Reports

Helium Flux from the Earth's Mantle as Estimated from Hawaiian Fumarolic Degassing

Abstract. *Averaged helium to carbon dioxide ratios measured from systematic collections of gases from Sulphur Bank fumarole, Kilauea, Hawaii, when coupled with estimates of carbon in the earth's crust, give a helium flux of 1 × 10⁵ atoms per square centimeter per second. This is within the lower range of other estimates, and may represent the flux from deep-seated sources in the upper mantle.*

The outflux of helium from the earth is of interest since it is associated with the composition of crustal and mantle rocks, with the generation of heat from radioactive decay, and with the balance of the budget of helium in the atmosphere. Measurements of this flux from a Hawaiian volcanic fumarole, Sulphur Bank, indicate that degassing through volcanic vents may be one of the important routes through which the venting of helium takes place from deep within the earth. Also it is a conveniently measured index of the flux of "excess volatiles" through volcanic and fumarolic vents, which are believed to be the major contributors of the components of the atmosphere and oceans (*1*).

Sulphur Bank is a fumarole situated near the edge of the caldera of Kilauea Volcano on the island of Hawaii. It is the most persistent of the many degassing areas that seem to define the edge faults of old craters (*2*). As a collecting device, a trio of pipes was set in this area to depths of 4.5 to 21 m in 1923. The temperature of the gases emitted through the pipe system is about that of boiling water (about 95°C) for an altitude of approximately 1.2 km at the fumarole. The gases generally are low in air content. Complete analyses of the gases have been made at irregular intervals since 1964. The average amounts of the major components [percent by volume ± 1 standard deviation (S.D.)] are: H_2O, 92 ± 2; CO_2, 8 ± 2; SO_2, 0.1 ± 0.2; H_2S, 0.02 ± 0.004. For minor components the ranges were (percent by volume): H_2, (0.2 to 5) × 10^{-4}; He, (0.3 to 6.0) × 10^{-4}; air, 0.000 to 0.4. The percentage of air was calculated from the N_2 content, although the N_2/O_2 ratio was always found to be greater than the value for ordinary air (O_2 deficiency).

Many have conjectured that there might be a functional correlation between the concentrations of some components in the fumarolic gases and the activity in the nearby volcanic vent at Halemaumau (*3*). If the concentrations of some components begin to vary before eruption, it might be possible to use this variation to predict volcanic eruptions. The abyssal gases that are most irritatingly evident to the observer are the sulfur-containing members, SO_2 and H_2S. We have found no consistent variation in the sulfur content with Kilauean eruptions that could be used predictively (*4*). If anything, an increase in the total sulfur content seemed to set in only after an eruption was underway.

Helium and carbon dioxide are gases that also might have their source deep in the volcanic system. Carbon dioxide is one of the major components that is present in far greater concentration than is likely to arise from aerial or surface water contamination. Its deep-seated source is supported by a "dead" or zero content of carbon-14 (*5*). The degree of incorporation of deep-seated carbon-bearing sediments into the volcanic system by subduction cannot be evaluated. It is assumed that the process is minor in Hawaiian volcanoes compared to their counterparts along the continental margins. Helium also is present in relatively high concentration, and probably is being fed to the system as a product of radioactive decay from the elements in the uranium-thorium series in the rocks of the crust and mantle. In addition, helium diffuses readily in hot silicate materials, and would be expected to permeate through the rocks of the volcanic pile, particularly as they are being heated and opened up just before an eruption. It might thus increase in concentration before the advent of an eruption.

Sampling and analysis for helium at Sulphur Bank have been carried on for almost 3 years, during which Kilauea has been in an almost constant state of eruption on its southeast flank at Mauna Ulu, with short periods of

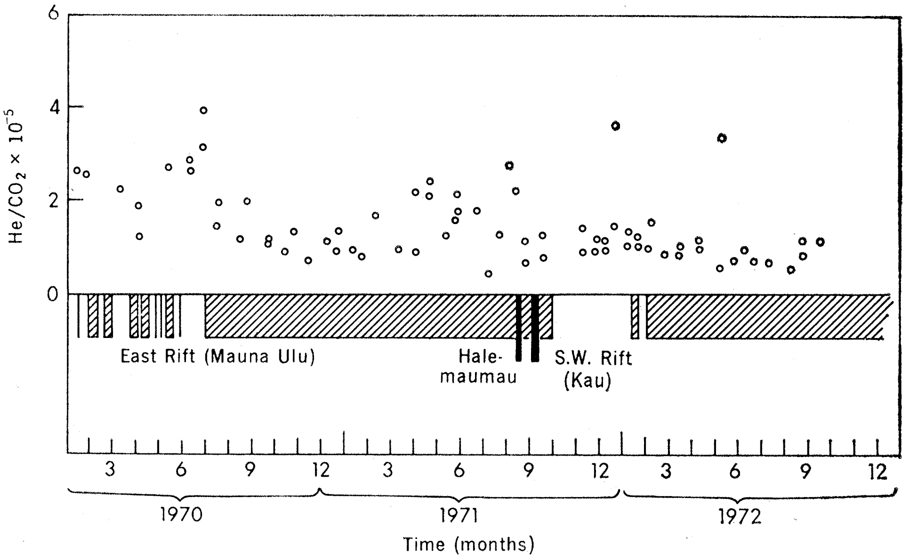

Fig. 1. The data points (circles) show the variation of the He/CO_2 ratio with the time of collection of gas samples from Sulphur Bank fumarole. The bar graph below shows the concurrent state of activity at Kilauea Volcano associated with the fumarole. The hatched bars indicate periods of eruption on the east rift zone of Kilauea, and the black bars are for periods of eruption in the summit caldera and nearby on the southwest rift zone.

eruption during 1971 on the southwest rift (Kau) and in the summit caldera near Halemaumau, which is the site nearest the Sulphur Bank fumarole.

For work with helium and carbon dioxide, the sampling tubes were of the evacuated type, in which water was taken up in one section by a P_2O_5 absorbent and the acid gases in a separate portion on a soda lime absorbent. These parts could be weighed before and after to give the amounts of these two major classes of components present. A large volume of gas (about 10 liters) could thus be taken into a relatively small collecting tube. The acid gases were assumed to be only carbon dioxide. Previous analyses have shown that this would result in a maximum error in the carbon dioxide measurement of less than 1 percent due to the other acid gases, H_2S and SO_2, found in appreciable concentration at Sulphur Bank. Detailed analyses of the absorbed sulfur gases were not attempted. Other gases, including helium, occupied the free space of the tube and were analyzed by gas chromatography. The concentration of helium found in the majority of samples approached the limit of detection for the equipment, so that the precision was poor. The error involved in the chromatographic output for repetitive measurements of helium in the samples indicates a precision of 16 ± 12 percent (relative standard deviation). From measurements of mixtures of known composition, with helium contents in the same range as in the fumarolic samples, the indicated accuracy to 1 S.D. was $\pm 0.7 \times 10^{-4}$ mole percent. The results are presented in Fig. 1 as the concentration ratio of the two substances of interest, He/CO_2, and are given as a function of the date of collection, along with an indication of the eruptive activity at Kilauea as demonstrated by visible effusions of lava.

The averaged value of the He/CO_2 ratio taken during this period is $(1.4 \pm 0.8) \times 10^{-5}$. The precision of the ratio as calculated from error considerations discussed above is expected to be $\pm 0.7 \times 10^{-5}$, so that the observed deviation is within the range of the prediction. Moreover, short-term variations in the ratio which can be noted in Fig. 1 cannot be correlated with any confidence with the phases of activity at Kilauea also shown in the figure. One can only conclude from the data taken so far that variations in the amount of helium or carbon dioxide (or both) in fumaroles as measured by these methods cannot be used to predict eruptions in associated volcanoes, at least under the conditions which presently exist at Kilauea. However, collections and analyses are being continued.

The role of volcanoes, fumaroles, and hot springs as avenues through which the crust and upper mantle are degassed has been evaluated most thoroughly by Rubey (*1*) in his work on the budget of volatiles on the earth's surfaces and their relationship to the genesis of the ocean and atmosphere. The flux of volatiles such as helium is often expressed as atoms per square centimeter per second through the entire surface of the earth, as if the seepage were general and uniform throughout. It is generally conceded, however, that even for an element as fugitive as helium, any appreciable flow must take place through faults and vents (*6*). Bieri and co-workers (*7*) have found an excess of helium in ocean water beyond air-saturation values, and they attribute some fraction of this to injection through the ocean bottom. Also, they note a particular excess in samples taken from regions of subcrustal upwelling, as in those from the crest of the East Pacific Rise. They suggest that helium transport may occur with the upward movement of mantle material. Seismic studies indicate that the source of magma in Hawaiian volcanoes exists at a depth of between 45 and 60 km (*8*), well within the upper mantle in this region. The flux of helium from such centers, then, may give an indication of the current contribution of mantle sources to helium outgassing, and the gas measurements at Sulphur Bank fumarole, which is associated with Kilauea Volcano, can act as a convenient source for this information.

The lack of any significant variation in the He/CO_2 ratio during the period of these measurements may be taken as an indication of the long-term constant nature of the flux of these substances. Thus, one can use the average value of the He/CO_2 ratio measured for the fumarole to calculate the average helium flux, by coupling this with estimates of the content of carbon in the earth's crust contributed as "excess volatiles" (*1*) from such volcanic sources. Estimates of the carbon content of the crust, mainly tied up in sediments, vary from (0.56 to 2.5) $\times 10^{23}$ g (*1, 9–11*), and trend upward as new sinks of carbon are discovered and included. The considered figure of $(10 \pm 5) \times 10^{22}$ g suggested by Holland (*11*) seems most reasonable. If we assume that this carbon has been contributed at a uniform rate over the entire history of the earth's crust, this would give a carbon flux of 7×10^{9} atom cm^{-2} sec^{-1}. Coupling this value with the reported He/CO_2 ratio of 1.4×10^{-5}, we obtain a helium flux of 1×10^{5} atom cm^{-2} sec^{-1}.

Other estimates (*12*) of the flux of helium from the earth have been based on rock-weathering rates, heat-flow measurements, estimates of the uranium, thorium, and potassium contents of source rocks combined with the argon content of the atmosphere, and the direct measurement of $^{4}He/^{40}Ar$ in natural gases. These estimates range from 1.4×10^{5} to 10^{7} atom cm^{-2} sec^{-1}, with a value of 3×10^{6} most frequently cited. The measurements included sources from which the flux of helium would be high due to segregation of the radioactive parent elements in the crust. If the vent measured in this work is fed with gases from sources in the upper mantle, the lower value reported would be expected. This value (1×10^{5} atom cm^{-2} sec^{-1}) is in agreement with the estimate made by Turekian (*13*) of 1.4×10^{5} atom cm^{-2} sec^{-1} for the helium flux from the mantle.

Several researchers (*10, 14*) have discussed evidence for a higher rate of degassing during the early stages of evolution of the earth's crust, rather than the uniform rate assumed here and also generally used in discussions of the genesis of the atmosphere and oceans. In calculations of the flux based on the accumulation of an element on the crust through degassing, such as have been made for carbon and argon, it is not possible to differentiate linear degassing from some nonlinear form. However, one may invert the above argument and accept the value of the helium flux as suggested by Turekian (*13*) and others, combine this with the measured He/CO_2 ratio reported here, and show that the present rate of degassing would supply enough carbon to take care of estimates of its content in the crust, without the need to invoke periods of enhanced or catastrophic degassing.

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Ductile Superconducting Copper-Base Alloys

Abstract. *A new class of ductile superconductors has been prepared by casting and appropriate heat treatments. These alloys superconduct between 4° and 18°K and contain at least 90 atom percent copper and a superconducting phase such as Nb_3Sn or niobium. They can be processed into wires by conventional metallurgical techniques.*

Ductile superconducting materials are essential in many engineering applications, such as superconducting magnets, power transmission lines, motors, and generators (*1*). The superconducting materials used in these applications should have a reasonably high transition temperature, a high critical field, and a high critical current density. They should be easy to manufacture and inexpensive. Furthermore, they should exhibit high thermal stability under the influence of high magnetic field and current density. I report here a new class of ductile superconducting alloys, the members of which are composed primarily of a ductile metal such as Cu with a small amount of some superconducting element such as Nb or Sn. These alloys can be cast into ingots and processed by conventional metallurgical techniques. Typical examples are $Cu_{93.0}Nb_{5.0}Sn_{2.0}$ and $Cu_{90}V_{7.5}Si_{2.5}$ (the subscripts represent atom percentages). These ductile alloys are superconducting at a temperature between 4° and 18°K (the superconducting temperature depends on the alloy composition and the heat treatment). Preliminary experiments indicate that they are high-field superconductors and can be manufactured into wires (~0.2 mm in diameter) or sheets (0.2 mm thick) on a mass production scale and at a cost comparable to that of ordinary copper wires.

The alloys were prepared by the induction melting of the appropriate quantities of the constituents in a water-cooled silver boat (*2*) in an argon atmosphere. The alloys were melted several times and were then cooled at a rate of about 100°C/sec in the silver boat. The as-cast ingot is ductile enough to be rolled into wires with a cross section of 1 by 1 mm. For some of the alloys, an appropriate heat treatment is necessary to increase and sharpen the superconducting transition temperature. The heat treatment varies from alloy to alloy, and usually consists of annealing in a vacuum at a temperature between 500° and 900°C for from a few hours to a few days. For example, the alloy $Cu_{93.0}Nb_{5.0}Sn_{2.0}$ with a superconducting transition temperature (T_c) of about 12°K was annealed at 600°C for 2.5 days or at 800°C for 5 hours. I determined the T_c by measuring the electrical resistivity as a function of temperature with a standard four-probe technique. The criterion for superconductivity is that the potential drop across a 15-mm length of a specimen 0.5 by 0.5 mm is less than 10^{-8} volt at a current of 100 ma. This corresponds to an upper bound in resistivity of about 10^{-10} ohm-cm. Typical results of the resistivity measurements on two Cu-Nb-Sn alloys are shown in Fig. 1. It is apparent that the resistive superconducting transition is affected by rolling, annealing, and the addition of a small amount of P. On the basis of these results, the following statements can be made:

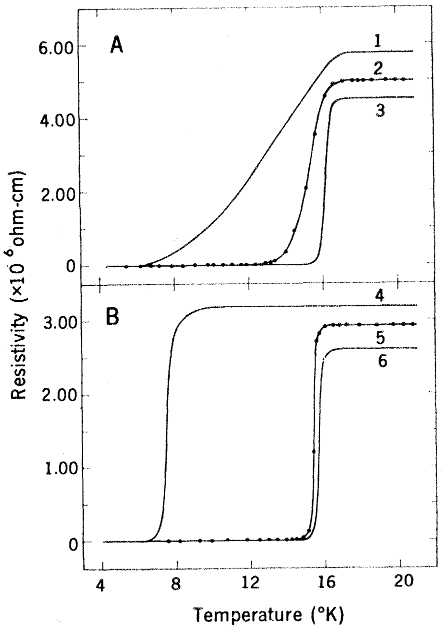

Fig. 1. Electrical resistivity as a function of temperature for two alloys of different compositions: (A) alloy $Cu_{93.0}Nb_{5.0}Sn_{2.0}$ as cast (curve 1), rolled (curve 2), and doped with less than 0.1 atom percent P and then rolled (curve 3) (all alloys were annealed at 800°C for 5 hours); (B) alloy $Cu_{93.5}Nb_{5.0}Sn_{1.5}$ as rolled (curve 4), and then annealed at 800°C for 2 hours (curve 5) and 6 hours (curve 6).

1) A resistive superconducting state has been observed in all the new alloys.

2) If the alloy is first rolled and then annealed, the superconducting transition is sharpened. For instance, the resistivity of the $Cu_{93.0}Nb_{5.0}Sn_{2.0}$ alloy cast and then annealed at 800°C for 5 hours starts to decrease at 17.5°K, and a complete superconducting state is reached at about 5°K (Fig. 1, curve 1). The rolled sample heat-treated in the same manner becomes superconducting around 12°K (Fig. 1, curve 2).

3) The addition of a small amount of P (< 0.1 atom percent) results in an increase in T_c and a sharper transition. As shown in Fig. 1, curve 3, the T_c of the $Cu_{93.0}Nb_{5.0}Sn_{2.0}$ alloy containing less than 0.1 atom percent of P is increased to 15.5°K and the transition is only 1.5°K wide.

4) The effect of annealing at a given temperature for different lengths of time is shown in Fig. 1, curves 4–6, for the $Cu_{93.5}Nb_{5.0}Sn_{1.5}$ alloy. The as-rolled sample superconducts at 6.5°K. The superconducting transition temperature of the same alloy can be increased to 12°K by annealing at 800°C for 2 hours and to 15°K by annealing at 800°C for 6 hours. Moreover, the ratio of Nb to Sn does not always