Geochemistry of Apollo 15 Basalt 15555 and Soil 15531

Abstract. *Major and trace element concentrations have been determined by atomic absorption spectrophotometry, colorimetry, and isotope dilution in Apollo 15 mare basalt 15555 from the Hadley Rille area; trace element concentrations have also been determined in plagioclase and pyroxene separates from basalt 15555 and in soil 15531 from the same area. Basalt 15555 most closely resembles in composition the Apollo 12 olivine-rich basalts. The concentrations of lithium, potassium, rubidium, barium, rare-earth elements, and zirconium in basalt 15555 are the lowest, and the negative europium anomaly is the smallest, reported for lunar basalts; this basalt might be the least differentiated material yet returned from the moon. Crystallization and removal of about 6 percent of plagioclase similar to that contained in the basalt would account for the observed europium anomaly; if plagioclase is not on the liquidus of this basalt, a multistage origin is indicated. Mineral data indicate that plagioclase and pyroxene approached quasi-equilibrium. Most of the chemical differences between basalt 15555 and soil 15531 would be accounted for if the soil were a mixture of 88 percent basalt, 6 percent KREEP (a component, identified in other Apollo soils, rich in potassium, rare-earth elements, and phosphorus) and 6 percent plagioclase (anorthosite?).*

As part of the preliminary examination of samples returned by the Apollo 15 mission, we received a 0.5-g piece of sample 15555, a mare olivine-basalt from station 9a near Hadley Rille. We present here major and trace element concentration data on this sample and compare these data with those of rocks from previous lunar missions and an Apollo 15 soil from the same area.

Analyses of the bulk chemical composition of sample 15555, given in Table 1, were carried out on duplicate 50-mg aliquants by the atomic absorption spectrophotometric procedure previously described (*1*), except for Ti and P, which were determined colorimetrically with the use of H_2O_2 and molybdivanado-phosphoric acid complex, respectively, on aliquots of the same solution used for atomic absorption. Accuracy checks were made for the various constituents by coanalysis of the respective U.S. Geological Survey (USGS) reference silicate rocks as listed in Table 1. The precision of the atomic absorption and colorimetric determinations was approximately ± 1 percent (relative) for all elements. The trace elements listed in Table 2 were determined by mass spectrometric stable isotope dilution. Modifications of our standard procedure have been described in a recent paper on Luna 16 analyses (*2*). We carried out the analyses of the Apollo 15 samples reported here immediately after our Luna 16 analyses, using the same batch of reagents; blank analyses for K, Rb, and Sr show that the lower contamination levels reported in the Luna 16 paper [blank A, table 1 of (*2*)] are applicable to the present work. For whole rock 15555 and soil 15531 the blank corrections were negligible, less than 1 percent in all cases, except for K, Rb, Zr, Ba, and Eu in sample 15555 where the blank corrections were between 1 and 2.5 percent. Blank corrections for the mineral separate samples were larger. For 15555 plagioclase the blank corrections (in percent) were as follows: Rb, 36; Ce, 29; Nd, 22; Sm, 15; Yb, 12; all others, less than 10. For 15555 pyroxene the blank corrections were as follows: Rb, 16; K, 14; Ba, 11; Eu, 11; all others, less than 10.

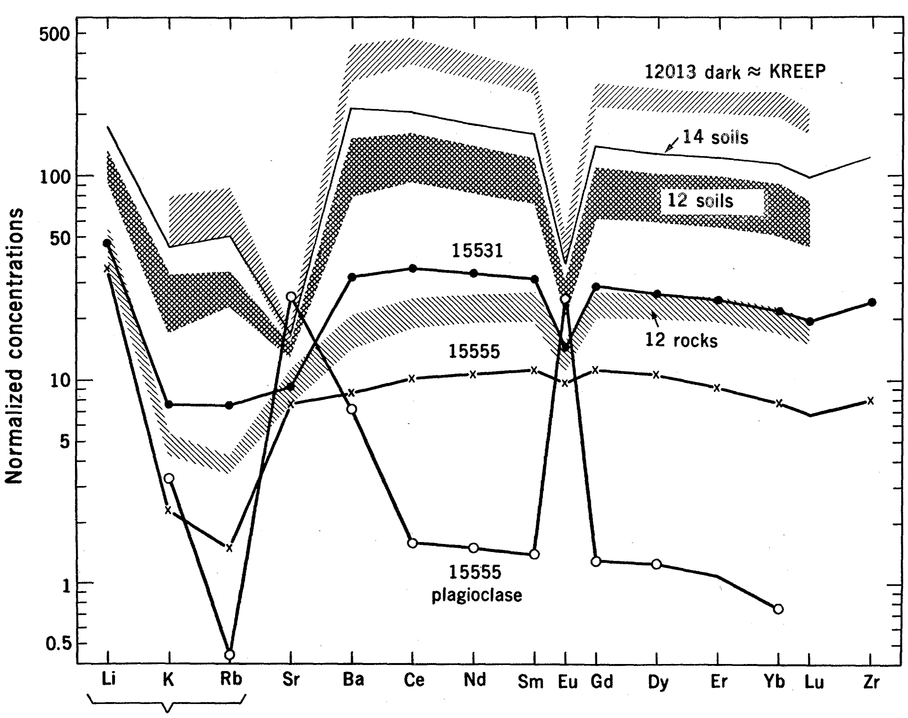

Fig. 1. Trace element concentrations normalized to chondritic abundances (alkali elements times 10) in igneous rock 15555 (×), plagioclase separated from rock 15555 (○), and soil 15531 (●). Also shown are the normalized concentrations observed in six Apollo 14 soils [(*1*) and unpublished results], and the concentration ranges observed for the dark-colored portion of sample 12013, Apollo 12 soils, and the Apollo 12 "normal sequence" igneous rocks (*5, 10*). Normalizing values are listed in Table 2.

Comparison of the bulk chemical composition of our specimen of sample 15555 with the x-ray fluorescence analysis reported by the Preliminary Examination Team (*3*) showed significant differences for Ti, Fe, Al, Mg, and Cr contents. Microscopic examination of a thin section (section 31) of this rock showed layering of opaque and silicate minerals; such mineralogical heterogeneity might well account for the differences in these two analyses, particularly in view of the relatively small sample sizes.

Rock 15555 has major and trace element concentrations similar to those of the Apollo 12 mare basalts. The trace element concentrations, reported in Table 2 and shown normalized to chondritic abundances in Fig. 1, are lower (except for Sr) than for any reported lunar basalt. They most closely match in absolute concentrations the olivine-rich basalt 12035 (*4*) and those from the Apollo 12 core at a depth of 13.2 to 14.4 cm (*5*), which undoubtedly was a partially disintegrated clod of an olivine-rich rock. The negative Eu anomaly in sample 15555 is the smallest observed in lunar basalts. The low concentrations of large cations, which tend to increase with differentiation, and the small Eu anomaly suggest that the Apollo 15 mare basalts might be the least differentiated material yet returned from the moon.

Plagioclase and pyroxene mineral separates were obtained from rock 15555 by an electromagnetic technique. The purity of the separates was estimated to be more than 95 percent. Ratios of trace element concentrations in the mineral to those in the whole rock obtained for this sample are in good agreement with those obtained on Apollo 11, Apollo 12 (exclusive of sample 12021), and Apollo 14 samples, even though the rock concentrations range over an order of magnitude and there are differences in relative abundances (*5*, *6*). In addition, these mineral/whole rock ratios agree fairly well with determinations of phenocryst/matrix ratios made on a number of terrestrial rocks (*7*). This agreement suggests that these minerals approximate quasi-equilibrium phases in equilibrium with liquids similar to their whole rocks. On the assumption that the plagioclase/whole rock ratios represent partition values and that 15555 whole rock represents a liquid, it is possible to determine the amount of feldspar removal necessary to generate the small negative Eu anomaly from a non-anomalous parent liquid. Either equilibrium or fractional crystallization of about 6 percent plagioclase by itself would produce the observed anomaly from a parent liquid with normalized Sm and Eu values of 10.7 each. As in the case of other lunar mineral separates, essentially all the Li, Sr, and Eu in sample 15555 can be accounted for in terms of the major mineral phases, if one uses modal mineral compositions (*8*). Approximately 72 percent of the K is accounted for on the basis of these two analyzed phases; for the other elements the two separated minerals contain less than 50 percent of the amounts in the whole rock.

Ratios of Eu^{2+} to Eu^{3+} for the pyroxene, plagioclase, and whole rock 15555 have been calculated according to the method of Philpotts (*9*). Two values were calculated for each phase. The results were as follows: pyroxene Eu^{2+}/Eu^{3+} ratio, 1.43 ± 6 percent; whole rock ratio, 3.1 ± 10 percent; plagioclase ratio, 89.6 ± 4 percent. The good consistency of the results supports the idea of quasi-equilibration of the phases; it offers some further justification for the above use of plagioclase/whole rock ratios for Sm and Eu as an approximation of mineral/liquid partition coefficients. The Eu^{2+}/Eu^{3+} ratio for 15555 plagioclase is identical to that for 12040 plagioclase (*5*). The pyroxene ratio is slightly higher than those for 12040 and 12035 pigeonites but not as high as that for 12021 phenocryst pigeonite (*5*). We conclude on the basis of the Eu^{2+}/Eu^{3+} calculations that sample 15555 crystallized under conditions (including oxidation-reduction) similar, and probably intermediate, to those for the crystallization of samples 12035 and 12040, but that sample 15555 crystallized slightly more rapidly, but not nearly as fast as the matrix of sample 12021 or the Apollo 11 basalts (*5*, *6*). The grain sizes of these samples appear to be consistent with these conclusions.

Soil sample 15531 is the <1-mm size fraction of a scoop taken at site 9a, approximately 25 m from rock 15555; both samples were collected about 10 to 15 m from the edge of Hadley Rille. The <1-mm size fraction is about 90 percent of the total unsieved sample. Soil 15531 has the lowest concentrations of K, Sr, Ba, rare-earth elements, and Zr of any lunar fines material yet reported. It is most similar in absolute

Table 1. Bulk chemical analysis (in percentage by weight) by atomic absorption spectrophotometry and colorimetry; analyst, D. F. Nava.

Component	Basalt 15555	USGS reference rocks* W-1		BCR-1		PCC-1	
SiO_2	45.0	52.7	(52.6)			42.3	(41.9)
TiO_2	1.60			2.19	(2.23)	0.02	(0.02)
Al_2O_3	9.37	15.08	(14.85)	13.66	(13.66)		
MgO	12.22	6.63	(6.62)				
CaO	9.25	10.90	(10.96)				
Na_2O	0.26	2.11	(2.12)	3.34	(3.31)		
K_2O	0.03					0.02	(0.02)
FeO†	21.18			11.95	(12.22)		
MnO	0.26			0.18	(0.18)		
P_2O_5	0.07	0.12	(0.14)				
Cr_2O_3	0.47	0.018	(~0.016)	<0.002	(~0.002)		
Total	99.71						

*Reference silicate rocks W-1, BCR-1, and PCC-1 were analyzed concurrently with sample 15555 to provide accuracy checks. Data in parentheses are recommended values from the literature (*11*).
†Total iron is expressed as FeO.

Table 2. Trace element isotope dilution analyses of Apollo 15 material (in parts per million by weight).

Element	15555 whole rock	15555 plagioclase	15555 pyroxene	15531 (<1-mm fines)	Normalizing values
Li	6.36	11.3	4.97	8.38	1.8
K	230	361	105	757	1000
Rb	0.445	0.131	0.204	2.24	3
Sr	84.4	282	26.1	103	11
Ba	32.2	27.1	12.2	117	3.66
Ce	8.06	1.25	3.14	28.4	0.787
Nd	6.26	0.87	2.99	19.6	.580
Sm	2.09	0.27	1.19	5.81	.185
Eu	0.688	1.84	0.271	1.00	.071
Gd	2.90	0.34	1.88	7.44	.256
Dy	3.27	0.39	2.29	8.06	.303
Er	1.70		1.27	4.67	.182
Yb	1.45	0.14	1.04	4.14	.188
Lu				0.61	.034
Zr	57.3		45	173	7
			Weight (mg)		
	108.1	15.6	29.3	127.8	

abundances of the Luna 16 fines (*2*), but more closely resembles the Apollo 12 and Apollo 14 soils in relative abundances, particularly in the rare-earth element concentrations, and K/Rb ratios. Soil 15531 is enriched in all the trace elements listed in Table 2 as compared to the igneous rock 15555. These enrichments, although smaller, are reminiscent of the differences between Apollo 12 rocks and soils, as shown in Fig. 1. In the case of Apollo 12 soils, the enrichment was ascribed to a component rich in trace elements called KREEP (so called as it is especially rich in potassium, rare-earth elements, and phosphorus) (*4*), with a composition similar to that of the dark-colored portion of the rock 12013 (*10*). The amounts of this material in the Apollo 12 soils varied from about 15 to 50 percent. Likewise, the compositions of Apollo 14 soils (also shown 15555 and soil 15531 are representative of material in this area, preliminary calculations on the amount of KREEP in Fig. 1) suggest they could be very rich in KREEP. If we assume that rock in the soil can be made. Using the portion of dark sample 12013 that is most enriched with trace elements as an end member representing KREEP (the analyses of which are quite variable), somewhere between 5 and 7 percent of KREEP in the soil can account for most of the observed concentration differences between samples 15555 and 15531. Exceptions are Eu and Sr, whose concentrations would be low in such a mixture. The addition of approximately 6 percent 15555 feldspar (or anorthosite?) would account for the Sr, but not quite all of the Eu. This mixture of 88 percent 15555 basalt, 6 percent KREEP, and 6 percent plagioclase would also produce a close match for most of the major elements. If the Apollo 14 soils, which are quite uniform in composition, are taken as the high trace element end member, the amount of Apollo 14 soils necessary to produce the soil enrichment rises to between 11 and 14 percent; here again, an addition of about 5 percent plagioclase is necessary to account for the Sr and Eu concentrations.

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Age of a Lunar Anorthosite

Abstract. *The crystallization age of an Apollo 15 anorthosite rock, 15415,9, returned from the lunar highlands has been measured to be* $(4.09 \pm 0.19) \times 10^9$ *years. The primitive lunar crust must have been formed in the first 300 to 400* $\times 10^6$ *years. The results give some credence to the hypothesis that the primitive lunar surface was molten and large-scale fractional crystallization occurred in the early history of the moon.*

Anorthosite rock fragments and glasses were unexpectedly found in the lunar material brought back by the Apollo 11 mission. The light color, low density, and chemical resemblance to the Surveyor 7 analyses (*1*) of material in the lunar highlands led Wood *et al.* (*2*) to believe that the anorthosite fragments were derived from the older lunar highlands. Wood *et al.* (*2*) proposed a lunar model which suggests that anorthosite formed the primitive outer crust of the moon because of fractional crystallization in magma chambers near the lunar surface and that its rise to the moon's surface was due to its low density (2.7 to 2.8 g/cm^3) compared to that of lunar basalt (3.2 to 3.3 g/cm^3). The lunar surface was later extensively modified by bombardment with large meteoritic or planetary bodies, thus limiting the abundance of large crystalline complexes of anorthosite to the lunar highlands. If this model is correct, radiometric ages for anorthosite should greatly help us to understand the evolution of the lunar crust by placing limits on the time of formation of the anorthosite complexes.

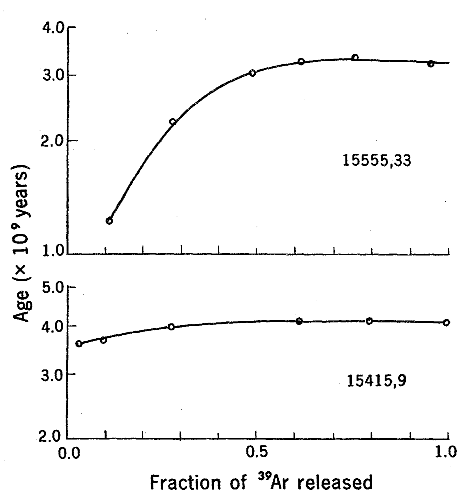

Fig. 1. The ^{40}Ar-^{39}Ar release pattern of lunar rocks 15555,33 and 15415,9-1.

The first large specimen of lunar anorthosite to be collected was found in the Apennine Mountains by astronauts David Scott and James Irwin. This rock presents a delicate challenge to lunar chronologists because it is extremely poor in radioactive elements; and its potassium concentration is only about 100 parts per million. We now report on the measurements of the age of this rock, as well as on the age of a lunar basalt from Hadley Rille.

The lunar rocks 15415,9-1 and 15555,33 were dated by the ^{40}Ar-^{39}Ar method, which has been described by Merrihue and Turner (*3*), Turner (*4*), and Mitchell (*5*). In brief, this technique consists of converting a fraction of ^{39}K in the rock to ^{39}Ar by a ^{39}K (neutron, proton) ^{39}Ar reaction with fast neutrons. By heating in stages, ^{39}Ar is released, along with radiogenic ^{40}Ar. The ^{40}Ar/^{39}Ar ratio is then measured in a mass spectrometer. From temperature release data one can calculate the retention ages and deduce information about its postcrystallization thermal history.

The lunar anorthosite, 15415, was collected from the north-northwest rim of Spur crater. From an examination of a thin section, this rock consisted of 99 to 98 percent polysynthetically twinned