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RADIOCARBON DATING OF CALCAREOUS TUFA: HOW RELIABLE DATA CAN WE EXPECT?

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ABSTRACT. Systematic dating of tufa samples has been undertaken to establish a chronology of tufa deposits in Plitvice National Park, Yugoslavia. We conclude that tufa samples give reproducible data within the time span of ≈ 40,000 years up to recent. The $^{14}C/^{12}C$ ratio of carbon in the ambient biosphere and hydrosphere gives a detailed picture of the distribution of carbon isotopes in the investigated system. Despite the susceptibility of calcareous material to ambient conditions in the hydrosphere, the original ^{14}C composition of tufa has not been substantially changed. A vertical profile which was cut in tufa during pathway construction showed that the tufa isochrones run vertically in the investigated area. The vertical isochrones and the ^{14}C gradient were horizontal due to tufa build-up in Plitvice National Park which occurs on vertical escarpments that have been flooded. The relatively uniform radiocarbon content of most tufa deposits indicates redistribution of radiocarbon during the formation period. While detailed stratigraphy is often obscured, a general chronology of tufa deposits in the investigated area has been established.

INTRODUCTION

A multidisciplinary project is in progress to establish the geochronology of the unique karstic phenomenon of travertine lakes in Plitvice National Park, central Croatia, Yugoslavia. Radiocarbon dating appears to be the most promising method if it covers the period of calcareous tufa formation, and if samples are not environmentally altered. A systematic investigation of dating tufa samples has been undertaken to determine the reliability of the method. Results are presented here with the conclusion that tufa samples give reproducible data despite their spongy nature and physically and chemically fragile structure. Because tufa is predominantly a postglacial feature, its time span of origin falls, in most cases, within radiocarbon dating limits. Tufa presents an ideal case for experimental determination of the $^{14}C/^{12}C$ ratio "in statu nascendi", *ie,* immediately upon the growth of the sample. Simultaneously, the $^{14}C/^{12}C$ ratio of carbon in the ambient biosphere and hydrosphere has been determined, giving a complete picture of the distribution of these carbon isotopes in the investigated system. The relatively rapid growth of tufa in a well-defined system that has been systematically investigated and monitored over the past 100 years enabled us to present accurate data on the $^{14}C/^{12}C$ ratio in freshly deposited tufa. Providing that the changes in environmental conditions in the past have not influenced substantially the $^{14}C/^{12}C$ ratio during tufa deposition, accurate dating of tufa is quite feasible. Our research indicates that, despite the susceptibility of calcareous material to ambient conditions in hydrosphere, there are good reasons that the original composition of tufa has not been substantially changed. Porous old tufa is exposed to atmospheric water if located above water level or soaked in a lake or stream, if it is below

the surface. In both cases, there are chances for changes in composition and/or isotopic fractionation. Fortunately, we found solid organic material (wood branches) embedded in tufa which enabled us to compare the $^{14}C/^{12}C$ ratio in organic material in the same stratum.

With all relevant information on hand, we chose a vertical profile that was cut in tufa during pathway construction and took samples, each 40cm from the pathway base up to approximately 4m height. The dating results were very interesting: contrary to the usual chronology of strata, where the oldest stratum is expected to be in the lowest lying region, the tufa isochrones run vertically in the investigated area. This was not a surprise since a great deal of tufa in Plitvice Park is deposited in waterfalls. The tufa buildup occurs on vertical escarpments flooded by water. Hence, the vertical isochrones and the age gradient were found in a horizontal direction.

Methods

Chemical processing of calcareous tufa poses no problem since it consists of relatively pure $CaCO_3$, easily soluble in acid. Calcareous tufa samples were cleaned mechanically from intrusions; the outer part of samples was scraped off. The clean sample was treated with diluted HCl and the developed CO_2 trapped for subsequent purification and conversion to methane. Wood, algae, and moss samples were treated with 4 percent HCl, washed to neutrality, and dried prior to combustion. Atmospheric CO_2 was absorbed in the NaOH solution exposed to air in a tray. The purification of gases, the catalytic hydrogenation of CO_2, and the counting procedure are described in a previous paper (Srdoč, Breyer, and Sliepčević, 1971).

Distribution of radiocarbon in the Karstic environment

Radiocarbon activity of the biosphere of lakes has been monitored over the past 4 years. Samples of recent plants (leaves, twigs), aquatic plants, moss, algae, water, carbonates, air, and tufa have been collected and measured at regular intervals. Tufa samples were collected by scraping the freshly deposited material, not older than a year. Water samples were processed using the modified IAEA method for $BaCO_3$ precipitation. Recent CO_2 samples were collected by exposing the concentrated carbonate-free NaOH solution to atmospheric air. A consistent picture of radiocarbon activity throughout the monitored period has been obtained, as shown in table 1, for Spring 1978. It is interesting to note the pronounced effect of the surrounding water on the aquatic plants and tufa (so-called, hard water effect). When the activity of water bicarbonates is compared with that of CO_2 in the atmosphere or recent plants, a ratio equal to 0.65 ± 0.02 is obtained. It should be pointed out that the mean retention time of underground water in Karstic regions is very short. We have checked the tritium activity of surface water and have found a close correlation with the precipitation activity. The ratio tufa/biosphere activity is 0.67 ± 0.02, which is slightly higher than that of water biocarbonate, presumably due to the intermittent exposure to

atmospheric CO_2 during low water levels. Aquatic plants, algae, and moss have an activity ratio between 0.6 and 0.7, again, very close to that of bicarbonates. However, when the ratio, 0.67, was applied to recent tufa deposits of the pre-bomb period, an unacceptable age was obtained, pointing at a ratio that is too low. It seems that lake water flowing over tufa barriers reaches isotopic equilibrium for the bicarbonate. Due to the enormous amount of uncontaminated pre-bomb tufa deposits in stream beds, barriers, and lake bottoms, the equilibrium activity of these dissolved bicarbonates has not been affected appreciably by the bomb test radiocarbon. This assumption is consistent with the described uniform activity of tufa beds in the formative stage. The initial activity ratio of 0.85 seems to be appropriate for tufa age calculation in the investigated region.

Dating of calcareous tufa

The conditions for tufa precipitation, such as water hardness, pH, temperature, aeration, etc, are still ambiguous. The same is true for biogenic factors. Tufa is always associated with specific algae (*Schizotrix*) and often deposited on moss (*Cratoneurum commutatum, Bryum pseudotriquetrum)* in the whole region, which supports the hypothesis of the importance of the biogenic factor in carbonate precipitation. Our measurements of distribution in the biosphere and hydrosphere of carbon isotopes support this hypothesis. It is obvious that aquatic plants, algae, and moss, having the same radiocarbon content as bicarbonates, use CO_2

TABLE 1
Radiocarbon activity of modern samples from Plitvice National Park

Sample no.	Sample description and location	^{14}C, % of modern	Comment
Z-672	Lake Kozjak water	85.0 ± 0.9	Coll Spring 1978
Z-659	Fresh tufa M Trnina falls	88.5 ± 1.0	Coll Spring 1978 Inundated by lake water
Z-657	Moss *(Cratoneurum Commutatum)* M Trnina falls	91.7 ± 1.0	Coll Spring 1978 Partially submerged in lake water
Z-677	Aquatic plant *(Potamogetum perfoliatus* L) Lake Galovac	78.6 ± 0.9	Coll Spring 1978 Submerged in lake water
Z-656	Twigs *(Salix cinerea* L) M Trnina falls	130.6 ± 0.8	Coll Spring 1978
Z-668	Leaves *(Fagus sylvatica* L) Lake Kozjak area	134.2 ± 0.8	Coll Fall 1976
Z-673	Atmospheric carbon dioxide Lake Kozjak area	131.5 ± 0.8	Coll Spring 1978

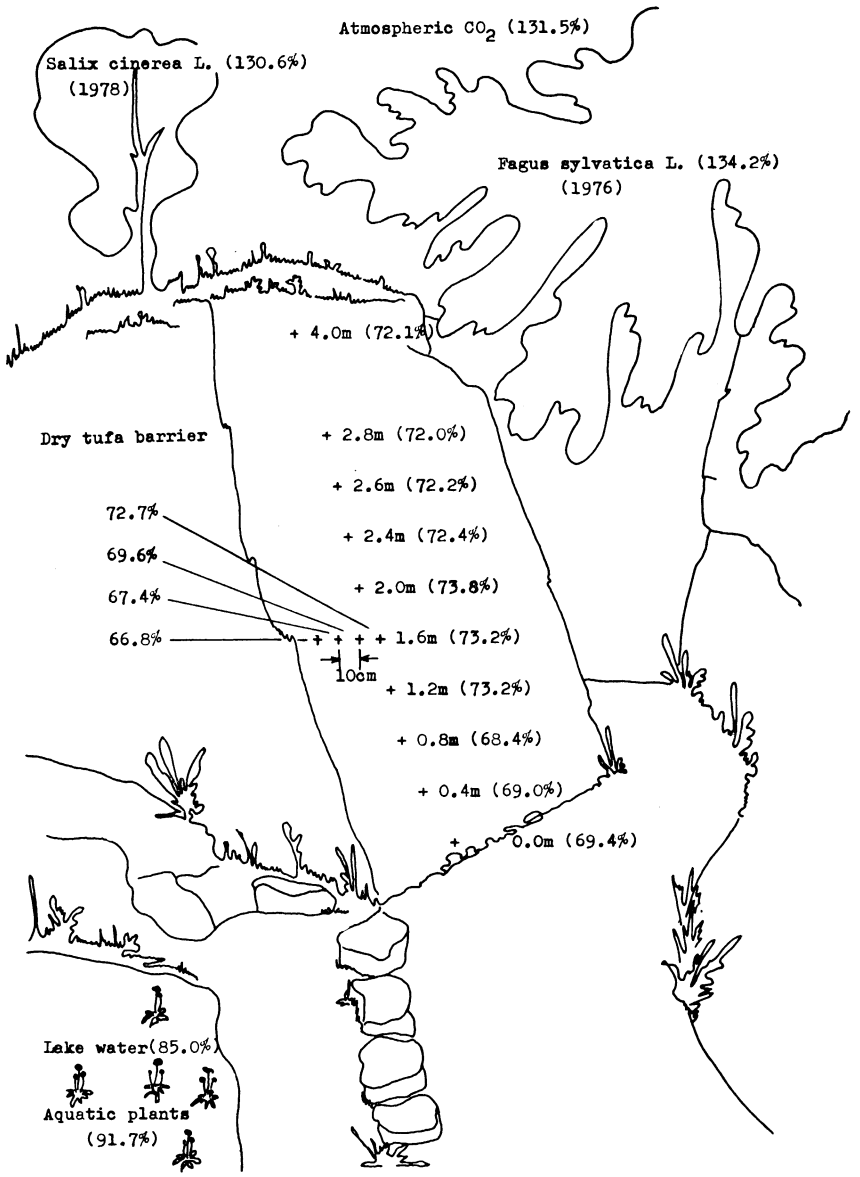

Fig 1. Shematic drawing of the dry tufa barrier, 4m above the present water level, Plitvice National Park. The vertical profile was cut during pathway construction. Sampling sites and tufa activity, expressed in percent of modern, are shown.

from water, promoting the precipitation of $CaCO_3$. The process of precipitation seldom occurs in slow-moving water. Most tufa is deposited in turbulent waters, forming barriers, overhanging draperies, thick layers having cavernous structure, etc. In most cases, the initial stratigraphy is perturbated by frequent change of intensity and direction of water flow, penetration of surrounding water into porous tufa layers, erosion, etc. More often than not, whole blocks of tufa have a uniform distribution of radiocarbon concentration, indicating exchange of carbonate ions during the build-up of the porous structure. Once the formation of a structure is completed because of the change, eg, of water flow, the isotopic composition of the whole structure tends to be preserved. This factor makes the radiocarbon dating of tufa possible.

A typical example of a tufa barrier, now 4m above water level, is shown schematically in figure 1. This dry barrier was chosen because of the cut that enabled us to take samples in a vertical profile, as shown. The results of radiocarbon analyses showed that the difference in activity along the vertical profile did not exceed several percent, being on the average, 71 ± 3.5 percent modern. The same is true in a lateral direction, as well as in the depth of the structure. One layer had a distinct ^{14}C gradient, indicating a horizontal direction of barrier growth (see fig 1). This mode of tufa growth is typical of barriers flooded by water, forming cascades or waterfalls. Several thick deposits of tufa with activity within the specified value of 71 ± 3.5 percent modern were found scattered along the gorge above the present level of water. This gives a consistent picture of one of the past water levels and the approximate time span between past and present levels of 2600 ± 250 yr.

A wooden branch, fairly well-preserved and covered with a thick layer of tufa was found in a nearby cave. Radiocarbon analysis showed that the difference between the activity of wood and that of tufa was relatively small. The difference could be explained by considering the growth time for wood and tufa deposits. Although more evidence is required to prove that tufa does not change its isotopic composition over a long period of time and under varying environmental conditions, the described measurement supports the opinion that tufa is stable in composition once it is hardened and no longer in active formation.

CONCLUSION

The interpretation of measured ^{14}C activity of tufa samples requires knowledge of several factors peculiar to tufa formation. One factor is the initial activity of fresh tufa, which we found to be close to the activity of bicarbonates dissolved in surrounding water. During the formative period, radiocarbon tends to spread throughout the deposit, obliterating the detailed stratigraphy. Inactive, dry tufa deposits preserve their isotopic composition, which changes only by radioactive decay, making the dating of tufa possible.

REFERENCE

Srdoč, Dušan, Breyer, B, and Sliepčević, Adela, 1971, Rudjer Bošković Institute radiocarbon measurements I: Radiocarbon, v 13, p 135-140.