APPLICATION OF ^{14}C METHOD TO CHRONOLOGY OF THE CROATIAN DINARIC KARST – A CASE OF THE PLITVICE LAKES

Ines Krajcar Bronić*, Jadranka Barešić, Andreja Sironić

Ruđer Bošković Institute, Bijenička c 54, 10000 Zagreb, Croatia

*corresponding author: krajcar@irb.hr

ORCID ID: IKB 0000-0002-6534-4125, JB 0000-0003-4634-5859, AS 0000-0001-7256-206X

ABSTRACT. Karst environments preserve some of the best archives of past climate, vegetation, hydrology, anthropogenic impact, and landscape evolution providing that a reliable chronology can be established. Here we present an example of the system of the Plitvice Lakes (Dinaric karst, Croatia), which is characterized by intensive tufa and lake sediment formations. Radiocarbon dating method, combined with some other dating methods and various geochemical and isotope analyses, showed that the Plitvice Lakes system in the present form has existed for about 8000 years. Older tufa deposits were dated to warm interglacial periods. A long-term comprehensive multi-proxy study showed that all environmental compartments (atmosphere, various water bodies, soil, bedrock, DIC, terrestrial and aquatic biota, and of course various secondary carbonates) must be included in order to obtain trustworthy results.

KEYWORDS: ^{14}C, karst, geochronology, tufa, lake sediments, Plitvice Lakes, Croatia

INTRODUCTION

Karst environments develop in many locations around the globe, where limestones and dolomite rocks crop out, and where there is sufficient flowing water for rock dissolution to induce process of karstification. [Note: In exceptional cases karst also forms on quartz-bearing rocks (Wray, 1997)]. Later, under favorable conditions by degassing and/or biomediated, precipitation of secondary carbonate features, such as speleothem, tufa, travertine, lake sediment, etc., occurs. As a result of these processes, a special type of karst landscape is formed, which is characterized by landforms derived from dissolution as well as by various depositional forms such as tufa barrages and cascades, among others (Ford and Pedley 1996, Ford and Williams 2007).

Karst environments preserve some of the best archives of past climate, vegetation, hydrology, human impact, and landscape evolution (Fairchild et al. 2007; Frisia and Borsato 2010). The climate and environmental data can be framed in a precise time span because karst deposits can be dated by various methods. The two most important dating methods applied in karst regions are radiocarbon and ^{230}Th-^{234}U-^{238}U disequilibrium radiometric dating (in further text U-Th dating) techniques.

The aim of this paper is to present research based on radiocarbon chronology of secondary carbonates at a specific location within the Croatian Dinaric karst - the Plitvice Lakes. The dominant carbonate deposits in the area are tufa and carbonate sediments deposited in karst lakes (later referred as lake sediments) and this overview is restricted to research on their isotope composition. They archive multi proxy data that allow the reconstruction of past climate and environmental changes, as well as trace the carbon cycle and anthropogenic influence in the area.

In what follows, a short introduction to the process of karstification is given, the study site is described, and the basic history of the research at the Zagreb Radiocarbon Laboratory of the Ruđer Bošković Institute (RBI) and the most important results are presented. The complete list of publications describing the corresponding research and the methods applied can be found in the Supplementary document.

KARST PROCESSES

The processes of carbonate rock dissolution and precipitation of secondary carbonate sediments have been described in detail in literature (Ford and Williams 2007; Srdoč et al. 1985a; Horvatinčić et al. 2003; Frisia and Borsato 2010; Tanner 2010). The process referring to tufa and karst lake sediments is schematically presented in Figure 1.

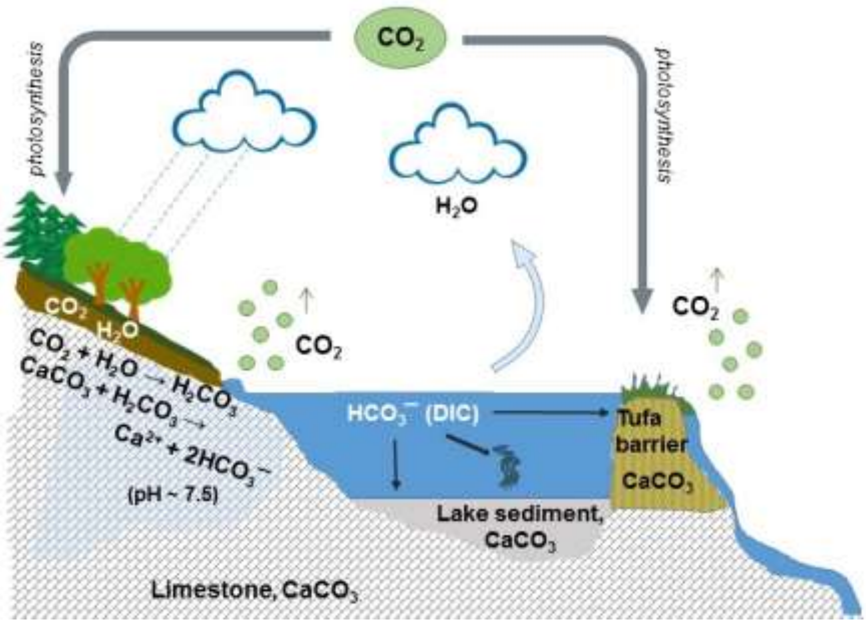

Figure 1 Schematic presentation of the karstification process (restricted to tufa and lake sediment formation) and the carbon cycle in karst.

The first step in the formation of karst archives is the dissolution of carbonate bedrock by meteoric water with dissolved carbon dioxide (eq. 1).

$$CaCO_3 + H_2O + CO_2 \rightleftharpoons Ca^{2+} + 2\,HCO_3^- \qquad (1)$$

The origin of the karst water is precipitation which enters the soil and dissolves soil CO_2 that is a product of root respiration and organic matter decomposition and the carbonic acid (H_2CO_3) is formed. Concentration of CO_2 in soil atmosphere can be several orders of magnitude higher than that in the air. [Note: Soil, however, is not always present. In arid or high mountain regions there might be little or no soil, and CO_2 is supplied directly from the atmosphere (Frisia and Borsato 2010; Horvatinčić et al. 2003)]. The carbonic acid dissolves bedrock carbonates forming bicarbonate ions HCO_3^-. Thus, water becomes enriched with dissolved inorganic carbon (DIC). Under geochemical conditions typical of karst, where pH in spring waters ranges between 7 and 8, DIC is composed mostly of HCO_3^-.

Precipitation of calcite from the solution can occur if the solution is supersaturated with respect to this phase. Where karst groundwaters come to the surface at springs, CO_2 passes from aqueous solution to the air (Figure 1) because of higher CO_2 partial pressure in water than in the atmosphere. Degassing typically results in calcite supersaturation and shifts reaction (1) to the left, leading to calcite precipitation. Rapid CO_2 degassing is aided at rapids and waterfalls (Chen et al. 2004; Della Porta 2015).

Besides physico-chemical conditions the plants/biota have important role in tufa precipitation process in surface karst environments. Calcium-carbonate deposition may be actively promoted by CO_2 removal related to photosynthesis. Thus, the level of saturation increases and biota (vegetation and microbial biofilms) act also as a convenient substrate for trapping calcite seed crystals (Chafetz et al. 1994; Golubić et al. 2008; Zippel and Neu 2011, Della Porta 2015). Tufa formation is favored where well-developed plants exist in streams and waterfalls. The process is known as biogenically enhanced or biomediated carbonate deposition (Pedley 2009; Tanner 2010).

The international karst terminology can be very confusing, specifically the use of the term "tufa" (Ford and Williams 2007). In this paper the term 'tufa' indicates fresh-water surface calcium carbonate deposits precipitated at or near ambient temperature, which commonly contain the remains of macro- and microphytes (Capezzuoli et al. 2014; Della Porta 2015; Gandin and Capezzuoli 2008; Ford and Pedley 1996; Ford and Williams 2007; Horvatinčić et al. 2000; Frančišković-Bilinski et al. 2004; Pedley 2000; 2009). Historically, some authors referred to the Plitvice Lakes deposits as "travertine" (e.g., Golubić et al. 2008). The term 'meteogene tufa' was suggested for deposits precipitated from waters in which the dissolved CO_2 comes from soil and atmosphere as opposed to the 'thermogene travertine" for deposits which precipitated from waters in which the dissolved CO_2 predominantly comes from deep fluids (Pentecost 1993).

Karst processes have also an important role in the carbon cycle since they are dependent on rainfall, temperature and vegetation changes. Carbon and oxygen stable isotope compositions archive data on environmental conditions at the time of formation of carbonate deposits, so in addition to their role in deciphering secondary mineral precipitation in karst environments they can point to both global and local changes in the past and in the present. Carbon isotope records in karst sediments could help determining the beginning of the recently proposed new epoch of Anthropocene (Zalasiewicz et al. 2015 and references therein).

STUDY AREA

Dinaric karst, known worldwide as the *locus typicus* of classical karst, occupies half of the Croatian territory including the islands and the Adriatic coast, the high mountain regions, and part of central Croatia between the eastern Adriatic coast and the Pannonian Plain (Figure 2) (Surić et al. 2020 and references therein).

The Plitvice Lakes (PL) is a unique system of 16 cascade flow-through lakes, situated in the Dinaric karst, Central Croatia (44°53'N, 15°37'E) (Figure 2). Tufa precipitates very intensively in the presence of macrophytes and microphytes forming numerous barriers or barrages that dam the lakes. Calcium carbonate also precipitates as lake sediment. The system lies on dolomites in the southern part, while four smaller and shallower lakes and the Korana River canyon sit on highly permeable limestone (Polšak et al. 1977; Sironić et al. 2021). The two main streams (Crna Rijeka, Bijela Rijeka, Figure 2c) form the first Lake Prošće. The lakes discharge into the Korana River which is a part of the Danube River watershed area. The total distance from the springs to the Korana River is approximately 12 km. The largest and the deepest is Lake Kozjak, followed by the uppermost Lake Prošće ("big lakes").

The PL area has been protected as a national park since 1949, and since 1979 it has been included in the United Nations Educational, Scientific, and Cultural Organisation (UNESCO) World Heritage

List. The lake system covers 1 % of the total park area of 298 km^2 with the remainder being largely deciduous forest (75 %) and meadows (23 %) (Horvatinčić et al. 2018). The area is scarcely populated and thus protected from direct anthropogenic influence; however, it cannot be protected from global changes such as the current climate change.

The climate is typical continental classified as Cfb type (temperate humid climate without dry season with warm summer) according to Köppen-Geiger climate classification (Köppen 1936; Filipčić 1998; Peel et al. 2007). The average annual air temperatures at the Plitvice Lakes range from 8.0 to 10.8 °C (1986–2019), with the mean value of 9.2 ± 0.5 °C. An increase of mean annual air temperature of 0.06 ± 0.01°C per year was observed, $p < 0.05$ (Krajcar Bronić et al. 2020). Annual precipitation amount at the Plitvice Lakes ranges between 1148 mm and 2113 mm in the same period (Meteorological data were obtained on request (free of charge) from the Croatian Meteorological and Hydrological Service). Monthly precipitation at the Plitvice Lakes is distributed relatively uniformly throughout the year.

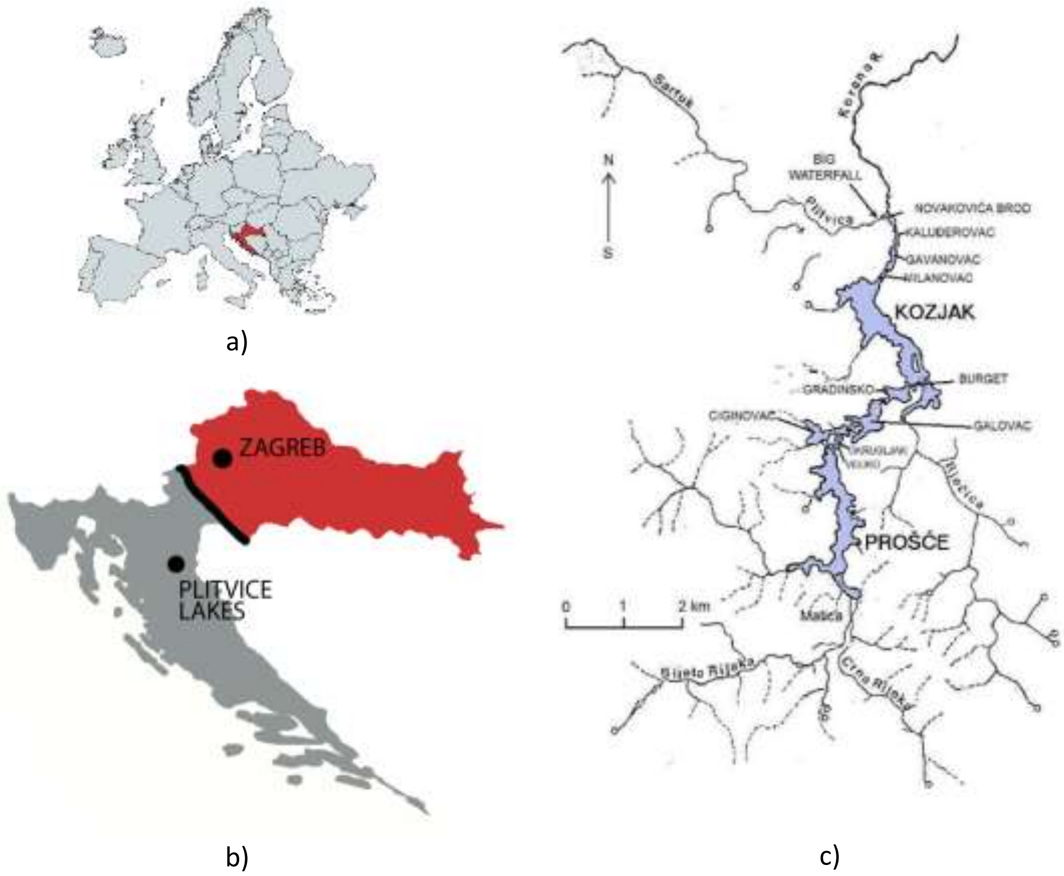

Figure 2 (a) Map of Europe with the position of Croatia. (b) Position of the Plitvice Lakes on the map of Croatia. Black line divides karst region (grey, below the line) from the rest of the country. (c) Lake area of the National Park Plitvice Lakes from the main streams (Crna Rijeka and Bijela Rijeka) along 16 lakes to the outflow of the Korana River.

HISTORICAL OVERVIEW OF RESEARCH AT RBI

The Plitvice Lakes area is one of the most studied karst areas in Croatia, where various scientific studies have been performed since the beginning of 20th century (Bencetić Klaić et al. 2018). Scientific projects stopped during the Homeland War (1991-1995) and after that they were continued with the aim to monitor and protect the ecosystem of the National Park.

The Zagreb Radiocarbon Laboratory, the first of this kind in the south-eastern Europe, was founded in 1968. The first radiocarbon dating results were obtained in 1970 (Srdoč et al. 1971). Dating of inorganic/carbonate samples (speleothem, shell, tufa) was soon implemented with the idea of determining the age of carbonate deposits in caves of the Dinaric karst (Sliepčević and Planinić 1973). Gas proportional counting technique was used in the beginning. Later, it was replaced by liquid scintillation counting in benzene matrix (Horvatinčić et al. 2004) and accelerator mass spectrometry, AMS (Krajcar Bronić et al. 2010; Sironić et al. 2013). Several Zagreb Radiocarbon Laboratory data lists were devoted partially or exclusively to the dating of various materials from the Dinaric karst (Data lists no 4, 7, 9, 12, 13, 14, 17 in the Supplementary file).

During the 1970s, the RBI group commenced research at the Plitvice Lakes with the initial aim of establishing geochronology of tufa and lake sediments (Srdoč et al. 1980). However, before long, the research was supplemented by systematic measurements of physico-chemical parameters of the waters to determine conditions required for the calcium carbonate precipitation in the form of tufa or lake sedimentary particles and by application of different isotope methods (Srdoč et al. 1985a). It turned out that the comprehensive studies should include analyses of isotope composition of DIC, tufa, lake sediments, atmosphere, soil, terrestrial and aquatic plants, i.e., various environmental compartments that contribute to the secondary carbonate precipitation. With this approach the aim was expanded to paleoclimate and paleoenvironmental reconstructions, as well as to effects of recent climate change and anthropogenic impact on the system. In addition to the use of radiocarbon (for dating and as a marker of the carbon cycle), stable isotopes of carbon and oxygen were used, as well as various dating methods of tufa and lake sediment, such as U-Th, ^{210}Pb and ^{137}Cs (Srdoč et al. 1986a; 1994; Horvatinčić et al. 2000; 2003; 2008; 2014; 2018). Radioactive (^{3}H, ^{14}C) and stable isotopes (^{2}H, ^{18}O, ^{13}C) were applied also to studies of various water bodies (precipitation, groundwater, surface and lake waters) (Krajcar Bronić et al. 2020). The 30-year long record of various physico-chemical parameters enabled determination of the impact of climate change on geochemical conditions for tufa precipitation (Sironić et al. 2017). The knowledge acquired in the studies of the Plitvice Lakes tufa and lake deposits was later extended to studies of other types of secondary carbonates, such as submerged speleothems (Surić et al. 2005) and algal rims (Faivre et al. 2019) that are out of the scope of this paper.

RESULTS

DIC and tufa

The presentation of results concerning secondary carbonate precipitation must start with the analyses of water solution from which they are formed. Both the isotope and physico-chemical data at springs in the PL area showed atmospheric (meteoric) origin of waters (Srdoč et al. 1985a; Krajcar Bronić et al. 2020) with constant values in different seasons, implying that the recharge water was well mixed with the existing water in aquifer. Short mean residence time of the water was determined based on the tritium activity concentration (Srdoč et al. 1985a; Krajcar Bronić et al. 1986; 2020). Fast decrease in CO_2 concentration within a short distance after emerging in springs causes oversaturation with calcium carbonate and precipitation occurs. As a consequence, a decrease in bicarbonate and calcium ion concentrations and increase in pH were observed from springs to the end of the lake series (Srdoč et al. 1985a; 1986b; Barešić et al. 2011a; Sironić et al. 2017). The ^{13}C (δ^{13}C) and ^{14}C (a^{14}C) isotope composition of DIC in karst springs is mostly a result of limestone bedrock dissolution by CO_2 dissolved in water. While δ^{13}C values were almost equal in the main springs, the a^{14}C was lower and more variable in the spring of the Crna Rijeka Stream (Krajcar Bronić et al. 1986; Sironić et al. 2020). Farther on, along the lake series, no large seasonal variation was observed in isotope composition of

DIC, but the increase in both $a^{14}C$ and $\delta^{13}C$ values along the water course became a distinct characteristic of the system, as will be discussed below.

A partial origin of carbon from limestone in the DIC in karst waters makes the radiocarbon dating of secondary carbonates precipitated from DIC more difficult than dating of organic material. Secondary carbonates are depleted in ^{14}C at the moment of calcite formation yielding too old radiocarbon ages. The effect is known as hard-water effect (Philippsen 2013 and reference therein) that may be quantified differently: as dead carbon proportion, as the reservoir age or as the initial activity a_0. Here we use the term initial activity a_0 as the ^{14}C activity of the secondary carbonate at the moment of formation assuming the atmospheric and biogenic ^{14}C activity equals 100 pMC. Hard-water effect in the PL area was identified in early stages of the isotope studies (Srdoč et al. 1980; Pedley 2009).

An attempt was made to estimate the initial ^{14}C activity of the two main karst springs by using several theoretical models (Krajcar Bronić et al. 1986). The results justified an assumption of karst system as the geochemical system open to the atmospheric CO_2 through karst fractures and showed that application of theoretical models to the complex natural site may lead to erroneous a_0 values. Therefore, the initial ^{14}C activity was determined empirically from available experimental data by several methods (Krajcar Bronić et al. 1992). Ratio of ^{14}C activities of carbonate and organic matter associated with it resulted in similar a_0 values as the extrapolation of measured $a^{14}C$ of long sediment cores from both Prošće and Kozjak lakes (Figure 2) (Srdoč et al. 1986a). However, it was noted that the terrestrial origin of the organic matter had to be checked by $\delta^{13}C$ measurements. When the associated organic matter (e.g., in lake sediments) consisted of aquatic plants that used carbon from DIC for photosynthesis, the a_0 values were not realistic since the aquatic plants themselves exhibited some hard-water effect, thus having their own a_0 values.

To make radiocarbon dating of tufa possible, it was necessary to show that the tufa preserved the isotopic composition from the time of formations and changes occurred only by radioactive decay. The equivalence of the ^{14}C activities of DIC and the precipitated tufa was shown (Srdoč et al. 1980). Some examples of tufa coating on old wood proved that tufa deposits preserve their isotopic composition and can give the age of tufa formation if the correct a_0 value is applied (Srdoč et al. 1983). Tufa was thus recognized as a potential source of information on climatic conditions in the past (Srdoč et al. 1983, Pedley 2009). Diagenetic alteration of primary precipitates starts contemporaneously with carbonate deposition, but in the porous calcareous tufa, diagenesis is uneven, and primary precipitates remain locally preserved (Chafetz et al. 1994; Golubić et al. 2008). However later contamination by younger calcite precipitated over the inactive tufa can affect the tufa age. No appreciable effect was observed for the Holocene tufa, while, porous older tufa gave in such cases unexpectedly young ages (Srdoč et al. 1986c).

Systematic dating of tufa samples from active barriers and old deposits revealed two distinct groups of deposits: tufa deposits from the Holocene, with an age limit of app. 6000 BP (ages corrected with the appropriate a_0 values), and old tufa outcrops found far from the current lakes with ^{14}C ages older than 25,000 BP (Srdoč et al. 1985a; Horvatinčić et al. 2003). Implications of such a result were that paleoclimatic conditions favoring tufa formation must have been similar in all periods of tufa growth, and that the old tufa deposits should be associated with warm interstadials. Although based on a limited number of data, these conclusions were later justified by dating outcrops of old tufa deposits found at the PL area by the U-Th dating method (Srdoč et al. 1994; Horvatinčić et al. 2000). Most of the old tufa samples clustered around marine isotope stage MIS 5, MIS 7 and MIS 9. ^{14}C and U-Th ages thus demonstrated that the formation of tufa barriers in the PL area was stimulated during interglacial periods with warm and humid climate (Horvatinčić et al. 2003).

Carbon isotope data obtained after intensive sampling of DIC and precipitated carbonates enabled an important observation of an increase of both a^{14}C and δ^{13}C values of DIC and precipitated carbonates downstream along the water course, similarly as observed earlier by Thorpe et al. (1980). It was explained by CO_2 exchange among DIC, atmospheric CO_2 and organic matter (Srdoč et al. 1986b; Horvatinčić et al. 2008). This observation enabled estimates of variable contributions of atmospheric and plant carbon to the DIC and lake sediment carbonate at different flow regimes (e.g., lakes, waterfalls, steady flow) (Barešić et al. 2011a; 2011b; Sironić et al. 2020; 2021). A semi-empirical model of the mechanism controlling the carbon isotope composition (a$^{14}C_{DIC}$ and δ$^{13}C_{DIC}$) attributed the observed changes to simultaneous processes of (1) degassing of dissolved CO_2, (2) exchange of dissolved CO_2 with atmospheric CO_2 and (3) exchange with CO_2 from surface soil and decomposed organic matter in almost equal proportions (Sironić et al. 2020).

Tufa systems are often associated with specific algae and calcium carbonate precipitation on mosses in the whole region, which supported the hypothesis of the importance of the biomediation in carbonate precipitation in these karst environments (Srdoč et al. 1985a; Chafetz et al. 1994; Pedley 2000; 2009; Della Porta 2015). Recently it was demonstrated that true aquatic and amphiphyte moss species use different sources of carbon for photosynthesis, which may have an impact on tufa chronology (Sironić et al. 2021). Since secondary carbonates contain also a certain small amount of organic fraction, knowing its origin through its carbon isotope composition, may help refining chronology of carbonate sedimentation. For example, if the organic fraction is of terrestrial origin, the reservoir age could be determined from the ratio of ^{14}C activities of the carbonate and the contemporary terrestrial organic fraction (Krajcar Bronić et al. 1992). However, if the organic fraction is of aquatic origin having itself some inherent reservoir age, a simple ratio of carbonate to the organic fraction ^{14}C activities would not yield the proper a_0 value. In that sense, a study of isotopic composition of plants such as mosses that grow in karst water and can use CO_2 of different origins (atmospheric CO_2 and/or DIC) presents an important contribution to radiocarbon chronology of karst deposits, namely tufa and karst lake sediments (Sironić et al. 2021).

Lake sediments

The studies of the Plitvice Lakes sediments included comprehensive investigation of: 1) the 12-m-long cores from two big lakes, Prošće and Kozjak (Srdoč et al. 1986a), 2) recent sediments (top ≈40 cm) from the same lakes (Srdoč et al. 1992), 3) recent sediments (top ≈40 cm) from four lakes (Horvatinčić et al. 2006; 2008; 2014), and 4) sediment from different locations with different characteristics from the same lake (Horvatinčić et al. 2018). The main results proved that lake sediments record recent and past environmental changes, both local and global, and both carbonate and organic components of lake sediment should be used for better interpretation of the data obtained by isotope and classical geochemical methods.

Sediment cores from Lakes Prošće and Lake Kozjak, of total length of ≈12 m, were extracted in 1983. The performed analyses (seismic profiling of lakes, geochemical and sedimentological analyses, dating of lake sediment and organic detritus, δ^{13}C and δ^{18}O analyses, analyses of pollen and diatoms) contributed to the understanding of lake geochronology (Srdoč et al. 1986a). Dominantly carbonate sediments contained only a minor fraction of organic matter (< 4 %). The Lake Prošće cores reached the bedrock at the deepest point, while in Lake Kozjak the bedrock was not reached and a large disturbance of the layers was observed at about 2 kyr ago. ^{14}C dating showed that the sedimentation in Lake Prošće began about 8000 yr ago, and in Lake Kozjak the deepest layer was formed 6500 yr ago. The a_0 was determined by the use of the contemporaneous organic material of terrestrial origin found in the sediment core. Sedimentation rate of 1.5 mm/yr in Lake Prošće was uniform throughout the whole profile. In Lake Kozjak the uniform sedimentation rate of 0.8 mm/yr was determined for the upper ≈2 m of the core. Steady $\delta^{18}O$ values along the sediment profile (Lake Prošće -9.0 ± 0.3 ‰, Lake Kozjak -9.3 ± 0.2 ‰) pointed to stable climatic conditions during the deposition of sediment. Good correlation of data obtained by ^{14}C dating of active tufa (Srdoč et al. 1994), lake sediments and peat deposits (Srdoč et al. 1985b) confirmed that the formation of the Plitvice Lakes started about 8000 years ago (Horvatinčić et al. 2003). For comparison, speleothem growth in the Dinaric karst started several thousand years earlier than tufa growth (Horvatinčić et al. 2003). Such a delay was explained by 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), whereas speleothem formation in caves was initiated by the change of climatic conditions at the beginning of the Holocene.

The top ≈40 cm layers of the lake sediments were used to study natural environmental changes or human-induced impact. These sediment cores, dated by ^{210}Pb and ^{137}Cs, encompass time span of ≈100 to 150 years. The reflections of global ^{14}C bomb peak and ^{137}Cs fallout were observed in the sediment profiles, as well as changes in isotope compositions $\delta^{18}O$ and $\delta^{13}C$ as consequences of modern global warming (Srdoč et al. 1992; Horvatinčić et al. 2008; 2014). No significant contamination caused by local anthropogenic influence was found in the sediments (Horvatinčić et al. 2006).

In all cores taken from four lakes (lakes Prošće, Gradinsko, Kozjak, Kaluđerovac), stratigraphic variations in $a^{14}C$ in both carbonate and organic fractions were observed and interpreted as a delayed and damped response to bomb-produced ^{14}C in the atmosphere. The increase of $\delta^{13}C$ of carbonate sediments in the last two decades, better visible in the small lakes, was attributed to an increase in primary productivity that enhanced biologically-induced calcite precipitation (Horvatinčić et al. 2008; 2014; 2018) due to the contemporaneous increase of the lake water temperature (Sironić et al., 2017; Krajcar Bronić et al. 2020).

A study of sediment cores retrieved from three locations having different characteristics from two karst lakes by combined geochemical and isotopic analyses of both carbonate and organic sediment components showed no significant difference between the sediments found away from the tributaries and shores in both lakes (Horvatinčić et al. 2018) – *in situ* calcite precipitation and aquatic OM produced in both lakes were observed. However, in the big Lake Prošće, surrounded with mostly deciduous forest, the sediment composition at the location close to the shore and the confluence of the feeding stream was significantly different. Significant fractions of land-derived both carbonate and organic components were recognized in the shallow, coastal area, showing that the local water inputs could have had great influence on the sediment. Such sediments are more appropriate for the determination of local short-term paleoenvironmental events. Indeed, extreme hydrological events in 1981 and 2010 were identified by disturbances in carbon isotopes distributions along the sediment profile. If regional and long-term paleoclimatic records in lake sediments are to be studied, the chosen sampling location should be far from local-scale influences.

The sedimentation rate was determined based on the radiocarbon (AMS) dating of macrofossils in Lake Kaluđerovac sediments (3 – 7 mm/yr) and the known occurrence of extreme hydrological events in Lake Prošće sediments (7 mm/yr). These values are in good agreement with the previously determined sedimentation rates obtained by ^{210}Pb dating (Horvatinčić et al. 2008).

CONCLUDING REMARKS

Comprehensive multi-proxy study of the secondary carbonate sediments (tufa and lake sediment) from the Dinaric karst resulted in some new knowledge on present and past of the karst system of the Plitvice Lakes. Several problems were recognized and discussed during almost half a century of research, and most of them are related with the geochronology. Secondary carbonates can be used for establishment of the time scale and give information of the past if the problem of initial radiocarbon activity a_0 is properly taken into account. Other dating techniques can be also applied extending the dating possibility to either ages beyond the radiocarbon limit or to recent periods characterized by anthropogenic radiocarbon disturbance. Stable isotopes of carbon, oxygen and nitrogen can provide additional information on the origin of secondary carbonates and processes involved in their formation.

One of the most important results obtained at the Plitvice Lakes system is that they have existed in the present shape during the last about 8000 years, while in the past, during warm interglacial stages, water took different water courses, as proved by the outcrops of old tufa far from the current lakes. Tufa, as the most prominent secondary carbonate feature in the area, as well as lake sediments, can provide valuable information on climate and environmental changes in the past. Combination of various geochemical and isotope methods is *conditio sine qua non* (a necessary condition) for understanding the complex system in which all environmental compartments must be included into the study (atmosphere, various water bodies, soil, bedrock, DIC, terrestrial and aquatic biota, and of course various secondary carbonates).

The research opened also some new questions and new possibilities, coupled with advances in experimental techniques, especially implementation of the AMS radiocarbon dating technique that enabled studies of organic matter in sediment, usually present in low concentrations. Future studies will include relation of organic matter of aquatic origin with the ages of tufa. Long-term data (geochemical and isotope) of the Plitvice Lakes karst system will also help in studying the impact of recent climate changes on lakes in general and on tufa in particular and thus help in determining the epoch of the Anthropocene.

ACKNOWLEDGMENTS

This paper presents a tribute to Dušan Srdoč, who initiated establishment of the Zagreb Radiocarbon Laboratory and the application of isotope techniques in environmental karst studies. We appreciate also indispensable contributions of former and present laboratory scientific and technical staff, especially Nada Horvatinčić, Bogomil Obelić and Adela Sliepčević. Without exquisite co-operation of the National Park Plitvice Lakes (NPPL) this long-term comprehensive study would not have been possible. The investigations were performed within various projects of the Croatian Ministry of Science and Education. Croatian Science Foundation funded project HRZZ-IP-11-2013-1623, Reconstruction of the Quaternary environment in Croatia using isotope methods (REQUENCRIM) 2014 – 2018, and NPPL financed projects Influence of environmental and climate changes on the biologically induced calcite precipitation in form of tufa or lake sediment at the Plitvice Lakes, 2011 – 2014, and JN – 75/19, 2018 – 2019. Some studies were performed also within projects funded by the European Commission: FP5 - ANTHROPOL.PROT, FP7 - SOWAEUMED and FP7 - STRAVAL.

REFERENCES

Barešić J, Horvatinčić N, Roller-Lutz Z. 2011a. Spatial and seasonal variations in the stable C isotope composition of dissolved inorganic carbon and in physico-chemical water parameters in the Plitvice Lakes system. Isotopes in Environmental and Health Studies 47:316-329.

Barešić J, Horvatinčić N, Vreča P, Sironić A. 2011b. Distribution of authigenic and allogenic fractions in recent lake sediment: isotopic and chemical compositions. Acta carsologica 40(2):293-305. doi:10.3986/ac.v40i2.14.

Bencetić Klaić Z, Rubinić J, Kapelj S. 2018. Review of research on Plitvice Lakes, Croatia in the fields of meteorology, climatology, hydrology, hydrogeochemistry and physical limnology. Geofizika 35:189–278, doi:10.15233/gfz.2018.35.9.

Capezzuoli E, Gandin A, Pedley M. 2014. Decoding tufa and travertine (fresh water carbonates) in the sedimentary record: The state of the art. Sedimentology 61:1–21.

Chafetz HS, Srdoč D, Horvatinčić N. 1994. Early diagenesis of Plitvice Lakes waterfall and barrier travertine deposits. Geographie Physique et Quaternaire 48:247-256.

Chen JA, Zhang DD, Wang SJ, Xiao TF, Huang RE. 2004. Factors controlling tufa deposition in natural waters and waterfall sites. Sedimentary Geology 166,3532366.

Della Porta G. 2015. Carbonate build-ups in lacustrine, hydrothermal and fluvial settings: comparing depositional geometry, fabric types and geochemical signature. Geological Society, London, Special Publications, 418(1):17–68. doi:10.1144/sp418.4

Fairchild IJ, Frisia S, Borsato A, Tooth A. 2007. Speleothems. In: Nash DJ, McLaren SJ (Eds), Geochemical Sediments and Landscapes. Blackwell Publishing, Oxford, pp. 200-245.

Faivre S, Bakran-Petricioli T, Barešić J, Horvatić D, Macario K. 2019. Relative sea-level change and climate change in the Northeastern Adriatic during the last 1.5 ka (Istria, Croatia). Quaternary Science Reviews 222:105909.

Filipčić A. 1998. Klimatska regionalizacija Hrvatske po W. Köppenu za standardno razdoblje 1961–1990. u odnosu na razdoblje 1931–1960 [Climatic regions of Croatia according to W. Köppen for 1961–1990 and 1931–1960 periods]. Acta Geographica Croatica 33:7–14. In Croatian.

Ford TD, Pedley HM. 1996. A review of tufa and travertine deposits of the world. Earth-Science Reviews 41, 117-175.

Ford DC, Williams P. 2007. Karst Hydrogeology and Geomorphology. John Wiley, Chichester, 562. https://doi.org/10.1002/9781118684986

Frančišković-Bilinski S, Barišić D, Vertačnik A, Bilinski H, Prohić, E. 2004. Characterization of tufa from the Dinaric karst of Croatia: mineralogy, geochemistry and discussion of climate conditions. Facies 50:183-193.

Frisia S, Borsato A. 2010. Karst. Chapter 6. In: Alonso Zarza AM, Tanner LH (Eds), Carbonates in continental settings – Facies, environments and processes. Developments in Sedimentology 61, 269 – 318, DOI 10.1016/S0070-4571(09)06106-8.

Gandin A, Capezzuoli E. 2008. Travertine versus calcareous tufa: distinctive petrologic features and stable isotopes signatures. Italian Journal of Quaternary Sciences 21:125-136.

Golubić S, Violante C, Plenković-Moraj A, Grgasović T. 2008. Travertines and calcareous tufa deposits: an insight into diagenesis. Geologia croatica 61:363-378.

Horvatinčić N, Čalić R, Geyh M. 2000. Interglacial growth of tufa in Croatia. Quaternary Research 53:185-195.

Horvatinčić N, Krajcar Bronić I, Obelić B. 2003. Differences in the ^{14}C age, δ^{13}C and δ^{18}O of Holocene tufa and speleothem in the Dinaric Karst. Palaeogeography. Palaeoclimatology. Palaeoecology 193;139–157.

Horvatinčić N, Barešić J, Krajcar Bronić I, Obelić B. 2004. Measurement of low ^{14}C activities in a liquid scintillation counter in the Zagreb Radiocarbon Laboratory. Radiocarbon 46(1):105-116.

Horvatinčić N, Briansó JL, Obelić B, Barešić J, Krajcar Bronić I. 2006. Study of pollution of the Plitvice Lakes by water and sediment analyses. Water Air and Soil Pollution: Focus 6;475-485.

Horvatinčić N; Barešić J; Babinka S, Obelić B, Krajcar Bronić I, Vreča P, Suckow A. 2008. Towards a deeper understanding how carbonate isotopes (^{14}C, ^{13}C, ^{18}O) reflect environmental changes: A study with recent ^{210}Pb-dated sediments of the Plitvice Lakes, Croatia. Radiocarbon 50:233-253

Horvatinčić N, Sironić A, Barešić J, Krajcar Bronić I, Todorović N, Nikolov J, Hansman J, Krmar M. 2014. Isotope analyses of the lake sediments in the Plitvice Lakes, Croatia. Central European Journal of Physics 12(10):707-713. doi:10.2478/s11534-014-0490-7

Horvatinčić N, Sironić A, Barešić J, Sondi I, Krajcar Bronić I, Borković D. 2018. Mineralogical, Organic and Isotopic Composition as Palaeoenvironmental Records in the Lake Sediments of Two Lakes, the Plitvice Lakes, Croatia. Quaternary International 494;300–313, doi:10.1016/j.quaint.2017.01.022.

Köppen W. 1936. Das geographische System der Klimate. In: Köppen W, Geiger G (Eds), Handbuch der Klimatologie. Gebrueder Borntraeger, Berlin, Germany, pp. 1-44.

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, Obelić B, Horvatinčić N, Barešić J, Sironić A, Minichreiter K. 2010. Radiocarbon application in environmental science and archaeology in Croatia. Nuclear Instruments and Methods in Physics Research A 619(1-3):491-496 doi:10.1016/j.nima.2009.11.032

Krajcar Bronić I, Barešić J, Sironić A, Lovrenčić Mikelić I, Borković D, Horvatinčić N, Kovač Z. 2020. Isotope Composition of Precipitation, Groundwater and Surface and Lake Waters from the Plitvice Lakes, Croatia. Water 12(9):2414. doi:10.3390/w12092414

Pedley M. 2000. Ambient temperature freshwater microbial tufas. In: Riding RE, Awramik SM (Eds). Microbial sediments. Berlin: Springer; 2000. pp. 179–186.

Pedley M. 2009. Tufas and travertines of the Mediterranean region: a testing ground for freshwater carbonate concepts and developments. Sedimentology 56(2998):221-246.

Peel MC, Finlyanson BL, McMahon TA. 2007. Updated world map of the Köppen-Geiger climate classification. Hydrology and Earth System Sciences 11:1633-1644.

Pentecost A. 1993. British travertines: a review. Proceedings of the Geologists' Association104:29-39.

Philippsen B. 2013. The freshwater reservoir effect in radiocarbon dating. Heritage Science 1:24. doi.org/10.1186/2050-7445-1-24

Polšak A, Juriša M, Šparica M, Šimunić A. 1977. Osnovna geološka karta, SFRJ, list Bihać, 1:100 000 (Basic geological map SFRY, Sheet Bihać; 1:100 000. The Bihać Sheet). Savezni geološki zavod, Beograd, SFR Yugoslavia.

Sironić A, Krajcar Bronić I, Horvatinčić N, Barešić J, Obelić B, Felja I. 2013. Status report on the Zagreb radiocarbon laboratory – AMS and LSC results of VIRI intercomparison samples. Nuclear Instruments and Methods in Physics Research B 294;185-188. doi:10.1016/j.nimb.2012.01.048.

Sironić A, Barešić J, Horvatinčić N, Brozinčević A, Vurnek M, Kapelj S. 2017. Changes in the geochemical parameters of karst lakes over the past three decades – The case of Plitvice Lakes, Croatia. Applied Geochemistry 78;12–22. doi:10.1016/j.apgeochem.2016.11.013.

Sironić A, Krajcar Bronić I, Horvatinčić N, Barešić J, Borković D, Vurnek M, Lovrenčić Mikelić I. 2020. Carbon isotopes in dissolved inorganic carbon as tracers of carbon sources in karst waters of the Plitvice Lakes, Croatia. In: Bojar AV, Pelc A, Lecuyer C, (Eds). Stable isotope studies of the water cycle and terrestrial environments. London: Geological Society; 2020 (Art. 49). (Geological Society of London Special Publications; 507). doi.org/10.1144/SP507-2020-49.

Sironić A, Alegro A, Horvatinčić N, Barešić J., Brozinčević A, Vurnek M, Krajcar Bronić I, Borković D, Lovrenčić Mikelić I. 2021. Isotope Fractionation in Karst Aquatic Mosses. Isotopes in environmental and health studies 57:142-165, DOI: 10.1080/10256016.2020.1852235

Sliepčević A, Planinić J. 1974. Određivanje starosti sekundarnih vapnenačkih taloga metodom radioaktivnog ugljika (Age determination of secondary carbonate sediments by radiocarbon method). Naše jame 15:71-75. In Croatian.

Srdoč D, Breyer B, Sliepčević A. 1971. Ruđer Bošković Institute Radiocarbon Measurements I. Radiocarbon 13:135-140.

Srdoč D, Obelić B, Horvatinčić N, Sliepčević A. 1980. Radiocarbon Dating of Calcareous Tufa; How Reliable Data Can We Expect?. Radiocarbon 22;858-862.

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 posebnim osvrtom na Plitvička jezera (Calcite deposition processes in karstwaters with special emphasis on the Plitvice Lakes, Yugoslavia). Carsus Iugoslaviae (Krš Jugoslavije) 11(4-6):101–204. In Croatian with English abstract.

Srdoč D, Obelić B, Horvatinčić N, Culiberg M, Šercelj A, Sliepčević A. 1985b. Radiocarbon dating and pollen analyses of two peat bogs in the Plitvice National Park area. Acta Botanica Croatica 44;41-46.

Srdoč D, Obelić B, Horvatinčić N, Krajcar Bronić I, Marčenko E, Merkt S, Wong H, Sliepčević A. 1986a. Radiocarbon Dating of Lake Sediments from two Karstic Lakes in Yugoslavia. Radiocarbon 28:495-502.

Srdoč D, Krajcar Bronić I, Horvatinčić N, Obelić B. 1986b. The Increase of ^{14}C Activity of Dissolved Inorganic Carbon Along the River Course. Radiocarbon 28:515-521.

Srdoč D, Horvatinčić N, Obelić B, Krajcar Bronić I, O'Malley P. 1986c. The Effects of Contamination of Calcareaous Sediments on Their Radiocarbon Age. Radiocarbon 28:510-514.

Srdoč D, Horvatinčić N, Ahel M, Giger W, Schaffner C, Krajcar Bronić I, Petricioli D, Pezdič J, Marčenko E, Plenković A. 1992. Anthropogenic influence on the ^{14}C activity of recent lake sediment. A case study. Radiocarbon 34:585-592

Srdoč D, Osmond J, Horvatinčić N, Dabous A, Obelić B. 1994. Radiocarbon and Uranium-Series Dating of the Plitvice Lakes Travertines. Radiocarbon 36(2):203-219.

Surić M, Juračić M, Horvatinčić N, Krajcar Bronić I. 2005. 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 214:163-175. doi:10.1016/j.margeo.2004.10.030.

Surić M, Czuppon G, Lončarić R, Bočić N, Lončar N, Bajo P, Drysdale R. 2020. Stable Isotope Hydrology of Cave Groundwater and Its Relevance for Speleothem-Based Paleoenvironmental Reconstruction in Croatia. Water 12(9): 2386, 23. doi:10.3390/w12092386.

Tanner LH. 2010. Continental Carbonates as Indicators of Paleoclimate. Chapter 4. In: Alonso Zarza AM, Tanner LH (Eds), Carbonates in continental settings – Facies, environments and processes. Developments in Sedimentology 61, 179 – 214, DOI 10.1016/S0070-4571(09)06204-9

Thorpe PM, Otlet RL, Sweeting MM. 1980. Hydrological implications from ^{14}C profiling of UK tufa. Radiocarbon 22(3):897-908.

Wray RAL. 1997. A global review of solutional weathering forms on quartz sandstones. Earth-Science Reviews 42:137-160. https://doi.org/10.1016/S0012-8252(96)00056-6

Zalasiewicz J, Waters CN, Williams M, Barnosky AD, Oreskes N. 2015. When did the Anthropocene begin? A mid-twentieth century boundary level is stratigraphically optimal. Quaternary International 383:196-203.

Zippel B, Neu TR. 2011. Characterization of glycoconjugates of extracellular polymeric substances in tufa-associated biofilms by using fluorescence lectin-binding analysis. Applied and Environmental Microbiology 77:505-516.