

**A POSSIBLE SOURCE OF ERROR IN <sup>14</sup>C DATES:  
VOLCANIC EMANATIONS (EXAMPLES FROM THE  
MONTE AMIATA DISTRICT, PROVINCES OF  
GROSSETO AND SIENNA, ITALY)**

FRANCIS SAUPÉ\*, OSVALDO STRAPPA\*\*, RENÉ COPPENST†,  
BERNARD GUILLET††, and ROBERT JAEGY†

**ABSTRACT.** Wood from regular timbering of a shallow seated mine in Tuscany gave <sup>14</sup>C ages of 5730 ± 100 years BP, much too old to be attributed to one of the known civilizations of Italy. This mine is located in a region of declining volcanic activity, noticeable especially through numerous emanations (natural or incidentally induced by drillings). It was suspected that the analyzed wood had grown in an environment where the normal atmosphere had been diluted by volcanic emanations. To check this hypothesis, living plants (trees, bushes and reeds) and volcanic emanations have been sampled and their <sup>14</sup>C content measured. All present day plants are depleted in <sup>14</sup>C, giving a fictitious age different from 0 (1805, 1820, 2540, 4350 years BP). Of the gaseous emanations sampled, two have a high pressure and show virtually no <sup>14</sup>C (>41,000 years BP). Two others have a pressure close to atmospheric, and small amounts of <sup>14</sup>C were introduced by atmospheric contamination (22,570 and 30,580 years BP).

Conclusion: plants grown in the vicinity of volcanic emanations have <sup>14</sup>C activities that are too low because of a natural <sup>14</sup>C dilution and yield anomalously high ages. The δ<sup>13</sup>C values obtained for two of these plants (-27.4‰ and -23.7‰) are close to the average for plants in general (-25‰), whereas the CO<sub>2</sub> of mofettes is heavier than atmospheric CO<sub>2</sub>.

INTRODUCTION

*Historic background*

The mercury deposits of the Monte Amiata district (fig 1) have been worked since prehistoric times and during the Etruscan period (Haupt, 1889; Squarzina, 1965; Strappa, 1977). Mining, and especially metallurgy, seem to have reached a high level of development under the Etruscans. Mines worked by these people, or at least the shafts, are recognizable by the absence of timbers or of supports (Squarzina, 1965, p 30).

The mine of Solforate was worked from 1852 on, and some 20 years later, traces of antique and mediaeval mining activity were found (Haupt, 1889). A zone of old workings, with several timber sets made of trunks 40 to 60cm in diameter, was intersected at "fossone 28", at the first level, *ie*, at a depth of 30 to 34m, by one of us (OS). It was considered that routine radiocarbon dating would give the age of the timber and interesting details of the history of mining techniques. But the age obtained, 5730 ± 110 years BP, clearly conflicted with our historical knowledge. This introduced the interesting methodological problem of natural overaging of samples. The word "age" will be used in the following discussion to designate the result of a physical measure, without chronological connotation. Further, it is not possible to suggest a correction for calculating the true age, because the dilution of the <sup>14</sup>C concentration in the local environment is variable with time for a given sample.

\* CRPG CO n° 1, F-54500 Vandoeuvre, France

\*\* Viale Sta Maria 1, I-01023, Bolsena, Italy

† ENSG, BP 452, F-54001 Nancy Cédex, France

†† CPB, BP 5, F-54500 Vandoeuvre, France

*Geologic setting*

The Monte Amiata is a recent volcano, 430,000 years, according to Evernden and Curtis (1965). It produced predominantly ignimbrites, and subordinately, rhyolites, quartz-latites, and trachytes (Mazzuoli and Pratesi, 1963). No eruptive activity was observed during historical times, but important geothermal anomalies remain. One such anomaly is presently being used at the vapor-dominated field of El Bagnore (Calamai and others, 1970; Cataldi, 1967). Hot springs and mofettes<sup>1</sup> (= putizze) are known in a broad zone and have been catalogued. Therefore, it is not surprising that development tunnels periodically meet mofettes, which flow into the workings. They are collected for the sake of security. They have rarely been analyzed, but we refer to the following average composition of the noncondensable part, determined on samples from the "Solforate" mine:

CO <sub>2</sub>	96.0%
CH <sub>4</sub>	2.0%
O <sub>2</sub>	1.5%
H <sub>2</sub> S	0.2
nd	0.3
	<hr/>
	100.0%

(Pellizer, 1971, p 480).

*"Aging"*

It was postulated that the timber had been cut in the immediate vicinity of the mine. The aberrant radiometric age determined could thus be explained by the growth of the tree<sup>2</sup> in an atmosphere with a <sup>14</sup>C content lowered by dilution by mofettes devoid of <sup>14</sup>C. This working hypothesis was successfully tested.

ANALYTIC DATA: <sup>14</sup>C*Sampling*

Different living ligneous plants were collected in the vicinity of mofettes or ventilation shafts of mines known to collect mofettes. A branch of an oak (*Quercus robur*) growing outside of the active zones was used as reference material. Its <sup>14</sup>C activity is considered to be in equilibrium with the normal atmosphere, not subjected to dilution through mofettes and soffioni.<sup>3</sup> Carbon dioxide of mofettes and soffioni was sampled by prolonged bubbling in 1L flasks containing normal NaOH. The solutions were stabilized at pH <7 immediately after sampling by addition of strontium chloride.

<sup>1</sup> Mofette (fr) — the exhalation of carbon dioxide in an area of late-stage volcanic activity (AGI: Glossary of Geology).  
Putizze (it) —

<sup>2</sup> The timber is oak, not typically Mediterranean, and possibly *Quercus robur*. The determination on a polished radial section was done by H Polge, Inst Natl Recherches Forestières, Champenoux, F-54280 Seichamps, France, whose help is gratefully acknowledged.

<sup>3</sup> Soffioni (it, pl) — steam type fumaroles (AGI: Glossary of Geology).

*Measurement*

$^{14}\text{C}$  activity was measured by liquid scintillation counting in the  $^{14}\text{C}$  laboratory of the Ecole Nationale, Supérieure de Géologie Appliquée. The carbon of the samples was converted into benzene according to the techniques described by Scharpenseel and Pietig (1969) and Hassko and others (1974).

Background values for the counting vials were  $6.06 \pm 0.05\text{cpm}$  whereas the figure of merit is approximately 700. The activity of 4ml of benzene was counted for 24h. Radiometric ages were calculated using  $T = 5568$  years and taking 95 percent of the activity of NBS oxalic acid

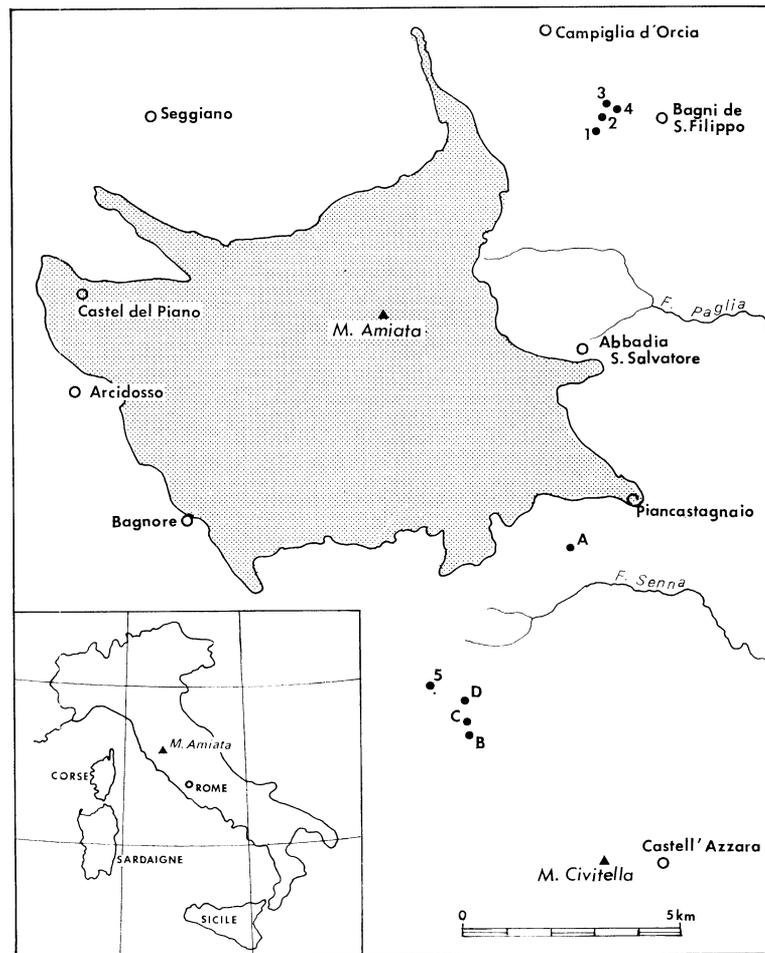


Fig 1. Position of analyzed samples (letters: mofettes; figures: plants; shaded area: Mte Amiata volcanics).

TABLE 1  
Results of  $^{14}\text{C}$  measurements

Sample	No. (fig 1)	Locality	Ref no.	$\delta^{14}\text{C}$ %	BP (years)
1. Old mine timber		Solforate mine			
			Ny-411a	$-510.1 \pm 6.5$	$5730 \pm 110$
			Ny-411b	$-509.5 \pm 6.5$	$5720 \pm 110$
			Ny-411c	$-509.3 \pm 5.9$	$5720 \pm 100$
				$-508.6 \pm 5.9$	$5710 \pm 100$
				$-512.2 \pm 5.9$	$5770 \pm 100$
				$\bar{x}$	$= 5730 \pm 104$
2. Living plants					
2.1 Outside presently active mofette	2	NW of Palazzo di Pietrineri	Ny-535	$+406.5 \pm 15.6$	modern
Oak ( <i>Quercus robur</i> )					
2.2 Proximity of active mofettes.	2	Putizze di Pietrineri	Ny-518	$-418.3 \pm 5.6$	$4350 \pm 80$
Broom ( <i>Sarothamnus scoparius</i> )	3	Putizze di S Giovanni	Ny-517	$-270.9 \pm 7.7$	$2540 \pm 80$
Broom ( " )	5	Putizze di Renaioli (Abetosso Creek)	Ny-516	$-202.5 \pm 10.2$	$1820 \pm 100$
Reed ( <i>Phragmites</i> sp)					
2.3 Proximity of mine shafts					
Alder ( <i>Alnus</i> sp)	1	Pietrineri mine	Ny-483	$-64.5 \pm 8.5$	$535 \pm 75$
Cherry ?	4	S Giovanni shaft	Ny-484	$-44.4 \pm 8.7$	$365 \pm 75$
Wild cherry ( <i>Cerasus</i> sp)	4	"	Ny-519	$-418.3 \pm 6.3$	$4350 \pm 90$
3. Mofettes					
Drill hole "SENNA 2" (surface)	A	Plant Piacastagnaio	Ny-526	$-939.8 \pm 7.1$	$22,570 \pm 1000$
Hole 10, Level 12 (mine)	B	Solforate mine	Ny-524	$\sim -1000$	$>41,000$
Drill hole (surface)	C	100m N of Argus mine	Ny-525	$\sim -1000$	$>41,000$
Drill hole ENEL "PN 4" (surface)	D	1km N of Argus mine	Ny-522	$-977.8 \pm 2.6$	$30,580 \pm 1010$
					$-900$

as the modern standard. The error is given as the value of one standard deviation. The  $\delta^{14}\text{C}$  was calculated by using the following relation:

$$\delta^{14}\text{C} = \left( \frac{\text{Specific activity of sample}}{\text{Specific activity of NBS standard}} - 1 \right) \times 1000$$

### Results

Good agreement on repeated measurements made on two samples of the timber from Solforate (Ny-411) excludes the possibility of an analytical error and indicates reproducibility.

Plants in the vicinity of mofettes or ventilation shafts yield a radiometric "age", indicative of variable depletion of  $^{14}\text{C}$ . This depletion does not occur in sample Ny-535 taken outside of the zone of influence of active mofettes. Its high  $^{14}\text{C}$  activity, due to A-bomb contamination, agrees well with recent data on the northern hemisphere (Paul and Van Veen, 1978).

It is assumed that the depletion in  $^{14}\text{C}$  in plants reflects, through photosynthetic assimilation, a lower activity of  $^{14}\text{CO}_2$  in the local atmosphere. This lower activity is induced by local dilution of atmospheric  $^{14}\text{CO}_2$  by  $\text{CO}_2$  of volcanic origin, which is isotopically inactive as indicated by two determinations (Ny-524, Ny-525) made on mofettes. The small, but detectable  $^{14}\text{C}$  activity of two other gas samples (Ny-522, Ny-526) is due to atmospheric contamination during sampling because these two soffioni have only slight overpressure.

An average dilution coefficient can be calculated for each sample from the following relation, linking the dilution coefficient  $x$  to the local ( $\delta^{14}\text{C}_l$ ) and general ( $\delta^{14}\text{C}_g$ ) activities.

$$x = \left[ 1 - \frac{1000 - \delta^{14}\text{C}_l}{1000 - \delta^{14}\text{C}_g} \right]$$

For the studied samples the dilution coefficient varies between 0.59 (Ny-518, Ny-519) and 0.32 (Ny-484). This means that during the growth of these plants from 30 to 60 percent of the incorporated  $\text{CO}_2$  was of volcanic origin, and thus, inactive, as previously shown. As this dilution is variable, it is not possible to solve the initial archaeological problem.

### ANALYTIC DATA: $^{13}\text{C}$

$\delta^{13}\text{C}$  was determined for three samples: two plants and the  $\text{CO}_2$  of a mofette. The latter is significantly heavier than the present atmosphere ( $\delta^{13}\text{C} \sim -8\text{‰}$ ; Keeling, Mook, and Tans, 1979).

TABLE 2  
Results of  $^{13}\text{C}$  measurements

Sample	$^{14}\text{C}$ ref no.	$\delta^{13}\text{C}$ (‰)
Alder ( <i>Alnus</i> sp)	Ny-483	-27.4
Broom ( <i>Sarothamnus scoparius</i> )	Ny-517	-23.7
Mofette	Ny-524	8.6

Values obtained for the two plants are essentially within the normal range for higher plants following the  $\text{C}_3$  photosynthetic cycle (or Calvin

cycle) ( $-24$  to  $-34\%$ ; Smith and Epstein, 1971). Thus, even in the case of a dilution with heavy  $\text{CO}_2$ , plants seem to regulate their  $^{13}\text{C}$  concentration mainly according to the biochemical characteristics of the photosynthesis. Our sampling is insufficient to determine the magnitude of second order changes in the  $\delta^{13}\text{C}$  values as a function of the concentration and of the isotopic composition of atmospheric  $\text{CO}_2$ . Of our two samples, the most  $^{13}\text{C}$  rich plant, broom, Ny-517 with  $-23.7\%$ , also has the lower  $^{14}\text{C}$  content. Thus, it is possible that this value reflects the  $^{13}\text{C}$ -rich composition of the local environment.

The result obtained for the mofette is far from  $\delta^{13}\text{C}$  measured elsewhere for mofettes: between  $-3$  and  $-13\%$  for about ten different geothermal zones (Panichi and Tongiorgi, 1977). The mean for central and southern Italy is  $-4.1\%$ , with  $-2.0\%$  and  $-1.1\%$  for the  $\text{CO}_2$  from the soffioni of El Bagnore and Piancastagnaio, respectively (fig 1). Such high  $\delta^{13}\text{C}$  cannot be explained by metamorphic decarbonation of carbonates. The enrichment of  $\text{CO}_2$  formed in this way, relative to calcite, reaches a maximum of  $+3\%$  for a reaction temperature between  $400$  and  $600^\circ\text{C}$  (Friedmann and O'Neil, 1977). Thus, for the mofette sample, Ny-524, the initial carbonate should have a minimum  $\delta^{13}\text{C}$  of  $+5$  to  $+6\%$ . This is improbable for sedimentary carbonates, even if deposited in an evaporitic environment. Only travertines could have a  $\delta^{13}\text{C}$  high enough to produce such an enrichment, and there is no evidence for such material at depth. Because our sampling method was designed for very small quantities of available  $^{14}\text{C}$ , it is possible that the high  $^{13}\text{C}$  character of  $\text{CO}_2$  reflects a fractionation during sampling.

#### CONCLUSIONS

An over-estimation of ages measured by  $^{14}\text{C}$  methods can occur in plants grown in a volcanic environment, even at a solfataric stage, because part of the atmospheric  $\text{CO}_2$  is of volcanic origin and contains no  $^{14}\text{C}$ . The dilution of atmospheric  $\text{CO}_2$  by volcanic  $\text{CO}_2$  can be considered as a natural  $^{14}\text{C}$  dilution. It was previously noted for Hawaii (Chatters, Crosby, and Engstrand, 1969).

#### ACKNOWLEDGMENTS

The authors are indebted to Ing de Salvo, Director General, Società Mercurifera Monte Amiata, for permitting sampling on the company property and in the Solforate mine, as well as to Messrs Marsili, Gasperi, and Martinci who assisted one of us (FS) in the field. R Letolle contributed the  $^{13}\text{C}$  determinations and S M F Sheppard reviewed the text.

#### REFERENCES

- Calamai, A, Cataldi, R, Squarci, P, and Taffi, L, 1970, Geology, geophysics and hydrogeology of the Monte Amiata geothermal fields: Geothermics, Spec issue, v 1, 8 p.  
 Cataldi, R, 1967, Remarks on the geothermal research in the region of Monte Amiata (Tuscany-Italy): Bull Volcanol, v 30, p 243-269.  
 Chatters, R M, Crosby, J W, and Engstrand, L G, 1969, Fumarole gaseous emanations: their influence on carbon-14 dates: Washington State Univ, Coll Eng, circ 32, 9 p.  
 Evernden, J F and Curtis, G H, 1965, The potassium-argon dating of Late Cenozoic rocks in East Africa and Italy: Current Anthropol, v 6, p. 343-385.

- Friedman, I and O'Neil, J R, 1977, Compilation of stable isotope fractionation factors of geochemical interest, in Fleischer, M, ed, Data of geochemistry, 6th ed: US Geol Survey Prof Paper 440, 12 p.
- Hasko, Bertalan, Guillet, Bernard, Jaegy, Robert, and Coppens, René, 1974, Nancy natural radiocarbon measurements III: Radiocarbon, v 16, p 118-130.
- Haupt, Theodor, 1889, Il rendiconto del mio stato de servizio: Firenze, Le Monnier.
- Keeling, C D, Mook, W G, and Tans, P P, 1979, Recent trends in the <sup>13</sup>C/<sup>12</sup>C ratio of atmospheric carbon dioxide: Nature, v 277, p 121-123.
- Mazzuoli, R, and Pratesi M, 1963, Rilevamento e studio chimico-petrografico delle rocche vulcaniche del Monte Amiata: Soc Toscana Sci naturale Atti, ser A, v 70, p 355-429.
- Panichi, Costanzo and Tongiorgi, Ezio, 1975, Carbon isotopic composition of CO<sub>2</sub> from springs, fumaroles, mofettes, and travertines of Central and Southern Italy: a preliminary prospection method of geothermal area: UN symposium on development and use of geothermal resources, 2nd, Proc: San Francisco, Lawrence Berkeley Lab, Univ California.
- Paul, E A, and Van Veen, S A, 1978, The use of tracers to determine the dynamic nature of organic matter, Internatl conf on soil sci, Proc: Edmonton, Canada, v 1, p 61-102.
- Pellizer, Renato, ed, 1971, La Toscana meridionale: Soc Mineralog e Petrolog italiana Rend, v 27, (fasc spec), 571 p.
- Scharpenseel, H W, and Pietig, F, 1969, Einfache Boden- und Wasserdatierung durch Messung der <sup>14</sup>C- oder Tritiumkonzentration: Geoderma, v 2, p 273-289.
- Smith, B N and Epstein, Samuel, 1971, Two categories of <sup>13</sup>C/<sup>12</sup>C ratios for higher plants: Plant Physiology, v 47, p 380-384.
- Squarzina, Federico, 1965, Italia Mineraria: Assoc Min Italiana, 742 p.
- Strappa, Osvaldo, 1977, Storia delle miniere di mercurio del Monte Amiata: Industria Min, v 28, nos. 4-6, 27 p.

#### DISCUSSION

*Willkomm:* You mentioned  $\delta^{13}\text{C}$  values up to +8‰ in CO<sub>2</sub> gas of mofettes. We found similar positive values in the HCO<sub>3</sub><sup>-</sup> from water of the Laacher See, lake in the Eifel mountains, West Germany. Perhaps, these high positive values may be explained as follows. First, CaCO<sub>3</sub> is thermally cracked forming CO<sub>2</sub> of the same isotopic composition ( $\delta^{13}\text{C} \sim 0\%$ ). Second, if this gas comes into contact with water, the dissolved HCO<sub>3</sub><sup>-</sup> ions will get positive equilibrium values of  $\delta^{13}\text{C}$ . When pressure is lowered later on, CO<sub>2</sub> of the same high positive  $\delta^{13}\text{C}$  may escape without coming into equilibrium with the remaining dissolved HCO<sub>3</sub><sup>-</sup>.