## REGIONAL SOURCES OF VOLCANIC CARBON DIOXIDE AND THEIR INFLUENCE ON <sup>14</sup>C CONTENT OF PRESENT-DAY PLANT MATERIAL

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ABSTRACT. <sup>14</sup>C measurements were made on present-day plant material with short integration times (tree leaves and sprouts) in the Eifel area, western Germany, where ancient volcanism produces gaseous emanations of considerable yield. Plants growing near sources emanating <sup>14</sup>C-free CO<sub>2</sub> show a significant depletion in the period of their growth. The same effect is found in the <sup>14</sup>C content of recent samples from the Thera (Santorini) Archipelago/Greece. This mixing of "dead" CO<sub>2</sub> may lead to pseudo ages in archaeologic or geologic samples of up to 1600 years in samples from the vicinity of CO<sub>2</sub> emanating sources.

The influence of volcanic  $CO_2$  on the global <sup>14</sup>C budget is considered to be negligible (Libby, 1972). Several series of radiocarbon measurements from material used in dating the destruction of the Greek site, Akrotiri, on the Mediterranean island, Thera (Santorini), around 1500 Bc, indicate remarkable discrepancies, especially in short-lived samples (Weinstein and Betancourt, 1978). These variations are much greater than what natural <sup>14</sup>C changes might produce. Several samples show ages up to 1000 years older. It was therefore suggested (Michael, 1978) that admixture of volcanic  $CO_2$  during photosynthesis could be responsible for these discrepancies.

Investigations (Sulerzhitzky, 1970; Chatters and others, 1969) on the possible influence of volcanic  $CO_2$  on plant material have been reported before. They show that active volcanism as well as volcanic gaseous emanations may lead to considerable pseudo ages in archaeologic or recent material.

Therefore, we started <sup>14</sup>C measurements on a series of present-day plant material from the Eifel area, western Germany, close to Wehr and Maria Laach (50° 25′ N, 7° 17′ E). This region (last active volcanism 10,000 BP) shows several sources with CO<sub>2</sub> gaseous emanations, partly used commercially for production of tank CO<sub>2</sub>. These emanations are visible as fields of bubbles in some brooks and lakes. Ten samples, mainly leaves and sprouts, grown at different distances from the emanating sources, were taken from Lake Maria Laach and the basin of Wehr. The <sup>14</sup>C was measured with proportional counters, sample pretreatment, and cleaning procedures (see Levin, Münnich, and Weiss, 1980; Schoch and others, 1980).

The influence of mineral/volcanic  $CO_2$  on the <sup>14</sup>C content of plant material can be seen in the depression of the <sup>14</sup>C values of plant material from the site compared to the "clean air" level at the time of growth, as, eg, monitored continuously in air samples taken at Vermunt/Vorarlberg, Austria (see Levin, Münnich, and Weiss, 1980). The <sup>14</sup>C data of table 1

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shows that during daytime, on the average, depending on the distance from the source, up to 16 percent of mineral/volcanic origin "dead"  $CO_2$ is admixed to the "normal" atmospheric  $CO_2$  and assimilated by the plants. It can be seen from table 1 that the dead  $CO_2$  influence decreases rather rapidly with increasing distance from the source due to horizontal and vertical atmospheric mixing. A possible influence of fossil fuel  $CO_2$ in this region from the highly industrialized areas about 80 to 100km north of Maria Laach (Ruhrgebiet) can be estimated (see Levin, Münnich, and Weiss, 1980) as not exceeding two percent of the natural concentration. Therefore, an only anthropogenic origin of the depression can be excluded.

We shall now discuss the Maria Laach data in more detail. Assuming that the total bubbling area (about  $50 \times 50$ m) observed on the lake is represented by an equivalent point source in the center of the area, we might try to calculate the concentration pattern in the neighborhood of the source with a meteorologic dispersion model (Pasquill, 1974). For this purpose, the curve given by Pasquill (p 371) has been extrapolated down to 50m source distance, and the predicted concentration versus

	Sample	Description, location, distance to source area	Δ <sup>14</sup> C[% <sub>0</sub> ]	V[%] admixed volcanic CO <sub>2</sub>	"Age"	δ <sup>13</sup> C <sub>PDB</sub> [%e]
Basin of Wehr	H-5637. Wehrer Kessel 1	Salix, sprouts, 1978, 1.5-2m above brook showing strong emanations	$128 \pm 5$	15.6	1360	-26
	H-5638. Wehrer Kessel 2	Species unknown, 200m E of center, 1-2m above ground, sprouts, 1977- 78, 200m E of sources	$325 \pm 5$	.1	90	-22.2
	H-5639. Wehrer Kessel 3	Reed, 1978, 2m SE of emanating source	$201 \pm 5$	10.1	860	-25.1
Lake Maria Laach	H-5630. Maria Laach 6	Unknown species, sprouts and twigs, 1976-78, 1-2m above ground, 30m N of emanations	$395\pm5$			-30.2
	H-5634. Maria Laach 7	Oak, leaves, 1978, 2m above ground, 5m from lake, near strong emanations	$205\pm7$	9.8	830	-28.2
	H-5631. Maria Laach 8	Birch, sprouts 1978, 1m above lake, bubbling emanations	$219\pm5$	8.8	736	-28.9
	H-5636. Maria Laach 10	Beech, leaves, 1978, 20m from lake, 5-7m above	$259\pm5$	5.8	480	-30.5
	H-5632. Maria	Alder, sprouts, 1978 directly	$262\pm7$	5.5	460	-29.3
	H-5635. Maria Laach 4	Beech, leaves, 1978, 200m from lake, 1-2m above ground	$334\pm7$		—	-30.3
	H-5633. Maria Laach 5	Beech, leaves, 1978, 50m from lake, 8m above lake level	329 ± 8			-30.0

TABLE 1		
Results of <sup>14</sup> C measurements of recent	plant material from	Eifel area

source distance relationship has been normalized to the measured concentration at 70m. The result is shown in figure 1. From this curve, then, the total source strength of our equivalent point source can be estimated. According to Pasquill, the emission of one unit admixture per minute leads (under average daytime atmospheric conditions-category B/C-with a mean wind speed at ground level of 4m/sec) to a concentration of 5.5 • 10<sup>-6</sup> units/m<sup>3</sup> at 70m downwind distance from the source. This is assumed to produce just the observed CO<sub>2</sub> admixture of about 6 percent of the normal atmospheric CO2 concentration (meaning additional 0.039 grams  $CO_2/m^3$ ). The observed concentration of dead  $CO_2$  thus would be caused by an emission of 10.2 tons of CO<sub>2</sub> per day or about 7kg/min. If we divide this by the estimated source area of  $2.5 \cdot 10^3$  m<sup>2</sup> we obtain a  $CO_2$  production flux density of about 4kg  $CO_2/m^2$  day. This is about 100 times the natural soil  $CO_2$  respiration flux (25 to 50g  $CO_2/m^2$  day; Lundegardh, 1924; Dörr and Münnich, 1980). It should be noted that our source estimate presumably is a lower limit since it assumes that our sampling points were always downwind of the source. This is not true, although it is, in fact, the main wind direction. This quick calculation indicates that at least a rough idea of the source strength can be deduced, in such cases, from a few simple measurements.

The influence of "dead"  $CO_2$  on the plant material samples causes "pseudo ages" up to 1500 years (column 5, table 1) exceeding the usual uncertainty due to global <sup>14</sup>C variations ( $\approx 2$  percent variation  $\approx 250$  to 300 years dating uncertainty).



Fig. 1. Percent contribution of volcanic  $CO_2$  to the atmospheric  $CO_2$  assimilated at different distances from the  $CO_2$  source region. Data from table 1 atmospheric dispersion curve, after Pasquill (1974) fitted to the observed data (see text).

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Sample	Description, location distance to source area	Δ <sup>14</sup> C[%]	V[%] admixed volcanic CO <sub>2</sub>	"Age"	δ <sup>13</sup> C <sub>PDB</sub> [%]
H-5742. Palea Kameni 2	SW end of Bay, species unknown, 2m above ground, 25m above NN, 1977-78, 100m from emanations	$382 \pm 5$			-23.2
H-5745. Palea Kameni 5	SW of bay, species un- known, 2m above NN, 5m from source, 70cm above ground, 1977-79	133 ± 4	15.9	1390	-21.8
H-5748. Palea Kameni 8	NW end of bay, species unknown, 5m above NN, 10m from source, 50cm above ground, 1977-1979	$185 \pm 5$	12.0	1030	-22.1

## TABLE 2 Results of <sup>14</sup>C measurements of recent plant material; Palea Kameni/Thera

In the Eifel region the <sup>13</sup>C values of the emanating CO<sub>2</sub> ( $\delta^{13}C = -4$ to -5%) (Puchelt and Hubberten, 1979) are too similar to the clean air  $CO_2$  (-8%) to be significantly reflected after photosynthesis in the  $\delta^{13}C$ of the plant material. This seems to be different in the case of Thera.

Within the archipelago of Thera (last period of volcanic activity in 1950) several hot CO<sub>2</sub> sources are found, partly submarine, primarily around a little bay with pronounced submarine emanations on the Kameni islands in the caldera (from the burst around 1500 BC). A few measurements made so far on recent samples (see table 2) confirm the results obtained from the Eifel series, showing a locally restricted, but considerable influence of these emanations. Here, an effect on the 13C values of the plant samples seems also to be visible. This is due to the fact that the  $\delta^{_{13}}\!C$  of the Thera emanations is more positive ( $\delta^{_{13}}\!C\,\approx\,0$ ) than in the Eifel.

This study was suggested by Prof A Boettcher, Jülich. The samples were taken in cooperation with the Demokritos Atomic Center, Attika.

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