CONSTRAINTS ON THE GENESIS AND EVOLUTION OF THE MOON'S MAGMA OCEAN AND DERIVATIVE CUMULATE SOURCES AS SUPPORTED BY LUNAR METEORITES

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Abstract: It is generally considered that the outer portion of the Moon was molten in its early history. Antarctic lunar meteorites support this supposition, indicating the presence of a global plagioclase-rich crust derived from magma ocean flotation cumulates. Lunar meteorites also contain a significant very low-Ti (VLT) mare basalt component which was likely generated by the melting of a cumulate mantle formed in an early moon-wide magma ocean. Early in the evolution of the mantle, when the lunar magma ocean (LMO) still was largely liquid, it is likely that vigorous convection was an important factor in crystallization. Such convection would allow crystals to remain suspended and in equilibrium with the LMO liquid for relatively long periods of time. This extended period of equilibrium crystallization would then have been followed by fractional crystallization once plagioclase became a liquidus phase and began to float to form the lunar highlands crust. The residual liquid after 80-90 percent crystallization was very evolved (in fact KREEPy) and, even in small proportions (1-5%), would have a noticeable effect on the trace-element chemistry of melts generated from these cumulates. This trapped residual liquid would elevate total REE abundances in the cumulate pile, while synchronously deepening the already negative Eu anomaly. The LMO liquid calculated after extensive crystallization (>99.5% crystallized) has a composition which is similar to that recorded in quartz monzodiorites. This evolved liquid could be represented by the sparse KREEP component found in lunar meteorites. The mare basalt component found in such meteorites as EET87521 can be generated by fractional crystallization of a more primitive magma similar in composition to Apollo VLT picritic glass beads. This picritic magma can be produced by melting of a cumulate source in the lunar upper mantle.

1. Introduction

The Moon appears to have had a shorter and simpler history than the Earth and is the only planetary body, outside the Earth, which we have sampled in a relatively systematic way. Whereas continuous cycles of weathering and subduction have inexorably altered the Earth and adulterated the composition of its primitive mantle, the Moon has retained a vestige of its beginning. Though debate continues on the origin of the Moon and its relationship to Earth, we nonetheless have created a substantial base of geologic, physical, and chemical groundtruth upon which to test our hypotheses. Mare basalts in excess of 4.0 Ga and crustal rocks of even greater antiquity have remained unaltered since their creation on the surface of the Moon (except for weathering by meteorite impact). For this reason alone, the Moon is the type-planet against which hypotheses of the early evolution of other planets must be logically compared. Therefore, the study of lunar samples continues to be paramount to our understanding of planetary evolution. However, with the completion of the U.S. Apollo and Soviet Luna missions in 1974 also came the possibility that lunar sampling may have ended for a generation.

The lunar meteorites have been an unexpected addition to the once-considered static collection of lunar rocks. Meteorites of lunar origin, which have been collected on Antarctic ice fields (and one from Australia), are the only new samples that have been added to the data base of lunar rocks in almost twenty years. As of the date of this writing, twelve samples of lunar meteorites have been collected. However, these twelve samples likely represent only nine different falls, or nine distinctly different meteorites (including two paired samples and a triplet). Still, the addition of these nine meteorites to the lunar collections has potentially doubled the number of sites which have been sampled from the Moon (previously, six Apollo sites and three Luna sites). With these nine lunar meteorites, it is even possible that we have sampled the back side of the Moon. Certainly, we have gained a clearer picture of the composition of the lunar crust through this more wide-spread sampling of the Moon's surface.

2. Evidence for a Magma Ocean from Lunar Meteorites

The magma ocean concept has been an integral part of the lunar literature practically since the return of the first lunar samples (*e.g.*, SMITH *et al.*, 1970; WOOD *et al.* 1970; WARREN, 1985). Several authors have indicated problems and inconsistencies inherent in an early Moon-wide magma ocean and have challenged its validity (WALKER, 1983; SHIRLEY, 1983; LONGHI and ASHWAL, 1985). However, the bulk of petrologic, geochemical, and geophysical data for the highlands and mare basins of the Moon point to a common, ancient, global reservoir.

The nine lunar meteorites have gone a long way in confirming various lunar hypotheses and yielding information on the global character of the Earth's moon. One meteorite, EET87521, is composed wholly of brecciated very low-Ti (VLT) mare basalt (WARREN and KALLEMEYN, 1989; 1991b; TAKEDA et al., 1992) with a characteristic negative Eu anomaly. Two others, Yamato (Y)-793169 and Asuka (A)-881757, are of mare affinity, but are texturally considered to be cumulates (WARREN and KALLEMEYN, 1991a). A fourth meteorite, Y-793274, contains both mare basalt and highlands components in the ratio of 2:1 (KOEBERL et al., 1991). Other lunar meteorites, including MAC88105, exhibit clasts of very low-Ti (VLT) mare basalts and ferroan anorthosite (NEAL et al., 1991; WARREN and KALLEMEYN, 1991b) which confirm the complementary negative and positive Eu anomalies, respectively, of these basic lunar rock types. Furthermore, numerous clast-rich impact melt breccias have been described in MAC88105 which are extremely aluminous (Al₂O₃ = 28 wt%; TAYLOR, 1991). These complementary basaltic and anorthositic clasts, and aluminous melts, confirm that the crust and mantle of the Moon were formed from the same reservoir, the lunar magma ocean (LMO), early in its history. Studies of lunar Antarctic meteorites have confirmed the high global Al₂O₃ signature of the upper crust of the Moon concluded from studies

of the Apollo collections (WARREN and KALLEMEYN, 1991b). This high global Al_2O_3 concentration (25–27 wt%) is consistent with the presence of a lunar magma ocean (LMO) early in the Moon's history. Furthermore, the abundance of mare material in these meteorites (three being completely of mare affinity) indicates the importance of volcanism in lunar evolution (*e.g.*, NEAL and TAYLOR, 1992). In this paper, results are reported of an ongoing study into the physics and chemistry of the lunar magma ocean and the consequent evolution of the Moon's interior, particularly its upper mantle (outer 400–500 km). It is emphasized that the basaltic lunar meteorites place important new constraints upon the composition and evolution of the LMO and its derivative cumulate sources.

3. Important Concepts in Lunar Magma Ocean Modeling

The proceeding discussion will assume the existence of an early Moon-wide magma ocean. Many variations of the lunar magma ocean (LMO) concept have been proposed (e.g., SHIH and SCHONFELD, 1976; HUGHES *et al.*, 1988, 1989), but a few aspects appear to be common in currently favored models: (1) formation of a Moon-wide melt layer, followed by (2) crystallization and settling of mafic (olivine, pyroxenes, spinel) cumulates, and (3) flotation of plagioclase to form the lunar highlands. It is the mafic cumulate pile which is of greatest concern to those interested in modeling the source regions for mare basalts (*e.g.*, NEAL and TAYLOR, 1992), and remelting of various layers of this mafic cumulate pile could have generated liquids which were parental to mare basalts (WALKER *et al.*, 1975).

The body of studies on lunar rocks and meteorites which has accumulated over the years has consistently been refined, and therefore, as resulted in production of ever more complicated models of igneous differentiation. Perfect adcumulates (*i.e.*, absolutely no trapped liquid) are rare as are perfectly monomineralic rocks However, models for the evolution of the lunar magma ocean (LMO) generally have not reflected this fundamental observation. It is the intent of this paper to present a more realistic model for evolution and solidification of the LMO, which encompasses considerations of the inefficiency of crystal-crystal and crystal-liquid separations.

Several parameters must be considered when developing a model for mare basalt source regions: (1) the bulk composition of the initial LMO; (2) the relevant phase equilibria at required pressures in order to map crystallization paths of the LMO; (3) the amount and composition of a trapped liquid component; (4) appropriate, lunar-relevant mineral/melt partition coefficients for the trace elements; (5) the possible extent of equilibrium crystallization and degree of perfect fractional crystallization of the LMO and subsequent crystal-crystal and crystal-liquid separation; and (6) the depth in the cumulate pile at which melting must occur to generate a mare basalt parent magma.

The mare basalt component of lunar meteorites generally is considered to have originated by the melting of a cumulate mantle formed during the crystallization of this LMO (e.g., PHILPOTTS and SCHNETZLER, 1970). However, the nature and chemistry of this cumulate mantle and the logistics of its origin have remained elusive. In fact, many workers have suggested that the stratigraphy of the lunar upper mantle has been overturned during subsolidus convection due to inherent density contrasts in the

cumulate pile (HERBERT, 1980; RYDER, 1991; SPERA, 1992). This convective overturn has been proposed on mineral/chemical grounds to explain the relatively high Mg# $[(Mg^{2+}/(Mg^{2+} + Fe^{2+}));$ as reflected in mare basalts] of late-stage ilmenite-bearing LMO cumulates. However, large-scale convective overturn of the lunar mantle may not be required if equilibrium crystallization was an important process in LMO differentiation (SNYDER and TAYLOR, 1992).

Early in the evolution of the lunar mantle, when the LMO still was largely liquid, it is possible that vigorous convection was an important factor in crystallization. Such convection would allow crystals to remain suspended and in chemical equilibrium with the LMO for relatively long periods of time. During this interval, equilibrium crystallization would control the differentiation of the LMO. However, plagioclase began to crystallize and float later in the evolution of the LMO (when convection was less vigorous) and was effectively separated from the rest of the cumulate. It is also assumed that the plagioclase does not react significantly with the residual liquid. At that time, fractional crystallization would take over as the controlling mode of differentiation.

In this paper, we will attempt to model the sources of the VLT mare basalts (specifically EET87521) by the consideration of a modified mafic cumulate source formed during the combined equilibrium and fractional crystallization of a moon-wide magma ocean. A refined approach to our previous work (SNYDER *et al.*, 1992b) was adopted for modelling the evolution of the LMO. Due to inherent complexities, previous studies modelled either trace elements or major elements, but generally failed to integrate the two. In this study, both trace and major elements have been modeled in the evolution of the LMO. As shown below, major elements tightly constrain the composition of mare basalt sources and the pathways to their creation.

Our presentation of this mare basalt source model will be in two stages. First, we will consider the parameters which influence the depth and composition of the initial LMO and its subsequent crystallization. Second, through a case study involving the VLT basalt, EET87521, we will test this LMO model, and its ability to generate viable mare basalt source regions.

4. Physical Constraints on the Depth of the Magma Ocean

The seismic velocity structure of the Moon has been determined by NAKAMURA (1983) through inversion of arrival time data collected during an eight year period. Analysis of this data has led NAKAMURA to place the transition from the upper to the middle mantle at 500 km. Furthermore, he has estimated the average thickness of the lunar crust to be 58 ± 8 km. This average crustal thickness is comparable to that proposed by TAYLOR (73 km; 1987) and HOOD and JONES (60–80 km; 1987), to name just a few. This means that the upper mantle of the Moon is approximately 440 km deep. This depth is consistent with maximums inferred from experimental data and modelling of mare basalt sources (DELANO, 1980) and other estimated depths of a global, near-surface, magma ocean (*see* WARREN, 1985). It is reasonable, therefore, to assume that the upper mantle of the Moon is the crystallization product of an early global magma ocean.

If, indeed, it consisted of a 500 km deep pool at the surface of the Moon, the LMO

must have been a high percentage melt of the total Moon. In fact, the outer 500 km shell of the Moon represents 63% of the total volume of the Moon. The plausibility, cause, and nature of this melting will not be debated here. Suffice it to say that even if only a 250 km deep ocean were formed (minimum depth from WARREN, 1985), this means that over 37% of the Moon was melted in its formation.

5. Bulk Composition of the Lunar Magma Ocean

A myriad of bulk lunar compositions have been offered based on mineralogic, petrologic, chemical, and geophysical constraints. Fewer workers have hazarded an estimate of the initial LMO composition. These include the SI composition of WARREN (1986a) and the compositions of JONES and DELANO (1989) and O'NEILL (1991). A few major-element parameters are key, as they define the appearance of key minerals on the LMO liquidus. The abundance of Al_2O_3 is important as it determines the relative appearance of plagioclase on the liquidus, as well as its abundance, and thus, the onset of crustal formation via flotation of this plagioclase. Of course, the Mg[#] is also key and determines the extent of mafic mineral fractionation. WARREN (1986a, 1986b) insisted, based upon convincing geochemical and geophysical arguments, that the initial LMO Mg[#] must be between 0.8 and 0.9. TAYLOR (1982) quoted an Mg[#] of 0.84 for the primitive lunar mantle. Based on pristine glass compositions, JONES and DELANO (1989) argued for a bulk lunar Mg[#] of 0.82–0.84, whereas LONGHI (1981) preferred an Mg[#] of 0.86 using mineralogic and chemical criteria. MUELLER et al. (1988) suggested an upper mantle Mg# of 0.78, and O'NEILL (1991) has come out in favor of a bulk Moon Mg[#] of 0.83. From these studies, we consider it likely that the initial LMO contained 5-7 wt% Al₂O₃ and had a bulk Mg[#] of 0.78-0.83. This translates into plagioclase becoming a liquidus phase in the LMO after 57-78% crystallization of olivine-orthopyroxene cumulates (SNYDER et al., 1992b). Assuming an initial LMO depth of 400–500 km, this early appearance of plagioclase (after 57% crystallization) is inconsistent with the proposed thickness of the mostly anorthositic lunar crust (60–100 km; TAYLOR, 1987; MUELLER et al., 1988). In other words, the largely anorthositic crust would be expected to be somewhat thicker than observed. Therefore, the later appearance of plagioclase (at 75-80 PCS; [Per Cent Solid by volume, as originally defined by MORSE, 1979]) is preferred.

Postulated TiO₂ abundances for an initial LMO are uniformly low and would likely be <0.4 wt%. This translantes into ilmenite (an important mineral in high-Ti basalt genesis) becoming a liquidus phase after at least 92% of the LMO has crystallized (SNYDER *et al.*, 1992b). Regardless of the chosen initial LMO composition, the following generalizations hold for differentiation: (1) olivine is always the first liquidus phase, and crystallizes alone over a very broad range (up to 40–65% fractional crystallization), and (2) the final total proportion of plagioclase after complete crystallization of the LMO never exceeds 21% (also *see* WARREN, 1986b, for a similar conclusion based upon modelling of pristine nonmare rocks).

Much has also been written about the siderophile-element content of the Moon (e.g., RINGWOOD and SEIFERT, 1986; TAYLOR, 1987; NEWSOM and TAYLOR, 1989; RINGWOOD et al., 1991; and O'NEILL, 1991; and references therein). Due, in part, to a

paucity of high-pressure siderophile-element partitioning data (see URAKAWA, 1991; JONES and WALKER, 1991), a good deal of debate has centered around the siderophileelement content of the bulk Moon and its LMO. Furthermore, siderophile-element abundances in an initial LMO are predicated on a precise knowledge of the nature and extent of core/silicate and accretionary partitioning—speculative endeavors at best. However, as will be shown, modelling of large-ion lithophile elements (LILE), which are incompatible with most of the crystallizing phases, avoids this problem.

Our proposed chemical model assumes a starting composition for the LMO which is modified from BUCK and TOKSOZ (1980): $SiO_2 = 48.4 \text{ wt\%}$, $TiO_2 = 0.40 \text{ wt\%}$, $Al_2O_3 = 5.0 \text{ wt\%}$, FeO = 12.0 wt%, MgO = 29.9 wt%, CaO = 3.83 wt%, and Mg# = 0.82(SNYDER *et al.*, 1992b). This composition is intermediate in most respects (specifically Mg# and Al_2O_3 content) to those which have been proposed. However, it must be pointed out that even this intermediate Mg# would be considered by some workers to be too low. Some would contend that the Mg# of the upper mantle of the Moon may even be as high as that of the Earth (approximately 0.89–0.90). An initial magma ocean depth of 400 km is also specified, though not necessary to the conclusions presented.

For the lithophile trace elements (including the REE), TAYLOR (1982) suggested the bulk Moon should have approximately $2.5 \times$ chondritic abundances. However, if it is presupposed that the bulk Moon underwent a previous differentiation event which included the crystallization of olivine alone (TAYLOR, 1982; JONES and DELANO, 1989), the "residual" LMO (the initial LMO for our model) would then have been enriched further in these elements (as olivine has extremely low mineral/melt distribution coefficients for the lithophile elements; see MCKAY, 1986). With this rationale, a value of $3 \times$ chondritic ($4-5 \times$ Cl chondrites; WASSON and KALLEMEYN, 1988) is preferred for the trace elements (*c.f.*, HUGHES *et al.* 1988; 1989) and would be consistent with this differentiation event if approximately 20% of the total Moon had fractionated to yield olivine alone. This initial lithophile-element composition is similar to that of SNYDER *et al.* (1992b) with two important changes: both Rb and Sr have been reduced in the initial LMO by $3 \times$ and $4 \times$, respectively. This change in the model is consistent with the known volatile-element depletion of the Moon.

6. LMO Crystallization Path

The debate continues as to where crystallization occurs within a magma ocean. In recent years, *in situ* crystallization (*i.e.*, crystallization at depth, near the base of a magma chamber) has become popular (LANGMUIR, 1989). The modelling presented in this paper assumes crystal nucleation at or near a boundary layer where the temperature gradient and heat flux are the greatest. Again, this assumption does not grossly affect the model, as equilibrium crystallization is expected to dominate during the first three-quarters of LMO evolution. Because of the increased heat flow and larger thermal gradient expected near the surface of a cooling body, the bulk of crystal nucleation and growth should occur within the upper and outer portions of the LMO. This location corresponds in the Moon to the upper portion of a bulk Moon-wide melt layer (the LMO) adjacent to the nascent lunar crust. Mafic crystals formed near the boundary layer would then become entrained in the vigorously convecting liquid. Once the

temperature has decreased and the liquid has become sufficiently laden with crystals (78 PCS in the model presented herein), mafic crystals would begin to sink in response to their density contrast with the residual LMO, be carried downward by convection currents within the LMO, or otherwise be transferred to the lower reaches of the LMO "chamber" by a process which is a hybrid of both processes. Undoubtedly, it is true that during the crystallization of the LMO in this fashion, early-formed crystals will not settle to the floor without interaction with the intervening magma. Resorption and recrystallization phenomena are possible, even likely, but are not considered to be within the scope of this paper.

In order to more precisely constrain the crystallization sequence for the LMO, the programs MAGPOX and MAGFOX (Longhi, pers. comm.) were utilized. The model includes equilibrium crystallization for the first three-quarters of LMO differentiation during rapid convection (at 6 kb pressure) using the equation,

$$C_L = C_0 / [F + D_0 (1 - F)],$$
 (1)

where C_L = concentration of the trace element in the residual liquid, C_0 = concntration of the trace element in the original liquid, F = fraction of liquid remaining, and D_0 = bulk minerals/melt distribution coefficient. This is then followed by low-pressure fractional crystallization of the magma ocean above 78 PCS using the relation,

$$C_{L} = C_{0} * F^{(D_{0} - 1)} .$$
 (2)

This latter phase of crystallization was accompanied by inefficient crystal-crystal and crystal-liquid separation. Most of the crystallizing plagioclase floated to form the lunar highlands. The trace-element composition of the cumulates at each stage in the crystallization was calculated using the simple relation,

$$C_s = D_0 * C_L , \qquad (3)$$

where C_s = concentration of the element in the solid (cumulate). The fractionation sequence, as determined by using modified output from the programs MAGPOX and MAGFOX, is as follows (SNYDER *et al.*, 1992b):

- (a) 0-40 PCS = olivine
- (b) 40-78 PCS = orthopyroxene (with some olivine resorption)
- (c) 78-86 PCS = 53% plagioclase +25% olivine +22% pigeonite
- (d) 86-95 PCS = 38% clinopyroxene + 36% plagioclase + 26% pigeonite
- (e) 95–99.5 PCS = 34% pigeonite + 31% plagioclase + 24% clinopyroxene + 11% ilmenite.

The stratigraphy of the upper mantle, which is a product of the equilibrium/ fractional crystallization model presented here, is similar to others previously presented (Fig. 1). The major difference is the relatively late appearance of clinopyroxene (*after* plagioclase) in the present model (at 86 PCS). Ilmenite begins to precipitate above 95 PCS, as opposed to 92–93 PCS in other models (SNYDER *et al.*, 1991; SNYDER and TAYLOR, 1992; TAYLOR, 1982). After approximately three-quarters of the LMO has crystallized, plagioclase becomes a liquidus phase. The bulk of this plagioclase floats and does not become part of the mafic cumulate + trapped liquid pile. Based on our earlier work with high-Ti basalts (SNYDER *et al.*, 1992b), we assume that a small pro-



Fig. 1. Comparison of the lunar upper mantle presented in this paper with others presented recently (SNYDER et al., 1991; S. R. TAYLOR, 1982). Abbreviations (used throughout diagrams): cpx = clinopyroxene, ilm=ilmenite, olv=olivine, opx=orthopyroxene, pig=pigeonite, plag=plagioclase. The lowermost 2/3 of the upper mantle in the model presented herein would be harzburgitic in bulk composition, and grade from an olivine-rich bottom to an orthopyroxene-rich top. In the mantle model at left, the dashed line in the lower unit represents the interface above which orthopyroxene is dominant over olivine.

portion of this plagioclase (2-5 wt%; see below) is entrained into the sinking cumulate mush. Generation of mare basalts from a cumulate containing only mafic minerals, left behind after plagioclase removal by flotation, is not a unique idea (see TAYLOR, 1982). However, previous geochemical models for the genesis of mare basalt sources do not include both the trapped instantaneous residual liquid (TIRL) component and an entrained plagioclase component.

7. Inefficiency of Crystal-Liquid and Crystal-Crystal Separation

The model presented here for crystallization of the LMO that is believed to more closely approximate both the early turbulent history of the LMO and its later, more quiescient phase, when imperfect fractional crystallization was the controlling method of differentiation. In this model, the LMO is allowed to undergo equilibrium, followed by fractional, crystallization. However, once fractional crystallization became the dominant mode of differentiation, both crystal-liquid and crystal-crystal separations were inefficient. At successively greater stratigraphic heights in the cumulate pile, a variable (1-5%) proportion of instantaneous residual liquid was trapped in the cumulate pile. In this model, 1 and 5% TIRL are used, and we assume that perfect adcumulates do not exist. The composition of the trapped liquid is calculated assuming equilibrium with the mafic cumulate and that, once trapped in the cumulate pile, the liquid does not communicate chemically with the residual LMO.

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In terrestrial layered mafic intrusions, it is known that the separation efficiency of crystals of grossly different densities is seldom 100% (*e.g.*, IRVINE, 1980). For instance, layers of troctolitic composition are much more common than those of purely anorthositic or dunitic composition. There is ample reason to believe that crystal-crystal separations in an LMO would be similarly inefficient, as evidenced by the lack of truly pure anorthosites in the highlands crust. Once plagioclase becomes a liquidus phase, a small proportion of this less dense mineral is also entrained into the sinking mafic cumulate mush. In turn, entrainment of a small proportion of more dense material (mafic cumulate) is likely to be entrained into the floating plagioclase cumulate. Furthermore, plagioclase is a difficult mineral to nucleate. It is likely that it would nucleate heterogeneously, preferring a mineral surface for a nucleation site. With this in mind, we will model the LMO cumulate pile with both the TIRL component ($\leq 5\%$) and, once it begins to crystallize, a small amount ($\leq 5\%$) of entrained plagioclase.

The presence of trapped liquid elevates the extremely low REE abundances found in the mafic cumulates alone (as first pointed out by SHIH and SCHONFELD, 1976). Only prohibitively low degrees of melting ($\ll 1\%$) of this mafic cumulate could generate a liquid with the appropriate *abundances* of the REE present in mare basalts. However, at these extremely low degrees of partial melting, derived liquids would be extremely LREE-enriched and would not match the analyzed REE *patterns* of mare basalts. Therefore, the addition of this TIRL component has a three-fold effect: (1) to elevate the REE abundances of the total cumulate pile; (2) to moderate the LREE-depletion in the cumulate pile; and (3) after plagioclase starts to crystallize, it is integral to the generation of the requisite negative Eu anomaly in the mare basalt source region.

8. Major-Element Evolution of the LMO

Using the proposed fractionation assemblage, starting composition, and exchange-reaction distribution coefficients from the literature, as discussed above, major elements have been modeled for the fractionated LMO up to 99.5 PCS. Above about 98 PCS, it becomes exceedingly difficult to model the major element evolution, due to uncertainties in exact mineral compositions and proportions (*e.g.*, one starts to exhaust major oxides if the mineral compositions and proportions are not well known). Also, it is likely that any residual liquid which occurs after 98 PCS will have already split into two immiscible liquids (HESS *et al.*, 1975), if that liquid has continued to follow Fenner trend evolution.

The progressive changes of the major oxides and Mg[#] of the residual LMO are shown in Fig. 2. MgO decreases continuously from start to end. SiO₂ is nearly constant for the first 90 PCS of LMO evolution and then decreases until ilmenite becomes a liquidus phase, at which point it increases. CaO increases steadily to a maximum of 12 wt% at about 85 PCS, and Al₂O₃ increases to a maximum of approximately 14 wt% where plagioclase first becomes a liquidus phase (78 PCS). From this point on both CaO and Al₂O₃ decrease. The point at which the LMO reaches saturation with respect to ilmenite affects the shape of the curves for FeO and Al₂O₃, but in opposing manners. Note that Al₂O₃ is in the range of 10–12 wt% between 90 to 95 PCS. The oxide TiO₂ shows a similar relation to FeO, increasing rapidly, until ilmenite reaches the liquidus



Fig. 2. A plot of wt% oxides (and Mg#×100) vs. PCS (Per Cent Solid) for the LMO liquid. This plot indicates the evolution of the LMO as the ocean fills with cumulates (after SNYDER et al., 1992b).

(at 93–95 PCS), and then dropping off rapidly. Extended equilibrium crystallization of the LMO leads to the "buffering" of the liquid at relatively high Mg#s. At 86 PCS the Mg# of the liquid has still only fallen to 0.49 (Fig. 2). The Mg# of the mafic cumulate at 86 PCS is 0.78. However, from this point on the Mg# of the liquid, and the corresponding Mg# of the mafic cumulate, drops off markedly (due to fractional crystallization becoming the dominant process for differentiation of the liquid). Ilmenite does not become a liquidus phase until 95 PCS, at which point the Mg# of the liquid is 0.15 and that of the corresponding mafic solid is 0.34.

The mafic cumulates (Fig. 3) show sympathetic trends to the melt, albeit in a more stepwise fashion. It has been stated previously that the LMO could have convected vigorously for most of its differentiation history, thus keeping crystallizing minerals suspended. Therefore, it is likely that the lower three-quarters of the lunar upper mantle consists of nearly equal proportions of olivine and orthopyroxene, with the ratio of orthopyroxene/olivine decreasing gradually with depth. In this case, the trends seen on Fig. 3 would be smooth up to 78 PCS. Figure 3 indicates the major element trends if olivine and orthopyroxenite layer above. Again, it is important to point out the precipitous drop in MgO and Mg[#] above 86 PCS, once clinopyroxene comes on the liquidus. Note also the expected jump in FeO and TiO₂ once ilmenite begins to crystallize at 95 PCS.

For instructive and display purposes, the composition of the LMO cumulate pile will be dealt with in a three-step manner in the following discussions. First, the composition of the mafic cumulate alone will be presented; then the mafic cumulate + varying percentages of TIRL; and finally, the complete model featuring the mafic cumulate + TIRL + varying proportions of entrained plagioclase. By using this stepwise approach to the presentation, we hope to indicate the relative importance and



Fig. 3. A plot of wt% oxides (and Mg*) vs. PCS for the mafic LMO cumulate pile (including only 1 wt% plagioclase once it comes on the liquidus). Open triangles are for TiO₂, closed triangles are for CaO. It must be pointed out that the major element compositions are for instantaneous solids crystallizing. However, it is very likely that these solids remained suspended in the turbulently convecting LMO for lengthy periods before actual precipitation. Therefore, the lower 0–78 PCS is likely a mixture of olivine and opx in subequal proportions, rather than an olivine layer overlain by an opx layer. In this case, major element trends would be smooth and would not include the abrupt changes in SiO₂ and MgO at 40 PCS (after SNYDER et al., 1992b).

effect of each component at successive stages in the evolution of the LMO and lunar mantle.

9. Trace-Element Evolution of the LMO

Trace-element evolution of the residual liquid and the mafic-cumulate pile + trapped liquid + entrained plagioclase pile are illustrated in Figs. 4–5 and labelled with the respective PCS values. Partition coefficients used in this study are given in Table 1 and the rationale for the choice of values is elucidated in SNYDER *et al.* (1992b). Extended equilibrium crystallization (for 78 PCS) is nearly indistinguishable from the trace-element evolution of the LMO displayed by simple fractional crystallization (SNYDER *et al.*, 1991; SNYDER and TAYLOR, 1992). This is due to the fact that most trace elements are incompatible with mafic minerals. Due to the low kDs, resulting in low bulk Ds for the cumulates, equilibrium crystallization mathematically reduces to fractional crystallization.

As pointed out by many previous workers (e.g., GROMET et al., 1981; HUGHES et al., 1988), REE evolution of the LMO residual melt becomes more and more KREEPy as crystallization of the LMO continues (Fig. 4). Once plagioclase starts to crystallize, the LMO residual melt takes on a pronounced negative Eu anomaly. Because of the continual removal of mafic minerals (which generally fractionate the HREE relative to



Fig. 4. Plot of a suite of modeled trace elements at various stages (40 PCS, 55 PCS, 78 PCS, 86 PCS, 90 PCS, 95 PCS and 99 PCS, where PCS=per cent solid) in the evolution of the LMO liquid normalized to the C1 Chondrites. High-K KREEP (WARREN, 1989) is also plotted for comparison.

the LREE), the LMO also begins to show LREE enrichment as the final dregs of melt are approached. Based in part on $^{143}Nd/^{144}Nd$ ratios, NYQUIST *et al.* (1976) have also pointed this out and concluded that the LMO may have started out LREE-enriched. If this is so, then this places even more stringent restrictions on the percentage of melting of cumulate sources produced from such an ocean. It is evident in Fig. 4 that late-stage, magma-ocean, residual liquids are similar to lunar high-K KREEP (WARREN, 1989).

On the other hand, the mafic cumulate pile alone displays LREE depletion throughout its evolution (Fig. 5a), but also begins to take on a pronounced negative Eu anomaly once plagioclase comes on the liquidus (Table 2). Addition of only 1% trapped instantaneous residual liquid (TIRL) boosts the total REE (by an order of magnitude for the LREE) and moderates the LREE depletion, but maintains the strong negative Eu anomaly (Fig. 5b; Table 2). Addition of 5% or greater TIRL all but eliminates the LREE depleted signature of the cumulate pile (which is required for the mare basalt source, as will be shown later). Above 90 PCS, the mafic cumulate takes on a pronounced LREE-depleted signature, due in part to the crystallization of clinopyroxene and pigeonite. Melts taken from above this level would retain relatively depleted Nd isotopic signatures over time. Above about 78 PCS (after plagioclase becomes a liquidus phase), the Eu anomaly varies little with the proportion of trapped liquid in the cumulate. However, the degree of LREE depletion (as indicated by the ratio (La/Sm)n) is drastically decreased by addition of just a few % of TIRL (Fig. 5). Above about 5% added TIRL, the mafic cúmulate after 90 PCS is effectively swamped by the LREE pattern of the LMO residual liquid (SNYDER et al., 1992b).

It is evident at this point that the modelling encounters two competing problems. In order to get the absolute abundances of the REE in the mare basalt source up to levels that will make it appropriate for melting to generate high-Ti basalts, an added



Fig. 5. Plots of a suite of trace elements for evolution of the mafic cumulate pile: (a) LMO mafic cumulates alone; (b) mafic cumulate pile + 1% TIRL and 1% entrained plagioclase.

component with higher REE (TIRL) must be included. However, the TIRL component has either a chondritic LREE pattern or is slightly LREE-enriched and, therefore, must make up a small proportion of the source in order to maintain the required overall LREE-depleted signature.

Also noteable are the large *depletions* of Sc, Sr, and Rb in the evolving LMO liquid (Fig. 4). This is mirrored by the *enrichment* of Sc in the earliest LMO mafic cumulates. Nb and Th are enriched, relative other elements, in the mafic cumulate throughout its precipitation with Th becoming relatively more depleted above 95 PCS, once ilmenite starts to crystallize. Cr is depleted early in the LMO liquid and is enriched in the earliest cumulates (where chromite is likely to crystallize with olivine). Cr becomes more depleted in the cumulate with increasing PCS (Table 2). This modelling of Cr may be contrary

Element	oliv ¹	opx²	cpx ³	pig ⁴	plag ⁵	ilm ⁶
Sc	0.27	1.6	1.6	1.6	0.0071	1.5
Cr	3	5	5	[5]	0.0332	4.2
Co	5	1.3	1.2	[1.3]	0.0202	4.3
Ni	30	2.5	2.5	[2.5]	[0.01]	3.5
Rb	0.0001	[0.023]	0.0257	[0.0026]	0.088	[0.001]
Sr	0.0001	0.018	0.097	0.0020	1.61	[0.001]
Zr ⁹	0.013	0.063	0.063	0.063	0.0128	0.406
Nb@	0.0001	[0.02]	0.02	[0.02]	0.005	0.80
Ba	0.0001	0.013	0.013	0.013	0.686	0.005
La	0.0001	0.007	0.023	0.0009	0.0418	0.0024
Ce	0.0001	0.009	0.039	0.00172	0.0302	0.0019
Nd	0.0001	0.014	0.104	0.0058	0.0236	0.0012
Sm	0.0006	0.022	0.17	0.011	0.0170	0.0023
Eu	0.0007	0.015*	0.16	0.0068	1.2*	0.0009
Gd	0.001	0.037	0.20	0.021	0.0105	0.0053
Tb	0.002	0.048	0.21	0.027	0.0095	0.0082
Dy	0.003	0.060	0.23	0.034	0.0089	0.013
Er	0.008	0.10	0.26	0.055	0.0077	0.031
Yb	0.019	0.170	0.29	0.087	0.0065	0.057
Lu	0.03	0.22	0.30	0.11	0.0068	0.070
Hſ	0.013	0.063	0.063	0.063	0.0128	0.406
Th	0.03	0.13	0.13	0.13	0.0208	0.55

Table 1. Mineral/melt partition coefficients.

References: ¹ MCKAY (1986); ² 1200°C run from WEILL and MCKAY (1975) and as estimated from their Fig. 6; ³ MCKAY *et al.* (1986); ⁴ MCKAY *et al.* (1991); ⁵ PHINNEY and MORRISON (1990); ⁶ NAKAMURA *et al.* (1986); ⁷ SHIMIZU (1974); ⁸ MCKAY and WEILL (1977); ⁹ Zr partition coefficients were assumed to be the same as those of Hf; ^(a) Nb data were taken or estimated from MCCALLUM and CHARETTE (1978). Many REE "data" are interpolated from data in these sources; * Eu value for opx is estimated assuming a similar magnitude Eu anomaly as pigeonite and that for plagioclase is from WEILL and MCKAY (1975). Some "gaps" in the data base (especially in Sc, Ba, Ta, Hf, and Th) have been filled in by previously used estimates generated in NEAL *et al.* (1989). Rb data for opx and pigeonite were calculated assuming Rb/Sr ratios given in ARTH (1976) and Sr partition coefficients from above. Transition metal (Cr, Co, Ni) partition coefficients were taken from VILLEMANT *et al.* (1981), BIRD (1971), and LINDSTROM (1976).

to some studies which suggest that Cr acts as an incompatible-element due to its reduced (2+) nature in the lunar environment (SCHREIBER, 1977). Ba becomes *relatively* more depleted in the liquid with time (especially above 78 PCS where plagioclase starts to crystallize). Above 78 PCS, Rb partitions into the residual LMO (*i.e.*, is incompatible with the mafic cumulate) increasing the Rb/Sr ratio with PCS value (Fig. 4). Hf is depleted in the cumulate early, but becomes even relative to the normalized REE above 95 PCS, when ilmenite is crystallizing (Table 2).

The entrainment of a small proportion of plagioclase into the cumulate source has some interesting effects. If the proportion is small (<5%), there will be little effect on the major-element composition of the bulk source; however, if plagioclase was an early melting phase, and melting percentages were low, it could exert an important influence on the major-element composition of the derivative melt. Even small amounts of plagioclase will have a significant effect on both the Eu and Sr values of the bulk cumulate (Fig. 5b). Eu and Sr are more compatible with plagioclase than with mafic

	1 PCS	40 PCS	55 PCS	78 PCS	95 PCS	99 PCS
Ba	0.10	0.18	0.55	1.1	3.1	10
Rb	0.0035	0.0059	0.025	0.050	0.16	0.59
Sr	0.10	0.17	0.61	1.2	4.4	6.3
Th	0.0061	0.0097	0.043	0.075	0.30	1.7
Nb	0.014	0.022	0.086	0.17	0.72	16
La	0.011	0.019	0.041	0.083	0.49	1.8
Ce	0.029	0.048	0.12	0.24	1.8	6.4
Nd	0.022	0.036	0.11	0.22	2.8	8.9
Sm	0.0073	0.012	0.048	0.095	1.36	4.1
Eu	0.0028	0.0046	0.014	0.028	0.24	0.39
Gd	0.010	0.017	0.094	0.18	2.1	6.3
ТЬ	0.0021	0.0034	0.021	0.041	0.40	1.2
Dy	0.015	0.025	0.17	0.32	2.9	8.8
Er	0.013	0.022	0.18	0.31	2.0	6.3
Yb	0.021	0.035	0.27	0.46	2.0	6.5
Lu	0.0045	0.0071	0.051	0.080	0.30	0.96
Zr	0.391	0.646	2.7	5.0	20	156
Hf	0.012	0.019	0.079	0.15	0.61	4.7
Sc	6.5	9.2	45	38	48	41

Table 2. Calculated LMO cumulate (+1% trapped liquid+1% entrained plagioclase) trace element compositions (in ppm) at various PCS levels.

minerals by over an order of magnitude (Table 1). Thus, as seen in Fig. 5b, addition of an entrained plagioclase component drastically alters the requisite negative Eu anomaly and Rb/Sr ratio of the source. In fact, addition of only 10% plagioclase to the source regions of the mare basalts will effectively delete the required negative Eu anomaly. By this observation, any model involving addition of plagioclase into the source is tightly constrained to be much less than 10 wt% plagioclase in the cumulate.

10. Late-Stage LMO Liquid, Similarity to Quartz Monzodiorites, and Evolution of the KREEP Component in Lunar Meteorites

It has been suggested (WARREN and WASSON, 1979), and widely accepted, that urKREEP represents the dregs (near final crystallization products) of the LMO. This so-called KREEPy component is evident in a plethora of highlands rocks from the near-side of the Moon. Abundances of KREEP indicator elements such as K and Th indicate that lunar meteorites contain significantly less KREEP material than rocks in the Apollo collections. However, WARREN and KALLEMEYN (1991b) have convincingly shown that K/Th ratios of lunar meteorite breccias are fairly constant with increasing Th (their Fig. 11). They use this observation as evidence that a single uniform component (KREEP) will account for this trend (WARREN and KALLEMEYN, 1991b), thus indicating again the importance of KREEP in lunar petrogenesis. However, the definition of a pure urKREEP end-member composition has remained elusive. Some authors have speculated that the rare quartz monzodiorites could represent the actual crystallization products of urKREEP (WARREN, 1988; SNYDER *et al.*, 1992a). In support of this

	15403,24 ¹	15405,851	15405,152 ¹	14161 ²	LMO (99.5) ³
Sc	34.0	30.7	29.0	30.2	24
Cr	1020	1220	1510	361	0.2
Со	9.91	7.8	8.0	7.15	
Rb	34	40.6		52	55
Sr	140	154		160	208
Ba	1370	1490	1900	2050	1400
La	281	217	183	228	196
Ce	726	557	413		510
Nd	470	328	287		354
Sm	121	92.5	77.4	97	106
Eu	2.82	2.60	2.75	3.35	8.7
Tb	24.9	19.7	14.9	18.7	24.0
Yb	81.2	63.0	55.2	73.6	74.4
Lu	10.5	8.50	8.20	10.2	9.9
Zr	1400		1620	4240	2320
Hf	44.9	51.0	44.7	100	69
Та	5.85	13	10.1	9.2	
Th	50.1	43	39.4	44	15.1

 Table 3. Trace element compositions (ppm) of lunar quartz monzodiorites compared to residual LMO liquid at 99.5 PCS.

¹ MARVIN et al. (1991). ² JOLLIF et al. (1991). ³ SNYDER et al. (1992b).

hypothesis, the trace-element compositions of the quartz monzodiorites are similar to the urKREEP composition considered by MORRIS *et al.* (1990) and the high-K KREEP composition of WARREN (1989).

As indicated above, the residual LMO above 80 PCS is KREEPy (LILE enriched). However, even at 99% crystallization, the LMO has still not achieved the enrichment seen in the quartz monzodiorites and calculated urKREEP (as per WARREN, 1989; NEAL and TAYLOR, 1989; MORRIS *et al.*, 1990). Not until 99.5% of the LMO has crystallized will the trace-element composition of the modelled LMO reach the enrichments seen in quartz monzodiorites. Table 3 compares trace-element compositions of four quartz monzodiorites (which are relatively free of accessory phosphates) with our modelled residual LMO at 99.5 PCS. The model LMO trace-element composition after 99.5 PCS is nearly indistiguishable from the compositions of the quartz monzodiorites. This consistency between model calculations and actual petrologic groundtruth lends credence to the LMO crystallization model presented within. Therefore, the KREEP component indicated in many *lunar meteorites* may have been derived from magmas similar to those which produced the quartz monzodiorites sampled by the Apollo missions.

11. Mare Basalt Source Regions: A Case Study from EET87521

In a previous paper (SNYDER *et al.*, 1992b), we demonstrated the applicability of this LMO crystallization model to the generation of viable source(s) for the Apollo high-Ti mare basalts. The high-Ti basalts were chosen as the test case because this suite

is somewhat unique among mare basalts, including their obvious high-Ti contents and their LREE-depleted patterns. It was felt that if the model was successful in explaining this complex suite of basalts, modelling of the petrogenesis of other basalt types could be even more readily accomplished. One of the keys to generating the high-Ti basalt source was the introduction of a small trapped liquid component. Too much KREEPy trapped liquid in the source would yield a melt which was LREE-enriched. However, this is generally not a consideration with other mare basalt groups, like the VLT-types found in EET87521 and Y-793274, as the basalts contain lower REE abundances and are LREE-enriched from the outset (WARREN and KALLEMEYN, 1991a, b).

Though brecciated, only sample EET87521 can be considered a true basalt both in terms of chemistry and grain size (WARREN and KALLEMEYN, 1991b). However, the Mg# of this sample (37; Table 4) indicates that, though.it may be considered a liquid composition, it is likely a differentiate of a more primitive parent. Previous workers have suggested that lunar picritic glasses could be parental to the Apollo VLT basalts (DELANO, 1986; LONGHI, 1987). Therefore, we attempted to *model the chemical composition of basalt EET87521 with picritic glass beads from the Apollo 17 landing site*. Approximately 35% fractional crystallization of olivine and plagioclase (3:1) from an average VLT picritic glass will achieve a major element composition which is quite similar to EET87521 (Table 4). However, trace elements, especially the incompatible

	EET07601	A-17 VLT	35%	+4%	
	EE18/321	average	Frac. Cryst.	KREEP	
SiO ₂	48.34	45.3	48.36		
TiO ₂	1.13	0.66	0.93		
Al_2O_3	12.47	9.60	11.72		
FeO	19.17	19.6	19.18		
MnO	0.24	0.26	0.26		
MgO	6.30	15.0	6.34		
CaO	11.67	9.40	12.63		
Na ₂ O	0.41	0.27	0.37		
K ₂ O	0.07	0.04	0.06		
Cr_2O_3	0.21	0.40	0.12		
Mg ♯	0.37	0.58	0.37		
Ba (ppm)	88	26	40	88	
Sr	104	57	88	79	
La	8.3	1.98	3.05	7.31	
Ce	20.9	4.74	7.28	18.2	
Nd	13.0	3.46	5.32	12.2	
Sm	3.86	1.35	2.07	3.91	
Dy	4.8	2.19	3.34	5.83	
Er		1.48	2.24	3.78	
Yb	3.19	1.26	1.89	3.29	
Sc	44	35	54	53	

 Table 4. Composition of VLT mare basalt EET87521, average apollo VLT picrite and model crystallization products.

Sources: LMO = BUCK and TOKSOZ (1980) for major elements; EET87521 = WARREN and KALLEMEYN (1989); A-17 VLT glass average = DELANO (1986) for major elements, SHEARER *et al.* (1991) for trace elements.

elements, in the fractionated VLT glass do not match the composition of EET87521. Addition of an incompatible element-rich component, similar to high-K KREEP (WARREN, 1989) is required. Assimilation of (or metasomatism by) only 4% of this KREEP component will achieve the requisite trace-element abundances found in EET87521 (Table 4), without perceptibly changing the major-element composition. It is therefore considered likely that a primary melt of composition similar to the Apollo 17 VLT picritic glass beads was parental to this basalt. However, could this primary VLT magma have its ultimate source in the cumulate upper mantle? To answer this question, we have modelled the REE during melting of a possible source from our LMO crystallization scheme using the batch modal melting equation,

$$C_{L} = C_{0} / [D_{0} + F(1 - D_{0})], \qquad (4)$$

which is identical to the equilibrium crystallization equation (1), except that $C_o =$ concentration in the initial solid.

The Mg# (57) of the VLT picritic parent indicates that the cumulate source must be quite primitive (Mg= 70–75). Therefore, the source must have been from below about the 50 PCS level (see Fig. 3) and be comprised of only orthopyroxene and olivine. Because this is in the region of the cumulate source formed during equilibrium crystallization of the LMO, it is difficult to constrain the actual proportions of olivine and orthopyroxene. However, due to the density contrast between olivine and orthopyroxene, allowing olivine to sink preferentially to orthopyroxene, it is likely that orthopyroxene is the dominant mineral at this level. We will assume that the source is at the 50 PCS level and consists of 60% orthopyroxene and 40% olivine. The REE pattern for a residue of 1-5% melting has been calculated from the VLT picrite parent and is shown in Figure 6 with the REE pattern of the LMO cumulate at 50 PCS. As can be seen, the modelled 50 PCS orthopyroxene + olivine (+1%) trapped instantaneous liquid) cumulate lies, for the most part, within the field for 1-5% melting residues of a VLT picritic glass. This coincidence of calculated and modelled residues lends creedence to the hypothesis that VLT picritic glasses are melts of the lunar upper mantle. This cumulate upper mantle is similar in composition to that predicted by our LMO crystallization model.

12. Conclusions

Mantle cumulates (comprised of sub-equal proportions of orthopyroxene and olivine) produced after approximately 50% fractional crystallization of the LMO, and which contain 1% trapped instantaneous residual liquid, have the requisite REE abundances and relative proportions to generate magmas parental to VLT basaltic meteorites such as EET87521 (Fig. 6). In general, mare basalt source regions can be generated by simple crystallization of the LMO (accompanied by bulk flotation of plagioclase) and settling of the mafic phases with a small amount of trapped instantaneous residual liquid and entrained plagioclase (above 78 PCS). Furthermore, evolved model residual LMO compositions resemble actual evolved rocks (quartz monzodiorites) returned from the Apollo missions and may represent the minor KREEP component found in lunar meteorites. This LMO crystallization model is capable of

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Fig. 6. Plot of the REE (normalized to the initial LMO) for the modeled lunar mantle cumulates (at 50 PCS) with reference to the VLT picrite parent pattern. A field of residues-of-melting for 1–5% melting with 60% orthopyroxene + 40% olivine in the residue and the VLT picrite as the derived melt is also indicated.

explaining the precursor rocks/protoliths to both the VLT mare basalt and KREEP components found in lunar meteorites.

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