



## VARIATION OF $\delta^{13}\text{C}$ IN FUMAROLIC GASES FROM KILAUEA VOLCANO

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### ABSTRACT

Values of  $\delta^{13}\text{C}$  in fumarolic gases from Sulphur Bank, the Puhimau thermal area, and a fumarole at Halemaumau have been determined for samples collected from June 1984 through December 1985. Samples from Sulphur Bank and Halemaumau have a  $\delta^{13}\text{C}$  of  $-3.5 \pm 0.2$  parts per thousand (permil) and show little change during this period. In contrast, the  $\delta^{13}\text{C}$  of samples from the Puhimau thermal area increased from  $-3.5$  to values of  $-2.7$  permil at the end of the collection period. Applying an equilibrium fractionation factor of 1.004 for the  $^{13}\text{C}$  distribution between carbon dissolved in the magma and the  $\text{CO}_2$  gas in equilibrium with the magma resulted in a calculated primary  $\delta^{13}\text{C}$  value of  $-7.5$  permil for carbon dissolved in the Kilauea magma. The change of  $\delta^{13}\text{C}$  at Puhimau can be the result of cooling of a pod of magma beneath Puhimau caused by the closure of its feeder passage from the main magma body.

### INTRODUCTION

The  $\delta^{13}\text{C}$  values of fumarolic gases are of interest for several reasons. The isotopic composition of mantle carbon is still a matter of conjecture, and the isotopic composition of mantle-derived gases is of importance in understanding the carbon cycle. Fumarolic gases are an important source of  $\text{CO}_2$  to the atmosphere, and a knowledge of the  $\delta^{13}\text{C}$  of such gases will help in understanding the atmospheric  $\text{CO}_2$  cycle.

The first analyses of fumarolic gases from Hawaii were made by Naughton and Terada (1954). Conversion of their published atomic ratios to modern  $\delta$  notation gives the following values in parts per thousand, permil to a precision of about  $\pm 2$  permil.

Sulphur Bank fumarolic gas	
1949, Mauna Loa in eruption	0 permil
1952, Kilauea in eruption	0 permil
1953, both volcanoes quiet	0 permil
Gas collected from Mauna Loa lava flow	-24 permil
$\text{CO}_2$ extracted from 1950 Mauna Loa olivine basalt	-19 permil

Those authors commented on the constancy of the Sulphur Bank ratios and on the relative enrichment of Sulphur Bank samples in  $^{13}\text{C}$  as compared to the gas extracted from the chilled lava or from above the active lava flow. Thomas (1977) reported data on samples collected at Sulphur Bank as well as at 1971 and 1974 fissures at Halemaumau. His data are given in table 32.1.

### EXPERIMENTAL PROCEDURE

In order to determine whether the variations found by Thomas were related to eruptive events, we initiated frequent sample collec-

tions at Sulphur Bank, Halemaumau, and at the Puhimau thermal area. Samples were collected by drawing the gases with a hand vacuum pump through a metal sample tube fitted with valves at both ends. The samples have been shipped to our laboratory in Denver where they were drawn through a metal trap cooled with liquid nitrogen. After the water was separated from the  $\text{CO}_2$  at dry ice temperature,  $\text{SO}_2$  was separated from the  $\text{CO}_2$  by distillation at the temperature of melting ethanol. Analysis for  $\delta^{13}\text{C}$  was carried out in the conventional manner on a 12-inch, triple-collector  $90^\circ$ -sector mass spectrometer.

### RESULTS

Our results are given in table 32.2 and plotted in figure 32.1. Analysis of probable errors indicates two standard deviations ( $2\sigma$ ) equal 0.1 permil.

There does not appear to be any correlation between  $\delta^{13}\text{C}$  values of gases collected at any of the three collection sites and the short-term phases of the eruption at Puu Oo.

TABLE 32.1.—Values of  $\delta^{13}\text{C}$  obtained by Thomas (1977) for samples of fumarole from Sulphur Bank, Kilauea Volcano, Hawaii

[Values given in permil (parts per thousand)]

Location	Date	$\delta^{13}\text{C}$
Sulphur Bank	5 Aug 75	-3.2
		-2.6
	18 Aug 75	-3.4
		-2.3
	8 Nov 75	-3.2
		3.0
	Dec 75	2.5
	13 Aug 76	-3.4
	17 Aug 76	-3.4
	13 Aug 76	-3.0
	1 Dec 76	-2.7
	28 Dec 76	-3.5
	28 Jan 77	-3.3
1971 fissure	13 Aug 75	-3.4
	19 Aug 75	-3.2
	8 Nov 75	-3.3
		-3.2
	1 Dec 75	-3.3
	9 Aug 76	-3.2
		-3.3
	26 Aug 76	-3.4
		-2.8
	13 Oct 76	-2.8
	-3.5	
	1 Dec 76	-3.2
	28 Dec 76	-4.2
	29 Dec 76	-3.6
1974 fissure	29 Jan 77	-3.1
	10 Feb 77	-3.0

TABLE 32.2.—Values of  $\delta^{13}\text{C}$  for samples of fumarolic gas from localities on Kilauea Volcano, Hawaii

[Values given in permil; date is date of collection of sample]

Date	Puhimau	Halemaumau	Sulphur Bank
1984			
26 June	-3.6	-3.5	-----
25 July	-3.2	-3.8	-3.9
6 Aug	-3.1	-3.6	-3.2
24 Aug	-3.0	-3.2	-3.4
11 Sept	-3.3	-3.6	-----
19 Sept	-3.2	-3.5	-3.3
26 Sept	-4.0	-3.9	-3.3
2 Oct	-3.0	-3.6	-3.5
12 Oct	-3.2	-3.8	-3.4
29 Oct	-2.7	-3.5	-3.5
31 Oct	-2.8	-3.6	-3.4
13 Nov	-2.5	-3.5	-3.5
27 Nov	-2.7	-3.5	-3.4
4 Dec	-2.7	-3.4	-3.3
1985			
10 Mar	-2.9	-3.5	-3.3
21 Mar	-2.9	-3.5	-3.4
1 Apr	-2.9	-----	-3.1
3 Apr	-----	-----	-3.3
12 Apr	-2.6	-3.4	-----
19 Apr	-2.6	<sup>1</sup> -1.9	-3.1
1 May	-2.6	-3.0	-3.1
14 May	-2.6	-----	-3.0
20 May	-2.7	-3.1	-3.3
31 May	-2.6	-3.5	-----
4 June	-2.7	-----	-3.4
17 June	-2.7	-3.5	-3.5
24 June	-2.7	-3.5	-3.2
28 June	-2.7	-3.4	-3.6
3 July	-2.8	-3.4	-3.5
19 July	-2.6	-3.3	-3.7
24 July	-2.7	-3.3	-3.4
9 Aug	-2.6	-3.4	-3.4
20 Aug	-2.8	-3.3	-3.5
13 Sept	-2.8	-3.4	-3.5
23 Sept	-2.5	-3.2	-3.3
30 Sept	-2.6	-3.5	-3.2
4 Oct	-2.7	-3.3	-3.3
11 Oct	-2.7	-----	-----
16 Oct	-2.8	-3.7	-3.6
25 Oct	-2.7	-3.4	-----
31 Oct	-2.8	-3.3	-3.5
8 Nov	-2.7	-3.4	-3.4
14 Nov	-2.1	-2.8	-3.5
19 Nov	-1.9	-3.3	-3.4
22 Dec	-3.2	-3.5	-3.5
30 Dec	-3.2	-3.5	-3.4

<sup>1</sup>We have no explanation for this apparent anomalous value.

The  $\delta^{13}\text{C}$  values of gases from both Halemaumau and Sulphur Bank appear to be fairly constant at  $-3.5 \pm 0.3$  permil, in reasonable agreement with the results of Thomas. We plan to continue to research long enough to determine if this constancy of  $\delta^{13}\text{C}$  will persist during periods of quiescence at Kilauea.

Gases emitted at the Puhimau thermal area show greater variation and indicate an increase in  $\delta^{13}\text{C}$  from  $-3.6$  permil in late June, 1984, to  $-2.7$  permil in November, followed by a slow decrease to  $-2.9$  permil in March 1985. The  $\delta^{13}\text{C}$  at Puhimau remained constant until early November, when it increased to  $-1.9$ , and then decreased to  $-3.2$  in late December. These changes may have been caused by a temperature decline in the gas source, related to either cooling of an isolated body of magma beneath the thermal area or to withdrawal of magma from under the site, followed in December by reintroduction.

## DISCUSSION

Pineau and others (1976) found the  $\delta^{13}\text{C}$  of  $\text{CO}_2$  released from vesicles in tholeiitic basalt from the mid-Atlantic ridge to be  $-7.6 \pm 0.5$  permil and postulated that this value represents the  $\delta^{13}\text{C}$  of primary deep-seated carbon in the ridge area. Matthey and others (1983) postulated that the  $\delta^{13}\text{C}$  of volcanic carbon is  $-4.2$  to  $-7.5$  for basalt midocean ridges,  $-2.8$  to  $-6.7$  permil in glass from Hawaiian and Explorer Seamounts, and  $-7.7$  to  $-16.3$  permil for glass from basalts in backarc basins.

The  $\delta^{13}\text{C}$  of dissolved carbon in 11 samples of glass from midocean basalt was determined by Des Marais and Moore (1984) to range from  $-5.6$  to  $-7.5$ .

Javoy and others (1978) determined experimentally that  $\text{CO}_2$  in equilibrium with carbon dissolved in tholeiitic magma at  $1,120$ – $1,280$  °C and  $7.0$ – $8.4$  Kb, is enriched in  $^{13}\text{C}$  by  $4.0$  to  $4.6$  permil relative to the magma. Therefore, if basaltic magma containing dissolved carbon with a  $\delta^{13}\text{C}$  of  $-7.5$  permil loses carbon dioxide to the atmosphere, we can expect that the initial fumarolic  $\text{CO}_2$  will have a  $\delta^{13}\text{C}$  of about  $-3$  to  $-3.5$  permil. Our results obtained at Halemaumau and Sulphur Bank agree with these expected values.

If the magma continues to lose  $\text{CO}_2$  in an equilibrium distillation (a Rayleigh process), then the  $\delta^{13}\text{C}$  of the  $\text{CO}_2$  will continuously decrease as the amount of carbon in the magma decreases with time because of  $\text{CO}_2$  loss.

The fairly constant  $\delta^{13}\text{C}$  of the gases sampled at Halemaumau and Sulphur Bank indicate that only a small amount of  $\text{CO}_2$  is lost from a large amount of magma, or that new magma enters the system in a continuous manner.

The increase of  $\delta^{13}\text{C}$  with time observed at Puhimau thermal area can be explained by a decrease in the temperature of isotopic equilibration from about  $1,250$  to  $1,100$  °C. This could occur by the cooling of a small pod of magma isolated by interruption of its feeder dike from a larger magma body, which has been the source of heat for the thermal area since its formation in 1936 or 1937. If this explanation is correct, the isolation must have occurred just before our initial sampling in late June 1984. The decrease in  $\delta^{13}\text{C}$  observed in December 1985 may be due to reintroduction of fresh magma beneath the site.

Monitoring the  $\delta^{13}\text{C}$  of fumarolic  $\text{CO}_2$  at Kilauea can yield important insights into magma movement and the opening and closing of feeder dikes.

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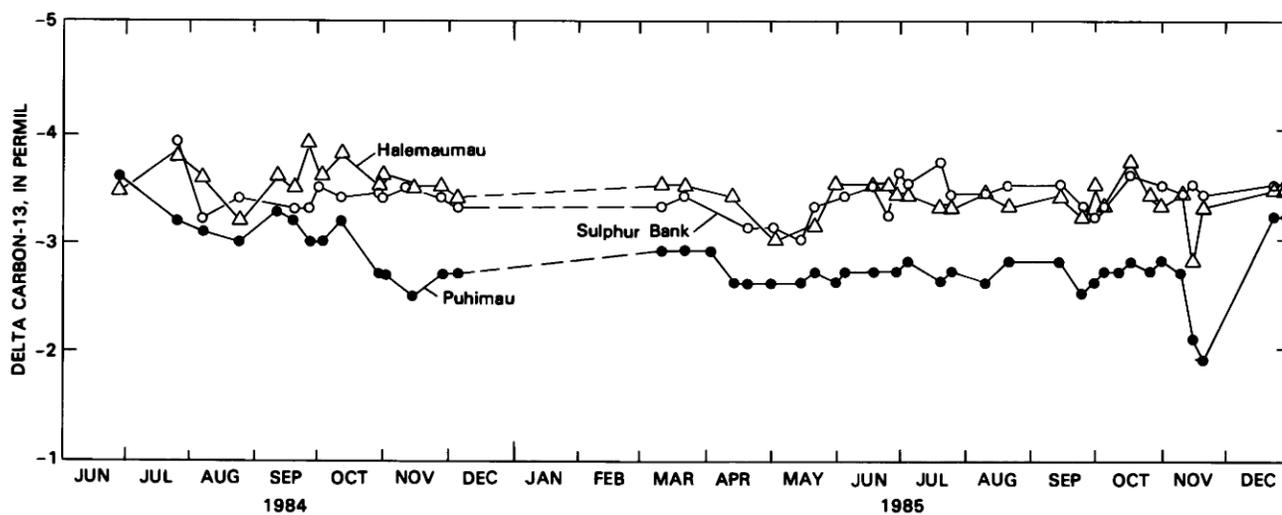


FIGURE 32.1.—Variation of  $\delta^{13}\text{C}$  in samples of fumarolic gas from three localities on Kilauea Volcano, Hawaii.

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