

## **<sup>14</sup>C TEPHROCHRONOLOGY WITH DIFFERENT FRACTIONS OF PALEOSOL HUMIC MATTER AT PROCIDA ISLAND, ITALY**

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**ABSTRACT.** <sup>14</sup>C apparent ages along with  $\delta^{13}\text{C}$  values for three different fractions of humic matter (HM) isolated from a suite of four paleosols (PAs) interbedded within tephra are reported. The dated HM fractions were: 1) HA, the easily released humic acids; 2) HA<sub>tot</sub>, the bulk of humic acids; 3) RES, the insoluble HM. The <sup>14</sup>C sequence dated from 13,000–25,000 BP, in agreement with stratigraphy and previous data. Age differences up to 2540±430 were statistically significant among fractions; their order of magnitude being independent from C content and depth. All the PAs showed a common pattern of among-fraction age variation, <sup>14</sup>C aging trending from RES to HA<sub>tot</sub> through HA. As the HM fractions exhibited quite comparable  $\delta^{13}\text{C}$  values ( $\delta^{13}\text{C} = -25.4 \pm 0.2\text{‰}$ ), it is inferred that the primitive organic matter (OM) input to PAs was dominantly supplied by vegetation of C-3 photosynthetic pathway which underwent complete decomposition during diagenesis.

### INTRODUCTION

In large areas of southern Italy which have experienced recurrent volcanic activity, there is often a dramatic shortage of reliable materials for <sup>14</sup>C dating. Such areas, however, depending on climatic conditions and nature of parent rocks, also are characterized by fast pedogenesis. Thus, significant pauses of intermittent volcanic activity are recorded by PAs interbedded within tephra.

The growing need for chronological data by Quaternary scientists determined continuing research at the radiocarbon dating laboratory of the University of Rome. Implementing a detailed time scale for the tephra levels is essential to assess frequency, importance and patterning of volcanic activity.

<sup>14</sup>C dating of HM is intriguing, for soil genesis includes dynamic processes involving both decomposition and accumulation of OM. For this reason, <sup>14</sup>C dating of HM yields the "apparent mean residence time" (AMRT), *ie*, a figure not necessarily correspondent to the PA "true age," *eg*, the beginning of pedogenesis. AMRT should be regarded as a peculiar parameter of the physicochemical system represented by PA; to what extent it approaches the "true age" depends on the PA history prior and subsequent to its burial.

A literature survey shows that <sup>14</sup>C dating of the whole HM may greatly limit the validity of the date. However, although the use of "individual" HM fractions does not guarantee a better date, a better approximation of the "true age" along with valuable information on PA history are generally achieved.

We are concerned here with determining apparent <sup>14</sup>C ages of HM fractions from a PAs suite, to understand the geochemistry and detect the HM component yielding the higher AMRT in the geologic context of the study area.

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## EXPERIMENTAL

*Sampling Site and Materials*

The PAs originated in the island of Procida (Fig 1), Tyrrhenian Sea. The island is made up only of tephra which, apart from the uppermost levels, was totally erupted by local volcanoes. The PAs, selected for their importance as reference levels, were sampled at Sancio Cattolico (40°45'52"N, 14°02'07"E). Figure 2 provides evidence of volcanic activity in a profile of a cliff section. Comprehensive geologic accounts of the area have been made (Rittmann, 1951; Di Girolamo & Stanzione, 1973) and <sup>14</sup>C dates were reported (Nonno, 1973; Alessio *et al*, 1976).

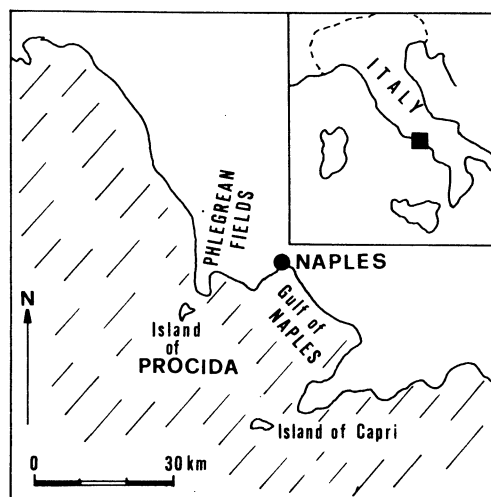


Fig 1. The island of Procida where the PAs were collected

The main analytical and field features for the PAs, which lie several meters above the groundwater table and show weakly developed profiles represented by B or possibly A/B horizons, are given in Table 1. Values for pH, NaF reaction (indicating abundant allophanic material), organic C content along with mineralogic data (Calderoni & Miles, 1983, ms) and particle size distribution (Fig 3) fairly match the characteristics reported by Violante and Wilson (1983) for modern Andosols from sites close to the study area.

*Sample Processing*

Each PA sample, visible contaminants removed, was split into two parts. Part 1 was repeatedly hydrolyzed at 100°C with 6N HCl, washed with distilled water and finally exhaustively extracted with 2N NaOH. Following acidification of the combined extracts with 6N HCl, the coagulate was boiled, washed with distilled water and oven-dried. The extract and the PA residue made up the HA<sub>tot</sub> and RES fraction, respectively.

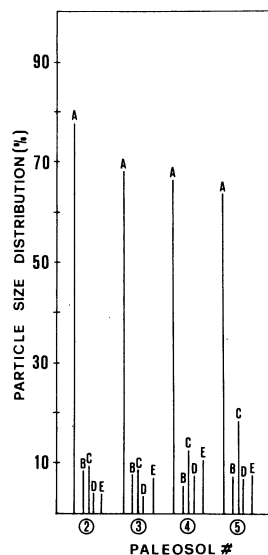


Fig 3. Particle size distribution of the <2 mm fraction for the studied PAs. Key: A = sand (0.05–2 mm); B = coarse silt (20–50  $\mu$ ); C = medium silt (5–20  $\mu$ ); D = fine silt (2–5  $\mu$ ); E = clay (<0.2–2  $\mu$ ).

Part 2 was used to recover fraction HA *via* the procedure recommended by the International Humic Substances Society (Calderoni & Schnitzer, 1984a).

After convenient C enrichment of fraction RES as reported by Polach and Costin (1971), the three HM fractions were burned to obtain  $\text{CO}_2$  used as counting gas in the proportional counters. Procedures for  $\text{CO}_2$  purification and  $^{14}\text{C}$  measurement were reported elsewhere (Alessio *et al*, 1970).

#### RESULTS AND DISCUSSION

##### $^{13}\text{C}/^{12}\text{C}$ Ratios

The  $\delta^{13}\text{C}$  values for the HM fractions (Table 2) highlight some important aspects of the diagenetic history as well as the nature of the HM precursors.  $\delta^{13}\text{C}$  does not show a definite trend with depth (hence age) and further, individual HM fractions are indistinguishable in terms of isotope signature. Such features strongly suggest that the parental OM underwent natural decomposition processes during the short-term diagenesis and rule out significant occurrence of preserved vegetation relics in the analyzed HM fractions. In fact, during the early diagenetic stages, the OM supplied by the vegetation input to soils undergoes both biological and chemical maturation which mainly results in 1) dramatic loss in both proteinaceous compounds and carbohydrates, 2) breakdown of the weaker C-C bonds, and 3) interactions among the newly formed molecules leading to formation of high molecular weight compounds. Such a biochemical pathway is responsible for and paralleled by carbon isotope fractionation yielding an overall  $^{13}\text{C}$  enrichment of

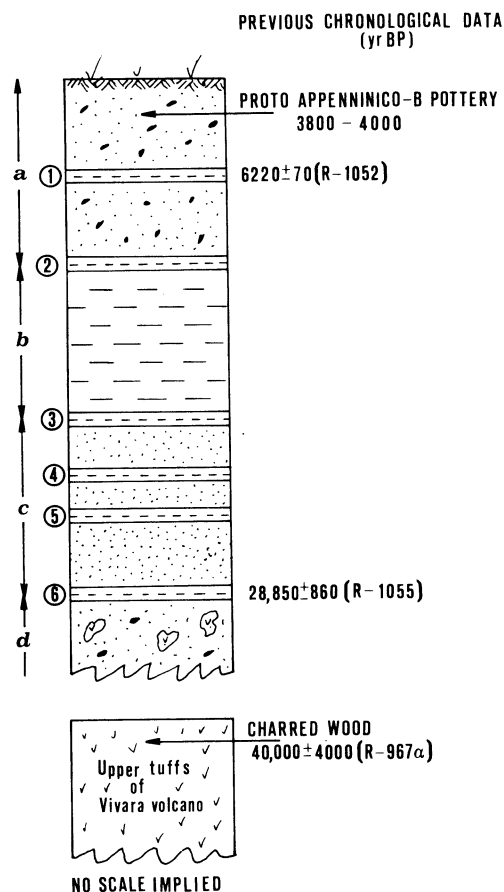


Fig 2. The section exposed at Sancio Cattolico site. The suite of dated PAs (1–6) and the main volcanoclastic terranes are shown. Previous  $^{14}\text{C}$  ages for a charred wood and  $\text{HA}_{\text{tot}}$  from PAs # 1 and 6, along with the estimated age for potsherds, are also given. The depicted upper tuffs of Vivara volcano are not exposed in this site. Key: a = Phlegrean tephra; b = Solchiaro formation; c = cinder pyroclasts; d = tephra of Punta della Lingua volcano.

TABLE 1

General analytical and field data for the studied PAs

PA no.	L no.	Depth from surface (m)	Thickness (cm)	Parent material	pH		C %	N %	C/N
					H <sub>2</sub> O	NaF			
2	R-1053	3	40	Leucitic tephritic hyaloclastite	8.5	8.9	1.04	0.11	9.4
3	R-1054	8	60	Weathered ash and pumice levels from recurrent explosive volcanic activity	8.1	10.0	1.10	0.7	1.4
4	R-1769	19	45	Weathered ash and pumice levels from recurrent explosive volcanic activity	7.9	10.4	0.96	0.35	2.7
5	R-1922	22	30	Weathered ash and pumice levels from recurrent explosive volcanic activity	8.3	10.2	1.02	0.48	2.1

TABLE 2  
Apparent  $^{14}\text{C}$  age,  $\delta^{13}\text{C}$  data and C percentage of the dated HM fractions

PA no.	HM fraction	C* (%)	$^{14}\text{C}$ age (yr BP)	$\delta^{13}\text{C}$ (‰)	$R \pm \sigma_R^{**}$
2	HA	27.8	13,350 $\pm$ 100	-25.2	1.098 $\pm$ 0.025
	HA <sub>tot</sub>	47.1	14,100 $\pm$ 150	-25.8	1.000
	RES	25.2	12,650 $\pm$ 100	-25.3	1.197 $\pm$ 0.027
3	HA	28.6	19,140 $\pm$ 150	-25.1	1.062 $\pm$ 0.063
	HA <sub>tot</sub>	33.3	19,620 $\pm$ 270	-25.6	1.000
	RES	38.1	17,500 $\pm$ 200	-25.6	1.303 $\pm$ 0.053
4	HA	9.6	21,530 $\pm$ 340	-25.4	1.104 $\pm$ 0.063
	HA <sub>tot</sub>	57.9	22,300 $\pm$ 290	-25.8	1.000
	RES	32.5	19,950 $\pm$ 260	-25.6	1.346 $\pm$ 0.072
5	HA	27.9	24,930 $\pm$ 450	-25.1	1.053 $\pm$ 0.073
	HA <sub>tot</sub>	56.2	25,340 $\pm$ 330	-25.2	1.000
	RES	15.9	22,800 $\pm$ 280	-25.5	1.372 $\pm$ 0.074

\* Percentages of the paleosol-C occurring in the three HM fractions. Fulvic acids, which were previously removed from PAs, are not considered in the C balance for their low abundance ( $\leq 100$  ppm)

\*\*  $^{14}\text{C}$  specific activities normalized to HA<sub>tot</sub>

the newly synthesized geopolymers, as the molecules made available during the humification are higher in  $^{13}\text{C}$  relative to the correspondent residues. As a result, the HM that escapes diagenetic decay, eg, that is preserved through interaction with metals and/or clay minerals and accumulated in B horizons, exhibits  $\delta^{13}\text{C}$  values close to  $-25\%$ , fairly comparable to those measured for the studied PAs. In turn, residues of the humification as well as "litter" are significantly  $^{13}\text{C}$ -depleted, their  $\delta^{13}\text{C}$  ranging from  $-30$  to  $-27\%$  (Becker-Heidmann & Scharpenseel, 1986 and references therein).

Comparison between  $\delta^{13}\text{C}$  data for Procida PAs and modern soils confirms that the direct relationship  $^{13}\text{C}$  enrichment vs time of diagenesis only holds over the relatively narrow time span of humification, the subsequent diagenetic modification being almost uninfluential on the isotope composition of HM.

Carbon isotope data reveal that the primitive OM input to the PAs was dominantly supplied by vegetation of the C-3 photosynthetic (Calvin cycle) pathway. The almost constant proportion of C-3/C-4 fixed C in the HM fractions, as expressed by  $^{13}\text{C}/^{12}\text{C}$  ratios, may indicate that paleoenvironmental temperature, irradiation and humidity under which PAs formed did not change appreciably with time.

#### $^{14}\text{C}$ Dating

Table 2 lists conventional  $^{14}\text{C}$  age and C content for the dated HM fractions along with  $^{14}\text{C}$ -specific activities normalized to HA<sub>tot</sub>. Dates are not corrected for isotopic fractionation as the measured  $\delta^{13}\text{C}$  values averaged

-25.4±0.2‰, thus producing a quite insignificant mean <sup>14</sup>C age decrease. We did not attempt to date fulvic acids (FA) due to their extreme depletion (concentration range: 10–100 ppm); <sup>14</sup>C dating of FA, however, is narrow in scope due to their high mobility and fast turnover.

Values for HA- and RES-<sup>14</sup>C-specific activity normalized to HA<sub>tot</sub> averaged 1.091±0.021 and 1.243±0.021, respectively, this pointing to a fairly distinct, constant distribution of <sup>14</sup>C among the HM fractions.

Among-fractions age discrepancy exhibits a constant pattern throughout the PAs suite, the apparent <sup>14</sup>C age decreasing on the order of

$$\text{HA}_{\text{tot}} > \text{HA} > \text{RES}.$$

Although the observed aging trend is far less common than its reversal, *viz.*, RES>HA, it has been previously reported for hydromorphic soils and accounted for by the occurrence, in the humin fraction, of cellulose remains which could escape degradation due to favorable environmental conditions (Scharpenseel, 1972). Further studies, however, revealed the same trend for a wide variety of pedogenic soil types sharing alkaline reaction (Gilet-Blein, Marien & Evin, 1980). Campbell *et al* (1967) found, in a modern Chernozemic black soil, almost indistinguishable AMRTs for HA and humin, likely because these two HM fractions behaved very similarly in terms of turnover.

At Procida, pedogenesis occurred in a well-drained, moderately oxidizing environment, conditions opposed to marshy, acidic, organic-rich soils. Thus, parental OM (including cellulose) could hardly be preserved, which is in line with the carbon isotope data.

The peculiar geologic context of the dated PAs suite supports the actuality of the among-fractions <sup>14</sup>C age difference, as biases depending on HM contamination can be reasonably ruled out. The lack of “fossil C” and carbonate rocks throughout the area prevented an admixture of “old” carbon as well as OM with a “hard-water effect” imprint. Also, the sampling site paleorelief and mineralogic features are inconsistent with PAs contamination by reworked, organic carbon-bearing sediments and wind-borne soil particles, respectively.

The chemical features of the dated HM fractions have been partly reported in four companion papers (Calderoni & Schnitzer, 1984a,b; Schnitzer & Calderoni, 1985; Senesi & Calderoni, 1988). Concerning the amount and chemical composition of the extracted humic acids, the data point to two main differences between fractions HA and HA<sub>tot</sub>. It appears that only HA<sub>tot</sub> includes, to a significant extent, the humic acids portion strongly stabilized against extraction by interactions (eg, absorption and complexation) with the PA's clay minerals and metals. Our data for this agree fairly well with those of Stevenson and Cheng (1970), proving that quantitative recovery of HM from allophanic-rich soils requires preliminary chemical breakdown of the mineral matrix.

As HA<sub>tot</sub> fractions exhibited higher AMRTs than corresponding HA samples, there is the possibility that, due to selective preservation, the strongly retained humic acids could include some relics of HM produced during the early humification stages. Further, because of the harsh hydrolysis

performed before their extraction, HA<sub>tot</sub> fractions were completely depleted of proteinaceous compounds (*ie*, amino acids and amino sugars) and carbohydrates relative to HA fractions. Data from Stevenson (1985), suggest that hydrolysis removes some of the younger C from humic acids, eg, that carried by decomposable substrates. Further investigations are underway to establish the importance of the above-mentioned mechanisms, sympathetic to producing HA<sub>tot</sub> aging.

The term RES, *ie*, the HM fraction yielding lower AMRT than both HA and HA<sub>tot</sub>, herein refers to humin devoid of hydrolyzable components (mainly carbohydrates). Data on the origin and significance of humin are too controversial to discuss the AMRTs yielded by RES fractions. Results of laboratory experiments are consistent with simultaneous synthesis of humin, FA and humic acids through the Maillard reaction between carbohydrates and proteinaceous compounds (Yamamoto, 1983) as well as with lipid conversion to humin during diagenesis (Shioya & Ishiwatari, 1983). On the other hand, structural data reveal that humin, unlike humic acids, contains significant amounts of macromolecular paraffinic-C refractory to both solvent extraction and hydrolysis with 6N HCl and thus is hardly accounted for by lipidic or proteinaceous components.

Both humin and humic acids from the studied PAs were low in lignin-derived constituents. This could suggest that at Procida Island, depending on the environmental conditions, the humification process was mainly governed by the Maillard reaction rather than the lignin pathway (eg, semiquinones polymerization).

#### CONCLUSIONS

We were unable to check the validity of the <sup>14</sup>C ages herein reported due to the lack of organic materials other than fossil HM. Sparse chronological data can only indicate a 3800–4000 to 40,000±4000 BP age bracket for the whole tephra sequence (Fig 2). The upper chronological limit, provided by archaeological findings, refers to the topmost tephra level, which in turn overlays PA # 1, previously dated at 6200±70 BP (R-1022, Alessio *et al*, 1976). The lower limit is provided by the <sup>14</sup>C age of charred wood (R-967α, Alessio *et al*, 1976) collected in the upper Vivara tuff.

We are well aware that, despite the efforts in selecting the most “reliable” HM fraction, <sup>14</sup>C dates only provide an intermediate age between the beginning and end of pedogenesis for each PA. In this respect, <sup>14</sup>C ages, particularly those for HA<sub>tot</sub> fractions, are intended to provide fixed points in time on a relative time scale. However, HM-bearing PAs enabled us to outline the chronology of Procida Island during the last 30,000 yr in considerably greater detail than would have been possible with stratigraphic criteria.

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