Reports

Iridium Enrichment in Airborne Particles from Kilauea Volcano: January 1983

Abstract. *Airborne particulate matter from the January 1983 eruption of Kilauea volcano was inadvertently collected on air filters at Mauna Loa Observatory at a sampling station used to observe particles in global circulation. Analyses of affected samples revealed unusually large concentrations of selenium, arsenic, indium, gold, and sulfur, as expected for volcanic emissions. Strikingly large concentrations of iridium were also observed, the ratio of iridium to aluminum being 17,000 times its value in Hawaiian basalt. Since iridium enrichments have not previously been observed in volcanic emissions, the results for Kilauea suggest that it is part of an unusual volcanic system which may be fed by magma from the mantle. The iridium enrichment appears to be linked with the high fluorine content of the volcanic gases, which suggests that the iridium is released as a volatile* IrF_6.

Atmospheric particulate material has been collected at Mauna Loa Observatory (MLO) for the past 4 years as part of the Global Monitoring for Climatic Change (GMCC) program of the National Oceanic and Atmospheric Administration (NOAA). Samples are collected on a weekly basis on three separate filters that yield three types of samples, including nighttime, downslope samples and daytime, upslope samples. Downslope samples are representative of clean, midtropospheric air, which flows down the mountain slopes at night. Upslope samples are collected during the day, when the dark lava absorbs radiation and warms the air, forcing it to rise convectively. This rising air comes from the vicinity of the marine boundary layer and contains materials generated at altitudes lower than MLO on the island of Hawaii (*1*). Figure 1 shows the location of the observatory and the site of the recent Kilauea eruptions. During nighttime sampling, if wind conditions are inappropriate for the downslope samples or if a condensation nuclei counter (CNC) detects a very high particle count (usually indicative of contamination), a sampling control unit shuts off the downslope sampling and activates the pump on the daytime sampler. Particle samples were collected on Nuclepore filters (110 mm in diameter and 0.4 μm in pore diameter), using plastic filter holders to minimize contamination by metals. As the goal of this project was to monitor the trace element content of remote atmospheric particles, no metallic parts were used near the samples. Filters were analyzed by nondestructive neutron activation analysis for 37 elements (*2*).

The first eruption of the 1983 activity of Kilauea occurred at 0031 on 3 January. Fortunately for observation of the volcanic plume, concentrations of most elements are normally quite constant and at their lowest levels of the year during December and January (*3*). As shown in Table 1, the upslope, daytime sample taken during the first week of January showed 500-fold increases in Se and In concentrations compared to those in normal samples and greatly enhanced concentrations of many other species.

According to the usual weekly sampling schedule, samples were changed at noon on 4 January, so the volcanic material had to have reached the observatory during the day on 3 January. According to the light-scattering and CNC records at MLO, a massive influx of material reached the observatory between noon and 6 p.m. on 3 January. Thus, most of the material from the volcanic eruption that was picked up in the first-week sample (28 December to 4 January) arrived over a 6-hour period. As we report only the average weekly concentrations in Table 1, concentrations during the 6-hour period must have been an order of magnitude greater. Concentrations were somewhat lower, but still much greater than normal, in the upslope sample during the second week.

Downslope samples were relatively unaffected by Kilauea during the first week of January, with only small increases in Se and In (factors of 10 and 4, respectively). This suggests that only a small quantity of plume material reached the observatory during the night of 3 January. Downslope samples collected during the second week of January showed an additional fivefold increase in concentrations of Se and In, bringing the concentrations up to levels nearly 50 times that under normal clean, downslope conditions.

Elements showing large increases in concentration—As, Cu, Zn, Cd, Hg, Se, In, Au, and Ir—are clearly from a source other than crustal weathering, the oceans, or anthropogenic emissions. During the past 4 years of observation at MLO, no concentration increases of this magnitude have been observed, and data for normal conditions are representative of upslope conditions at this time of year. Even though the sampling site is 50 km from the Kilauea eruption and at an altitude of 3400 m, which is above the marine trade-wind inversion, concentrations of Se and In were more than 400 times their normal values. Upslope samples collected during the first week of January contained only a slight excess of crustal material (indicated by Al concentrations), which was probably in volcanic ash particles. Particulate sulfur increased by a factor of 10 from 0.15 μg/m^3 to 1.7 μg/m^3, but most of the sulfur from the volcano should have been in the gas phase, which we did not measure. Abundances of the highly enriched elements relative to each other were approximately constant, with an Se/In ratio of 68 and 80 for the two upslope samples. The ratio was 130 in the downslope samples, which may indicate fractionation of the more volatile Se into a higher layer of the atmosphere as a gas by thermal buoyance. Since the Se/In ratio for Hawaiian basalt is only 0.1, Se is enriched much more than In in the plume. If the Se was released in the gas phase, it may have been partially separated from the emitted particles as a portion of a hot gas plume, which later cooled and condensed onto particles.

Iridium is clearly present in the samples, as all of its major γ-rays (295, 308, 316, 468, and 604 keV) were observed in the proper abundance ratios without chemical separation. Cadmium, which is not normally observed at MLO, was also observed in γ-ray spectra of these samples. Despite a careful search of the spectra for the 811-keV line of ^{58}Co [from ^{58}Ni(n,p)^{58}Co], we could not observe it at the National Bureau of Standards reactor used for irradiations, as its neutrons are so well thermalized that few (n,p) products are observed. The In/Ir ratio was 870 and 700 for the two upslope samples, which is half the ratio for Hawaiian basalt (1800) and suggests that Ir

Table 1. Composition of atmospheric particulates at MLO.

Element	Downslope samples (pg/m^3)			Upslope samples (pg/m^3)		
	Normal*	First week†	Second week‡	Normal*	First week†	Second week‡
S	80,000	58,000	400,000	150,000	1,700,000	590,000
Al	4,900	4,500	2,100	16,000	20,000	3,800
As	13	4.5	11	39	1,600	310
Se	11	110	580	22	10,100	3,200
In	< 0.2	0.77	4.2	< 0.4	148	40
Au	0.15	< 0.2	< 0.2	0.28	2.8	0.59
Ir	< 0.003	< 0.003	< 0.003	< 0.003	0.17	0.057

*Geometric mean concentration during clean season (July to mid-February), 1979 to 1982 (*1*). †Collected between 28 December 1982 and 4 January 1983. ‡Collected between 4 and 11 January 1983.

is enriched more than In. The two upslope samples have the same relative composition for the elements enriched by the volcanic emissions. After subtraction of the normal concentrations of the enriched elements (Table 1), ratios of excess concentrations between the two samples are 3.9, 5.8, 3.2, 3.7, 4.8, and 3.0 for S, As, Se, In, Au, and Ir, respectively. This relatively good agreement suggests that the emissions carried a chemical signature of the volcanic system that was consistent over at least the 2-week sampling period reported here.

Other elements also showed enrichments larger than normally observed at this site, as shown in Fig. 2. Enrichment factors are shown for the upslope sample collected during the first week of January and are defined by

$$\mathrm{EF}_{\mathrm{BHVO}} = \frac{(\mathrm{X/Al})_{\mathrm{air}}}{(\mathrm{X/Al})_{\mathrm{BHVO}}}$$

where X is the concentration of the element of interest in the air sample and reference material, in this case Hawaiian basalt BHVO-1, a U.S. Geological Survey (USGS) standard rock (*4, 5*). Aluminum is used for normalization, as it is easily measured and, at MLO, is found to be a quantitative measure of the crustal dust component (*3*). The highest enrichments observed are for Se and Hg, both of which exceed 10^6 relative to basalt. The mercury data are for particulate Hg only and reflect a lower limit because of potential losses of radioactive Hg during activation analysis. Several enriched elements are naturally enriched in the atmosphere (I, Br, Cs, Na, and Cl) and are not as strongly enhanced by the volcanic activities.

Table 2 shows groups of elements that are enriched by various amounts owing to volcanic activity. From Table 2 and Fig. 2, it is apparent that most of the enrichments result from volcanic activity. Most mafic and rare-earth elements show a distribution pattern similar to that of Hawaiian basalt, which must have been the dominant component of the sample. The Ir enrichments are 13,000 and 22,000 for the first and second upslope samples, which are highly significant. In recent years we have studied six active volcanoes—Augustine, Mount St. Helens, El Chichón, Arenal, Poas, and Colima—and found no evidence of an Ir enrichment, although each spectrum was examined for γ-rays characteristic of Ir. Enrichments of Se and In are also much greater than previously observed at most volcanoes (*6–9*).

These observations suggest several questions: (i) why Ir is enriched in this volcanic eruption but not in the other volcanoes studied, (ii) what mechanism could be responsible for the Ir enrichment, and (iii) whether there are implications for the Ir anomaly at the Cretaceous-Tertiary (K-T) boundary layer, which has been explained as an artifact of a cataclysmic meteoritic impact (*10*).

The Hawaiian volcanoes, including Kilauea, are geologically different from the other volcanoes we have studied in that they represent a so-called volcanic hot spot (*11*). Some theories suggest that these volcanoes are fed by magma from very deep in the earth, possibly from the mantle. The F/Cl ratio in the gases and the fume from Kilauea during this eruption is 0.45, similar to that observed by Naughton *et al.* (*12*) during previous eruptions and about ten times greater than normally observed at other volcanoes (*13*), which suggests that it is fed by magma from the mantle. The other known high-fluorine volcanic vents are associated with Hekla in Iceland (*14*). In the case of Iceland, the fluorine-rich vents are probably being fed magma

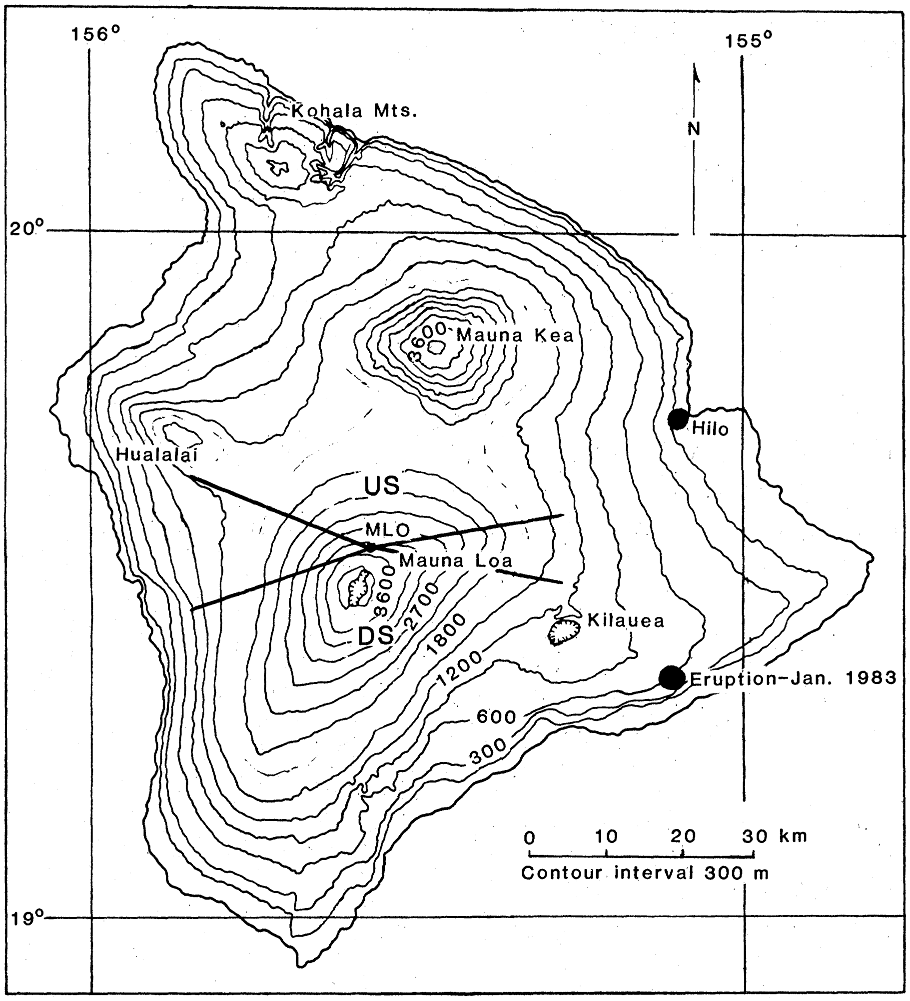

Fig. 1. Map of the island of Hawaii, showing the location of MLO (including upslope and downslope wind sectors) and the site of the 3 January eruption.

from the oceanic spreading center (*15*). No measurements of Ir from Hekla have been reported.

The high fluorine concentration may be partly responsible for the Ir enrichment. The most volatile compound of Ir is IrF_6, with a melting point of 44.4°C and boiling point of 53°C (*16*). The Ir is probably released as volatile IrF_6, which is formed only in the presence of excess fluorine. Fluorine gases are found only in volcanoes fed by a deep magma source, possibly the mantle. The IrF_6 can be formed easily by direct action of F_2 on Ir metal, but there are no data on F_2 in volcanic gases and it cannot be proved that this reaction takes place (*17*). Volatile Ir acids in which Ir is in a lower oxidation state might be formed, but such compounds are not known.

The implication of this Ir source for the K-T boundary problem depends on the magnitude of the Ir release and its association with other platinum group metals. Alvarez *et al.* (*10*) suggested that the Ir anomaly resulted from the impact of a meteorite 10 ± 4 km in diameter with the earth. During the recent eruption of Kilauea, a minimum of about 50×10^6 m^3 of magma was released prior to the June-July sequence (*18*). The Ir content of this magma, based on a concentration of 0.055 ppb (*5*), is only about 9 kg. If one uses 0.44 ppb for the Ir content of BHVO, as reviewed by Gladney and Goode (*4*), then the amount of Ir would be almost ten times as large. Since the Ir was released in the fume, initially as a gas and then adhering to airborne particles, it is difficult to know what fraction to use in calculating the gas-phase enrichment, especially in light of the remoteness of the sampling site from the vents. It is therefore not possible to calculate gas-phase emission rates based on the data presented here. The calculated mass of Ir in the K-T boundary layer is approximately 200 kilotons and would require an eruption much larger than that which occurred at Kilauea in 1983. Volcanic events, such as those that formed the Deccan Flood basalts, are known to have occurred during the Cretaceous and Tertiary periods and were of sufficient magnitude to have introduced the Ir found in the K-T layer (*19*).

Table 2. Degree of enrichment of the elements observed at MLO.

Degree of enrichment*	Element
1–3	Na, Mg, Al, Cl, Ca, Sc, Ti, V, Mn, Fe, Co, Ga, Br, I, Cs, La, Ce, Sm, Eu, Yb, Hf, Ta
3–10	Sb, Ag, K, Rb, Au
10–50	S, Cu, Zn, As
> 50	Se, Hg, Cd, In, Ir

*Ratio of concentration in January samples to normal concentration.

An important point is that the enrichment observed at the K-T boundary is in the other platinum group elements as well as Ir, and that these elements are present in ratios similar to those observed in meteorites (*10, 20, 21*). The only other platinum-group element that we were able to observe was Au, which was significantly enriched. Gold is normally enriched in the atmosphere and the enrichments are usually quite variable, but at this stage the enrichments due to Kilauea are higher than normally observed and can be used to estimate the Au/Ir ratio. This ratio for the K-T boundary is approximately equal to the cosmic abundance ratio of 0.30, whereas we observed a value between 10 and 16, almost 50 times higher. More data are needed on the other platinum-group elements before we can evaluate the importance of the volcanic enrichments as a potential source for the K-T boundary anomaly.

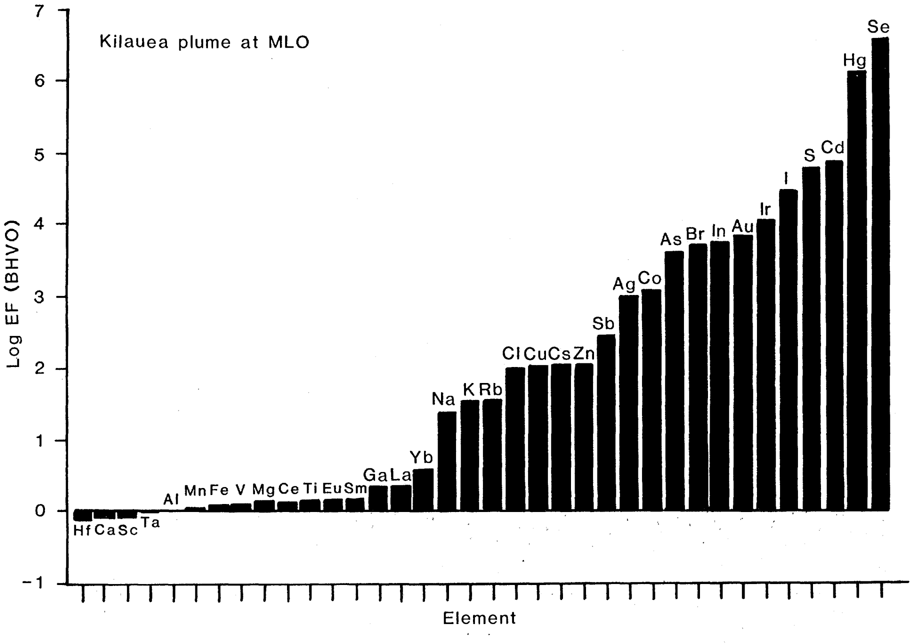

Fig. 2. Enrichment factors relative to Hawaiian basalt for Kilauea plume sample collected at MLO between 4 and 11 January 1983.

It is possible that changes in the elemental distribution occurred during the sedimentation process as sulfides were apparently formed in a reducing environment, and under these conditions one would expect Ir to become fixed and Au to be mobile.

The enhanced concentrations of Se, As, and Sb in the K-T layer have been difficult to explain on the basis of meteoritic material (*12*). Some authors (*5*) suggest that those volatile elements are due to a volcanic component. This is consistent with our observation that these elements are always highly enriched in volcanic plumes, but a great deal of chemical fractionation has probably taken place. Selenium, As, and Sb would be expected to be more mobile in the geological strata than Ir under reducing conditions.

In conclusion, we have observed Ir release from an active volcano at a concentration much greater than that in the magma. The mechanism apparently involves the formation of a volatile fluoride compound. Although the Au/Ir ratio is not the same as that at the K-T boundary, the presence of Sb, Se, and As in the plume and at the K-T boundary suggests that volcanic components may have been involved. If volcanism was instrumental in producing the K-T boundary layer, the volcano was certainly not Kilauea but may have been similar to the one that formed the Deccan Flood basalts.

Following the observation of Ir in the MLO samples, a trip was taken to the hot vents at Kilauea in May 1983 and samples were obtained directly in the fume from the vents. Analyses of these samples are not complete, but Ir, Au, and all the elements observed at MLO have also been found in extremely high concentrations in the samples.

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Equatorial Undercurrent Disappears During 1982–1983 El Niño

Abstract. *The equatorial undercurrent at 159°W decayed during August 1982, partially reversed during September, and rapidly reappeared in January 1983. The virtual disappearance is consistent with the basin-wide adjustment of sea surface slope to the strong westerly winds in the western and central Pacific that caused the 1982–1983 El Niño event.*

El Niño events are usually described in terms of sea-surface temperature, sea level, winds, rainfall, and, to a lesser extent, hydrographic structure (*1*). Until the 1982–1983 event there were few measurements of currents near the equator during El Niño. Current measurements made along 159°W from March 1982 through June 1983 (*2*) show that currents, like the winds, reverse during El Niño.

During March through July 1982, currents at the equator (Fig. 1) were marginally weaker than during the same season in 1979 and 1980. The Equatorial Undercurrent (EUC) flowed east with a maximum speed of 1 m/sec at a depth near 150 m. Western flow in the South Equatorial Current (SEC) was weak. The EUC surfaced in April and eastward surface flow remained through most of the boreal summer (*3*).

During August the upper and middle parts of the EUC vanished, and a westward current appeared at the core depth (150 m) during September and October. Below 160 m the EUC was reduced to a small remnant during September. This is the first time, to our knowledge, that direct current measurements in the central Pacific have failed to show a substantial EUC. A meridional section of current profiles during late September confirms that the EUC was really absent rather than shifted off the equator.

During November, eastward flow returned at 150 m due to the deepening of a strong surface current rather than the restoration of a normal EUC. The EUC, with a strong SEC above it, returned abruptly in January. From mid-February through the last observations in June, the maximum speed of the EUC remained over 0.7 m/sec while that of the SEC varied from 0.2 to 1 m/sec.

What caused this disappearance of the undercurrent?

Ship and island wind measurements from 160°E to the date line show westerly anomalies beginning in June, with westerly winds persisting from July through November (Fig. 2). The rapid return of easterly winds at Tarawa in December was accompanied by a strong northerly component and by continued westerlies south of the equator. At 159°W within 3° of the equator, steady easterly trade winds prevailed until September, when they rapidly weakened. Winds were light and variable during October. Starting in November, bursts of strong westerlies were associated with vigorous convection and precipitation in the normally arid equatorial band.

Monthly average sea levels at islands near the equator (Fig. 3) show the basin-wide adjustment of the sea surface during El Niño. In June the sea levels were near their long-term averages, with the normal slope down to the east (*4*). Starting in July, the sea surface began a gradual fall in the far west. At Nauru, Christmas Island, and the Galápagos Islands, sea level rose and then fell at successively later times. By January there was essentially no slope across the basin at the zonal scales resolved by these widely separated islands.

The disappearance of the EUC at 159°W in September coincided with the peak in sea level at Christmas Island (157°W) and with the collapse of the local trade winds. The high sea level is consistent with a reduced or reversed pressure gradient, hence with weak westward flow replacing the EUC core. The

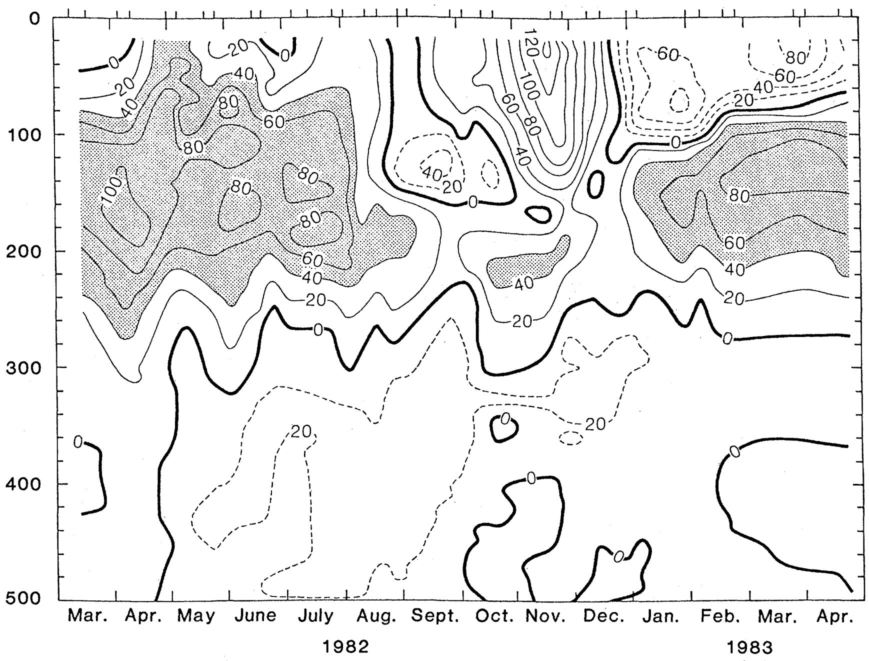

Fig. 1. Zonal velocity component on the equator at 159°W. Contour intervals are 20 cm/sec, with westward flow indicated by dashed lines. Tick marks at top show observation times. The EUC (shaded) was virtually absent from September through December 1982.