and a new approach. *Water Resour. Res.* 15, 399–413.
- Ford, T.D., Pedley, H.M., 1996. A review of tufa and travertine deposits of the world. *Earth Sci. Rev.* 41, 117–175.
- Ford, D., Williams, P., 1989. *Karst Geomorphology and Hydrology*. Chapman and Hall, London.
- Gascoyne, M., 1992. Palaeoclimate determination from cave calcite deposits. *Quat. Sci. Rev.* 11, 609–632.
- Genty, D., Massault, M., 1997. Bomb ^{14}C recorded in laminated speleothems: calculation of dead carbon proportion. *Radiocarbon* 39, 33–48.
- Genty, D., Vokal, B., Obelić, B., Massault, M., 1998. Bomb ^{14}C time history recorded in two modern stalagmites – importance for soil organic matter dynamics and bomb ^{14}C distribution over continents. *Earth Planet. Sci. Lett.* 160, 795–809.
- Genty, D., Massault, M., 1999. Carbon transfer dynamics from bomb ^{14}C and $\delta^{13}\text{C}$ time series of a laminated stalagmite from SW France – Modelling and comparison with other stalagmite records. *Geochim. Cosmochim. Acta* 63, 1537–1548.
- Genty, D., Massault, M., Gilmour, M., Baker, A., Verheyden, S., Kepens, E., 1999. Calculation of past dead carbon proportion and variability by the comparison of AMS ^{14}C and TIMS ages on the Holocene stalagmites. *Radiocarbon* 41, 251–270.
- Genty, D., Baker, A., Massault, M., Proctor, C., Gilmour, M., Poms-Branchu, E., Hamelin, B., 2001. Dead carbon in stalagmites: Carbonate bedrock paleodissolution vs. ageing of soil organic matter. Implications for ^{13}C variations in speleothems. *Geochim. Cosmochim. Acta* 65, 3443–3457.
- Geyh, M.A., 1972. On the determination of the initial ^{14}C content in ground water. In: Rafter, T.A., Grant-Taylor, T. (Eds.), *Proc. 8th Int. ^{14}C Conf.*, Wellington, New Zealand. R. Soc. NZ, pp. D58–D69.
- Geyh, M.A., Hennig, G.J., 1986. Multiple dating of a long flowstone profile. *Radiocarbon* 28, 503–509.
- Golubić, S., 1973. The relationship between blue–green algae and carbonate deposits. In: Carr, N.G., Whitton, B.A. (Eds.), *The Biology of Blue–Green Algae*. Blackwell, Oxford, pp. 434–472.
- Gonfiantini, R., Panichi, C., Tongiorgi, E., 1968. Isotopic disequilibrium in travertine deposition. *Earth Planet. Sci. Lett.* 5, 55–58.
- Goslar, T., Hercman, H., Pazdur, A., 2000. Comparison of U-

- series and radiocarbon dates of speleothems. *Radiocarbon* 42, 403–414.
- Hendy, C.H., 1971. The isotopic geochemistry of speleothems. I. The calculation of the effects of different modes of formation on the isotopic composition of speleothems and their applicability as palaeoclimatic indicators. *Geochim. Cosmochim. Acta* 35, 801–824.
- Hennig, G.J., Grün, R., Brunnacker, K., 1983. Speleothems, travertines and paleoclimates. *Quat. Res.* 20, 1–29.
- Herman, J.S., Lorah, M., 1988. Calcite precipitation rates in the field: Measurements and prediction for a travertine-depositing stream. *Geochim. Cosmochim. Acta* 52, 2347–2355.
- Horvatinčić, N., Srdoč, D., Šilar, J., Tvrđiková, H., 1989. Comparison of the ^{14}C activity of groundwater and recent tufa from Karst areas in Yugoslavia and Czechoslovakia. *Radiocarbon* 31, 884–892.
- Horvatinčić, N., Obelić, B., Krajcar Bronić, I., Srdoč, D., Čalić, R., 1999. Ruđer Bošković Institute radiocarbon measurements XIV. *Radiocarbon* 41, 199–214.
- Horvatinčić, N., Čalić, R., Geyh, M.A., 2000. Interglacial growth of tufa in Croatia. *Quat. Res.* 53, 185–195.
- Krajcar Bronić, I., Horvatinčić, N., Srdoč, D., Obelić, B., 1986. On the initial ^{14}C activity in karst aquifers with short mean residence time. *Radiocarbon* 28, 436–440.
- Krajcar Bronić, I., Horvatinčić, N., Srdoč, D., Obelić, B., 1992. Experimental determination of the ^{14}C initial activity of calcareous deposits. *Radiocarbon* 34, 593–601.
- Krajcar Bronić, I., Horvatinčić, N., Obelić, B., 1998. Two decades of environmental isotope record in Croatia: reconstruction of the past and prediction of future levels. *Radiocarbon* 40, 399–416.
- Lauritzen, S.E., 1995. High-resolution paleotemperature proxy record for the last interglaciation based on Norwegian speleothems. *Quat. Res.* 43, 133–146.
- Lauritzen, S.E., Lovlie, R., Moe, D., Ostbye, E., 1990. Paleoclimate deduced from a multidisciplinary study of a half-million-year-old stalagmite from Rana, Northern Norway. *Quat. Res.* 34, 306–316.
- Lorah, M., Herman, J., 1988. The chemical evolution of a travertine-depositing stream, chemical processes and mass transfer reactions. *Water Resour. Res.* 24, 1541–1552.
- Marčenko, E., Srdoč, D., Golubić, S., Pezdić, J., Head, M.J., 1989. Carbon uptake in aquatic plants deduced from their natural ^{13}C and ^{14}C content. *Radiocarbon* 31, 785–794.
- Mook, W.G., 1976. The dissolution-exchange model for dating ground water with ^{14}C . In: *Interpretation of Environmental Isotope and Hydro-Chemical Data in Groundwater Hydrology*. IAEA, Vienna, pp. 213–225.
- Mook, W.G., van der Plicht, J., 1999. Reporting ^{14}C activities and concentrations. *Radiocarbon* 41, 227–239.
- Obelić, B., 1989. The radiocarbon data base at Ruđer Bošković Institute Radiocarbon Laboratory. *Radiocarbon* 31, 1057–1062.
- Pazdur, A., Pazdur, M.F., Szulc, J., 1988. Radiocarbon dating of Holocene calcareous tufa in Southern Poland. *Radiocarbon* 30, 133–151.
- Pazdur, A., Pazdur, M.F., Pawlyta, J., Gogny, A., Olszewski, M., 1995. Paleoclimatic implications of radiocarbon dating of speleothems from the Cracow–Wielun Upland, Southern Poland. *Radiocarbon* 37, 103–110.
- Pazdur, A., Goslar, T., Pawlyta, M., Hercman, H., Gradzinski, M., 1999. Variations of isotopic composition of carbon in the karst environment from Southern Poland, present and past. *Radiocarbon* 41, 81–97.
- Pedley, M., 2000. Ambient temperature freshwater microbial tufas. In: Riding, R.E., Awramik, S.M. (Eds.), *Microbial Sediments*. Springer, Berlin/Heidelberg, pp. 179–186.
- Pedley, M., Andrews, J., Ordonez, S., Garcia del Cura, M.A., Gonzales Martin, J.A., Taylor, D., 1996. Does climate control the morphological fabric of freshwater carbonates? A comparative study of Holocene barrage tufas from Spain and Britain. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 121, 239–257.
- Pentecost, A., 1995. The Quaternary travertine deposits of Europe and Asia minor. *Quat. Sci. Rev.* 14, 1005–1028.
- Pentecost, A., 1998. The significance of calcite (travertine) formation by algae in a moss-dominated travertine from Matlock Bath, England. *Arch. Hydrobiol.* 143, 487–509.
- Pentecost, A., Thorpe, P.M., Harkness, D.D., Lord, T.C., 1990. Some radiocarbon dates for tufas of the Craven district of Yorkshire. *Radiocarbon* 32, 93–97.
- Salomons, W., Mook, W.G., 1986. Isotope geochemistry of carbonates in the weathering zone. In: Fritz, P., Fontes, J.Ch. (Eds.), *Handbook of Environmental Isotope Geochemistry*, 2. The terrestrial environment. Elsevier, Amsterdam, pp. 239–269.
- Srdoč, D., Breyer, B., Sliepčević, A., 1971. Ruđer Bošković Institute radiocarbon measurements I. *Radiocarbon* 13, 135–140.
- Srdoč, D., Sliepčević, A., Planinić, J., Obelić, B., Breyer, B., 1973. Ruđer Bošković Institute radiocarbon measurements II. *Radiocarbon* 15, 435–441.
- Srdoč, D., Sliepčević, A., Planinić, J., 1975. Ruđer Bošković Institute radiocarbon measurements III. *Radiocarbon* 17, 149–155.
- Srdoč, D., Sliepčević, A., Obelić, B., Horvatinčić, N., 1977. Ruđer Bošković Institute radiocarbon measurements IV. *Radiocarbon* 19, 465–475.
- Srdoč, D., Obelić, B., Horvatinčić, N., Sliepčević, A., 1979. Measurement of the ^{14}C activity of the ANU sucrose secondary standard by means of the proportional counter technique. *Radiocarbon* 21, 321–328.
- Srdoč, D., Sliepčević, A., Obelić, B., Horvatinčić, N., 1981. Ruđer Bošković Institute radiocarbon measurements VI. *Radiocarbon* 23, 410–421.
- Srdoč, D., Horvatinčić, N., Obelić, B., Sliepčević, A., 1982. Ruđer Bošković Institute radiocarbon measurements VII. *Radiocarbon* 24, 325–371.
- Srdoč, D., Horvatinčić, N., Obelić, B., Sliepčević, A., 1983. Radiocarbon dating of tufa in palaeoclimatic studies. *Radiocarbon* 25, 421–428.
- Srdoč, D., Horvatinčić, N., Obelić, B., Krajcar, I., Sliepčević, A., 1985a. Procesi taloženja kalcita u krškim vodama s po-

- sebnim osvrtom na Plitvička jezera (Calcite deposition processes in karst waters with special emphasis on the Plitvice Lakes, Yugoslavia) (in Croatian with English abstract). *Carsus Iugoslaviae* (Krš Jugoslavije) 11, 101–204.
- Srdoč, D., Obelić, B., Horvatinčić, N., Culiberg, M., Šercelj, A., Slipečević, A., 1985b. Radiocarbon dating and pollen analyses of two peat bogs in the Plitvice National Park. *Acta Bot. Croat.* 44, 41–46.
- Srdoč, D., Krajcar Bronić, I., Horvatinčić, N., Obelić, B., 1986a. The increase of ^{14}C activity of dissolved inorganic carbon along the river course. *Radiocarbon* 28, 515–521.
- Srdoč, D., Obelić, B., Horvatinčić, N., Krajcar Bronić, I., Marčenko, E., Merkt, S., Wong, H., Slipečević, A., 1986b. Radiocarbon dating of lake sediments from two Karstic lakes in Yugoslavia. *Radiocarbon* 28, 495–502.
- Srdoč, D., Horvatinčić, N., Obelić, B., Krajcar Bronić, I., Slipečević, A., 1987. Ruđer Bošković Institute radiocarbon measurements IX. *Radiocarbon* 29, 115–134.
- Srdoč, D., Horvatinčić, N., Ahel, M., Giger, W., Schaffner, C., Krajcar Bronić, I., Petricoli, D., Pezdič, J., Marčenko, E., Plenković, A., 1992a. Anthropogenic influence on the ^{14}C activity of recent lake sediment. A case study. *Radiocarbon* 34, 585–592.
- Srdoč, D., Horvatinčić, N., Krajcar Bronić, I., Obelić, B., Slipečević, A., 1992b. Ruđer Bošković Institute radiocarbon measurements XII. *Radiocarbon* 34, 155–175.
- Srdoč, D., Osmond, J., Horvatinčić, N., Dabous, A., Obelić, B., 1994. Radiocarbon and uranium-series dating of the Plitvice Lakes travertines. *Radiocarbon* 36, 203–219.
- Turner, J.V., 1982. Kinetic fractionation of carbon-13 during calcium carbonate precipitation. *Geochim. Cosmochim. Acta* 46, 1183–1191.
- Urbanc, J., Pezdič, J., Dolenc, T., Perko, S., 1985. O izotopih kisika in ogljika v jamskih vodah in sigah Slovenije (Isotopic composition of oxygen and carbon in cave water and speleothems of Slovenia). *Acta Carsologica* XIII, 99–112 (in Slovenian).
- Urbanc, J., Pezdič, J., Krajcar Bronić, I., Srdoč, D., 1987. Comparison of isotopic composition of different forms of calcite precipitated from fresh water. In: *Isotope Techniques in Water Resources Development, Proc. Int. Symp. on the Use of Isotope Techniques in Water Resources Development*. IAEA, Vienna, pp. 783–787.
- Uzdowski, E., Hoefs, J., Menschel, G., 1979. Relationship between ^{13}C and ^{18}O fractionation and changes in major element composition in a recent calcite-depositing spring – a model of chemical variations with inorganic CaCO_3 precipitation. *Earth Planet. Sci. Lett.* 42, 267–276.
- Vogel, J.C., 1983. ^{14}C variations during the Upper Pleistocene. *Radiocarbon* 25, 213–218.
- Vokal, B., 1999. The Carbon Transfer in Karst Areas – An Application to the Study of Environmental Changes and Paleoclimatic Reconstruction. Ph.D. Thesis, Nova Gorica Polytechnic, Slovenia, 90 pp.
- Vokal, B., Obelić, B., Genty, D., Kobal, I., 1999. Chemistry measurements of dripping water in Postojna Cave. *Acta Carsologica* 28, 305–321.