

# Reports

## Helium/Carbon Dioxide Ratios as Premonitors of Volcanic Activity

**Abstract.** *The composition of the gaseous emissions of two fumaroles at the summit of Kilauea Volcano was monitored for more than 2 years. Magma was released from the summit reservoir on three occasions during this period; prior to or during each event the ratios of helium to carbon dioxide in the fumarole gases decreased substantially from that observed during periods of quiescence.*

Attempts to forecast volcanic eruptions through a study of changes in the chemistry of fumarolic emissions have been made for several years (1). Although a preeruptive change has been observed in both the total outgassing rate and the gas compositions of several volcanic systems, no successful predictions of eruptive activity have yet been made through observations of changes in the gas chemistry.

During the last few years, we have monitored the fumarole emissions of Kilauea Volcano in an effort to determine whether there are significant changes in the gas compositions that occur consistently prior to eruptive or intrusive activity. Results of earlier related work on Kilauea have been reported by Naughton *et al.* (1); recent modifications made to the original sampling and analysis procedures have allowed a considerably improved interpretation of the most recent data.

Although gas samples (2) were obtained from several fumaroles at the

Kilauea summit, only two sampling sites were found to consistently provide reliable (low air) samples, Sulphur Bank and the 1971 Fissure fumarole. Sulphur Bank, located in a shallow graben at the northern edge of the Kilauea caldera, has been active throughout recorded history. The 1971 Fissure fumarole is located along one of the eruptive fissures of the August 1971 eruption that took place near the southern edge of the Kilauea summit caldera.

Even though the gas chemistry and temperature of these two sites are markedly different (3), we strongly believe that both are in communication with the summit magma reservoir of Kilauea. Both fumaroles consistently have produced He concentrations well above atmospheric values ( $\text{He}/\text{N}_2 = 2.6 \times 10^{-3}$  for Kilauea,  $\text{He}/\text{N}_2 = 6.6 \times 10^{-6}$  for air); the observed  $^3\text{He}/^4\text{He}$  isotope ratios are also well above that observed in the atmospheric helium [ $^3\text{He}/^4\text{He} = 2 \times 10^{-5}$  for Kilauea,  $^3\text{He}/^4\text{He} = 1.4 \times 10^{-6}$  for air (4)]. Thus, it is highly probable

that the primary source of the acid gases and rare gases in these fumaroles is the summit magma reservoir of Kilauea.

In the analysis of the fumarolic gas samples, we used standard gas chromatographic procedures with a slightly modified detector arrangement. Details of the equipment and procedures have been reported elsewhere (5).

Data on the ratios of  $\text{SO}_2$  to  $\text{CO}_2$  and of He to  $\text{CO}_2$  observed for the Sulphur Bank and 1971 Fissure fumaroles are presented in Figs. 1 and 2; also indicated are three events that occurred during the course of this study. The first two, in August 1976 and in February 1977, were substantial noneruptive deflations of the summit magma reservoir, as indicated by continuous monitoring of tiltmeters at the Kilauea summit. It is believed that each such deflation of the summit reservoir was accompanied by an injection of magma into the east-rift zone of Kilauea (6). The third event shown in Figs. 1 and 2 was the summit deflation associated with a 19-day eruption of the lower part of the east-rift zone of Kilauea in September–October 1977.

Although the  $\text{SO}_2/\text{CO}_2$  ratios exhibit a substantial variation over the period of this study, there appears to be very little relationship between the  $\text{SO}_2$  concentrations and the activity or state of the summit magma reservoir. Although space does not permit a complete discussion of the fumarole sulfur chemistry here (5), we believe that large short-term variations (arising from near-surface phenomena) mask long-term changes in the fumarole sulfur concentrations.

In contrast to the case for the sulfur gases, the long-term variations in the He/ $\text{CO}_2$  ratios are substantially larger than

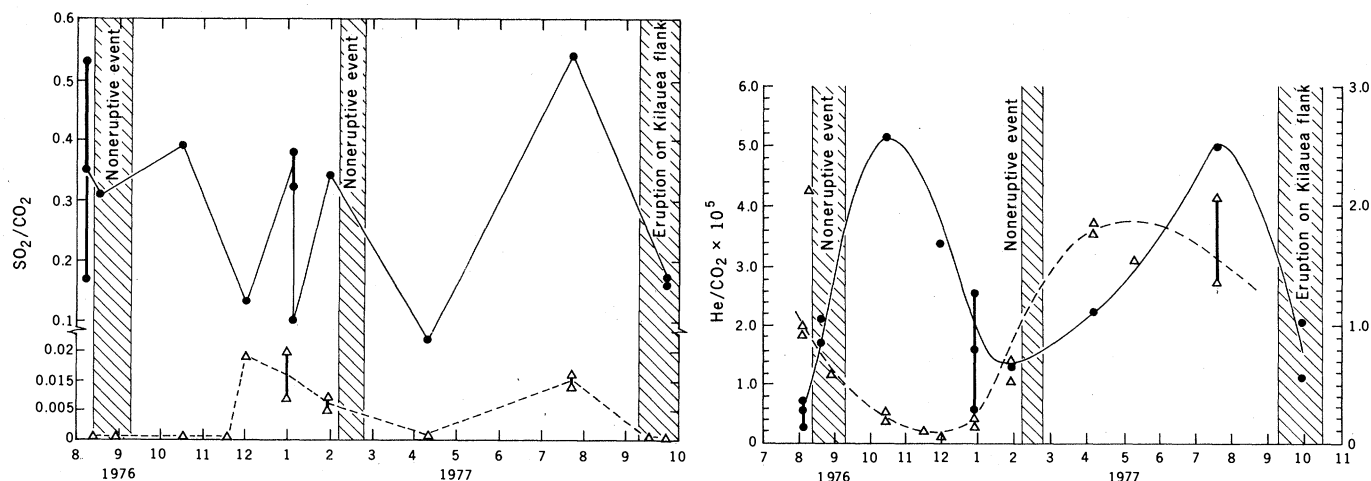


Fig. 1 (left). Ratios of  $\text{SO}_2$  to  $\text{CO}_2$  observed at the 1971 Fissure fumarole (—●—●—) and at Sulphur Bank (---△---△---). Points connected by heavy vertical lines indicate samples taken on the same day. Fig. 2 (right). Ratios of He to  $\text{CO}_2$  observed at the 1971 Fissure fumarole (—●—●—, left scale) and at Sulphur Bank (---△---△---, right scale) as a function of time. Points connected by heavy vertical lines indicate samples taken on the same day.

the short-term variations. Further, the He/CO<sub>2</sub> ratios drop dramatically in the 1971 Fissure fumarole prior to or during the summit deflation for all three of the events. We propose the following explanation for this behavior. Under conditions of moderate inflation of the Kilauea summit magma reservoir, the overburden above the chamber is relatively impermeable to most magmatic volatiles. The resistance of the rocks to the release of these gases impedes the flow of CO<sub>2</sub>, SO<sub>2</sub>, and other large molecular gases more effectively than the flow of He because of the high mobility of He in silicate glasses. This results in a much higher relative ratio of He to CO<sub>2</sub> in the fumarole gases than is actually present in the magma. As the inflating summit reservoir approaches the point of "failure" (that is, the migration of magma), the overburden rock is dilated and incipient fracture systems open, thus releasing considerably more of the volatiles in the magma chamber. The resulting decrease in resistance encountered by the gases reduces the relative advantage of He over the other magmatic volatiles and brings about a net decrease in the He/CO<sub>2</sub> ratio in the fumarole gases.

The cycle present in the Sulphur Bank gases appears to be displaced forward in time relative to that in the 1971 Fissure fumarole gases (the decrease in the He/CO<sub>2</sub> ratio for Sulphur Bank occurs later than that for the 1971 Fissure fumarole). This shift may result from differences in travel time for the gases between the summit magma reservoir and the two surface fumaroles. The 1971 Fissure fumarole is thought to be located almost directly above the summit reservoir, whereas Sulphur Bank is displaced several kilometers to the north.

We conclude that the He/CO<sub>2</sub> ratios observed at the 1971 Fissure fumarole may possibly provide us with a means of predicting impending eruptive activity of Kilauea several weeks prior to the event. With further observations to extend the data base, we may be able to refine this technique sufficiently to forecast the probability of an eruptive event several days beforehand.

DONALD M. THOMAS  
J. J. NAUGHTON

Hawaii Institute of Geophysics,  
University of Hawaii at Manoa,  
Honolulu 96822

#### References and Notes

1. J. J. Naughton, J. H. Lee, D. Keeling, J. B. Finlayson, G. Dority, *Science* **180**, 55 (1973).
2. Samples were taken in evacuated stainless steel tubes partially filled with silica gel, which was used to immobilize the acid gases that both protected the stainless steel from acid attack and increased the effective volume of the sample tube.

3. The temperature of Sulphur Bank is 97°C (the boiling temperature of water at 1200-m altitude); the temperature measured in the 1971 Fissure fumarole during the period of study was in the range of 140° to 150°C. Sulphur Bank emissions contain only small concentrations of the acid gases (CO<sub>2</sub> ≈ 2 percent, SO<sub>2</sub> ≈ 0.5 percent), whereas the 1971 Fissure fumarole is much richer in the acid gases (CO<sub>2</sub> = 10 percent, SO<sub>2</sub> ≈ 5 percent).
4. The Kilauea isotope ratios were determined for us by Dr. W. Jenkins of Woods Hole Oceanographic Institution and will be reported by D. M. Thomas and P. M. Kroopnick (in preparation); the air value is from B. Z. Mamyrin, G. S. Anuf-

riyev, I. L. Kamenskiy, and I. N. Tolstikhin, *Geokhimiya* No. 6 (1970).

5. D. M. Thomas and J. J. Naughton, in preparation.
6. D. Dzuirsin *et al.*, *Eos (Trans. Am. Geophys. Union)* **59**, 1025 (abstr.) (1978).
7. We thank the staffs of Hawaiian Volcano Observatory of the U.S. Geological Survey, Hawaii Volcanoes National Park, and the Sciences Department of the University of Hawaii-Hilo. Work was supported in part by grants EAR-73-00201-A01 and EAR-78-14763. Hawaii Institute of Geophysics contribution No. 968.

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## Application of Carbon Isotope Stratigraphy to Late Miocene Shallow Marine Sediments, New Zealand

**Abstract.** A distinct (0.5 per mil) carbon-13/carbon-12 isotopic shift in the light direction has been identified in a shallow marine sedimentary sequence of Late Miocene age at Blind River, New Zealand, and correlated with a similar shift in Late Miocene Deep Sea Drilling Project sequences throughout the Indo-Pacific. A dated piston core provides an age for the shift of  $6.2 \pm 0.1$  million years. Correlations based on the carbon isotopic change require a revision of the previously established magnetostratigraphy at Blind River. The carbon shift at Blind River occurs between  $6.2$  and  $6.3 \pm 0.1$  million years before present. A new chronology provides an age for the evolutionary first appearance datum of *Globorotalia conomiozea* at  $6.1 \pm 0.1$  million years, the beginning of a distinct latest Miocene cooling event associated with the Kapitean stage at  $6.2 \pm 0.1$  million years, and the beginning of a distinct shallowing of water depths at  $6.1 \pm 0.1$  million years. The Miocene-Pliocene boundary as recognized in New Zealand is now dated at  $5.3 \pm 0.1$  million years. Extension of carbon isotope stratigraphy to other shallow Late Miocene sequences should provide an important datum for international correlation of Late Miocene shallow and deep marine sequences.

The stable isotope composition of foraminiferal tests is often used to determine the paleoceanographic and paleoclimatic history of the oceans through the Cenozoic and, to a much lesser extent, the Mesozoic. Recognizable changes in stable isotope composition, shifts or events, also serve as chronostratigraphic markers where biostratigraphic correlation is difficult between locations underlying different water masses (1, 2). Shackleton (3) considered that Quaternary isotopic composition changes are of greater value for stratigraphic correlation than the paleotemperature record they provide. Until recently (4, 5), isotope stratigraphy was mostly restricted to latest Neogene studies and utilized only the oxygen isotope record.

Although changes in the <sup>13</sup>C/<sup>12</sup>C ratio in foraminifera are little understood, Shackleton and Kennett (2) called for the collection of <sup>13</sup>C data for coherent patterns to emerge. Since then, Keigwin (5) and workers in the Cenozoic Paleocceanography (CENOP) program (6) have recorded a Late Miocene permanent shift in the <sup>13</sup>C record of about 0.5 to 0.8 per mil in the light direction. This occurs at approximately 6.5 million years in Deep Sea Drilling Project (DSDP) sites 158 and 310 in the east equatorial and

central north Pacific, respectively. Unpublished work by Shackleton on piston core RC12-66 shows the existence of the carbon isotopic shift in the upper part of magnetic Epoch 6.

Since the carbon isotopic shift was established as a potential criterion for interoceanic correlation and for chronology, its stratigraphic occurrence needed to be tested in a shallow marine sedimentary sequence on land and a logical choice was the Blind River section, New Zealand. The Blind River section is a relatively continuous, freshly exposed land section containing a rich assemblage of benthonic foraminifera for isotopic analysis. Previous paleomagnetic dating (7) suggested that the Blind River section was of the right age to find the carbon isotope shift if it occurs in shallow marine sedimentary sequences.

The Blind River section is also important for two other reasons. First, it contains a well-established evolutionary sequence of globorotalids (*Globorotalia miozea conoidea*, *Globorotalia conomiozea*, *Globorotalia puncticulata*), which is important for global correlation of temperate sequences (7-9). Second, it contains an excellent paleoclimatic record including a dramatic Late Miocene cooling and was important in providing a