# Parental Magmas of Lunar Troctolites: Genetic Problems and Estimated Original Compositions

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Abstract—The paper presents a review of hypotheses of the early magmatic differentiation of the Moon and petrogenetic processes responsible for the origin of the parental magmas of the magnesian suite of the highland crust. An important role of hybridism of the parental magmas is discussed in the context of the transformations of the melting products and the differentiation of the subchondritic mantle via anorthosite assimilation. These processes are thought to have proceeded simultaneously with the consolidation of the anorthosite crust and resulted in high-Mg magmas, which later gave rise to troctolites, norites, and gabbronorites. An updated version of the METEOMOD model was utilized for simulations of the composition of primitive troctolite melts corresponding to equilibrium with olivine of the composition  $Fo_{88}$  and  $Fo_{91}$ . The differences between the simulated melt compositions are interpreted with regard for variations in the temperature and composition of the parental magnesian liquids that assimilated compositionally similar feldspathic material. The compositional data obtained are a necessary component of a thermochemical model of assimilation that would also involve the enthalpy of phase transitions and the heat capacity for the reactants and products of crystallization associated with the partial dissolution of anorthosites in high-temperature magmas.

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## **INTRODUCTION**

The interpretation of the Moon's inner structure involves the estimation of the average composition of this planetary body and its principal units and the elucidation of mechanisms of differentiation of its interiors and the conditions of this process, as well as the specifics of the origin of the geochemical reservoirs corresponding to the sources of highland and mare magmatic rocks. A particularly important issue is the genesis of the primary lunar crust, whose development can be analogous in certain respects with processes that took place early in the Earth's evolution [1, 2]. It is commonly believed that the average thickness of the modern lunar crust is close to ~60 km in the near side of the moon and may exceed 100 km in its other side [3]. These estimates are underlain by geophysical and gravimetric models popular in the 1970s. The past years were marked by attempts of the revision of the Apollo seismic data and the "shift" of the crust-mantle boundary to depths of 45–30 km [4, 5]. In any event, the relative volume of the lunar crust does not exceed 8-10% of the overall Moon's volume. The lunar crust is laterally and vertically heterogeneous. Its surface rocks are the brecciated material of ancient highland areas and the basalts of younger maria (with the ratio of their surface areas of approximately 83/17). Considering the depth of depressions filled with basaltic lavas, the relative contribution of the "mare component" to the total crust mass is no greater than 1% [6].

In the vertical section, the lunar crust is traditionally subdivided into upper and lower parts [7]. This subdivision is based on a combination of the results of petrological research and data of geological and geophysical observations. The ubiquitous occurrence of calcic plagioclase ( $An_{96-99}$ , up to monomineralic anorthosites) in the polymictic breccias, pristine rock samples, and regolith at highland landing sites of space probes led to the conclusion about an "anorthositic" composition of lunar plateaus and mountainous areas, which were thought to be dominated by feldspathic rocks with 26-28 wt % Al<sub>2</sub>O<sub>3</sub> [7, 8]. This composition is provisionally ascribed to the whole zone of fractured and brecciated rocks, which extends to depths of about 20 km and is identified with the lunar upper crust [9, 10]. General information on the composition of the lower crust can be obtained from data on the ejecta of large craters. These data point to a less aluminous composition of the lavas (~20% Al<sub>2</sub>O<sub>3</sub>, for example, [11]) and an increase in pyroxene content toward the crust-mantle boundary.

The results of *Clementine* spectral data have introduced certain corrections into these estimates [12]. The analysis of mulispectral images of the central peaks of 109 large (40–180 km in diameter) impact craters provided more detailed information on the mineralogy of rocks within the depth range of ~5–30 km (beneath highlands) and ~25–55 km (beneath maria). According to these data, the composition of the upper crust turned out to be even more anorthositic (82% modal plagioclase on average), which corresponds to 27–



**Fig. 1.** Bimodality of the compositions of plagioclase and mafic minerals in the ferroanorthosites and rocks of the magnesian plutonic suite of the lunar highland crust. The diagram is constructed for pristine samples >0.1 g in mass [16]: (1) ferroanorthosite (>95% An in plagioclase), magnesian suite (>85% An in plagioclase); (2) dunite; (3) troctolite (mg# > 80); (4) norite (mg# > 75); (5) gabbronorite (mg# > 60).

29 wt % Al<sub>2</sub>O<sub>3</sub>. The material of the lower crust also suggests strong plagioclase accumulation (71–75%) at depths of >20 km. Hence, the average composition of the lunar crust corresponds to hypothetical anorthositic norite that contains from 18–20% [7–11] to 27–28% [12] alumina. The diversity of highland rocks comprises a number of their groups, which differ in mineralogy, petrochemistry, and geochemistry.

The scope of these groups depends on the aim of the research and the observation scale [13]. The point is that the rock material delivered to the Earth provided no evidence of geologic bodies measured in kilometers or at least tens of meters and consisted of variably sized megaregolith fragments. Some samples represent rock blocks or nodules a few meters across in megabreccia. The other end of this range includes fragments a few millimeters across and the fine fraction of the regolith. This situation is further complicated by the presence of rock mixtures affected by impact remelting and their crystallization and disintegration products. These processes were widespread and played an important role in the reworking of the material of the upper crust of the Moon throughout its whole evolutionary history [14]. Thus, distinguishing between fragments of endogenic rocks and the products of impact mixing and melting is a challenging and complicated problem, which can not always be unambiguously solved. The main criterion proposed to be used to recognize rocks that were not contaminated with the material of the impactor was low concentrations of siderophile elements: no higher than  $3 \times 10^{-4}$  CI [15]. Additional criteria included texturalpetrographic, isotopic, and some other features of the rocks. The work resulted in a list of 260 pristine samples and fragments that highly probably had a magmatic genesis and showed no traces of significant contamination or melting of the original material [16]. Most of these fragments were small: the samples with high pristinity indices equal to 7–9 included only 46 samples with masses greater than 1 g [13].

The most conspicuous characteristic of this selection is the clearly pronounced bimodality of the rocks, which can be readily seen in a diagram showing the composition of plagioclase (its anorthite percentage) vs. the Mg mole fraction (mg#) of mafic minerals (Fig. 1). The diagram was constructed based on the data in [16] for samples with masses >0.1 g. The contrasting character of the lunar crustal rocks is manifested in the occurrence of two major groups demonstrating (1) a vertical trend of the mg# of the pyroxenes (42 < mg# < 75) within a narrow range of plagioclase composition (96-99% An) and (2) a trend of normal crystallization evolution, which is characterized by co-variations in the compositions of the minerals. These compositional relations are correlated with the modal composition of the pristine samples: the first group comprises ferroanorthosites, which usually contain >95% plagioclase (FAS), and the second group consists of the rocks of the high-Mg suite (HMS). Early in the course of the petrological research, the Mg-suite was thought to include dunites, troctolites, norites, and gabbronorites. Later this "magmatic series" without definite spatial boundaries was expanded to include rarer and lower-temperature products of crustal magmatic evolution as anorthosites, norites, gabbroids, and monzodiorites under the common name of alkali suite (HAS) and some aluminous and KREEP basalts [13]. The petrological justification of this combining was, however, doubted by some researchers. For example, Shearer and Floss [17] stressed that HMS and HAS rocks are the cumulates of various parental magmas, whose genetic relationships are still not fully clear. No less curiosity was provoked by the nature of the KREEP material and high-Al volcanism at lunar highlands, which could be a volcanic analogue of the HMS and HAS plutonic complexes.

The isotopic–geochemical results indicate that the high-Mg members of the plutonic suite (dunite 72415-18 and some norites and troctolites) and most ferroanorthosites represent the oldest lunar crustal material. The Rb–Sr and Sm–Nd systematics points to close crystallization ages of these rocks at 4.4–4.56 Ga [18]. The parental magmas of the troctolite–gabbronorite plutons were definitely produced at that time simultaneously with the growth of the upper part of the lunar crust, with some samples of anorthosites depleted in LREE having relatively young ages of 4.29  $\pm$  0.06 Ga, which suggests that the formation of the highland crust was a long-lasting process [19]. The age range of 4.4–4.5 Ga was also marked by the development of the geochemical reservoir of the KREEP component and the mantle source of the mare basalts (according to the Hf–W systematics [20]). Hence, the upper mantle and crustal sources of lunar magmatic rocks were generated relatively quickly, possibly, within the first 40–100 m.y. of the Moon's history [21]. There are no apparent indications of the chemical chronology of the events. Conversely, it is reasonable to believe that the major types of highland rocks and the bimodal character of the corresponding mineralogical characteristics (Fig. 1) were produced practically simultaneously, during the coupled processes of the consolidation, destruction, and intrusion of the anorthosite crust by mafic plutons.

The considerations presented above led to the conclusion that it is possible to estimate the compositions of the earliest and primitive parental magmas of the primary lunar crust and to test the models of the bulk composition of their possible source (undifferentiated lunar mantle or cumulates of the magmatic ocean). Searches for the parental melts are based on the selection of highland rocks that have old crystallization ages and petrological-geochemical features corresponding to those of the primitive magmas that formed these rocks. The obvious candidates for this role are the least ferrous ferroanorthosites (Fig. 1) and high-Mg plutonic rocks, including the known dunite samples [22, 23] and a representative group of pristine troctolites [3, 13, 16]. The genetic informativeness of anorthosites is underlain by the subchondritic ratios of plagiophile elements in them (Ga, Eu, and Al; Fig. 2) and their predominance in the ancient lunar crust [10, 21]. An interesting petrological problem is the high *fe*<sup>#</sup> of these feldspathic rocks, which is manifested in the absence of mafic minerals with mg# > 75 (Fig. 1). This situation calls for the construction and examination of differentiation schemes that allow for the simultaneous existence of relatively primitive melts and their derivatives (see below).

## SCHEMES OF THE MOON'S EARLY MAGMATIC DIFFERENTIATION AND THE PROBLEMS OF THE GENESIS OF TROCTOLITE MAGMAS

Most of the troctolites are also characterized by subchondritic proportions of plagiophile elements, and these rocks represent the most magnesian material of the highland crust (Fig. 2). This follows not so much from the Mg/(Mg + Fe) ratios of these rocks (these ratios reflect the degree of the accumulation of mafic minerals) as from the high Fo concentrations in the olivine. Figure 3 shows a diagram of the compositions of olivine from 30 samples of pristine troctolites, which is based on the data from [16] for samples >0.1 g in mass and with <95% modal plagioclase. This plot indicates that 18 troctolite samples contain olivine of the composition 87-90 mol % Fo (spinel troctolite was determined to contain 92% Fo). This richness in forsterite suggests that the parental magmas of the troctolites meet the main criterion of primitiveness in terms of possible relations to a subchondritic or differentiated



**Fig. 2.** Dependence of the Eu/Al ration on the *mg*# of pristine highland rocks (modified after [24]).

(1) Ferroanorthosites; rocks of the magnesian suite: (2) dunite, (3) troctolites, (4) norite, and (5) gabbronorites. The shaded field includes the compositions of monzodiorites and KREEP basalts.



**Fig. 3.** Histogram of the forsterite concentration in olivine from high-Mg troctolites.

Thirty-five samples >0.1 g in mass were selected from thirty-eight pristine troctolite samples [16]. The histogram shows data on thirty samples for which information is available on their olivine composition.

mantle source. At the same time, the high mg# of olivine in these rocks highlights a serious problem of lunar petrology [25]. The point is that the schemes proposed for the early magmatic differentiation of the Moon imply relatively late plagioclase crystallization from Fe-enriched evolutionary products of the parental magmas. The predominant cotectic mineral in the anorthosites is thereby not magnesian olivine but hypersthene and (in more ferrous varieties) pigeonite.<sup>1</sup> This places serious limitations onto the possible genesis of the troctolite magmas, which usually cannot be produced by the direct melting of the lunar mantle because the stability fields of olivine and plagioclase in chondritic systems under low pressures are separated by the appearing orthopyroxene [24]. Another problem is the geochemistry of lunar troctolites, which show evidence of notable enrichment in REE (by approximately one order of magnitude compared to anorthosites), which is thought to be explained by the certain contamination with the KREEP component [20, 24]. These contradictions with the composition of the possibly chondritic (?) source were the main reasons to put forth hypotheses admitting that the troctolite magmas may have had a hybrid genesis (see review [10]). The appreciation of the petrological significance of these hypotheses varied as concepts concerning the early magmatic evolution of the Moon evolved. Their starting point was always the postulate of the complete or partial melting of the lunar mantle with the development, in the upper planetary shell, of (1) a melt zone in the form of a "magmatic ocean" (LMO), (2) a global "magmosphere" with possible significant variations in the amounts of liquid with depth, or (3) local chambers separated by undifferentiated mantle material.

The scale and duration of the melting of the lunar material were controlled by the amount of the stored heat and the occurrence of external heating sources. Most researchers believe that the major heat source was the kinetic energy released during the accretion of the planetary body. The key problem here is the possible sizes of the impactors and the rate of the process. The complete melting of lunar interiors to a depth of hundreds of kilometers requires the rapid (106-108 years) accretion of bodies at least 40 km across [28]. Schemes with a relatively slow and low-energy accretion process lead to models of the magmosphere [29, 30] or numerous separated magma chambers and pools, which characterize the development of so-called serial magmatism [31, 32]. It is worth noting that the incomplete melting of the silicate mantle leading to the origin of a thick (hundreds of kilometers) magma ocean also implies the heterogeneity of significant volumes of the lunar mantle, which should have been a transitional layer with moderate and low degrees of melting of the primitive material.

The petrological aspect of the proposed schemes involves the development of models for the differentiation of the LMO or magmosphere, which results in an anorthositic crust and major geochemical reservoirs corresponding to the sources of the Mg-suite, KREEP, and low- and high-Ti mare basalts. This aspect should be examined with regard for the phase and chemical succession of derivatives, which predetermines the primary vertical layering of the crust and mantle and the probable chronology of the events [28, 33-35]. A principal issue in the development of these models is related to the analysis of the gravitational stability of differentiation products that form the stratigraphic sequence of cumulates. In particular, attention was paid to the fact that origin of heavier phases (including ferrous silicates, ilmenite, and melt enriched in FeO) during the intermediate and final stages of LMO crystallization can bring about a global overturn of the multiphase heterogeneous system with the emplacement of primitive magnesian components to upper mantle levels (for example, [36]). This idea won numerous proponents among geochemists because the opposite displacement of the primitive and evolved crystallization products was considered to be a natural mixing mechanism of the primary geochemical reservoirs and the potential heat source for the melting of hybridized cumulates and the formation of the source of mare basalts [35, 37]. According to Spera [34], the process of convection stirring of lunar interiors and the origin of hybrid reservoirs lasted for approximately 200 m.y.

Among the aforementioned (in fact, qualitative) schemes of the early lunar differentiation, it is worth noting a computer model developed by M.Ya. Frenkel, who was the first to try to simultaneously solve the problems of the cooling of the postaccretionary Moon and the origin and differentiation dynamics of mantle melting zones with the development of the major petrological and geochemical reservoirs of the lunar material [30, 38]. The model allowed for the development of a global sphere of the partial melting of the lunar mantle, including a relatively short-lived magmatic ocean (>90% melt) and an underlying heterogeneous zone with >5% pore melt. This model is unique because partial melting in the lower part of a magma-generating system is temporally coupled with the cooling and crystallization of the protocrust. This implies that the anorthositic material and complementary systems of basite-hyperbasite composition were produced simultaneously, which was a stumbling block to many models based on the successive crystallization of the magmatic ocean. The leading differentiation mechanism of lunar interiors was thereby thought to be infiltrationcontrolled metasomatism related to the compaction of the cumulates, migration of the interstitial liquid, and the reequilibration of the primitive melts with the differentiation products at upper levels. This model can, in fact, be regarded as another scenario for the origin of the anorthositic crust and the hybridization of the "primary cumulates" [30].

With regard for these hypotheses, the following three scenarios can be proposed for the genesis of the primitive magmas of the magnesian suite: (1) the products of LMO crystallization, (2) contaminated systems that developed during the assimilation of anorthosites by the partial melts of the primitive mantle [24], and (3)

<sup>&</sup>lt;sup>1</sup> The selection of samples of the pristine anorthosites >1 g in mass includes two unusual fragments (62236 and 62237) with elevated contents of olivine  $\sim Fo_{60}$  [13].

the result of the reworking of the feldspathic crust by impact melts during the melting of a subchondritic impactor [39] or early olivine cumulates [25]. As was mentioned above, the concept of magmatic ocean faces insurmountable difficulties when trying to derive troctolites (Ol-Pl cotectics) from a primitive system with characteristics close to chondritic ones (Fig. 4). It can be added to this that the high *mg*<sup>#</sup> of troctolite magmas (Fig. 3) is inconsistent with the long-lasting crystallization of olivine, a process that should have resulted in aluminous (cotectic) melts with elevated FeO/MgO ratios. The hypotheses of assimilation and impactmagmatic effects present models that can "shift" the final hybridization product to the olivine-plagioclase cotectic at the preservation of high mg# typical of the magnesian source [24, 25, 39] (Fig. 4). The topology of the Ol-An-SiO<sub>2</sub> diagram demonstrates that this can be done by adding a certain amount of material enriched in anorthite (this material approximates the composition of the anorthositic crust; point A) to the primitive component PM. Principal uncertainties are related here to the nature of the initial high-Mg material and the reworking mechanism of the crust.

A less plausible model was proposed by Taylor [39], who suggested that the composition of the completely remelted impactor corresponded to the average composition of the Moon itself. Criticizing this concept, Hess [25] highlighted two aspects. First, the impact melting with varying proportions of the crustal and impactor materials implies the formation of a continuous spectrum of derivative compositions and rules out the bimodality of the anorthosites and hybrid troctolite magmas (Figs. 1, 2). Second, it is known that the mass of the impact melt rarely exceed 10% of the mass of the impactor, which, in turn, casts doubt onto the possibility of the predominance of olivine lithology of the composition (mg#) of subchondritic material in the hybrid products. Moreover, Clementine data indicate that the development of troctolite liquid pools could hardly be an occasional (i.e., equally probable anywhere) process because only six of the 65 large highland craters show appreciable traces of mafic materials [12]. The distribution of non-anorthositic ejecta in the central peaks of the craters is more consistent with the concept of a sporadic emplacement of high-Mg endogenic magmas into the lunar crust.

The problem of the composition of endogenic picrite-basaltic magmas and the main mechanism of their hybridism remains unresolved. According to [25], such magmas can be the melts of olivine cumulates from the upper subcrustal levels, which were mechanically mixed with impact melting products of the anorthositic crust. This model is consistent with the primitive MgO/(MgO + FeO) ratio in the hybridized magmas but requires high degrees of melting of the crustal and mantle materials. Warren [24] also favored the concept of the thermochemical effect of high-Mg magmas and believed that they were formed in the magmosphere via the partial melting of the undifferentiated



**Fig. 4.** Scheme displaying possible genetic relations between the main products of the Moon's magmatic differentiation.

Phase boundaries in the Ol-An-SiO<sub>2</sub> system are given according to [26, 27]. Data points: *PM*—primitive high-Mg melt produced by the melting of the chondritic mantle *CH* or the crystallization of the magmatic ocean; *A* anorthositic crust; compositions of troctolite magmas:  $T_1$  generated by the mixing of the melts of *PM* and *A*;  $T_2$ —produced by the assimilation of the anorthositic crust by the primitive melt. The direction of the *CH-PM* line indicates the crystallization succession of chondritic magma:  $Ol \longrightarrow$  $Ol + Opx \longrightarrow Ol + Opx + Pl$ . Projection routines are according to [26] from the apex of normative wollastonite (CaSiO<sub>3</sub>).

mantle. The hybridization process occurs in this situation as the assimilation of "hot" but solid anorthositic crust by high-temperature chondritic melts.

The problem is that magmatic assimilation does not act as a simple mixing of two or more components and does not necessarily result in a cotectic (Ol + Pl) melt  $T_1$  lying on the *PM*-A mixing line (Fig. 4). In fact, it is necessary to take into consideration that the temperature of the magnesian melt should be, by definition, higher than the temperature of the assimilant. This is a necessary prerequisite that ensures the dissolution of feldspathic component because of the partial crystallization of the original liquid along with the overall cooling of the hybrid system [40]. Thus, the assimilation process should be coupled with phase transitions, including the partial dissolution of the anorthositic material, crystallization of a certain amount of olivine, and the origin of a cotectic melt that has a lower mg# than that of the source (point  $T_2$ ). Obviously, the extent of this compositional shift,  $T_1 \longrightarrow T_2$ , is controlled by the amount and temperature of the assimilant: the greater the amount of the dissolved cold component, the more significant the cooling of the system and the higher the proportion of olivine crystallization. A complete characterization of this process would involve such parameters as total heat and mass balance and phase proportions in the evolved systems at any given moment. The estimates previously obtained for the thermochemical parameters of assimilation of lunar anorthosites are contradictory. According to [24], the heat stored in the overheated (because of their adiabatic ascent) melts of the subchondritic mantle is sufficient for the dissolution of the anorthositic material and the generation of troctolite magmas. The calculation results in [25] point to inevitable assimilation *n*-induced crystallization of a significant amount of olivine notably decreasing the mg# of the derivative troctolites compared to their observed characteristics (see Ol compositions in Fig. 3).

The materials of this paper represent the initial stage of the investigation aimed at the estimate of the compositions of the most primitive magmas of the magnesian suite: the parental melts of high-Mg troctolites.

## THE COMPOSITION OF THE PARENTAL TROCTOLITE MELTS

The relations between the parental picrite magma of PM, assimilant A, and derivative liquid  $T_2$  in the Ol-An-SiO<sub>2</sub> diagram (Fig. 4) highlight the important role of the identification of the composition and amount of newly formed troctolite melt. These characteristics should be taken into account in the thermochemical balance and analysis of the evolution of phase proportions during anorthosite assimilation [24]. With regard for the cumulus genesis of troctolites, the composition of the melt from which they crystallized can be approximated by the composition of the intergranular material. However, available literature data on the composition of the intercumulus liquid of lunar troctolites commonly include only data on the concentrations of trace elements (usually REE) (see, for example, [41]), and such information on major components is practically absent. Most researchers simply emphasize that these rocks are enriched in anorthitic plagioclase crystals, and that the parental magmas were likely restricted to the olivine-plagioclase cotectic, which was constructed by Walker et al. [26, 27]. For example, Yaroshevskii [42] analyzed the correlations between the normative plagioclase composition and the alumina content in highland lunar rocks and proposed an initial composition of a magma corresponding to the troctolite system containing approximately 10 wt % MgO and 23 wt %  $Al_2O_3$ . In [24], the composition of the modeled troctolite melt  $(17-18 \text{ wt }\% \text{ Al}_2\text{O}_3)$  is given as the final result of picrite magma contamination with anorthosite, and no such composition is presented at all in [25]. However, experimental and theoretical methods have been developed for the reconstruction of the composition of intercumulus material.

The experimental approach involves partial melting of samples at subliquidus temperatures and the subsequent studying of glasses filling the space between grains of incompletely melted (perhaps, primary) crystals. Examples of such studies are described in [43, 44], which present the results of a series of experiments with gabbroids from the principal zones of the Layered Series of the Skaergaard intrusion. Recently obtained data on the melting of natural and synthetic troctolites from the Kiglapait intrusion, Labrador, were published in [45]. Principal difficulties in the identification of intercumulus in these experiments arise from the fact that the researcher never knows beforehand the equilibrium temperature of the primary crystals and liquid and thus runs the risk, when interpreting the results, of entering the compositional field notably differing from the original characteristics. This possibility becomes even greater when multiphase assemblages are studied that contain less than 50% of the intergranular liquid.

Theoretical approaches are based on the calculations of the intercumulus compositions from data on crystal-melt distribution coefficients (for example, [46]). In the late 1980s, we proposed a universal method for the geochemical thermometry of magmatic rocks that makes it possible to assay the initial composition of the melt by simulating the equilibrium crystallization of intrusive or volcanic basic rocks [47]. The method is founded on the COMAGMAT model of crystallization [48] that is used for simulations for genetically interrelated rocks corresponding to close differentiation stages of a parental magma. This approach is not an alternative of experimental studies and is characterized by its own limitations, but its application sometimes makes it possible to eliminate uncertainties in estimates of the original temperatures. This notably narrows the range of the possible compositions of the corresponding liquid [49]. The methodological fundamentals and examples of genetic reconstructions of intrusive basites with the use of the COMAGMAT program are described in detail in [50]. In the context of this publication, it is interesting that one of the pioneering attempts of geochemical thermometry of extraterrestrial materials (with the aim to test a version of the crystallization model of basaltic magmas) was undertaken for lunar highland rocks [47, 51].

## FIRST ATTEMPTS TO MODEL THE COMPOSITION OF HIGHLAND MAGMAS

It is important to stress that attempts to interpret that the genesis of terrestrial intrusive rocks were fairly successful, because the rock samples were preliminarily carefully positioned relative to the contact zones or principal units within layered series [50]. However, ideally, on can imagine a situation when information on the conditions under which a rock was crystallized would be derived from separate rock fragments that are not accompanied by clear descriptions of their geological setting. For this, a rock must be crushed and divided into several fractions enriched in different cumulus minerals, the bulk compositions of these fractions should be evaluated, and these compositions should then be utilized as starting for the modeling of equilibrium crystallization [49]. Evidently, these artificial "cumulates" were formed, by definition, from a single magma and at the same temperature, and thus, the intersection of the calculated crystallization trajectories in composition-temperature space must uniquely identify the composition of the intercumulus liquid, which was the same for discrete fractions and the rock as a whole. It is hard to say whether this approach can be fully applied to terrestrial rocks. However, the simulation of the crystallization or melting of separate rock fragments has been proven to be an efficient tool for the identification of the parental melt of lunar rocks. Indeed, lunar regolith consists of rock and mineral aggregates that were highly probably produced by the destruction of the same geological bodies: lava flows, sills, or intrusions. These breccias offer an example of strongly disintegrated and sorted systems whose compositionally contrasting character possesses a potential for the application of geochemical thermometry. At a great number of initial compositions (fragments), the results of these simulations acquire a statistical (stochastic) character [52].

This idea was utilized as the basis for the estimations of the temperatures and compositions of highland magmas from data obtained on 72 particles of sample 63500 (Apollo 16) and 88 regolith particles (Luna 20) [47, 51]. The chemical composition of these rocks was examined by INAA and defocused microprobe or was estimated by means of mass balance calculations based on the modal composition of these rocks and the compositions of their minerals. As a result of thermometric calculations and searches for compact clusters of the model liquids, five average compositions were identified that characterized the most probable parental melts at temperatures of 1400/1240/1200°C (for the Apollo 16 rocks) and 1250/1200°C (for the Luna 20 rocks) (see Table 2 in [51]). The high-temperature feldspathic liquid in equilibrium with anorthitic plagioclase at 1400°C was likely a calculation artifact, while the estimates of the compositions of the troctolite melts at 1240 and 1250°C looked quite realistic. In both situations, they suggested a high-Mg composition of the melt, which contained ~19.5 wt % Al<sub>2</sub>O<sub>3</sub> and ~11.8 wt % MgO and was in equilibrium with olivine  $\sim Fo_{90}$ . The group of 24 Luna 20 rocks turned out to be particularly representative and included fragments of spinel troctolites [53].

These estimates are still of importance in the context of solving the problem of troctolite genesis but leave uncertain as to how much can the results of geochemical thermometry of fragments of sample 63500 and the *Luna 20* rocks be extended over lunar troctolite magmatism as a whole. The particles were not examined in terms of the "pristinity" of the rocks, showed evidence of moderate *fe*# of their mafic minerals, and reflected various degrees of disintegration of the regolith material [54]. We set ourselves the task of continuing this research by simulating the most primitive melts corresponding to the intercumulus of obviously pristine samples [16], containing olivine with 87–90% *Fo* (Fig. 3).

### SELECTION OF THE CRYSTALLIZATION MODEL AND TEST SIMULATIONS

When starting thermometric calculations, it is necessary to choose a model for phase equilibria. Currently available computer programs enable the researcher to calculate the liquid lines of descent of natural magmas corresponding to terrestrial tholeiitic and mildly alkaline basalts (COMAGMAT [48, 49]), lunar highland basalts (LUNAMAG [55]), and the melting products of ordinary chondrites (METEOMOD [56]). The selection of an optimal model depends on the composition of the system to be examined. The results of experiments with highland rocks [26, 27] and the first results of geochemical thermometry (see above) testify that the most conspicuous feature of troctolite cotectics is their high alumina contents (approximately 20% Al<sub>2</sub>O<sub>3</sub>), high mg# values, and low concentrations of alkalis (usually below 0.7%). With respect to Al<sub>2</sub>O<sub>3</sub>, the aforementioned crystallization models show no advantages over one another, because all of them were calibrated within the compositional region with no more than 15–17% Al<sub>2</sub>O<sub>3</sub>. The COMAGMAT model is more suitable in terms of mg# value, but it was calibrated on compositions of higher alkalinity, up to 5%  $Na_2O$  + K<sub>2</sub>O. The LUNAMAG and METEOMOD programs were tuned for low-alkali compositions, but the crystallization model for lunar basalts was originally tailored for iron enriched systems. This led us to choose the METEOMOD computer program, which makes it possible to solve problems related to genetic relations between troctolite magmas and a chondritic source.

The additional tuning of the model was carried out using experimental compositions available from the INFOREX database [50] and corresponding to high-Al  $(17-22\% \text{ Al}_2\text{O}_3)$  and low-alkali  $(\text{Na}_2\text{O} + \text{K}_2\text{O} < 2\%)$  $Ol + Pl \pm Opx$  cotectics at 1200–1300°C. Preliminary calculations had demonstrated that the METEOMOD program underestimates the plagioclase crystallization temperature by approximately 20°C within this compositional region and overestimates the crystallization temperatures of mafic mineral by 15°C on average. These corrections were introduced into the computation algorithm of the corresponding temperatures. The plausibility of the corrected model can be assayed from the calculated trajectory of equilibrium crystallization for samples of feldspathic basalt 68415.82 and spinel microtroctolite 62295.48, which were used in the experiments on locating the *Ol-Pl* cotectic in the Ol-An-SiO<sub>2</sub> system [27].

The simulations were conducted with a crystallization step of 1% at a pressure of 1 atm, near the iron– wustite buffer, up to the point where orthopyroxene appears. Figure 5a shows the modeled evolutionary trends, which include regions where excess olivine (~6%, sample 62295) and Pl (~60%, sample 68415) crystallize and give way to the cotectic crystallization of both minerals. These data indicate that the compositions of troctolite melts calculated by the METEO-MOD model are in good agreement with the experimentally established olivine-plagioclase phase boundary. The relatively steep slope of the calculated cotectics in the Ol-An-SiO<sub>2</sub> diagram is explained by the continuous change in the mg# of the systems, and the insignificant shift of the troctolite crystallization products into the field of feldspathic compositions was caused by the high mg# value (0.81) of the initial melt. It should be mentioned that the appearance of orthopyroxene in the modeled systems is also consistent with the phase diagram (see the terminations of cotectic lines in Fig. 5a). We also conducted additional test calculations for the compositions of the two most primitive melts ("1240" and "1250") identified based on the data of geochemical thermometry of fragments of samples 63500 and Luna 20 [51]. Both compositions unambiguously corresponded to the *Ol-Pl* cotectic ( $\pm 1\%$ ) excess mineral), although the temperatures calculated by the METEOMOD program occurred to be 20-30°C higher than the quoted modeled values. Obviously, the reason for the temperature underestimates in the papers published in the 1980s was the use of less accurate thermometers in our earlier crystallization models [49].

## SELECTION OF SAMPLES AND CORRECTION OF INITIAL COMPOSITIONS

In selecting samples for the simulations, we applied the following criteria: the troctolites should have had high "pristinity indices" (from 6 to 9) [16], consisted of olivine of the composition  $Fo_{87-90}$  (Fig. 3), and contained no more than 95% modal plagioclase. We identified ten such fragments ranging from 0.1 to 155 g in mass, for which petrochemical and geochemical data were available (Table 1). During the first stage of our research, we accomplished preliminary calculations of the equilibrium crystallization trajectories for the melts of these rocks: in the crystallization field of excess minerals (Ol or Pl) and along the Ol-Pl cotectic. The problem was that the liquid lines of descent were characterized by a wide scatter of the SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> concentrations for the cotectic compositions, with some of the trajectories very soon deviating to the systems strongly undersaturated in silica (<35% SiO<sub>2</sub>) and hyperaluminous (up to 30% Al<sub>2</sub>O<sub>3</sub>). The analysis of this problem indicates that the "problematic" compositions were characterized by the presence of normative nepheline and kyanite, and sample 15426c137 [60] contained monticellite (Table 1). The absence of these minerals from the list of the modal phases of lunar troctolites and the actual differentiation trend toward more "acid" systems (gabbronorites and monzodiorites) suggest that the deviations toward silica-undersaturated compositions were not related to inaccuracies of the model simulations but were caused by some features of the raw



**Fig. 5.** Verification of the corrected METEOMOD program [56] and the results of the simulation of troctolite melts. (a) Tested position of modeled cotectics representing the equilibrium crystallization trajectories of melts of feldspathic basalt 68415.82 and spinel microtroctolite 62295.48 [27]; (b) simulation results for selected troctolites and dunite (see Tables 1 and 2 for the numbers of the compositions). Solid circles show the average compositions of troctolite melts "T=1320," " $Fo_{88}$ ," and " $Fo_{91}$ " listed in Table 3. The simulations were carried out with a crystallization step of 1% under a pressure of 1 atm, at the IW buffer, up to the appearance of orthopyroxene.

Parameter	1	2	3	4	5	6	7	8	9	10	11
PI	7	7	6	6	6	9	8	7	7	6	9
Mass, g	0.23	89	0.67	2	0.1	155	0.49	0.34	0.49	0.14	55.2
SiO <sub>2</sub> , wt %	43.63	(43.14)*	42.56	43.42	(35.41)	42.9	42.14	(43.6)	(43.7)	(44.2)	39.93**
Average compositions of minerals, mol %											
Fo	87.2	87.3	87.5	87.5	88	87.5	88.7	89	89	89.9	87.2
An	94.7	93.5	94.4	94.5	95	95.5	95.1	95.1	95.3	97.1	94
Modal proportions of minerals, vol %											
Ol	nd	~45	30	nd	65	37	38	37***	nd	nd	93
Pl	70	55	70	70	35	58	61	29	~40	>90	4
Characteristics of normative composition, wt %											
Ne	0.15	-	0.24	0.29	0.82	_	1.37	_	-	1.05	_
Als	2.02	0.37	-	0.14	-	-	0.62	-	_	_	-
Mon	-	-	-	—	16.12	-	-	—	_	-	-

 Table 1. Characteristics of the troctolites and dunite that can be used to reconstruct the compositions of the initial high-Mg melts

Notes: (1–10) Troctolites: (1) 14305c264 [57]; (2) 14304c95("a") [58], (3) 14179c6 [59], (4) 14303c194 [57], (5) 15426c137 [60], (6) 76535.21-22 [41], (7) 72705c1 [61], (8) 14305c317 [62], (9) 14305c358 ("w6") [63], (10) 14305c361MgA ("w7"); (11) dunite 72415 [22]. PI is the pristinity index [16]. Normative components: *Ne*—NaAlSiO<sub>4</sub>; *Als*—Al<sub>2</sub>SiO<sub>5</sub>; and *Mon*—Ca(Mg,Fe)SiO<sub>4</sub>; nd—no data.

\* Evaluated as difference from 100%.

\*\* Calculated from mass balance.

\*\* Plus 33% modal orthopyroxene.

analytical data. This looks most plausible for silica, whose concentrations are often evaluated as the difference between 100% and INAA data.

Because of this, we corrected the problematic compositions using the trial and error approach and varying the SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> concentrations within the errors of instrumental analysis (~2%). The concentrations were varied to preclude the appearance of normative minerals (*Ne*, *Als*, and *Mon*) that are absent from natural samples. The SiO<sub>2</sub> concentrations in compositions *1*, *3*, and *4* in Table 1 were increased by 0.5–0.6 wt %, and the Al<sub>2</sub>O<sub>3</sub> concentrations were decreased by 0.1–0.5 wt %. Compositions 5, 7, and 10 required more fundamental corrections, which likely extended beyond the analytical errors, so that we rejected these three compositions from further consideration. Compositions 2, 6, 8, and 9 were left without corrections. Thus, the final selection consisted of seven troctolite samples, whose compositions are listed in Table 2. In addition, we used data on the composition of dunite 72415, which is thought to show evidence of genetic links with troctolite 76535 [22, 23, 41].

Component	1	2	3	4	6	8	9	11
SiO <sub>2</sub>	43.74	43.21	43.32	43.60	43.13	43.74	43.84	40.90
TiO <sub>2</sub>	0.04	0.17	0.03	0.03	0.05	0.13	0.13	0.03
$Al_2O_3$	27.17	16.64	23.05	26.72	20.81	21.97	21.77	1.46
FeO	2.80	5.54	4.46	3.14	5.02	4.21	4.01	11.62
MnO	0.03	0.07	0.05	0.03	0.07	0.05	0.05	0.13
MgO	11.31	25.24	16.14	11.68	19.20	17.66	17.76	44.67
CaO	14.41	8.69	12.50	14.31	11.46	11.74	11.94	1.17
Na <sub>2</sub> O	0.43	0.28	0.38	0.41	0.20	0.44	0.45	0.02
K <sub>2</sub> O	0.07	0.15	0.08	0.08	0.03	0.06	0.06	0.00
$P_2O_5$	_	-	_	-	0.03	_	_	_

Table 2. Corrected compositions of troctolites and dunite used to reconstruct the compositions of the initial high-Mg melts

Notes: (1–9) Troctolites; (11) dunite 72415. Compositions are normalized to 100 wt %. Numbers of compositions are the same as in Table 1.

# **RESULTS OF MODEL SIMULATIONS**

Simulations with the updated version of the METEOMOD model were conducted on the selected compositions (Table 2) at a pressure of 1 atm, under conditions corresponding to the iron-wustite buffer, at a crystallization step of 1%, and the maximum amount of solid phases reaching 98%. The significant crystallinity of the modeled systems was caused by potentially high contents of cumulus minerals and attempts to trace the evolution of the melt composition up to the appearance of relatively low-temperature phases (*Opx* or *Pig*) at  $T < 1250^{\circ}$ C. Our simulations for troctolites demonstrate that olivine was the first to crystallize (~1410– 1580°C) in five samples. Plagioclase was the liquidus phase at 1350 and 1349°C in the two most aluminous compositions (Table 2, 1 and 4). Regardless of the crystallization sequence, all troctolite composition comes to the Ol-Pl cotectic at 1308–1326°C. The third crystallizing phase was orthopyroxene-in all cases at contents of crystals higher than 94% (the maximum temperature of its appearance was 1234°C). The liquid line of descent for the dunite showed an extensive field of olivine stability (1728-1261°C, 0-93% crystals), and plagioclase and orthopyroxene appeared at higher proportions of solid phases (96%, 1242°C).

For further analysis of our simulation results, it is important to mention that the initial compositions of all seven high-Mg troctolites fall within the spinel field when projected onto the Ol-An-SiO<sub>2</sub> diagram (Fig. 5b). This means that the early crystallization stages of the modeled troctolite system should have included pleonaste (noble spinel). Depending on the initial composition, this spinel could later dissolve in the low-temperature melts or be preserved as a relic phase among later crystallization products. With regard for this fact, the *Ol-Pl* cotectics in the spinel field should be regarded as an artifact of the high-temperature simulations, which should not, however, affect the plausibility of the melt compositions outside the spinel stability field.

The character of the evolution of these modeled liquids can be seen in the plots of Fig. 6. Table 2 displays the temperature dependencies of the concentrations of major components for the melts of the selected troctolites and dunite. The lines of the troctolite melts characterize the usual evolution with decreasing temperature, which are somewhat different in the field of excess Ol and Pl but nevertheless display similar tendencies along the trajectory of cotectic equilibrium. Because of this, when expressed as normative components of the Ol-An-SiO<sub>2</sub> system, the liquid lines of descent of the troctolite liquids define a fairly compact group of Ol-Pl cotectics (Fig. 5b). This consistency does not, however, provide genetic information but characterizes the topology of the model system. The variations in the contents of major components in Fig. 6 enabled us to evaluate some of the crystallization parameters.

This concerns, first of all, the temperature. The characteristic sheaflike morphology of the family of the calculated trajectories testifies that the compact clusters of modeled compositions group near 1320°C, a value that can be regarded as the upper limit for the probable temperature of the troctolite magmas. The average composition of the modeled liquid calculated for the seven troctolite melts at 1320°C is presented in Table 3. This is a fairly aluminous ( $\sim 25\%$  Ål<sub>2</sub>O<sub>3</sub>) and highly magnesian (12.6% MgO) melt, which can be, in principle, assumed as the composition of the most primitive magmas reconstructed from the compositions of lunar rocks. However, the realism of this compositions provokes doubt. First, a liquid of this composition should be, according to our simulations, in equilibrium with  $Fo_{94}$ , but no olivine of this composition was found in the pristine troctolites (Fig. 3). Second, when projected onto the Ol-An-SiO<sub>2</sub> diagram, this composition plots in the high-temperature region of the spinel field (Fig. 5b), casting doubt onto the reliability of the estimate. Because of this, in reconstructing the primitive magmas of lunar troctolites, we decided to substitute analysis of the temperature-composition dependences with analysis of the correlation between the compositions of olivine and melt.

Figure 7 displays the dependence between the Fo in olivine and the compositions of the modeled liquids for the results of the same simulations that were used to construct Fig. 6. These data show that, proceeding from the compositions of modeled olivine, one can obtain a more realistic estimate of the composition of the troctolite liquids. To solve this problem, we selected two possible olivine compositions:  $Fo_{91}$  and  $Fo_{88}$ . The former is close to the most primitive olivine, and the latter corresponds to the maximum of the histogram of the pristine samples (Fig. 3). The results of our simulations make it possible to obtain the average characteristics of melts in equilibrium with  $Fo_{91}$  and  $Fo_{88}$ . These estimates are presented in Table 3.<sup>2</sup> The average temperature of the more magnesian melt is  $1288 \pm 10^{\circ}$ C and it plots near the point of four-phase *Ol-Pl-Sp*-melt equilibrium when projected onto the Ol-An-SiO<sub>2</sub> diagram. The second melt characterizes the Ol-Pl-melt equilibrium at  $1254 \pm 10^{\circ}$ C and plots in the middle part of the line cotectic control, close to the liquid line of descent of the for dunite 72415 (Fig. 5b). This convergence of the liquid lines of descent of the troctolites and dunite (Figs. 6, 7) confirms the cotectic nature of olivineenriched fragments of sample 72415-18. The same conclusion was previously drawn from geochemical evidence [22, 23].

The genetic relations between such troctolite melts as " $Fo_{88}$ " (1254°C) and " $Fo_{91}$ " (1288°C) can be interpreted in two manners. The traditional interpretation is

<sup>&</sup>lt;sup>2</sup> Only three of the seven liquid lines of descent were simulated up to the appearance of olivine of the composition  $Fo_{88}$ .



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Component	I ( <i>n</i> = 24)	II ( <i>n</i> = 7)	$III (Fo_{88}, n = 3)$	$IV (Fo_{91}, n = 7)$
SiO <sub>2</sub>	46.77	43.82 (0.25)	47.91 (2.15)	45.14 (0.94)
TiO <sub>2</sub>	0.53	0.11 (0.08)	0.59 (0.13)	0.36 (0.22)
$Al_2O_3$	19.52	25.07 (0.28)	17.91 (0.97)	22.73 (0.94)
FeO	7.82	4.41 (0.52)	8.18 (0.42)	6.76 (0.28)
MnO	_	0.05 (0.01)	0.13 (0.02)	0.10 (0.01)
MgO	11.89	12.61 (0.08)	11.18 (0.10)	11.58 (0.23)
CaO	12.88	13.37 (0.32)	12.95 (0.73)	12.37 (0.56)
Na <sub>2</sub> O	0.45	0.45 (0.09)	0.64 (0.18)	0.72 (0.18)
K <sub>2</sub> O	0.14	0.10 (0.05)	0.24 (0.09)	0.20 (0.10)
$P_2O_5$	-	0.01 (0.01)	0.26 (0.11)	0.05 (0.03)
<i>T</i> , °C	1250	1320	$1254 \pm 10$	1288 ±10
<i>Fo</i> (mol %)	88–89	$94.2 \pm 0.6$	88	91
<i>An</i> (mol %)	95–96	$97.9 \pm 0.4$	$95.4 \pm 1.0$	$95.8 \pm 1.0$

**Table 3.** Compositions of primitive melts of the magnesian suite calculated with earlier and the modern models for equilibrium crystallization of lunar highland rocks

Note: Modeled melts simulated for the following: (I) particles of *Luna 20* regolith [51]; (II–IV) selected troctolites (Table 2), with the use of the corrected version of the METEOMOD model: (II) using the analysis of melt–temperature diagrams (Fig. 6), (III, IV) based on the condition of equilibrium with olivine  $Fo_{88}$  and  $Fo_{91}$  (Fig. 7). The compositions are normalized to 100 wt %, numerals in parentheses are the standard deviations (1 $\sigma$ ).

based on the idea of fractionation and admits that the less magnesian melt is a crystallization product of a more primitive source (Table 2, composition " $Fo_{91}$ "). The other possibility is underlain by the hybridization concept: in this case, the compositions " $Fo_{88}$ " and

" $Fo_{91}$ " can be treated as assimilation products of anorthosites with subchondritic melts, which were derived from the primitive mantle or olivine cumulates produced during the early Moon differentiation (see discussion of Fig. 4).



**Fig. 7.** Dependences of the forsterite concentration in olivine on the composition of residual liquid calculated from the simulation results of the equilibrium crystallization of melts of the troctolites and dunite 724215 (Table 2). Horizontal dashed lines correspond to 88 and 91 mol % *Fo*. The line of dunite equilibrium crystallization enters the field of troctolite compositions in equilibrium with  $Fo_{87}$ . Open circles show the average compositions of troctolite melts "T=1320," " $Fo_{88}$ ", and " $Fo_{91}$ " listed in Table 3.

#### CONCLUSIONS

The review of hypotheses concerning the genesis of parental magmas for the rocks of the magnesian suite of the lunar crust led us to the conclusion about the important role of hybridization processes, which involved the origin of products of the melting and differentiation of the subchondritic mantle via anorthosite assimilation. These processes were simultaneous with the consolidation of the anorthositic crust and resulted in high-Mg troctolite magmas, which served as the source (parental magma) for the rocks of the magnesian suite of lunar highlands.

Based on simulation by a modified version of the METEOMOD model, estimates were obtained for the composition of high-Mg troctolite melts that corresponded to equilibrium with olivine of the composition  $Fo_{88}$  and  $Fo_{91}$  (Table 3). These melts contained approximately 11.5 wt % MgO and variable Al<sub>2</sub>O<sub>3</sub> concentrations (~18 and 23%). The less magnesian and aluminous composition likely corresponds to the most widely spread type of primitive troctolite magmas and, when projected onto the Ol-An-SiO<sub>2</sub> diagram, plots on the olivine-plagioclase line of cotectic olivine-plagioclase equilibrium at a temperature of  $1254 \pm 10^{\circ}$ C. The relatively aluminous composition " $Fo_{91}$ " has a higher temperature (1288  $\pm$  10°C), and the corresponding data point is projected near the point of the Ol-Pl-Sp-melt four-phase equilibrium (Fig. 5b). This highlights the important role of spinel troctolites as the most primitive highland material among currently available lunar rocks.

The compositional relations between the modeled melts can be interpreted within the scope of the hybridization concept. A self-evident fact is the differences between the temperatures and compositions of the initial chondritic liquids that assimilated compositionally similar anorthositic material. The process could also be slightly dependent on the temperature of the assimilant [24, 25]. Systematic analysis of these issues should involve the development of a thermochemical model based on data such as melt compositions, heat capacities of all phases and enthalpy of melting/crystallization reactions for all reactants of the heterogeneous mixture in which anorthite dissolves due to olivine crystallization [40]. The results of our thermochemical simulations of troctolites using modern techniques for the calculation of phase equilibria in crystallizing systems [50] enabled us to evaluate the probable temperature of the protocrust and the composition of the picritic melts that could be derived from the protomantle during various stages of the Moon's differentiation. The solution of these problems provides potential for the elucidation of the composition of the undepleted lunar mantle and the initial material from which this planetary body was formed [64].

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