Reports

Terrestrial Ratio of Potassium to Rubidium and the Composition of Earth's Mantle

Abstract. *The ratios of potassium to rubidium determined for a series of oceanic volcanic rocks suggest that the K/Rb ratio of the upper mantle exceeds 1500. The similarity between this inferred K/Rb ratio for the mantle and that found in some achondritic meteorites suggests a similar overall composition for these materials.*

The hypothesis that chondritic meteorites approximate the composition of the earth has been seriously questioned by Gast (*1*) and Wasserburg *et al.* (*2*); both studies indicate that the chemical composition of the earth resembles that of the basaltic achondrites more than the chondrites. One of the most unusual characteristics of the basaltic achondrites is fractionation of the alkali metals with respect to other large ions and to each other (*3*). Their K/Rb ratios are three to seven times higher than those found in most other meteorites or in most terrestrial basalts. This unique feature of the basaltic or calcium-rich achondrites suggests that knowledge of the terrestrial K/Rb ratio may furnish a further test of the hypothesis that the mantle is similar to these objects.

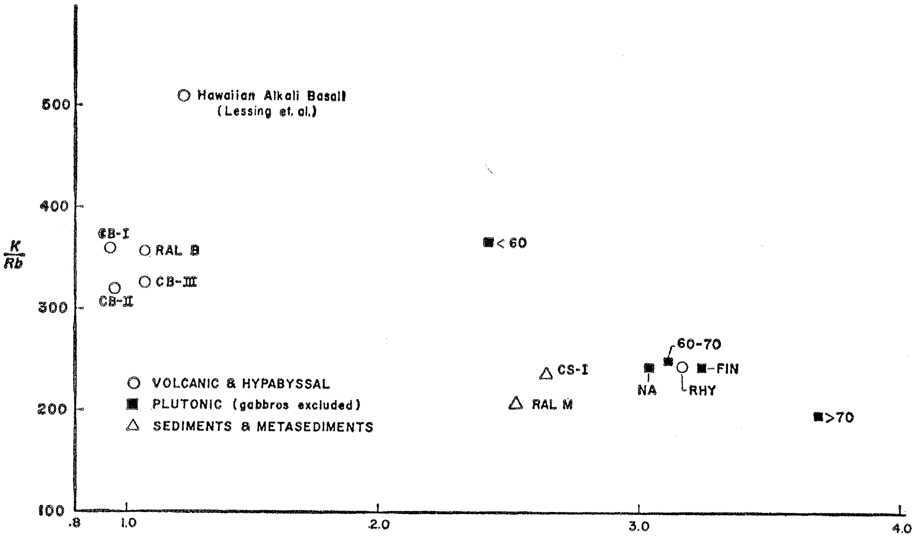

Fig. 1. Potassium/rubidium ratios and the potassium content of some composite rock samples. The points labeled *CB-I, CB-II,* and *CB-III* are composite basalts from (*1*). Points labeled *FIN* and *NA* are a composite of 27 intrusive granites from Finland and 50 granites and granite gneiss from the western U.S., respectively; the data for these samples are from (*1*). The points labeled *60, 60-70,* and *70* are composite samples made up from all the analyzed granites of the Minnesota Rock Analysis Laboratory; they were arbitrarily divided into these three groups on the basis of their SiO_2 content. The points labeled *RHY* and *RAL B* are a rhyolite and a basalt composite made up from the analyzed samples of the Rock Analysis Laboratory. Most of the volcanic rocks from both the *CB* and *RAL* composites are from continental regions. The new data shown on this figure were determined by x-ray fluorescence analysis. Analytical uncertainty for both the K and Rb content is approximately ± 10 percent.

The relative abundance of potassium and rubidium in common rocks is widely accepted as being nearly constant ($K/Rb \cong 300$) (*4*), but several recent studies (*1, 5*) of rocks with low potassium contents have shown that ratios may be as high as 1200 in some basaltic rocks. Lessing *et al.* (*5*) in particular show that the K/Rb ratio in Hawaiian basalts is about 510; they suggest that this is the ratio in the upper mantle under the Hawaiian Islands. To test the achondrite hypothesis, I have determined the potassium and rubidium contents of a series of oceanic volcanic rocks including eight submarine flows of the type recently described by Engel and Engel (*6, 7*). I have also determined the K/Rb ratio for a series of composite basalt, granite, and sediment samples; their K/Rb ratios and K contents are presented in Figs. 1 and 2. Detailed descriptions and locations for individual samples will be reported later. The composite samples (Fig. 1), especially the three composites separated on the basis of SiO_2 content, show that the K/Rb ratio is not constant even in plutonic granitic rocks. The sediment and metasediment composites suggest that there is some enrichment in Rb during sedimentation and diagenesis. The K/Rb ratios in the oceanic volcanic rocks (Fig. 2) show quite clearly that the K/Rb ratio varies systematically with the K content of these rocks. This observed K/Rb fractionation accords with that found for other lithophile elements (for example, Zr and Hf or the rare earth elements) where the larger ions increase in abundance relative to the smaller ions as the composition of a rock proceeds toward higher SiO_2 and alkali metal contents. There is also a suggestion of systematic differences between different oceanic islands: only one of nine samples from Ascension and St. Helena falls outside the area outlined for these islands in Fig. 2. The K/Rb ratios for both chondritic and achondritic meteorites (*3, 8*) are also shown in Fig. 2.

The K/Rb ratios for the oceanic tholeiites are surprisingly variable and clearly support the suggestion of Engel and Engel (*6*) that these materials are closely related to a material similar in composition to the basaltic achondrites. If the ionic radii of K and Rb do in fact control the behavior of these elements during formation and crystallization of the oceanic tholeiites, it is difficult to see how these rocks can derive from a source with a K/Rb ratio similar to that shown for the chondrites. On the contrary, if the potassium content of the upper mantle source-material of the oceanic tholeiites is 500 parts per million or less, the covariance of the K/Rb ratio and the K content indicate that the upper mantle source region has a K/Rb ratio greater than 1500. To the extent that the K/Rb ratio may be used to infer a more general composition, the inferences drawn here support the hypothesis that the upper mantle is similar in composition to the basaltic achondrites.

Data for the individual oceanic tholeiite samples and the four achondrite samples are further compared in Table 1. Although the data at this point are rather sparse, those additional facts that are available indicate that these volcanic rocks and the achondrites are remarkably similar materials.

Both the textures and the mineral assemblages found in the basaltic achondrites have led many observers to the conclusion that these objects were derived from a chondritic magma by an igneous differentiation process (*9*). The high concentrations, relative to chondrites, of certain elements, for example, Sr, Ba, U, Th, and the lanthanides, are attributed to this process by analogy with concentration patterns observed in terrestrial differentiated rock series. However, in terrestrial igneous rock series enrichment in the elements named is accompanied by enrichment in the heavy alkali metals, and an enrichment of the light rare earths relative to the heavy rare earths. Thus the unusually low abundance of the heavy alkali metals in the achondrites and the similarity of the relative rare earth abundances in the chondrites, and the eucrites and howardites (*10*), are not consistent with the hypothesis that the composition of the basaltic achondrites is entirely the result of igneous differentiation.

An alternative to the igneous differentiation hypothesis is that the alkaline earths and lanthanide elements were already enriched, and that the alkali metals were already depleted in the parent material of the basaltic achondrites. This enrichment of some elements and depletion in others could have been the result of a volatilization process similar to the one described by Urey (*11*). The qualitative chemical similarities of the earth's upper mantle and the basaltic achondrites may there-

Table 1. Concentrations (parts per million) of alkali metals and alkaline earth metals in basaltic achondrites and oceanic tholeiite. All concentrations for the achondrites except those of uranium are from (*4*) and (*8*) or from my unpublished results. All concentrations for basalts except those for the first sample are published here for the first time. All alkali-metal determinations except those for the sample from station 8 are made by the stable isotope dilution method.

Source	K	Rb	Cs	K/Rb	Sr	Ba	U
			Achondrites				
Pasamonte	425	0.23	0.011	1850	82.7	38	0.05*
Sioux County	335	.24	.012	1300	68.8	25	.06
Nuevo Laredo	367	.37	.018	990	84.4	44	.126†
Moore County	187	.16	.005	1150	79.5	22	
			Basalts				
Atlantic							
Station 7 I‡	1400	0.98	.04	1430	106	40	.085
Station 7 II	875	.75		1165	69		
Station 8	4500	9.5		475	115		
Station 20	3040	5.61		540	95		
D2-1	1345	1.42		950			
Pacific							
D-3	1560	1.14		1370			
D-4	641	0.35		1830			
PV-17	2285	3.69		620			

* From Konig and Wanke (*12*). † From Reed *et al.* (*13*). ‡ This sample is identical with that studied by Carr and Kulp (*14*); the uranium content is from their study.

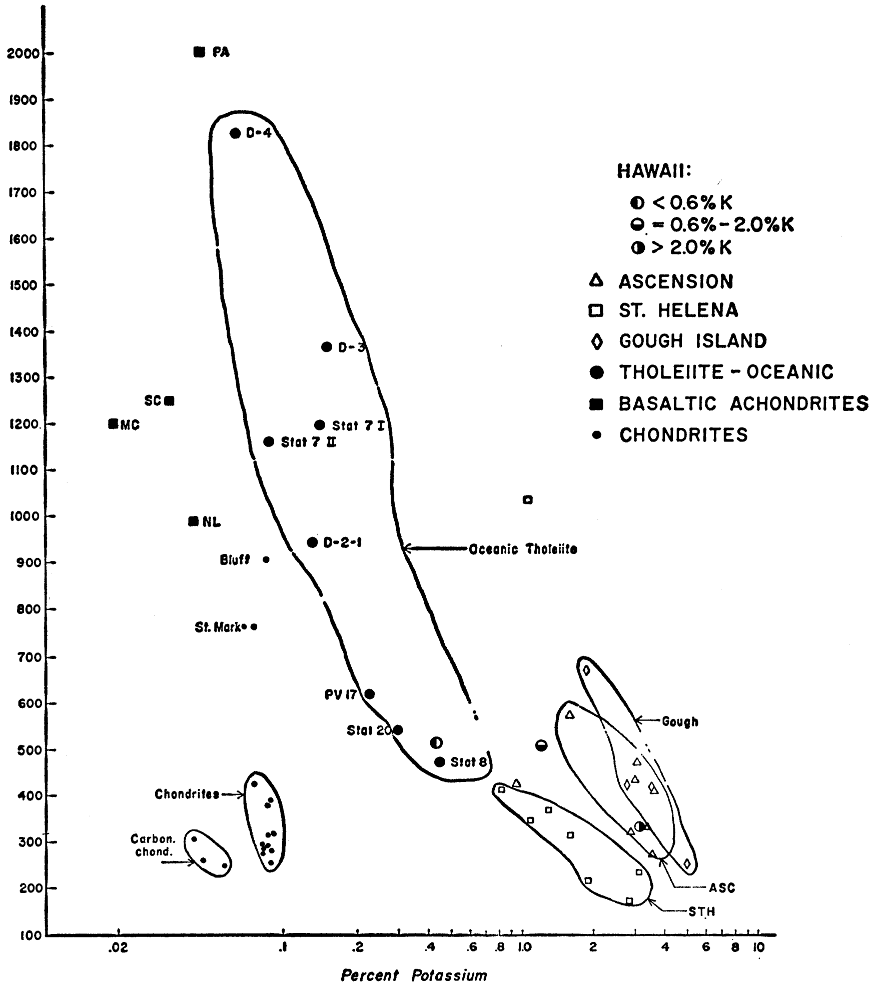

Fig. 2. Potassium/rubidium ratios and the potassium content of some oceanic volcanic rocks. The achondrites shown are *PA*, Pasamonte; *NL*, Nueva Laredo; *MC*, Moore County; and *SC*, Sioux County. Locations and descriptions for samples *D-2-1*, *D-3*, *D-4*, and *PV 17* are given in (*6*). Locations 7, 8, and 20 are given by Shand, *J. Geol.* **57**, 9 (1949). The three points for Hawaii are from (*5*). All K and Rb contents other than those given in Table 1 were determined by x-ray fluorescence, with an analytical uncertainty of ± 10 percent.

fore be an indication that such a process did indeed operate on a planetary scale in the early solar system, as proposed by Urey. Thus I suggest that Earth accreted from reduced iron and a silicate portion enriched in Ca, Al, Sr, Ba, U, Th, and rare earths and depleted in K, Rb, Cs, and other volatile elements.

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References and Notes

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High-Pressure Transitions of Germanium and a New High-Pressure Form of Germanium

Abstract. *Some transitions in germanium and other semiconductor systems have been detected after very long exposure to high pressures followed by various quenching techniques. In the case of Ge, a new high-pressure polymorph, Ge-IV, has been synthesized above 110 kilobars with a body-centered-cubic structure. The pressure for the Ge-I ⇌ Ge-III (body-centered-tetragonal structure) transition has been revised from about 120 to 25 kilobars at 30°C. The transition from the Ge-I (diamond structure) to the Ge-II (white tin structure) is metastable up to 140 kilobars. Thus some phase diagrams based on discontinuities observed in essentially dynamic systems may be inaccurate.*

Investigations of phase transitions in germanium under high pressures have revealed (i) that the melting point decreases with increasing pressure (*1*); (ii) that resistivity methods (*2*) detect a reversible, nonquenchable transition which high-pressure x-ray methods (*3*) indicate are related to the $\alpha \rightleftharpoons \beta$-tin transition [$\text{Ge-I}_{(\text{diamond})} \rightleftharpoons \text{Ge-II}_{(\beta\text{-tin})}$] at about 120 kb; (iii) that the shift of absorption edge with pressure goes through a maximum at about 45 kb (*4*); (iv) that a crystalline phase designated as Ge-III can be formed at pressures "exceeding 120 kb" (*5*) and "quenched" to ambient conditions.

We report on our intensive study of the relationships existing in the high-pressure crystalline phases of Ge under conditions designed to approach equilibrium. Another crystalline form has now been found, and this phase (Ge-IV) is the analog of the quenchable high-pressure body-centered-cubic (bcc) phase reported for silicon (*6*).

In order that the germanium might approach equilibrium between 35 to 140 kb and −78° to 450°C, "long-run" experiments were undertaken with opposed anvil apparatus (*7–9*).

Our Bridgman compound anvils were of tungsten carbide (type 886 or K96) force-fitted into thick right cylinders of Rene 41 alloy (*8*). The familiar configuration for the sample was used for most of the runs at lower pressures, the anvils having working faces of 6.35 mm and 4.76 mm diameter; the sample (99.999 percent Ge) was contained in a nickel ring 0.25 mm thick and was covered with discs of foil (0.025 mm thick and made of platinum containing 10 percent rhodium). For runs above about 80 kb the nickel retaining ring was omitted because of "blowouts," and a packed sample 0.50 mm thick was sandwiched between the aforementioned foil discs. Owing to extrusion of sample under pressure, the thickness of this wafer was decreased to 0.23 mm for a 4.76-mm diameter anvil face and to 0.178 mm for a 3.17-mm face, the ratio of diameter to thickness comparing favorably with the ideal ratios of 15 to 20 reported by Myers *et al.* (*9*).

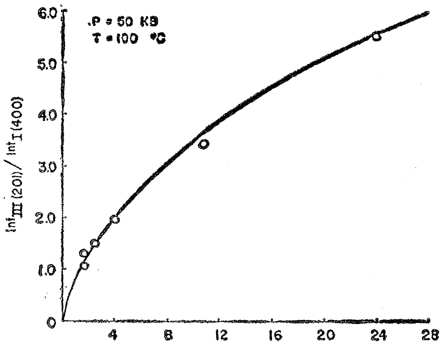

Fig. 1. X-ray diffraction intensity (*Int*) ratio of the $\text{Ge-III}_{(201)}$ and $\text{Ge-I}_{(400)}$ as a function of time at a fixed pressure and temperature, illustrating the sluggishness of the transition.

Actual pressures on the samples were probably not higher than we report. In assigning the pressure values we have considered diameter-to-thickness ratios (*9*) and results of varying such ratios in many runs with Ge. Furthermore, since the metallic sample assembly flows easily on the application of pressure, inhomogeneities of packing conducive to intensification of local pressure must tend to diminish with time.

Thus our achieving the transition at lower pressures cannot be attributed either to intense local shear on first raising the pressure or to hypothetical large pressure inhomogeneities; first raising the pressure up to 140 kb produced no quenchable transitions, and it was only after 10 hours at a stable configuration of the sample assembly that the dense phases were detectable by x-ray methods. The addition of continuous displacive shearing of small amplitude (*10*) did not change the transition pressures or the interval required for conversion.

Our investigation of the pressure-temperature phase relations of the Ge-I ⇌ Ge-III transition reported by Bundy and Kasper (*5*) to take place at pressures in excess of 120 kb indicated that the transition could be obtained at pressures as low as 25 kb at room temperature. However, at such low pressures, runs several days long were required to obtain an appreciable amount of Ge-III phase (see Fig. 1). The data shows that the "working" time required for an appreciable amount of GE-III to form is 4 to 5 days. Short runs (minute) would not re-