

A Chemical Model for Lunar Non-Mare Rocks

Norman J. Hubbard
*NASA/Johnson Space Center
Houston, Texas*

J. Michael Rhodes
*Lockheed Electronics Corporation
Houston, Texas*

Nearly all rocks returned from the Moon are readily divided into three broad categories on the basis of their chemical compositions: (1) mare basalts, (2) non-mare rocks of basaltic composition (KREEP, VHA), and (3) anorthositic rocks. Only mare basalts may unambiguously be considered to have original igneous textures and are widely understood to have an igneous origin. Nearly all other lunar rocks have lost their original textures during metamorphic and impact processes. For these rocks one must work primarily with chemical data in order to recognize and define rock groups and their possible modes of origin. Non-mare rocks of basaltic composition have chemical compositions consistent with an origin by partial melting of the lunar interior. The simplest origin for rocks of anorthositic chemical composition is the crystallization and removal of ferromagnesian minerals. We propose that the rock groups of anorthositic and non-mare basaltic chemical composition could have been generated from a single series of original, but not necessarily primitive, lunar materials.

Lunar rock samples can be subdivided according to three important types of criteria: the physiographic or geologic province where the sample was collected, the petrographic features of the sample, and its chemical composition. The lunar rocks thus far collected have come from three physiographic regions: (1) mare regions (Apollo 11 and 12), (2) a non-mare area (Apollo 14), and (3) a highland area (Apollo 16). The Apollo 15 and 17 sites were chosen to sample mare boundaries. In the broadest sense, two petrographic types of rocks have been returned: rocks with igneous textures and brecciated and metamorphosed rocks that are often visually poly-mict. Rocks with igneous textures were collected from all three physiographic regions but are scarce among the samples returned from the non-mare and highland regions. They are common, even characteristic, of the mare regions. Using chemical data, lunar rocks are readily separated into three major

groups: (1) mare basalts, including a more aluminous feldspathic subcategory sometimes called "mare-like" basalts (ref. 1); (2) rocks with basaltic chemical composition, but distinct from the chemical compositions of mare basalts and characteristically brecciated; and (3) a group of rocks with broadly anorthositic chemical compositions.

The mare basalts, as the name implies, are typical of mare regions and have not been returned as large rocks from any other regions. In this paper the term "mare basalt" will be used to denote a combination of physiographic or geologic province, chemical composition, and basaltic igneous texture, i.e., as commonly used. Mare basalts are not a major topic in this paper and have been included for contrast and comparison with other lunar rocks of basaltic chemical composition.

Other rocks of basaltic chemical composition have been returned as large rocks from the Apollo 14, 16, and 17 sites, and were re-

turned from the Apollo 12 and 15 sites as large fragments (rake fragments and coarse fines). The term non-mare basalt will be used to denote this group of samples because a prominent member of this group, KREEP, is typical of the non-mare Apollo 14 site. This group is identical to the KREEP plus VHA compositions defined earlier (refs. 2 and 3). This usage broadens the range of chemical compositions indicated by Hubbard and Gast (ref. 2) when they introduced the term "non-mare basalt," but continues to denote a group of lunar rocks with basaltic chemical composition which we believe records some of the earliest magmatic activity on the Moon. The non-mare basaltic group contains three groups of samples that we have kept separate in earlier publications. They are the common Apollo 14 KREEP group at lower Al_2O_3 values, the Apollo 16/17 KREEP group at intermediate Al_2O_3 values, and the VHA group at higher Al_2O_3 values. They are grouped together here because the purposes of this general paper are better served by emphasizing the similarities within the non-mare basaltic group of samples and the differences between this group and the

mare basalt and anorthositic groups.

Large rocks with anorthositic chemical compositions have been returned from Apollo 15, 16, and 17 and are present as small fragments in the samples returned by Apollo 11, 12, and 14 and Luna 20. A predominant subset of this group of rocks will be referred to as the Low-K Anorthositic Series (LKAS) (ref. 4). These rocks may be samples of the oldest chemical compositions returned from the Moon, and appear to have been a major component in the lunar crust for at least the last 4.0×10^9 yr (ref. 5).

The approach of this paper is to start with the returned rocks and to work backward in an attempt to deduce the chemical composition of the outer part of the Moon before these rocks were formed. In doing this, no assumptions are made about the material that formed the Moon or about an early lunar differentiation.

Presentation of Data

The chemical data used in this report were all obtained on samples of large rocks, large

Table 1.—Precision of Major Element Data for Lunar Soils

	10084 Mean Rel. Dev. ^(a) N = 9		12070 Mean Rel. Dev. ^(a) N = 6		14163 Mean Rel. Dev. ^(a) N = 6		15101 Mean Rel. Dev. ^(a) N = 4		66081 Mean Rel. Dev. ^(a) N = 3		72701 Mean Rel. Dev. ^(a) N = 4	
SiO ₂	41.98	0.6	45.83	0.2	47.66	0.9	46.21	0.3	44.97	0.9	45.13	0.6
TiO ₂	7.49	1.7	2.81	0.7	1.80	2.6	1.31	5.2	0.67	0.9	1.53	2.5
Al ₂ O ₃	13.75	2.1	12.71	1.6	17.45	1.6	17.55	0.7	25.99	0.8	20.64	0.4
FeO	15.83	0.8	16.52	1.2	10.26	1.3	11.61	0.9	5.99	2.5	8.84	1.7
MnO	0.21	3.7	0.22	2.3	0.14	2.9	0.16	0.0	0.08	0.0	0.12	5.3
MgO	7.90	1.6	10.14	3.3	9.29	0.9	10.32	1.9	6.40	0.6	9.95	0.6
CaO	12.02	0.8	10.45	0.4	10.95	2.0	11.63	0.9	15.17	1.1	12.77	0.5
Na ₂ O	0.44	8.4	0.45	9.7	0.70	9.1	0.40	6.5	0.48	21.5	0.46	10.8
K ₂ O	0.14	10.4	0.25	6.2	0.57	2.7	0.18	5.4	0.14	8.5	0.16	4.8
P ₂ O ₅	0.10	26.5	0.31	6.9	0.50	4.8	0.16	15.4	0.13	15.4	0.15	4.0
S	0.13	8.4	0.09	29.4	0.09	9.1	0.07	20.8	—	—	0.07	16.4
Cr ₂ O ₃	0.30	7.9	0.41	13.0	0.21	13.5	0.29	21.0	0.13	—	0.22	11.4
Total	100.29		100.19		99.62		99.89		100.15		100.04	

NOTE: (1) Standard deviation (1σ) expressed as a percentage of the mean.

Sources of data:

10084: References 6 through 12.

12070: References 9, 13, 14, and 15.

14163: References 9, 12, and 16 through 19.

15101: References 9, 12, 20, and 21.

66081: References 22, 23, and 24.

72701: References 10, 25, 26, and 27.

breccia clasts, or rake samples. (Data for soil samples are given in figures 1, 2, 4, and 5 for comparison.) The major element data are largely from X-ray fluorescence analyses, and the trace element data are predominantly from stable isotope dilution mass spectrometric analyses done in our laboratory and reported in numerous papers by Hubbard and coauthors. Neutron activation and X-ray fluorescence data have been included when needed to fill critical gaps for the elements Eu and Sr.

DATA QUALITY

The quality of data from a purely analytical standpoint is best assessed using analyses of lunar soils. The chief advantage of this approach is that samples covering a broad range of chemical compositions were analyzed in an analytical environment that was "real" in the sense that these analyses were made in order to supply scientists with chemical data for research purposes rather than to obtain data on rock standards for the purpose of interlaboratory comparison. The analyses were commonly performed without the knowledge of other analyses of the same samples. In table 1 we list the means and percent-relative deviations for one soil sample with three or more chemical analyses from each Apollo mission. This comparison extends over the entire Apollo program and includes results from eight research groups. In an earlier paper (ref. 28), we documented the degradation of chemical data for mare basalts that resulted from the allocation of excessively small subsamples (commonly only 0.5 g) of coarse-grained Apollo 15 mare basalts. This sampling problem is severe when attempting to use such analyses to interpret the detailed petrogenesis of individual coarse-grained mare basalts, but less troublesome when studying mare basalts as a chemical group. In contrast, lunar rocks of non-mare and anorthositic chemical compositions contain so many complexities that it has not proven feasible to interrelate individual samples; their study is therefore

largely limited to consideration of the chemical groups. The analysis of a large clast in a breccia of different composition is treated as a separate sample. The chemical analyses often reflect the heterogeneities due to the intimate but incomplete mixing of two different rocks with two widely different chemical compositions (e.g., 61016), and also reflect variability in the plagioclase/ferromagnesian ratio (e.g., 67075, 14310, 65015).

In order to test the reproducibility of our trace element data we recently reanalyzed the very first lunar sample analyzed by us (10084) and the first Apollo 12 sample analyzed by us (12070). In all cases the new values are within 12 percent of the original values, and about 80 percent of the new values are within 5 percent of the first values. This comparison covers a 4-year period and a total change of laboratory, equipment, and materials.

In view of the above results, we conclude that the chemical data used in this paper are fully adequate to support detailed study, with due respect for sampling problems, and are free of analytical error for the types of interelement comparisons and correlations made in this study.

THE DATA

Chemical data for soils are included in some figures for comparison and to demonstrate that lunar soils from the Apollo sites are composed of varying proportions of material, chemically similar or identical to the material found in the local rocks. However, estimates of the relative abundances of these rock types based on soil composition may differ drastically from their relative abundances in the returned sample collection (ref. 26). The three main chemical groups used in this paper have been recognized on several bases, including the chemical one used in this paper. Individual samples that are inconsistent with this broad chemical classification will be noted where considered appropriate.

In figure 1 we have plotted data for FeO versus Al_2O_3 , which, with the exception of

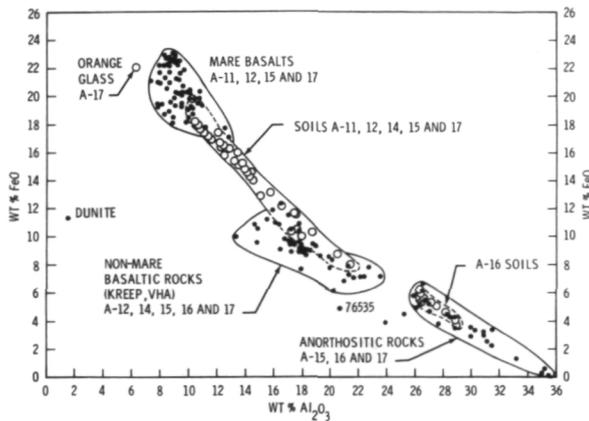


Figure 1.—FeO versus Al_2O_3 for lunar rocks and soils. Data are from references 4, 9, 10, 12 through 15, 17, 23, 24, 26, and 28 through 31.

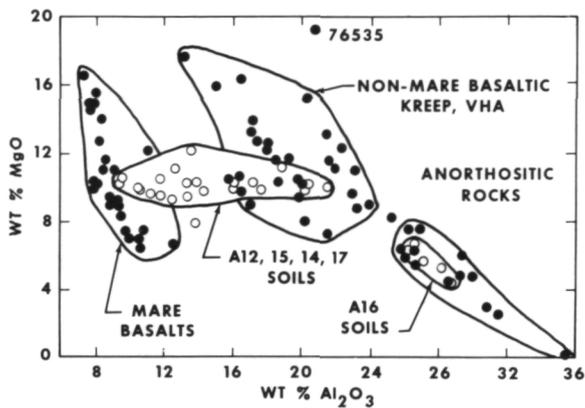
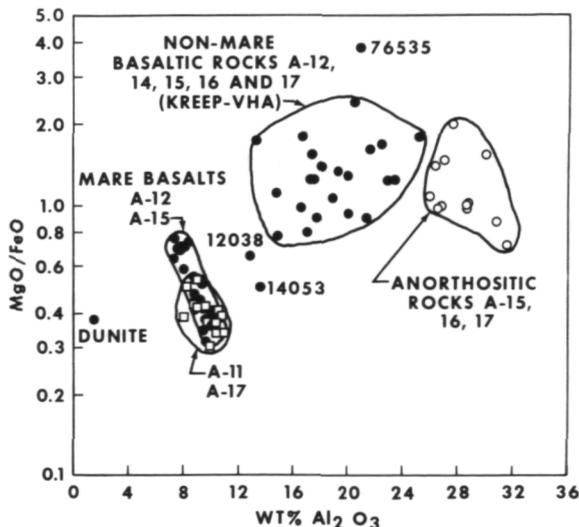


Figure 2.—MgO versus Al_2O_3 for lunar rock and soils. Data are from the same sources as for figure 1.



Ti, are the major elements that show the most variance in lunar rocks. The anorthositic rocks have a relatively well-defined inverse variation of FeO and Al_2O_3 . Extrapolation of the FeO- Al_2O_3 trend seen in these rocks toward the non-mare basaltic rocks shows that the non-mare basaltic rocks generally have less FeO for a given Al_2O_3 value than predicted from the extrapolation. This demonstrates that non-mare basaltic rocks and anorthositic rocks are two populations and not simply one population with internal variation in plagioclase abundance. The mare basalts have, on the contrary, more FeO than expected from the extrapolation. In figure 2, MgO is plotted versus Al_2O_3 , where it is shown by extrapolating from the data for anorthositic rocks that mare basalts have far less MgO than expected. Non-mare basaltic rocks show a wide range in MgO and Al_2O_3 concentrations, with their range in MgO concentrations nearly identical to the range in MgO concentrations for mare basalts. Figure 3 shows MgO/FeO ratios versus Al_2O_3 and demonstrates that anorthositic rocks have the widest range of MgO/FeO ratios of any group of lunar rocks and that the ranges of MgO/FeO ratios for non-mare and mare basalts are similar even though mare basalts have much lower MgO/FeO ratios. The range in MgO/FeO ratios in mare basalts suggests that the similar variations in the non-mare basalt group may also be due to fractional crystallization even though these samples have lost any original igneous textures. Figure 4 illustrates the variation of TiO_2 relative to Al_2O_3 . The major features of this diagram are the steady rise in average TiO_2 concentrations in the series anor-

Figure 3.—MgO/FeO ratio versus Al_2O_3 for lunar rocks. Note that the rocks with the highest Al_2O_3 concentrations have the widest range in MgO/FeO ratios. Data are from the same sources as for figure 1.

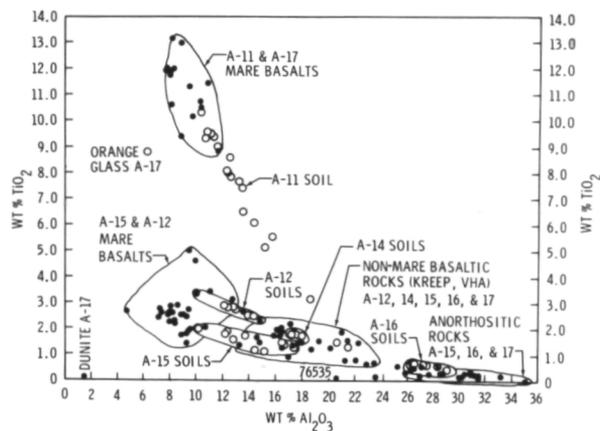


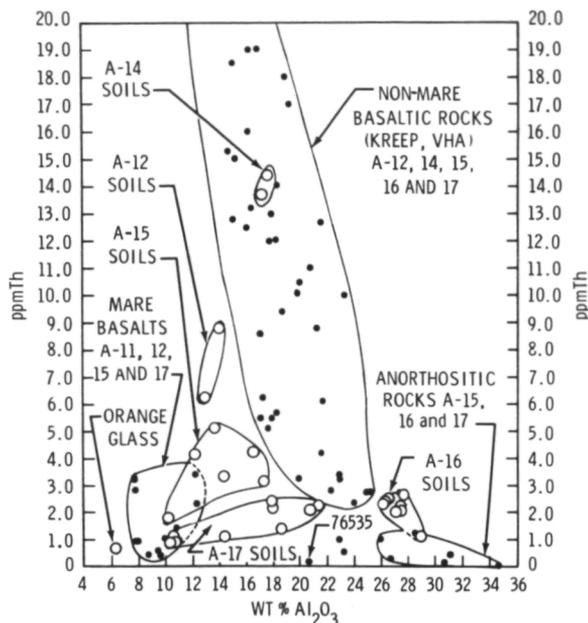
Figure 5.—Th versus Al_2O_3 for lunar rocks and soils. This plot serves to demonstrate that it is the non-mare basaltic group of rocks that has high concentrations of lithophile trace elements such as Th, U, rare earths, Ba, Zr, etc. Data are from the same sources as for figure 1, plus numerous other papers published in the Lunar Science Conference volumes.

thositic rocks → non-mare basaltic rocks → Apollo 12 and 15 mare basalts and the three-fold to fourfold higher TiO_2 concentrations of the Apollo 11 and 17 mare basalts.

Figure 5 shows the variation of Th relative to Al_2O_3 and serves to make the transition between major element and trace element data, and identifies the non-mare basaltic rocks as the group of rocks that have high concentrations of lithophilic trace elements such as Th, U, REE, Ba, Zr, etc.

The data for one set of lithophilic trace elements, the REE, and Ba are summarized in figure 6 for a wide range of Apollo 15, 16, and 17 non-mare basaltic rocks and anorthositic rocks. The data in this diagram can be divided into two major groups: (1) rocks with deep negative Eu anomalies and high concentrations of REE and Ba and (2) rocks with almost no Eu anomalies or positive Eu anomalies and low REE concentrations. Not surprisingly, the samples in group 2 have

Figure 4.— TiO_2 versus Al_2O_3 for lunar rocks and soils. Note that only the Apollo 11 and 17 mare basalts and associated soils have TiO_2 values greater than 6 percent. Data are from the same sources as for figure 1.



anorthositic major element chemistry and are the anorthositic samples in figures 1 through 5. The samples in group 1 are the non-mare basaltic rocks (KREEP, VHA) that cluster together in terms of major element variables (figures 1 through 5). Taken together, the data in figures 1 and 6 amply demonstrate that non-mare basaltic rocks and anorthositic rocks are two separate chemical groups.

Rare Earth, Ba, U, and Sr data are presented in figure 7 for anorthositic rocks only. There is a high degree of regularity in the REE, Ba, and U abundance patterns of these rocks, in that the concentrations of REE, Ba, and U generally decrease with increasing Al_2O_3 concentrations, suggesting that we may be dealing with a series of anorthositic rocks where the major chemical variations are a function of plagioclase concentration. However, some samples deviate from the simple requirements of an anorthositic series—in this case, a specific correlation of REE

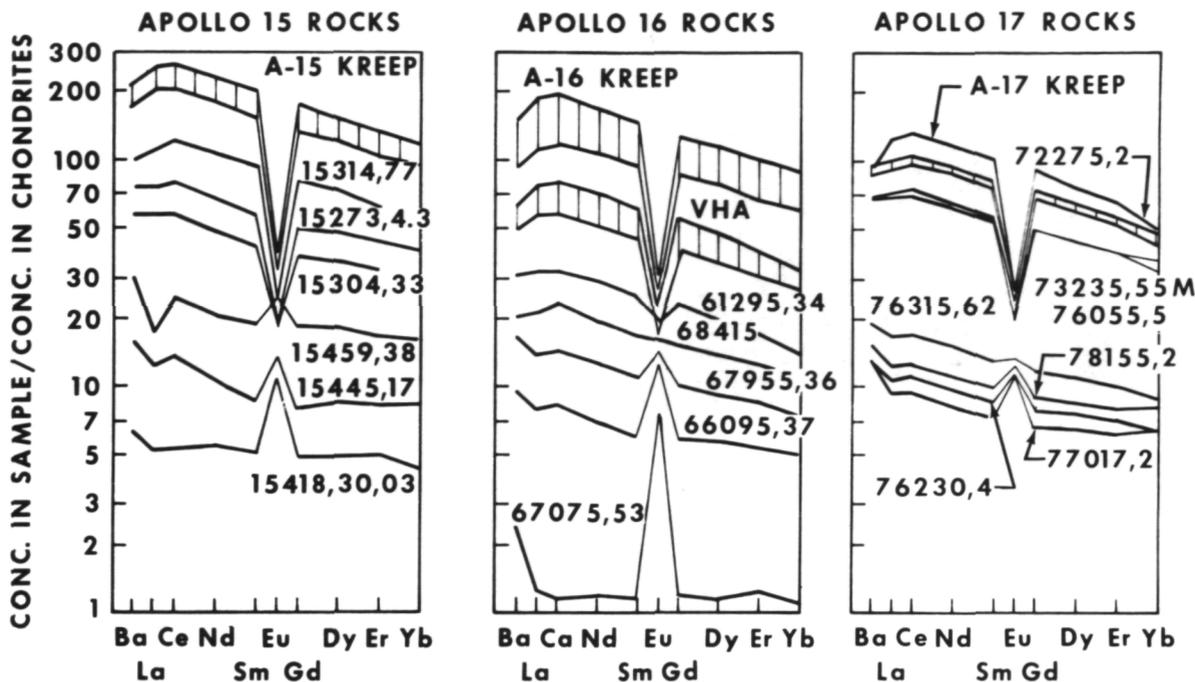


Figure 6.—Rare earth and Ba data for a large number of Apollo 15, 16, and 17 rocks. The main features of these data are that the rocks with deep negative Eu anomalies belong to the group of nonmare basaltic rocks in figures 1 through 5, and the rocks with positive Eu anomalies belong to the anorthositic group in figures 1 through 5, as do samples 68415 and 61295. All of the data are from publications by Hubbard and coworkers.

abundance patterns with Al_2O_3 versus Eu, Sr, and Sm (ref. 4). Further subdivision or reduction to conditional membership in the main subgroup is made on other chemical parameters such as the slope of the trivalent rare earth abundance patterns, MgO/FeO ratio, and abnormally low or high concentrations of any rock-forming element like Si, K, Ti, Cr, etc. On this basis we can immediately reject 63335,36, 15459,38, 61295,34, 68415,10 and 63549,2 from the rest of the samples because 63335,36 has an abnormal Eu anomaly and 15459,38, 61295,34, 68415,10, and 63549,2 have too much Eu, Sr, and Sm for their Al_2O_3 concentrations. Samples 15418, 67075, and 15445,17 are conditionally retained with the majority of samples even though sample 15418 has low Sm for its Al_2O_3 value of 26 percent and also has a flatter trivalent rare earth pattern. Sample 67075,53 also has a flat trivalent rare earth pattern and has the lowest MgO/FeO ratio of anorthositic samples included in this

study. Sample 15445, 17 has low Al_2O_3 , a high MgO/FeO ratio, and a high SiO_2 concentration. The white portion of sample 15445 (ref. 32) has not been included in the LKAS group because of its high MgO/FeO ratio, low TiO_2 , very high Eu concentration, and the steep slope of its trivalent rare earth pattern. There are more than 10 samples remaining, after the deletions, with a simple and regular pattern of major and trace element chemical compositions. These have been named the Low-K Anorthositic Series (LKAS). This series has been proposed to be a major subset of anorthositic lunar rocks (ref. 4).

A thorough consideration of the behavior of Eu in lunar rocks requires accurate knowledge of the $\text{Eu}^{+3/+2}$ ratio during petrogenesis. Lunar rocks formed in rather reducing conditions, i.e., about 10^{-13} atm of oxygen partial pressure at temperatures about 1200°C (ref. 33), and it is reasonable to assume, as is commonly done, that Eu is largely

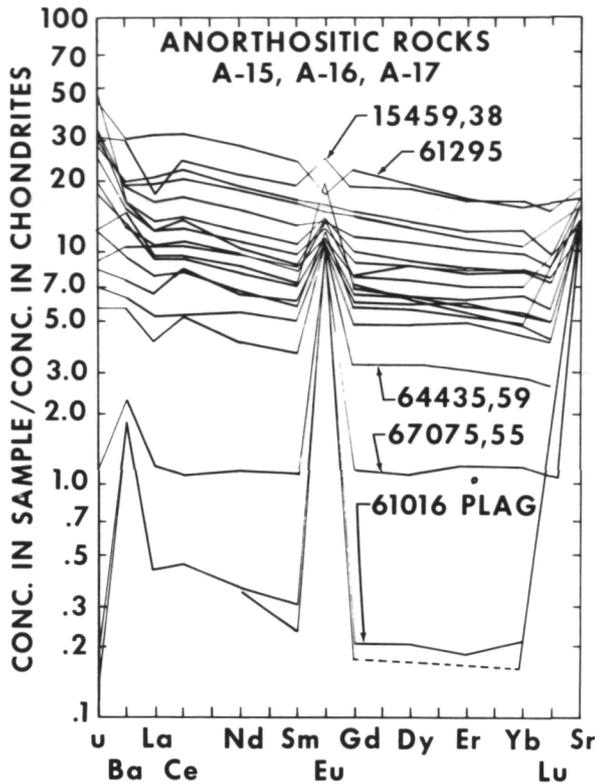
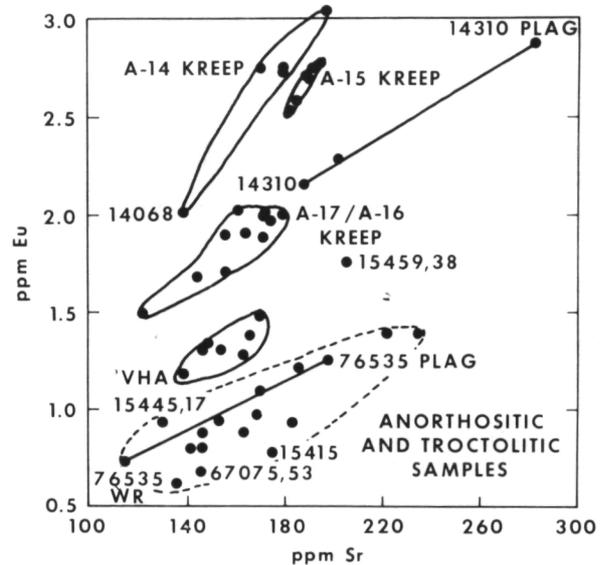


Figure 8.—Eu versus Sr for the entire range of non-mare basaltic and anorthositic lunar rocks. If Eu were entirely divalent and the lunar rocks were formed from a common parent with a single Eu/Sr ratio, this Eu versus Sr plot should be very nearly a single narrow band of data points. Instead, for a twofold range in Sr concentration there is a fourfold range in Eu concentrations. As discussed in the text, this greater range in Eu concentrations is explained as the result of 10 to 20 percent of the Eu having been in the trivalent oxidation state during magma genesis.

divalent. A plot of Eu versus Sr (fig. 8) and the overall rare earth data shown in figure 6 provide fundamental information about the ratio of $\text{Eu}^{+3/+2}$ in the lunar petrogenetic environment for non-mare and anorthositic rocks. If Eu was entirely divalent during lunar petrogenesis, then Eu should closely follow Sr. Instead, Eu has a much wider range of concentration than Sr in lunar non-mare and highland rocks. If one considers that this is due to the presence of substantial Eu^{+3} , then the rare earth data

Figure 7.—Rare earth, Ba, U, and Sr data for anorthositic rocks from Apollo 15, 16, and 17. Nearly all of the data are from Hubbard et al. (1974). The remainder are from earlier publications. In order of increasing Sm concentrations, the samples plotted are 61016, plag, 67075,53, 64435,59, 15418,30,03, 66095,37, 15418,30,07A, 76230,4, 63335,36, 61016,3, 77017,2, 15445,17, 78155,2, 67955,56, 76315,62, 68415,10, 63549,2, 15459,38, and 61295.



in figure 6 allow one to estimate that the percentage of Eu that is trivalent is 10 to 20 percent, on the assumption that trivalent Eu is intermediate between trivalent Sm and Gd in its chemical behavior. Some recent experimental work is directly relevant to this question. Morris and Haskin (ref. 34) found that for a fixed $p\text{O}_2$, the $\text{Eu}^{+3/+2}$ ratio is strongly dependent on the bulk composition for glasses in the compositional range from anorthite to Ca-Mg pyroxene. Specifically, the nearer the glass composition to the pyroxene

end member the higher the $\text{Eu}^{+3/+2}$ ratio. Related research by Morris et al. (ref. 35) found that even in glass of anorthite composition ($\text{CaAl}_2\text{Si}_2\text{O}_8$) at 1370 to 1600°C the Eu^{+3} was about 10 percent of the total Eu at $p\text{O}_2 = 10^{-12}$, and about 4 percent of the total at $p\text{O}_2 = 10^{-14}$. Thus, even a pure anorthite liquid at lunar $p\text{O}_2$ may have a few percent of trivalent Eu. Glass of diopside composition ($\text{CaMgSi}_2\text{O}_6$) at 1450°C at $p\text{O}_2 = 10^{-14}$ was found to have $\text{Eu}^{+3/+2} \sim 0.5$. These experimental data suggest that silicate liquids on the Moon of non-mare basaltic composition (KREEP, VHA), i.e., 50 percent or less pyroxene, will have about one-fourth or less of their Eu in the trivalent oxidation state, thus substantiating the above interpretation of the chemical data for lunar rocks.

The Chemical Model

INTRODUCTORY REMARKS

This model is primarily concerned with the origin of the non-mare basaltic and anorthositic rocks. There will be no attempt to further decipher the genesis of mare basalts. With both non-mare basaltic and anorthositic rocks there is a fundamental need to directly determine which rocks have had their chemical compositions seriously contaminated by material from non-cogenetic rocks and the nature and extent of such contamination. Typically for current studies of lunar rocks, such data are almost nonexistent for the chips of samples used in this study. It is expected that accurate and verifiable knowledge of such contamination will result in a sharper view of the chemical processes described in this paper because the "noise" introduced by contamination will be reduced and seriously contaminated rocks can be excluded from this type of study. Impact-related mixing processes are the accepted means of mixing (i.e., contaminating) non-cogenetic lunar rocks, as well as mixing the members of a cogenetic suite of rocks.

There is an apparent paradox in that there is an extensive cratering history in the lunar

highlands (ref. 36) which is consistent with the brecciated nature of nearly all lunar samples except mare basalts. Yet, the bulk of the chemical data shown in this paper is compatible with igneous processes, suggesting that igneous processes have produced a wide range of chemical compositions. From this we conclude that igneous processes were either more effective or lasted longer than the homogenizing effect of impact processes, or, perhaps, simply that impact mixing was not adequately efficient to erase the chemical record. This apparent paradox between the extensive cratering record and the extensive range of chemical compositions seen among the non-mare and highland rocks, as well as the existence of preferred chemical groups, has led one group of researchers (ref. 37) to propose that the impacts both homogenize (through mixing) and differentiate (through partial fusion) the material involved in the impact. We find it difficult to accept the hypothesis that impact events can produce the observed abundance of material that has an apparent igneous origin because of a lack of evidence that impact processes cause significantly more igneous differentiation than mixing. Since mixing reverses the processes of differentiation, Warner et al. (ref. 37) are dependent on an unproven efficiency of impact-related differentiation.

Mixing processes must operate on existing material and, if mixing processes are of any importance, that material must have initially had at least as wide a range of chemical composition as presently observed, because mixing processes will decrease the probable range of chemical compositions available for sampling. The observed range of chemical compositions was either produced on the Moon, already existed in the material that accreted to form the outer tens to hundreds of kilometers of the Moon, or some combination of the two possibilities. At least one model (ref. 38) proposes that the Moon was made from partially disrupted preexisting planetary bodies and thus provides for lunar material that has a prelunar igneous history. In the absence of unambiguous data to the contrary, and for simplicity, we presume that

igneous differentiation on the Moon was the cause of the range of chemical compositions observed in the non-mare basaltic and anorthositic rocks and that homogenization due to impact-related mixing has been minimal. We will describe what we consider to be the general features of that differentiation. We believe that the hypothesis we have chosen to emphasize has the greatest potential for revealing fundamental internal lunar processes and evolution. In this paper we will not consider heat sources that could have caused the inferred igneous differentiation. If an igneous interpretation of the chemical data is correct, then an adequate heat source must have existed. Current interpretations of the Rb-Sr data (refs. 5, 39, and 40) suggest that the heat source was adequate about 4.3×10^9 years ago.

THE MODEL

We will first consider the non-mare basaltic and anorthositic groups independently and then combine the requirements of these groups in order to arrive at an overall model. The genesis of mare basalts will not be discussed below. Interested readers are referred to reference 4 and earlier papers where we have presented arguments for the generation of mare basalts from a different source material than non-mare basaltic rocks and proposed that much of the inferred chemical differences were the result of heterogeneous accretion of the outer part of the Moon.

Non-Mare Basaltic Rocks

This group of rocks is identical with the KREEP and VHA rocks described earlier (refs. 1 through 4, 30, and 31). The recent experimental paper of Walker et al. (ref. 41) provides the clearest insight into the origin of the non-mare basaltic rock types so far as major elements are concerned. Briefly, they are the result of partially melting any of a wide range of rocks having variable amounts of plagioclase, pyroxene, olivine, and, for the VHA samples, sometimes spinel.

The deep negative Eu (also Sr) anomalies of these rocks are explained as the result of partially melting plagioclase-bearing source rocks that retain significant plagioclase in the residue after the partial melting episode (ref. 2). These samples have a characteristic slope in their trivalent rare earth abundance patterns (chondrite normalized $\text{La/Yb} \approx 2.0$). This was initially explained (ref. 2) as the result of partially melting a plagioclase, clinopyroxene, olivine source rock to a very limited extent (only a few percent liquid generated). This specific partial melting model depended on the combination of clinopyroxene and small amounts of liquid to produce the observed La/Yb slope from material that had the rare earths in absolutely chondritic relative abundances. Even with the enrichments provided by the small amounts of liquid produced, this model requires the source to have about tenfold chondritic concentrations. However, clinopyroxene is absent or of minor importance in both non-mare basaltic and anorthositic rocks, as well as in their probable source materials and their P-T conditions of origin (refs. 41 and 42), thus invalidating partial melting models that depend on clinopyroxene for fractionation of the La/Yb ratio. Recently Hubbard and Shih (refs. 43 and 44) considered partial melting models that are more realistic for lunar non-mare basaltic samples, i.e., no clinopyroxene. In addition, distribution coefficient data obtained using phenocrysts were preferred to those obtained using high-pressure metamorphic mineral pairs. The resulting model, using only plagioclase, olivine, and orthopyroxene does very little differentiation of La/Yb ratio, essentially transmitting the trivalent rare earth abundance pattern of the unmelted source material into the liquid. It is possible to use an orthopyroxene-rich source material (fig. 9) to produce La/Yb ratios approaching the observed ratios from a source material with chondritic relative abundances of the rare earths, but only with the generation of 1 percent or less liquid. Increasing the plag/opx ratio of the source reduces the La/Yb ratio of the liquid, as does the generation of larger

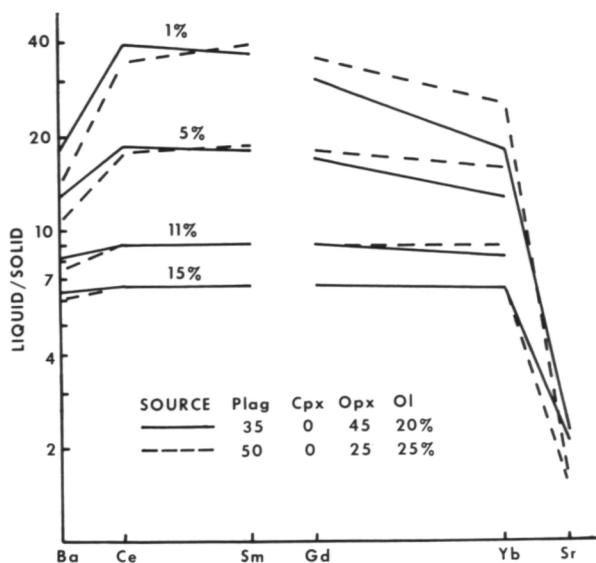


Figure 9.—Two partial melting models that are capable of producing the range of trivalent rare earth concentrations observed in the non-mare basaltic group of rocks. See Gast (ref. 45) for the most recent version of the old clinopyroxene bearing models. Sr serves to indicate the behavior of Eu^{+2} , which is not plotted in order to emphasize the trivalent rare earths.

percentages of melt. This model requires that the observed La/Yb ratio and the characteristic slope of the trivalent rare earth abundance pattern must have already been in the source material. The deviation from absolutely chondritic relative abundances for the rare earths is not large, in fact only requiring La to be $1.35 \times$ and Yb $0.675 \times$ chondritic. Since the chemical compositions of the returned lunar samples are grossly nonchondritic, this deviation is quite permissible. Partial melting events that produce about 4 to 5 percent of liquid (fig. 9) have about twentyfold more rare earths, etc., in the liquid than in the initial material, and can thus produce even the rare earth concentrations in Apollo 14 KREEP if the initial material had tenfold chondrite concentrations of these elements.

There is an inverse correlation between Al_2O_3 and Eu and the trivalent rare earths within the non-mare basaltic group of rocks for the series VHA through Apollo 16/17

KREEP to Apollo 14 common KREEP (figs. 1, 6, and 8 and ref. 4). This can be explained by coupling the pseudoternary silica-anorthite-olivine diagram of Walker et al. (ref. 41) with trace-element-derived partial melting model calculations. On the pseudoternary diagram the series of compositions from Apollo 14 common KREEP to Apollo 16/17 KREEP to VHA becomes more aluminous and moves toward higher liquidus temperatures. The Eu and trivalent rare earths decrease in this series, implying, in terms of partial melting models, increasing percentages of liquid (melting). This in turn is consistent with the higher liquidus temperatures of the more Al_2O_3 -rich compositions. This is not meant to imply that the entire series of chemical compositions within the non-mare basaltic group was generated from a single source material, but rather that many of the predictable chemical features are consistent with this concept, even though some allowance must be made for the MgO/FeO ratio differences (ref. 41). Schemes that properly combine partial melting models and experimental data require that partial melting models be tuned to produce the observed variations in major element chemical composition and attendant changes in the permissible mineralogical composition of the source material. This is presently very difficult to do for the observed wide range in MgO/FeO ratios, but has been taken into consideration for plagioclase/orthopyroxene/olivine ratios.

The Anorthositic Group

The LKAS subset of the anorthositic samples was anticipated by Hubbard et al. (ref. 1) when they calculated the REE, Ba, and Sr concentration in a hypothetical silicate liquid in equilibrium with anorthosite sample 15415. The crystal plus equilibrium liquid model behind those calculations is still the most satisfactory chemical explanation of the internal, plagioclase-related chemical variations. Samples like 77017 and 66095,37 have major and trace element compositions

approximating the equilibrium liquid of the model.

It is easier to say, with qualifications, how the group of rocks with anorthositic chemical compositions were not formed than how they were formed. Although the major cause of internal chemical variations is clearly a result of plagioclase control, the anorthositic group itself is probably not the result of plagioclase fractional crystallization because of the consistent lack of negative Eu and Sr anomalies for this group. One could avoid this constraint by assuming a precursor with positive Eu and Sr anomalies; that is, by assuming an even more Al_2O_3 - and plagioclase-rich precursor and further increasing the difficulty of accounting for these rocks. The consistent lack of negative Eu and Sr anomalies also rules against the production of this group by partial melting because again negative anomalies in the observed rocks and more Al_2O_3 and plagioclase precursors are the predicted result. If the process is to be igneous, we are left with either plagioclase accumulation or fractional crystallization of ferromagnesian minerals. Plagioclase accumulation due to flotation of plagioclase has been popular (refs. 46 and 47), but it remains unproven that plagioclase will float in feldspathic silicate liquids. On the other hand, ferromagnesian minerals will almost surely sink unless there is a prohibitive mesh of earlier crystallizing plagioclase. A prohibitive mesh of plagioclase crystals is increasingly likely as the Al_2O_3 concentration increases, thus progressively reducing the efficiency of this process as more feldspathic compositions are reached. So long as sinking of ferromagnesian minerals is the proposed mechanism for generating the anorthositic group, plagioclase does not move relative to the liquid, and we have no knowledge of the olivine/pyroxene ratio, the MgO/FeO ratio of the parental material is very poorly defined. Although likely, it is not essential that the parent material have plagioclase on the liquidus, but it must have had an even higher MgO/FeO ratio than presently found in anorthositic lunar rocks in order to allow removal of ferromagnesian minerals, es-

pecially extensive removal. If extensive removal of orthopyroxene occurred, then the La/Yb ratio would have been increased somewhat, but probably no higher than one and one-half times the initial ratio in the source material (ref. 44). Also, if large volumes of material were removed by the fractional crystallization of ferromagnesian minerals, then the initial Eu and Sr concentrations would have been lower and the early crystallizing plagioclase crystals would have had to completely reequilibrate in order to produce the observed consistent minimum concentrations of Eu and Sr. This difficulty decreases as the amount of ferromagnesian minerals removed decreases after the onset of plagioclase crystallization. In summary, we consider the removal of ferromagnesian minerals to be the most reasonable means of making the anorthositic rocks on the Moon, or any other similar planetary body, mainly because the alternate means considered here are even less probable. Another alternative is to provide a precursor that has a chemical composition very near to or within the field of compositions for anorthositic rocks.

A Common Precursor

The chemical similarities of the parental materials inferred for the non-mare basaltic and anorthositic chemical groups is suggestive of a common precursor for these groups. It does not seem possible to describe material with a single chemical composition because some of the requirements of the two groups are mutually inconsistent, in particular the inferred initial concentrations of rare earths and related lithophile trace elements. However, definition of a series of closely related precursors seems appropriate and possible at the present time. The goal is to define the limits of a probable set of lunar materials that could have been parental to the chemical groups observed in the returned lunar samples. The result of this exercise is expected to change, perhaps radically, as further data are obtained and the approach is further developed.

First, the materials do not have to be plagioclase rich. Thirty percent plagioclase is adequate to produce the observed deep negative Eu and Sr anomalies of the non-mare basaltic group, and the ferromagnesian fractional crystallization deduced for the anorthositic group can produce the required plagioclase enrichments. Conversely, nothing prohibits a plagioclase-rich material so long as the requirements imposed by large percentages of plagioclase are not considered prohibitive. The natural limit on plagioclase enrichment is reached when it becomes prohibitively difficult to produce an adequate volume of the non-mare basaltic composition liquid, probably around 70 percent plagioclase.

Second, the pyroxene/olivine ratio is not very well determined and neither is the MgO/FeO ratio, although the MgO/FeO ratio must be greater than about 1.5 in order to produce liquids with MgO/FeO greater than 1.5. Ratios of MgO/FeO increasingly greater than 1.5 are probably compatible with decreasing pyroxene/olivine ratios.

Third, there is no independent way of postulating the trace element concentrations and ratios of these lunar materials unless one adopts a specific model for making the material that was later incorporated into the Moon. We have adopted no such model because we are attempting to work backwards from the chemical compositions of analyzed lunar rocks. If the REE concentrations are to be produced by single-stage partial melting and the problems of extracting very small percentages (~ 1 percent) of liquid are to be avoided, this approach requires that the parental material for the non-mare basaltic group had at least tenfold chondritic concentrations of REE for the Apollo 14-type KREEP and perhaps as little as threefold to fourfold for the VHA compositions. A source with tenfold chondritic concentrations of REE can also be used as the source for the Apollo 16/17-type KREEP and VHA basaltic compositions. The anorthositic rocks require parental material with less than tenfold chondritic concentration for the LKAS subgroup and similar concentrations for the other samples. Threefold to fivefold lower

concentrations are possible if extensive fractional crystallization occurred during the genesis of these rocks.

In summary, the plausible outer bounds for a set of precursors that could have been parental to the non-mare basaltic group and the anorthositic group are quite far apart. The plagioclase concentration could be as low as about 30 percent or as high as about 75 percent. The Al_2O_3 concentration could be as low as about 10 percent or as high as about 26 percent. The MgO/FeO ratio can only be constrained to be greater than 1.5 and can be highly variable. Concentrations of lithophile trace elements may be as low as threefold chondritic values or as high as more than tenfold. This wide range in chemical composition is easily converted into a set or spectrum of compositions if the realistic assumption is made that the concentration of lithophile trace elements is inversely correlated with plagioclase concentration. However, if the anorthositic rocks require a plagioclase-rich source material with nearly tenfold chondritic concentrations of rare earths, etc., then the series cannot be so simple as just suggested. Although we consider it improbable that the precursor for non-mare lunar rocks was as simple as deduced here, we do consider a precursor consisting of a related series of chemical compositions to be much more reasonable than one with a single chemical composition. The old Rb-Sr model ages of the KREEP rocks and the low initial $\text{Sr}^{87/86}$ ratios of some anorthositic samples suggests that this precursor may be original lunar material (refs. 5, 39, and 40).

If the type of precursor suggested here is basically correct, the hypothesized increase of rare earths, etc., with ferromagnesian content implies that it was not produced by crystal accumulation because the relevant minerals, orthopyroxene, olivine, and plagioclase, all reject rare earths (except Eu^{+2}) to a very similar extent. We are left with two poorly defined possibilities: (1) the precursor was a residual liquid produced by extensive differentiation of the Moon or (2) the precursor was the material that accumu-

lated to form the outer part of the Moon, altered by thermal metamorphism prior to melting. In view of the inferred old ages for the chemical compositions of lunar non-mare rocks (refs. 5, 39, and 40), this approach may get us as close as any to the chemical composition of original lunar crustal material and is certainly more comprehensive than approaches using individual and unique lunar rocks such as 76535, 72415, or 15415.

References

- HUBBARD, N. J., P. W. GAST, C. MEYER, L. E. NYQUIST, C. SHIH, AND M. WIESMANN, Chemical Composition of Lunar Anorthosites and Their Parent Liquids. *Earth Planet. Sci. Letters*, Vol. 13, 1971, pp. 71-75.
- HUBBARD, N. J., AND P. W. GAST, Chemical Composition and Origin of Nonmare Lunar Basalts. *Proc. Second Lunar Science Conference, Geochimica et Cosmochimica Acta*, Supplement 2, Vol. 2, 1971, pp. 999-1020.
- HUBBARD, N. J., J. M. RHODES, AND P. W. GAST, Chemistry of Very High Al_2O_3 Lunar Basalts. *Science*, Vol. 181, 1973, pp. 339-342.
- HUBBARD, N. J., H. WIESMANN, C. SHIH, B. BANSAL, AND J. M. RHODES, The Chemical Definition and Interpretation of Rock Types Returned From the Non-Mare and Highland Regions of the Moon. *Proc. Fifth Lunar Science Conference, Geochimica et Cosmochimica Acta*, Supplement 5, Vol. 2, in press, 1974.
- NYQUIST, L. E., B. M. BANSAL, H. WIESMANN, AND B. JAHN, Taurus Littrow Chronology: Some Constraints on Early Lunar Crustal Development. *Proc. Fifth Lunar Science Conference, Geochimica et Cosmochimica Acta*, Supplement 5, Vol. 2, in press, 1974.
- AGRELL, S. O., J. H. SCOON, I. D. MUIR, J. V. P. LONG, J. D. C. McCONNEL, AND A. PECKETT, Observations on the Chemistry, Mineralogy and Petrology of Some Apollo 11 Lunar Samples. *Proc. Apollo 11 Lunar Science Conference, Geochimica et Cosmochimica Acta*, Supplement 1, Vol. 1, 1970, pp. 93-128.
- COMPSTON, W., B. W. CHAPPELL, P. A. ARRIENS, AND M. J. VERNON, The Chemistry and Age of Apollo 11 Lunar Material. *Proc. Apollo 11 Lunar Science Conference, Geochimica et Cosmochimica Acta*, Supplement 1, Vol. 2, 1970, pp. 1007-1027.
- ENGEL, A. E. J., AND C. G. ENGEL, Lunar Rock Compositions and Some Interpretations. *Proc. Apollo 11 Lunar Science Conference, Geochimica et Cosmochimica Acta*, Supplement 1, Vol. 2, 1970, pp. 1081-1084.
- LSPET (Lunar Sample Preliminary Examination Team), The Apollo 15 Lunar Samples: A Preliminary Description. *Science*, Vol. 175, 1972, pp. 363-375.
- LSPET (Lunar Sample Preliminary Examination Team), Apollo 17 Lunar Samples: Chemical and Petrographic Description. *Science*, Vol. 182, 1973, pp. 659-674.
- MAXWELL, J. A., L. C. PECK, AND H. B. WIJK, Chemical Composition of Apollo 11 Lunar Samples 10017, 10020, 10072 and 10084. *Proc. Apollo 11 Lunar Science Conference, Geochimica et Cosmochimica Acta*, Supplement 1, Vol. 2, 1970, pp. 1369-1374.
- WILLIS, J. P., A. J. ERLANK, J. J. GURNEY, R. H. THEIL, AND L. H. AHRENS, Major, Minor and Trace Element Data for Some Apollo 11, 12, 14 and 15 Samples. *Proc. Third Lunar Science Conference, Geochimica et Cosmochimica Acta*, Supplement 3, Vol. 2, 1972, pp. 1269-1274.
- COMPSTON, W., H. BERRY, M. J. VERNON, B. W. CHAPPELL, AND M. J. KAYE, Rubidium-Strontium Chronology and Chemistry of Lunar Material From the Ocean of Storms. *Proc. Second Lunar Science Conference, Geochimica et Cosmochimica Acta*, Supplement 2, Vol. 2, 1971, pp. 1471-1486.
- CUTTITTA, F., H. J. ROSE, JR., C. S. ANNELL, M. K. CARRON, R. P. CHRISTIAN, E. J. DWORNIK, L. P. GREENLAND, A. W. HELZ, AND D. T. LIGON, JR., Elemental Composition of Some Apollo 12 Lunar Rocks and Soils. *Proc. Second Lunar Science Conference, Geochimica et Cosmochimica Acta*, Supplement 2, Vol. 2, 1971, pp. 1217-1320.
- WILLIS, J. P., L. H. AHRENS, R. V. DANCHIN, A. J. ERLANK, J. J. GURNEY, P. K. HOFMEYER, T. S. MCCARTHY, AND M. J. ORREN, Some Inter-Element Relationships Between Lunar Rocks and Fines, and Stony Meteorites. *Proc. Second Lunar Science Conference, Geochimica et Cosmochimica Acta*, Supplement 2, Vol. 2, 1971, pp. 1123-1138.
- CHAPPELL, B. W., Personal communication, 1972.
- ROSE, H. J., JR., F. CUTTITTA, C. S. ANNELL, M. K. CARRON, R. P. CHRISTIAN, E. J. DWORNIK, L. P. GREENLAND, AND D. T. LIGON, JR., Compositional Data for Twenty-One Fra Mauro Lunar Materials. *Proc. Third Lunar Science Conference, Geochimica et Cosmochimica Acta*, Supplement 3, Vol. 2, 1972, pp. 1215-1230.
- SCHNETZLER, C. C., AND D. F. NAVA, Chemical Composition of Apollo 14 Soils 14163 and 14259. *Earth Planet. Sci. Letters*, Vol. 11, 1971, pp. 345-350.
- WIJK, H. B., J. A. MAXWELL, AND J. L. BOUVIER,

- Chemical Composition of Some Apollo 14 Lunar Samples. *Earth Planet. Sci. Letters*, Vol. 17, 1973, pp. 365-368.
20. CARRON, M. K., C. S. ANNELL, R. P. CHRISTIAN, F. CUTTITTA, E. J. DWORNIK, D. T. LIGON, JR., AND H. J. ROSE, JR., Elemental Analyses of Lunar Soil Samples From Apollo 15 Mission. *The Apollo 15 Lunar Samples*, Lunar Science Institute, Houston, 1972, pp. 198-200.
 21. SCOON, J. H., Chemical Analysis of Lunar Samples 15101,65 and 15211,6. *The Apollo 15 Lunar Samples*, Lunar Science Institute, Houston, 1972, pp. 255-256.
 22. COMPSTON, W., M. J. VERNON, B. W. CHAPPELL, AND R. FREEMAN, Rb-Sr Model Ages and Chemical Composition of Nine Apollo 16 Soils (abs.). *Lunar Science*, Vol. IV, Lunar Science Institute, Houston, 1973, pp. 158-158b.
 23. LSPET (Lunar Sample Preliminary Examination Team), The Apollo 16 Lunar Samples: Petrographic and Chemical Description. *Science*, Vol. 179, 1973, pp. 23-34.
 24. ROSE, H. J., JR., F. CUTTITTA, S. BERMAN, M. K. CARRON, R. P. CHRISTIAN, E. J. DWORNIK, L. P. GREENLAND, AND D. T. LIGON, JR., Compositional Data for Twenty-Two Apollo 16 Samples. *Proc. Fourth Lunar Science Conference, Geochimica et Cosmochimica Acta*, Supplement 4, Vol. 2, 1973, pp. 1149-1158.
 25. DUNCAN, A. R., A. J. ERLANK, J. P. WILLIS, AND M. K. SHER, Compositional Characteristics of the Apollo 17 Regolith (abs.). *Lunar Science*, Vol. V, Lunar Science Institute, Houston, 1974, pp. 184-186.
 26. RHODES, J. M., K. V. RODGERS, C. SHIH, B. M. BANSAL, L. E. NYQUIST, H. WIESMANN, AND N. J. HUBBARD, The Relationship Between Geology and Soil Chemistry at the Apollo 17 Landing Site. Submitted to *Proc. Fifth Lunar Science Conference*.
 27. SCOON, J. H., Chemical Analysis of Lunar Samples From the Apollo 16 and 17 Collections (abs.). *Lunar Science*, Vol. V, Lunar Science Institute, Houston, 1974, pp. 690-692.
 28. RHODES, J. M., AND N. J. HUBBARD, Chemistry, Classification and Petrogenesis of Apollo 15 Mare Basalts. *Proc. Fourth Lunar Science Conference, Geochimica et Cosmochimica Acta*, Supplement 4, Vol. 2, 1973, pp. 1127-1148.
 29. DUNCAN, A. R., A. J. ERLANK, J. P. WILLIS, AND L. H. AHRENS, Composition and Inter-Relationships of Some Apollo 16 Samples. *Proc. Fourth Lunar Science Conference, Geochimica et Cosmochimica Acta*, Supplement 4, Vol. 2, 1973, pp. 1097-1114.
 30. HUBBARD, N. J., P. W. GAST, J. M. RHODES, B. M. BANSAL, H. WIESMANN, AND S. E. CHURCH, Nonmare Basalts: Part II. *Proc. Third Lunar Conference, Geochimica et Cosmochimica Acta*, Supplement 3, Vol. 2, 1972, pp. 1161-1179.
 31. HUBBARD, N. J., J. M. RHODES, P. W. GAST, B. M. BANSAL, C. Y. SHIH, H. WIESMAN, AND L. E. NYQUIST, Lunar Rock Types: The Role of Plagioclase in Non-Mare and Highland Rock Types. *Proc. Fourth Lunar Science Conference, Geochimica et Cosmochimica Acta*, Supplement 4, Vol. 2, 1973, pp. 1297-1312.
 32. TAYLOR, S. R., M. P. GROTON, P. MUIR, W. NANCE, R. RUDOWSKI, AND N. WARE, Lunar Highlands Composition: Apennine Front. *Proc. Fourth Lunar Science Conference, Geochimica et Cosmochimica Acta*, Supplement 4, Vol. 2, 1973, pp. 1445-1460.
 33. SATO, M., N. L. HICKLING, AND J. E. McLANE, Oxygen Fugacity Values of Apollo 12, 14 and 15 Lunar Samples and Reduced State of Lunar Magmas. *Proc. Fourth Lunar Science Conference, Geochimica et Cosmochimica Acta*, Supplement 4, Vol. 1, 1973, 1066-1079.
 34. MORRIS, R. V. AND L. A. HASKIN, EPR Measurement of the Effect of Glass Composition on the Oxidation States of Europium. *Geochimica et Cosmochimica Acta*, in press, 1974.
 35. MORRIS, R. V., L. A. HASKIN, G. M. BIGGARS, AND M. J. O'HARA, Measurement of the Effects of Temperature and Partial Pressure of Oxygen on the Oxidation States of Europium in Silicate Glasses. *Geochimica et Cosmochimica Acta*, in press, 1974.
 36. SHORT, N. M., AND M. L. FORMAN, Thickness of Impact Crater Ejecta on the Lunar Surface. *Modern Geology*, Vol. 3., 1972, pp. 69-91.
 37. WARNER, J. L., C. H. SIMONDS, AND W. C. PHINNEY, Impact Induced Fractionation in the Highlands. *Lunar Science*, Vol. V, 1974, pp. 823-825.
 38. WOOD, J. A., AND H. E. MITLER, Origin of the Moon by Modified Capture Mechanism, or Half a Loaf Is Better Than a Whole One. *Lunar Science*, Vol. V, 1974, pp. 851-853.
 39. NYQUIST, L. E., N. J. HUBBARD, P. W. GAST, S. E. CHURCH, B. M. BANSAL, AND H. WIESMANN, Rb-Sr Systematics for Chemically Defined Apollo 14 Breccias. *Proc. Third Lunar Science Conference, Geochimica et Cosmochimica Acta*, Supplement 3, Vol. 2, 1972, pp. 1515-1530.
 40. NYQUIST, L. E., N. J. HUBBARD, P. W. GAST, B. M. BANSAL, H. WIESMANN, AND B. JAHN, Rb-Sr Systematics for Chemically Defined Apollo 15 and 16 Materials. *Proc. Fourth Lunar Science Conference, Geochimica et Cosmochimica Acta*, Supplement 4, Vol. 2, 1973, pp. 1823-1846.
 41. WALKER, D., T. L. GROVE, J. LONGHI, E. M. STOLPER, AND J. F. HAYS, Origin of Lunar Feldspathic Rocks. *Earth Planet. Sci. Letters*, Vol. 20, 1973, pp. 325-336.
 42. WALKER, D., J. LONGHI, T. L. GROVE, E. STOLPER, AND J. F. HAYS, Experimental Petrology and

- Origin of Rocks From the Descartes Highlands. *Proc. Fourth Lunar Science Conference, Geochimica et Cosmochimica Acta*, Supplement 4, Vol. 1, 1973, pp. 1013-1032.
43. HUBBARD, N. J., AND C. SHIH, Opposing Partial Melting Models and the Genesis of Some Lunar Magmas (abs.). *36th Annual Meeting Meteoritical Society*, 1973, pp. 72-73.
44. HUBBARD, N. J., AND C. SHIH, *Partial Melting Models and the Precursors of Lunar Non-Mare Magmas*. In preparation.
45. GAST, P. W., The Chemical Composition and Structure of the Moon. *The Moon*, Vol. 5, 1972, pp. 121-148.
46. WOOD, J. A., J. S. DICKEY, JR., U. B. MARVIN, AND B. N. POWELL, Lunar Anorthosites and a Geophysical Model of the Moon. *Proc. Apollo 11 Lunar Science Conference, Geochimica et Cosmochimica Acta*, Supplement 1, Vol. 1, 1970, pp. 965-988.
47. SMITH, J. V., A. T. ANDERSON, R. C. NEWTON, E. J. OLSEN, P. J. WYLLIE, A. V. CREWE, M. S. ISAACSON, AND D. JOHNSON, Petrologic History of the Moon Inferred From Petrography, Mineralogy and Petrogenesis of Apollo 11 Rocks. *Proc. Apollo 11 Lunar Science Conference, Geochimica et Cosmochimica Acta*, Supplement 1, Vol. 1, 1970, pp. 897-925.