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RADIOCARBON DATING OF TUFA IN PALEOCLIMATIC STUDIES

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ABSTRACT. Calcareous deposits known as tufa or travertine contain biogenic carbon and are a potential source of geochronologic information. Many dated samples from Karstic regions in Yugoslavia proved that ^{14}C analyses of tufa can provide reliable data reflecting climatic conditions in the past. Systematic dating of tufa samples revealed two distinct groups of deposits: recent tufa deposits, with a sharp age limit of ~6000 ± 500 years BP, and old tufa deposits with ^{14}C age ranges from 25,000 ± 2300 years BP to the lowest limit of our ^{14}C dating system (~37,000 years). A histogram based on the initial activity A_o = 0.85 shows the age distribution of randomly sampled tufas vs sample frequency. A time gap between ~6000 BP and ~23,000 BP is evident, reflecting cooler climatic conditions. The start of peat deposition is coincident with that of tufa growth in the Holocene.

Paleoclimatic implications of tufa growth periods obtained by ^{14}C dating are as follows: climatic conditions that favor tufa formation at least in karstic regions, are very stringent. Therefore, climatic conditions, such as mean annual temperature and humidity, as well as hydrologic and vegetational conditions, must have been very similar in periods of tufa growth. While recent tufa deposits are coincident with the warm Holocene period, old tufa can be associated with warm interstadials in the Würm.

INTRODUCTION

Tufa concretions are found in predominantly karstic

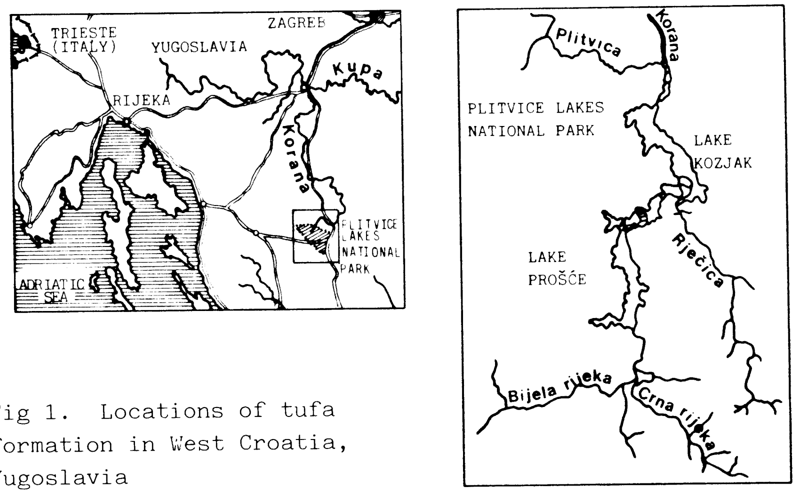

Fig 1. Locations of tufa formation in West Croatia, Yugoslavia

areas in Yugoslavia, always associated with present or past surface water flow. Tufa is usually deposited as a crust on aquatic plants near cascades and waterfalls or finely dispersed in lakes, forming thick basal sediments. Tufa deposits range in thickness from several centimeters to tens of meters, usually preserving the structure of objects on which it was originally deposited. Since tufa contains carbon of biogenic origin it can be used, in principle, for ^{14}C dating. We carried out ^{14}C measurements of tufa deposits from Plitvice Lakes National Park, Central Croatia (fig 1). This is a typical karst area where tufa formations are dominant in an area of $2km^2$ along the Korana River and its tributaries.

According to Polšak (1979), the entire Park area ($200km^2$) consists of Mesozoic carbonate beds of folded and faulted structures. Faults run in a NW-SE direction which is typical of Dinarides. The Upper Triassic dolomites form impermeable beds which influence surface flow and karst spring locations. Recent tufa is found along streams and lakes, whereas old tufa outcroppings emerge from alluvial deposits, or are preserved on top of present-day hills or gorge rims.

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^{14}C DATING OF TUFA

Several factors influence the accuracy of the age of ^{14}C-dated tufa samples. Some preliminary values were encouraging (Srdoč et al, 1980); we continued ^{14}C dating a substantial number of randomly selected samples of tufa in the Plitvice Lakes National Park area. The following factors play an important role in measuring and calculating the age of tufa: 1) initial ^{14}C activity of groundwater or, more specifically, the activity of dissolved bicarbonates, which precipitate in the form of calcium carbonate (tufa) following the loss of CO_2 after surfacing and warming up of groundwater 2) contamination of old tufa beds by recent calcareous material and/or bomb-test-produced ^{14}C.

Initial groundwater activity was measured at several karst springs, and surface water activity along the creeks, lakes, and the Korana River. An increase of ^{14}C activity A_o was observed from 60% modern at the karst spring, Crna Rijeka, to 92% modern in the Korana River. The large difference between the groundwater activity and the subsequently increased activity of river water introduces a large error in calculating tufa age unless a proper value of A_o is associated with every tufa sample, depending on the sampling location. Fortunately, tufa is precipitated for a very short stretch (6 to 7km) of the Korana River where the surface water attained a practically constant ^{14}C activity equal to 85% modern. A more serious problem is contamination of recent groundwater with bomb-test-produced ^{14}C. A relatively short mean residence time makes groundwater in karstic areas susceptible to bomb-test contamination, proven by a high tritium concentration of groundwater. Use of the present-day initial activity of groundwater introduces another error in age calculation of pre-bomb-test tufas which cannot be easily estimated. Thus, we sought "pre-war" samples of tufa of known age, associated with organic material (wood, moss, etc). These measurements gave a mean initial activity A_o = 85% modern, which is in accordance with the expected values for karst areas (Geyh, 1973). It should be emphasized that groundwater activity has not followed the sharp increase of atmospheric CO_2 activity after nuclear weapon tests of 1953 and after.

Contamination of old tufa beds through exposure to atmospheric CO_2 or seepage of precipitation water is another potential source of error in dating tufa. However, we found tufa layers that had been exposed to rain and snow or even surface water, which were "dead", ie, their ^{14}C concentration was below the detectable limit of our system. This indicates that exposure to recent surface or precipitation water does not necessarily result in contamination.

RESULTS

The following were measured: 146 samples of tufa, 32 samples of peat, 10 samples of ground and surface water, and 20 samples of various organic materials (wood, plants, etc). A complete list appears elsewhere (Srdoč et al, 1982), whereas data relevant to paleoclimatic studies are presented in figure 2. The ^{14}C age of tufa and peat samples is calculated using 5730±40 years for the half-life of ^{14}C; it is assumed that the initial activity of tufa samples was 85% of modern standard. All Holocene samples are dendrochronologically--corrected using MASCA curves (Ralph, Michael, and Han, 1973).

PALEOCLIMATIC IMPLICATIONS

The coincident start of tufa and peat formation shown in figure 3 is certainly not fortuitous. A relatively thick layer of organic detritus plays a decisive role in aquatic chemistry through enrichment of seeping water with CO_2, which in turn dissolves $CaCO_3$ in karstic areas. Under favorable conditions, the excess of dissolved calcium bicarbonate is precipitated in the form of tufa in a relatively short period which makes the organic material (peat, gyttja, humus) and tufa practically contemporaneous on the ^{14}C time scale. However, the dissolution of limestone by groundwater introduces an uncertainty in the initial ^{14}C activity of tufa which must be considered when comparing the ^{14}C age of these materials, as explained previously.

The environmental conditions under which tufa precipitates are very stringent. The list of parameters that determines the environmental conditions favorable for tufa formation is not yet complete, but the most important parameters are climatic, hydrogeologic, limnologic, and biologic factors. There is, of course, a strong interplay among these factors. Groundwater alkalinity, temperature, an increase of

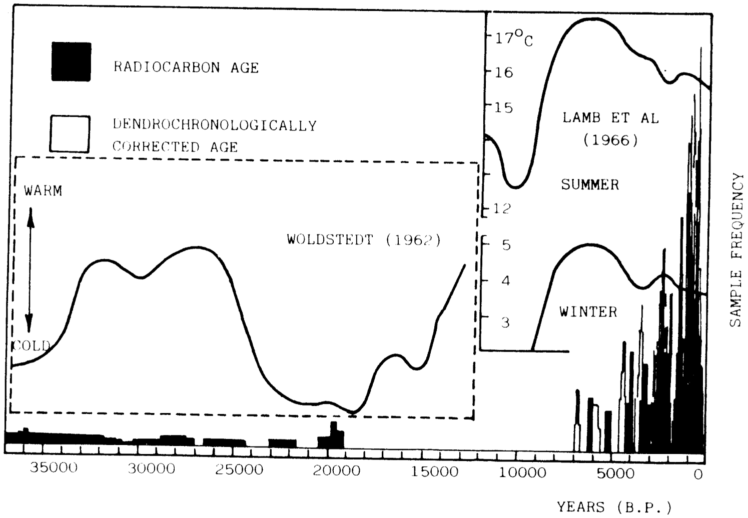

Fig 2. Frequency of randomly collected tufa samples (62) vs ^{14}C age. The general trend of mean annual temperature in the Würm is according to Woldstedt (1962) and summer and winter temperatures in England during the Holocene (Lamb, Lewis, and Woodroffe, 1966).

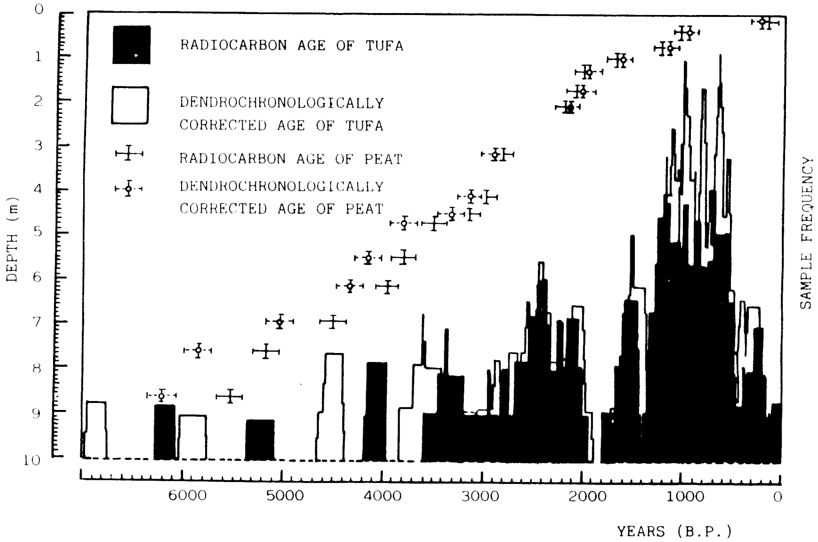

Fig 3. Expanded histogram showing frequency of randomly selected tufa samples (48) vs ^{14}C age. The age of peat found in the same area is shown vs depth. Very abundant recent tufa deposits (age <200 yr) are not included.

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surface water temperature, and a drop of hardness due to tufa precipitation are of primary importance. They all depend on the mean annual temperature and precipitation. Consequently, periods of tufa formation in a specific area must have had very similar climatic conditions. Thus, ^{14}C dating of tufa (or associated organic material such as embedded wood) provides a useful tool in paleoclimatic studies. In our case, the climate that favors tufa precipitation in karstic areas, is close to or identical with the present climate. The mean annual temperature curve for the past 7000 years (Lamb, Lewis, and Woodroffe, 1966) supports our reasoning, even though the curve is given for England which has a different climate.

Our ^{14}C measurements of tufa in Plitvice National Park revealed two distinct groups of beds belonging to two geologic epochs. Whereas ^{14}C dates of Holocene tufa beds, tested by measuring organic material (wood) found in tufa beds and pollen analysis, are quite reliable, the dating of old tufa (~30,000 years) is less reliable. Some contamination of very old tufa samples with recent calcareous material will result in an error or shifting the age of old tufa. The ^{14}C date will be too young. Thus, we seek other dating methods to compare with the old dates shown in figure 2. These dates are close to the lower limit of the ^{14}C method. It should be noted, however, that contamination with recent tufa probably does not exceed 1 or 2% in well-preserved samples of old tufa, which introduces a shift of 1000 to 1800 years for tufa that is ca 23,000 years old (Olsson, 1980). This is an error comparable to that due to the uncertainty of the initial groundwater activity A_o. Consequently, the total inherent error of ^{14}C dates of tufa samples in the range between 20 and 25,000 years is ca ± 2300 years. Continuity of tufa ages stretches from $25{,}000 \pm 2300$ years BP down to the lowest limit of our ^{14}C measurements with the exception of two samples, 19,000 and 20,000 years old, as shown in figure 2. This implies a warm climate, like the present, from $25{,}000 \pm 2300$ years BP extending at least to the limit of our measurements, $37{,}000^{+3500}_{-2500}$ years. This period coincides with the warm interstadial often referred to in older literature as Paudorf-Arcy (Woldstedt, 1962), and more recently, as Denekamp and Hengelo interstadials in the Weichselian period in Central Europe (Geyh and Rohde, 1972).

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