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FURTHER INVESTIGATIONS ON ^{14}C DATING OF CALCAREOUS TUFA[1]

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ABSTRACT. Systematic studies on ^{14}C dating of tufa profiles in southern Poland have resulted in developing a simple phenomenological model which enables us to estimate the reservoir correction factor of ^{14}C dates of individual carbonate samples. We made further studies to test model assumptions and to verify relationships between the value of reservoir correction factor T_R and ^{13}C content of tufa carbonate. Two new study sites, Rudawa and Szklarka, are close to previously studied sites. Four tufa samples with associated organic fraction from ca 2000m asl in South America (Peruvian Andes) were measured to test the possible application of the developed model to tufas in different geochemical and climatic environments. Finally, a series of calcareous tufa samples from the Villers-devant-Orval profile (Belgium) were dated, although no direct comparison with organic matter dates is available for this profile.

INTRODUCTION

In earlier studies of tufa profiles from southern Poland (Pazdur, Pazdur & Szulc 1988; Pazdur 1988) we found highly different values of the reservoir correction factor T_R of the carbonate fraction of tufa samples, ranging from 900–11,000 yr. Observed values of T_R are related to the lithologic type of tufa. The highest values are observed for tufas deposited in highly turbulent water (oncoids, stromatolites, moss travertines), whereas the lowest values correspond to peloidal muds deposited in semilimnic environments. We observed constant values of T_R in most profiles (Racławka, Rzerzuśnia, Sieradowice).

The aim of this study is to extend the experimental base of the geochemical model developed for interpretation of ^{14}C ages of tufa profiles (Pazdur 1988) and to check its validity by dating tufa samples from other regions.

SITE DESCRIPTIONS

Rudawa and Szklarka, Southern Poland

These sites are in the Cracow-Wielún Upland, close to the Racławka site studied previously (Pazdur, Pazdur & Szulc 1988). Tufa horizons are incorporated in a thick series of fluvial sediments of various origins, with variable admixtures of organic matter. A detailed description and discussion of sedimentology and stratigraphy of the profile in the Rudawa site was published elsewhere (Pazdur & Rutkowski 1987). The sequence of sediments in the Szklarka site, ca 5km from the Rudawa site in the valley of a small tributary to the Rudawa stream, is similar.

Checras, High Andes, Peru

This site is in the valley of the Checras River near Churin (10° 48′ S, 76° 45′ W), Prov Cajatambo, Dept Lima. Moss travertines occur in two series of gravels in Terraces I and III ca 2400m and 2100m asl, respectively, separated by a series of lacustrine sediments ca 300m thick (*cf* Pazdur 1989).

Villers-devant-Orval, Belgium

The profile of tufaceous sediments, >12m thick, consists of calcareous gyttja, fine- and coarse-grained tufas, fine calcareous detritus, and several layers of stromatolite in the upper part of the profile. Distinct sedimentologic changes in the lowermost part of the profile may suggest the presence of reworked carbonate. A detailed site description, including discussion of the results of pollen analysis, was published by Geurts (1976).

[1] This paper was presented at the 13th International Radiocarbon Conference, June 20-25, 1988, in Dubrovnik, Yugoslavia.

FIELD AND LABORATORY TECHNIQUES

Samples from profiles in Rudawa and Szklarka were collected in 1987 from natural exposures by J Rutkowski and S W Alexandrowicz, as part of systematic studies of the stratigraphy and sedimentology of Holocene fluvial deposits of the Vistula River and tributaries near Cracow (Rutkowski 1987) and malacologic studies of calcareous sediments in the Cracow-Wieluń Upland (Alexandrowicz 1983). Samples from the Checras site were collected in 1985 by P Libelt and members of the Polish Expedition to High Andes, Peru, from a natural outcropping. Samples from the Villers-devant-Orval profile were collected in 1975 by MA Geurts from natural exposures and submitted for dating in 1988.

All samples submitted for dating were first subjected to careful visual examination and lithological identification before further laboratory processing. A detailed description of laboratory methods was given elsewhere (Pazdur, Pazdur & Szulc 1988).

RESULTS AND DISCUSSION

Tufa profiles with Organic Matter

Experimental data were obtained from two new sites in southern Poland, situated close to the Racławka site studied previously (Pazdur, Pazdur & Szulc 1988), and one site in High Andes, Peru. In each site, both carbonate and organic matter fractions were dated to determine experimentally the value of reservoir correction T_R. The results are given in Table 1. $\delta^{13}C$ values of carbonate of four samples of moss travertine from the Checras site are shown in Figure 1 as functions of ^{14}C dates of organic and carbonate fractions. The clearly outlying result obtained on the organic fraction of sample I/O2 may be suspect because of very little organic matter (ca 60% dilution with inactive carbon) and possible contamination with recent organic dust. After rejecting this point, the remaining results show good regularity and can be approximated by least squares lines with equations:

$$\delta^{13}C = (3.0 \pm 0.93) - (0.21 \pm 0.03)T_c\,, \tag{1a}$$

$$\delta^{13}C = (-0.36 \pm 0.27) - (0.16 \pm 0.02)T_{ORG}. \tag{1b}$$

Experimentally determined values of T_R, listed in Table 1, are plotted as functions of $\delta^{13}C$ in Figure 2, together with data previously obtained from tufa profiles in Racławka and Folkestone, UK (Pazdur 1988, Fig 2, p 12; see also Pazdur, Pazdur & Szulc 1988, Table 1). The new data points fit the previously obtained dependence very well (Pazdur 1988, line C, Fig 2). The least square line approximating the dependence of T_R (in ka) upon $\delta^{13}C$ is described by equation

$$T_R = (17.35 \pm 0.71) + (1.34 \pm 0.09)\,\delta^{13}C. \tag{2}$$

TABLE 1
Comparison of ^{14}C dates of organic and carbonate fractions of tufa

Sample	T_{ORG} yr BP	T_c yr BP	T_R yr	$\delta^{13}C$ % wrt PDB
Rudawa Rd-4	6140 ± 100	10,970 ± 70	4830	−9.20
Szklarka Sk-121-C	7600 ± 130	10,240 ± 100	2640	−11.17
Checras I/O1	19,900 ± 540	34,500 ± 1300	14,600	−3.71
I/O2	24,500 ± 2800	35,400 ± 1700	10,900*	−4.83
III/O3	1000 ± 100	17,100 ± 200	16,100	−0.65
III/O4	9500 ± 1200	23,600 ± 400	14,100	−1.67

*Values estimated from Eq 2

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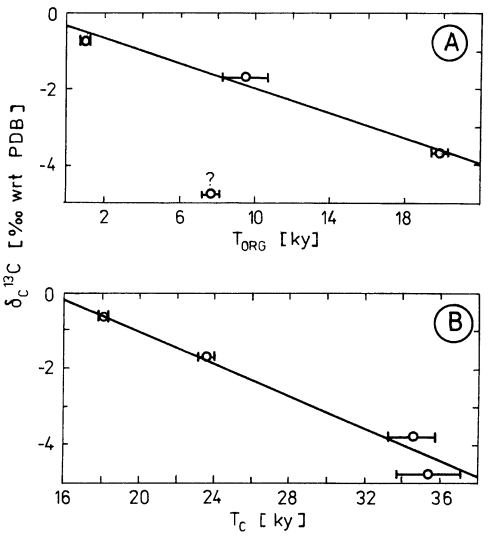

Fig 1. Values of $\delta^{13}C$ in carbonate fraction of tufa samples from Checras, High Andes, as functions of ^{14}C ages of organic matter (A) and carbonate (B)

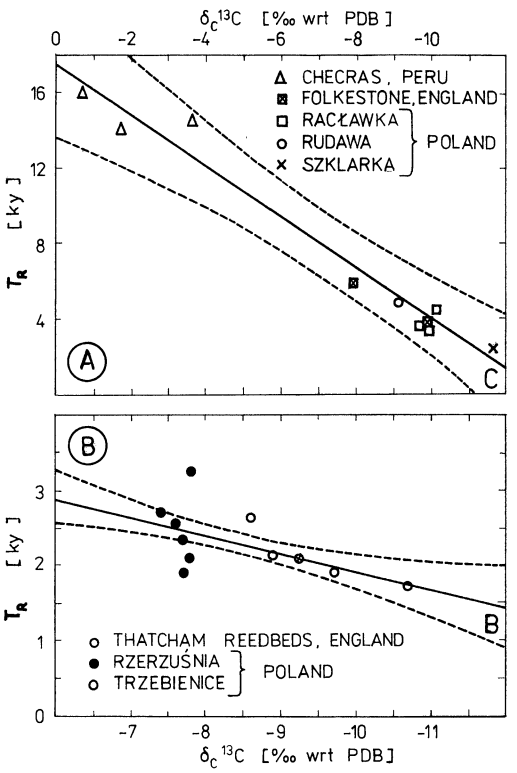

Fig 2. Dependence of experimentally determined values of the reservoir correction T_R on $\delta^{13}C$ values of tufa carbonate for tufas deposited in high-energy water flow (line C, A) and in medium-energy water (line B, B). Dashed lines show 1σ confidence limits (after Pazdur 1988, Fig 2, p 12, modified and completed with new data).

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TABLE 2
Radiocarbon and palynologic age estimates of tufa samples from the Villers-devant-Orval profile, Belgium

Sample	T_c yr BP	$\delta^{13}C$ % wrt PDB	T_R yr	T_{corr} yr BP	Palynologic age*
O2/221	9830 ± 140	−8.79	2210 ± 140	7620 ± 200	Early Atlantic
O2/249	11,230 ± 180	−8.78	2220 ± 140	9010 ± 230	Late Boreal
O2/253	9860 ± 130	−8.94	2180 ± 150	7680 ± 200	Middle Boreal
O2/258	10,300 ± 80	−10.08	1890 ± 260	8410 ± 270	Early Boreal
O2/274	27,200 ± 700	−0.83	16,240 ± 3640	10,960 ± 3700	Late Preboreal
O2/286	21,340 ± 250	−2.28	14,290 ± 3050	7050 ± 3100	Preboreal

*According to the subdivision of the Holocene, accepted by Geurts (1976, Fig 3, p 58), the Preboreal phase extends from 10,500 to 8500 BP, the Boreal phase from 8500-7500 BP, and the Atlantic phase from 7500-4500 BP.

This dependence can thus be used for estimating the real age of sample Checras I/O2. According to equation (2), the value of the apparent age is equal to 10,900 ± 2200, and the resulting age can be estimated as equal to 24,500 ± 2800 BP.

Tufa Profiles Without Organic Matter

Six samples from the lower part of the Villers-devant-Orval profile were dated. The organic content in all the samples was too low for ^{14}C dating. The profile showed much differentiation of lithologic types of calcareous sediments, as well as distinct bipartition in $\delta^{13}C$ values of carbonate. The two oldest samples, O2/286 and O2/274, show very high values of $\delta^{13}C$ and ^{14}C age (Table 2). ^{14}C ages and $\delta^{13}C$ values of four younger samples form a compact group and indicate different mechanisms of deposition of the younger series. Two distinct age inversions also occur in the profile. The $\delta^{13}C$ values show a very high correlation with ^{14}C ages of carbonate (Fig 3). This dependence, described by

$$\delta^{13}C = (-14.4 \pm 0.8) + (0.52 \pm 0.05)T_c, \quad (3)$$

is similar to that obtained for tufas from the Gliczarów and Folkestone sites (Pazdur 1988).

The presence of two significantly different groups of $\delta^{13}C$ values and ^{14}C ages in the profile suggests that they should be treated separately. High values of $\delta^{13}C$ of samples O2/274 and O2/286 indicate that the reservoir correction factors of these samples should be estimated from the dependence of T_R upon $\delta^{13}C$ given by line C in Figure 2 (*cf* Pazdur 1988). The corrected ages (Table 2) are subjected to large errors (ca 30%), but indicate the beginning of sedimentation of tufas in the early Holocene. The mean value, equal to 9000 ± 2100 BP, is consistent with palynologic results by Geurts (1976:50) indicating a Preboreal age of the lowermost part of the profile (Fig 4).

Lithologic features and $\delta^{13}C$ values of the second group of four samples suggest that corresponding reservoir corrections should be estimated from the dependence of T_R on $\delta^{13}C$ observed in profiles in Rzerzuśnia and Trzebienice (S Poland) and Thatcham Reedbeds

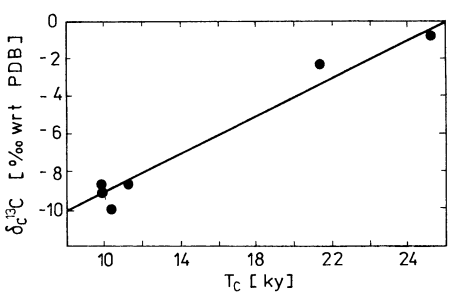

Fig 3. Values of $\delta^{13}C$ of tufa samples from the Villers-devant-Orval profile, Belgium, as functions of ^{14}C dates

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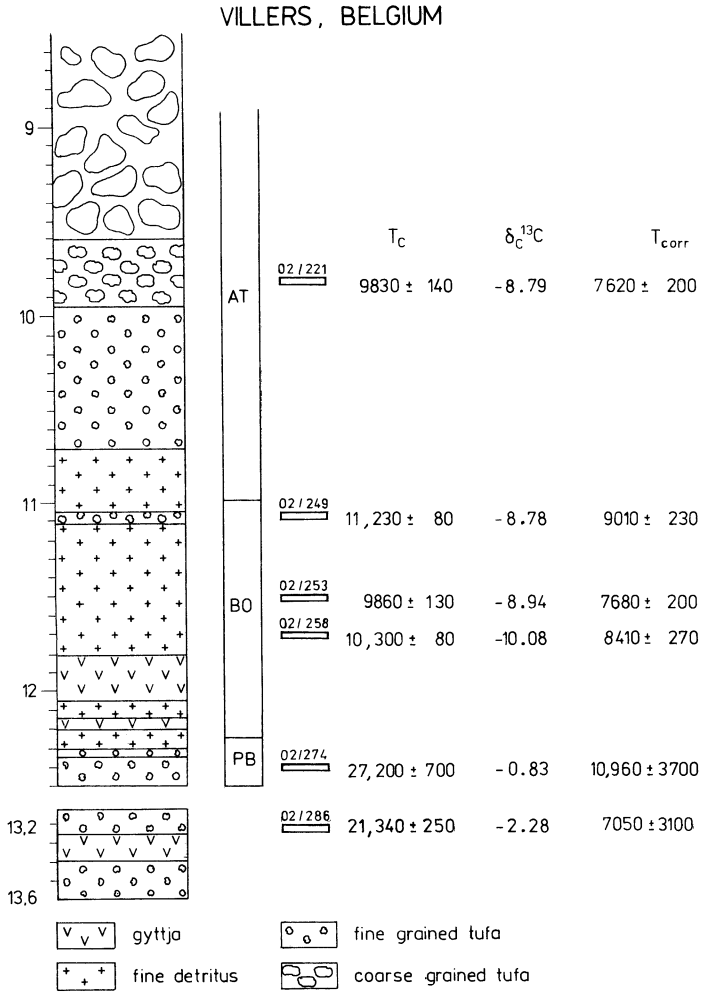

Fig 4. Lower part of the tufa profile in Villers-devant-Orval, Belgium, with ^{14}C and ^{13}C data. Lithology and stratigraphy after Geurts (1976).

(S England), described by equation (Pazdur 1988:11)

$$T_R = (4.41 \pm 0.98) + (0.25 \pm 0.11)\,\delta^{13}C \quad (4)$$

shown by line B in Figure 2. Estimated values of T_R and corrected ages are listed in Table 2. An inversion of dates of samples O2/249 and O2/253 also occurs after correction.

There is general agreement between the corrected ages of this set of tufa samples and the palynologic results (Geurts 1976) which indicate an early Boreal age for sample O2/258 and an early Atlantic age for the youngest dated sample, O2/221. However, the inversion of ages of samples O2/249 and O2/253 occurs after correction. Sample O2/249, with a corrected ^{14}C age equal to 9010 ± 230 BP was collected from a thin layer of coarse-grained tufa, embedded in a series of fine-grained calcareous detritus, >1m thick. This distinct sedimentologic change in the profile may suggest the presence of reworked carbonate.

CONCLUSIONS

The results obtained on paired organic and carbonate samples quoted in Table 1 seem to confirm that the validity of model considerations (Pazdur 1988) is not limited to local or

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regional conditions of southern Poland. Application of this model to data obtained on samples from a profile in Villers-devant-Orval shows reasonable agreement of corrected ^{14}C ages of tufas with palynologic age estimates in the group of four younger samples. However, there are significant age inversions. A very rough lithologic description of the dated profile leads to conclusions that age inversions are associated with reworked sediments. It should be pointed out that very regular data from High Andes tufas were obtained on autogenic material with no evidence of redeposition or diagenetic changes. Therefore, it seems appropriate to repeat the conclusion from our previous study (Pazdur, Pazdur & Szulc 1988) that a detailed lithologic investigation of the dated profile and careful selection of tufa samples for ^{14}C dating is of crucial importance for reliable dating.

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