Geochemical Zoning and Early Differentiation in the Moon[1]

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The large volume of geochemical, petrological, and geophysical data (refs. 1 and 2) now available place many constraints on the composition and evolution of the Moon. For example, one of the first-order facts that appears to be well established is that the volatile elements (e.g., Rb, Pb, Tl, Bi, Cs) had already been depleted (refs. 3 and 4) at the time of accretion. Accordingly, it may be assumed that the Moon initially accreted from refractory material. Whether the siderophile elements (e.g., Ir, Au, Ni) were depleted before accretion is a current question.

The good correlation between volatile/involatile element ratios (e.g., Cs/U, K/La, K/Zr) in both highland and maria samples means that element distribution in lunar crustal rocks is not governed by volatility differences. This and other evidence (refs. 5, 6, and 7) encourages the view that the Moon was accreted homogeneously. Theories that the highlands represented a late addition of chemically distinct refractory material have been abandoned.

A consequence of homogeneous accretion theories is that very efficient large-scale element fractionation is required to account both for the high near-surface concentrations of refractory elements (e.g., Th, U, REE, Zr, Ba, etc.) and for the Ca-Al-rich crust.

There are several independent constraints of varying severity that indicate a high re-fractory trace element abundance for the Moon:

(1) Near-surface concentrations of many refractory elements are two orders of magnitude higher than those in primitive (Type I carbonaceous chondrite) meteorites (CCI). The latter are taken to represent a good approximation of the abundances of non-volatile elements in the solar nebula (ref. 8).

(2) The high heat flow (~ 0.7 HFU) (HFU = 10^{-6} cal cm^{-2} s^{-1}) indicates that the total lunar abundance of uranium is about 60 ± 15 ppb (ref. 9). The abundance of U in CCI is variable (ref. 10), but generally estimated at about 12 ppb. On this basis the Moon is enriched at least five times over the CCI abundances. Even the extreme value of 17 ppb (ref. 10) still requires about $4 \times$ CCI levels.

(3) The orbital gamma ray value for Th averages about 1.5 ppm (ref. 11). If the 60-km-thick crust (10 percent of the Moon) has this value, then $4 \times$ CCI levels (35 ppb) are required just to provide for the crustal concentrations. In addition there must have been some Th in the lunar interior to provide radioactive heating during the period 3.8 to 3.2 aeons in order to produce the maria basalts.

(4) The highland element trace abun-

dances (refs. 5 and 12) set further limits. If the concentration levels are representative of the 60-km-thick crust and not some thinner surficial zone, then 3 to 4 $\times$ CCI abundances are required to provide enough Ba and light REE. Maria basalts, derived from deeper levels by partial melting after the highland crust was formed, also contain high levels of Ba, U, Th, REE, Zr, Hf, Nb, etc. (relative to CCI abundances), increasing the abundance problem.

(5) The uniform interelement ratios in lunar samples (e.g., K/La, K/Ba, K/Th, K/Ar, etc.) (refs. 7 and 13) set limits for the lunar abundance of K. Assuming 5 $\times$ CCI for the *involatile* elements, the K concentration is ~ 100 ppm. On this basis, about 80 percent of the K (and associated Rb and Cs) is in the highland crust.

Some of these arguments depend on the vertical element distribution in the lunar crust. It is assumed here that the overall 60-km-thick crust has similar element abundances. The 40 observed ringed basin-forming events (ref. 14) must have effectively overturned large segments of the deep crust. Many

lunar models predict somewhat exhanced KREEP-type components with depth, so that the abundance problem is likely to be exacerbated rather than alleviated by lack of thorough mixing.

In summary, some limits can be set. The lower limit of 4 $\times$ CCI appears well established by the element abundance levels. The heat flow values set upper limits of perhaps 7 $\times$ CCI. An overall lunar average for the involatile elements of about 5 $\times$ CCI appears reasonable and is adopted here.

The major element abundances in the Moon may then be estimated as follows. The refractory elements Ca, Al, and Ti are taken as 5 $\times$ CCI. The iron content is set at 10.5 percent FeO to accommodate density and magnetic requirements (ref. 15). The Si/Mg ratio in chondrites is used to obtain Si and Mg concentrations (table 1). This composition is very close to that proposed by Ganapathy and Anders (ref. 17).

The Moon's moment of inertia (0.3953 ± 0.0045) suggests a nearly uniform density distribution with depth (ref. 18). This and the low bulk density of the Moon (3.34 g/cm^3) rules out the existence of dense (eclogitic) phases at depth (refs. 16 and 19). Thus, neither the highlands anorthosites nor the maria basalts are suitable compositions for the deep lunar interior. The lack of major

Table 1.—*Major Element Compositions*

	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
SiO$_2$	44.0	44.3	45.2	44.9	43.3	53.1	48.9	42.73
TiO$_2$	0.3	—	0.6	0.56	0.7	1.0	0.15	0.42
Al$_2$O$_3$	8.2	0.6	16.9	24.6	14.4	5.0	3.6	8.21
FeO	10.5	9.9	6.8	6.6	12.6	13.5	10.5	10.95
MgO	31.0	44.7	18.3	8.6	17.7	22.5	34.2	30.70
CaO	6.0	0.7	12.5	14.2	11.3	4.0	2.7	7.68

Explanation of column headings:
(1) Bulk Moon (this study).
(2) Composition of 300 to 1000 km of Moon (this study).
(3) Composition of upper 300 km of Moon.
(4) Average highlands, composition of upper 60 km of Moon (ref. 12).
(5) Composition of 60 to 300 km of Moon (including source of maria basalts).
(6) Composition of source of maria basalts (200 to 400 km pyroxenite, ref. 16).
(7) Carbonaceous chondrite (CCl-Orgueil); volatile and siderophile elements subtracted and Fe taken as in column 1.
(8) Bulk Moon (ref. 17).

seismic discontinuities between the base of the crust at 60 km and a depth of 1000 km suggests a rather uniform interior with gradational boundaries in mineralogy and chemical composition. The interior of the Moon is divided into (a) crust (upper 60-km), (b) lithosphere (60–1000 km), and (c) asthenosphere (1000–1738 km), with at least the upper portion of this zone partially liquid (refs. 9 and 20). The presence of orthopyroxene (with some Al and Ca) below 300 km is inferred from P-wave velocities that fit an olivine-orthopyroxene mixture better than olivine alone.

Experimental petrology studies indicate that the source region of the maria basalts lies between depths of 100 to 300 km (refs. 16 and 21). Among the maria basalts, several types are distinguished using major and trace element criteria; their common feature is a high Ca/Al ratio, relatively low Mg/Fe, varying degrees of REE enrichment with Eu depletion, and varying but low contents of Ni. Although the maria basalts could be related by petrological schemes involving different degrees of partial melting, the TiO_2 and Al_2O_3 contents (accompanied by Eu anomalies) and the Fe/Ni ratios suggest as well that partial melting of slightly different mineralogies involving a combination of pyroxene, olivine, Fe-Ti phases, and plagioclase (and sulphides) has taken place. The REE abundances in maria basalts suggest that plagioclase was removed from their source region (refs. 22 and 23).

The highland rocks contain three distinct and incompatible geochemical components: (a) high Ca, Al, Sr, and Eu (anorthite); (b) high Mg and Cr contents; and (c) high abundances of REE, Th, U, Zr, Hf, etc. Conventional theories involving crystal fractionation cannot account for this association.

We now attempt to reconcile this geochemical information with the geophysical constraints, derive the composition of the deep lunar interior, and correlate the overall composition with the sequence of geological events, beginning with a homogeneously accreted Moon that underwent partial or total melting due to accretional heating.

Toksöz et al. (ref. 9) have shown that early heating and melting of large parts of the Moon are compatible with the later thermal history of the Moon. Melting of a large part of the Moon can be achieved if short accretional times of order 100 to 1000 yr are considered (ref. 24).

Three alternative models may account for the deep lunar interior (asthenosphere) (below 1000 km):

(1) An immiscible Fe-FeS liquid sinks to form a core effectively removing most siderophile and chalcophile elements (ref. 25). The core radius is restricted to less than 700 km by the moment of inertia (0.395). Enough sulfur (~ 0.5 percent) is retained in the whole Moon to form FeS. The partially liquid zone as suggested by the seismic evidence below 1000 km is interpreted as due to dispersed Fe-FeS in an olivine-orthopyroxene matrix. The magnetic field appearing in remanently magnetized rocks results from a core dynamo mechanism.

(2) The initial melting did not extend below 1000 km. The central part of the Moon is formed of primitive unfractionated material now in a partially molten state from heating due to trapped initial K, U, and Th. The seismic data are satisfied by 0.5- to 1-percent partial melting. This model precludes core formation, since sinking Fe-FeS will drive these incompatible elements upward. In this model, the remanent magnetism of lunar rocks is caused by external magnetic fields (ref. 26).

(3) The molten zone is a relic of early melting. The choice between these models for the lunar interior depends critically on the amount of the early siderophile and chalcophile element depletion. If the siderophile elements were accreted, even in the amounts corresponding to low bulk Fe content of the Moon, a lunar core is required

to remove them in a very efficient manner. The evidence at present for a chemically distinct core is equivocal (ref. 27).

We assume in the following discussion that a core did not form and that an inner zone 700 km thick (10 percent volume) was not melted initially (model 2). Following accretional melting of 90 percent of the Moon, the first silicate phase to separate from the primitive molten Moon is Mg-rich olivine. The early precipitation of olivine removes Ni^{2+} and lesser amounts of Cr^{2+} and Co^{2+}.

The surface of the Moon cools rapidly forming a "frozen crust," although this is continually broken up by the declining meteoritic bombardment. This frozen surface layer, analogous to the chilled margins of terrestrial intrusions, retained high concentrations of Mg, Cr, etc., in near-surface regions. Thus, its composition is probably representative of the melt composition during the early stages of crystallization of the lower interior. This chilled early lunar crust is later incorporated into the overall highland composition and contributes the Mg and Cr "primitive" component. If this model is correct, the high Cr/Ni ratios in the highlands indicate that the primitive lunar composition was deficient in siderophile elements.

As crystallization proceeds and Si/Mg changes, orthopyroxene precipitates. This has a similar effect on the composition of the residual melt, as does olivine, except for Si/Mg ratios. Most cations, except Mg, Fe, Ni, Co, and Cr^{2+}, are excluded from the olivine and orthopyroxene lattice sites and migrate upward, concentrating in the still voluminous residual melt. These include Ca and Al. The high Cr^{3+} abundances in most accessible lunar materials indicate that separation of clinopyroxene, if any, was minor, and that olivine and orthopyroxene were probably the major components.

The density and seismic properties and the Si/Mg ratio in the deep lunar interior are satisfied by 80-percent olivine ($\geq Fo_{85}$) and 20-percent orthopyroxene ($\leq En_{85}$). The composition of the lower part of the Moon below 300 km (assuming 2.2 percent Al_2O_3 and 2.5 percent CaO in the orthopyroxene) is given in table 1, column 2. The model requires, however, that even the lower parts of the Moon are compositionally and mineralogically zoned. Orthopyroxene with Al_2O_3 and CaO content is present at shallower depths, together with olivine, whereas Mg-rich olivine is present in deeper parts.

Increasing crystallization of Mg-rich olivine, later accompanied by orthopyroxene at depth, leads to an increasing concentration of refractory elements (Ca-Al) trapped between the already crystallized lower (Ol-Opx) lunar interior and the chilled surface layer. The composition of this zone (the upper 300 km of the Moon) is given in table 1, column 3. When the concentration of Al reaches 12- to 17-percent Al_2O_3, An-rich plagioclase precipitates and concentrates or remains suspended beneath the frozen surface, whereas the Mg-Fe phases continue to crystallize and sink (ref. 28). The Ca-Al-rich region (plagioclase) incorporates Sr^{2+} and Eu^{2+}, but most other elements are unable to enter the Ca^{2+} sites in significant amounts.

Experimental petrology provides constraints on the Al_2O_3 content of melts to precipitate plagioclase together with Fe-Mg silicates (olivine and pyroxene). Values above 12-percent Al_2O_3 are necessary (ref. 29). If the Moon has initially the Ca/Al ratio of meteorites, the corresponding value for CaO at that stage is 9.0 percent or higher. The composition of the highland crust is given in table 1, column 4. The composition of the zone from 60 to 300 km is given in table 1, column 5.

The removal of plagioclase from the source region of maria basalts explains the high Ca/Al ratios, negative Eu anomalies, low content of Al in maria basalts, and relative depletion of larger REE (ref. 23). Plagioclase is not a liquidus phase in maria basalts (ref. 30) (note the exception of high Al mare basalts such as 14053 and 12038) (ref. 31), and prior removal of plagioclase is required to account for the above-mentioned features.. We suggest therefore that the

source region of maria basalts is zoned in respect of Ca-Al and also Mg/Fe and, consequently, in mineralogy (ref. 23).

The high-Al maria basalts come from plagioclase-bearing regions shallower than other maria basalts (ref. 32) ; our model suggests that the content of plagioclase decreases from the base of the crust (60 km) downward, whereas the contents of Fe-Mg silicates increase. These silicates become more Mg-rich with depth. Pockets or zones of Fe-Ti oxides and FeS in shallower regions account for the high Ti and S contents of the Apollo 11 and 17 basalts (ref. 33). The source region of 15555 (Great Scott) and the green glass (ref. 34) may represent a lower boundary of plagioclase precipitation. We assume that plagioclase separation commenced when a large part ($\simeq 40$ percent) of the Moon was still molten, i.e., during formation of the source region of maria basalts above 300 km depth. The composition of the source region of the maria basalts (200 to 300 km) is given in table 1, column 6.

As crystallization of the source region of maria basalts and crust proceeds, elements unable to enter the Ca-Al sites in plagioclase (above) or the Mg-Fe sites (below) are trapped between. In this trapped or residual zone, all the remaining elements concentrate. These include K, Ba, Rb, Cs, REE, Th, U, Zr, and Nb. It is a geochemical characteristic of great importance that the principal lunar mineral phases do not readily accommodate the refractory trace elements. The evidence of high concentrations of these elements near the surface of the Moon is a dramatic consequence of this crystal chemical fact. Thus, following the primordial fractionation, a chemically zoned Moon is produced, with residual phases enriched below chilled margin and plagioclase crust and above the source region of maria basalts.

This crustal zonation established at about 4.5 aeons is changed very quickly. The declining stages of the meteoritic bombardment pulverize the chilled zone, and larger impacts mix in the underlying anorthosite. The high concentration of heat-producing elements K, U, and Th (and Zr, Hf, REE,

etc.) trapped beneath the plagioclase zone provide the high element abundances for the Fra Mauro or KREEP basalts. Possibly this zone did not solidify, but residual liquids invaded the crust where impact mixing of the primitive surface layer, the Ca-Al plagioclase-rich layer, and the residual liquids beneath produced the parent material for the anorthositic gabbro (highland basalt) and the Fra Mauro basalts. The average composition of the highland crust is given in table 1, column 4. The activity continues to 3.9 aeons, culminating in the production of the ringed basins and the cessation of the intense highland cratering.

Partial melting next occurs in successively deeper layers as the smaller amounts of the heat producing elements induce partial melting and a succession of "maria-type" basalts are erupted. The high-Al maria basalts formed in this model at shallow depths beneath the crust. This emplacement of basalts overlaps with the later stages of the bombardment and predates the Imbrium collision in part, as shown by their presence in Fra Mauro breccias. Some of the high-Al maria basalts were emplaced later (≈ 3.4 aeons), suggesting that partial melting in shallower zones was not limited to early periods of maria formation (Luna 16 rocks, 12038).

Following these, the Ti-rich Apollo 11 and 17 basalts were extruded during the period 3.8 to 3.6 aeons from a zone where Fe-Ti oxides and FeS accumulated. They have about 1 ppm Ni. Later (3.4 to 3.2 aeons), the Apollo 12 and 15 quartz and olivine normative basalts were extruded. These contain nickel, indicating extensive partial melting involving olivine, and many show evidence of near-surface fractionation. A negative Eu anomaly is characteristic of all maria basalts and contrasts with the deepest material erupted, the Apollo 15 emerald green glass (15426) (refs. 34 and 35) with 180-ppm Ni and primitive REE patterns, low total REE (3 to 5 times chondrites), and a small Eu anomaly (ref. 36). This material is the least fractionated lunar material that has been sampled (ref. 37). The thickness of the crust

above this zone, as well as the residual high melting point material and lack of heat sources due to the upward concentration of K, U, and Th, causes cessation of lunar vulcanism at 3.2 aeons. A diagrammatic view of the model proposed here is given in figure 1.

Acknowledgment

Figure 1.—*Geochemical model of the lunar interior at about 4.4 aeons.*

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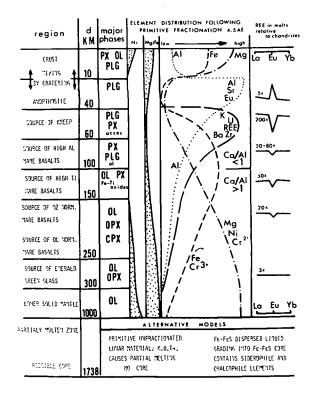13. WÄNKE, H., H. BADDENHAUSEN, G. DREIBUS, E. JAGOUTZ, H. KRUSE, H. PALME, B. SPETTEL, AND F. TESCHKE, *Proc. Fourth Lunar Science Conference*, 1973, p. 1461.
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