Reports

Rare Gas Isotopes in Hawaiian Ultramafic Nodules and Volcanic Rocks: Constraint on Genetic Relationships

Abstract. *Differences in the rare gas isotopic ratios, especially the ratios of helium-3 to helium-4 and of argon-40 to argon-36, in Hawaiian ultramafic nodules and phenocrysts in volcanic rocks indicate that the nodules and phenocrysts were derived from different sources. The isotopic ratios in ultramafic nodules are similar to those in oceanic tholeiites. The phenocrysts seem to have formed in equilibrium with source materials richer in primordial components than those of the oceanic tholeiites. Mixing between the sources is quite likely.*

Many investigations (petrographical, mineralogical, and geochemical studies) have been directed toward determining the origin of Hawaiian volcanic rocks (*1*). In studies of this kind, it is often assumed that the ultramafic nodules included in Hawaiian volcanic rocks represent either the source materials of or cumulates from these volcanic rocks (*2*). However, to our knowledge no definite evidence has been presented that they have a common genetic relationship. Even isotope studies have not resolved the problem, since most studies are mainly concerned with volcanic materials of different types. The few isotopic investigations of ultramafic nodules have lacked the analytical precision to settle the question (*3*). We have attempted to resolve this problem by using rare gas isotopes. Recent rare gas isotope studies in terrestrial materials of deep origin have revealed the remains of primordial rare gas components within the earth (*4*).

We analyzed three ultramafic nodules (two spinel-lherzolites and one garnet-pyroxenite) from the Salt Lake Crater, Oahu Island (SLC samples), and three large phenocryst samples (one olivine and two augite samples) from the Haleakala Volcano, Maui Island (HA samples). Two dunite nodules from Hualalai and one olivine phenocryst sample of the Kapoho lava, Kilauea, Hawaii Island, were analyzed earlier (*5*), and the results are included in Fig. 1. Olivine and augite phenocrysts were handpicked under a microscope. Their grain size ranges from about 1 to 5 mm. We have analyzed large phenocrysts instead of bulk samples of the volcanic rocks in an effort to characterize their rare gas isotopes on the ground that large phenocrysts are considered to have solidified at depth in a magma reservoir, where atmospheric contamination should be less serious. The isotopic composition of the rare gases in the phenocrysts will represent those of the magma as long as isotopic equilibrium of the rare gases was maintained in the magma reservoir.

A Nier-type mass spectrometer equipped with a secondary multiplier was used to measure all rare gas isotopes including the ^{3}He/^{4}He ratio. This instrument has a resolving power of about 600 and can separate ^{3}He from HD + H_3. All vacuum lines are made of stainless steel except the sample holding part (*6*). A two-stage (700° and 1800°C, 30 minutes) stepwise heating was used for some of the samples to examine the effect of surface atmospheric contamination. Samples were melted in a tantalum crucible with a resistance heater, and the temperature was measured with an optical pyrometer.

The rare gas concentrations are shown in Table 1, and selected isotopic ratios are listed in Table 2. All isotope ratios other than those in Table 2 were of atmospheric composition within the experimental uncertainty. For the samples that were exposed to stepwise heating, the low-temperature fraction always showed a more atmospheric composition than the high-temperature fraction. Since the ^{3}He/^{4}He ratio is rather insensitive to the effect of surface atmospheric contamination, this ratio is a good indicator with which to characterize source materials.

Our results indicate that the ultramafic nodules and phenocrysts in volcanic rocks have different isotopic compositions. The difference is especially clear in the ^{3}He/^{4}He and ^{40}Ar/^{36}Ar ratios (Fig. 1 and Table 2). Ultramafic nodules from Hualalai and Salt Lake Crater show high ^{40}Ar/^{36}Ar ratios (> 1000) and relatively constant ^{3}He/^{4}He ratios of 1.0×10^{-5} to 1.4×10^{-5}. Both ratios are quite similar to those observed in the oceanic tholeiites (*7*). Olivine and augite phenocrysts from Kilauea and Haleakala volcanoes show lower ^{40}Ar/^{36}Ar ratios (< 1000) and higher ^{3}He/^{4}He ratios ($> 1.9 \times 10^{-5}$). Since the atmospheric ^{40}Ar/^{36}Ar and ^{3}He/^{4}He ratios are 295.5 and 1.4×10^{-6}, respectively, it is impossible to explain the difference on the basis of atmospheric contamination. Figure 1 shows a mixing trend between two possible source materials. One is represented by sample HA a with a ^{40}Ar/^{36}Ar ratio of about 400 and a ^{3}He/^{4}He ratio of

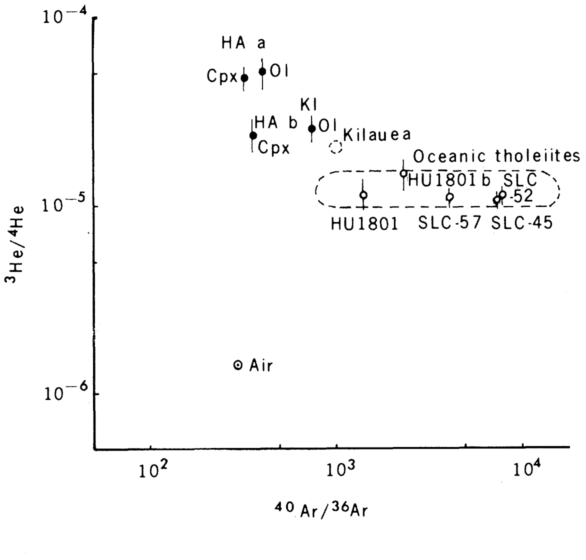

Fig. 1. The ^{3}He/^{4}He ratio versus the ^{40}Ar/^{36}Ar ratio for Hawaiian ultramafic nodules (open symbols) and phenocrysts of volcanic rocks (closed symbols). Abbreviations: *Ol*, olivine phenocrysts; *Cpx*, augite phenocrysts; *HU*, Hualalai, Hawaii Island; *SLC*, Salt Lake Crater, Oahu Island; *KI*, Kilauea, Hawaii Island; *HA*, Haleakala, Maui Island. The dotted area designated Kilauea is represented as the combination of data on the ^{3}He/^{4}He ratios of fumarolic gases (*8*) and the maximum ^{40}Ar/^{36}Ar ratio observed in pillow basalts from the East Rift zone (*14*). The oceanic tholeiite area is also defined by a combination of the published data. When samples were subjected to stepwise heating, the data in the higher temperature fraction are plotted.

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Table 1. Rare gas concentrations in Hawaiian ultramafic nodules and phenocrysts in volcanic rocks. Concentrations were determined by the peak height method with an uncertainty of about 10 percent; a calibrated air standard was used; STP, standard temperature and pressure.

Sample No.	Sample description	Temperature (°C)	^{4}He	^{20}Ne	^{36}Ar	^{84}Kr	^{132}Xe
			(× 10^{-8} cm^3 STP per gram)			(× 10^{-10} cm^3 STP per gram)	
HA a, Cpx	Augite phenocrysts (1.662 g)	1800	3.25	0.117	0.104	0.816	0.101
HA a, Ol	Olivine phenocrysts in a lava flow, White Hill, Haleakala Volcano, Maui (0.955 g)	700	0.34	0.0179	0.0789	0.424	0.0231
		1800	1.89	0.0120	0.0390	0.345	0.0972
HA b, Cpx	Augite crystal in ankaramite, west of Puu Oili, Haleakala Volcano, Maui (1.650 g)	700	0.23	0.0109	0.0617	0.126	0.0046
		1800	2.16	0.0263	0.160	0.223	0.0179
SLC-45	Spinel-lherzolite, Salt Lake Crater, Oahu (3.473 g)	700	0.74	0.0018	0.0083	0.022	0.0029
		1800	32.4	0.0075	0.0120	0.080	0.0136
SLC-52	Spinel-lherzolite, Salt Lake Crater, Oahu (3.086 g)	1800	27.8	0.0101	0.0189	0.141	0.0151
SLC-57	Garnet-pyroxenite, Salt Lake Crater, Oahu (1.309 g)	1800	132	0.0230	0.0279	0.182	0.0209
Blanks	(30 minutes)	1800	0.12	0.0020	0.0069	0.003	0.0035

Table 2. Rare gas isotopic ratios of Hawaiian samples. All tabulated data are those of the 1800°C fraction with an uncertainty of 1 standard deviation. Since all samples appeared on the surface less than a million years ago and their uranium (thorium) and potassium contents are generally low, no correction was applied for radiogenic components. Relatively large uncertainty in the ^{20}Ne/^{22}Ne ratio has been caused primarily by the large correction for doubly charged $^{44}CO_2$ on ^{22}Ne.

Sample No.	^{3}He/^{4}He (× 10^{-6})	^{20}Ne/^{22}Ne	^{40}Ar/^{36}Ar	^{129}Xe/^{132}Xe
		Maui Island		
HA a, Cpx	47.8 ± 6.1	9.94 ± 0.38	311.2 ± 0.8	0.990 ± 0.007
HA a, Ol	51.5 ± 9.7	8.8 ± 1.3	417.6 ± 4.9	0.994 ± 0.017
HA b, Cpx	23.5 ± 4.8	9.9 ± 0.5	334.1 ± 1.9	1.010 ± 0.032
		Oahu Island		
SLC-45	10.5 ± 0.6	10.2 ± 0.4	7563 ± 66	1.016 ± 0.012
SLC-52	11.3 ± 0.7	9.64 ± 0.17	8054 ± 56	0.987 ± 0.032
SLC-57	11.0 ± 0.7	9.70 ± 0.19	4039 ± 50	1.002 ± 0.010
Air	1.4	9.81	295.5	0.983

about 5 × 10^{-5}; the other is represented by the oceanic tholeiites with a ^{40}Ar/^{36}Ar ratio of about 16,000 and a ^{3}He/^{4}He ratio of 1.0 × 10^{-5} to 1.4 × 10^{-5}. Kilauea fumarolic gases also show high ^{3}He/^{4}He ratios (about 1.9 × 10^{-5}) (*8*). Such high ^{3}He/^{4}He ratios (> 1.9 × 10^{-5}) are typically observed in Hawaii, Iceland (*9*), and Yellowstone National Park (*10*) and are interpreted to be characteristic of a hot spot area (*10*). It is almost impossible to relate such a high ^{3}He/^{4}He ratio to that of the oceanic tholeiites on the basis of a simple mass fractionation process. Olivine and augite phenocrysts from sample HA a seem to show a similar ^{3}He/^{4}He ratio but different ^{40}Ar/^{36}Ar ratios (Fig. 1). However, this may be due to differences in the analytical procedures. Olivine phenocrysts were analyzed by the two-stage stepwise heating, and the values for the 1800°C fraction are shown in Fig. 1. Augite phenocrysts were analyzed as a total melt. Their total isotopic values are similar for both the ^{3}He/^{4}He (4.3 × 10^{-5} to 4.8 × 10^{-5}) ratio and the ^{40}Ar/^{36}Ar (310 to 330) ratio. Hence, we may argue that an isotopic equilibrium occurred between the two phases. On the other hand, even the 1800°C fraction of sample HA b shows lower ^{3}He/^{4}He and ^{40}Ar/^{36}Ar ratios than sample HA a. This may reflect either the heterogeneity of the source materials or the introduction of small amounts of atmospheric components into the magma reservoir at the relatively shallow depth from which sample HA b was derived. However, the ^{3}He/^{4}He ratio for sample HA b is still higher than those of ultramafic nodules from the Hawaiian Islands; this finding suggests different sources for these materials.

It has been reported that the ^{3}He/^{4}He ratios for the oceanic tholeiites from quite separated regions such as the East Pacific Rise and the Mid-Atlantic Ridge are rather uniform in spite of very large variation in the ^{4}He/Ne ratios (*11*). The variation in the ^{4}He/Ne ratios probably reflects the difference in the mobility for each element during geological processes. However, the uniformity of the ^{3}He/^{4}He ratios over large areas requires a special condition for the equilibration of helium. A simple estimation suggests that it is difficult for helium to be equilibrated over such large distance by diffusion through solids. Instead, the partial melting zone in the asthenosphere would probably play an important role in the equilibration of helium isotopes. Slight differences in the ^{3}He/^{4}He ratios between different regions may indicate less than complete equilibration at the regional scale. Argon may be less homogenized than helium. The occurrence of excess ^{129}Xe in Hawaiian ultramafic nodules (*5*) and no definite evidence for it in the recent oceanic tholeiites may also be due to heterogeneity in the xenon isotopes in the mantle.

The rare gas isotopic ratios do not exhibit the genetic relationships between Hawaiian volcanic rocks and ultramafic nodules found in the Hualalai and Salt Lake Crater nodules. On the other hand, the similarity of rare gas isotopic ratios between Hawaiian ultramafic nodules and the oceanic tholeiites may imply that the lithosphere under the Hawaiian Islands is composed of such ultramafic rocks and that they were formed from source materials similar to those of the oceanic tholeiites. We suppose that the uniformity of the ^{3}He/^{4}He ratios observed in the oceanic tholeiites is due to the existence of a partial melting zone in the asthenosphere, which is probably the source region for the production of the oceanic tholeiites.

Our results are compatible with the hot spot hypothesis for the genesis of the Hawaiian chain (*12*) and require that the hot plume originates deeper in the mantle than the bottom of the lithosphere. This study indicates that the source materials of the Hawaiian volcanic rocks are different from those of the oceanic tholeiites, which are presumably derived from the asthenosphere. We conjecture that mantle plumes must arise in the mantle below the asthenosphere. The source materials for the Hawaiian volcanic rocks have higher ^{3}He/^{4}He and lower ^{40}Ar/^{36}Ar ratios than those of the oceanic tholeiites. If we assume that the primordial components of rare gases are depleted in the source region of the oceanic tholeiites, we can explain the isotopic differences between the two sources. Such a model is compatible with the concept of a "depleted mantle" for the source region of the oceanic tholeiites (*13*). In this case, the source region from which a mantle plume arises still retains a relatively primordial character, including high ^{3}He/^{4}He and low ^{40}Ar/^{36}Ar ratios.

Our results also provide evidence of mixing between the mantle plume and the source materials of the oceanic tholeiites (materials of the asthenosphere or lithosphere, or both) as observed in the Hawaiian volcanic rocks. The strontium, lead, and neodymium isotopic ratios in the Hawaiian volcanic rocks may also be interpreted in this way.

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Stratospheric Sulfuric Acid Layer: Evidence for an Anthropogenic Component

Abstract. *Recent measurements of small aerosol particles in the stratosphere over Laramie, Wyoming, indicate low-concentration background conditions. A comparison of measurements made some 20 years ago with the present background concentration reveals the possibility of an increase of 9 percent per year. Since the aerosol particles are predominantly sulfuric acid droplets which form in the stratosphere from tropospheric sulfur-containing gases, such an increase may be related to man-made sulfur emissions.*

A layer of small aerosol particles has been known to be present in the stratosphere for some time. Although volcanic eruptions appear to increase the concentration of these particles, the question of whether such a layer would still be present in the absence of such volcanic activity has never been answered, to our knowledge. In this report we present measurements which address this question.

The stratospheric aerosol concentration has been measured by balloon-borne particle counters at Laramie, Wyoming (41°N), since 1971. Measurements at varying latitudes revealed the global time behavior of the aerosol layer during a low-concentration period in 1972 and 1973 (*1-4*). The enhancement of the stratospheric aerosol layer, due to the volcanic eruption of Fuego Volcano, Guatemala (14°N), in late 1974, was also studied in detail by means of particle counter measurements at Laramie (*5*). Continuation of the measurements during 1977 through 1979 has revealed another volcanically quiescent period, this time of greater duration than that in early 1974. These latter measurements now appear to have established the current background stratospheric aerosol concentration. The determination of such a background concentration is important because, being related to tropospheric sulfur-containing gases, it may be a measure of anthropogenic effects on the stratosphere and, because of the frequency and slow decay of large volcanic eruptions, this background concentration is probably reached, on the average, only every 10 or 20 years.

The layer of aerosol particles, which girdles the globe at a height of about 20 km, is responsible for the predawn and postsunset purple atmospheric glow and has become known as the stratospheric aerosol layer, sulfate layer, or Junge layer after its discoverer. Using particle impact samplers on balloons and aircraft during the period 1957 through 1960, Junge's group determined that for particles of radii 0.1 to 1.0 μm a relative concentration maximum exists in the altitude range from 18 to 23 km. Sample analysis revealed sulfur as the predominant element, and Junge and his coworkers postulated that a tropospheric sulfur-containing gas (such as SO_2 or H_2S), injected into the stratosphere, underwent a gas-to-particle conversion process (*6*).

Junge's pioneering measurements terminated shortly thereafter. Other researchers verified the existence of the layer, studied its composition, and delineated its structure (*7*). The substantial eruption in 1963 of Agung Volcano on Bali (8°S), considerably altered stratospheric conditions, increasing the stratospheric particulate loading by at least an order of magnitude in the Northern Hemisphere and probably more in the Southern Hemisphere (*7*). The observation of higher stratospheric aerosol concentrations for several years after 1963 cast suspicion and doubt on the considerably more conservative values Junge had measured before 1963. However, it now appears that during certain nonvolcanic periods the stratospheric aerosol concentration does decrease to very low but finite values and that Junge's measurements were probably correct.

The instrument that we used detects aerosol particles in situ during balloon ascent with a vertical resolution of about 250 m to an altitude of about 28 km. Through analysis of light scattered by individual particles as they are drawn through the instrument, the concentrations of particles in two size ranges, $r \geq 0.15\ \mu m$ and $r \geq 0.25\ \mu m$, are determined. A detailed description of the instrument has been given in (*1*).

The time history of the maximum in the stratospheric particle mixing ratio (number of particles per milligram of air) from monthly balloon soundings through 1979 at Laramie is given in Fig. 1. The altitudes at which these maxima occurred were generally in the range of 18 to 23 km. The enhancement due to the Fuego eruption in late 1974 is apparent in Fig. 1, as is the accompanying change in size distribution; that is, the volcanic aerosol is characterized by a ratio of the mixing ratios for $r \geq 0.15\ \mu m$ to $r \geq 0.25\ \mu m$ of about 3, whereas for nonvolcanic