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Orthopyroxene as a recorder of lunar crust evolution: An ion microprobe investigation of Mg-suite norites

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Abstract

The lunar Mg suite, which includes dunites, troctolites, and norites, make up to ~20–30% of the Moon's crust down to a depth of ~60 km. The remainder is largely anorthositic. This report focuses on norites (which consist of mostly orthopyroxene and plagioclase) because we have found that the chemical characteristics of orthopyroxene are effective recorders of their parental melt compositions.

The values of Mg′ for the parental melts calculated from those in orthopyroxene show that most melts have values of Mg′ in the range of 0.36–0.60. This compares with a range of Mg′ values for lunar volcanic picritic glass beads of 0.4–0.68 (Shearer and Papike, 1993). Therefore, although the cumulate whole-rock compositions of the Mg suite can be extremely magnesian (Mg′ > 0.90), the calculated parental melts are not anomalously high in Mg.

A chemical characteristic of the Mg-suite norites that is more difficult to explain is the high KREEP content of the calculated parental melts. The REE contents (especially HREE) for the calculated norite parental melts match or exceed the high-K KREEP component of Warren (1989). Therefore, the mixture of a KREEP component and a picritic melt, by itself, cannot explain the high estimated REE contents of the melts parental to norites. Advanced crystallization (>90%), especially of plagioclase, may also be required.

Introduction

Shortly after the first lunar rocks were returned to Earth in 1969, an extremely important discovery involved the realization that the early history of the Moon could have been dominated by a global magma ocean. Although this hypothesis has never been proved, it remains the leading model for the early differentiation of the Moon. One recent interpretation (Hess and Parmentier, 1994) of the global consequences of a lunar magma ocean with a depth of 800 km is that plagioclase could have floated, forming a 60-km anorthositic crust near the lunar surface. The denser olivine and pyroxene probably sank, forming a cumulate pile ~700 km thick with the denser [late-crystallizing, low Mg′ = Mg/(Mg + Fe) atomic] pyroxene assemblages near the top and the less dense, more magnesian, olivine and pyroxene assemblages near the bottom. Hess and Parmentier (1994) suggested that late-crystallizing melt was rich in trace incompatible elements forming a KREEP (K, rare earth elements, and P) residue that was also rich in ilmenite. If this model is correct, it leads to a gravitationally unstable cumulate pile, with dense cumulates overlying less dense cumulates. The predicted consequence of this instability (Spera, 1992; Hess and Parmentier, 1994) is convective overturn with the ilmenite layer (which also contains KREEP and heat-producing elements three to ten times the bulk Moon) sinking to deep mantle depths. Although this model is speculative, it potentially explains how KREEP (a late-crystallizing product of the magma ocean) can be brought to great depth in a zone of melting, which may include both Mg-rich cumulates and primitive mantle. This process could provide source regions for the picritic lunar basalts (Shearer and Papike, 1993) and Mg- and Al-rich magmas (the Mg suite), which intruded the anorthositic crust during the period 4.43–4.1 Ga, after most of the magma ocean had crystallized (Taylor et al., 1993; Warren and Kallemeyn, 1993). This paper focuses on the petrogenesis of the Mg-suite magmas (Papike et al., 1994), which apparently intruded the anorthositic crust and may have formed layered mafic complexes (James, 1980) similar to the Stillwater Complex, Montana.

Many of the samples representing the Mg suite are small and thus unrepresentative. In addition, they are cumulates and thus are difficult to study using whole-rock techniques. Therefore, we decided to study the Mg-suite rocks using SIMS techniques to analyze a suite of trace elements in cumulus orthopyroxene from Mg-suite norites. The 12 norite samples we report on in this paper were selected from a recent compilation by Warren (1993), who attempted to select the best candidates from the

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standpoint of their pristine character, i.e., those samples not formed by or contaminated by impact processes.

EXPERIMENTAL METHODS

Ion microprobe analyses of orthopyroxene in norites were conducted using a Cameca IMS 4f ion microprobe operated on the UNM campus by a UNM–Sandia National Laboratory consortium. Analyses were performed on the ion microprobe using a Kilbourne Hole augite standard and a Kakanui augite standard for all analyses. The analyses were conducted under the following operating conditions: a 10-kV O^- primary beam, a primary beam current of 30–40 nA, depending on beam density, a beam diameter of 25–35 μm, a sample voltage offset of −75 V, a 150-μm secondary-ion image field, a 250-μm contrast aperture, a 60-μm field aperture, and a 50-V energy window. Counting times and the number of cycles per analysis varied, depending on the concentration of the elements being analyzed, to achieve the precision of 5% or better, in most cases, a precision better than 2% was achieved. A minimum counting time of 20 s on a background peak was maintained to determine the detection limits.

All ion microprobe analyses were conducted in locations previously analyzed by electron microprobe. Care was taken to prevent the analysis of a contaminating phase by mass imaging of major elements prior to and following each analysis.

Major and minor elements of orthopyroxene were analyzed using a JEOL 733 Superprobe equipped with a backscattered-electron detector, five wavelength spectrometers, and a LINK exL II operating system. All analyses were performed using an accelerating voltage of 15 kV and a beam current of 20 nA. A beam diameter of 5 μm was used to reintegrate any fine augite lamellae. ZAF corrections were applied to all microprobe data.

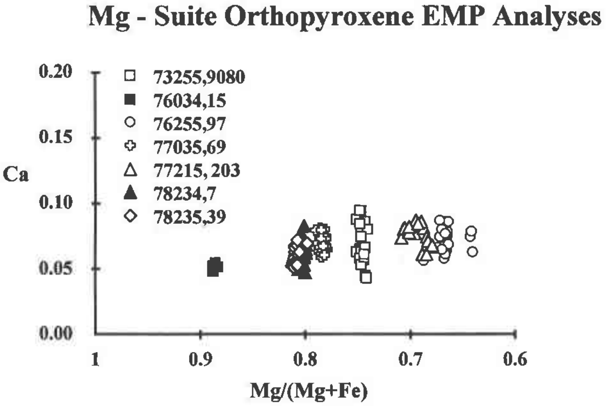


Fig. 1. Ca contents of Apollo 17 orthopyroxenes from Mg-suite norites. Mg′ [Mg/(Mg + Fe) atomic] increases to the left.

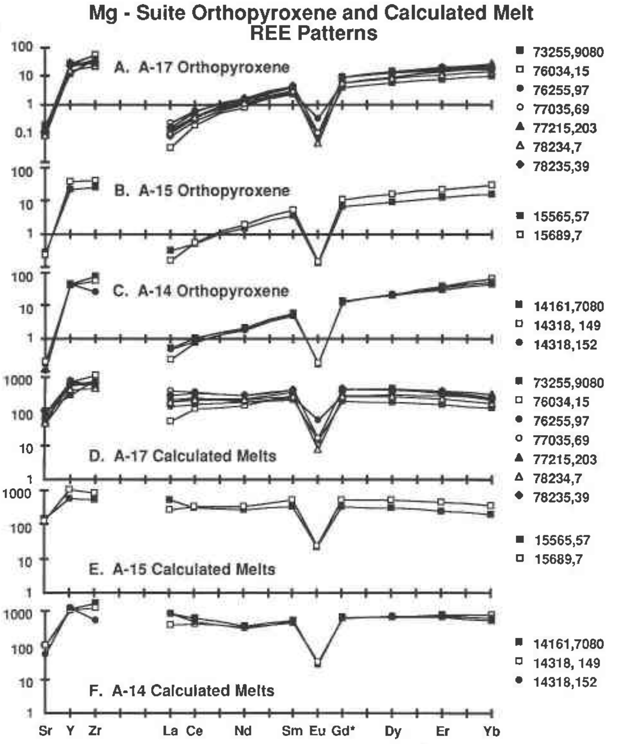
We used a screening technique to judge whether an individual electron microprobe analysis was acceptable. Only acceptable analyses were plotted in Figure 1 and used in calculating the averages reported in Table 1. The criteria we used for selecting acceptable analyses were as follows: (1) the oxide total must be between 98 and 102 wt%; (2) Si + Al must obey the relationship $1.98 < (Si + {}^{[4]}Al) < 2.02$ atoms per formula unit (apfu); (3) the sum of the cations (normalization to six O atoms) occupying the M2 and M1 sites must be between 1.98 and 2.02 apfu; and (4) Al ≥ Cr + Ti. The last criterion relates to the charge balance requirements for the minor-element coupled substitutions ${}^{[6]}Cr^{3+} + {}^{[4]}Al^{3+}$, ${}^{[6]}Al^{3+} + {}^{[4]}Al^{3+}$, ${}^{[6]}Ti^{3+} + {}^{[4]}Al^{3+}$, and ${}^{[6]}Ti^{4+} + 2{}^{[4]}Al^{3+}$.

The data base used in this paper includes ~300 EMP

TABLE 1. Average orthopyroxene EMP major and minor element analyses and SIMS trace element analyses of Mg-suite norites

	14161,7080	14318,149	14318,152	15565,57	15689,7	73255,9080	76034,15	76255,97	77035,69	77215,203	78234,7	78235,39
						Weight percent						
SiO_2	53.01	53.81	55.13	52.81	53.40	53.46	56.58	52.41	54.77	52.73	55.36	54.73
Al_2O_3	1.04	0.95	0.72	2.75	1.33	1.00	1.44	0.67	0.89	0.80	0.94	1.12
TiO_2	0.94	0.73	0.43	0.63	0.68	0.71	0.43	0.68	0.40	0.44	0.32	0.29
Cr_2O_3	0.43	0.34	0.27	0.94	0.68	0.37	0.64	0.29	0.57	0.57	0.58	0.55
MgO	24.97	25.98	28.07	28.18	26.12	25.69	32.49	22.56	27.25	23.13	28.50	28.54
FeO	16.06	14.79	13.48	11.82	14.70	15.59	7.36	20.21	13.37	18.26	12.40	12.07
MnO	0.24	0.22	0.21	0.20	0.23	0.26	0.15	0.32	0.23	0.34	0.21	0.22
CaO	1.90	1.78	1.16	1.45	1.58	1.68	1.39	1.82	1.78	1.91	1.61	1.54
Na_2O	0.01	0.02	0.01	0.01	0.02	0.01	0.00	0.01	0.00	0.01	0.01	0.01
Total	98.61	98.61	99.47	98.79	98.73	98.77	100.49	98.97	99.24	98.17	99.92	99.08
						Parts per million						
La	0.120	0.056	0.113	0.075	0.037	0.031	0.007	0.019	0.056	0.027	0.025	0.039
Ce	0.619	0.451	0.501	0.326	0.352	0.248	0.120	0.164	0.372	0.245	0.219	0.344
Nd	0.968	0.896	0.802	0.698	0.890	0.467	0.375	0.467	0.732	0.621	0.553	0.775
Sm	0.856	0.749	0.790	0.551	0.830	0.338	0.473	0.392	0.658	0.583	0.449	0.674
Eu	0.009	0.011	b.d.	0.007	0.008	0.005	b.d.	0.019	0.006	b.d.	0.003	b.d.
Dy	5.254	5.187	5.354	2.388	4.163	1.415	3.543	2.346	3.492	3.585	2.069	3.348
Er	5.113	6.210	5.621	2.043	3.709	1.269	2.933	2.345	2.886	3.176	1.812	2.624
Yb	7.558	11.200	8.948	2.721	5.041	1.718	2.993	3.365	3.611	4.484	2.333	2.931
Y	45.010	41.105	47.970	22.889	40.652	11.791	28.055	23.392	27.722	30.198	16.539	23.334
Zr	78.956	58.591	26.612	27.349	41.598	43.055	55.561	38.697	28.957	29.280	23.008	30.345
Sr	0.195	0.199	0.106	0.288	0.246	0.194	0.168	0.167	0.112	0.103	0.087	0.122

Note: b.d. = below detection.



* Gd values were extrapolated.

Fig. 2. Average normalized trace-element patterns for orthopyroxene and estimated patterns for parental melts.

analyses and ~50 SIMS analyses of orthopyroxene from 12 samples (three from Apollo 14, two from Apollo 15, and seven from Apollo 17).

RESULTS AND DISCUSSION

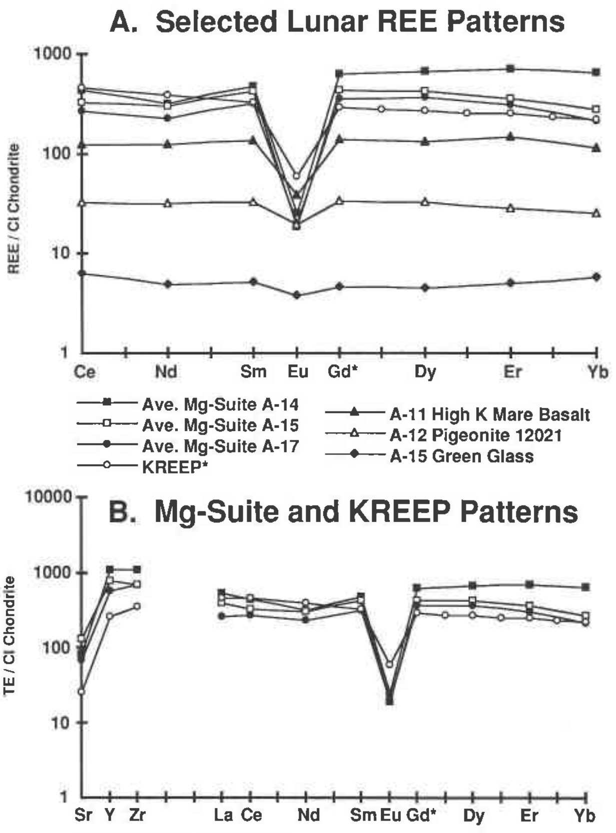
The compositions of the orthopyroxene grains that we analyzed are relatively homogeneous. Figure 1 illustrates Ca vs. Mg′ systematics for seven samples from the Apollo 17 collection. This is a rather remarkable set of samples because the range of Mg′ in orthopyroxene spans most of the known range for the Mg suite. Orthopyroxene from sample 76255,97 is the most Fe-rich. This sample is classified as a gabbronorite (James and Flohr, 1983), and the rest are classified as norites. The Mg-suite rocks have been considered quite rich in Mg relative to other lunar rock types, e.g., mare basalts and ferroan anorthosite. However, this observation was based largely on bulk analyses of mafic cumulate rocks, which are significantly more magnesian than the melts from which they crystallized. We therefore back-calculated the values of Mg′ for the melts parental to our norite suite using the Fe-Mg exchange coefficient $K_D = 0.28$ (1200 °C) for orthopyroxene of Grove and Bence (1977). The calculated values of Mg′ for the melts parental to the norites range from 0.36 for the gabbronorite 76255,97 to 0.60 (with one outlier, 76034,15, which has a calculated Mg′ = 0.69). For comparison, volcanic picritic glass beads from the Moon have values of Mg′ in the range 0.47–0.68 (Shearer and Papike, 1993). Therefore, although the melts parental to the lunar norites have values of Mg′ generally higher than most mare basalts, they are not anomalously high in Mg. Taylor et al. (1993) stated that it is difficult to reconcile the high Mg′ (>90) of the Mg-suite rocks with their high KREEP signature because the high Mg′ implies primitive melts, whereas high KREEP implies evolved parental melts. We argue that the relevant values of Mg′ are the calculated ones for the parental melts, not those measured on cumulate rocks. Also, although KREEP does involve advanced melt evolution, the estimated Mg′ for average high-K KREEP (Warren, 1989) is 0.60. Therefore, a mixture of KREEP and picritic lunar magmas poses no insurmountable problems in terms of high KREEP content and high Mg′.

Figure 2 shows both our chondrite-normalized (Anders and Grevese, 1989) REE and the Sr, Y, and Zr data for orthopyroxene in our 12 noritic samples and the estimated contents of these elements in the parental melts. Only averages are plotted from the ~50 SIMS analysis taken on the 12 samples. We used the partition coefficients (D) of McKay et al. (1991) for our calculations. The D values reported by McKay et al. (1991) for pigeonite with Wo = 5 are $D_{\mathrm{Ce}} = 0.00172$, $D_{\mathrm{Nd}} = 0.0058$, $D_{\mathrm{Sm}} = 0.011$, $D_{\mathrm{Eu\,(IW)}} = 0.0068$, $D_{\mathrm{Eu\,(IW/10)}} = 0.0050$, $D_{\mathrm{Gd}} = 0.021$, $D_{\mathrm{Yb}} = 0.087$, and $D_{\mathrm{Sr}} = 0.002$. We used $D_{\mathrm{Eu}} = 0.006$, which lies between the value taken at log f_{O_2} of iron + wüstite and iron + wüstite − 1. By using these values and a graphical relation between the trivalent REE and the ionic radius, we estimated $D_{\mathrm{La}} = 0.0006$, $D_{\mathrm{Dy}} = 0.032$, and $D_{\mathrm{Er}} = 0.050$. By similar logic we estimated $D_{\mathrm{Y}} = 0.04$. $D_{\mathrm{Zr}} = 0.05$ was taken from Johnson et al. (1990).

The REE contents of the orthopyroxenes are high and relatively uniform, reflecting very high REE concentrations of their parental melts (Table 1). The uniform nature of the REE, Zr, and Y concentrations in these pyroxenes strongly suggests that the concentrations were inherited from their parental melts and not the result of some fictive metasomatic fluid that added the trace elements to these noritic rock types after crystallization (e.g., Snyder et al., 1994a).

Figure 3 compares normalized trace-element concentrations for our estimated average Apollo 14 (A-14), A-15, and A-17 melts that were parental to our noritic rock types with several other lunar rocks. The KREEP estimate is from Warren (1989) for his average high-K KREEP. The estimated REE contents for A-14, A-15, and A-17 melts are extremely high, especially for the heavy REE. Therefore, no simple process of mixing a high-K KREEP with a picritic melt (e.g., A-15 green glass) can produce the enriched patterns we estimated. Similarly enriched REE patterns were reported by Shervais (1994) and Snyder et al. (1994b). Apparently, advanced fractionation of the Mg-suite plutons and especially plagioclase crystallization, superimposed on the addition of KREEP, must have contributed to the extreme HREE enrichments.

The KREEP component could have been added either



* Gd values were extrapolated.

Fig. 3. Estimated trace-element patterns (**A** and **B**) for melts parental to Mg-suite norites compared with other lunar rock types.

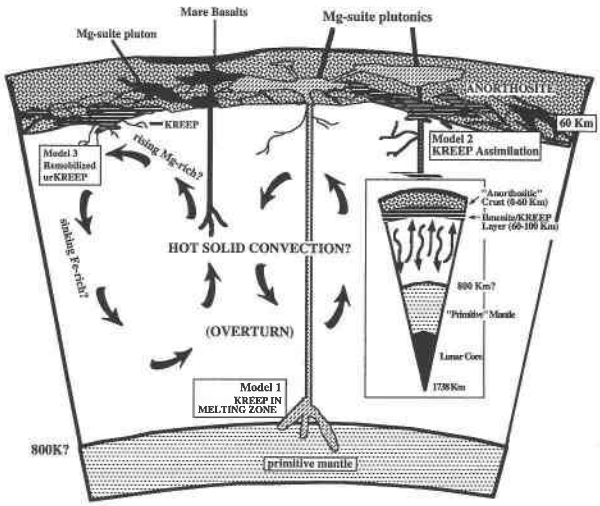

~ 4.4 - 4.3 Ga

Fig. 4. Schematic cross section of the Moon showing possible petrogenetic models for the origin of the Mg-suite rocks. Modified from a diagram provided by Graham Ryder (1994, personal communication).

to a Mg-rich (picritic?) melt deep in the Moon (model 1, Fig. 4; e.g., Shearer and Papike, 1993) or by the assimilation of KREEP (model 2, Fig. 4) at much shallower levels (60–100 km) below the anorthositic crust. The KREEP-rich sinking cumulates (Hess and Parmentier, 1994) could have had three to ten times the heat-producing elements contained in the bulk Moon and thus, potentially, provide the heat source for deep melting. The process of assimilation usually results in crystallization (AFC: DePaolo, 1981), and thus the Mg-suite magmas may have been arrested in their movement to the required shallow crustal regimes where meteorite impacts could excavate and deliver these lithologic types to the lunar surface. Model 3 is a scenario by which Ur KREEP is remobilized, possibly by decompressional melting caused by impact.

The Apollo 17 landing site provided a large variety of exciting samples, including a fascinating array of Mg-suite samples and includes the Mg-suite norites and gabbronorites reported on in this paper. Mg-suite norite 78235 is one of the largest and best-preserved noritic samples recovered by the Apollo mission. It was chipped from a glass-coated 0.5-m boulder near the base of Sculptured Hills at the Apollo 17 site. An early and complete description of this rock is provided by McCallum and Mathez (1975). Cumulus phases are plagioclase ~50% and orthopyroxene ~50%. In an early, detailed study that included three Apollo 17 Mg-suite rock types, Dymek et al. (1975) described dunite 72415, troctolite 76535, and norite 78235 and suggested that all three can be related in a fractionation sequence. Laul and Schmitt (1975) reported a detailed chemical study of dunite 72417 and pointed out that even the dunite (which presumably crystallized early) had a highly enriched KREEP content. The calculated Mg′ for the dunite parent melt is 0.65 (Roeder and Emslie, 1970). Therefore, it is highly likely that we sampled one or more Mg-rich plutons throughout much of their stratigraphic intervals at the Apollo 17 site.

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