The lherzolitic shergottite Grove Mountains 99027: Rare earth element geochemistry

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Abstract—We report here on an ion probe study of rare earth element (REE) geochemistry in the lherzolitic shergottite Grove Mountains (GRV) 99027. This meteorite shows almost identical mineralogy, petrology, and REE geochemistry to those of the lherzolitic shergottites Allan Hills (ALH) A77005, Lewis Cliff (LEW) 88516, and Yamato (Y-) 793605. REE concentrations in olivine, pyroxenes, maskelynite, merrillite, and melt glass are basically comparable to previous data obtained from ALH A77005, LEW 88516, and Y-793605. Olivine is the dominant phase in this meteorite. It is commonly enclosed by large (up to several mm) pigeonite oikocrysts. Non-poikilitic areas consist of larger olivine grains (~mm), pigeonite, augite, and maskelynite. Minor merrillite (up to 150 µm in size) is widespread in non-poikilitic regions, occurring interstitially between olivine and pyroxene grains. It is the main REE carrier in GRV 99027 and has relatively higher REEs (200–1000 × CI) than that of other lherzolitic shergottites. A REE budget calculation for GRV 99027 yields a whole rock REE pattern very similar to that of other lherzolites. It is characterized by the distinctive light REE depletion and a smooth increase from light REEs to heavy REEs. REE microdistributions in GRV 99027 strongly support the idea that all lherzolitic shergottites formed by identical igneous processes, probably from the same magma chamber on Mars.

Despite many similarities in mineralogy, petrography, and trace element geochemistry, subtle differences exist between GRV 99027 and other lherzolitic shergottites. GRV 99027 has relatively uniform mineral compositions (both major elements and REEs), implying that it suffered a higher degree of sub-solidus equilibration than the other three lherzolites. It is notable that GRV 99027 has experienced terrestrial weathering in the Antarctic environment, as its olivine and pyroxenes commonly display a light REE enrichment and a negative Ce anomaly. Caution needs to be taken in future chronological studies.

INTRODUCTION

Among the small number of described martian meteorites, roughly 70% have been classified as shergottites. These meteorites exhibit distinctive young ages (180–474 Ma) and characteristic depletion of light rare earth elements (LREEs) in whole rock compositions (except for Los Angeles). They are generally thought to have been derived from the martian crust, probably from a single young igneous province on Mars (McSween 1994). Shergottites can be further divided into two sub-groups—basalts and lherzolites. Basaltic shergottites mainly consist of pyroxene (pigeonite and augite) and maskelynite (plagioclase glass) with trace amounts of phosphates and opaques. Olivine is a minor phase and appears as a late, Fe-rich (~Fay) phase in basaltic shergottites and a Mg-rich (Fo70–90) phenocryst in olivine phric shergottites. These meteorites commonly display basaltic or diabasic textures. Representative members include Shergotty, Los Angeles, and Dar al Gani 476. Lherzolitic shergottites are cumulates consisting mostly of olivine and pigeonite with minor amounts of augite and maskelynite and trace amounts of phosphates and opaques. Olivine in lherzolites is very different from that of basaltic shergottites. It is Mg-rich (~Fay) and occurs as a cumulus
phase. This sub-group currently has five members, all recovered from Antarctica, Allan Hills A77005 (ALH A77005), Lewis Cliff 88516 (LEW 88516), Yamato-793605 (Y-793605), YA 1075, and Grove Mountains 99027 (GRV 99027) (Goodrich 2002).

GRV 99027 was collected from the ice field of the Grove Mountains, Antarctica, by the 16th Chinese Antarctic Research Expedition in 1999/2000. It weighs 9.97 g and is partially covered by fusion crust (Fig. 1). Its mineralogy, petrology, and hydrogen isotopic compositions have been reported elsewhere (Lin et al. 2002; Wang et al. 2002; Guan et al. 2003). Here, we report on an ion microprobe study of rare earth element (REE) geochemistry in this new lherzolitic shergottite.

EXPERIMENTAL METHODS

The sample used in this study is a one-inch polished thin section provided by Chinese National Antarctic Research Institute. The section was first examined with an optical transmission and reflectance microscope and a JEOL-845 scanning electron microscope (SEM) equipped with an IXRF energy-dispersive (EDS) detector system. Mineral chemistry was determined with an electron microprobe (JEOL JXA-8800M) at Nanjing University. Accelerating voltage was 15 keV with a 20 nA beam current. Both synthetic (NBS) and natural mineral standards were used, and matrix corrections were based on ZAF procedures.

The REE analyses were carried out with a Cameca-6f ion microprobe at Arizona State University, using the energy filtering technique described by Zinner and Crozaz (1986). An O⁻ primary ion beam of 1–4 nA was accelerated to −12.5 KeV. Secondary ions, offset from a nominal +10 KeV accelerating voltage by −100 eV, were collected in peak-jumping mode with an electron multiplier. To increase the transmission of the secondary ion signals, an imaged field of ~75 µm was used for REE measurements. The total counting time varied from ~30 min to ~4 hr depending the phases analyzed. Silicon and calcium were used as the reference elements for silicates and phosphates, respectively. NBS-610, NBS-612, synthetic titanium-pyroxene glass, and Durango apatite standards were measured periodically to account for any variation of ionization efficiencies caused by minor changes of operating conditions.

PETROGRAPHY AND MINERALOGY

Like other lherzolitic shergottites (Harvey et al. 1993; Ikeda 1997; Mikouchi and Miyamoto 2000), GRV 99027 contains three distinct petrographic units: poikilitic, non-poikilitic, and glassy to partially crystalline melt pocket (Fig. 2). In poikilitic areas, olivine occurs as round or euhedral crystals (0.1–0.5 mm) enclosed by large (up to several mm) oikocrystals of pigeonite (Fig. 3). Some of the oikocrysts have irregular exsolved augite rims. Maskelynite is
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rare and occurs only as a small patch in one poikilitic region. Non-poikilitic areas consist of larger olivine grains (~mm), pigeonite, augite, and maskelynite. Phosphates (mainly merrillite) are widespread in these areas. They usually occur interstitially between olivine and pyroxenes. Their size ranges from 10 to 150 µm (Fig. 4). On the left edge of the thin section, there are some shock melt pockets (Fig. 5). The pockets consist predominantly of quenched olivine and melt glass. Needle-shaped, crypto-crystalline materials are also commonly set in melt glasses.

Individual mineral grains of olivine, pyroxenes, maskelynite, and merrillite in GRV 99027 have essentially homogeneous chemical compositions. Inter-grain variations are generally small and comparable to intra-grain variations. Olivine in poikilitic areas is slightly more magnesian (Fo73 to Fo76) than that (Fo70 to Fo73) in non-poikilitic regions. The quenched olivine in shock melt pockets often displays strong chemical zoning from a magnesian core (Fo72) to a ferroan rim (Fo66). Unlike other lherzolitic shergottites, pigeonite in GRV 99027 shows no apparent major element zoning. However, it displays a systematically compositional variation. Pigeonite in non-poikilitic areas is more Ca- and Fe-rich than that in poikilitic areas. Augite in GRV 99027 has a similar chemical composition as other lherzolites. It ranges from En47Fs18Wo37 to En40Fs14Wo37, compared to a range from En53Fs15Wo32 to En48Fs14Wo38 in ALH A77005, from En52Fs17Wo31 to

Fig. 2. Backscattered electron image of the GRV 99027 thin section. The gray grains are pyroxenes enclosing light gray olivine crystals. Maskelynite (dark gray) occurs interstitially between olivine and pyroxene in non-poikilitic areas. Melt glass is present on the left edge of the thin section.

Fig. 3. Transmitted light photograph of a poikilitic area. Euhedral to subeuhedral olivine grains (gray) are enclosed by pyroxene (light gray). The field of view is 2.15 mm.

En47Fs16Wo37 in LEW 88516, and from En53Fs16Wo32 to En49Fs14Wo37 in Y-793605 (Mikouchi and Miyamoto 2000). Maskelynite shows a considerable inter-grain variation (from An44Ab25Or1 to An57Ab23Or10), in agreement with that of other lherzolites. Mikouchi and Miyamoto (2000) reported that the chemical composition of maskelynite ranges from

En47Fs16Wo37 in LEW 88516, and from En53Fs16Wo32 to En49Fs14Wo37 in Y-793605 (Mikouchi and Miyamoto 2000). Maskelynite shows a considerable inter-grain variation (from An44Ab25Or1 to An57Ab23Or10), in agreement with that of other lherzolites. Mikouchi and Miyamoto (2000) reported that the chemical composition of maskelynite ranges from
An48Ab49Or3 to An58Ab41Or1 in ALH A77005, from An48Ab49Or3 to An58Ab41Or1 in LEW 88516, and from An45Ab52Or3 to An55Ab44Or1 in Y-793605. Table 1 lists some representative mineral compositions of GRV 99027.

RARE EARTH ELEMENT DISTRIBUTIONS

REE analyses were carried out in olivine, pyroxene, maskelynite, melt glass, and merrillite of GRV 99027. One olivine, six pyroxene, one maskelynite, one melt glass, and five merrillite grains were measured. A total of 20 ion microprobe analyses were performed (1 in olivine, 8 in pyroxene, 2 in maskelynite, 2 in glass, 7 in merrillite). Representative REE abundances are reported in Table 2.

The olivine in the poikilitic area is depleted in REEs with a V-shaped pattern (Fig. 6a). CI chondrite-normalized REE abundances in this mineral decrease from La (0.35 × CI) to Sm (~0.03 × CI) and then gradually increase to Lu (~0.25 × CI). A negative Ce anomaly (Ce/Ce* ~0.4, where Ce* is the value interpolated between CI normalized abundances of La and Pr) is clearly present. Within the analytical errors, GRV 99027 olivine has essentially the same heavy rare earth element (HREE) abundances as that of ALH A77005, LEW 88516 and Y-793605. But GRV 99027 olivine displays a LREE enrichment and a negative Ce anomaly. This is an indication of terrestrial weathering.

Six pyroxene grains from both poikilitic and non-poikilitic areas were analyzed. As expected, pigeonite shows an HREE-enriched pattern. CI-normalized REE abundances increase gradually from Pr to Lu. However, the patterns display varying degrees of an upturn at La and a negative Ce anomaly (Ce/Ce* 0.3–0.5) (Fig. 6b). Eu anomalies are negligible. A V-shaped REE pattern similar to that of olivine is also observed in this mineral (3 out of 5 analyses). Augite appears to be affected by terrestrial weathering as well. Pigeonite is generally depleted in REEs relative to CI chondrites (0.03–1 × CI). Augite has higher REEs than pigeonite. REE patterns for this mineral are similar to that of pigeonite but have a smaller slope. From Ce to Sm, CI-normalized REEs increase gradually. From Gd to Lu, the pattern is almost flat. There is also an upturn at La and a small negative Eu anomaly (Fig. 6c). In general, REEs are essentially homogeneous within an individual pyroxene grain but show small inter-grain variations (by a factor of 2 to 5). In particular, pyroxene in non-poikilitic regions has higher REEs than those in poikilitic areas. REE abundances and patterns of pyroxenes in GRV 99027 are comparable with those of other lherzolitic shergottites (Harvey et al. 1993; Wadhwa et al. 1994; Wadhwa et al. 1999).

Maskelynite is generally depleted in REEs (except for Eu) with a LREE-enriched pattern and a positive Eu anomaly (Fig. 6d). GRV 99027 maskelynite has relatively higher REEs (La ~0.8 × CI) than those of other lherzolitic shergottites (La ~0.3 × CI). Shocked melt glass in GRV 99027 usually contains crypto-crystalline olivine and pyroxene. REE analyses were made in a homogeneous crystallite-free area. The glass has a REE pattern parallel to that of ALH A77005 whole rock but with elevated REE abundances (Fig. 6e), indicating localized partial melting of bulk sample. Similar results were previously observed in melt glasses of LEW 88516 and Y-793605,
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although they have relatively lower REEs than that of GRV 99027 (Harvey et al. 1993; Wadhwa et al. 1999).

Seven measurements were made in five merrillite grains. Three are in one grain, and there is one each in the other four grains. REEs are highly homogeneous within the merrillite grain and among the grains studied. Merrillite has the highest concentrations of REEs (200–1000 × CI). The REE pattern for this mineral is HREE-enriched with a negative Eu anomaly (Fig. 6f). This pattern is generally similar to that of lherzolitic shergottite whole rocks (except for Eu). It is noted that GRV 99027 merrillite has higher REEs than those of ALH A77005 and LEW 88516, especially the HREEs (Yb ~1000 × CI versus ~200 × CI) (Wadhwa et al 1994).

DISCUSSION AND CONCLUSIONS

Several lines of evidence suggest that lherzolitic shergottites were derived by the same igneous processes on Mars. These meteorites have an essentially identical mineral assemblage, consisting predominantly of coarse-grained olivine and poikilitic pigeonite with minor augite and maskelynite and trace phosphates and opaques (McSween 1994). Individual mineral chemistry is very similar among all lherzolitic shergottites and largely overlaps within the range of compositional variations (Ikeda 1997; Treiman et al. 1994; Wang et al. 2002; Yanai 2002; this study). It is also noted that pyroxene and maskelynite in ALH A77005, LEW 88516, and Y-793605 display similar major and minor element zoning patterns (Mikouchi and Miyamoto 2000). Petrographically, these rocks commonly contain three distinct lithologies: poikilitic, non-poikilitic, and glassy to partially crystalline melt pocket (Harvey et al. 1993; Ikeda 1994; Mikouchi and Miyamoto 2000; this study). By bulk compositions, ALH A77005, LEW 88516, and Y-7 93605 have the same REE pattern, characterized by the distinctive LREE depletion (Ma et al. 1981; Wänke et al. 1986; Dreibus et al. 1992; Gleason et al. 1997; Ebihara et al. 1997; Warren and Kallemeyn 1997). Lherzolitic shergottites appear to be the youngest of any known group of meteorites. Jagoutz (1989) obtained a Rb-Sr age of 156 ± 6 Ma and a Sm-Nd age of 135 ± 40 Ma.
for ALH A77005. Borg et al. (2002) reported a Rb-Sr age of 185 ± 11 Ma and a Sm-Nd age of 173 ± 6 Ma for ALH A77005 and 183 ± 10 Ma and 166 ± 16 for LEW 88516, respectively. Morikawa et al. (2001) obtained a Rb-Sr age of 173 ± 14 Ma for Y-793605. The Sm-Nd ages of lherzolitic shergottites are basically concordant with their respective Rb-Sr ages, which, in turn, agree well with the U-Pb systematics as determined by Chen and Wasserburg (1986; 1993) and Misawa et al. (1997). In these meteorites, they found that there was a lead loss event at 170–200 Ma. Despite these similarities among lherzolitic shergottites, some differences were also observed. In particular, their

Fig. 6 Representative REE concentrations in olivine, pyroxenes, maskelynite, melt glass, and merrillite of GRV 99027 and comparison with previous data of other lherzolites (Ma et al. 1981; Harvey et al. 1993; Wadhawa et al. 1994, 1999).
initial Sr and Nd isotopic compositions are analytically distinct, suggesting that these meteorites were derived from different sources (Jagoutz 1989; Borg et al. 2002).

These observations point to a scenario as illustrated by Harvey et al. (1993). Olivine, chromite, and pigeonite initially crystallized from the parent melt of lherzolitic shergottites, which was generated from a LREE-depleted source in the Mars mantle. As fractional crystallization continued, some early formed pigeonite crystals grew large and enclosed olivine and chromite and developed a poikilitic texture. Accumulation and separation of cumulus phases from the parent melt would lead to the formation of poikilitic and non-poikilitic lithologies. As the process proceeded, augite and plagioclase began to crystallize from the magma. This was followed by more evolved phases such as phosphates and ilmenite. These phases tended to fill in the interstices of early formed cumulus phases (olivine and pigeonite). Finally, sub-solidus re-equilibration of major elements in the cumulus phases occurred and produced exsolved augite rims on pigeonite oikocrysts.

In this study, we analyzed REE microdistributions in individual phases of GRV 99027. Our results are basically compatible with previous data obtained from ALH A77005, LEW 88516, and Y-793605 (Harvey et al. 1993; Lundberg et al. 1990; Wadhwa et al. 1999). REE microdistributions in GRV 99027 and in other lherzolitic shergottites strongly support the crystallization history proposed above. Although the REE zoning was not observed in GRV 99027, it is notable that pyroxenes in its non-poikilitic areas generally have higher REE abundances than the ones in poikilitic regions. As expected, the late-stage phase merrillite usually occurs in non-poikilitic regions and contains the highest REE concentrations. Its REE pattern is characterized by a LREE depletion and is essentially parallel to the whole rock REE pattern of lherzolitic shergottites.

In principle, we can calculate the bulk REE compositions of GRV 99027 using appropriate modal abundances and the average REE concentrations of individual mineral phases. Instead of using the modal abundance determined on a specific thin section, we would like to use the average results of all previously reported data for lherzolitic shergottites. Because these rocks are highly heterogeneous in mineral distributions, especially for minor phases, the modal abundance determined on a given cross section varies widely and, therefore, is not representative. But, the average results of a large number of analyses should be close to the real values if we assume that all lherzolitic shergottites were derived from a single petrologic unit on Mars. Overall, the dominant phase in these meteorites is olivine, followed by pyroxenes (Ma et al. 1981; Mason 1981; Treiman et al. 1994; Wadhwa et al. 1994; Gleason et al. 1997; Ikeda 1997; Kojima et al. 1997; Mikouchi and Miyamoto 1997). The large variations reported by different workers reflect the sample heterogeneity and analytical uncertainties. For major phases like olivine and pyroxenes, the variation contributed from analytical methods is relatively small compared to that from the sampling. The average of all reported results will generally represent the mineral modal abundance in lherzolitic shergottites. They are olivine (50%), pyroxene (38%), maskelynite (9%), and melt glass (11%) (Ma et al. 1981; Mason 1981; Treiman et al. 1994; Wadhwa et al. 1994; Gleason et al. 1997; Ikeda et al. 1997; Kojima et al. 1997; Mikouchi and Miyamoto 1997). But, for accessory minerals such as merrillite, the analytical uncertainty may weigh as equally as the sample heterogeneity because these minerals are usually very small (µm-sized) and difficult to detect during analyses. In the case of merrillite, it becomes even more critical, as this mineral is the major REE carrier in lherzolitic shergottites and largely controls their REE budgets.

With the average REE concentrations in mineral phases of GRV 99027, we performed three simple mixing calculations for GRV 99027 using the average modal proportions of olivine, pyroxene, maskelynite, and melt glass from literatures and 0.1%, 0.3%, and 0.5%, respectively, for merrillite. The results are shown in Fig. 7 along with bulk analyses of ALH A77005 (Ma et al. 1981), LEW 88516 (Gleason et al. 1997), and Y-793605 (Ebihara et al. 1997). The calculation with 0.1% merrillite yields a whole rock pattern for GRV 99027 that has low REEs and a positive Eu anomaly relative to those of ALH A77005 and LEW 88516. The calculation with 0.5% merrillite generates an opposite result. A modal abundance of 0.3% merrillite in GRV 99027 will create a whole rock REE pattern essentially identical to those of ALH A77005 and LEW 88516. From the calculation, we can see that the estimated REE budget of GRV 99027 is largely controlled by the amount of merrillite. Although the absolute REE concentrations of GRV 99027 are difficult to determine in this study, its whole rock REE pattern appears to be very similar to that of other lherzolitic shergottites.

It is notable that olivine and pyroxenes in GRV 99027 frequently show a LREE enrichment with a negative Ce anomaly. This has been a common phenomenon for Antarctic meteorites (Floss and Crozaz 1991; Harvey et al. 1993; Hsu and Crozaz 1996; Wadhwa et al. 1994). It reflects the terrestrial weathering in the Antarctic environment. From this work and previous ones, mineral phases such as olivine and pyroxenes that originally contained very low REEs, especially LREEs, are most severely affected by weathering. Minerals with high REE contents like merrillite are essentially unaltered. In addition, REE mobilization was found only over limited (i.e., µm- to mm-scale) distances (Wadhwa et al. 1994). Therefore, the bulk REE concentrations of GRV 99027 remain largely unaffected.

Because of the addition of LREEs from alteration, REE concentrations of olivine and pyroxenes are not suitable for calculating the parent melt composition of GRV 99027 by inverting. Caution is also urged for future studies of Sm-Nd systematics in this meteorite.

Each olivine grain in poikilitic areas of Y-793605 shows chemical zoning of the major elements Mg and Fe (Mikouchi
and Miyamoto 2000); while in LEW 88516, some olivines exhibit Fe/Mg zoning from core (high Mg) to rim (low Mg) (Harvey et al. 1993). ALH A77005 olivine has a much restricted range of compositions (Fo$_{69}$ to Fo$_{73}$) and shows no major element zoning (Mikouchi and Miyamoto 2000; Treiman et al. 1994). Pigeonite in these three lherzolitic shergottites commonly displays major element zoning and has an almost identical compositional range (Mikouchi and Miyamoto 2000). Maskelynite also shows minor element zoning of Fe, Mg, and K. The zoning in ALH A77005 is smoother than that in Y-793605, and LEW 88516 is intermediate between the two (Mikouchi and Miyamoto 2000). Mg and Fe cations in olivine have relatively high diffusion rates under sub-solidus conditions (Freer 1981). Pigeonite is more resistant to thermal metamorphism than olivine. And maskelynite is intermediate between olivine and pigeonite. The homogenization of ALH A77005 olivine indicates that this meteorite suffered more intense thermal metamorphism than LEW 88516 and Y-793605. The major and minor element zoning preserved in pigeonite and maskelynite further suggests different degrees of re-equilibration experienced by these meteorites (ALH A77005 >LEW 88516 >Y-793605) (Mikouchi and Miyamoto 2000). In GRV 99027, olivine, pyroxenes, and maskelynite show no chemical zoning, implying that it suffered a higher degree of sub-solidus equilibration than the other three lherzolites.

In conclusion, GRV 99027 shares many similarities in mineralogy, petrology, and geochemistry with ALH A77005, LEW 88516, and Y-793605. REE microdistributions in GRV 99027 are essentially identical to those of other lherzolitic shergottites. The estimated bulk REE pattern for this meteorite is compatible with that of ALH A77005, LEW 88516, and Y-793605. It follows that GRV 99027 could also have formed by progressive fractional crystallization within a closed system from which other lherzolitic shergottites were derived. These meteorites experienced different degrees of sub-solidus re-equilibration after their formation (GRV 99027 >ALH A77005 >LEW 88516 >Y-793605). And, GRV 99027 appears to have suffered extensive terrestrial weathering during its long residence in the Antarctic environment.

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