Bulk chemical composition of lherzolitic shergottite Grove Mountains 99027 —Constraints on the mantle of Mars

Yangting LIN1*, Liang QI2, Guigin WANG3, and Lin XU4

¹Key Laboratory of the Earth's Deep Interior, Institute of Geology and Geophysics, Chinese Academy of Sciences, Beijing 100029, China ²State Key Lab of Ore Deposit Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang 550002, China ³Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou, China ⁴National Astronomic Observatory, Chinese Academy of Sciences, Beijing, China *Corresponding author. E-mail: linyt@mail.igcas.ac.cn

(Received 31 December 2006; revision accepted 05 February 2008)

Abstract—We report the concentration of 50 elements, including rare earth elements (REEs) and platinum group elements (PGEs) in bulk samples of the Grove Mountains (GRV) 99027 lherzolitic shergottite. The abundances of REEs are distinctly lower than those of Allan Hills (ALH) A77005 and other lherzolitic shergottites, indicating that GRV 99027 is not paired with them. It may, nevertheless, sample the same igneous unit as the others (Lin et al. 2005b; Wang and Chen 2006). The CInormalized elemental pattern of GRV 99027 reveals low (0.004–0.008 × CI) and unfractionated PGEs (except for Pd of 0.018 × CI) without depletion of W or Ga relative to lithophile element trends. Fractionation between siderophile and lithophile elements become less pronounced with increase of volatility, except for high abundances of Ni and Co. These characteristics are probably representative of the mantle of Mars, which is consistent with previous work that the Martian mantle formed in a deep magma ocean followed by a later accretion of chondritic materials.

INTRODUCTION

Lherzolitic shergottites are a small subgroup of shergottites (6 out of 48 samples). Grove Mountains (GRV) 99027 was the fourth lherzolitic shergottite reported (Lin et al. 2002, 2003). The first three Allan Hills (ALH) A77005, Yamato (Y-) 793605, and Lewis Cliff (LEW) 88516 were known to be very similar in petrography and mineral chemistry (McSween et al. 1979; Harvey et al. 1993; Treiman et al. 1994; Ikeda 1997; Mikouchi and Miyamoto 1997, 2000), trace element compositions of minerals (Lundberg et al. 1990; Wadhwa et al. 1999), bulk compositions (Warren and Kallemeyn 1997), and ejection ages (Nyquist et al. 2001), suggesting a paired ejection event. The close relationship of these meteorites was also confirmed by their platinum group elements (PGEs), as summarized by Jones et al. (2003). Only initial Sr and Nd isotopic compositions of ALHA77005 and LEW 88516 require derivation from unique sources (Borg et al. 2002). Recently, two other lherzolitic shergottites, Northwest Africa (NWA) 1950 and GRV 020090, have been reported. NWA 1950 was probably ejected together with ALHA77005 and others (Gillet et al. 2005), whereas GRV 020090 has a distinctly low abundance of olivine (29 vol%)

with its silicates being high in FeO content (e.g., Fa_{30-42} of olivine and Fs_{26-31} of low Ca pyroxene) (Miao et al. 2004).

Grove Mountains 99027 is a small (9.97 g) achondrite with partial intact fusion crust. To clarify the formation and evolution history of this new Martian meteorite, and to understand its genetic relationship to the other lherzolitic shergottites, detailed petrography, major and trace element microanalysis of minerals, and H isotopic compositions of GRV 99027 were carried out (Hsu et al. 2004; Lin et al. 2005b; Wang and Chen 2006). These studies showed that texturally and mineralogically GRV 99027 is in general indistinguishable from ALHA77005, Y-793605 and LEW 88516. GRV 99027 has two textural regions: poikilitic and non-poikilitic areas. The poikilitic areas consist mainly of pigeonite oikocrysts that contain rounded olivine and euhedral chromite grains. The non-poikilitic areas are composed of olivine, pigeonite, augite, and plagioclase with small amounts of chromite, ilmenite, merrillite, apatite, and trace amount of sulfides (pyrrhotite and pentlandite). Olivine and pigeonite in the poikilitic areas are FeO-poor (Fa_{26.8+1.3}, $Fs_{21.3\pm1}$) relative to those in the non-poikilitic areas $(Fa_{29.3\pm0.8},$ Fs_{24.5+1.3}) (Lin et al. 2005b), similar to ALHA77005, LEW 88516 and Y-793605 (Harvey et al. 1993; Treiman et al. 1994;

Ikeda 1997). Concentrations of REEs in pyroxenes, plagioclase, and merrillite are within the ranges of ALHA77005 (Lin et al. 2005b). A distinct difference is severe post-shock thermal metamorphism of GRV 99027, as indicated by complete re-crystallization of maskelynite and homogeneity of the minerals (Lin et al. 2005b; Wang and Chen 2006). In this study, we analyzed bulk concentrations of 50 elements in GRV 99027, including REEs and PGEs, to clarify its genetic relationship to the other lherzolitic shergottites, and to constrain composition of the mantle of Mars. Preliminary results were reported by Lin et al. (2005a).

SAMPLES AND EXPERIMENTS

A 2.34 g sample of GRV 99027 was allocated for a cooperative study. The sample was first gently crushed to mm-size with an agate mortar and pestle, and the pieces with adhered fusion crust were picked out by hand under stereomicroscope. 1.6 g of the fusion crust free sample obtained was ground with the mortar and pestle and sieved to <150 μ m. An aliquot of 0.82 g of the sample was then ground to < 75 μ m and used as the bulk sample for chemical analysis of GRV 99027. 39.6 mg of the bulk sample and 39.2 mg of another fine-grained (<50 μ m) fraction were analyzed for major, REE, and other trace elements. Platinum group elements (PGEs) were determined using a separate 101.2 mg aliquot of the bulk sample.

The sample digestion procedures and the instrumental measurements for major, REE and other trace elements are the same as described by Wang and Lin (2007). The bulk sample and the fine-grained fraction were dissolved with 0.6 ml of concentrated HF, 0.3 ml of 6 M HCl and 5 drops of concentrated HClO₄ in screw-capped Teflon vessels. The vessels were heated to 120 °C and maintained at this temperature for 3 days on a hotplate, and then sealed in stainless steel bombs that were heated at 190 °C for 24 h in an oven. After cooling, the solutions were evaporated to dryness, re-dissolved in 3 ml of 4 M HNO₃ and diluted to 20 ml of 3% HNO₃. Five ml of the aliquots were analyzed for major elements using inductively coupled plasma atomic emission spectrometry (ICP-AES). The remaining 15 ml solutions were diluted to 60 ml of 3% HNO₃, with 10 ppb Rh as internal standard. The final solutions were analyzed for REE and other trace elements using the inductively coupled plasma mass spectrometry (ICP-MS). The ICP-AES was a VISTA-PRO, and the ICP-MS was a Perkin-Elmer Sciex ELAN 6000, both in the Key Lab of Isotope Geochronology and Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences. The standards used were various natural igneous rocks from the National Research Center for Certified Reference Materials of China (GBW) (GSR-1 granite, GSR-15 plagio-amphibolite and GSR-17 kimberlite), U.S. Geological Survey (USGS) (W-2 diabase and AGV-1 andesite), Canadian Certified Reference Materials Project

(CCRMP) (UM-2 ultramafic rock, UMT-1 ultramafic ore tailings, UB-N serpentinite and MRG-1 gabbro), the Council for Mineral Technology, South Africa, National Bureau of Standards (MINTEK) (SARM-4 norite). In addition, pure solutions of Ga and Zn were used as standards for both elements, because some of the above rock standards contain high P or Ti that could result in interference of ⁷¹Ga from ³¹P⁴⁰Ar⁺, and ⁶⁶Zn from ⁵⁰Ti¹⁶O⁺. A powder sample of the Allende (split 8) carbonaceous chondrite (CV3) was also analyzed as a reference material, and the results are in good agreement with the literature values (Table 1) except for Cu which shows a large deviation (>20%).

The analysis of PGEs followed the Carius tube digestion technique combined with ICP-MS (VG PQ ExCell). The bulk sample of 101.2 mg and appropriate amounts of enriched isotope spike solution containing ¹⁹⁴Pt, ¹⁰⁵Pd, ¹⁰¹Ru, ¹⁹³Ir, and ¹⁹⁰Os were digested with 5 ml of aqua regia in a 20 ml Carius tube. The Carius tube was placed in a sealed stainless steel high-pressure autoclave and filled with water to balance the internal pressure and to avoid possible explosion. After digestion at 320 °C for 15 hours, the Carius tube was cooled and the content transferred to a 15 ml centrifuge tube. After centrifuging, the supernatant was used for Os distillation, the OsO₄ vapor was trapped with 5 ml of 8% HCl solution cooled in an ice-water bath. The remainder of the solution was used to pre-concentrate PGEs by Te coprecipitation. The precipitate was dissolved with aqua regia and then passed through a mixed ion exchange column containing a Dowex 50 WX 8 cation exchange resin and a P507 extraction chromatograph resin to remove the main interfering elements, including Cu, Ni, Zr, and Hf, as described by Qi et al. (2004). The eluant was evaporated to 1 ml and then used for ICP-MS measurement. Platinum, Pd, Ru, Ir, and Os were measured by isotope dilution, while ¹⁹⁴Pt was used as the internal standard to calculate the abundance of the mono-isotope element Rh as described by Qi et al. (2004). The total procedural blanks were lower than 0.002 ng/g for Os; 0.003 ng/g for Ru, Rh and Ir, and 0.020 ng/g for Pd and Pt. Analytical results for the standard reference material, WPR-1 (peridotite), are shown in Table 2. The results are in excellent agreement with the certified values.

RESULTS

The bulk compositions of GRV 99027 are summarized in Tables 1 and 2. Figure 1 shows a smooth and hump-shaped REE pattern of GRV 99027, with CI-normalized concentrations increasing from La (0.84 × CI) to Dy (3 × CI), and then decreasing to Lu (2.2 × CI). It has no Ce or Eu anomalies. The bulk REE pattern of GRV 99027 is nearly parallel to those of other lherzolitic shergottites (e.g., ALHA77005, Y-793605 and LEW 88516) except for variations in Ce and probably Eu from literature values. However, bulk GRV 99027 has a distinctly lower total REE

Table 1. Bulk compositions of GRV 99027 (µg/g, unless otherwise noted).

| Weight | GRV bulk | RSD% | GRV < 350μm | RSD% | Allende-8 | RSD% | | ende ² |
|--------|----------|------|-------------|------|-----------|------|-----------|-------------------|
| (mg) | 39.6 | 1 | 39.2 | 2 | 39.2 | 3 | Certified | Other |
| Si%1 | 20.2 | | 20.0 | | 17.3 | | 17.5 | 17.5 |
| Al% | 1.09 | 1 | 1.29 | 2 | 1.75 | 2 | 1.74 | 1.74 |
| Ca% | 2.46 | 1 | 2.58 | 1 | 1.85 | 2 | 1.85 | 1.84 |
| Fe% | 14.9 | 1 | 14.8 | 2 | 23.6 | 2 | 23.6 | 23.6 |
| Mg% | 17.9 | 1 | 17.4 | 1 | 15.2 | 2 | 14.9 | 14.8 |
| Ti | 2020 | 1 | 2380 | 2 | 886 | 2 | 900 | 900 |
| Na | 3120 | 3 | 3200 | 4 | 3510 | 5 | 3400 | 3400 |
| P | 1080 | 4 | 2280 | 2 | 1040 | 3 | 1100 | 1050 |
| Ni | 314 | 4 | 341 | 5 | 15200 | 3 | 14200 | 14200 |
| K | 156 | 11 | 148 | 2 | 203 | 3 | 268 | 288 |
| Sc | 21.4 | 4 | 20.5 | 2 | 10.2 | 2 | 12.7 | 11 |
| V | 122 | 4 | 156 | 4 | 72.4 | 2 | 93 | 85 |
| Cr | 7200 | 4 | 11400 | 2 | 3670 | 2 | 3600 | 3630 |
| Mn | 3530 | 6 | 3420 | 3 | 1380 | 3 | 1500 | 1470 |
| Co | 65.6 | 5 | 66.3 | 4 | 700 | 2 | 610 | 557 |
| Cu | 4.24 | 3 | 5.49 | 4 | 99.4 | 3 | 130 | 135 |
| Zn | 59 | | 97 | | 129 | | 120 | 114 |
| Ga | 7.4 | | 13 | | 7.0 | | 5.9 | 7 |
| Ge | 0.606 | 6 | 0.629 | 8 | 15.7 | 3 | 17 | 11 |
| Rb | 0.717 | 5 | 0.729 | 4 | 1.12 | 4 | 1.1 | 1.2 |
| Cs | 0.035 | 7 | 0.041 | 5 | 0.083 | 8 | 0.082 | 0.096 |
| Ba | 3.66 | 2 | 4.55 | 2 | 5.19 | 2 | 4.8 | 4 |
| Sr | 7.5 | 5 | 9.53 | 2 | 12.6 | 3 | 13 | 12 |
| Zr | 15.0 | 4 | 15.8 | 2 | 7.23 | 3 | 5.9 | 9 |
| Nb | 0.455 | 3 | 0.576 | 3 | 0.524 | 3 | 0.7 | 0.6 |
| W | 0.455 | 4 | 0.162 | 6 | 0.156 | 6 | 0.15 | 0.2 |
| Hf | 0.438 | 3 | 0.496 | 3 | 0.187 | 9 | 0.19 | 0.21 |
| Pb | 0.327 | 4 | 0.07 | 13 | 1.00 | 4 | 1.1 | 1.4 |
| Th | 0.031 | 5 | 0.067 | 6 | 0.065 | 6 | 0.062 | 0.063 |
| U | 0.009 | 14 | 0.015 | 14 | 0.014 | 14 | 0.015 | 0.016 |
| Y | 4.77 | 1 | 8.75 | 2 | 2.86 | 2 | 3.1 | 3.1 |
| La | 0.196 | 6 | 0.436 | 3 | 0.516 | 3 | 0.44 | 0.52 |
| Ce | 0.499 | 2 | 1.13 | 2 | 1.33 | 3 | 1.25 | 1.33 |
| Pr | 0.076 | 5 | 0.171 | 4 | 0.207 | 4 | 0.2 | 0.21 |
| Nd | 0.452 | 6 | 1.02 | 3 | 1.01 | 5 | 0.91 | 0.99 |
| Sm | 0.254 | 12 | 0.571 | 4 | 0.306 | 8 | 0.29 | 0.34 |
| Eu | 0.138 | 6 | 0.255 | 4 | 0.113 | 7 | 0.107 | 0.11 |
| Gd | 0.568 | 3 | 1.16 | 3 | 0.401 | 8 | 0.43 | 0.42 |
| Tb | 0.105 | 6 | 0.206 | 3 | 0.071 | 6 | 0.074 | 0.081 |
| Dy | 0.731 | 5 | 1.37 | 4 | 0.475 | 4 | 0.42 | 0.42 |
| Но | 0.155 | 7 | 0.29 | 2 | 0.103 | 5 | 0.12 | 0.1 |
| Er | 0.433 | 6 | 0.768 | 3 | 0.283 | 4 | 0.31 | 0.29 |
| Tm | 0.06 | 7 | 0.113 | 7 | 0.054 | 6 | 0.049 | 0.064 |
| Yb | 0.366 | 4 | 0.662 | 3 | 0.313 | 5 | 0.32 | 0.3 |
| Lu | 0.053 | 6 | 0.09 | 5 | 0.045 | 6 | 0.058 | 0.052 |

RSD: Relative standard deviation of counting.

content as compared to the other lherzolitic shergottites. The only possible exception to this is Y-793605. Ebihara et al. (1997) reported REEs for Y-793605 that are even lower than in GRV 99027 (Fig. 1). However, their results could be due to an unrepresentative sample, since analyses of Y-793605 by other groups (e.g., Warren and Kallemeyn 1997) revealed no differences from ALHA77005 and LEW 88516.

In comparison with the bulk sample, the fine-grained fraction of GRV 99027 has clearly higher concentrations of REEs, but its REE pattern is nearly parallel to that of the bulk sample (Fig. 1). In addition, the fine-grained fraction contains higher Al, Cr, P, Y, U, and Th in comparison with the bulk sample (Table 1).

Figure 2 shows the CI-normalized abundances of

¹Calculated based on mass balance for a total of 100%.

²The certified values of Allende after Mason (1979) and other literature values after Jarosewich et al. (1987).

Table 2. Platinum group elements of GRV 99027 (ng/g).

| | <u> </u> | | (0 0 | | | | |
|---------------|----------|----------------|----------------|----------------|--------------|----------------|--------------|
| | Weight | | | | | | |
| | (mg) | Os | Ir | Ru | Pt | Rh | Pd |
| GRV bulk | 101.2 | 2.5 | 2.4 | 3.0 | 8.1 | 0.75 | 10 |
| RSD% | | 4 | 13 | 6 | 5 | 13 | 1 |
| WPR-1 \pm S | 5000 | 13.5 ± 0.5 | 13.2 ± 1.2 | 23.5 ± 1.9 | 272 ± 13 | 12.7 ± 0.7 | 225 ± 17 |
| Certified | | 13 | 13.5 | 22 | 285 | 13.4 | 235 |

RSD: Relative standard deviation of counting; S: Standard deviation (n = 3).

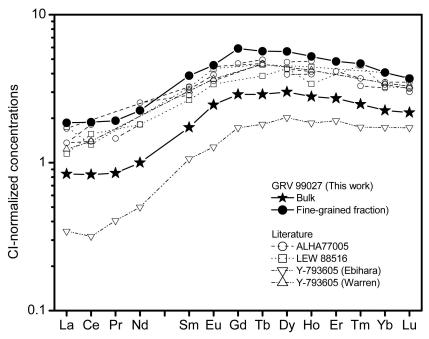


Fig. 1. REE patterns of GRV 99027 showing a "hump" shape parallel to those of other lherzolitic shergottites without any Ce anomaly. However, the bulk sample of GRV 99027 contains lower REEs except for the analysis of Y-793605 (open triangle down, dash double dot line) reported by Ebihara et al. (1997). The fine-grained fraction of GRV 99027 has higher concentrations of REEs, close to the upper range of the lherzolitic shergottites. Literature data of ALHA77005 (open circle, dash line) from Smith et al. (1984), Dreibus et al. (1992), Warren et al. (1999); LEW 88516 (open square, dot line) from Dreibus et al. (1992), Gleason et al. (1997), and Y-793605 (open triangle up, dash dot line) from Warren et al. (1999).

siderophile and chalcophile elements of the bulk GRV 99027. The elements are arranged from right to left, with increase of the 50% condensation temperature, i.e., more refractory toward left. The Os/Ir ratio of GRV 99027 is chondritic $(1.03 \times \text{CI})$, and all PGEs (except for Pd) have a nearly flat pattern with $0.004 \sim 0.008 \times \text{CI}$ (Fig. 2). The CInormalized abundances of Pd, Ni and Co increase to 0.018, 0.029, and $0.13 \times \text{CI}$, respectively. When compared with other lherzolitic shergottites, GRV 99027 contains slightly lower concentrations of Os and Ir and a higher concentration of Pt (Fig. 2).

The analyses of GRV 99027 show different trends of lithophile and siderophile elements, and obvious fractionation between them (Fig. 3). The fractionation becomes more pronounced with the 50% condensation temperature. Co and probably Ni plotted above the trend of other siderophile elements, and Ge is apparently depleted. W and Ga plotted along the trend of lithophile elements.

DISCUSSION

Genetic Relationship to Other Lherzolitic Shergottites

Compared with ALHA77005, Y-793605 and LEW 88516, GRV 99027 contains distinctly lower REEs (Fig. 1). All analyses of ALHA77005, Y-793605 and LEW 88516 have nearly identical compositions of REEs (Smith et al. 1984; Dreibus et al. 1992; Gleason et al. 1997; Warren et al. 1999), except for the lower REE concentrations of Y-793605 reported by Ebihara et al. (1997), which could be due to heterogeneously sampling as mentioned above. The sample of Y-793605 analyzed by Ebihara et al. may be dominated by poikilitic areas and hence deficient in the most REE-rich merrillite (e.g., Lundberg et al. 1990; Lin et al. 2005b). This is supported by the higher concentrations of REEs in the fine-grained fraction of GRV 99027 (Fig. 1). Besides REEs, the fine-grained fraction contains more Al, Cr, and P than the bulk sample (Table 1), suggesting higher abundances of

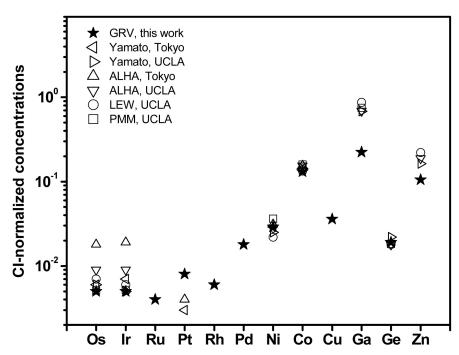


Fig. 2. The CI-normalized concentrations of siderophile and chalcophile elements of GRV 99027. The elements are arranged from the left to the right with increase of volatility. PGEs (except for Pd) of GRV 99027 are nearly flat, without negative anomaly of Pt as in other lherzolitic shergottites. Also plotted is the primitive mantle of Mars (PMM) after Warren et al. (1999). Other literatures data are from the groups of Tokyo (Ebihara et al. 1997) and UCLA (Warren and Kallemeyn 1996; Warren et al. 1999).

plagioclase, chromite, and merrillite in the former. This is consistent with the coexistence of plagioclase, chromite and merrillite in the non-poikilitic areas (Lin et al. 2005b), which may be more sampled by the fine-grained fraction.

However, the low REE concentrations of the bulk GRV 99027 compared with other lherzolitic shergottites cannot be due to heterogeneous sampling, as the analyzed sample was prepared from a relatively large mass (2.34 g) as described above. Furthermore, the ICP-MS analysis of the bulk sample is consistent with the previous result calculated from modal composition and in situ analyses of constituent phases (Lin et al. 2005b, Fig. 12d). In addition, during fractional crystallization of a closed system with the bulk composition of GRV 99027, the REE concentrations of the liquids calculated based on mass balance agree well with those determined by partitioning of REE between liquids and minerals (Lin et al. 2005b). The lower bulk REE concentrations of GRV 99027, together with its lower modal abundance of olivine, very homogenous compositions of major silicates and well recrystallized maskelynite reported in previous studies (Lin et al. 2005b; Wang and Chen 2006), confirm that this meteorite is not a fragment of (in other words, not paired with) ALHA77005, Y-793605, or LEW 88516. On the other hand, the differences in petrography, mineral chemistry, and bulk composition might be explained by variation within the same magma body, therefore a possible pairing ejection of GRV 99027 with other lherzolites cannot be completely excluded. GRV 99027 might sample a different portion of the same igneous unit as ALHA77005 and other lherzolites. After

crystallization, GRV 99027 was heavily shocked and reburied in a deep location, followed by a slow cooling. The depletion of LREE of GRV 99027 suggests little contamination by the incompatible element-enriched Martian crust (Herd et al. 2002), and the absence of a Ce anomaly indicates little terrestrial weathering.

Constraints on the Martian Mantle

Chondritic PGEs

The Os/Ir ratio of GRV 99027 is chondritic $(1.03 \times CI)$, consistent with previous analyses of other lherzolitic shergottites (e.g., Ebihara et al. 1997; Kong et al. 1999; Warren et al. 1999). Furthermore, the CI-normalized abundances of siderophile elements in GRV 99027 show a flat pattern of PGEs, with exception of a slight enrichment of Pd that has the lowest 50% condensation temperature of PGEs (Fig. 2). Pt and Ru in ALHA77005 were measured by Ebihara et al. (1997) and Kong et al. (1999), and both are significantly depleted relative to Os and Ir (Fig. 2). However, their analyses of Os and Ir are unusually higher than those determined by other groups (e.g., Warren et al. 1999) and in other lherzolitic shergottites (Warren and Kallemeyn 1996; Ebihara et al. 1997; Kong et al. 1999; Warren et al. 1999). Hence, the abundances of Pt and Ru in ALHA77005 are not unusual relative to most analyses of Os and Ir in lherzolitic shergottites. Jones et al. (2003) cited unpublished data of PGEs in ALHA77005 analyzed by Ely and Neal, which are close to the chondritic ratios. The new analysis of GRV 99027

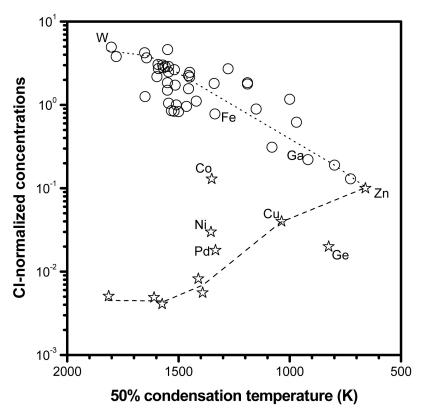


Fig. 3. The elemental pattern of GRV 99027, indicative of the lithophile (circle) and siderophile (star) element trends and fractionation between them. A dot line through the upmost plots of lithophile elements and another dash line through the downmost plots of siderophile elements (excluding Ge) were drawn as references to the element trends. It is noted that the fractionation between siderophiles and lithophiles increases with the 50% condensation temperature (Lodders 2003). W and Ga are not depleted relative to the lithophile element trend, and Co and probably Ni are higher and Ge is lower relative to the siderophile element trend.

confirms that the relative abundances of PGEs in lherzolitic shergottites are near-chondritic (Jones et al. 2003).

GRV 99027 and other lherzolitic shergottites are probably representative of the Martian mantle with respect to PGEs, as these highly siderophile elements are almost unfractionated. Small degrees of partial melting or large degrees of fractional crystallization will produce fractionated PGE patterns, as these highly siderophile elements show different behaviors from compatible to incompatible (Barnes and Picard 1993; Bockrath et al. 2004; Righter et al. 2004). Shergotty and Zagami represent large degrees of fractional crystallization, and Nakhla is a result of a small degree of partial melting, both are strongly depleted in highly siderophile elements and have subchondritic Os/Ir ratios (Jones et al. 2003). Lherzolitic shergottites crystallized from melts derived from the Martian mantle. Neither large degrees of fractional crystallization nor small degrees of partial melting can be invoked for these meteorites. This is consistent with a closed system crystallization of GRV 99027 based on the petrography and REE microdistribution (Lin et al. 2005b). In addition, the concentrations of Os and Ir in GRV 99027 (2.5 and 2.4 ppb, respectively) are identical to the estimated values for the Martian mantle (both 2.5 ppb, Warren et al. 1999).

The LREE-depleted patterns of GRV 99027 and other lherzolitic shergottites also indicate little contamination by the crust of Mars. In contrast, basaltic shergottites show various degrees of interaction between the basaltic parent magmas, derived from a source in the Martian mantle, and the oxidized and LREE-enriched crust (Wadhwa 2001; Herd et al. 2002). Another evidence for primitive characteristics of lherzolitic shergottites was demonstrated on a Al/Si versus Mg/Si diagram by Dreibus et al. (1992), with ALHA77005 and LEW 88516 plotting at or near a cross point of a cosmochemical fractionation line and a shergottite parent body fractionation line, suggesting that their compositions are close to that of the Martian mantle. GRV 99027 has the same Al/Si (0.05) and Mg/Si ratios (0.89), confirming the previous results.

The high and unfractionated abundances of PGEs of the mantle cannot be explained by partitioning between the silicate mantle and metal core, but reconciled with a later accretion of chondritic materials after the core-mantle segregation (Chou 1978; Morgan et al. 2001; Jones et al. 2003). Given the concentrations of PGEs in the upper Martian mantle similar to those of GRV 99027, it requires about 0.5% of chondritic materials adding into the mantle after the core formation of Mars.

No Depletion of W or Ga

In Fig. 3, the bulk composition of GRV 99027 shows fractionation between lithophile and siderophile elements, which is related to volatility. As the 50% condensation temperature decreases, the CI-normalized abundances of lithophile elements decrease, whereas those of siderophile elements increase. It is noted that W plots on the lithophile element trend, indicative of no depletion relative to other refractory lithophiles. This is consistent with previous analyses of W in ALHA77005 (0.9 × CI, Wänke et al. 1986), Y793605 (<2.7 × CI, Dreibus et al. 1992), and LEW 88516 $(1.5 \times CI, Gleason et al. 1997)$. The absence of W depletion cannot be resulted from partial melting of the Martian mantle or the subsequent crystallization, but inherited from the reservoir. Melting and/or crystallization may change concentrations of W and other refractory lithophile elements, but have little effect on ratios of W to the latter. This is consistent with previous results that shergottites plot on a straight line in the W-La diagram (Wänke and Dreibus 1986; Righter and Drake 1996). Similarly, the concentration of Ga in GRV 99027 plots on the lithophile element trend, indicating neither depletion relative to chondrites and the 50% condensation temperature. The absence of Ga depletion is also attributable to the Martian mantle for the same reasons as W.

The elemental pattern of GRV 99027 confirms previous work that the Martian mantle has no or small depletion of W (Righter and Drake 1996), different from the W-depleted terrestrial mantle (Righter and Drake 1997; Walter and Tronnes 2004). The significant depletion of W in the terrestrial mantle suggests that W was partitioned more in the metal core than in the silicate mantle under reducing and high pressure conditions during the core-mantle segregation, as the partition coefficients of W between metal and silicates increase with pressure (Righter et al. 1997). In contrast, the Martian mantle probably formed under more oxidizing conditions in comparison with the Earth, as suggested by the lack of W depletion in the Martian mantle. The difference in W depletion between the terrestrial and martial mantles cannot be solely attributed to their different pressures, because that W depletion of the terrestrial mantle can be expected based on W partition coefficients at one bar pressure (Righter et al. 1997).

High Abundances of Ni and Co

The CI-normalized concentrations of Ni (0.03) and Co (0.13) in GRV 99027 are consistent with previous analyses of other lherzolitic shergottites (Dreibus et al. 1992; Ebihara et al. 1997; Gleason et al. 1997; Warren et al. 1999). Figure 3 reveals deviations of Ni and especially Co in GRV 99027 from the siderophile element trend. The relatively high abundances of Ni and Co probably originated from the mantle source rather than being due to variable partial melting and/or subsequent crystallization.

As discussed above, GRV 99027 probably crystallized from a closed system, hence has little change in the bulk composition during the process. In addition, the nearly chondritic PGEs of GRV 99027 and other lherzolitic shergottites argue against large degrees of fractional crystallization or small degrees of partial melting. The ratios of Ni/Ir and Ni/Co of GRV 99027 (CI-normalized) are 5.8 and 0.22, respectively, nearly similar to the estimated values of the primitive mantle of Mars (7 and 0.23, respectively, Warren et al. 1999).

The high relative abundances of Ni and Co in the Martian mantle cannot be explained by equilibrium partition with the core under oxidizing conditions. As discussed above, the core-mantle segregation of the Earth probably took place under more reducing conditions as compared to Mars based on W depletion. However, the terrestrial mantle has higher abundance of Ni (0.18–1.19 × CI) and ratio of Ni/Co (0.85– 0.87) (Righter et al. 1998; Warren et al. 1999), in comparison with the Martian mantle. Measurement of partition coefficients of Ni and Co between metal and silicate under high P-T conditions reveals that both elements become less siderophile with pressure and the effect is much more pronounced for Ni (Li and Agee 1996; Righter et al. 1997). The abundances of Ni and Co in both terrestrial and Martian mantles are consistent with metal-silicate partitioning in magma oceans with various depths (Li and Agee 1996; Righter et al. 1997).

SUMMARY

The bulk composition of 50 elements including REEs and PGEs of GRV 99027 were determined using ICP-AES, ICP-MS and the Carius-tube technique combined with ICP-MS. The LREE-depletion and lack of Ce anomaly suggest little contamination of GRV 99027 by Martian crust materials or by terrestrial weathering. GRV 99027 contains distinctly lower REEs than other lherzolitic shergottites, confirming the petrographic and mineral chemical differences reported in previous studies (Lin et al. 2005b; Wang and Chen 2006). GRV 99027 is not paired with other Martian lherzolites, but probably has sampled an unique portion of the same igneous unit as the latter.

The abundances of Os and Ir of GRV 99027 are within the range of lherzolitic shergottites and all PGEs (except for Pd) show a flat pattern normalized to CI chondrites. The unfractionated PGEs of GRV 99027 are probably inherited from the Martian mantle, consistent with the later accretion of chondritic materials after the core-mantle segregation of Mars. The CI-normalized elemental pattern of GRV 99027 reveals no depletion of W or Ga and high abundances of Ni and Co relative to lithophile and siderophile element trends, respectively. These characteristics are attributable to the Martian mantle, consistent with previous work.

Acknowledgments—The authors thank Ying Liu, Guangqian Hu, and Xianglin Tu for laboratory assistance. The thorough and constructive reviews by K. Righter, T. Mikouchi, R. Walker and an anonymous reviewer, and the comments by the associate editor C. Goodrich significantly improved the paper. The sample was provided by the Polar Research Institute of China, and this study was supported by the Knowledge Innovation Program (kzcx2-yw-110) and One-Hundred-Talent Program of the Chinese Academy of Sciences, and by the Natural Science Foundation of China (grant no. 40232026).

Editorial Handling—Dr. Cyrena Goodrich

REFERENCES

- Barnes S. J. and Picard C. P. 1993. The behavior of platinum-group elements during partial melting, crystal fractionation, and sulfide segregation: An example from the Cape Smith Fold Belt, northern Quebec. *Geochimica et Cosmochimica Acta* 57:79–87.
- Bockrath C., Ballhaus C., and Holzheid A. 2004. Fractionation of the platinum-group elements during mantle melting. *Science* 305: 1951–1953.
- Borg L. E., Nyquist L. E., Wiesmann H., and Reese Y. 2002. Constraints on the petrogenesis of Martian meteorites from the Rb-Sr and Sm-Nd isotopic systematics of the Iherzolitic shergottites ALH 77005 and LEW 88516. Geochimica et Cosmochimica Acta 66:2037–2053.
- Chou C. L. 1978. Fractionation of siderophile elements in the Earth's upper mantle. Proceedings, 9th Lunar and Planetary Science Conference. pp. 219–230.
- Dreibus G., Jochum K. H., Palme H., Spettel B., Wlotzka F., and Wänke H. 1992. LEW 88516: A meteorite compositionally close to the "Martian mantle." *Meteoritics* 27:216–217.
- Ebihara M., Kong P., and Shinotsuka K. 1997. Chemical composition of Y-793605, a Martian Iherzolite. *Antarctic Meteorite Research* 10:83–94
- Gillet P., Barrat J. A., Beck P., Marty B., Greenwood R. C., Franchi I. A., Bohn M., and Cotten J. 2005. Petrology, geochemistry, and cosmic-ray exposure age of lherzolitic shergottite Northwest Africa 1950. Meteoritics & Planetary Science 40:1175–1184.
- Gleason J. D., Kring D. A., Hill D. H., and Boynton W. V. 1997. Petrography and bulk chemistry of Martian Iherzolite LEW 88516. Geochimica et Cosmochimica Acta 61:4007–4014.
- Harvey R. P., Wadhwa M., McSween H. Y., Jr., and Crozaz G. 1993. Petrography, mineral chemistry and petrogenesis of Antarctic shergottite LEW88516. *Geochimica et Cosmochimica Acta* 57: 4769–4783.
- Herd C. D. K., Borg L. E., Jones J. H., and Papike J. J. 2002. Oxygen fugacity and geochemical variations in the Martian basalts: Implications for Martian basalt petrogenesis and the oxidation state of the upper mantle of Mars. Geochimica et Cosmochimica Acta 66:2025–2036.
- Hsu W., Guan Y., Wang H., Leshin L. A., Wang R., Zhang W., Chen X., Zhang F., and Lin C. 2004. The lherzolitic shergottite Grove Mountains 99027: Rare earth element geochemistry. *Meteoritics & Planetary Science* 39:701–709.
- Ikeda Y. 1997. Petrology and mineralogy of the Y-793605 Martian meteorite. *Antarctic Meteorite Research* 10:13–40.
- Jarosewich E., Clarke R. S. J., and Barrows J. N. 1987. The Allende meteorite reference sample. Smithsonian Contributions to the Earth Sciences 27:1–49.

- Jones J. H., Neal C. R., and Ely J. C. 2003. Signatures of the highly siderophile elements in the SNC meteorites and Mars: A review and petrologic synthesis. *Chemical Geology* 196:5–25.
- Kong P., Ebihara M., and Palme H. 1999. Siderophile elements in Martian meteorites and implications for core formation in Mars. *Geochimica et Cosmochimica Acta* 63:1865–1875.
- Li J. and Agee C. B. 1996. Geochemistry of mantle-core differentiation at high pressure. *Nature* 381:686–689.
- Lin Y., Qi L., Wang G., and Xu L. 2005a. Major, trace, and platinum-group elements of the Martian lherzolite Grove Mountains (GRV) 99027 (abstract). *Meteoritics & Planetary Science* 40: A92.
- Lin Y., Guan Y., Wang D., Kimura M., and Leshin L. A. 2005b. Petrogenesis of the new lherzolitic shergottite Grove Mountains 99027: Constraints of petrography, mineral chemistry, and rare earth elements. *Meteoritics & Planetary Science* 40:1599–1619.
- Lin Y., Wang D., Miao B., Ouyang Z., Liu X., and Ju Y. 2003. Grove Mountains (GRV) 99027: A new Martian meteorite. Chinese Science Bulletin 48:1771–1774.
- Lin Y., Ouyan Z., Wang D., Miao B., Liu X., Kimura M., and Jun Y. 2002. Grove Mountains (GRV) 99027: A new Martian Iherzolite (abstract). *Meteoritics & Planetary Science* 37:A87.
- Lodders K. 2003. Solar system abundances and condensation temperatures of the elements. *The Astrophysical Journal* 591: 1220–1247.
- Lundberg L. L., Crozaz G., and McSween H. Y., Jr. 1990. Rare earth elements in minerals of the ALHA77005 shergottite and implications for its parent magma and crystallization history. *Geochimica et Cosmochimica Acta* 54:2535–2547.
- Mason B. 1979. *Data of geochemistry*, 6th ed. Washington D. C.: U.S. Government Printing Office. p. B114.
- McSween H. Y., Jr., Stolper E., Taylor L. A., Muntean R. A., O'Kelley G. D., Eldridge J. S., Biswas S., Ngo H. T., and Lipschutz M. E. 1979. Petrogenetic relationship between Allan Hills 77005 and other achondrites. *Earth and Planetary Science Letters* 45:275–284.
- Miao B., Ouyang Z., Wang D., Ju Y., Wang G., and Lin Y. 2004. A new Martian meteorite from Antarctica: Grove Mountains (GRV) 020090. Acta Geologica Sinica 78:1034–1041.
- Mikouchi T. and Miyamoto M. 1997. Yamato-793605: A new lherzolitic shergottite from the Japanese Antarctic meteorite collection. *Antarctic Meteorite Research* 10:41–60.
- Mikouchi T. and Miyamoto M. 2000. Lherzolitic Martian meteorites Allan Hills 77005, Lewis Cliff 88516, and Yamato-793605: Major and minor element zoning in pyroxene and plagioclase glass. Antarctic Meteorite Research 13:256–269.
- Morgan J. W., Walker R. J., Brandon A. D., and Horan M. F. 2001. Siderophile elements in Earth's upper mantle and lunar breccias: Data synthesis suggests manifestations of the same late influx. *Meteoritics & Planetary Science* 36:1257–1276.
- Nyquist L. E., Bogard D. D., Shih C.-Y., Greshake A., Stöffler D., and Eugster O. 2001. Ages and geologic histories of Martian meteorites. Space Science Reviews 96:105–164.
- Qi L., Zhou M., and Wang C. Y. 2004. Determination of low concentrations of platinum group elements in geological samples by ID-ICP-MS. *Journal of Analytical Atomic Spectrometry* 19: 1335–1339.
- Righter K. and Drake M. J. 1996. Core formation in Earth's Moon, Mars, and Vesta. *Icarus* 124:513–529.
- Righter K. and Drake M. J. 1997. Metal-silicate equilibrium in a homogeneously accreting Earth: New results for Re. Earth and Planetary Science Letters 146:541–553.
- Righter K., Drake M. J., and Yaxley G. 1997. Prediction of siderophile element metal-silicate partition coefficients to 20 GPa and 2800 °C: The effects of pressure, temperature,

- oxygen fugacity, and silicate and metallic melt compositions. *Physics of the Earth and Planetary Interiors* 100:115–134.
- Righter K., Hervig R. L., and Kring D. A. 1998. Accretion and core formation on Mars: Molybdenum contents of melt inclusion glasses in three SNC meteorites. *Geochimica et Cosmochimica Acta* 62:2167–2177.
- Righter K., Campbell A. J., Humayun M., and Hervig R. L. 2004. Partitioning of Ru, Rh, Pd, Re, Ir, and Au between Cr-bearing spinel, olivine, pyroxene, and silicate melts. *Geochimica et Cosmochimica Acta* 68:867–880.
- Smith M. R., Laul J. C., Ma M. S., Huston T., Verkouteren R. M., Lipschutz M. E., and Schmitt R. A. 1984. Petrogenesis of the SNC (shergottites, nakhlites, chassignites) meteorites: Implications of their origin from a large dynamic planet, possibly Mars. *Journal Geophysical Research* 89:B612–B630.
- Treiman A. H., McKay G. A., Bogard D. D., Mittlefehldt D. W., Wang M. S., Keller L., Lipschutz M. E., Lindstrom M. M., and Garrison D. 1994. Comparison of the LEW 88516 and ALHA 77005 Martian meteorites: Similar but distinct. *Meteoritics* 29:581–592.
- Wänke H. and Dreibus G. 1986. Die chemische Zusammensetzung und Bildung der terrestrischen Planeten. *Mitteilungen der Astronomischen Gesellschaft Hamburg* 65:9–24.
- Wänke H., Dreibus G., Jagoutz E., Palme H., Spettel B., and Weckwerth G. 1986. ALHA 77005 and on the chemistry of the Shergotty parent body (Mars) (abstract). 17th Lunar and Planetary Science Conference. pp. 919–920.

- Wadhwa M. 2001. Redox state of Mars' upper mantle and crust from Eu anomalies in shergottite pyroxenes. *Science* 291:1527–30.
- Wadhwa M., McKay G. A., and Crozaz G. 1999. Trace element distributions in Yamato-793605, a chip off the "Martian lherzolite" block. *Antarctic Meteorite Research* 12:168–182.
- Walter M. J. and Tronnes R. G. 2004. Early Earth differentiation. *Earth and Planetary Science Letters* 225:253–269.
- Wang D. and Chen M. 2006. Shock-induced melting, recrystallization, and exsolution in plagioclase from the Martian lherzolitic shergottite GRV 99027. Meteoritics & Planetary Science 41:519–527.
- Wang G. and Lin Y. 2007. Bulk chemical composition of the Ningqiang carbonaceous chondrite: An issue of classification. Acta Geologica Sinica 81:141–147.
- Warren P. H. and Kallemeyn G. W. 1996. Siderophile trace elements in ALH 84001, other SNC meteorites, and eucrites: Evidence of heterogeneity, possibly time-linked, in the mantle of Mars. *Meteoritics & Planetary Science* 31:97–105.
- Warren P. H. and Kallemeyn G. W. 1997. Yamato-793605, EET 79001, and other presumed Martian meteorites: Compositional clues to their origins. *Antarctic Meteorite Research* 10:61–81.
- Warren P. H., Kallemeyn G. W., and Kyte F. T. 1999. Origin of planetary cores: Evidence from highly siderophile elements in Martian meteorites. *Geochimica et Cosmochimica Acta* 63: 2105–2122.