EFFECTS OF VOLCANIC EMANATIONS ON CARBON-ISOTOPE CONTENT OF MODERN PLANTS NEAR KILAUEA VOLCANO

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ABSTRACT

Measurement of stable and unstable carbon isotopes were made on growing plants at various distances from fumarolic volcanic vents on the Island of Hawaii. Samples of CO_2 from volcanic gas vents were also measured, as well as control samples of unaffected atmosphere and plants. Results indicate that the proximity of the sample to the source of volcanic emanation does affect the ^{14}C concentration as anticipated, but for a variety of reasons the $^{13}C/^{12}C$ ratio, although significantly altered, does not relate directly to ^{14}C activity. Depending on how close a plant grows to fumaroles, the radiocarbon age can appear to be 1,400 years too old, with extremes of 4,000 years not unlikely.

INTRODUCTION

During investigations of the age of a pyroclastic ash on Kilauea (the mostly A.D. 1790 Keanakakoi Ash Member of the Puna Basalt) using buried charcoal, a negative correlation was observed between the radiocarbon age and the collection distance from the caldera (fig. 9.1). In order to test whether a $^{13}C/^{12}C$ ratio on the charcoal could give an indication of how much, or if any, non-radiogenic, juvenile carbon from volcanic vents was incorporated in the plants during growth, a series of samples was collected from living plants at various distances from active vents as well as control samples that could not have incorporated volcanic CO_2. From previous work

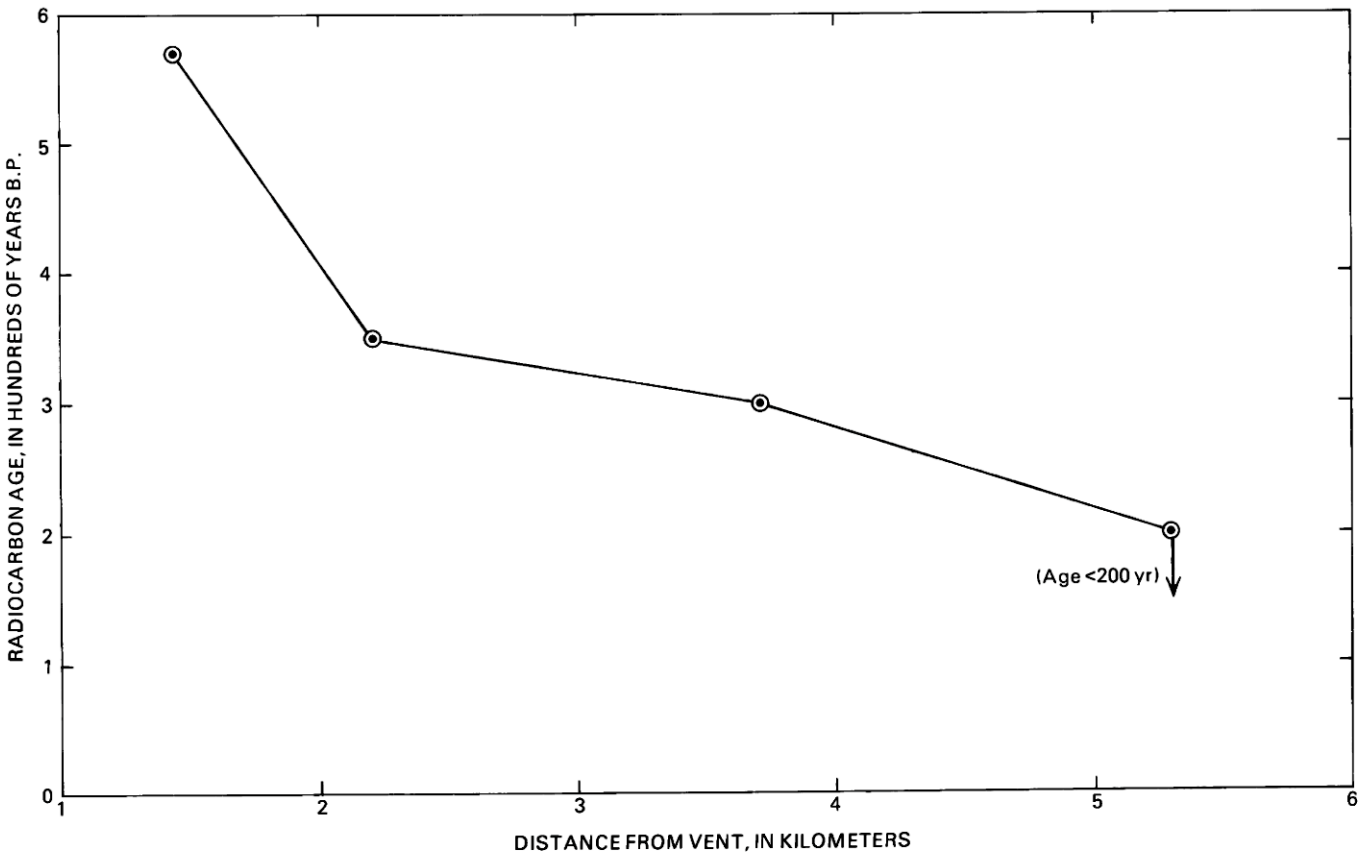

FIGURE 9.1.—Carbon-14 ages on charcoal from the mostly A.D. 1790 Keanakakoi Ash Member of the Puna Basalt as a function of collection distance from steam vents.

TABLE 9.1.—*Isotopic composition of Hawaiian plants*

Lab number	Description	$\delta^{13}C$ PDB (in permil)[1]	^{14}C (percent of modern)[2]	Apparent age (in ka)[3]
W-5476	Ohia[4] leaves from living trees overhanging the ocean on the windward Hamakua coast, Kukui Point.	-28.9	124	0
W-5477	Ohia leaves from anomalous kipuka south of Bird Park.	-24.5	124	0
W-5474	Ohia leaves from Puhimau Thermal Area.	-25.8	108	1.4
W-5482	Root of living Ohia tree at edge of fumarole at margin of Puhimau Thermal Area.	-26.3	108	1.4
W-5480	Fern[5] growing directly in hot steam at margin of fumarole at Puhimau Thermal Area.	-26.8	82	4.3
3464-6	Gas sample, Puhimau vent.	-3.0	--	--
3464-7	Gas sample, Halemaumau.	-3.5	--	--
W-1957	Gas sample, Sulfur Bank no. 2, Kilauea 1966.	-3.6	.1	>45
W-1958	Gas sample, Sulfur Bank no. 1.	--	.0	>45
W-3983	Gas sample, Sulfur Bank, 1971.	--	.2	>40
W-3989	Gas sample, 1971 fissure, Kilauea.	--	.5	>40

[1] CO_2 from samples of air collected weekly for 4 yr on Mauna Loa at 3,048 m elevation range from -7.1 to -8.4 permil.

$$\delta^{13}C_{PDB} = \left(\frac{R\ sample}{R\ standard}\right) - 1 \quad 1{,}000, \text{ where } R = \text{the ratio } {}^{13}C/{}^{12}C.$$

[2] Measured in comparison to the National Bureau of Standards 1960 oxalic acid standard. Modern equals 95 percent of the activity of this standard.

[3] Using present-day wood activity as 124 percent of modern.

[4] *Metrosideros polymorpha.*

[5] *Nephrolepsis exaltata.*

(Chatters and others, 1969; Sulerhitzky, 1970; Libby and Libby, 1972; Panichi and Tongiorgi, 1975; Michael, 1978; Weinstein and Betancourt, 1978; Puchelt and Hubberten, 1979; Bruns and others, 1980; Saupe and others, 1980), juvenile CO_2 from volcanic vents was found to be "dead" (contains no ^{14}C), and plants growing immediately adjacent to the vents could give anomalous ages as much as several thousand years too old. What was not known, however, was whether the ^{13}C measurements could help in determining possible old carbon contamination in the hundreds of previously dated samples from Hawaii.

METHODS

Grab samples were collected of living, native vegetation growing under different conditions of exposure to volcanic gases, from the worst case of ferns growing directly in the hot steam of a fumarole to leaves of trees overhanging the Hamakua coast bathed in the uncontaminated northeast trade winds (table 9.1). Samples were taken of first-year leafy growth to verify that the biologically fixed carbon was obtained from the atmosphere in the year of sampling (1983). The $^{13}C/^{12}C$ measurements were made in Denver, Colorado, on an aliquot of the same samples that were dated by ^{14}C measurements in Reston, Virginia. The dried plant material was oxidized at 900 °C and the purified CO_2 was analyzed on a 12-inch triple-collector magnetic-sector mass spectrometer. The analytical precision is ±0.1 percent (2 sigma). All $^{13}C/^{12}C$ ratios are reported in permil relative to the Peedee belemnite (PDB) standard. A value of −28.1 permil was obtained for NBS–21 graphite. The Sulfur Bank gas samples were collected in 1966 by Bruce

Hanshaw and Meyer Rubin and measured by the same methods. The 1971 gas samples were collected by Meyer Rubin and Elliott Spiker. The gas for ^{14}C determinations was collected by absorption in NaOH. The leaves, collected from several growing plants in a localized area, were only given a hot water wash as a pretreatment, then counted in gas proportional counters as acetylene.

DISCUSSION

As anticipated, the ^{14}C data show the dilution effect of the "dead" CO_2 of juvenile volcanic origin. The Sulfur Bank gas has a ^{14}C activity of juvenile gas. Within our background error of ± 1 percent, there is no measurable ^{14}C. The gas samples from Puhimau vent and Halemaumau crater as well as from Sulfur Bank and the 1971 fissure have $\delta^{13}C$ values ranging from -3.0 to -3.6 permil. Pure air has a $\delta^{13}C$ of approximately -8 ± 0.3 permil. This 5 permil difference between the pure air and the volcanic gas should show up in the $\delta^{13}C$ of the leaves if the plants incorporated the isotopically heavier volcanic gas. The Kilauea samples are about 2 permil heavier than those from a tree growing on the seacliff remote from volcanic CO_2. If 40 percent of the CO_2 assimilated by the plants was of volcanic origin, we would expect the $\delta^{13}C$ of the plant material to be heavier by about 2 permil. Inasmuch as Puhimau gas contains 1 to 5 percent CO_2 (L.P. Greenland, oral commun., 1985) only 1 percent of this gas mixed with 99 percent air (0.035 percent CO_2) could account for this change in $\delta^{13}C$. However, the $\delta^{13}C$ values of the leaves and roots are probably affected by factors such as moisture availability and temperature as well as the $\delta^{13}C$ of the ingested CO_2, and the $\delta^{13}C$ values of the samples collected on Kilauea do not relate directly to the ^{14}C activity, as can be seen in table 9.1.

The ^{14}C results (table 9.1) may appear slightly confusing because they are compared to 0.95 times the activity of an oxalic acid standard, which gives the modern or present-day atmospheric activity if there had been no bomb testing. The ^{14}C produced by the nuclear weapons tests since 1953 first elevated the activity to 200 percent of the 95 percent oxalic acid standard; absorption by the oceans and other buffering mechanisms has subsequently lowered it to approximately 124 percent (as of 1985).

If the present-day activity is represented by the two samples at 124 percent ^{14}C activity, then the samples growing in a thermal area are depressed by 16 percent, giving the plants an initial age of approximately 1.4 ka. The fern leaves growing at the very edge of a fumarole, a worst case situation, were depressed approximately 42 percent, differing from normal living plants by 4,300 years.

Thus, the charcoal from plants buried by an ash or lava flow could have an initial built-in age of as much as 4.3 ka, but more likely not more than 1.4 ka, depending on how close to a volcanic fumarole the plants grew at the time of burial. This dilution is also possible near central volcanic areas, particularly downwind, decreasing in effect rapidly away from the source of the dead CO_2 (fig 9.1). Nonmeteoric CO_2 is higher in abundance at Kilauea summit fumaroles, but decreases in abundance away from the caldera, along both the east and southwest rift zones (L.P. Greenland, written commun., 1985).

CONCLUSIONS

Carbonaceous samples dating volcanic activity are probably usually correct to within twice the stated one-sigma counting error. However, because one cannot always reconstruct the locations of volcanic fumaroles or determine the original juvenile CO_2 gas activity, radiocarbon samples from volcanic areas may appear too old by about 1,400 years. In rare situations samples may date 4,300 years too old.

Most contaminants of charcoal collected for radiocarbon chronology studies result in geologically young ages (modern rootlets, humic acids, and so on). Our studies show that samples collected from the immediate vicinity of CO_2-emitting volcanic fumaroles can also incorporate contaminants that result in radiocarbon ages that are too old. Considerable caution should be used in the evaluation of ages from central volcanic areas. Given the present sparse data one cannot use $\delta^{13}C$ to predict possible old carbon contamination.

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