Trace Elements

Abundance of Alkali Metals, Alkaline and Rare Earths, and Strontium-87/Strontium-86 Ratios in Lunar Samples

Abstract. *The variation in trace element abundance patterns indicates that lunar igneous rocks are the product of extensive igneous fractionation. Variations in the* Sr^{87}/Sr^{86} *ratio indicate that these rocks crystallized* $3.5 \pm 0.3 \times 10^9$ *years ago.*

The concentrations of K, Rb, Cs, Sr, Ba, La, Ce, Nd, Sm, Eu, Gd, Dy, Er, Yb, Lu and the isotopic composition of Sr have been determined mass spectrometrically. By using quantitative ion exchange separation procedures the concentrations of Na, Ca, Zn, and Ti were determined on the same samples using other techniques. Results of the analysis of individual 200- to 300-milligram samples of seven igneous rocks, one breccia, and one soil sample are given in Table 1.

The chemical data obtained in this study and in the preliminary examination (*1*) show that the nine samples analyzed are remarkably similar in terms of a wide range of chemical characteristics. These characteristics clearly distinguish the Tranquillity Base basalts from basaltic meteorites and terrestrial basalts. The primary distinguishing characteristics are (i) the high concentration of titanium, zirconium, and rare earth elements (REE); (ii) the two- to fourfold depletion of Eu relative to Sm and Gd; (iii) the low abundance of sodium relative to other major elements.

On a finer scale the data clearly distinguish three groups of samples from each other. The fine grained (type A) samples 10071, 10017, and 10049 are very similar. In fact, 10071 and 10049 are almost identical for all the elements reported here.

Coarser grained (type B) rocks 10020, 10003, 10062, and 10058 form a second distinguishable chemical group. In the rocks we have analyzed, the fine grained rocks have higher K and Rb contents, lower K/Rb ratios, higher REE abundances, higher Sm/Eu ratios, lower La/Sm ratios, and higher Ba/Sr ratios than the coarse grained rocks.

Our soil and breccia samples are

Table 1. Concentrations of 20 elements in nine samples from Tranquillity Base. All concentrations except CaO and TiO_2 are given in parts per million. Those shown in roman were determined by stable isotope dilution; others were determined by the methods indicated.

Element	Soil sample 10084	Analytical error (%)*	Breccia sample 10073	Fine grained igneous rocks			Coarse grained igneous rocks			
				10049	10017	10071	10062	10020	10003	10058
Na†	*3200*	±*10*	*3500*	*4000*	*3800*	*3900*	*3300*	*2800*	*2900*	*2900*
K	1200	±3	1200	2730	2610	2770	628	486	470	877
Rb	2.79	±3	2.89	6.24	5.63	5.93	0.90	0.63	0.49	0.98
Cs	0.104	±10	0.098	0.166	0.155	0.170	0.032		0.022	0.027
Sr	171.4	±2.5	167.5	160.8	174.8	160.9	141.6	149.8	158.6	218.3
Ba	176	±5	175	338	308	327	79.9	77.1	108	117
La	16.3	±3		29.2	26.2	27.8	13.8	7.95	15.1	11.7
Ce	47.6	±3	46.5	84.2	77.2	83.5	42.7	25.8	47.2	40.2
Nd	36.8	±3	35.4	64.2	59.7	64.8	37.0	24.1	40.0	41.2
Sm	13.1	±3	12.4	22.5	21.0	22.7	13.3	9.49	14.5	17.1
Eu	1.77	±3	1.70	2.31	2.15	2.29	2.02	1.61	1.82	2.64
Gd	17.2	±5	16.9	28.0	27.0	29.2	17.2	12.8	20.2	23.6
Dy	19.7	±5	19.2	36.1	34.1	34.5	20.4	16.2	22.4	27.3
Er	12.1	±5	11.5	19.9	19.2	21.1	12.0	9.99	13.7	16.3
Yb	11.5	±5	10.7	20.2	18.8	20.2	12.1	9.77	12.7	15.2
Lu	1.58	±7	1.56		2.66	2.87	1.73	1.43	1.81	2.14
Ni‡	*198*	±15	*161*	*12*	*17*	*24*	*13*	*10*	*18*	*13*
Zn†	*24*	±15	*24*	*9.3*	*30*	*11*	*9.9*	*10*	*7.4*	
CaO%§	*11.4*	±3	*11.0*	*10.4*	*10.1*	*10.9*	*10.8*	*10.8*	*10.3*	*12.3*
TiO_2*%*§	*7.7*	±5	*7.5*	*11.5*	*12.4*	*13.8*	*10.7*	*10.4*	*9.2*	*8.3*
La/Sm	1.24			1.29	1.25	1.22	1.04	.837	1.04	.679
Sm/Eu	7.40		7.30	9.74	9.76	9.90	7.58	5.90	7.92	6.47
Ba/Sr	1.025		1.045	2.10	1.77	2.03	0.564	.517	0.677	.542
K/Rb	430		415	437	464	467	698	772	959	895
$Sr^{87/86}$‖	0.7015 ±.0005		0.7025 ±0.0006	0.7043 ±0.0006	0.7046 ±.0003	0.7041 ±.0004	0.7002 ±.0004	0.7005 ±.0006	0.6993 ±.0004	0.6996 ±.0005

*90 percent confidence limits based on replicate analysis of other samples. †Atomic absorption analysis of separated fraction. ‡X-ray fluorescence analysis of powder. §Colorimetric or titrimetric analysis of separated fraction. ‖ Normalized to 8.375.

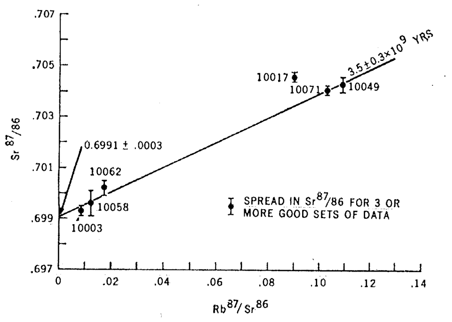

Fig. 1. Chondrite normalized abundance patterns for nine rare earth elements and Sr and Ba. Chondrite REE concentrations are from Frey *et al.* (*9*), Dy is interpolated to be 0.335 ppm, Ba is taken to be 3 ppm, and Sr 11 ppm. Data for sample V21-40 and average ORB are from Kay *et al* (*5*).

nearly identical and in most respects chemically intermediate between the coarse and fine grained igneous rocks. However, both samples of these materials are clearly distinguished from the igneous rocks by higher nickel and zinc contents and lower TiO_2 contents. (We conjecture that the high zinc content of our sample—a surface chip—from rock 10017 is an indication that the surface composition of this rock may be different from the bulk of the rock.) The soil and breccia samples may have been modified with respect to the underlying bedrock by (i) a mixture of meteorite impact material, (ii) addition of material by the solar wind and (iii) enrichment in materials that may have condensed out of the lunar atmosphere after vaporization out of superheated silicate liquids produced by impact melting. The high nickel content is probably due to the first of these causes—that is, the admixture of about 0.1 percent of nickel iron or approximately 1 percent of average chondrites. The low TiO_2 content of the soil and breccia indicates that rocks with TiO_2 contents much lower than those analyzed here make up a significant fraction of the soil.

The large variations in K, Rb, Cs, and Ba content within the otherwise similar igneous rocks are quite puzzling. If explained in terms of simple fractional crystallization processes they would require 80 to 90 percent crystallization of the "coarse grained" liquid to produce the "fine grained" liquid. Such extensive crystallization seems inconsistent with the near identity of the major element composition of these two groups of rocks. Another possible explanation of the nearly fivefold variation on K, Rb, Cs, and Ba content involves the existence of a third liquid containing 2 to 4 percent K, 50 to 100 ppm rubidium, and 2000 to 4000 ppm barium. Several percent of such a liquid added to the "coarse grained" liquid would explain the difference between these two groups of rocks. The low K, Rb, and Cs contents may also be explained if the coarse grained rocks are locally accumulated from a liquid having most of the observed characteristics—that is, large Eu anomalies and low Sr content.

Tentatively accepting this hypothesis, we now consider the origin of most of the chemical characteristics of both the coarse and fine grained igneous rocks. At the outset we observe that it is quite unlikely that the observed composition is entirely primary in the sense that it is material formed directly from dispersed matter in the solar nebula. The extreme enrichment of Ti, REE, U, and Th (*1*), the fractionation of the REE, and the depletion of Eu, Ba, Sr, Ti, and Al are all difficult to explain by the volatilization or fractional condensation processes. On the other hand, the low abundance of elements which may be volatile at high temperature, e.g., the alkalis, Zn, and Ni, can be ascribed to the primitive composition of the moon. Both the low K/U ratio (*1*) and Rb/Sr ratio (see below) indicate that some chemical fractionation has taken place during the formation of both the moon and the earth. Therefore, one need not call upon igneous fractionation processes to explain all of the nonchondritic relative abundances observed in the lunar samples. In the following discussion we examine the possible fractionation of large refractory ions with respect to each other in terms of igneous processes. The abundances of these ions relative to chondritic abundances are illustrated in Fig. 1. The dominant characteristics illustrated are (i) the general and extensive depletions of Sr and Eu with respect to the other ions and (ii) the increasing depletion of the elements Nd, Ce, La and sometimes Ba (opposite to the general case for terrestrial basalts). The REE and Ba abundance patterns in the Tranquillity Base basalts are similar to those observed for oceanic ridge basalts (ORB) but much higher in total REE plus Ba abundances.

It has been shown that most mafic minerals (e.g., pyroxenes, amphiboles, garnets, and spinels) that contain significant concentrations of REE and Ba tend to fractionate the REE with respect to each other (*2*, *3*). Thus any igneous processes that involve a significant distribution of REE between such mafic phases and a basaltic liquid would tend to fractionate the REE in the liquid relative to the associated crystalline phases. In spe-

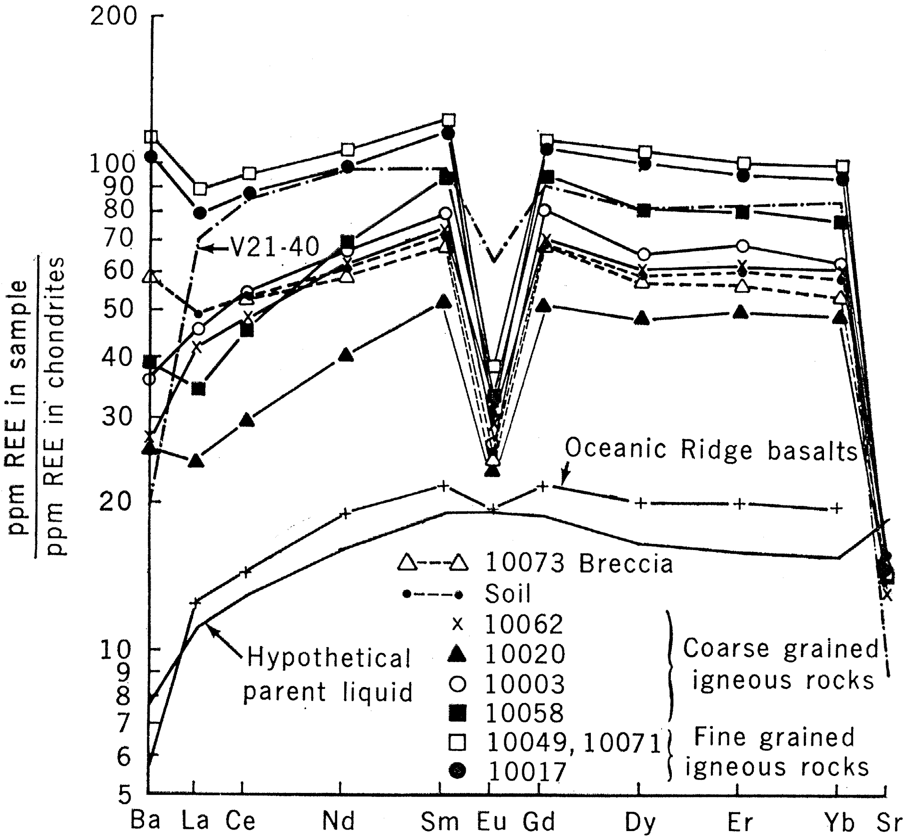

Fig. 2. Isochron diagram for six lunar rocks ($\lambda = 1.39 \times 10^{-11}$ year^{-1}).

cific cases it may be possible by arranging proper combination of phases, e.g., basaltic liquid, pyroxene, and spinel, to obtain a situation where the liquid REE abundances are unfractionated with respect to the bulk solid. This is, however, a special case that would probably not produce the other element abundances and ratios, e.g., Ti, Zr, Al, and Cr (*1*), observed in the Tranquillity Base basalts. It has been proposed that the relative lack of REE fractionation in the ORB is due to complete extraction of the REE from the earth's mantle (*4*). The low Al content and high Ti content found for the lunar materials is quite inconsistent with this hypothesis for the lunar case. A detailed study of the ORB shows that the total REE, FeO, and TiO_2 contents increase together and, furthermore, that those rocks high in total REE have small negative Eu anomalies (*5*). The explanation proposed for these variations in the ORB abundance patterns is the removal of basic plagioclase and olivine (*5*). A similar hypothesis is proposed here to explain the abundance patterns observed in the lunar basalts. The original composition and pattern of a liquid consisting of 6 parts of plagioclase (An 96), 1½ parts olivine (Fo 80) and 2½ parts of "coarse grained" liquid (10062 and 10003 averaged) are shown in Fig. 1. We recognize that absence of pyroxene from such a liquid may be unusual. If pyroxene were removed from the parent liquid in significant amounts, less than 10 percent, the Cr content of this initial liquid would have to be over 1 percent by weight (*4*). Assuming that the distribution coefficients between liquid and plagioclase for Eu, Sr, Ba, and REE are 1.3, 0.7, 10, and 20 (*2*), respectively, the CaO, Al_2O_3, TiO_2, FeO, and MgO concentrations of such an original liquid would be about 15, 25, 3, 7½, and 8 percent, respectively. If this hypothesis is correct, we infer that cumulates rich in plagioclase should occur on the lunar surface. It is also of some interest that the results of the Surveyor 7 analysis (*6*) indicate unusually high Al_2O_3 (21 percent) and CaO (15 percent) contents and relatively low Fe contents are found in highland regions.

The depletion of Ba and La relative to heavy REE and broad peak at Sm and Gd is not explained by this process. These features could be due to other minor phases that have crystallized and separated from the liquid or to fractionation that takes place during production of parent liquid in the lunar interior. If the proposed original liquid is produced by partial melting in a lunar mantle (< 20 percent) we infer that the U, Th, and K contents of the parent lunar mantle are less than 0.08, 0.3 and 100 ppm, respectively.

The Sr^{87}/Sr^{86} ratios and Rb^{87}/Sr^{86} ratios of six igneous rocks are shown in an isochron diagram in Fig. 2. With the exception of sample 10017, these data define an isochron indicating that the time of crystallization was 3.5 ± 0.3 billion years ago. We have no explanation for sample 10017 but note again that our sample was a surface chip. The limits placed on the difference between the initial ratio (0.6991) and the achondrite initial ratio, 0.6989 (*7*), indicate that the source of these igneous rocks has a rubidium-strontium ratio less than one-tenth that of chondrites. If the igneous liquids were derived from the interior of the moon 3.5 ± 0.3 billion years ago, we conclude that large portions of the moon must be even more depleted in rubidium relative to strontium than the earth (*8*). The possibility that the high abundance of refractory elements e.g., Ca, Al, TiO_2, REE, and so forth, is a primary characteristic of a large part of the moon should not be overlooked. Unless this possibility is excluded one cannot infer general differentiation of the moon from the existence of basaltic rocks on the lunar surface.

PAUL W. GAST
NORMAN J. HUBBARD
Lamont-Doherty Geological Observatory, Palisades, New York

References and Notes

1. Lunar Sample Preliminary Examination Team, *Science,* **165**, 1211 (1969).
2. C. C. Schnetzler and J. A. Philpotts, *Geochim. Cosmochim. Acta,* in press.
3. F. A. Fay, *ibid.* **33**, 1429 (1969).
4. P. W. Gast, *ibid.* **32**, 1057 (1968).
5. R. Kay, N. J. Hubbard, P. W. Gast, *J. Geophys. Res.,* in press.
6. J. H. Patterson, E. J. Franzgrote, A. L. Turkevich, W. A. Anderson, T. E. Economou, H. E. Griffin, S. L. Grotch, K. P. Sowinski, *ibid.* **74**, 6120 (1969).
7. D. A. Papanastassiou and G. J. Wasserburg, *Earth Planet. Sci. Lett.* **5**, 361 (1969).
8. P. W. Gast, in *History of the Earth's Crust,* R. A. Phinney, Ed. (Princeton Univ. Press, Princeton, N.J., 1968), pp. 15-27.
9. F. A. Frey, M. Haskin, J. Poetz, L. Haskin, *J. Geophys. Res.* **73**, 6085 (1968).
10. This research was supported by NASA grant NAS 9-7895. The chemical separations, data reductions, and Na and Zn determinations were done by H. Wiesmann. We thank R. Kay for operating the computer and Chi-Yu Shih for doing the CaO and TiO_2 determinations. Lamont-Doherty Geological Observatory contribution No. 1441.

4 January 1970

Rare Earth Elements in Returned Lunar Samples

Abstract. *A linear correlation between concentrations of Sm and ratios of Sm to Eu for nine lunar samples suggests that those samples could correspond to liquids from equilibrium partial melting of a common source. On the basis of partition coefficients in terrestrial systems, the fraction of melting would not have exceeded about 15 percent and the immediate source could have been composed of olivine, orthopyroxene, and opaque minerals plus at least 25 percent feldspar, with at most a few percent calcic clinopyroxene and less than 1 percent apatite. The large Eu depletions could also have been produced by fractional crystallization if the ratio of* Eu^{2+} *to* Eu^{3+} *in lunar magmas significantly exceeds the values for terrestrial magmas.*

We present here concentrations for 12 of the rare earth elements (REE) in nine samples of lunar material returned to earth by the Apollo 11 astronauts (*1*). Included are five fine-grained igneous rocks (type A), one medium-grained igneous rock (type B), two breccias (type C), and "fine" material less than 1 mm in diameter (type D) from the lunar soil. The igneous rocks were received as 1-g chips, and the breccias and soil as cuts of powders. The concentrations of the REE were measured by neutron activation analysis; the REE were separated as a group from the irradiated samples and then were assayed by Ge-Li gamma-ray spectrometry.

The REE concentrations for the lunar samples plus those for a terrestrial basalt which was analyzed in the same irradiation as the lunar breccias are given in Table 1. The accompanying uncertainties are based strictly on counting statistics and are applicable to the comparison of one REE with the others in the same rock. Values for all the REE in any particular sample may be systematically in error by 1 to 2 percent.

Relative and absolute REE abundances for these samples are compared in Fig. 1 with those for a composite of nine chondritic meteorites (*2*). The ratios of the concentrations in parts per million for each element in a sample to the concentration in parts per million for the same element in the chondrites are plotted as a function of REE atomic number (*3*). Included as a dashed line