THE EFFECTS OF CONTAMINATION OF CALCAREOUS SEDIMENTS ON THEIR RADIOCARBON AGES

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ABSTRACT. Two principal reasons for the inherent uncertainty in ¹⁴C dating of calcareous sediments such as tufa or those of lacustrine origin are the unknown initial ¹⁴C activity (A_0) of the sediment, mainly affecting younger (Holocene) samples, and contamination of older sediments with recent carbonate, causing ¹⁴C ages to be excessively young. To assess the contamination effect, samples of old tufa from the Riss/Würm interglacial were examined. These sediments contain essentially no ¹⁴C except that contributed by surface contamination. Tufa samples were crushed and grains ranging in size from <1mm, 1 to 2mm, up to 4 to 5mm were separated for analysis; 2M HCl was then used to dissolve the samples in successive steps. ¹⁴C measurements indicated that each subsequent soluble fraction obtained from porous tufa gave a successively older age, indicating that the surface of the sample was contaminated by younger carbonates. No consistent effect of grain size on the ¹⁴C age was observed. Compact tufa proved to be less subject to contamination. ¹⁴C ages obtained on this material were also too young, yet older than the age obtained from porous tufa samples.

¹⁴C ages of interglacial tufa were cross-checked with the ²³⁰Th/²³⁴U dating method, using samples of very clean calcite which overlies the tufa blocks. Inferred ²³⁰Th/²³⁴U ages of the interglacial tufa (which had yielded ¹⁴C dates ranging from 25,000 to 37,000 yr) coincided with the last interglacial (Riss/Würm, Stage 5). Samples of Holocene tufa, in which contributions of recent ¹⁴C from surface contamination would pose less of a problem, yielded ¹⁴C and ²³⁰Th/²³⁴U dates which were in excellent agreement.

INTRODUCTION

¹⁴C dating of calcareous tufa yields reliable results providing that the tufa was deposited as a result of decomposition of dissolved calcium bicarbonate in cold fresh water. The source of CO2 that dissolves limestone bedrock is biogenic, thus introducing ¹⁴C in bicarbonates, and subsequently, in lacustrine sediments. This process is fast in comparison with the half-life of ¹⁴C, consequently, freshly deposited lacustrine sediments are practically contemporaneous with the surrounding living matter in the biosphere. However, due to the presence of inactive carbon from limestone, the specific activity of lacustrine sediments, as well as that of speleothems, is always lower than the specific activity of living matter. Stoichometrically, ¹⁴C activity of dissolved bicarbonates and speleothems should be 50% of the activity of biogenic CO₂. However, numerous measurements have shown that the actual 14C activity of recent freshwater bicarbonates, tufa, and speleothems ranges between 60% and 90% of the activity of atmospheric CO₂, prior to nuclear weapon tests contamination (Vogel, 1970; Geyh, 1972).

The increase of ¹⁴C activity of dissolved bicarbonates in fresh water is caused by an exchange of dissolved CO_2 in natural systems of groundwater circulation which are partly or completely open to the atmosphere. The wide range of the resulting ¹⁴C activity of the dissolved bicarbonates is the source of a serious error in the ¹⁴C age calculation of lacustrine sediments, unless such an activity is measured or estimated fairly precisely. Several

models for calculation of initial activity of groundwater bicarbonates have been developed (Tamers & Scharpenseel, 1970; Pearson & Hanshaw 1970; Mook, 1972; Fontes & Garnier, 1979; Eichinger, 1983) and comparison of calculated and experimental data are published (Krajcar-Bronić *et al*, this issue).

A typical error in age estimation of lacustrine sediments due to variability of the initial activity of freshwater bicarbonates ranges from ca 500 to 2500 yr. The relative standard deviation may reach unacceptable values for younger (Holocene) sediments (eg, 1000 ± 2500 yr), whereas the same absolute error is of the same order of magnitude as the standard deviation of the counting rate of very old samples. Therefore, a realistic assessment or an adequate measurement of the initial activity of sediments is of great importance for younger deposits.

Minor contamination of deposits with recent carbonates (of the order of several percent of total mass of carbonates), will not affect the ¹⁴C age of young samples significantly (Olsson, 1980). On the contrary, the same amount of contamination of old deposits with recent carbonates, renders the ¹⁴C ages of sediments, the actual age of which is between 20,000 and 40,000 yr, quite useless. The same applies to much older sediments; in this case the contamination with recent carbonates produces ¹⁴C ages within the range of the method (eg, <40,000 yr), whereas the actual age is beyond the limits of the ¹⁴C method, as revealed by the ²³⁰Th/²³⁴U method. In fact, the inconsistency of ¹⁴C ages of samples of old tufa taken from the same block, as well as the incompatibility of obtained ages with paleoclimatic conditions, prompted a more detailed study which is presented below.

EXPERIMENTAL

Radiocarbon Dating of Old Tufa Deposits

Tufa samples were selected from outcroppings or huge blocks which belonged to an interglacial phase of tufa growth in the Plitvice National Park, NW Yugoslavia. ¹⁴C dates of numerous samples were very inconsistent (Srdoč *et al*, 1980) ranging in age from ca 20,000 to 40,000 yr BP. Samples of calcite in the form of clean crystals that sporadically overlay the tufa blocks always gave the background counting rate, *ie*, their age was much older than the lowest detectable ¹⁴C age. These factors point to contamination of very old, porous tufa layers with young carbonate as the possible explanation for inconsistent ¹⁴C ages.

Experimental verification of the contamination of old deposits was based on the assumption that the surface layer which may contain the contaminant will dissolve first, when a sample of calcareous tufa is treated with diluted hydrochloric acid. Two samples of old tufa were chosen for chemical treatment with acid. The porous, spongy, structured samples were considered more susceptible to contamination, whereas compact tufa seemed less affected by contamination. Samples of tufa weighing ca 300g were crushed and separated into fine (<1mm in diameter), medium (1 to 2mm), and coarse grains (4 to 5mm). It was expected that this procedure could result in a difference in activity of evolved CO_2 by varying the ratio of freshly cut surface and the contaminated one. However, the activity of evolved CO_2 was much more dependent on the degree of etching the grains than on the grain size; therefore, no particular grain size could be specified as the most contaminated or as the cleanest one.

Dissolution of tufa samples was carried out in 2 or 3 steps (depending on the sample size), each step producing the amount of CO_2 sufficient to fill the gas processing system which converts the evolved CO_2 into methane. The amount of 2.0M HCl, sufficient to dissolve the whole sample, was divided in 2 or 3 portions and slowly dripped on the sample, which was constantly stirred in the reaction flask. The evolved CO_2 was removed from the reaction flask in a stream of nitrogen and trapped at liquid nitrogen temperature. Subsequent chemical and counting procedures are described elsewhere (Srdoč, Breyer & Sliepčević, 1971; Srdoč *et al*, 1979, 1982).

The results of succesive dissolution of porous and of compact tufa are presented in Table 1. For comparison, the result of ¹⁴C dating clean calcite crystalline aggregate is also given.

²³⁰Th/²³⁴U Dating of Old Tufa

 14 C dates of old tufa (Table 1) showed clearly that the true age of old tufa lies beyond the limits of 14 C dating. We also used the 230 Th/ 234 U dating method on clean calcite which can be found overlying tufa blocks as well as on porous tufa. First, a clean Holocene calcite sample was split into two halves and dated using both methods. The agreement between the obtained dates was excellent (1440 \pm 150 14 C yr vs 1400 \pm 600 230 Th/ 234 U yr). The

of old tufa samples from Plitvice National Park, Yugoslavia			
Grain size (mm)	No. of fraction*	% modern**	Apparent ¹⁴ C age (in yr BP)†
	P	orous tufa	
4 - 5	I (30%)	12.2 ± 1.0	$15,000 \pm 400$
4 - 5	II (30%)	5.9 ± 1.1	$21,100 \pm 800$
4 - 5	III (30%)	3.9 ± 0.7	$24,500 \pm 1200$
1 - 2	I (50%)	7.8 ± 0.8	$18,700 \pm 1600$
1 - 2	11 (50%)	1.7 ± 0.7	$31,000 \pm 400$
<1	I (50%)	10.8 ± 0.9	$16,000 \pm 400$
< l	II (50%)	3.6 ± 0.7	$25,000 \pm 1200$
	Сс	ompact tufa	
1 - 5	I (30%)	3.9 ± 0.3	$24,400 \pm 1100$
1 - 5	H (30%)	2.9 ± 0.3	$26,900 \pm 1600$
1 - 5	III (30%)	1.0 ± 0.3	>37,000
	Clean calcite	crystalline aggregate	
4 - 5	I (100%)	0.5 ± 0.6	>37,000

TABLE 1

The activity in percent modern and the apparent ¹⁴C age of successive fractions obtained by fractional dissolution of old tufa samples from Plityice National Park. Yugoslavia

* An approximate percentage of total sample weight dissolved in each step is given in parentheses

** % modern ref: activity of NBS oxalic acid $\times 0.95 = 100\%$

+ Initial ¹⁴C activity (A_o) = 75% modern standard

same procedure was applied to several old tufa samples with ¹⁴C ages that fell within the last glaciation period and which were not considered reliable. The ²³⁰Th/²³⁴U dates of clean calcite overlying tufa blocks coincided with the last interglacial (Riss/Würm, Stage 5), as opposed to ages obtained on porous tufa, which were not acceptable due to contamination with clay containing thorium. The 230 Th/ 234 U age of clean calcite, 119,000 ± 8500 yr, fits very well in the time sequence of tufa deposition based on the fact that a warm and humid climate is required for tufa growth.

CONCLUSIONS

¹⁴C dating of Holocene calcareous sediments, such as lake sediments or tufa poses no problem since a small percentage of younger calcite does not affect their ¹⁴C age appreciably. Moreover, the requested precision of tufa dating is usually much lower than that of archaeologic samples. However, in case of old, preglacial tufa, minor contamination with recent carbonate results in a false, unacceptable age. For example, most of the porous samples of old tufa collected in the karst region of the Plitvice National Park, Yugoslavia, showed an apparent ¹⁴C age 20,000 to 40,000 yr. This age would place the formation of tufa in Europe during the Würm glacial, which is unacceptable.

Porous tufa turned out to be contaminated with ²³⁰Th, and thus was unreliable for ²³⁰Th/²³⁴U dating. However, clean calcite crystal aggregates that frequently intersperse tufa formation, or overlie tufa blocks, yield reliable and reproducible data. The ²³⁰Th/²³⁴U data presented here were crosschecked at the Niedersächsisches Landesamt für Bodenforschung, Hannover, West Germany. ²³⁰Th/²³⁴U dates obtained on calcite aggregates at USGS and NLfB laboratories are in excellent agreement (Horvatinčić, ms). ²³⁰Th/²³⁴U dates of tufa deposits in the Plitvice National Park coincide with the warm and humid Riss/Würm interglacial. This is quite plausible on the basis of present knowledge about climatic conditions that favor tufa formation.

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