Trace element distributions in the Yamato 000593/000749, NWA 817 and NWA 998 nakhlites: Implications for their petrogenesis and mantle source on Mars

Meenakshi Wadhwa^{1*}, Ghislaine Crozaz² and Jean-Alix Barrat³

 ¹Department of Geology, The Field Museum, 1400 S. Lake Shore Dr., Chicago, IL 60605, U.S.A.
 ²Department of Earth and Planetary Sciences and Laboratory for Space Sciences, Washington University, St. Louis, MO 63130, U.S.A.
 ³CNRS UMR 6538 (Domaines Océaniques), U.B.O.-I.U.E.M., Place Nicolas Copernic, F-29280 Plouzané Cedex, France
 *Corresponding author. E-mail: mwadhwa@fieldmuseum.org

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Abstract: We report here results of ion microprobe analyses of rare earth element abundances in various phases in the new Antarctic (paired) nakhlites Yamato 000593 and Yamato 000749, as well as in two additional nakhlites recovered from the Saharan desert, NWA 817 and NWA 998. Although these nakhlites are all composed predominantly of augite and some olivine, they differ from each other, and from the three previously known nakhlites, in the abundance and degree of crystallinity of the interstitial mesostasis. Trace element abundances in various phases in these new nakhlites indicate that they are petrogenetically related to (and comagmatic with) each other and the previously known nakhlites. The calculated parent melt compositions (in equilibrium with augite core compositions) are LREE-enriched and have REE patterns parallel to those of their whole rocks. This suggests that subsequent to accumulation of the olivine and augite, the intercumulus trapped melt evolved in a closed system. The similarity in the estimated parent melt compositions and trace element zonation in the augites of the various nakhlites indicates that these rocks are likely to have formed within a single lithologic unit on Mars. In this scenario, the differences among these nakhlites may be explained in terms of differences in the depth of crystallization within the cumulus pile, represented by different horizons within the same lithologic unit. Based on the partitioning of Eu in their augite cores, the magmatic redox conditions for the nakhlites are estimated to be relatively oxidizing (~QFM), implying an oxidized source reservoir in the martian mantle. Late metasomatism of their mantle source by LREE-enriched, oxidizing fluids is suggested to be responsible for the LREE-enrichment and oxidation condition of the nakhlite parent melts.

key words: nakhlites, Mars, rare earth elements, trace elements, ion microprobe

1. Introduction

Although numerous new meteorites of purported martian origin have been found in recent years, most of these have been classified as belonging to the shergottite type. In

fact, of the more than two dozen meteorites thought to have originated on Mars, $\sim 70\%$ are shergottite basalts. Therefore, the recent finds of two paired nakhlites from the Antarctic, Yamato 000593 (Y000593) and Yamato 000749 (Y000749) (Imae *et al.*, 2002; Misawa *et al.*, 2003), and another two from the Sahara (NWA 817 and NWA 998) (Irving *et al.*, 2002; Sautter *et al.*, 2002) have doubled the number of martian pyroxenites available for study. The previously known non-desert nakhlites (Nakhla, Governador Valadares and Lafayette) are virtually identical in terms of their petrologic and geochemical characteristics (*e.g.*, Harvey and McSween, 1992; Wadhwa and Crozaz, 1995) and, thus, constraints on the petrogenesis of new and potentially diverse members of the nakhlite class are anticipated to provide new insights into the magmatic history of Mars. Towards this goal, we have made an investigation of trace element systematics in each of these new nakhlites and report here ion microprobe analyses of rare earth element abundances in various phases of Y000593, Y000749, NWA 817, and NWA 998.

2. Sample description and analytical methods

X-ray mapping and mineral identification were performed on one polished thin section each of Y000593, Y000749, NWA 817 and NWA 998 using either the University of Chicago JEOL JEM-5800LV scanning electron microprobe, equipped with an Oxford/Link ISIS-300 energy dispersive microanalysis system (for Y000593, Y000749 and NWA 998) or the Cameca SX50 electron microprobe located at the Université de Paris VI (for NWA 817). This information was used to identify the phases appropriate for trace element analyses. Concentrations of rare earth elements (REE) were then measured *in situ* in selected spots of the various phases, including the major silicates, glassy mesostasis and/or apatite, in each of the four nakhlite thin sections studied here (Y and Ti were additionally analyzed in the augites) using the Washington University modified CAMECA IMS-3f secondary ion mass spectrometer (SIMS). Analytical procedures for such measurements have been described in detail by Zinner and Crozaz (1986) and Lundberg et al. (1988). Typical primary (O^{-}) beam currents used in this study ranged from $\sim <1$ nA (for REE-rich phases like apatite) to ~ 10 nA (for REEpoor minerals such as olivines), and corresponding beam spot sizes ranged from ~ 10 to ~50µm.

3. Petrography and mineralogy

Petrographic descriptions, modal mineralogies and major element compositions of minerals of the Y000593/000749, NWA 817 and NWA 998 nakhlites have previously been reported (Imae *et al.*, 2003; Mikouchi *et al.*, 2003; Irving *et al.*, 2002; Sautter *et al.*, 2002) and are briefly summarized below to provide a context for the trace element microdistributions reported here.

3.1. Y000593/000749

Petrologic investigations of the paired Y000593/000749 nakhlites have been made by Imae *et al.* (2003) and Mikouchi *et al.* (2003). As can be seen in Fig. 1, these



Fig. 1. Optical photomicrographs in cross-polarized light of polished thin sections of (a) Y000593, (b) Y000749, (c) NWA 817 and (d) NWA 998. Field of view of each image is ~2 mm. AUG=augite; OL=olivine; PL=plagioclase; M=mesostasis.

meteorites are cumulates composed predominantly of augite (70–85%) and olivine (7–18%). The augites are subhedral to euhedral and are up to ~1.5 mm in length. The mesostasis areas (5–15%) have a microcrystalline texture (similar to that in Nakhla, Governador Valadares and Lafayette) and are composed mostly of radiating sprays of plagioclase (200–300 μ m long, 20 μ m wide) intergrown with silica and minor to trace phases such as K-feldspar, pigeonite, Ti-magnetite, Fe-sulfide and apatite. As in the non-desert nakhlites, olivines appear to be altered to rusty brownish colored weathering products (iddingsite) along rims and fractures. The mesostasis also contains abundant rust colored weathering products.

The augites in Y000593/000749 have large cores with uniform major element compositions ($En_{38}Fs_{22}Wo_{40}$), and thin (10–20 μ m) Fe-rich rims adjacent to the mesostasis. Olivines are extensively zoned (Fa_{58-82}), with the most Fe-rich compositions in rims adjacent to the mesostasis. The major element composition of the plagioclase is $An_{35-21}Or_{3-10}$.

3.2. NWA 817

The mineralogy and petrography of NWA 817 was recently reported by Sautter *et al.* (2002). Mineral modes in this rock are augite ~69%, olivine ~10%, mesostasis ~20%, and Fe-Ti oxides ~1%. As can be seen in Fig. 1, the augites and olivines are up to ~1 mm in length. The mesostasis is mostly glassy with fine-grained feldspar, pyroxene and olivine, Ti-magnetite, Fe-sulfide and apatite. The reddish-orange hydrous ferrous silicate that comprises the pre-terrestrial alteration product in this meteorite has been described by Gillet *et al.* (2002). It is present mostly in fractures in olivine, but can also be found in the mesostasis.

The augites have large homogeneous cores $(En_{38}Fs_{22}Wo_{40})$. The Fe-rich augite rims extend ~10 μ m beyond the cores and appear to develop only adjacent to the mesostasis. Olivines show smooth and extensive zonation from core to rim (Fa₅₆₋₈₆). The composition of the fine-grained feldspar in the mesostasis is typically An₁₃₋₁₇Or₁₄₋₁₅.

3.3. NWA 998

A preliminary petrographic description of NWA 998 has been provided by Irving *et al.* (2002). Like the other nakhlites, this rock is composed mostly of augite (core composition $\sim En_{39}Fs_{22}Wo_{39}$) and olivine (Fa₆₄). However, unlike all other nakhlites known so far, the plagioclase (An₃₅Or₄) occurs as well crystallized grains (displaying albitic twinning) in the areas interstitial to the augite and olivine (Fig. 1). Moreover, NWA 998 is also unusual in having low-Ca pyroxene (En₄₇Fs₄₉Wo₄) in greater modal abundance than in the other nakhlites. Minor and trace phases include K-feldspar, Ti-magnetite, pyrrhotite and apatite.

4. Results

Representative REE abundances in various phases of the Y000593, Y000749, NWA 817 and NWA 998 nakhlites are given in Tables 1–3 and Fig. 2. Apatites large enough for trace element analyses with the ion microprobe (*i.e.*, $\geq 10-20\,\mu$ m) were only found in the thin sections of Y000593 and NWA 998, and three apatite grains were analyzed in each of these two meteorites. This mineral is characterized in the nakhlites by a LREE-enriched pattern and a negative Eu anomaly (Fig. 2a). However, apatite in Y000593 is not as LREE-enriched (La ~670-810×CI; chondrite-normalized La/Yb ~14-17) as that in NWA 998 (La ~1450-1900×CI; chondrite-normalized La/Yb ~45-60).

Glass-rich mesostasis areas are present in Y000593, Y000749 and NWA 817. Analyses were made in one such area in each of the two Antarctic nakhlites, and in two such areas of NWA 817. Their REE patterns, like those of the apatites, are LREEenriched (Fig. 2b). The degree of LREE-enrichment in the glassy mesostasis of the paired Y000593 and Y000749 nakhlites (chondrite normalized La/Yb ~14 and ~6, respectively) appears to be variable. In NWA 817, the fine-grained glassy mesostasis has a chondrite normalized La/Yb ratio of ~5–6. REE concentrations in this phase in Y000593 and Y000749 (La ~20–40×CI) are lower than those in NWA 817 (La ~80– $100 \times CI$). As can be seen in Fig. 2b, a small positive Ce anomaly (defined as Ce/Ce^{*}, where Ce^{*} is the value interpolated between chondrite normalized abundances of La

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Table 1.

			Y000593				A	00749	
	Apatite	Mesostasis	Plagioclase	Augite Rim	Olivine	Mesostasis	Plagioclase	Augite Core	Inclusion*
La	167 ± 3	9.92 ± 0.24	2.27 ± 0.09	0.49 ± 0.03	0.0022 ± 0.0005	4.96 ± 0.16	3.06 ± 0.10	0.075 ± 0.005	3.67 ± 0.14
Ce	448 ± 6	28.0 ± 0.5	4.92 ± 0.18	5.67 ± 0.24	0.0086 ± 0.0011	26.7 ± 0.4	8.33 ± 0.19	0.39 ± 0.02	9.59 ± 0.26
Pr	58.6 ± 1.7	3.00 ± 0.13	0.66 ± 0.03	0.36 ± 0.02	0.0008 ± 0.0003	1.81 ± 0.08	0.93 ± 0.05	0.082 ± 0.006	1.40 ± 0.07
ΡN	280 ± 5	12.3 ± 0.3	2.22 ± 0.09	1.85 ± 0.08	0.0041 ± 0.0012	5.71 ± 0.17	3.22 ± 0.10	0.49 ± 0.01	5.25 ± 0.17
Sm	53.5 ± 3.0	2.06 ± 0.14	0.36 ± 0.03	0.59 ± 0.04	n.d.	1.40 ± 0.10	0.58 ± 0.05	0.14 ± 0.01	1.15 ± 0.09
Бu	12.3 ± 0.5	0.61 ± 0.09	0.63 ± 0.07	0.14 ± 0.01	<0.0006	0.62 ± 0.09	0.53 ± 0.06	0.041 ± 0.002	0.22 ± 0.09
Gd	45.4 ± 3.9	1.42 ± 0.22	0.34 ± 0.05	0.57 ± 0.06	0.0034 ± 0.0012	1.31 ± 0.13	0.52 ± 0.07	0.16 ± 0.01	0.64 ± 0.13
$^{\mathrm{dI}}$	8.61 ± 0.8	0.32 ± 0.04	0.067 ± 0.007	0.10 ± 0.01	0.0021 ± 0.0005	0.22 ± 0.02	0.095 ± 0.014	0.028 ± 0.004	0.16 ± 0.02
Dy	32.7 ± 1.5	1.24 ± 0.08	0.27 ± 0.02	0.69 ± 0.03	0.017 ± 0.002	1.24 ± 0.06	0.36 ± 0.02	0.16 ± 0.01	1.03 ± 0.06
Но	6.25 ± 0.50	0.25 ± 0.02	0.072 ± 0.009	0.14 ± 0.01	0.0080 ± 0.0010	0.23 ± 0.02	0.092 ± 0.009	0.034 ± 0.003	0.21 ± 0.02
ц	13.8 ± 0.8	0.66 ± 0.04	0.15 ± 0.01	0.40 ± 0.02	0.022 ± 0.002	0.71 ± 0.04	0.19 ± 0.02	0.090 ± 0.005	0.63 ± 0.04
Tm	1.95 ± 0.2	0.086 ± 0.010	0.018 ± 0.007	0.061 ± 0.006	0.0040 ± 0.0007	0.11 ± 0.01	0.017 ± 0.004	0.0092 ± 0.0019	0.063 ± 0.009
Yb	7.57 ± 0.70	0.44 ± 0.03	0.065 ± 0.009	0.42 ± 0.04	0.028 ± 0.002	0.58 ± 0.04	0.079 ± 0.012	0.090 ± 0.009	0.46 ± 0.03
* Gla	ssy magmatic	inclusion in oli	vine.						
Err	ors are 1σ fro	om counting stat	tistics only; uppe	r limits are 2σ (n.d.=not detected	, and no upper	limits could be	estimated).	



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and Pr) is present in the mesostasis of Y000593 (Ce/Ce^{*} \sim 1.2) and a larger one is present in the mesostasis of Y000749 (Ce/Ce^{*} \sim 2.1).

Feldspars in the mesostasis of NWA 817 are too fine-grained to be analyzed with the ion microprobe; they are sufficiently coarse in the Y000593/000749 mesostasis, and are the coarsest in NWA 998 (Fig. 1). We measured rare earth element abundances in two plagioclase grains in Y000593, one in Y000749, and one in NWA 998; we also analyzed one potassic feldspar grain in NWA 998. Figure 2c shows that although feldspars in Y000593, Y000749 and NWA 998 have LREE-enriched patterns, they differ in their absolute REE abundances, their degree of LREE-enrichment, and the sizes of their Eu anomalies (Eu/Eu^{*}, where Eu^{*} is the value interpolated between chondrite normalized abundances of Sm and Gd). Plagioclase of Y000593 (La ~6–10×CI; chondrite normalized La/Sm ~4; Eu/Eu^{*} ~3–5) and Y000749 (La ~13×CI; chondrite normalized La/Sm ~14; Eu/Eu^{*} ≥60). Compared to plagioclase, potassic feldspar in NWA 998 has somewhat lower REE abundances (La ~1×CI) but a similar sized Eu anomaly (Eu/Eu^{*} ~60).

Analyses were made on seven spots in two augite grains of Y000593, five spots in two augite grains of Y000749, seven spots in two augite grains of NWA 817, and six spots in two augite grains of NWA 998. Augites in the nakhlites studied here have the characteristic concave-downward REE patterns, with small Eu anomalies (Eu/Eu* \sim 0.7–0.9), similar to those of augites in the non-desert nakhlites (Fig. 2d). The absolute abundances of REE and other trace elements in this mineral vary from core to rim of this mineral in all the nakhlites (Fig. 2d and Fig. 3). La concentrations in augites of paired Antarctic nakhlites Y000593 and Y000749 vary by a factor of \sim 6.6 (Table 1 and Fig. 2d show the REE concentrations in two augites from Y000593/000749 with the highest and the lowest REE concentrations, which represent the compositions of the augite rims and cores in these paired samples, respectively). La abundances in augites of NWA 817 and NWA 998 vary by factors of \sim 3.0 and \sim 1.3, respectively. Augite cores in Y000593/Y000749 have the lowest REE abundances, while augite rims in NWA 817 have the highest REE concentrations in this mineral in the nakhlites analyzed so far. Ce anomalies are prevalent in augites of Y000593/Y000749. In Y000593, four

^{Fig. 2(opposite). Representative REE abundances in (a) apatites of Y000593 and NWA 998, (b) mesostasis of Y000593, Y000749 and NWA 817, (c) feldspars of Y000593, Y000749 and NWA 998, (d) pyroxenes of Y000593, Y000749, NWA 817 and NWA 998, (e) olivines of Y000593, NWA 817 and NWA 998, and (f) glassy magmatic inclusions in olivines of Y000749 and NWA 817, normalized to the CI chondrite values of Anders and Grevesse (1989). Symbols are as follows: ● Y000593 (apatite, mesostasis, plagioclase, augite and olivine); ○ Y000749 (mesostasis, plagioclase, augite and glassy magmatic inclusion); ● NWA 817 (mesostasis, augite, olivine and glassy magmatic inclusion); ■ NWA 998 (apatite, plagioclase, augite, olivine and glassy magmatic inclusion); □ NWA 998 (K-feldspar and low-Ca pyroxene). For comparison, the solid black lines show the REE abundances in (a) apatite, (c) plagioclase, (d) augites, and (e) olivine of Nakhla (Wadhwa and Crozaz, 1995). REE concentrations in whole rocks (WR) of Nakhla (Nakamura et al., 1982), Y000593 (Dreibus et al., 2003), and NWA 817 (Sautter et al., 2002) are shown as the gray solid lines in (a), (b) and (f).}



Fig. 3. Ti versus Y abundances in augites of Y000593, Y000749, NWA 817, and NWA 998. Shaded area shows the compositional range of augites in the non-desert nakhlites, Nakhla, Governador Valadares and Lafayette.

of the seven analyses (in a single augite grain) show positive Ce anomalies, with Ce/Ce^{*} ranging from ~1.9–7.9. In Y000749, three of the five analyses (in a single augite grain) show positive Ce anomalies, with Ce/Ce^{*} ranging from ~1.8–8.8.

Six analyses were made in a single low-Ca pyroxene grain in NWA 998. All analyses of this mineral show pronounced LREE-enrichment and V-shaped REE patterns (Fig. 2d). Similar LREE-enrichment and V-shaped REE patterns are also seen in the olivines of the nakhlites studied here (one grain of which was analyzed in Y000593, two in NWA 817 and one in NWA 998). As is evident from Fig. 2e, HREE abundances and patterns in olivines of Y000593 (Yb ~ $0.2 \times$ CI; chondrite normalized Yb/Gd ~10), NWA 817 (Yb ~ $0.7-1.1 \times$ CI; chondrite normalized Yb/Gd ~5-7) and NWA 998 (Yb ~ $1.0 \times$ CI; chondrite normalized Yb/Gd ~30) vary considerably.

Magmatic inclusions are commonly found in olivines of all the nakhlites studied here and we analyzed one each (that was mostly glassy) in Y000749, NWA 817 and NWA 998. These glassy inclusions are characterized by LREE-enriched patterns in each of these meteorites (chondrite normalized La/Sm \sim 2.0–2.6).

5. Discussion

5.1. Do trace element microdistributions support a pairing relationship between Y000593 and Y000749?

It has previously been suggested based on the petrographic, geochemical and isotopic constraints (including cosmic ray exposure ages), as well as on the close spatial association of their recovery sites, that the Antarctic nakhlites are most likely to be paired (Imae *et al.*, 2003; Mikouchi *et al.*, 2003; Misawa *et al.*, 2003; Okazaki *et al.*,

2003; Oura et al., 2003).

Our investigation shows that in their REE microdistributions, Y000593 and Y000749 are more similar to each other than to any of the other known nakhlites (Fig. 2). In particular, REE abundances and patterns of the glassy mesostasis and of the plagioclase in the Antarctic nakhlites show a remarkable similarity, whereas they are quite distinct from the REE abundances and patterns of these phases in other nakhlites (Figs. 2b and 2c). However, the range of trace element concentrations in the augites of the Antarctic nakhlites appears to be slightly different (Fig. 3). Specifically, Y abundances vary by factors of ~5.6 and ~3.0, and Ti concentrations vary by factors of \sim 4.0 and \sim 2.5, in augites of Y000593 and Y000749, respectively. Nevertheless, it is important to note that the trace element compositions of the augite cores in both Y000593 and Y000749 are almost identical (La \sim 0.3–0.4 \times CI; Y \sim 1 μ g/g and Ti \sim 550– $650 \mu g/g$), and the difference in range of concentrations of these elements is mainly due to apparent variations in the compositions of the augite rims in these meteorites. This may be expected since the highly zoned rims typically only extend to $\sim 20 \,\mu m$ beyond the large, relatively homogeneous cores, and several of the augite "rim" analyses may actually represent a partial overlap of the primary beam spots (typically $\sim 20 \,\mu m$ in diameter) with the augite cores. Given this, the trace element microdistributions reported here do indeed support a pairing relationship between the Y000593 and Y000749 Antarctic nakhlites.

5.2. Comparison of REE microdistributions in the nakhlites

Our previous investigation of the non-desert nakhlites, Nakhla, Governador Valadares and Lafayette, showed that these three martian clinopyroxenites are almost identical in their trace and minor element microdistributions (Wadhwa and Crozaz, 1995). Apatite, a mineral that occurs in only trace amounts in these meteorites, is the main REE carrier. It accounts for $\sim 80-90\%$ of the LREE, $\sim 20-30\%$ of Eu and $\sim 30-50\%$ of the HREE. With the exception of $\sim 20-30\%$ of the Eu in the plagioclase, the remainder of the REE in these nakhlites resides in the augite.

The present study of REE microdistributions in the two paired Antarctic (cold desert) nakhlites, Y000593 and Y000749, and the two hot desert nakhlites, NWA 817 and NWA 998, shows that there exists greater variability among these meteorites than was recognized previously based only on the three non-desert nakhlites. Since there are presently no reported data for REE abundances in the NWA 998 whole rock, we will only discuss the distributions of the REE between the various phases based on mass balance estimates in Y000593/000749 (modal mineralogies from Imae et al., 2003; and Mikouchi et al., 2003) and NWA 817 (modal mineralogy from Sautter et al., 2002). In Y000593/000749, apatite (although having lower REE concentrations than in the apatites of the non-desert nakhlites) is still the main REE carrier, but there is also a significant fraction of the REE in the glass-rich mesostasis. Taken together, the apatite along with the mesostasis (which includes the plagioclase) accounts for $\sim 90\%$ of the LREE, $\sim 60\%$ of Eu, but only $\sim 25\%$ of the HREE. The remainder of the REE is accounted for by the augite. In NWA 817, the main REE carrier phase is the abundant glassy mesostasis (which includes extremely fine-grained apatite and plagioclase). We estimate that this phase accounts for up to $\sim 95\%$ of the LREE, $\sim 75\%$ of Eu, and $\sim 60\%$

of the HREE; the remainder of the REE resides in the augite.

Therefore, it is evident that compared to Nakhla, Governador Valadares and Lafayette (Wadhwa and Crozaz, 1995), the distributions of the REE among the various phases present in the more recently recovered hot and cold desert nakhlites are quite different. In particular, REE abundances and patterns in apatite, mesostasis, plagioclase and olivine vary considerably in these meteorites (Figs. 2a, 2b, 2c and 2e). Additionally, the ranges of trace element concentrations in the augites of these nakhlites show significant differences amongst each other (Fig. 2d and Fig. 3) compared to the broadly similar ranges of such elemental abundances in Nakhla, Governador Valadares and Lafayette (Fig. 4a and Fig. 6 of Wadhwa and Crozaz, 1995). In particular, REE abundances in augite cores of Nakhla (La ~ $0.8 \times CI$), Governador Valadares (La ~ $0.4 \times CI$) and Lafayette (La ~ $0.4 \times CI$) are similar within a factor of ~2. In contrast, there is significant variation among the REE compositions of augite cores in Y000593/000749 (La ~ $0.3 \times CI$), NWA 817 (La ~ $2 \times CI$) and NWA 998 (La ~ $1 \times CI$).

The differences in the trace element microdistributions in the nakhlites investigated here imply differences in the degrees of evolution of their parent melts and their formation environments, and these will be discussed in more detail in the following sections. Nevertheless, despite the greater variability among the recently discovered hot and cold desert nakhlites, it is also important to note that there are still similarities that are indicative of a petrogenetic relationship between all known nakhlites. The broadly similar LREE-enriched patterns of the glassy mesostasis and the glassy magmatic inclusions in olivines (Figs. 2b and 2f) are indicative of a similarity in the REE patterns of their parent melts and in their crystallization histories. Moreover, as can be seen in Fig. 3, the compositions of augites in all of the known nakhlites fall along the same trend, consistent with comagmatism among all these martian clinopyroxenites.

5.3. Effects of weathering in a terrestrial environment

The predominant secondary alteration product in the non-desert nakhlites, Nakhla, Governador Valadares and Lafayette, is the iddingsite-like material (Reid and Bunch, 1975; Gooding *et al.*, 1991; Treiman *et al.*, 1993), although some siderite and evaporitic minerals are also present (Bridges and Grady, 2000). These secondary phases are suggested to be of pre-terrestrial origin, and are considered to have formed by interaction with aqueous fluids in a near-surface environment on Mars. The effects of any terrestrial alteration or weathering in these three meteorites are minimal, and their trace element microdistributions have remained relatively unaffected by such a process (Wadhwa and Crozaz, 1995).

The nakhlites studied here also contain the iddingsite-like secondary alteration products that are likewise considered to have formed on the surface of Mars (Irving *et al.*, 2002; Gillet *et al.*, 2002; Sautter *et al.*, 2002; Imae *et al.*, 2003; Mikouchi *et al.*, 2003). However, in contrast to the three previously known nakhlites, the four subsequently recovered from the hot and cold deserts show clear evidence of having been moderately to severely weathered in the terrestrial environment.

In Y000593/000749, the effects of terrestrial weathering are evident in the prevalence of Ce anomalies in the augite (Fig. 2d) and the mesostasis (Fig. 2f), and in the V-shaped REE pattern of the olivine (Fig. 2e). Ce anomalies are also found in pyroxenes of Antarctic shergottites and are thought to result from the partial oxidation of Ce^{3+} to Ce^{4+} , which is relatively insoluble compared to the rest of the trivalent REE in weakly acidic aqueous fluids, and is less mobile than the other REE during terrestrial weathering (Crozaz *et al.*, 2003, and references therein). The presence of such anomalies in 7 of the 12 augite analyses (in 2 of 4 analyzed grains) and in the two analyses of mesostasis areas in Y000593/000749 is indicative of severe weathering of the Antarctic nakhlites in an oxidizing terrestrial environment.

We note here that the absence of a Ce anomaly in the Y000593 whole rock (Dreibus et al., 2003), despite the presence of large Ce anomalies in several augites and mesostasis, indicates one of two possibilities. The proportion of augites and mesostasis with Ce anomalies are likely to represent a negligible proportion of the total LREE budget, and thus are not expected to perturb the whole rock REE pattern to any significant degree (*i.e.*, outside of 2σ of the analytical uncertainties on the measured whole rock REE composition). Alternatively (or additionally), it is also possible that the REE mobilization that results in the formation of Ce anomalies in these phases occurs only on small length scales (of tens to hundreds of micrometers), such that a bulk sample of several hundreds of milligrams would not be affected by a net loss/gain of REE (other than Ce), and so is not expected to show a Ce anomaly. The latter possibility is supported by the fact that although Ce anomalies are commonly present in pyroxenes of the Antarctic shergottites, their whole rock REE patterns typically never show Ce anomalies (Crozaz *et al.*, 2003).

The V-shaped REE pattern of the olivine in Y000593 (Fig. 2e) is indicative of the addition of LREE to this mineral (which is typically highly LREE-depleted) during terrestrial weathering. It is notable that, thus far, LREE-enrichment resulting from terrestrial alteration in minerals that are typically LREE-depleted (such as pyroxenes and olivines) has not been commonly observed in cold desert meteorites, but is known to occur mainly in the more severely altered hot desert meteorites (Crozaz *et al.*, 2003). This is further indication of the severe weathering that Y000593/Y000749 are likely to have encountered in the Antarctic. Finally, it is possible that the variable degree of LREE-enrichment in the mesostasis of Y000593/000749 (chondrite-normalized La/Yb \sim 6-14) is perhaps due to terrestrial contamination as well.

The preliminary Rb-Sr and Sm-Nd analyses of Y000593 (Shih *et al.*, 2002) also provide some indication of the extent to which terrestrial weathering may have affected these isotopic systematics. It is interesting that, although some of the leachates fall to the right of the ~ 1.3 Ga ⁸⁷Rb-⁸⁷Sr isochron, the unleached and leached whole rocks fall on the isochron. Additionally, all Sm-Nd data points (including leachates as well as unleached and leached whole rocks) fall along the ~ 1.3 Ga ¹⁴⁷Sm-¹⁴³Nd isochron. This may indicate, as also suggested earlier by the lack of Ce anomalies in the Y000593 whole rock, that the length scales of elemental mobilization (particularly for the REE, Rb and Sr) may be restricted to hundreds of micrometers or less, such that bulk samples greater than a few hundreds of milligrams have not suffered any net loss/gain of these elements. Alternatively, it is possible that the effects of weathering in Y000593/Y000749 are highly heterogeneous and that some portions are much more severely weathered than others.

The effects of terrestrial alteration are also pervasive in the two hot desert nakhlites,

NWA 817 and NWA 998. Specifically, the V-shaped REE patterns in all the analyses of olivine grains (2 in NWA 817 and 1 in NWA 998), and in all low-Ca pyroxenes analyses in NWA 998 (6 spots in a single grain) are suggestive of the addition of LREE during secondary alteration in a terrestrial environment. Sr-Nd-Hf-Pb isotopic data have recently been reported for NWA 998 and these also offer clear indications of perturbation resulting from terrestrial weathering (Carlson and Irving, 2004).

Despite the severe terrestrial alteration that appears to have affected the hot and cold desert nakhlites, we emphasize that it is still possible to make robust inferences regarding the parent melt compositions and petrogenetic histories of these martian clinopyroxenites based on the trace element microdistributions since it is possible to identify the particular analyses that have been compromised by such a process. For example, in our estimation of the parent melt compositions (in the following sections), we have used only those augite core compositions that showed no Ce anomalies.

5.4. Parent melt REE compositions and implications for nakhlite petrogenesis on Mars The REE compositions of the parent melts of the nakhlites studied here may be estimated by two independent means. Parent melt compositions can be estimated by inverting the REE compositions of the augite cores using appropriate mineral/melt distribution coefficients. Additionally, the REE compositions of mostly glassy magmatic inclusions within olivines can be used as a proxy for the REE composition of the parent melt (since such inclusions are assumed to be representative of the melt that was trapped in the early formed olivines).

Recently, McKay and coworkers reported REE augite/melt partition coefficients most appropriate for the nakhlites (Oe *et al.*, 2002; G. McKay, pers. comm.). Using these values, we have calculated the REE compositions of the melts in equilibrium with the augite core compositions (given in Tables 1–3) of Y000593/000749, NWA 817 and NWA 998. The estimated compositions of the parent melts of these nakhlites are characterized by LREE-enriched patterns (chondrite normalized La/Sm ~1.4–1.8) that are generally similar to those of their whole rocks (chondrite normalized La/Sm ~1.6–1.9) (Fig. 4). In fact, these REE patterns are also similar to those estimated for the parent melts of the non-desert nakhlites (Wadhwa and Crozaz, 1995).

The REE patterns of the glassy magmatic inclusions in olivines of Y000749, NWA 817 and NWA 998 (chondrite normalized La/Sm ~2.0–2.6; Fig. 4) provide independent evidence that their parent melts are LREE-enriched. It is interesting that the REE abundances estimated in the parent melts by inverting augite core compositions in each of the nakhlites studied here (*i.e.*, La ~11×CI for Y000593/000749, ~66×CI for NWA 817, and ~34×CI for NWA 998) are rather similar to the REE concentrations measured in their magmatic inclusions (La ~16×CI for Y000749, ~59×CI for NWA 817, and ~45×CI for NWA 998). This lends credence to our estimates of the REE compositions (REE patterns as well as absolute abundances) of the parent melts of each of these nakhlites and further suggests that although their LREE-enriched patterns were rather similar (*i.e.*, chondrite normalized La/Sm ~2), their absolute abundances were variable. Thus, it is evident that the parent melt of Y000593/749 had the lowest REE abundances (representing the least evolved composition), whereas that of NWA 817 had the highest (representing the most evolved composition), and the NWA 998 parent melt

had intermediate concentrations of the REE (and was correspondingly evolved to an intermediate degree).

The fact that the REE patterns of the parent melts estimated here mimic those of the whole rocks is significant since it indicates that subsequent to accumulation of the augite and olivine, the intercumulus trapped melt evolved in a predominantly closed system. There are several additional lines of evidence that point towards a closed system evolution of the intercumulus trapped melt in the nakhlites studied here. One of these is the broad similarity between the LREE-enriched patterns of the glassy mesostasis (the composition of which represents that of the intercumulus trapped melt) in Y000593/000749 and NWA 817, and those of their whole rocks (Fig. 4) (as noted in an earlier section, the degree of LREE-enrichment in the mesostasis of Y000593/000749 is variable and somewhat greater than in the whole rock, but terrestrial contamination may be the cause of this). Another line of evidence is provided by the REE composition of the melt estimated to be in equilibrium with apatite. Since this mineral is one of the last formed minerals in the nakhlites, its equilibrium melt composition is expected to be highly evolved. We have inverted the REE composition of the apatite of Y000593 and NWA 998 using appropriate mineral/melt partition coefficients (*i.e.*, same as those used by Wadhwa and Crozaz, 1995, for apatites in Nakhla) and the results are shown in Fig. 4. In the case of these two nakhlites, it is evident that this highly evolved melt composition is also LREE-enriched and has a REE pattern that is again broadly similar to that estimated for the parent melt (from augite core compositions and also from magmatic melt inclusions in olivines). Finally, as can be seen in the plot of Y versus Ti concentrations (Fig. 3), augite cores and rims of each of the nakhlites considered here fall along the same trend, indicative of progressive crystallization of the augite rims from the intercumulus trapped melt in a closed system. Figure 3 also demonstrates that augite compositions in all the known nakhlites define overlapping trends, and this clearly suggests a petrogenetic linkage between the martian clinopyroxenites and is consistent with comagmatism of these rocks.

Therefore, it is clear that each of the nakhlites originated from a parent melt that was LREE-enriched, but was different in terms of its absolute REE abundances from the parent melts of the other nakhlites. More specifically, we have shown that the parent melt of Y000593/000749 had the lowest REE concentrations (comparable to those in the parent melts of Nakhla, Governador Valadares and Lafayette since REE abundances in their augite cores are so similar), while that of NWA 817 had the highest, and that of NWA 998 had intermediate REE abundances. The parent melts of each of the nakhlites may then be related to each other in terms of different degrees of evolution resulting from different amounts of fractionation of augite and olivine from the original melt. Such a scenario would be consistent with comagmatism of all the nakhlites and with previous suggestions that these rocks originated from different horizons within a single lithologic unit on Mars (Harvey and McSween, 1992; Wadhwa and Crozaz, 1995). In fact, one may expect that Y000593/000749 (in having the least evolved REE parent melt composition, along with the three non-desert nakhlites), may have formed deeper in the cumulus pile, NWA 817 towards the top, and NWA 998 at some depth in between. It is interesting that, based on the compositions of olivines in the various nakhlites, it was also suggested that all the nakhlites formed within a single cumulus pile

Mesostasis	Aug	ite	Olivine	Inclusion*
	Core	Rim		
22.4 ± 0.3	0.44 # 0.03	1.30 ± 0.08	0.123 ± 0.009	13.8 ± 0.3
55.2 ± 0.5	2.09 ± 0.08	5.46 ± 0.20	0.258 # 0.013	36.4 ± 0.6
7.10 ± 0.14	0.45 ± 0.03	1.16 ± 0.06	0.022 ± 0.002	4.72 ± 0.18
29.6 ± 0.4	2.52 ± 0.09	6.44 ± 0.19	0.109 ± 0.003	18.6 ± 0.5
6.42 ± 0.29	0.82 ± 0.06	1.86 ± 0.13	0.061 ± 0.004	3.32 ± 0.29
2.06 ± 0.13	0.23 ± 0.01	0.51 ± 0.03	0.017 ± 0.003	1.04 ± 0.10
5.04 ± 0.32	0.75 ± 0.09	1.69 ± 0.21	0.031 ± 0.005	3.48 ± 0.37
0.88 ± 0.07	0.13 ± 0.02	0.33 ± 0.04	0.012 ± 0.001	0.53 ± 0.08
5.17 ± 0.17	0.94 ± 0.05	2.15 ± 0.10	0.083 ± 0.003	3.41 ± 0.21
1.11 ± 0.06	0.20 ± 0.01	0.34 ± 0.03	0.024 ± 0.002	0.74 ± 0.08
3.02 ± 0.12	0.51 ± 0.03	1.23 ± 0.06	0.107 ± 0.003	2.25 ± 0.15
0.39 ± 0.03	0.073 ± 0.007	0.16 ± 0.01	0.025 ± 0.001	0.33 ± 0.04
245 ± 013	0.52 ± 0.04	0.04 + 0.00	0.177 ± 0.007	174 ± 013

Table 2.	Representative	rare	earth	element	concentrations	(in	$\mu g/g$	in	min
	of NWA 817.								

Errors are 1σ from counting statistics only.

$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$		Apatite	Plagioclase	K-Feldspar	hV	gite	Low-Ca Pyroxene	Olivine	Inclusion*
$ \begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$					Core	Rim			
Ce 103 ± 16 1.07 ± 0.06 0.25 ± 0.02 0.80 ± 0.06 1.44 ± 0.06 0.760 ± 0.019 0.007 ± 0.009 27.1 ± 0.7 Pr 101 ± 4 0.12 ± 0.01 0.016 ± 0.002 0.18 ± 0.02 0.113 ± 0.004 0.007 ± 0.0005 3.71 ± 0.2 R 3.39 ± 11 0.33 ± 0.01 0.014 ± 0.006 0.55 ± 0.02 0.141 ± 0.005 0.025 ± 0.007 15.0 ± 0.5 Sm 3.28 ± 5.3 0.033 ± 0.007 0.021 ± 0.006 0.33 ± 0.03 0.094 ± 0.008 0.99 ± 0.103 Gd 41.1 ± 8.1 -0.018 0.30 ± 0.05 0.32 ± 0.03 0.032 ± 0.007 0.033 ± 0.010 $0.26 \pm 0.37 \pm 0.33$ Tb 9.06 ± 1.80 0.41 ± 0.06 0.30 ± 0.016 0.28 ± 0.01 0.019 ± 0.003 0.99 ± 0.13 Tb 9.06 ± 1.80 0.41 ± 0.06 0.30 ± 0.016 0.28 ± 0.010 0.0055 0.33 ± 0.01 0.099 ± 0.03 0.999 ± 0.010 0.25 ± 0.02 0.33 ± 0.01 0.019 ± 0.003 0.019 ± 0.001 0.0055 0.32 ± 0.02 0.33 ± 0.010 0.019 ± 0.003	La	414 ± 9	0.71 ± 0.05	0.24 ± 0.03	0.23 ± 0.02	0.29 ± 0.02	0.461 ± 0.008	0.0023 ± 0.0006	10.5 ± 0.4
$ \begin{array}{llllllllllllllllllllllllllllllllllll$	Ce	1003 ± 16	1.07 ± 0.06	0.25 ± 0.02	0.80 ± 0.06	1.44 ± 0.06	0.760 ± 0.019	0.007 ± 0.0009	27.1 ± 0.7
Nd 399 ± 11 0.33 ± 0.02 0.044 ± 0.006 0.95 ± 0.05 1.56 ± 0.06 0.438 ± 0.010 0.0025 ± 0.007 150 ± 0.5 Sm 52.8 ± 5.3 0.033 ± 0.007 0.021 ± 0.006 0.33 ± 0.03 0.43 ± 0.04 0.094 ± 0.008 <0.005 3.27 ± 0.37 Gd 41.1 ± 8.1 0.44 ± 0.06 0.30 ± 0.15 0.082 ± 0.007 0.13 ± 0.01 0.019 ± 0.003 <0.0068 0.99 ± 0.17 Tb 9.06 ± 1.80 0.44 ± 0.06 0.30 ± 0.004 0.28 ± 0.05 0.47 ± 0.00 0.019 ± 0.003 0.005 ± 0.010 $2.66\pm0.34\pm0.010$ Tb 9.06 ± 1.80 0.41 0.01 0.018 ± 0.009 0.005 ± 0.010 0.025 ± 0.010 0.99 ± 0.17 Dy 27.6 ± 2.6 0.41 0.01 0.025 ± 0.010 0.021 ± 0.009 0.005 ± 0.010 0.021 ± 0.000 0.003 ± 0.0005 0.38 ± 0.07 Th 0.25 ± 0.17 0.1 0.1 0.06 ± 0.007 0.12 ± 0.01 0.021 ± 0.000 0.031 ± 0.002 0.33 ± 0.005 0.15 ± 0.01 0.52 ± 0.01 Th 1.45 ± 0.26 0.141 ± 0.006 0.070 ± 0.001 0.16 ± 0.00 Th 1.45 ± 0.26 0.1 0.10 ± 0.01 0.25 ± 0.002 0.114 ± 0.006 0.070 ± 0.001 0.15 ± 0.01 0.15 ± 0.01 Th 1.45 ± 0.26 0.15 ± 0.01 0.15 ± 0.001 0.15 ± 0.001 0.15 ± 0.001 0.15 ± 0.001 0.15 ± 0.001 0.15 ± 0.001 0.15 ± 0.001 Th 1.45 ± 0.26 0.05 ± 0.002 0.075 ± 0.001 0.15 ± 0.001 0.005 ± 0.002 0.005 ± 0.002 0.005 ± 0.002 0.005 ± 0.002 0.005 ± 0.002 0.005 ± 0.002 0.005 ± 0.001 0.005 ± 0.000 0.005 ± 0.000 0.005 ± 0.000 0.005 ± 0.000 0.002 ± 0.000 0.002 ± 0.000 0.005 ± 0.000 0.005 ± 0.000 0.005 ± 0.000 0.005 ± 0.000 0.005 ± 0.000 0.005 ± 0.000 0.000 ± 0.000 0.000 ± 0.0000	Ρr	101 ± 4	0.12 ± 0.01	0.016 ± 0.002	0.18 ± 0.02	0.27 ± 0.02	0.113 ± 0.004	0.0005 ± 0.0002	3.71 ± 0.22
$ \begin{array}{llllllllllllllllllllllllllllllllllll$	ΡN	399 ± 11	0.33 ± 0.02	0.044 ± 0.006	0.95 ± 0.05	1.56 ± 0.06	0.438 ± 0.010	0.0025 ± 0.0007	15.0 ± 0.5
$ \begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	Sm	52.8 ± 5.3	0.033 ± 0.007	0.021 ± 0.006	0.33 ± 0.03	0.43 ± 0.04	0.094 ± 0.008	<.0005	3.27 ± 0.32
Gd 41.1 ± 8.1 <0.018 0.008 ± 0.004 0.28 ± 0.05 0.47 ± 0.05 0.087 ± 0.009 0.0054 ± 0.010 2.66 ± 0.33 Tb 9.06 ± 1.80 n.d. n.d. 0.051 ± 0.009 0.097 ± 0.010 0.021 ± 0.002 0.338 ± 0.005 0.38 ± 0.002 0.101 ± 0.001 0.46 ± 0.00 Ho 5.29 ± 0.73 n.d. n.d. 0.355 ± 0.01 0.12 ± 0.01 0.355 ± 0.02 0.011 ± 0.001 0.46 ± 0.00 Tir 10.22 ± 0.01 0.12 ± 0.01 0.25 \pm 0.02 0.11 ± 0.001 0.15 ± 0.001 0.15 ± 0.001 0.15 ± 0.001 0.15 ± 0.001 0.15 ± 0.001 0.15 ± 0.001 0.15 ± 0.001 0.15 ± 0.001 0.15 ± 0.001 0.15 ± 0.001 0.15 ± 0.001 0.15 ± 0.001 0.15 ± 0.001 0.15	Б	8.43 ± 0.84	0.44 ± 0.06	0.30 ± 0.15	0.082 ± 0.007	0.13 ± 0.01	0.019 ± 0.003	<0.0008	0.99 ± 0.17
Tb 9.06 ±1.80 n.d. 0.051 ±0.009 0.097 ±0.010 0.021 ±0.002 0.0030 ±0.0065 0.38 ±0.0 Dy 27.6 ±2.6 n.d. n.d. 0.39 ±0.03 0.50 ±0.065 0.31 ±0.002 2.26 ±0.1 Ho 5.29 ±0.73 n.d. n.d. 0.39 ±0.07 0.12 ±0.01 0.031 ±0.002 2.26 ±0.1 Ho 5.29 ±0.73 n.d. n.d. 0.060 ±0.007 0.12 ±0.01 0.033 ±0.003 0.031 ±0.001 0.46 ±0.00 Fr 10.2 ±1.4 n.d. n.d. 0.106 ±0.001 0.12 ±0.01 0.25 ±0.02 0.070 ±0.004 1.06 ±0.00 Tm 1.45 ±0.26 n.d. n.d. 0.026 ±0.003 0.026 ±0.004 0.15 ±0.001 0.15 ±0.001 0.15 ±0.001 0.15 ±0.001 0.15 ±0.006 0.59 ±0.005	Gd	41.1 ± 8.1	<0.018	0.008 ± 0.004	0.28 ± 0.05	0.47 ± 0.05	0.087 ± 0.009	0.0054 ± 0.0010	2.66 ± 0.39
Dy 27.6 ± 2.6 n.d. n.d. 0.39 ± 0.03 0.50 ± 0.03 0.152 ± 0.006 0.031 ± 0.002 2.26 ± 0.17 Ho 5.29 ± 0.73 n.d. n.d. 0.066 ± 0.007 0.12 ± 0.01 0.033 ± 0.003 0.011 ± 0.001 0.46 ± 0.00 Er 10.2 ± 1.4 n.d. n.d. 0.056 ± 0.007 0.12 ± 0.01 0.070 ± 0.001 0.46 ± 0.00 Tm 1.45 ± 0.26 n.d. n.d. 0.19 ± 0.01 0.25 ± 0.02 0.141 ± 0.006 0.070 ± 0.004 1.06 ± 0.00 Tm 1.45 ± 0.26 n.d. n.d. 0.026 ± 0.003 0.029 ± 0.004 0.025 ± 0.001 0.15 ± 0.001 0.15 ± 0.001 0.15 ± 0.006 0.59 ± 0.005 Yb 4.66 ± 1.16 n.d. n.d. 0.17 ± 0.02 0.26 ± 0.006 0.59 ± 0.06 0.59 ± 0.06	ЧЪ	9.06 ± 1.80	n.d.	n.d.	0.051 ± 0.009	0.097 ± 0.010	0.021 ± 0.002	0.0030 ± 0.0005	0.38 ± 0.07
Ho 5.29 ± 0.73 n.d. n.d. 0.066 ± 0.007 0.12 ± 0.01 0.033 ± 0.003 0.011 ± 0.001 0.46 ± 0.01 Er 10.2 ± 1.4 n.d. n.d. 0.19 ± 0.01 0.25 ± 0.02 0.141 ± 0.006 0.070 ± 0.004 1.06 ± 0.04 Tm 1.45 ± 0.26 n.d. n.d. 0.026 ± 0.003 0.025 ± 0.004 0.025 ± 0.001 0.15 ± 0.001 0.15 ± 0.001 0.15 ± 0.001 0.15 ± 0.001 0.15 ± 0.001 0.15 ± 0.001 0.15 ± 0.001 0.15 ± 0.001 0.15 ± 0.001 0.15 ± 0.001 0.15 ± 0.001 0.15 ± 0.001 0.15 ± 0.001 0.15 ± 0.005 0.59 ± 0.001 0.15 ± 0.005 0.59 ± 0.005 0.50 ± 0.005	Dy	27.6 ± 2.6	n.d.	n.d.	0.39 ± 0.03	0.50 ± 0.03	0.152 ± 0.006	0.031 ± 0.002	2.26 ± 0.17
Er 10.2 ±1.4 n.d. n.d. 0.19 ±0.01 0.25 ±0.02 0.141 ±0.006 0.070 ±0.004 1.06 ±0.04 Tm 1.45 ±0.26 n.d. n.d. 0.026 ±0.003 0.029 ±0.004 0.020 ±0.001 0.15 ±0.01 Yb 4.66 ±1.16 n.d. n.d. 0.17 ±0.02 0.26 ±0.006 0.59 ±0.006 0.59 ±0.00	Ю	5.29 ± 0.73	n.d.	n.d.	0.060 ± 0.007	0.12 ± 0.01	0.033 ± 0.003	0.011 ± 0.001	0.46 ± 0.06
Tim 1.45 ± 0.26 n.d. n.d. 0.026 ± 0.003 0.029 ± 0.004 0.020 ± 0.002 0.015 ± 0.001 0.15 ± 0.01 Yb 4.66 ± 1.16 n.d. n.d. 0.17 ± 0.02 0.26 ± 0.008 0.178 ± 0.008 0.156 ± 0.006 0.59 ± 0.01	Ē	10.2 ± 1.4	n.d.	n.d.	0.19 ± 0.01	0.25 ± 0.02	0.141 ± 0.006	0.070 ± 0.004	1.06 ± 0.09
Yb 4.66±1.16 n.d. n.d. 0.17±0.02 0.26±0.02 0.178±0.08 0.156±0.06 0.59±0.03	Πm	1.45 ± 0.26	n.d.	n.d.	0.026 ± 0.003	0.029 ± 0.004	0.020 ± 0.002	0.015 ± 0.001	0.15 ± 0.03
	Yb	4.66 ± 1.16	n.d.	n.d.	0.17 ± 0.02	0.26 ± 0.02	0.178 ± 0.008	0.156 ± 0.006	0.59 ± 0.08

Errors are 1 σ from counting statistics only; upper limits are 2σ (n.d. = not detected, and no upper limits could be estimated).



Fig. 4. Estimated REE compositions of the melts in equilibrium with augite cores (thick dashed lines) and apatite (thin dashed lines) of (a) Y000593/000749, (b) NWA 817 and (c) NWA 998, normalized to the CI chondrite values of Anders and Grevesse (1989). REE compositions of magmatic melt inclusions in olivine and in the glassy mesostasis are shown as solid and open circles, respectively. Whole rock REE compositions of Y000593 (Dreibus et al., 2003) and NWA 817 (Sautter et al., 2002) are shown as solid gray lines. The whole rock REE composition of NWA 998 has not yet been reported. in which the burial depths of Nakhla and NWA 817 are \sim 4–5 m and \sim 0.5 m respectively, and that of the Yamato nakhlites is intermediate between these (Mikouchi and Miyamoto, 1998, 2002; Mikouchi *et al.*, 2003). It was also suggested that the abundance of the mesostasis and its crystallinity may be related to the depth within the cooling cumulus pile. Our results are generally consistent with this picture, although our data indicate that the Yamato nakhlites may be closer to Nakhla in terms of their depth of formation within the cumulus pile.

5.5. Magmatic redox conditions and implications for the martian mantle

Based on the compositions of Fe-Ti oxides, it has been estimated that Nakhla and Lafayette were formed under relatively oxidizing conditions (Reid and Bunch, 1975). Magmatic redox conditions for the nakhlites may also be estimated through the partitioning behavior of Eu in their augites. The Eu oxybarometer has been applied successfully to shergottite pyroxenes (Wadhwa, 2001) and offers several advantages over the oxybarometer based on Fe-Ti oxide compositions. Pyroxenes in the martian meteorites are among the earliest formed minerals and they have been shown to have preserved their original magmatic REE zonation (e.g., Wadhwa et al., 1994; Wadhwa and Crozaz, 1995; this work). Therefore, it is expected that Eu distributions in this mineral have remained pristine since their original crystallization. In contrast, the Fe-Ti oxides are one of the last minerals to form in these meteorites and are additionally prone to subsolidus equilibration. The application of the Eu oxybarometer to nakhlite augites, however, requires that the partitioning of Eu in augites with compositions similar to those in the nakhlites be calibrated for a range of fO_2 conditions. So far, the only REE partitioning experiments relevant to the nakhlites have been conducted at ~QFM (e.g., Oe et al., 2002). Therefore, although there is insufficient experimental partitioning data at the current time to rigorously quantify the magmatic redox conditions for the nakhlites investigated here, we can constrain whether their magmatic redox conditions were more or less oxidizing than ~QFM.

Using a methodology similar to that of Wadhwa (2001), and the augite core compositions from Tables 1–3, we estimate that the D_{Eu}/D_{Gd} ratio (where D_{Eu} and D_{Gd} are the augite/melt partition coefficients for Eu and Gd, respectively) for augite cores in Y000593/000749 and NWA 817 is ~1.0. For this calculation, we assumed Eu/Gd ratios in their parent melts to be similar to those in their whole rocks (Dreibus et al., 2003; Sautter et al., 2002), since we have already demonstrated in the previous section the parallelism of the REE patterns of the nakhlite parent melts and their whole rocks. Whole rock REE concentrations for NWA 998 have not yet been reported, so we have assumed the Eu/Gd ratio in its parent melt to be similar to the average Eu/Gd ratio of the Nakhla, Y000593, and NWA 817 whole rocks (Nakamura et al., 1982; Sautter et al., 2002; Dreibus et al., 2003). With this assumption, we obtained a D_{Eu}/D_{Gd} value for NWA 998 augite of ~0.9. Moreover, using the augite core compositions of Nakhla, Governador Valadares and Lafayette (Wadhwa and Crozaz, 1995), and assuming parent melt Eu/Gd ratios to be similar to that in the Nakhla whole rock (Nakamura et al., 1982), we estimated D_{Eu}/D_{Gd} values of ~0.8-1.2 for these three nakhlites. In comparison, the D_{Eu}/D_{Gd} value for nakhlite augites determined from experiments conducted at ~QFM is ~1.1 (Oe et al., 2002; G. McKay, pers. comm.). Therefore, this implies that the magmatic redox conditions for all known nakhlites were close to ~QFM, and thus relatively oxidizing.

It follows from the above discussion that all known nakhlites are likely to have originated from a relatively oxidized source reservoir in the martian mantle. This situation is quite distinct from that of the basaltic shergottites, which record highly variable magmatic redox conditions (Wadhwa, 2001; Herd et al., 2002). Specifically, the variations of the magmatic redox conditions for the basaltic shergottites with their initial Nd and Sr isotopic systematics indicate that the parent melts of the basaltic shergottites originated from a highly reduced (~IW), depleted source in the martian mantle and interacted to different degrees with an enriched reservoir (in the martian mantle or crust) that was highly oxidized (>QFM). In the case of the nakhlites, the initial ¹⁴³Nd/¹⁴⁴Nd and ⁸⁷Sr/⁸⁶Sr ratios also indicate a depleted mantle source (Nakamura et al., 1982; Shih et al., 1999, 2002; Carlson and Irving, 2004). However, it is clear that the characteristics of this depleted mantle source require it to be distinct from the depleted mantle source from which the basaltic shergottites (such as QUE 94201) originated. In particular, as discussed above, the nakhlite source mantle is likely to be relatively oxidized (~QFM). Moreover, this mantle source is distinctive in having large ¹⁴²Nd (daughter product of ¹⁴⁶Sm; $t_{1/2}$ ~103 Ma) as well as ¹⁸²W (daughter product of ¹⁸²Hf; $t_{1/2}$ ~9 Ma) anomalies (Harper *et al.*, 1995; Lee and Halliday, 1997; Foley et al., 2004). It has been suggested that these isotopic characteristics are the result of coupled fractionation of Sm-Nd and Hf-W following early core formation and most likely during early silicate differentiation, while ¹⁴⁶Sm and ¹⁸²Hf were still extant, so that the nakhlite source was likely established on Mars well within ~50 Ma of solar system formation (Halliday et al., 2001; Foley et al., 2004). In contrast, Sm-Nd and Hf-W systematics in the basaltic shergottites are quite different from the nakhlites and, indicate that the shergottite source was established close to ~4.513 Ga, while ¹⁴⁶Sm was alive, but ¹⁸²Hf was largely extinct (Borg et al., 2003; Foley et al., 2004). The preservation of these distinct isotopic signatures in the mantle sources of the shergottites and nakhlites clearly indicates that the martian mantle is heterogeneous and has not undergone global convective mixing subsequent to the earliest phases of silicate differentiation that established the source reservoirs of the martian meteorites.

Finally, it is necessary to reconcile the fact that while the nakhlite parent melts are estimated to be LREE-enriched, their mantle source is required by its isotopic systematics to be characterized by a long term LREE-depletion. As noted by Longhi (1991), a LREE-rich partial melt may be derived from a LREE-depleted source through low degrees of partial melting, but such a scenario is at odds with the estimated major element composition of the nakhlite parent melts (which require higher degrees of partial melting). Borg *et al.* (2003) showed that the composition and source of the LREE-enriched component in the nakhlite source could be estimated using binary mixing calculations involving mixing of a LREE-depleted source (similar to the source of the shergottite QUE94201) with a LREE-enriched component prior to 1.3 Ga (*i.e.*, the crystallization age of the nakhlites). In such a scenario, the LREE-enriched component is required to originate from an ancient LREE-depleted source. Therefore, it is suggested that late metasomatism of the LREE-depleted source with LREE-enriched fluids or melts (derived from an ancient depleted mantle source) may be able

to reconcile the trace element and isotopic systematics in the nakhlites. We further suggest that metasomatism may also be responsible for the oxidation of the depleted nakhlite source.

6. Summary and conclusions

The following is a summary of the major findings resulting from our ion microprobe investigation of trace element abundances in various phases of the newly recovered Antarctic nakhlites, Y000593 and Y000749, and two other nakhlites from the Saharan desert, NWA 817 and NWA 998:

1) Comparison of trace element microdistributions in the two Antarctic nakhlites, Y000593 and Y000749, supports earlier suggestions that these two samples are paired. These paired Antarctic (cold desert) nakhlites as well as the two hot desert nakhlites show clear evidence of weathering in a terrestrial environment, such as the presence of Ce anomalies in augites and mesostasis and LREE-enrichment in olivines and low-Ca pyroxenes.

2) Distributions of trace elements in various phases of Y000593/000749, NWA 817 and NWA 998 demonstrate that there is greater variability among the nakhlites than had been previously recognized based on the three non-desert nakhlites (Nakhla, Governador Valadares and Lafayette). Nevertheless, there are still enough similarities to suggest that all the nakhlites are comagmatic and likely to have formed within a single lithologic unit on Mars. In this scenario, the noted variability may be the result of the differences in their formation environments (such as depth of formation in the cumulus pile) and, consequently, the degrees of evolution of their parent melts (which may be related to each other by differing degrees of augite/olivine fractionation).

3) We have estimated the REE compositions of the parent melts of Y000593/ 000749, NWA 817 and NWA 998. Like the parent melt compositions estimated for the non-desert nakhlites, these are LREE-enriched and have REE patterns parallel to those of their whole rocks. This (along with the REE distributions in the augites and mesostasis) indicates that subsequent to accumulation of augite and olivine, the intercumulus trapped melt in these nakhlites evolved in a closed system. Among the nakhlites studied here, the parent melt of Y000593/000749 is least evolved in terms of its REE abundances, that of NWA 817 is most evolved, and that of NWA 998 is intermediate between these two. This sequence of evolution may be consistent with their relative depths of formation in a cumulus pile.

4) Based on the partitioning of Eu in augites of nakhlites, we have estimated that magmatic redox conditions were relatively oxidizing (\sim QFM). It is suggested that the trace element composition, isotopic systematics, and degree of oxidation inferred for the nakhlite source reservoir in the martian mantle may be accounted for by late metasomatism of this source by LREE-enriched, oxidizing fluids.

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