

RADIOCARBON DATING OF TRAVERTINE SEDIMENTS
IN PLITVICE NATIONAL PARK

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ABSTRACT

Radiocarbon dating of travertine (calcareous tufa) sediments is in progress at our ^{14}C laboratory. The results obtained so far show two distinct periods of travertine deposits formation: a relatively recent one and another much older, close to the lower limit of radiocarbon method (\approx 30,000 to 40,000 years). The uncertainties involved in the age calculation of travertine samples, such as contamination with recent and/or thermonuclear blast produced ^{14}C , susceptibility of travertine to chemical and isotopic changes, etc are discussed in some details, as well as the assessment of the initial activity of groundwater. Experimental data are presented in 2 Tables showing present activity of biosphere (lake water, vegetation, atmospheric CO_2) and that of travertine samples ranging from recent deposits to very old layers.

INTRODUCTION

Radiocarbon dating has been successful applied to measure the age of samples composed of inorganic material such as groundwater hydrocarbonates, speleothems, shells etc. These substances contain radiocarbon of biogenic origin, which has been removed from the carbon cycle in the biosphere. We have attempted to measure the age of calcareous tufa or travertine by the radiocarbon dating method, since travertine contains carbon of biogenic origin as well. Our radiocarbon technique is described in general in ref 1, while details on the tufa dating have been

presented at the 10th Radiocarbon Conference, Bern/Heidelberg 1979 (2).

A substantial number of samples from the Plitvice National Park has been measured to establish geochronology of travertine sediments. Travertine is considered quintessential in lake formation in the National Park, therefore a study of travertine layers, its morphology and formation processes are recently in the focus of our research. Problems connected with radiocarbon dating of travertine such as sample contamination with modern carbon, absolute age calculation, etc are discussed in the following paragraphs.

Principles of radiocarbon dating of travertine

Travertine formation in waterfalls is caused by loss of carbon dioxide through aeration, temperature change and/or biogenic assimilation, which shifts the equilibrium in groundwater solution of hydrocarbonates toward calcium carbonate precipitation. The origin of larger part of carbon in groundwater hydrocarbonates is biogenic. Rainwater contains very small amount of carbon dioxide absorbed from the atmosphere. However, during seepage process rainwater is enriched with CO_2 from decaying detritus, which contains ^{14}C in equilibrium with the biosphere. On its further way, groundwater, now containing appreciable concentration of carbonic acid, dissolves mineral carbonates, mostly limestone and dolomite in the Park area. The net result is incorporation of ^{14}C into dissolved carbonate or bicarbonate anions. The ^{14}C specific activity of recent groundwater carbonates usually departs from stoichiometric value and ranges between 65 and 90% of present biosphere activity (4) (before the recent contamination with man-made ^{14}C from nuclear weapon tests). Precipitation of calcium carbonate in form of travertine eliminates it from further cycling in the carbonate reservoir. Radioactive decay of ^{14}C , which is the basis of radiocarbon dating, enables one to measure the age of travertine samples.

Experimental technique

Approximately 100 grams of dry travertine sample is mechanically cleaned from recent intrusions such as rootlets. Surface layer which contains usually lichens, moss or plants is removed by scraping. The clean sample is then dissolved in dilute HCl and the evolved CO₂ is trapped in liquid nitrogen. After purification, carbon dioxide is converted into methane via catalytic hydrogenation over Ru catalyst. Methane gas is then used for proportional counter filling, which is a frequent and precise technique for specific activity measurements. Details of this experimental technique are given in ref. (1). The experimental data are further processed on the computer to obtain statistical tests, calculated age etc.

Uncertainties in age measurement of travertine

Besides uncertainties in radiocarbon dating which are common to all organic samples such as variation of ¹⁴C concentration in atmosphere in the past, as discussed at the 12th Nobel Symposium (3), the radiocarbon dating of travertine involves several specific uncertainties. Carbonates are in general more susceptible to chemical and isotopic composition change, especially when exposed to open atmosphere and/or groundwaters over millenia. Travertine is specifically susceptible to such changes due to its spongy structure. Our recent research is aimed at precise measurement of travertine samples from the same site, having various morphology, which varies from sandy to crystalline structure with perfectly preserved substratum of moss. We believe that these measurement will give us quantitative data concerning the error in age measurement due to chemical or isotopic changes.

Another important question is the initial activity A₀ of groundwater or freshly deposited travertine. Generally accepted values (4) vary between

65 and 90 percent of modern standard (0.95 Oxalic, NBS), which causes an inherent error of approximately \pm 1050 years in the travertine age measurements, unless more precise data on the initial activity A_0 are available. A straightforward way to measure the A_0 value would be measurement of recent travertine deposits, had not the man-made ^{14}C contaminated the whole biosphere. According to our measurement presented at the 10th Radiocarbon Conference (2) and reproduced in this paper in Table 1, present ratio of recent travertine vs biosphere activity is equal to 0.65. However, when this value is used to calculate the absolute age of travertine, the result of calculation is meaningless for a large number of samples listed in Table 2. Obviously, the initial activity ratio must be much closer to the value 0.85 (present travertine activity vs 0.95 Oxalic) as if recent bomb-produced ^{14}C has not influenced the groundwater activity in the whole catchment area. The explanation of this phenomenon can be only guessed. It seems that underground water is flowing (or seeping) through huge deposits of travertine which was formed before contamination with bomb-test ^{14}C . Due to exchange between solid and liquid phase, the equilibrium concentration of $\text{H}^{14}\text{CO}_3^-$ ions is shifted toward the prevailing solid phase activity. In other words, large amount of porous travertine acts as a "buffer zone" by keeping the groundwater activity constant over a long period, in spite of short, sharp pulses of much higher activity, such as the man-made increase of ^{14}C concentration in the atmosphere which started in 1952. It should be pointed out here that the retention time of groundwater is very short in Karst. Our measurements of tritium activity of spring water in the same area showed that the average tritium concentration in water is very close to that of precipitation. Consequently, the above outlined process of isotopic equilibration is very fast and efficient.

We are searching for samples of prebomb-test travertine of known age. Measurement of activity of such samples would solve the question of

initial activity of travertine from the investigated area. Accepting tentatively an initial activity equal to 0.85 of modern standard, the age of numerous samples of travertine collected in the National Park and measured in our laboratory has been calculated. The results are shown in Table 2. We must emphasize that the number of samples, as well as the number of collecting sites is very limited due to the complex and expensive measuring technique. In spite of that, one fact is evident from the travertine ages listed in Table 2: There is a gap between two distinct groups of samples, one being the relatively young (0-3000 years) and the other much older, close to the lowest limit of radiocarbon dating method (30,000 to 40,000 years). Even though further refinement of our measuring technique and calculation may result in shifting the ages shown in Table 2 by several hundred years or more, the fact remains that we are dealing with travertine from two distinct geological periods. Instead of speculating now about the warm interglacial or interstadial periods which could be linked to the old travertine formation, we are pursuing extensive and systematic dating of travertine from Karstic regions in Yugoslavia. After collecting and measuring a representative number of samples we hope to present a conclusive picture of geochronology of travertine in Plitvice National Park.

TABLE 1.

^{14}C activity of samples collected from Plitvice Lakes National Park, expressed as percent of modern, relative to 0.95 NBS Oxalic Acid

Sample code	Descriptive name of sample	Percent of modern, %	Description of sample, site and comment
Z-672	Lake or stream water bicarbonate, Lake Kozjak	85.0 ± 0.9	Lake water, waterfalls between lakes Kozjak and Milanovac. Coll. spring 1978.
Z-692	Same, Crna Rijeka	60.2. ± 0.9	Crna Rijeka spring; Coll. spring 1978; contains lower ^{14}C activity.
Z-694	Same, Bijela Rijeka	79.6 ± 0.6	Bijela Rijeka stream water. Old mill, coll. fall 1979.
Z-710	Same, Rječica	87.7 ± 0.6	Rječica stream, col. fall 1979 near old bridge.
Z-708	Same, Plitvica	85,5 ± 0.7	Water catchment, Plitvica spring, coll. fall 1979.

Sample code	Descriptive name of sample	Percent of modern, %	Description of sample, site and comment
Z-709	Same, Korana	92.2 ± 0.9	Korana river, near bridge, coll. fall 1979.
Z-657	Moss (<i>Cratoneurum commutatum</i>)	91.7 ± 0.9	Moss, covering recently deposited travertine, waterfalls
Z-659	Recent travertine	88.5 ± 0.9	Recent travertine covered by moss. M. Trnina falls, coll. spring 1978.
Z-677	Aquatic plants	78.6 ± 0.9	Submerged aquatic plants <i>Potamogetum perfoliatum</i> , lake Galovac, coll. spring 1978.
Z-673	Atmospheric Carbon Dioxide	131.5 ± 0.8	Atmospheric CO ₂ trapped on NaOH, Mokinje, spring 1978.
Z-668	Dry leaves	134.2 ± 0.8	<i>Fagus sylvatica</i> , lake Kozjak shore, coll. fall 1976.
Z-656	Fresh twigs	130.6 ± 0.8	<i>Salix cinerea</i> , M. Trnina falls, coll. spring 1978.

Table 1, continued

TABLE 2

Radiocarbon dating of travertine samples from Plitvice Lakes National Park

Sample code	Description of sample	Site of sample collection	Radiocarbon age; Initial activity $A_0 = 0.85$	Percent of modern vs 0.95 NES Oxalic	Comment
Z-659	Recent travertine covered by moss	M.Trnina falls	-	89.4	
Z-658	Recent travertine, deeper layer	M.Trnina falls	-	88.5	
Z-701	Recent travertine, covered by moss (Cratoneuron)	Plitvica stream	-	90.3	Mean value is 88.8% of modern standard.
Z-704	Recent travertine covered by moss	Korana river, near bridge	-	88.8	
Z-400	Recent travertine covered by moss	Lake Gradina	-	87.2	

Sample code	Description of sample	Site of sample collection	Radiocarbon age; Initial activity $A_0=0.85$	Percent of modern vs 0.95 NBS Oxalic	Comment
Z-403	Dry travertine, above water level	Lake Gradina	1080 ± 100	74.8	
Z-663	Dry travertine, broken giant column Outer rim.	Travertine Caves	1165 ± 100	73.5	Group of travertine samples from various locations showing similar radiocarbon age.
Z-664	Same, 15 cm from surface	"	1200 ± 90	73.3	
Z-665	Same, 30 cm from surface	"	1150 ± 100	73.3	
Z-666	Same, 45 cm from surface	"	1190 ± 100	73.3	
Z-686	Travertine barrier, above water level	Lower Lakes	1290 ± 100	72.5	

Table 2, continued

Sample code	Description of sample	Site of sample collection	Radiocarbon age; Initial activity $A_0 = 0.85$	Percent of modern vs 0.95 NBS Oxalic	Comment
Z-405	Dry travertine barrier, bottom layer	Gavanovac, cut through dry barrier	2930 ± 110	59.7	
Z-620	Same - pathway level	"	3000 ± 120	59.0	
Z-624	Same - 120 cm above path	"	2790 ± 100	60.4	Group of travertine various sites showing similar radiocarbon age. No distinct gradient was found
Z-630	Same - 240 cm above path	"	2750 ± 80	60.8	
Z-632	Same - 405 cm above path	"	2630 ± 110	61.6	in huge travertine blocks in any direction.
Z-625	Same - 160 cm above path, surface layer	"	2630 ± 100	61.6	
Z-626	160 cm above path 10 cm depth	"	2650 ± 100	61.5	
Z-660	160 cm above path 20 cm depth	"	2940 ± 100	59.3	
Z-681	160 cm above path 30 cm depth	"	2970 ± 100	59.2	
Z-682	160 cm above path 40 cm depth	"	3110 ± 120	58.1	
Z-700	Dry travertine	Pl. Ljeskovac	3125 ± 120	57.6	
Z-676	Dry travertine barrier	Kozjak	2630 ± 100	61.6	

Table 2, continued

Sample code	Description of sample	Site of sample collection	Radiocarbon age; Initial activity A_0	Percent of modern vs 0.95 NBS Oxalic	Comment
Z-685	Dry travertine in form of wooden beams	Crna Rijeka estuary	24800 ± 650	6.1	
Z-745	Dry travertine in cave	Cave above Korana River	28150 ± 920	2.8	
Z-671	Dry travertine on top of hill Gradina	Gradina	30200 ± 1500	2.4	Very old travertine, close to the lower limits of the radiocarbon method
Z-684	Dry travertine barrier	Bijela Rijeka	34800 ± 3000	1.3	
Z-396	Dry travertine barrier, partly recrystallized	Pl. Ljeskovac, near monument	40000	0.5	

Table 2, Continued

References

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