

## **<sup>14</sup>C DATING OF CALCAREOUS TUFA FROM DIFFERENT ENVIRONMENTS**

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**ABSTRACT.** <sup>14</sup>C dates of carbonate and organic matter fractions are compared with a series of calcareous tufa samples from selected sites representing different geochemical environments and associated with different bedrocks. Results obtained in this study indicate values of apparent age ranging from  $940 \pm 110$  yr for calcareous tufas associated with Pleistocene sediments to  $2000 \pm 110$  yr and even ca 4000 yr for tufas from sites associated with Jurassic or Cretaceous limestone. It was found also that within each of the investigated sites the value of apparent age does not change significantly with the age of the tufa layer.

### INTRODUCTION

Calcareous tufa sediments occur very often in southern Poland, where they are related to Cretaceous or Jurassic bedrock, as well as with loesses of Upper Pleistocene age. Recent studies identify many tufa sites in northern Poland associated with Pleistocene sediments of glacial origin. The potential significance of dating tufa deposits in the reconstruction of paleoclimates and environments based on malacologic studies (Alexandrowicz, 1983; Alexandrowicz & Gerlach, 1983) necessitates the use of reliable dating techniques. We have begun research to determine the suitability and reliability of various dating methods applied to calcareous tufa sediments. These methods include TL, ESR, and <sup>14</sup>C dating. We present here the preliminary results of <sup>14</sup>C dating of tufa samples and other carbonate sediments and associated organic matter from selected sites representing various geologic and geochemical environments and compare them with the results of Thorpe *et al* (1980) and Srdoc *et al* (1980).

### SITE DESCRIPTIONS

Six sites, 5 from southern Poland and one from northern Poland, with calcareous tufa sediments were selected in the first stage of this work to obtain a preliminary pattern of regional variability of the apparent age and reservoir dilution factor.

#### *Trzebienice*

This site is in the Cracow Upland, in a valley of a small stream near Wolbrom. The valley was developed in Jurassic limestone and Cretaceous marls, with basal deposits of residual clays overlain by peat with thin tufa layers. At the top of the profile above the erosional surface are two oncolithic layers overlain by peat (Szulc, 1984, p 75-77, Fig 30).

#### *Rzerzuśnia*

This site is in the Cracow Upland, in the valley of the Gołczanka River, near Wolbrom. Holocene sediments, ca 8m thick, were deposited directly on Cretaceous marls. The Holocene series consists of various types of calcareous tufa sediments which include, according to Szulc (1983), peloidic slimes, oncoids, stromatholites and moss travertines. Tufa layers are sepa-

rated by other organogenic and carbonate sediments (Szulc, 1984, p 77–79, Fig 34).

#### *Raławka*

This site is in the Cracow Upland, Raławka River valley, northwest of Cracow. Different types of tufa sediments occur in the Holocene and Late Glacial series deposited directly on Carboniferous limestones (Szulc, 1984, p 62–65, Fig 20).

#### *Sieradowice*

This site is in the Świętokrzyskie (Holy Cross) Mts, near Bodzentyn. This Holocene series with tufa sediments was found (Klatka, 1968) in a valley of a small stream in loess cover, ca 20m thick, overlying Devonian limestones and marls. Tufa layers with varying admixtures of organic matter overlie a bog soil level with numerous plant fragments, dated to 9680 ± 60, Gd-1574, and overlain at the top with pararendzina soil, dated to 4870 ± 70, Gd-1572.

#### *Gliczarów*

This site is in the Podhale region. Tufa sediments consisting of stromatolites, moss travertines, and peloidic slimes form a wide cover in some parts overlain with peat, on the northern slope of a valley (Szulc, 1984, p 52–54, Fig 15).

#### *Czymanowo*

This site is in the Baltic coastal zone, northern Poland, northwest of Gdynia. Calcareous tufa occurs in thin layers within a peat layer ca 1m thick. This Holocene series overlies thick Pleistocene sediments.

### LABORATORY METHODS

Carbonate samples were treated with 8% HCl to obtain CO<sub>2</sub>, which was collected in traps cooled with liquid nitrogen, purified in a standard method, and stored for at least 4 weeks before counting. The remaining insoluble residue was washed, dried, and combusted to CO<sub>2</sub> if the amount of organic matter was sufficient. Small aliquots of CO<sub>2</sub> were collected for measurements of δ<sup>13</sup>C and δ<sup>18</sup>O (for carbonate samples only). <sup>14</sup>C measurements were made using CO<sub>2</sub>-filled proportional counters. <sup>14</sup>C ages of both carbonate and organic matter fractions were calculated based on <sup>14</sup>C activity equal to 0.95A<sub>ox</sub>.

### RESULTS AND DISCUSSION

The most crucial problem in dating calcareous tufa sediments lies in the determination of the apparent age of carbonate to be dated, as well as the magnitude of its temporal and regional variability. From among 70 samples, only 19 pairs of <sup>14</sup>C dates could be compared to obtain estimates of apparent age, defined here as the difference of corresponding <sup>14</sup>C dates of carbonate and associated organic matter. The results are presented in Figure 1, where <sup>14</sup>C dates obtained on CaCO<sub>3</sub> are plotted against dates

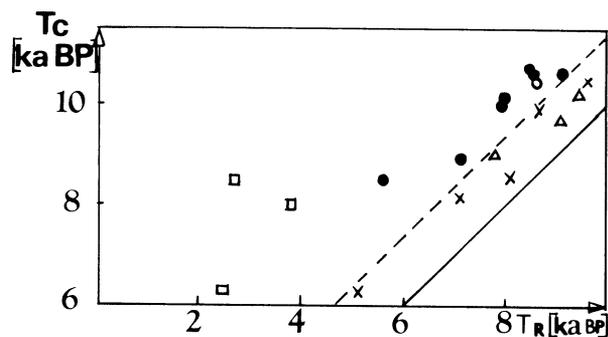


Fig 1.  $^{14}\text{C}$  dates on carbonate fractions as functions of corresponding dates on organic matter. Sites: x—Sieradowice,  $\Delta$ —Czymanowo, o—Trzebienice, ●—Rzerzuśnia, □—Raclawka.

on organic matter. It is evident that all results for tufa samples from sites lying in Pleistocene sediments (Czymanowo and Sieradowice) fall within the limits marked by the two straight lines, the solid line corresponding to initial  $^{14}\text{C}$  activity  $A_o = 0.95A_{ox}$ , and the dashed line corresponding to initial  $^{14}\text{C}$  activity equal to  $0.85A_o$ , which is recommended by Srdoc *et al* (1980). The dashed line corresponds to an apparent age equal to 1300 yr. Due to the relatively small scatter of data points it seems reasonable to calculate the mean value of apparent age for both sites,  $\bar{T}_{app} = 940$  yr. The mean standard deviation of a single measurement  $s_1 = 300$  yr; the standard deviation of the mean value  $s_m = 110$  yr. Such a value of  $T_{app}$  corresponds to the initial  $^{14}\text{C}$  activity equal to 89% modern.

All results obtained on samples from three sites (Trzebienice, Rzerzuśnia, Raclawka) where Holocene sediments with tufa were in close contact with old  $^{14}\text{C}$ -free Cretaceous or Jurassic marls or limestones, fall above the dashed line. With one outlying point rejected, both sites in Trzebienice and Rzerzuśnia could be characterized by the same value of  $T_{app} = 2000$  yr, corresponding to the initial  $^{14}\text{C}$  activity equal to 78% modern. The mean standard deviation of a single measurement and of the mean value are equal to 280 and 110 yr, respectively.

The estimated value of apparent age for tufas from the Raclawka site is not very precise because only one sample contained a sufficient amount of organic matter for dating in conventional large proportional counters. The resulting apparent age, equal to  $4300 \pm 450$  yr, is, however, supported by independent dates of tufa layers over- and underlying the soil level at the top of the profile. This set of three dates yields a value of  $3700 \pm 300$  yr. It seems reasonable, then, to consider the value of apparent age for the Raclawka tufas equal to  $4000 \pm 300$  yr, which corresponds to the initial  $^{14}\text{C}$  activity equal to 61% modern. An unexpectedly large difference in  $^{14}\text{C}$  dates of carbonates and organic matter in one sample (oncoids and associated soil) could be explained by redeposition of the dated oncoids. This statement is supported by significant age inversion on oncoids from subsequent layers, as well as by geologic evidence showing erosion and redeposition in this part of the profile (Szulc, oral commun, 1985).

An estimate of the apparent age for tufas from the Gliczarów site has not been possible by direct comparison of <sup>14</sup>C dates of carbonates and organic matter due to insufficient amounts of organic matter and an erosional hiatus in the profile selected for dating. In spite of this, we found an independent age estimate of this level, based on results of malacofauna analysis of sample Gl-Id. This sample contains characteristic malacofauna corresponding to the boundary of the Late Glacial and Holocene (Alexandrowicz, oral commun, 1984). Assuming a reasonable age for this boundary of ca 10,500 BP, and comparison with the measured tufa age of 14,530 ± 150, Gd-1680, we conclude that the apparent age is equal to ca 4000 yr. However, the question whether this value is valid for the whole site must remain open.

Another interesting question which also remains open is the enigmatic dependence of  $\delta^{13}\text{C}$  values of tufa carbonates upon sample age, shown in Figure 2. In three sites (Gliczarów, Sieradowice, Raławka) we found a well-defined and quite different time dependence of  $\delta^{13}\text{C}$ . Further detailed studies on samples from other sites (especially on tufas from the Rzerzuśnia site) have been undertaken to explain this question.

#### CONCLUSIONS

Our results indicate significant differences of apparent age of tufa samples from several loci. The lowest values of ca 900 yr were found for

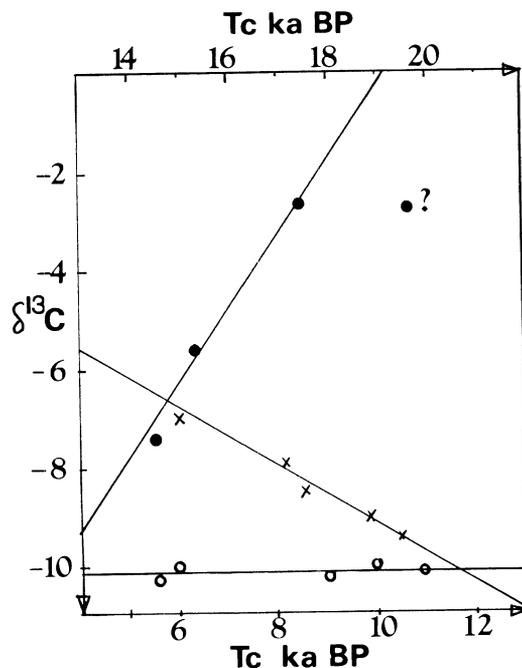


Fig 2. Values of  $\delta^{13}\text{C}$  of tufa  $\text{CaCO}_3$  from 3 sites as functions of the <sup>14</sup>C age of tufa carbonate uncorrected for apparent age. The lower time scale corresponds to Sieradowice (x) and Raławka (○) sites, the upper, to Gliczarów (●).

tufas associated with Pleistocene sediments; higher values of ca 2000 and 4000 yr were observed for tufas associated with Cretaceous and/or Jurassic bedrock. The value of the apparent age within each of the studied sites seems constant. The initial  $^{14}\text{C}$  activity equal to 78% modern which was found for the two tufa sites in the vicinity of Wolbrom (Trzebienice, Rzerzuśnia), associated with Cretaceous marls is close to the values obtained by Thorpe *et al* (1980) for tufas from the two sites (Gordale Scar, 80% modern, and Dunsley Spring, 79% modern), associated with Carboniferous Limestone. Also the value of 75% for the Priory Mill site, quoted by Thorpe *et al* (1980), seems to coincide with our value within the limits of error. It can be concluded then that the value of 75–80% modern seems to be typical for most tufa sites, though quite different values of  $^{14}\text{C}$  initial activity should also be expected. It is interesting to note that the mean value of the apparent age for four of our sites (Czymanowo, Sieradowice, Trzebienice, Rzerzuśnia) appears to be very close to the value found by Srdoč *et al* (1980).

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