# THE CHEMICAL COMPOSITION AND
# STRUCTURE OF THE MOON

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**Abstract.** Three types of igneous rocks, all ultimately related to basaltic liquids, appear to be common on the lunar surface. They are: (1) iron-rich mare basalts, (2) U-, REE-, and Al-rich basalts (KREEP), and (3) plagioclase-rich or anorthositic rocks. All three rock types are depleted in elements more volatile than sodium and in the siderophile elements when relative element abundances are compared with those of carbonaceous chondrites. The chemistry and age relationships of these rocks suggest that they are derived from a feldspathic, refractory element-rich interior that becomes more pyroxeni-tic; that is, iron/magnesium-rich; with depth.

It is suggested that the deeper parts of the lunar interior tend toward chondritic element abundances. The radial variation in mineralogy and bulk chemical composition inferred from the surface chemistry is probably a primitive feature of the Moon that reflects the accretion of refractory element-enriched materials late in the formation of the body.

Chemical and mineralogic studies of samples from five different points on the Moon have shown that more than 95% of the material returned from the lunar surface has a basaltic liquid somewhere in its ancestry; i.e. the great majority of materials from the lunar surface are derived from parent rocks that probably originated as an igneous liquid. The chemical compositions of these liquids are very different from any prim-itive material that could have separated from the dust and gas surrounding the Sun. This leads to the conclusion that the igneous liquids which have preceded most lunar rocks are produced by processes that involve extensive separation of igneous liquids and crystalline solids. At the outset of this discussion, I will make the rather plausible assumption that most of the igneous rocks on the lunar surface were the product of partial melting in the lunar interior, followed by segregation and upward transport of an igneous liquid. This does not preclude the possibility that many rocks on the lunar surface have undergone a second period of melting due to large collisions. The validity of the partial melting assumption has not been seriously questioned in the sense that internal melting does not take place. There is, however, real lack of agreement con-cerning the extent to which liquids produced in the lunar interior have been modified by shallow differentiation processes. If differentiation near the lunar surface takes place, I suggest that it has not been so extensive that fundamental differences in the composition of primitive deep-seated liquids have been obscured. This assumption will be discussed further in the analysis of minor and trace element data given below. If the assumption stated here is substantially correct, one can infer that the detailed chemical composition of deep-seated lunar liquids will be a prime source of information on the chemical and mineralogical composition of the lunar interior.

The main objective of this paper will be to determine constraints on the composition of the lunar interior that derive from the chemical composition of the lunar igneous rocks. Before attempting such an interpretation of the composition of the lunar inte-

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rior, the salient chemical characteristics of igneous rocks from the lunar surface will be summarized. These chemical characteristics will be compared to analogous characteristics of terrestrial volcanic rocks so that major similarities and differences between terrestrial and lunar basaltic rocks can be established.

## 1. Major Element Composition

The bulk chemical composition and ranges of concentrations of major elements in unambiguous igneous rocks from the Apollo 11, 12, and 15 sites are shown in Table I, along with the composition of a single igneous fragment in the Luna 16 sample.

TABLE I

Chemical composition of major lunar rock types

| Mare basalts | | | | KREEP | | Plagioclase rich rocks | | Silica rich rocks |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| XI[a] | XII[b] | XV[c] | L 16[d] | XII[e] | XIV[f] | 15415[g] | Anortho.[h] Gabbro | 12013[i] |
| $SiO_2$ 40.70 | 44.95 | 46.07 | 43.8 | 47.6 | 48.0 | 44.08 | 45.3 | 59.7 |
| $TiO_2$ 11.00 | 3.32 | 2.13 | 4.9 | 1.7 | 2.1 | 0.02 | 0.48 | 1.3 |
| $Al_2O_3$ 9.43 | 9.19 | 8.95 | 13.65 | 17.2 | 17.1 | 35.49 | 26.3 | 16.2 |
| $Cr_2O_3$ 0.32 | 0.51 | – | 0.55 | 0.17 | -- | 0.20 | ~.1 | 0.2 |
| FeO 17.42 | 20.53 | 21.19 | 19.35 | 9.4 | 10.5 | 0.23 | 5.3 | 10.7 |
| MgO 7.34 | 9.83 | 9.51 | 7.05 | 9.1 | 8.7 | 0.09 | 7.3 | -- |
| CaO 10.52 | 10.94 | 10.21 | 10.4 | 10.2 | 10.7 | 19.68 | 14.6 | 7.1 |
| $Na_2O$ 0.49 | 0.28 | 0.26 | 0.38 | 1.0 | 0.7 | 0.34 | 0.3 | 1.0 |
| $K_2O$ 0.18 | 0.058 | 0.034 | 0.15 | 0.7 | 0.5 | 0.01 | 0.07 | 1.7 |
| $P_2O_5$ 0.12 | 0.088 | 0.07 | – | 1.0 | – | -- | -- | – |
| MnO 0.23 | 0.27 | 0.28 | 0.20 | – | – | – | – | 0.16 |

[a] Average of 13 analyses reported in *Proceedings of the First Lunar Science Conference.*
[b] Average of 17 analyses reported in *Proceedings of the Second Lunar Science Conference.*
[c] Average of 7 analyses reported by LSPET, 1972.
[d] Composition of one crystalline fragment, Vinogradov, 1971.
[e] Average of 29 fragments, broad beam microprobe analyses given by Keil and Fuchs, 1971; Meyer *et al.*, 1971; Smith *et al.*, 1970.
[f] Average of Type B and C glasses, Apollo Soil Survey, 1971.
[g] Composition of Rock 15415, a very pure plagioclase from Apollo 15 site, LSPET, 1972.
[h] Average of high alumina feldspathic basalts, Reid *et al.*, 1972.
[i] Average composition of 12013, Wakita and Schmitt, 1970.

Studies of individual millimeter and submillimeter size fragments indicate that the soil at the Apollo 11 and 12 sites contains igneous rock types that were not found in the macroscopic rock specimens returned from these sites. The Apollo 12 soil sample, in particular, revealed a totally different type of basaltic rock characterized by the occurrence of orthopyroxene and very unusual relative and absolute abundances of large radius cations (U, Th, Ba, and rare Earth elements). The average major element composition

of these fragments and the range of compositions for a number of individual analyses are also given in Table I. These fragments which were designated norite by Marvin *et al.* (1971) and KREEP by Hubbard *et al.* (1971a) are remarkably similar in composition to most Apollo 14 samples. Some fragments with this composition have also been found in the Apollo 11 soil; for example, Luny Rock 1 (Albee and Chodos, 1970). In addition, fragments rich in basic plagioclase have been observed in soil samples from
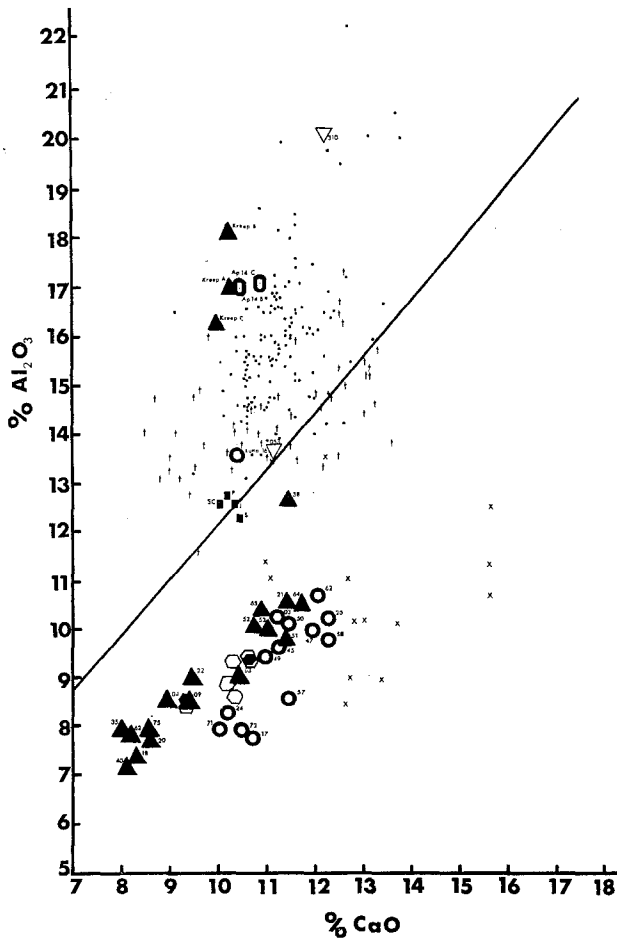


Fig. 1. CaO and Al₂O₃ contents of lunar basalts, basaltic achondrites, and terrestrial basalts. Symbols are as follows: ○ Apollo 11 basalts, ▲ Apollo 12 basalts, △ KREEP, 0 Apollo 14 samples, ⬡ Apollo 15 basalts, ■ basaltic achondrites, · oceanic ridge basalts, † Icelandic basalts, and × post-erosional Hawaiian basalts. The solid line shows the locus of chondrites and basaltic achondrites. Both terrestrial and lunar basalts appear to divide into groups that fall on either side of this line; i.e. the Al-rich (ORB on Earth and non-mare basalt on the Moon) group with an Al/Ca ratio greater than the meteorite ratio and the Al-poor rocks with low Al/Ca ratios (nepheline normative basalts on Earth and mare basalts on the Moon) lower than the meteorite ratio. Given the very plausible assumption that the Al/Ca ratio of both planets is meteoritic, this observation suggests that two distinct petrogenetic fractionation trends are involved in producing liquids with these compositions.

all points on the lunar surface that have been sampled. Such plagioclase-rich fragments also occur as clasts in most breccias returned from the lunar surface. Mineralogically, these fragments resemble terrestrial anorthosites or anorthositic gabbros. Many of these rock fragments cannot possibly represent a primitive liquid. The data discussed below also suggests that plagioclase-rich fragments cannot have been derived from a single parent liquid. Two compositions representing gabbroic anorthosite and rather pure anorthosite are shown in Table I. The existence of rocks enriched in plagioclase by segregation of this mineral from an igneous liquid was dramatically demonstrated by the discovery of a rock consisting of more than 99% pure plagioclase during the Apollo 15 mission. Finally – for completeness – the composition of the light portion of one very unusual rock – 12013 – which is similar to granite in composition is given in Table I.

The summary given in Table I shows that the elements iron, titanium, and aluminum – and to a lesser extent magnesium – account for most of the variance in the chemical composition between groups of lunar igneous liquids. This variation is il-
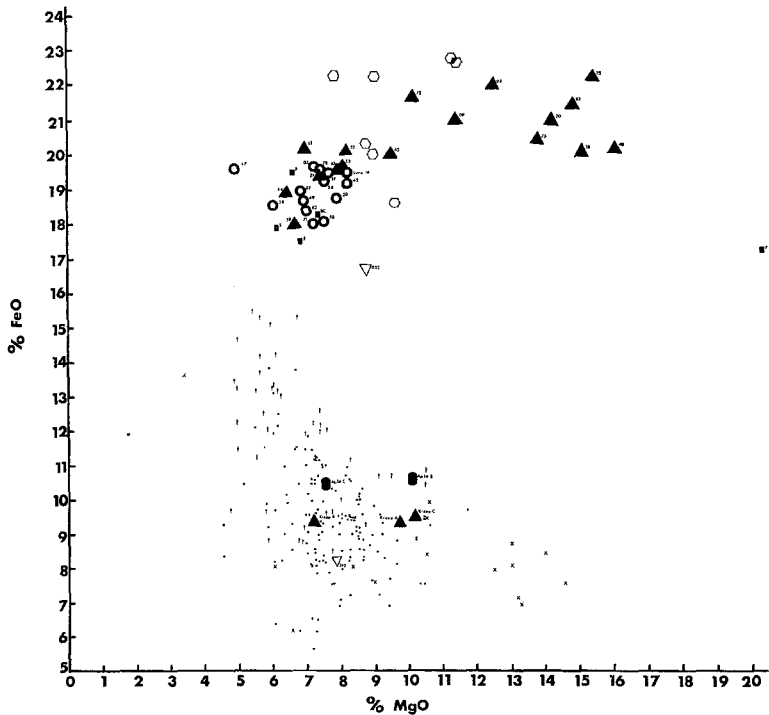


Fig. 2.   FeO and MgO contents of lunar basalts, basaltic achondrites, and terrestrial basalts. Symbols same as Figure 1. The three groups of terrestrial basalts shown here were chosen to illustrate the extremes in total Fe (as FeO), FeO, $Al_2O_3$, and $TiO_2$ contents found in terrestrial basalts. A much more extensive compilation – e.g. Manson (1967) – of terrestrial basalts would still show a very marked gap between the total Fe content of lunar and terrestrial basalts. The high MgO Apollo 12 basalts are probably the result of olivine (Fa 68–72) accumulation.

lustrated in three different plots of the concentrations of these elements shown in Figures 1, 2, and 3. The iron-magnesium and iron-titanium plots show rather clearly that there is a first-order separation of lunar samples into a high iron and low iron group. The calcium-aluminum diagram shows a similar variation in the aluminum content. In fact, the high aluminum and low iron group of samples appear to coincide as do the high iron and low aluminum group. The iron, titanium, and magnesium concentrations observed in some terrestrial basalts are also shown in Figures 1, 2, and 3.

The comparison of lunar and terrestrial compositions clearly indicates that the mare basalts have higher total iron concentrations than most terrestrial basalts. Furthermore, iron is consistently present only as $Fe^{++}$ except for very minor amounts of metallic iron, while terrestrial basalts always contain significant proportions of ferric iron. The CaO and $Al_2O_3$ concentrations of mare basalts are somewhat similar to
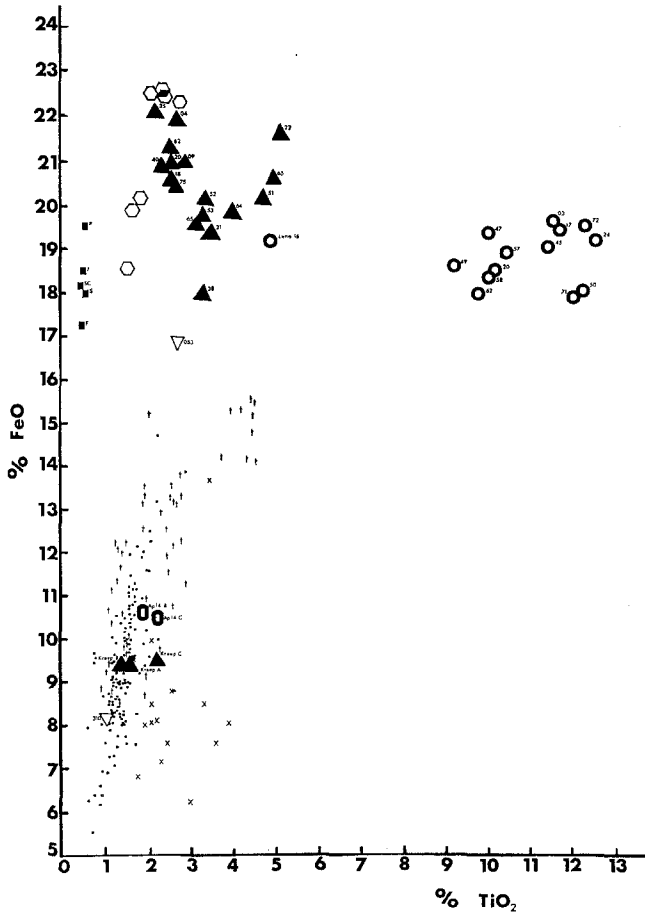


Fig. 3. Total Fe (as FeO) and $TiO_2$ contents of lunar basalts, basaltic achondrites, and terrestrial basalts. Symbols same as Figure 1. The extreme $TiO_2$ contents of Apollo 11 basalts are clearly shown here. However, other mare basalts (Luna 16) also tend to have relatively high $TiO_2$ contents relative to terrestrial basalts.

those of undersaturated olivine basalts, while the non-mare or low iron basalts are, in many respects, similar to the oceanic ridge basalts. Even though the comparison illustrated in Figures 1–3 is far from exhaustive, it is clear that variation in chemical compositions found in lunar basaltic rocks is much greater than that observed for terrestrial basaltic rocks. The $Na_2O$ and $K_2O$ content of terrestrial basalts, lunar basalts, and meteoritic materials are compared in Figure 4. These data show that lunar and meteoritic materials have consistently higher $Na_2O/K_2O$ ratios than terrestrial basalts. No adequate explanation of this systematic difference has been put forth to date.



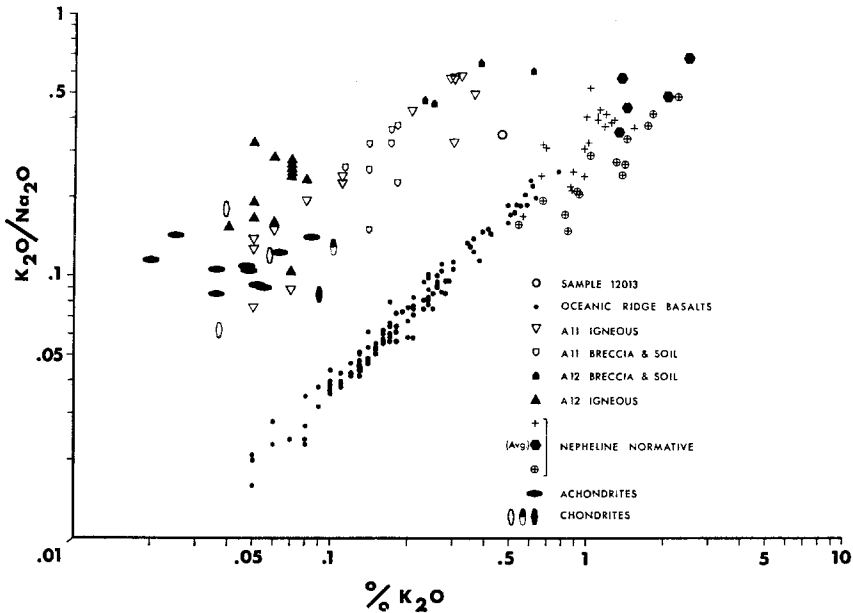Fig. 4.  $K_2O$ and $Na_2O$ content of terrestrial and lunar basalts. The ratio of $K_2O/Na_2O$ is systematically higher in meteoritic and lunar materials than all terrestrial basalts.

## 2. Minor Elements

In order to facilitate subsequent discussion of trace element concentrations, they will arbitrarily be divided into three groups: (1) The large ion lithophile elements – K, Rb, Cs, Ba, U, Th, REE, Sr, and Li (Li will be discussed with this group even though it is clearly a much smaller ion); (2) The siderophile elements – i.e. elements more easily reduced than iron; and (3) Elements that are volatile under reducing conditions at temperatures in excess of 1000–1200°C. The latter group includes many of the chalcophile elements (elements forming stable sulfur compounds) in addition to the halogens. It may also include Au and Ge which also belong to Group 2.

    The comparison of the chemistry of basalts from different points on the lunar surface will emphasize the large ion lithophile elements because the abundance of these

elements varies greatly from one type of lunar basalt to another. The latter groups will be discussed more generally. In all of the discussion of minor elements, the abundance of these elements in carbonaceous chondrites will frequently be employed as a convenient frame of reference.

## 2.1. SIDEROPHILE ELEMENTS

Elements that are concentrated into the iron-nickel phase in chondritic meteorites have been designated siderophile elements (Goldschmidt, 1954). The most unambiguous examples are Ni, Co, Ge, Au, Re, and the Pt metals. In the Earth these elements are thought to be largely concentrated into the Earth's core (Goldschmidt, 1954; Ringwood, 1966; Brett, 1971). Thus terrestrial basalts would be expected to be markedly depleted in these elements when compared to chondritic meteorites. The understanding of the geochemistry of these elements is, in general, very limited by the paucity of data, particularly for Re, Au, and most of the Pt elements. Even the very detailed studies of the lunar samples produced little or no accurate data for most Pt elements. Figure 5 is a summary of the concentration of these elements in lunar mare basalts and terrestrial basalts. The depletion of these elements is remarkably variable. It is significant that Os and Ir are much more depleted than Ni and Co. Furthermore, the appar-
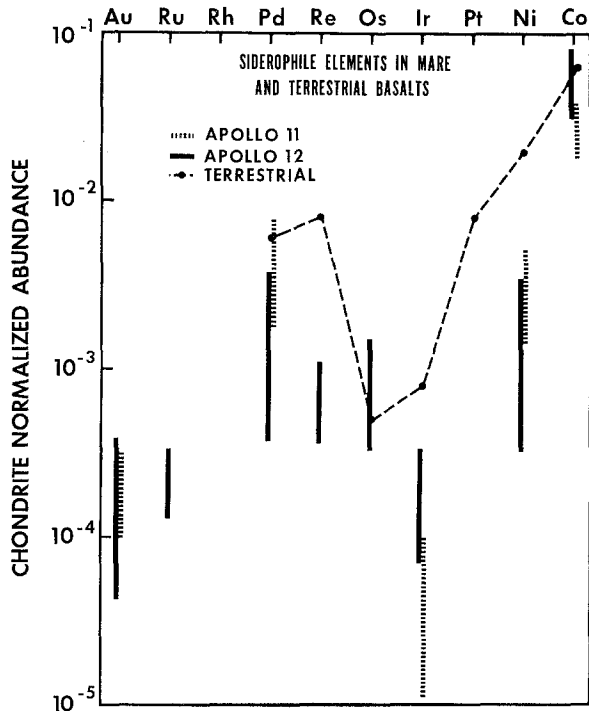


Fig. 5. Chondrite normalized siderophile abundance patterns. Chondrite data are taken from Crocket (1969). Lunar data are taken from Reed and Jovanovič (1971), Anders *et al.* (1971), Baedecker *et al.* (1971), Herr *et al.* (1971), and Laul *et al.* (1972).

ent removal of Ni from the Earth's mantle (Ringwood, 1966; Brett, 1971) is not nearly as extensive as would be inferred from the known distribution of Ni between silicates and metal. Terrestrial and lunar basalts are remarkably similar for the Ni, Co, and the platinum metals in this comparison. However, Ge and possibly Au are much more depleted than other siderophile elements. The depletion of the lunar basaltic rocks by as much as six orders of magnitude indicates that the parent liquids for these rocks must have been equilibrated with a metallic iron, which was separated from these liquids before they reached the surface (see also Reid *et al.*, 1970). O'Keefe (1970) has suggested that the similarity in terrestrial and lunar siderophile element abundances is strong evidence that the Moon must have separated from the Earth after formation of the Earth's mantle. This hypothesis does not explain the different Fe/Mg ratio of the lunar and terrestrial basalts or the different Na/K ratio. It is, furthermore, significant that some siderophile elements – in particular Au and Ge – are much more depleted in the lunar basalts than they are in terrestrial basalts. Other elements, e.g. Pb, Tl, Bi, and the halogens, are also extremely depleted. These differences are not readily explained by the fission hypothesis. However, a few percent of metallic Fe formed by reduction or present in the primitive Moon are probably sufficient to return siderophile elements in the lunar interior.
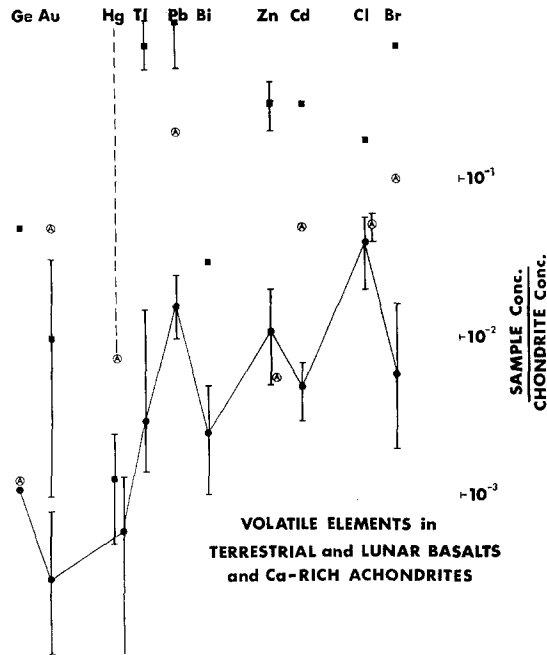


Fig. 6.   Chondrite normalized abundances of Ge, Au, Hg, Tl, Pb, Bi, Zn, Cd, Cl, and Br. The concentrations were divided by average of Type I and II carbonaceous chondrites given by Larimer and Anders (1967). Basalt and achondrite data were taken from Ehmann *et al.* (1970), Wasson and Baedecker (1970), Ehmann (1967), Turekian and Wedepohl (1961), Engel *et al.* (1965), Lieberman (unpublished results), Lieberman and Ehmann (1967); Reed and Jovanović (1971). Lunar data was taken largely from the work of Ganapathy *et al.* (1970). Pb[204] concentrations were estimated from the work of Tatsumoto (1970).

## 2.2. VOLATILE AND NONVOLATILE ELEMENTS

Anders (1965) has shown that many heavy metals are regularly depleted in hypersthene and bronzite chondrites when compared to Type I carbonaceous and Type I enstatite chondrites. Gast (1960, 1968a) has argued that many of these elements are also depleted in the Earth when compared to carbonaceous chondrites or normal chondrites. This naturally leads to a query regarding the abundance of these elements in the Moon. Carbonaceous chondrite normalized abundances of the elements Ge, Au, Hg, Tl, Pb, Bi, Zn, Cd, U, and Br in achondrites, terrestrial basalts, and lunar basalts are shown in Figure 6. Even though some of the concentrations of many of these elements cover a rather wide range, it is quite clear that lunar basalts, as well as achondrites, are much more depleted in this group of elements than terrestrial basalts. The only non-siderophile element that is strongly depleted in terrestrial basalts is Hg.

The marked depletion in volatile elements is also demonstrated when the abundance of moderately volatile elements such as the heavy alkali metals is compared to that of geochemically similar refractory elements like barium and uranium. The geochemical
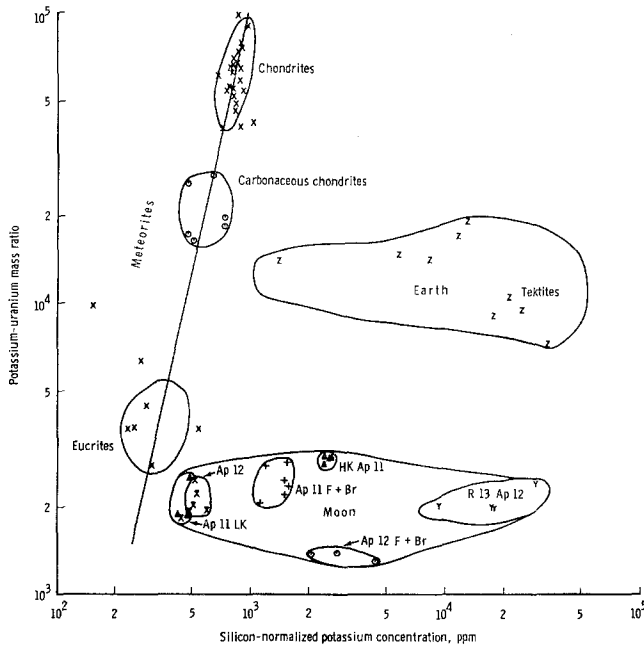


Fig. 7. Potassium/uranium mass ratios in the Earth's crust, chondritic meteorites, calcium rich achondrites, and lunar rocks and soil. The K concentrations have been normalized to a constant $SiO_2$ concentration, i.e. K plotted = K observed x Si observed 18.5. Terrestrial data are representative analyses of composites or averages taken from the literature. Chondrite analyses include 4 enstatite chondrites, 6 olivine bronzite chondrites, and 17 olivine hypersthene chondrites. Analyses are taken from the literature; K and U determinations are usually on different samples and by different analysts. Calcium-rich achondrites plotted for Nuevo Laredo, Stannern, Moore Co., Sioux Co, Pasamonte, Juvinas, and Macabini. Groups of lunar samples shown are Apollo 11 low K rocks, fines and breccia (Br), and high K (HK) rocks; Apollo 12 igneous rocks (X); Apollo 12 fines (F) and breccia (Br); and Apollo 12 rock 12013 (R 13).

similarity of potassium and uranium or thorium is well established by a large number of excellent analyses for these elements in a variety of terrestrial rocks. The relative abundance of potassium and/or thorium varies by less than a factor of 2 in rocks as diverse as oceanic ridge basalts containing less than 0.1% potassium and granites having more than 5% potassium. The constancy of the K/U ratio in a wide variety of terrestrial rocks is illustrated in Figure 7. The variation in the relative abundance of these elements in meteorites is in strong contrast with that found in terrestrial rocks. Achondritic meteorites are strongly depleted in potassium relative to uranium when compared to most chondrites. The wide range of K/U ratios observed for meteorites is also illustrated in Figure 7. The K/U ratio and K contents of all lunar rocks analyzed to date are compared with those of both meteorites and terrestrial rocks in Figure 7. The data shown there suggests that the Moon, like the Earth, has a distinctive K/U ratio and that the lunar ratio is even lower than that of the Earth. In addition, careful comparisons of various lunar rock types reveal that the high-K or KREEP basalts have systematically lower K/U ratios $(1500 \pm 300)$ than the mare basalts $(3000 \pm 700)$.

It is well known that the high temperature behavior of lithium is quite different from that of the heavier alkali metals. Its volatility is, in fact, similar to that of refractory elements like calcium and aluminum. The different behavior of these elements in complex natural systems has been clearly demonstrated by simple volatilization experiments on lunar samples (Gibson and Hubbard, 1972). A comparison of terrestrial, meteoritic, and lunar K/Li ratios similar to K/U ratios does, indeed, show a remarkable parallelism between these two element ratios. Both the alkali metal comparisons and the low abundance of other volatile elements suggest that that part of the Moon that is involved in the formation of the rocks now seen on the surface must be depleted in volatile elements when compared to more primitive solid systems such as carbonaceous chondrites which are generally accepted as representative in solar abundances.

## 2.3. LARGE ION LITHOPHILE ELEMENTS

The elements that normally occur as oxides or silicates in chondritic meteorites were first designated as lithophile elements by Goldschmidt (1954). A somewhat more restrictive class of elements are those lithophile elements that are strongly enriched in the Earth's crust relative to the whole Earth or the Earth's mantle. These are generally electropositive elements forming ions substantially larger than the major cations of the mantle, i.e. Mg, Fe, Ca, and Al. The heavy alkaline earths Sr and Ba, the rare earth elements, and uranium will be considered in the discussion that follows. The alkali elements K, Rb, and Cs are both volatile and form large electropositive ions. The concentrations of the refractory LIL (large ion lithophile) elements will be considered in a standard frame of reference, i.e. they will be compared to average concentration of these elements in chondrites. The chondrite normalized concentrations of this series of elements for igneous rocks from the Apollo 11, 12, 14, and 15 sites are shown in Figures 8 and 9.

Similar element abundance patterns in a group of terrestrial basalts are shown in Figure 10. The data shown there are chosen to represent the widest range of trace

element characteristics observed for these elements. They illustrate the relation be-
tween the degree of silica saturation and the slope in the abundance pattern that has
been observed for most basalts found in oceanic regions.

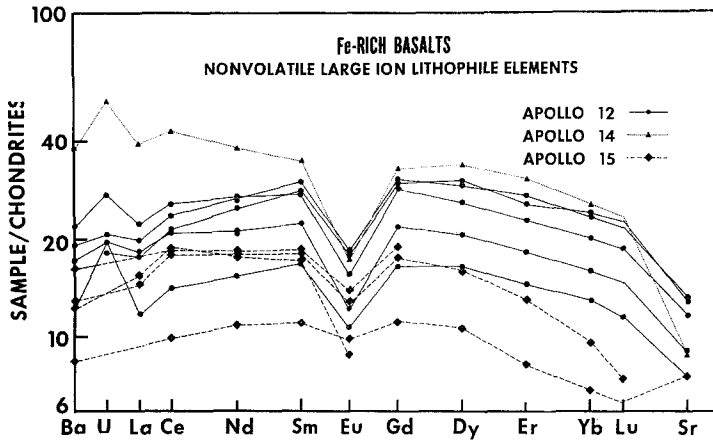The most remarkable characteristic of the lunar igneous rocks is the very marked



Fig. 8.   Chondrite normalized refractory large lithophile element abundances for Fe-rich basalts
from Apollo 11, 12, 14, 15 sites and Luna 16. Chondrite values and Apollo 12 samples are from
Hubbard and Gast (1971); Apollo 14 data are from Hubbard *et al.* (1972); sample 15555 data are from
Philpotts (personal communication, 1971); other Apollo 15 data are unpublished results.
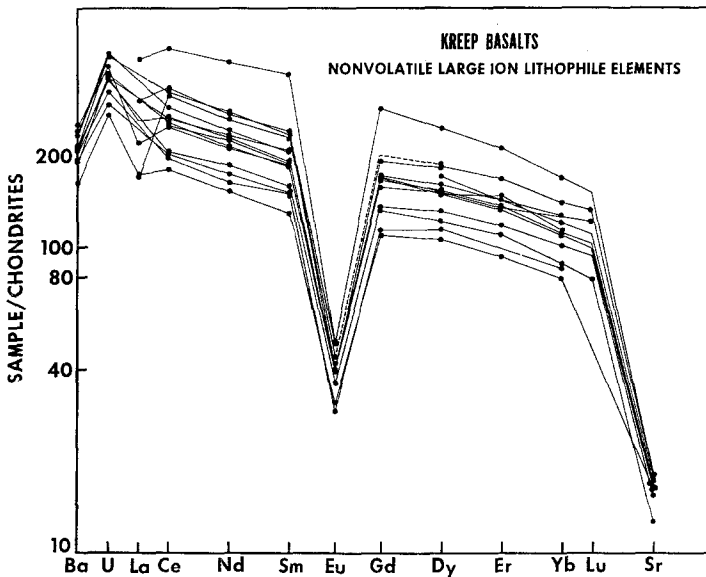


Fig. 9.   Chondrite normalized refractory large ion lithophile elements in KREEP basalt fragments
from Apollo 14 and Apollo 12 sites. Data are from Hubbard and Gast (1971) and Hubbard *et al.* (1972).
Some Eu and Sr concentrations for these fragments could not be plotted because of overlapping data
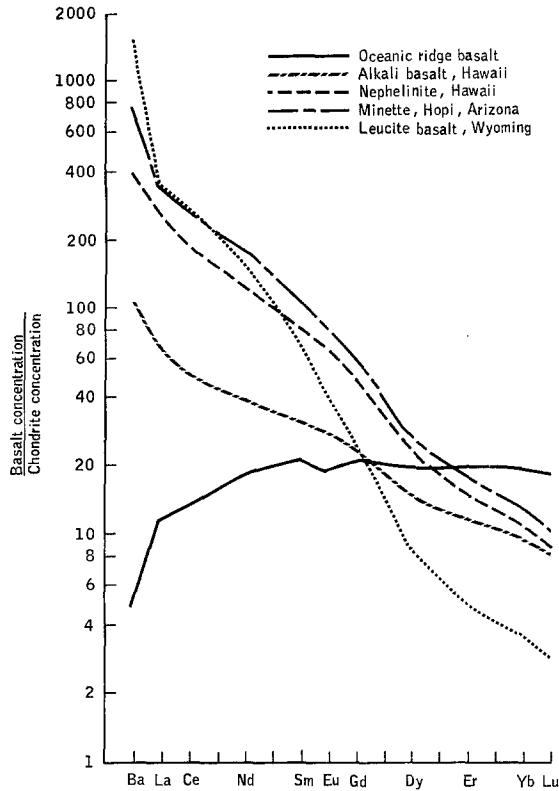points. Apollo 11 samples are from Gast *et al.* (1970).

Fig. 10.   Chondrite normalized terrestrial LIL abundance patterns. Data are from Kay (1970),
Kay et al. (1970), and unpublished data. Uranium data on oceanic basalts
were furnished by Tatsumoto (personal communication).

separation of europium and strontium from the remaining large ions. The anomalous abundance of europium is almost certainly related to the different oxidation states of terrestrial and lunar basalts. It was noted above that lunar basalts are virtually free of ferric iron. Terrestrial basalts rarely have less than 10% of their iron as $Fe^{+++}$. Trace element studies on a relatively reduced group of terrestrial basalts, i.e. the oceanic ridge basalts, show that europium is only partly reduced to $Eu^{++}$ ($Eu^{++}/Eu^{+++} \sim 0.2$). Careful analysis of europium concentrations in coexisting phases in lunar basalts shows that the $Eu^{++}/Eu^{+++}$ ratio in the parent liquid of these basalts was probably in excess of 5 (Philpotts, 1970). Since $Eu^{++}$ and $Sr^{++}$ have very similar ionic characteristics, it is not surprising that these two elements should behave quite similarly during igneous differentiation processes.

   The terrestrial and lunar characteristics of the other large ions shown in Figure 10 are also somewhat different. Terrestrial basalts are characterized by wide range of relative abundances of light and heavy rare-earths. The light and heavy rare-earths in lunar basalts are only mildly fractionated. Thus the variation in concentration of the heavy rare-earths in lunar basalts is much greater than that observed in terrestrial

basalts. We should also note that barium is frequently significantly depleted relative to light rare earths such as Ce and Nd in a number of lunar basalts where the light rare-earth elements are otherwise strongly enriched.

The distinctive europium and strontium fractionations observed in the lunar basalt indicate that the liquids from which these basalts crystallized must have separated from a phase enriched in large divalent ions. The only common mineral fitting this description is plagioclase. It was noted above that calcium-rich plagioclase fragments do occur in the lunar soil. Several individual plagioclase-rich fragments have been analyzed for the LIL elements. The relative abundances are shown in Figure 11. These
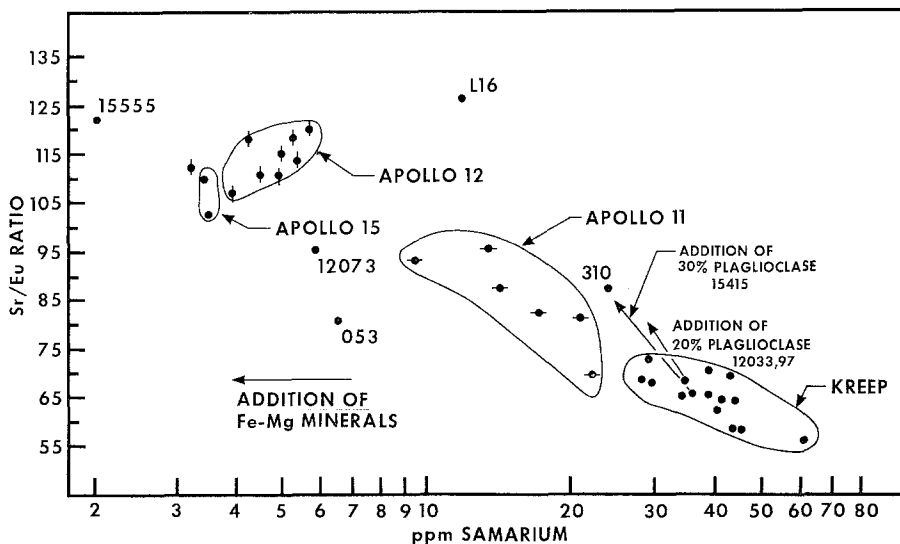


Fig. 11. Sr/Eu ratios versus Sm content of lunar basaltic samples.
Data are from references cited in Figures 8 and 9.

analyses clearly show that europium and strontium are, indeed, both enriched in plagioclase; however, the abundance of these two elements in different fragments rich in plagioclase appears to vary significantly. Hubbard *et al.* (1971a) conclude that some anorthosites are derived from Eu and Sr depleted liquids, while others are derived from liquids in which the relative abundance of these elements is nearly chondritic.

When the major element and LIL element compositions of various lunar rock types are compared, they reveal a very systematic correlation, i.e. all LIL-rich rocks are relatively rich in Al and poor in Fe, and the LIL element poor rocks are Fe-rich, and low in Al; that is, mare basalts. Detailed examination of the LIL abundance patterns reveal a number of significant regularities: (1) The high Al basaltic rocks have LIL abundance patterns in which the light REE and U are systematically enriched relative to the heavy REE. Only La and occasionally Ce depart from this regular pattern. (2) Many of the Fe-rich basalts have LIL abundance patterns with maxima in the region
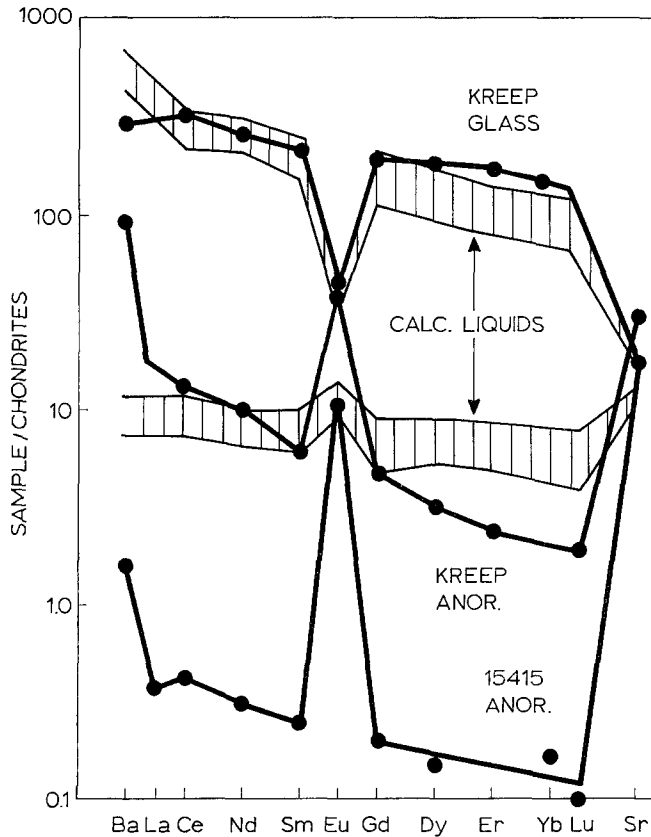
Fig. 12.   Chondrite normalized abundance of LIL elements in two different types of plagioclase-rich fragments. Data are from Hubbard *et al.* (1971b). Liquids in equilibrium with these two types are calculated using distribution coefficients estimated from plagioclase phenocryst matrix comparisons.

of Sm and Gd. (3) The abundances of Eu and Sr correlate rather well. (4) The ratio Sr/Eu varies in a regular way with the abundance of Gd and Sm. This is illustrated in Figure 12, which shows that the Sr/Eu ratio of lunar basalts approaches that of chondritic meteorites as the total LIL element abundance decreases. The LIL element data summarized here clearly shows that terrestrial and lunar basalts differ in at least two significant characteristics: (1) Some terrestrial basalts must be produced by processes which can fractionate the heavy rare-earth and light rare-earth elements very efficiently, and (2) The behavior of both Sr and Eu in terrestrial basalts is significantly different (particularly in nepheline-normative basalts) from that found in lunar basalts.

## 3. Summary of Chemical Characteristics

Generalizations regarding the chemistry of the lunar surface made at this writing are subject to serious limitations. First, the paucity of data and secondly, they are highly

susceptible to revision by new data obtained on forthcoming lunar landings. In this context, the proposed generalizations put forth here are somewhat in the nature of propositions rather than observations. Even though the data is limited and subject to revision, it furnishes us with a useful working hypothesis. The comparison of samples from four unambiguous mare regions with two somewhat ambiguous non-mare regions clearly suggests that the iron and aluminum concentrations in basaltic rocks on the lunar surface are major chemical characteristics that distinguish the lunar highlands and lunar maria.

Preliminary results from the Apollo 15 experiment that measured the intensity of characteristic aluminum and silicon $x$-radiation from the lunar surface (Adler *et al.*, 1972) show that the $Al_2O_3$-rich materials must be a major component of large areas of the highlands. Results of the measurement of the gamma ray intensity of the lunar surface (Metzger *et al.*, 1972) clearly indicate that the abundance of LIL-rich material may vary greatly from one highland material or summary region to another. The relative abundance of Al-rich basaltic rocks also rich in LIL elements and very Al-rich anorthositic rocks that are poor in LIL elements is at present one of the major unresolved questions about the lunar highlands.

Chemical and mineralogical analyses of individual grains from the lunar regolith have revealed several rock types not elaborated in the above summary; for example, ultramafic rocks, trachytic or silicic basalts, and extremely Fe- and Ti-rich glasses. The abundance and source of such rocks on the lunar surface is not known. In addition, optical (McCord *et al.*, 1972) and photographic studies of the lunar surface suggest that the very low albedo materials such as those found in the southeastern portion of Mare Serenitatis and in smaller occurrences like the dark halo craters in the Crater Alphonsus or the dark halo crater Copernicus H may represent a distinctive type of volcanic material. McCord *et al.* and McCord (personal communication) suggest that these dark materials contain a high proportion of Fe- and Ti-rich glass. The association of the low albedo materials with distinctive volcanic structures indicates that they may be a type of volcanic deposit that should be distinguished from the much more widespread mare basalts. Perhaps the very Fe- and Ti-rich glasses are derived from these young volcanic structures.

### 3.1. CHRONOLOGY OF LUNAR VOLCANISM

The absolute ages of mare basalts from four points on the lunar surface (Papanastassiou and Wasserburg, 1971a, b, 1972; Wasserburg and Papanastassiou, 1971) and studies of crater morphology (Soderblom and Lebofsky, 1972) indicate that most mare volcanism probably occurred during the interval 3.0–4.0 billion years ago. The age of crystallization in several non-mare basalts collected at the Apollo 14 site have also been determined (Wasserburg and Papanastassiou, 1971). These times cannot, however, be unambiguously ascribed to an extrusive igneous event; that is, they cannot be associated with extensive lunar volcanism. The widespread occurrence on the lunar surface of small fragments that yield Rb/Sr model ages 4.4–4.5 billion years suggests that many of the materials with crystallization ages of 3.9–4.0 billion years may, in fact, be derived

from igneous rocks formed much earlier in lunar history. Hubbard and Gast (1971) specifically suggest that the chemical and isotopic characteristics require liquids produced by partial melting 4.3–4.4 billion years ago. The absolute age of the dark halo or low albedo deposits can only be inferred from their morphology and relatively undisturbed character. The occurrence of one such crater on the ejecta of a young rayed crater, i.e. Copernicus, indicates that such materials were deposited substantially later than the youngest mare basalts.

When viewed together, the chemical and chronological data suggests that the character of lunar volcanism apparently changed with time, beginning with Fe-poor and Al-rich materials 4.4–4.5 billion years ago and ending with very Fe-rich materials perhaps as recently as 1 billion years ago. It should also be noted that the total volume of post-3 billion year volcanism is probably negligible or very small when compared to the volume of pre-3 billion year volcanic materials. The changing characteristics of lunar volcanism probably reflect both the increasing depth of the zone of melting and radial variations in the chemistry and mineralogy of the planet.

## 4. Lunar Interior and Petrogenesis of Lunar Mafic Liquids

Most of the major chemical characteristics of uncontaminated (by assimilation of continental crusts) terrestrial mafic liquids can be explained by two factors: (1) The extent of partial melting in the Earth's upper mantle and (2) the depth at which the melting or equilibration with the mantle takes place (see for example, Green and Ringwood, 1967; Gast, 1968b, 1970; Green, 1970). The andesites and tholeiitic basalts of the island arcs may be an exception to this generalization if they are produced by melting of an underthrust oceanic crust (Taylor et al., 1969). The application of this generally accepted model of the petrogenesis of terrestrial mafic liquids has provided important insights into the chemistry and mineralogy of the Earth's upper mantle. It is quite natural that a similar model of basalt petrogenesis should be invoked for the lunar mafic liquids. Before doing so, however, the validity of several alternative models must be considered. With virtually no knowledge of the detailed structure and stratigraphy of the lunar surface and very little information on the physical state of the lunar interior, it is difficult to make such an evaluation in a rigorous way. However, the inferences and implications of some alternative models of petrogenesis which have been proposed tend to support the partial melting model as the most plausible explanation of the observed chemical and physical characteristics. Specifically, the alternatives to partial melting at different depths in the lunar interior involve chemical fractionation on a Moon-wide scale (see for example, Smith et al., 1970; Wood et al., 1970) or very extensive differentiation by fractional crystallization near the lunar surface (O'Hara et al., 1970). These alternative models will not be reviewed in detail here, but some general characteristics and implications need to be noted. Any scheme of differentiation that produces the chemical characteristics of the lunar basalts in a single Moon-wide melting and crystallization event leads to the inference that the residual basaltic liquids produced by such an event should be quite

similar from place to place. The systematic and large difference between the Apollo 11, 12, and 15 basalts is not predicted by such a model and must thus be explained by additional local differentiation processes. The more than fivefold difference in abundance of many lithophile elements that is found for the Apollo 11 and 12 or 15 sites is an example of the scope of the local differentiation processes that need to be invoked. The early Moon-wide differentiation hypothesis has the inherent feature that it is associated with the heating of the Moon by release of gravitational potential energy during lunar accretion or by other cataclysmic heating processes. In this case, the melting of the Moon must take place in a very short interval, with subsequent cooling of the outer 100 km over a period of 10–30 million years. All rocks associated with this early melting and particularly with the formation of the crust must, therefore, date back to a single early event in lunar history and must fall within a very narrow range of absolute ages.

O'Hara *et al.* (1970) have emphasized massive near-surface fractional crystallization and the loss of volatile elements from the surface of lava extrusions, in particular, sodium and water, in explaining the petrogenesis of the Apollo 11 liquids. The loss of volatile ions and molecular species from large volumes of a silicate liquid is almost certainly controlled by the diffusion rate of these species in the liquid rather than the escape rate from the surface of the liquid. In this situation, one would conclude that depletion in volatiles should only be observed in a thin surface layer. Depletion of flows and intrusions that are hundreds of meters thick (or even tens of meters) requires both extreme convection and diffusion rate in these bodies. The complete absence of heterogeneities in sodium and water rich minerals in the lunar igneous rocks and soil is strong evidence against the efficacy of volatilization of these elements from liquids extruded on the lunar surface. The extent of fractional crystallization due to removal of plagioclase has been considered by Gast *et al.* (1970). They point out that the europium and strontium anomalies can only be accounted for in an extremely aluminum rich liquid. Thus, one chemical characteristic is explained by introducing another that is even more difficult to explain, i.e. postulating the existence of liquids that contain more than 80% anorthite.

In summary, it appears that the most comprehensive and generally satisfactory explanation of the chemical characteristics of the mare basalts and high aluminum KREEP liquids is the hypothesis that they were formed by partial melting, segregation of liquid, and upward transport of this liquid in the lunar interior. Proceeding from this working hypothesis, one can now inquire into the chemical and mineralogical composition of the lunar interior and the cause of the differences in terrestrial and lunar basalts.

### 4.1. PHASE COMPOSITION OF THE LUNAR INTERIOR

Ringwood and Essene (1970) have attempted to infer the phase composition of the lunar interior from the bulk composition of the Apollo 11 basalts in a series of laboratory experiments in which the phases in equilibrium with liquids of this composition at different pressures and temperatures were determined. They conclude that the

Apollo 11 basalts should be saturated with armalcolite, subcalcic augite, and nearly saturated with orthopyroxene. They also conclude that these liquids could not have been saturated with plagioclase. From these observations and the known distribution of density in the Moon, they are led to the suggestion that the lunar liquids are derived from a pyroxene rich assemblage. They propose a specific composition for this pyroxenite which is given in Table II. It should be noted that their composition implies a substantial fractionation between titanium and calcium or aluminum when it is com-

TABLE II

Model compositions of the lunar interior

|  | 1 | 2 | 3 | 4 |
|---|---|---|---|---|
| SiO$_2$ | 53.1 | 49.1 | 48 | 49.48 |
| TiO$_2$ | 1.0 | 0.45 | 0.8 | 0.46 |
| Al$_2$O$_3$ | 5.0 | 6.0 | 16 | 5.10 |
| FeO | 13.5 | 18 | 9 | 17.39 |
| Cr$_2$O$_3$ | 0.5 | 0.5 | – | 1.34 |
| MgO | 22.5 | 19.6 | 14 | 20.5 |
| CaO | 4.0 | 5.3 | 12 | 4.02 |
| Na$_2$O | 0.1 | 0.1 | – | 0.17 |
| MnO | 0.4 | 0.5 | 0.4 | 0.5 |

1. Lunar Interior, Ringwood and Essene, 1970.
2. Lower Lunar Mantle, this paper.
3. Mean Composition of the Upper 150 km, this paper.
4. Frankford, Howardite.

pared to the composition of chondritic meteorites. In the pyroxenite of Ringwood and Essene, plagioclase is stable to depths of 210 km at the temperature where basaltic liquid would be formed. At greater depths, plagioclase breaks down to spinel and pyroxene. Ringwood and Essene conclude from this diagram that the Apollo 11 liquids are produced by 1–2% partial melting of the spinel-bearing assemblage. This hypothesis conflicts with the strontium and europium anomalies; that is, the occurrence of plagioclase inferred from these anomalies.

The composition of the Apollo 14 samples; in particular, the uniformly high Al$_2$O$_3$ concentrations and high normative plagioclase content inferred from the bulk chemical composition of individual fragments and the average soil, indicates that non-mare basalts should commonly have plagioclase on the liquidus. Experimental studies (Walker *et al.*, 1972; Ringwood *et al.*, 1972) with liquids similar in composition to the Apollo 14 rocks have, indeed, shown that plagioclase is a liquidus phase. If liquids similar in composition to the Apollo 14 basalts are the product of partial melting in the lunar interior, one can safely infer that plagioclase is a phase that exists in the lunar interior in addition to clino- and orthopyroxene.

Thus, in the case of the KREEP basalts, the phase compositions derived for the source of these liquids by both experimental phase equilibria studies and from the trace element patterns are in rather good agreement. The phase composition of the

source of the mare basalts – in particular, the Apollo 11 basalts – remains as one of the unresolved questions in the petrogenesis of lunar materials. The evidence arising from trace element data will be further explored in the following section.

## 4.2. Minor element constraints on the composition of the lunar interior

The trace element characteristics of lunar igneous liquids enumerated above can be ascribed to: (1) the concentration and relative abundance of these elements in the source of the igneous liquids; i.e. the lunar interior and (2) the production, transport, and crystallization of these liquids. In other words, if the petrogenesis of the basaltic liquids is sufficiently well understood, the element abundance patterns observed for lunar basalts can yield information on the abundance of these elements in the lunar interior. The magnitude of the element abundances and the degree to which some elements are fractionated relative to each other allow us to state some conclusions on the composition of the lunar interior even before specific petrogenetic models are investigated. Due to the relatively large area-to-volume ratio of a small body like the Moon, the chemical composition of the surface can place a significant limit on the composition of the whole body. If, for example, it is assumed that the Apollo 14 materials and the KREEP fragments in the Apollo 12 soil are representative of a significant part of the non-mare lunar surface, one must infer certain constraints on the volume and composition of hypothetical source materials required to produce a lunar crust containing a significant portion of such rocks. In order to illustrate this point, I will assume that the mass of such materials now found near the lunar surface is equivalent to a shell 1 km thick. It should be noted that a 1 km thick low density crust can in no way account for the significant gravity anomalies (mascons) observed on the lunar surface. Reasonable density differences; that is, less than one gram per cc, require crustal thicknesses of low density material in excess of 20 km. Furthermore, the extensive cratering of the lunar surface; in particular, the lunar highlands, has resulted in some homogenization of the surface of the Moon so that samples now collected from the lunar surface must represent a vertical sampling that greatly exceeds 1 km, so a sample collected at several sites indicates vertical thicknesses far in excess of 1 km. The postulated 1 km layer is not equivalent to assuming that the entire lunar crust is similar to the Apollo 14 samples in composition; in fact, if the Moon has a crust 20–30 km thick, we assume that less than one-tenth of this crust is similar to the Apollo 14 materials in composition. Nevertheless, even this plausible assumption requires a shell of chondritic composition approximately 300 km thick to produce the postulated 1 km crust; that is, complete extraction of a group of elements from approximately 40% of the mass of the Moon would be required to make a relatively small fraction of the present lunar crust if the Moon had a chondritic concentration of elements like uranium, barium, and the light rare-earth elements. This simple calculation clearly illustrates the difficulties that are associated with a chondritic lunar composition.

The extension of this heuristic calculation to include a larger crust with lower uranium concentrations is quite obvious. A 30 km thick crust with an average uranium content of 0.5 ppm requires complete extraction of uranium from a mass much

larger than the 60% of the Moon that remains after a 1 kilometer thick layer of KREEP is accounted for.

In summary, the uranium concentrations observed in surface rocks appear to imply very deep and extremely efficient differentiation very early in lunar history. At present, this possibility probably cannot be rigorously excluded. However, it leads to several serious problems – in particular, a heat source for complete melting of the primitive Moon is required. Also, it implies that the source of the mare basalts is extensively depleted in LIL elements. This implication is in direct conflict with the element abundance patterns observed for these basalts.

We have already noted that chondritic concentrations of volatile elements in the lunar interior are inconsistent with the observed chemistry of the lunar surface; i.e. much lower concentrations of volatile elements are inferred. It now appears that we must further conclude that the lunar abundance of certain refractory elements is also nonchondritic, but enriched rather than depleted. This conclusion has already been tentatively derived from the LIL element abundance patterns observed in mare basalts (Haskin et al., 1970; Gast and Hubbard, 1970). The high abundance of these elements in the Apollo 11 basalts is inconsistent with any plausible petrogenetic model which derived liquids of this composition from a chondritic source. It is quite clear that similar models applied to the non-mare basalts with even higher concentrations of these elements will lead to even stronger similar conclusions. The basic model used to relate observed or postulated igneous liquid compositions to the composition of the source of these liquids is that of Gast (1968b) and Shaw (1970). This model has been used with some success in explaining LIL element abundances in terrestrial basalts (Kay, 1970). It will be utilized here to further elucidate the LIL element patterns in lunar basalts.

As a rather good first approximation, the major elements or components, e.g. $SiO_2$, $Al_2O_3$, CaO, and (MgO + FeO), in a silicate liquid produced by partial melting of the multi-phase assemblage are controlled by the mineral phases in equilibrium with that liquid part are independent of the proportion of these phases. This is not the case for minor elements that exist as dilute solutions in coexisting solid phases and liquid phases. The proportion of different phases, in particular, the proportion of liquid relative to solid phases, has a drastic effect on the composition of the liquid in addition to the specific phases that may be present. For the simple case where all phases are assumed to be in thermodynamic equilibrium, the composition of the liquid relative to the bulk composition of the system producing this liquid can be readily determined from the phase composition and dilute solution distribution coefficients. The usefulness of this simple model is at present restricted by the quality and paucity of data for distribution coefficients for elements of interest between coexisting mafic phases. However, even the present poorly-known distribution coefficients are sufficient to explain a number of qualitative characteristics of the LIL element abundance patterns and, furthermore, they lead to some semi-quantitative estimates of the phase and trace element composition of the source of the lunar and terrestrial basaltic liquids. Relevant observations and data on the appropriate distribution coefficients needed to explain the observed element patterns are summarized in Figure 13. The data shown there are
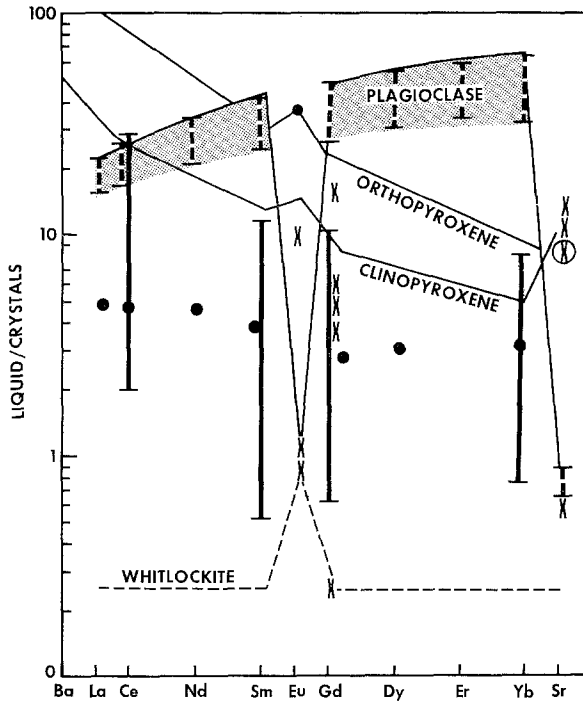
Fig. 13. Distribution coefficients for some LIL elements. The value plotted is the concentration in the liquid over the concentration in various crystalline phases. Individual symbols are results from synthetic systems reported by Green *et al.* (1971) – ×; Masuda and Kushiro (1970) – ⊗; and Shimizu and Akimoto (1971) – ●. The estimates shown by vertical bars are based on studies of phenocrysts in basaltic rocks (Schnetzler and Philpotts, 1970; Shih, personal communication). It is clear that the uncertainty in these constraints is still very significant. Some of this uncertainty clearly results from variations in the distribution coefficients with the bulk composition of the solid phases. Green *et al.* (1971) have shown, for example, that the Al content of clinopyroxene significantly effects the distribution of trivalent REE between a liquid and the coexisting clinopyroxene. In particular, the ratios $K_{REE}^{1/cpx}$ are much higher for diopside than augite. Furthermore, subcalcic clinopyroxenes may have higher ratios than pure diopside. The relatively high values in the calculations made here are, at least in part, justified by this observation; i.e. the phase undergoing melting is not the same as the common pyroxene observed as phenocrysts in basaltic rocks. The distribution coefficients for divalent europium are entirely based on synthetic studies. The values for Sr are based both on experimental data and on phenocryst data. The solid lines are those used in model calculations shown in Figures 14 and 15.

largely based on phenocryst-basalt groundmass pairs, with some key additions from recent experimental measurements. With regard to the Moon, the significant values in this figure are the clinopyroxene/basalt liquid values for the trivalent REE and the plagioclase/basalt liquid values for $Sr^{++}$ and $Eu^{++}$. The data shown in Figure 11 suggests that in the absence of garnet, clinopyroxene will be the dominant solid phase carrying the REE in an ultramafic assemblage, while plagioclase is the dominant solid phase carrying $Eu^{++}$ and $Sr^{++}$. It is, of course, also possible that accessory phases such as apatite, perovskite, sphene, or zircon may carry a significant proportion of

some of the elements under consideration. However, it is important to note that the effect of these phases can only be significant if they persist in the presence of a significant amount of liquid phase. In an equilibrium model, the effect of a minor phase must disappear as soon as that phase is eliminated from the system. In the case of apatite, we must postulate that the initial system must contain sufficient $P_2O_5$ to stabilize a phosphate phase. The low concentration of phosphorus in the mare basalts along with the relatively small amounts of partial melting generally inferred to produce these basalts suggests that phosphorus is very rare in the lunar interior; that is, makes up less than 0.01% of the source of these basalts. There is no evidence at present that equilibrium systems with such low concentrations of $P_2O_5$ will contain a phosphate as a stable phase. As a first approximation, the effect of accessory minerals in the equilibrium model will be neglected. However, incomplete specification of the phase composition of the lunar interior may be a significant omission in the calculations that follow. Phases such as perovskite and melilite may be particularly significant since they contain sites that could accommodate large divalent and trivalent ions.

A series of model calculations for two possible phase compositions are shown in Figures 14 and 15. The distribution coefficients used in these calculations are shown in Figure 13. These values have been chosen to maximize the concentration of most elements in the liquid. The choice of distribution coefficients for clinopyroxene is particularly crucial. The rather arbitrary use of high values is probably justified by the evidence that diopside excludes trivalent REE more effectively than augite. The two phase compositions used in these calculations anticipate the later conclusion that the Ca and Al content of the Moon decreased toward the lunar interior. The high plagioclase assemblage represents a six- to eightfold enrichment in the concentration of these ele-
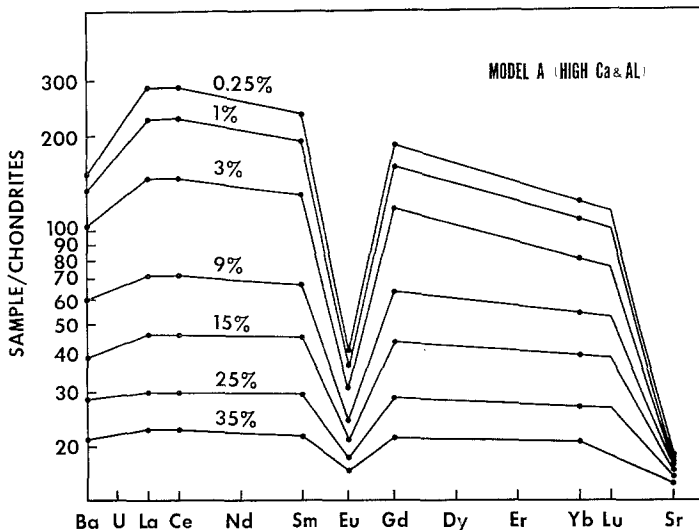


Fig. 14. Calculated abundance patterns using model of Shaw (1970). Phase composition is plagioclase 35%, clinopyroxene 20%, orthopyroxene 25%, and olivine and spinel 20%. Values shown on each line are the percentages of liquid at the time of extraction.
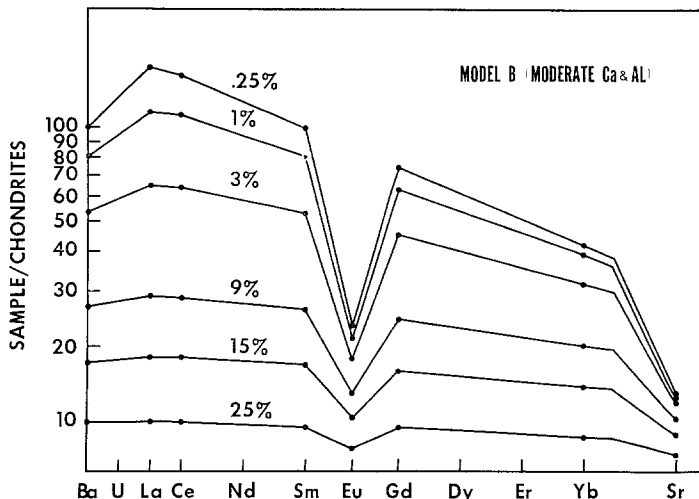
Fig. 15. Calculated abundance patterns using model of Shaw (1970). Phase composition is plagioclase 16%, clinopyroxene 16%, orthopyroxene 38%, and olivine and spinel 40%. Values shown on each line are the percentages of liquid at the time of extraction.

ments over that of chondrites. The low plagioclase composition represents a two- to fourfold enrichment. The approximate bulk compositions for both of these assemblages, along with bulk compositions given by Ringwood and Essene (1970), are shown in Table II.

It is quite clear that the simple model used here can explain the basic characteristics of the abundance patterns inferred for lunar basaltic liquids if plagioclase is present in the lunar interior. Indeed, the abundance of plagioclase dominates over all other factors in determining the depth of the strontium and europium anomalies.

Both cases illustrated in Figures 14 and 15 show that it is difficult to produce the extreme enrichments of LIL elements by simply varying the degree of partial melting of a given phase composition, even when the distribution coefficients have been chosen to favor the concentration of these elements into the liquid. The model calculations show that plausible amounts of partial melting will not produce some of the observed liquids from a source with chondritic concentrations of the LIL elements. The exact answer to this question depends on the ability to extract and concentrate small amounts of liquid evenly dispersed through a solid. There is no well-established or definite limit to this process. It seems likely, however, as the proportion of liquid approaches 1–2% by volume, it will be extracted or physically separated from the residual solid with ever increasing difficulty. In any case, the phase compositions and distribution coefficients used in the model illustrated here suggest that even infinitesimally small amounts of liquid will not be extremely enriched in the trace elements under consideration. For the rather arbitrary limit of 1% partial melting, the concentration of LIL elements in the source of the Apollo 12 liquid probably must be 3–5 times that of chondrites. For similar assumptions, the KREEP liquids require a source with 7–9 times the chondritic concentration of these elements.

One of the characteristics of the trace element patterns seen in Figures 14 and 15 is a relatively wide range of europium concentrations compared to the range of observed strontium concentrations. If the europium distribution coefficients for plagioclase and basaltic liquid is unity or less, this characteristic difference in the behavior of the europium and strontium becomes difficult to explain unless it is assumed that the $Eu^{+++}/Eu^{++}$ ratio is greater than 0.05. The calculated values illustrated in Figures 14 and 15 assume that this ratio is 1/10. Alternatively, one could have assumed that the $Eu^{++}$ distribution coefficient is between 1.1 and 1.3.

The variations in Sr/Eu ratios provide a significant constraint on partial melting models that will not be discussed here except to note that this variation can only be explained by assuming that the concentration of refractory LIL elements in the source of different basalts must vary if we begin with the assumption that the relative abundance of these elements is chondritic and assume that both liquids are produced by similar mechanisms.

The possibility that LIL element abundance patterns similar to those observed for the KREEP basalts can be produced by fractional crystallization processes has been discussed in several previous papers (Gast *et al.*, 1970; Gast and Hubbard, 1970; Hubbard *et al.*, 1971b). In order to further illustrate the difficulties associated with this hypothesis, let us consider what is involved in forming such a residual liquid from a plausible starting liquid. Assume that the starting or initial liquid is probably similar to the initial liquid from which one might derive an anorthositic cumulate. For example, it will have the following properties: (1) It is rich in normative plagioclase or $Al_2O_3$, (2) It is rich in normative olivine with a relatively high content of forsterite, i.e. it has 10–14% MgO and 8-10% FeO, (3) It has a $Cr_2O_3$ content similar to that of mare basalts, i.e. 0.4–0.5%, and (4) It has a chondritic LIL abundance pattern where the abundance of these elements is 15–20 times that of average chondrites. (This is 2–3 times the abundance of howardite or eucritic achondrites.)

In order to produce the KREEP LIL element patterns from such a liquid, it is clearly necessary that it must crystallize both plagioclase and olivine and/or pyroxene. The two KREEP characteristics that are not difficult to produce are (1) The twenty- to thirtyfold increase in uranium and cerium concentration which immediately implies that the residual liquid is less than 5% of the initial or starting liquid and (2) The relatively high Mg/Fe + Mg ratio of the KREEP basalts. The latter characteristic can only be achieved if there is substantial crystallization of ilmenite or other iron-rich oxides along with olivine and orthopyroxene. The chromium content of KREEP basalts (0.2%) is somewhat lower than that of the presumed starting liquid. It is well known, however (Gast, 1968b; Ringwood and Essene, 1970) that Cr is very rapidly depleted in liquids that crystallize substantial amounts of ortho- or clinopyroxene. A residual liquid of the type proposed should be virtually free of Cr; that is, it should contain less than 100 ppm. This is clearly not observed. Finally, the extreme Eu and Sr depletions observed in the KREEP basalts require that plagioclase must dominate over ferro magnesium minerals during fractional crystallization. This will have two effects: (1) It will result in extensive depletion of the residual liquid and $Al_2O_3$ and (2) it will strongly deplete the residual

liquid in Sr, i.e. the residual liquid will have a much lower Sr concentration than the initial liquid (see e.g. Gast and Hubbard, 1970). Neither of these characteristics are observed for KREEP basalts.

In summary, a variety of qualitative characteristics that are predicted for residual or extensively differentiated igneous liquids are in strong contrast with those actually observed for KREEP basalts. It is concluded that these basalts do not represent fractional crystallization products and that the most plausible explanation of their observed characteristics is the partial melting mechanism similar to the one discussed above. The primitive Ca- and Al-rich outer layer inferred from the KREEP basalts also suggests a rather straightforward origin for the widespread occurrence of very plagioclase-rich rocks. Complete melting of such a layer by external heating or release of accretional energy during the terminal phases of lunar accretion would produce a liquid that would naturally give rise to large quantities of liquidus plagioclase.

The chemical compositions and petrologic characteristics of the more abundant igneous rocks that occur on the surface of the Moon thus suggest the following conclusions: (1) Partial melting of a primitive U-, Ca-, and Al-rich feldspathic assemblage made up of about one-third plagioclase took place about 4.4 billion years ago. This primitive source contained 5–10 times the refractory LIL element content of chondrites, (2) Partial melting (3–30%) of a Fe/Mg-rich source with abundant Fe-rich pyroxene took place between 3.8 and 3.0 billion years ago. This source may also have contained small amounts of plagioclase, i.e. $\sim 10\%$. The abundance of LIL refractory elements in this region was 2–4 times that of chondrites, (3) Plagioclase-rich (anorthositic) highland rocks were formed by complete or nearly complete melting of the upper portion of the Al-rich zone that produced the KREEP basalts, and (4) It is suggested that the dark halo materials will have higher Fe/Mg ratios and abundances of volatile elements than the mare basalts.

The depth of formation of lunar volcanic liquids must be intimately involved with the early thermal evolution of the Moon and the initial thermal condition of the Moon. Thermal history calculations (McConnell and Gast, 1972) suggest that the upper Al- and Ca-rich zone proposed here must extend to a depth of at least 150 km in order to produce the KREEP basalts. Similarly, the source of the mare basalts may extend from depths of 150–450 km. When combined with initial temperatures that decrease from 1300 K at the surface to 270 K at the center of the Moon, the radioactive heat production inferred from the partial melting models given here provides a self-consistent thermal evolution that includes very early shallow melting and virtual cessation of melting 2 billion years ago at depths of 600–800 km.

The composition of the deep interior – below 400 km – of the Moon can be constrained in two ways: (1) The U and K content must be consistent with the observed thermal history and present state of the Moon and (2) The proposed interior must give rise to the correct moment of inertia. Neither of these constraints can at present be applied in a quantitative way. Hays (1971) has shown that the U content of the interior is probably much lower than that here inferred for the outer 400 km of the Moon. In addition, Wetherill (1968) and Ringwood and Essene (1970) have shown that the Ca

and Al content of the deep interior must be limited by compositions that will not contain garnet-rich assemblages at high pressures. This constraint probably requires that the Al content of the interior must be much lower than that here inferred for the upper 400 km. It is, therefore, concluded that the primitive Moon had a zoned structure in which the abundance of refractory elements such as Ca, Al, U, and REE increased going from the interior to the surface of the Moon. Such a zoned structure places significant constraints on any theory of lunar origin.

These inferences lead to the further significant conclusion that the matter that made up our sister planet was separated from more primitive matter over a wide range of temperatures. This conclusion is, in fact, quite in accord with similar observations derived from the chemistry of meteorites and the chemistry of the Earth. The abundance of a large number of volatile elements, e.g. Bi, Tl, Pb, Zn, Br, Cl, and others, in chondritic meteorites varies by several orders of magnitude. These abundance variations have been elegantly interpreted in terms of temperatures of accretion (Larimer and Anders, 1967).

Variations in the abundance of refractory elements in meteorites have also been observed (Ahrens and von Michaelis, 1969). The abundance of Ca and Al varies by a factor of 2 or more in chondritic meteorites and by a factor of more than 6 in all meteorites. Other elements, notably strontium and europium, vary by similar factors. The relative abundance of Ca and Al is much more constant in these objects than that observed in terrestrial and lunar igneous rocks. This argues against the possible explanation of these variations by igneous differentiation processes. Detailed studies of several Type 3 carbonaceous chondrites; in particular, the meteorites Allende and Leoville (Marvin *et al.*, 1970; Keil and Fuchs, 1971) provide evidence for even more extensive enrichment of this group of refractory elements. The observations for the Earth are less detailed than those for meteorites. The low relative abundance of alkali metals; in particular, K and Rb, appears to be well-established (Gast, 1960; Wasserburg *et al.*, 1964). The evidence that the Earth is depleted in other more volatile elements; for example, Tl, Cl, and Br, is also rather clear. Enrichment of the Earth in refractory elements has been suggested as a hypothesis (Gast, 1968a, 1972).

The combined observations made on meteorites, the Earth, and the Moon suggest that the fractionation of volatile (gaseous) and refractory (solid) materials in the early solar system took place over a wide range of temperatures. When and where this separation occurred is an open question. Two classes of explanations can be noted. First, that the separation takes place during the condensation of the gas to small solid bodies; that is, the release of gravitational potential energy and local gravitational fields had no role in the chemical fractionation; or, alternatively, that the chemical fractionation was associated with the rapid formation and heating of planetary-sized objects – the energy source for this heating coming from the release of gravitational potential energy. The loss of very substantial hot, dense, atmospheres from planetary-sized objects is unavoidable in the second type of explanation.

The relative importance of these two mechanisms in separating volatile from non-volatile material during the formation of the planets will not be explored in detail in

this report. It is intuitively clear, however, that five- to tenfold enrichments in refractory elements by vaporization of more volatile material is unlikely or difficult for Moon-sized objects. In other words, refractory element enrichment on the scale proposed here implies chemical fractionation during condensation from a gas as the most plausible mechanism that can account for the observations.

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