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Large-ion lithophile element fractionation during the early differentiation of Mars and the composition of the martian primitive mantle

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Abstract–Basaltic shergottites display a systematic decrease in K/Th, K/U, and K/La ratios with increasing K content. These trends are interpreted as mixing lines between relatively young martian magmas derived from highly depleted mantle sources and an ancient large-ion lithophile (LIL) element-enriched crustal component. One implication of this is that a substantial fractionation of these ratios occurs during the early crustal differentiation on Mars. Isotopic evidence from SNC meteorites and compositional data from Pathfinder and orbital gamma ray spectroscopy suggest that in excess of 50% of the LIL element complement of Mars resides in the crustal reservoir. If so, the primitive mantle of Mars is significantly more volatile-depleted (i.e., lower K/Th, K/U, K/La) than previously thought but probably (though not necessarily) still less volatile-depleted than the primitive mantle of the Earth. The La/Th ratios of virtually all SNC meteorites are subchondritic, including those with the most severe LREE-depletion. Extrapolation of the basaltic shergottite trend suggests that both the depleted mantle end member and the enriched crustal end member have subchondritic La/Th ratios. This is in contrast with the Earth where basalts from LIL element-depleted sources such as MORB have superchondritic La/Th ratios, complementary to the subchondritic ratios of the continental crust. Accordingly, assuming that the refractory elements are in chondritic proportions for the Mars primitive mantle, an additional major geochemical reservoir must exist on Mars that may not yet have been sampled.

INTRODUCTION

Among the most important constraints on the formation, composition, and evolution of terrestrial planets are the ratios of moderately volatile large-ion lithophile (LIL) elements, such as K, Rb, and Cs, and refractory LIL elements, such as Th, U, and the largest rare earth elements, notably La (see Taylor [2001] for recent review). These LIL elements are typically highly incompatible ($D \ll 1$) during the partial melting of planetary mantles and, thus, ratios such as K/U, K/Th, K/La, Rb/La, and so forth should change relatively little during magmatic differentiation. Ratios measured in exposed igneous rocks across a broad compositional range are typically rather uniform and, thus, thought to be representative of the overall planetary values (Fig. 1). Accordingly, variations in these ratios between planets and certain other solar system objects (meteorites, comets, etc.) are thought largely to reflect the degree of depletion of moderately volatile elements and, thus, provide important information about the conditions and processes of planetary accretion and early evolution.

Most of the direct information regarding the composition of the martian primitive mantle comes from the SNC meteorites that generally are accepted to have originated from Mars (e.g., McSween 1985, 2002; McSween and Treiman 1998; Treiman et al. 2000). Wänke and coworkers have evaluated the SNC geochemical data thoroughly (e.g., Dreibus and Wänke 1985; Wänke and Dreibus 1988; Wänke 1991; Halliday et al. 2001) and have concluded that Mars is a volatile-rich planet with the ratio of moderately volatile elements to refractory elements being about a factor of 2 greater than the Earth. These results are also consistent with the U-Pb and Rb-Sr isotope systematics of SNC meteorites that suggest a Pb-rich and Rb-rich primitive mantle for Mars (Chen and Wasserburg 1986; Jagoutz 1991; Dreibus and Jagoutz 2002).

A number of relatively recent developments suggest that various aspects of the models for the chemical composition of the martian primitive mantle should be re-evaluated. The first is the evidence from the Mars Pathfinder mission for a well-constrained moment of inertia factor of 0.3662 ± 0.0017 for Mars (Folkner et al. 1997). The Mars bulk compositional

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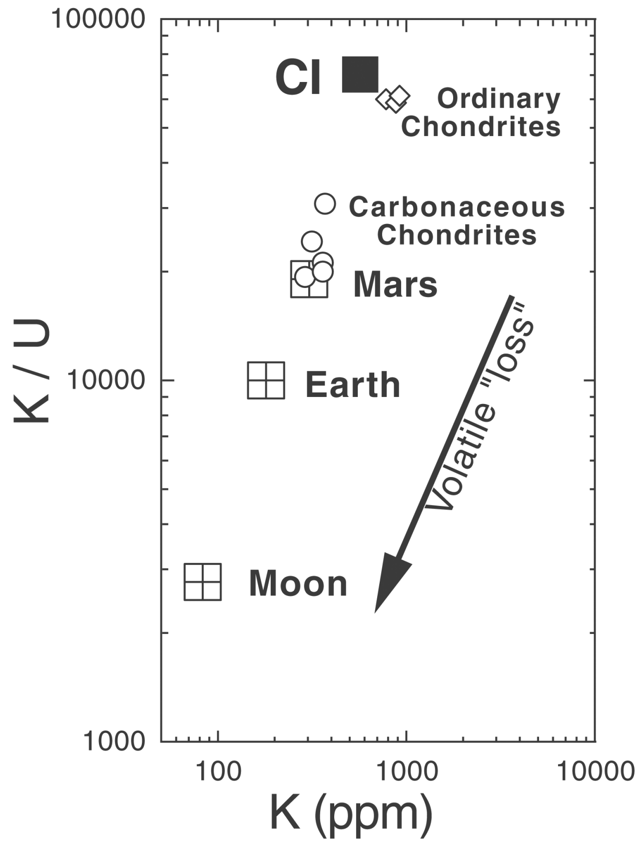

Fig. 1. Plot of K/U versus K abundances for various chondritic meteorites and previously proposed primitive mantle compositions for Earth, the moon, and Mars. The decrease of the K/U ratio results from loss of moderately volatile elements before or during accretion of the planets. The average compositions of chondritic meteorites are from Lodders and Fegley (1998).

models of Wänke and coworkers' earlier studies (e.g., Dreibus and Wänke 1985; Wänke and Dreibus 1988; Wänke 1991) assumed chondritic proportions of all refractory elements, including Fe and Si, for the entire planet (i.e., including the core). However, a moment of inertia factor of 0.3662 is inconsistent with chondritic Fe abundances and an Fe/Si ratio (Bertka and Fei 1998a, b; Spohn et al. 2001). A complete discussion of the implications of the moment of inertia factor value for the bulk composition of Mars can be found in Bertka and Fei (1998b; also see Halliday et al. [2001] for explanations of a lower Fe content of Mars).

The second development is the recent spate of new SNC meteorite finds, especially of basaltic shergottites (e.g., Dreibus et al. 2000, 2002; Folco et al. 2000; Rubin et al. 2000: Zipfel et al. 2000; Barrat et al. 2001a, b, 2002a, b; Jambon et al. 2001; Taylor et al. 2002) that, among the SNC meteorites, are most likely to be representative of the mantle of Mars. This increased sampling expands the compositional range of this meteorite group and makes it more likely that systematic geochemical behavior can be identified. The third factor is the inference, from Pathfinder geochemical data, orbital gamma ray spectroscopy, and isotopic data for SNC meteorites, that a very large fraction of the LIL element complement of Mars was transferred into the crust shortly after planetary accretion (see further discussion below). One implication of this is that a full understanding of the composition of the martian primitive mantle likely requires a reasonable appreciation of the composition of the martian crust—to a degree even greater than for Earth. Consequently, the purpose of this paper is to examine the relationships among moderately volatile and refractory LIL elements in SNC meteorites and evaluate how any systematic variations might influence models for the composition of the primitive mantle of Mars.

SNC METEORITE DATA

For the purposes of this study, SNC meteorites have been divided into "basaltic shergottites," "lherzolitic shergottites," and "other SNC meteorites" that include various ultramafic lithologies, including the nakhlites. Basaltic shergottites generally appear to represent lavas that erupted onto the surface of Mars while the ultramafic (mostly cumulate) SNC meteorites crystallized at depth (e.g., Nyquist et al. 2001). Although ultramafic cumulates are likely to provide some important information about their sources, the basaltic shergottites are far more likely to provide relatively unambiguous information about their mantle sources.

The basaltic shergottites for which appropriate chemical data are available include Shergotty, Zagami, EETA79001A, EETA79001B, QUE 94201, Los Angeles, Dhofar 019, Dhofar 378, Dar al Gani (DaG 476 and DaG 489 are likely to be from the same fall [Folco et al. 2000] and are considered here as one analysis), SaU 005, NWA 856 (Djel Ibone), NWA 480, and NWA 1068. Lherzolitic shergottites include ALHA77005, LEW 88516 and Y-793605. Other SNC meteorites for which appropriate chemical data are available include the nakhlites Nakhla, Lafayette, Governador Valadares, and NWA 817, the orthopyroxenite ALH 84001, and Chassigny (dunite).

The compositions adopted in this study for SNC meteorites for which multiple chemical analyses are available are based on averages of high precision data obtained from the compilations provided by Meyer (2002). Other data sources included Dreibus et al. (2000, 2002) for SaU 005 and Dhofar 378, Folco et al. (2000) and Zipfel et al. (2000) for Dar al Gani, Rubin et al. (2000) for Los Angeles, Barrat et al. (2001a, b) for NWA 480 and Dar al Gani, Jambon et al. (2001) for NWA 856, and Taylor et al. (2002) for Dhofar 019.

An important but rarely discussed consideration is the generally poor reproducibility of SNC meteorite data. For some samples where multiple analyses are available (e.g., Shergotty, Nakhla, ALH 84001), variations in critical trace elements, such as La, by as much as a factor of 2 are not uncommon (see compilation in Meyer 2002). Although some of this discrepancy may be due to analytical error, the relatively coarse grained nature of many of the SNC meteorites and the common presence of trace element-enriched phosphatic phases, coupled with the small amounts of sample typically available for analysis, are also likely to be significant factors. For this study, a "best estimate" of the average composition of each meteorite was made where multiple analyses were available, but in cases where very few or only one analysis was available, appropriate caution is warranted.

CRUSTAL COMPOSITION AND EVOLUTION ON MARS

Although the detailed radiogenic isotope systematics and age relationships of SNC meteorites are complex, some type of LIL element-enriched reservoir (likely a crustal reservoir) is generally agreed to have separated from the martian primitive mantle very early in the planet's history. The exact age of this differentiation event(s?) is unclear but is well in excess of 4.0 Ga (e.g., Chen and Wasserburg 1986; Jagoutz 1991; Harper et al. 1995; Blichert-Toft et al. 1999; Brandon et al. 2000; Halliday et al. 2001; Nyquist et al. 2001; Dreibus and Jagoutz 2002). Although crust formation continued after this date (for example, most SNC meteorites have crystallization ages <1.5 Ga), the mean age of the martian crust is probably approaching twice the mean age of the terrestrial continental crust and 4 times the mean age of the overall terrestrial crust (e.g., Jacobsen and Yin 2002; Hauck and Phillips 2002).

Available geochemical data for the surface of Mars are also consistent with a LIL element-enriched crust. Soils and rocks at the Pathfinder site are characterized by surprisingly high potassium contents (Rieder et al. 1997; Brückner et al. 2001; Foley et al. 2001). In addition, orbital gamma ray spectroscopy (GRS) from the Phobos-2 mission suggests relatively high K, Th, and U abundances in surficial deposits preserved at equatorial latitudes (Surkov et al. 1994). In compiling the available data, McLennan (2001) concluded that, on average, the exposed portion of the martian crust contained approximately 5,000 ppm K and that a similar composition may also be applicable to the bulk crust. Preliminary GRS data from Mars Odyssey appear to confirm these high levels of K and Th in exposed martian crust (Taylor et al. 2003).

The degree to which LIL elements are enriched in the crust depends on both crust/mantle compositions and the relative mass of the "enriched" crust. Recent geophysical measurements from the Mars Global Surveyor mission have led to estimates of crustal thickness in the range of about 30–100 km, likely averaging about 50 km (e.g., Zuber et al. 2000; Nimmo and Stevenson 2001; Turcotte et al. 2001). A crust this thick amounts to slightly more than 3% of the mass of the planet and about 4.5% of the mass of the primitive mantle. Although the fraction of this crust that is LIL-enriched is not known with certainty, the crustal composition given by McLennan (2001) would suggest that on the order of 50% or more of the LIL element of Mars reside in the crust.

Such a large degree of crustal enrichment of LIL elements is also consistent with modeling of REE/Nd-isotope systematics in SNC meteorites (Norman 1999, 2002). Many of the SNC meteorites, and notably most basaltic and lherzolitic shergottites, are characterized by severe LREE-depletion, indicating derivation from a highly depleted mantle (Fig. 2). In general, a relationship exists between the degree of LREE-depletion, REE abundances, and Nd-isotopic composition. Norman (1999, 2002) modeled the REE/Nd-isotope characteristics of shergottites as a mix between a highly depleted mantle and a LREE-enriched crustal component. If one of the most LREE-depleted samples (e.g., QUE 94201) is assumed to be representative of the depleted mantle end member, some constraints can be placed on the REE composition of the martian crust. The most recent calculations by Norman (2002) suggest a LREE-enriched crustal reservoir containing as much as 70% of the planet's complement of Nd.

In fact, such estimates are likely to have large uncertainties. Although REE patterns of basaltic shergottites clearly indicate that they are derived from a highly depleted mantle, no reason necessarily exists to accept that the most depleted sample is characteristic of the average composition of that depleted end member. Local effects, such as the degree of partial melting, complex magmatic history, pressure and temperature effects on bulk distribution coefficients and mineral stabilities, and so forth, could all result in any given sample being more depleted in LREE than the average mantle sources. Nevertheless, the modeling carried out by Norman (1999, 2002) is clearly consistent with other calculations that suggest that 50% or more of the LIL complement of the martian primitive mantle has been sequestered into the crust of the planet.

In summary, basaltic shergottites sample a highly depleted mantle with variable amounts of assimilation of an LREE-enriched martian crust. On average, the crust of Mars appears to be LIL element-enriched and likely contains 50% or more of the planet's complement of elements such as K, Th, U, Cs, and Rb. The differentiation of this LIL element-enriched crust largely took place very early in Mars' geological history, in contrast to the crust of Earth, and, thus, possibly by processes that differ from typical crust-forming processes on Earth.

LARGE ION LITHOPHILE ELEMENT RELATIONSHIPS IN SNC METEORITES

Models of the Bulk Composition of the Primitive Mantle of Mars

A number of models have been proposed for the composition of the primitive mantle of Mars (e.g., Morgan and

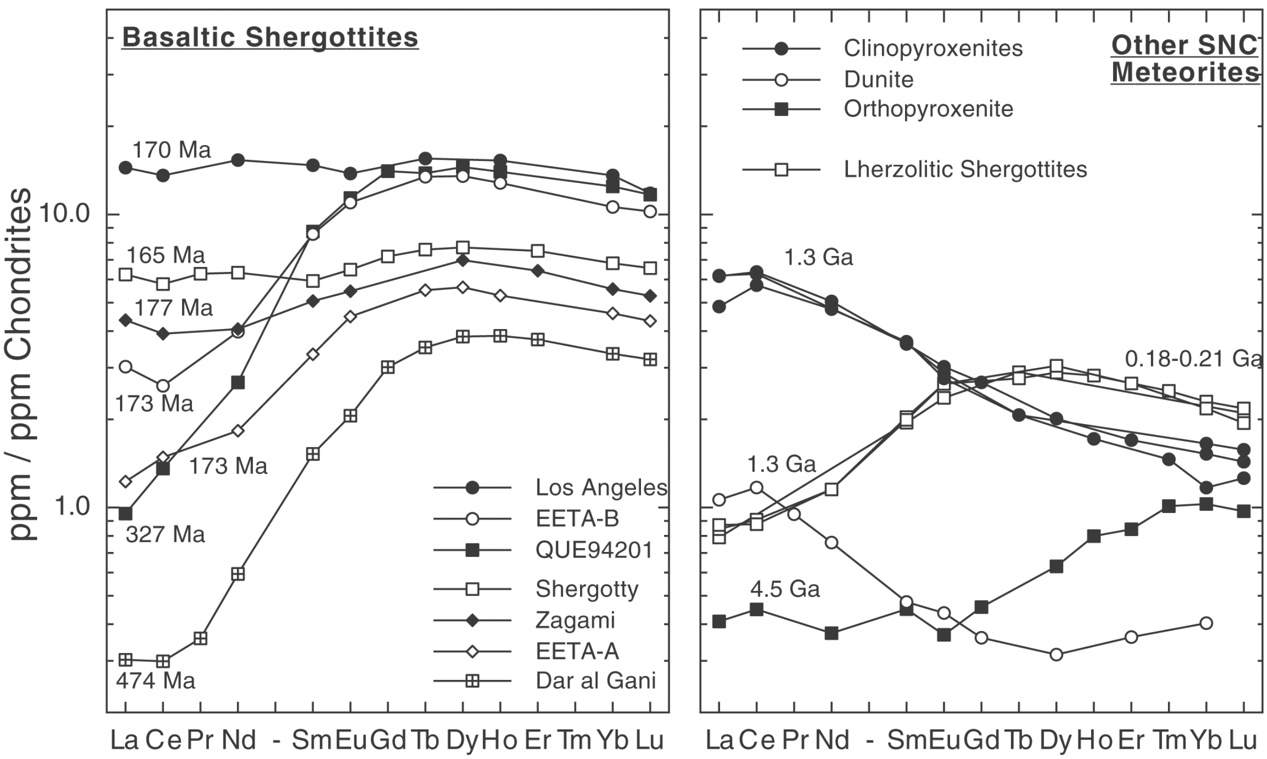

Fig. 2. Chondrite-normalized REE plots of selected SNC meteorites (see text for data sources). The estimates of the crystallization ages are from a compilation in Nyquist et al. (2001). Basaltic shergottites and lherzolitic shergottites are characterized by young ages and highly variable degrees of LREE-depletion and total REE abundances. Variations in LREE-depletion are thought to be related to variable degrees of crustal contamination during eruption (e.g., Norman 1999, 2002). The 1.3 Ga nakhlites (clinopyroxenites) and Chassigny (dunite) are the only SNC meteorites that are characterized by LREE enrichment.

Anders 1979; Wänke and Dreibus 1988; Lodders and Fegley 1997; Sanloup et al. 1999; Lodders 2000). The model of Morgan and Anders (1979) was developed before the martian origin of SNC meteorites was appreciated. This model adopted an extremely low ratio of moderately volatile to refractory elements based on the single Mars-5 orbital gamma ray spectrometric analysis that suggested very low K/U (3,000) and K/Th (600) ratios for the martian surface. In sharp contrast, the composition of Lodders and Fegley (1997) is characterized by very high K/U (>50,000) because it assumes a volatile depletion pattern for the moderately volatile lithophile elements (K, Rb, Na, etc.) that is similar to H and CV chondrites (also see Lodders [2000] and Sanloup et al. [1999]).

By far, the most influential model for the composition of the martian primitive mantle is that of Wänke and coworkers (e.g., Dreibus and Wänke 1985; Wänke and Dreibus 1988; Wänke 1991; Halliday et al. 2001) based on the geochemistry of SNC meteorites and basic principles of cosmochemistry. In estimating the abundances of moderately volatile elements, Wänke and coworkers relied largely on the K-La systematics of SNC meteorites. For the SNC meteorites available at the time, Wänke and Dreibus (1988) calculated a martian primitive mantle K/La ratio of 635 using the average of all SNC meteorites. This value is much lower than the chondritic value of ~2,300 but significantly higher than the terrestrial primitive mantle value of ~325 (Taylor and McLennan 1985). Figure 3 plots K against La for the currently available SNC meteorites. Most of the SNC meteorites generally plot along the K/La ratio of 635. However, some exceptions exist. A number of recently discovered SNCs have been found in desert environments and some of these have anomalously high K/La ratios. This is likely a terrestrial weathering effect and is discussed at greater length in the following section.

Assuming that refractory lithophile elements are present in the martian primitive mantle in chondritic proportions (see further discussion below), the K/La of 635 leads to estimates of K/U = 19,000 and K/Th = 5,450. These compare to terrestrial values of about K/U = 10,000 and K/Th = 2,810 (Taylor and McLennan 1985), suggesting that the primitive mantle of Mars is enriched in moderately volatile lithophile elements, relative to refractory lithophile elements, by nearly a factor of 2 over Earth.

Terrestrial Weathering Effects

Many of the recent SNC meteorite finds have been from desert environments. A variety of petrographic and geochemical relationships indicates that some of these meteorites have been affected by terrestrial weathering

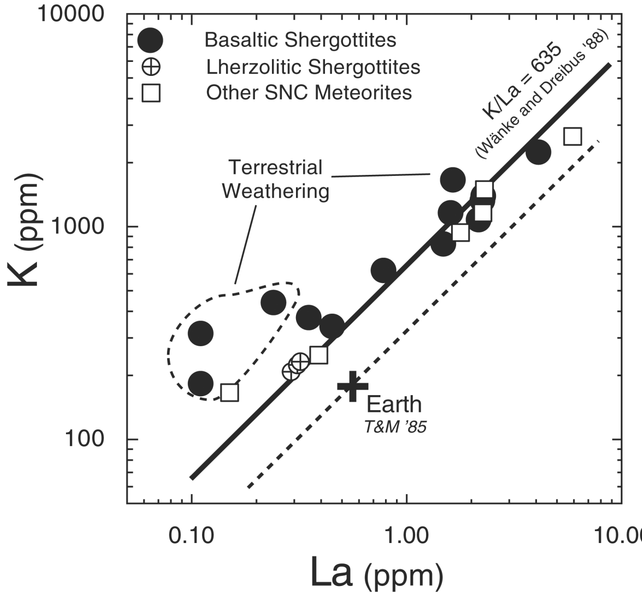

Fig. 3. Plot of K versus La for SNC meteorites. The K/La ratios for the model of primitive martian mantle from Wänke and Dreibus (1988) and for the terrestrial primitive mantle from Taylor and McLennan (1985) are shown for reference. The samples with anomalously high K/La ratios are all for SNC meteorites found in desert environments and are thought to reflect the addition of potassium (and other elements) during terrestrial weathering. Note that samples with low K and La abundances tend to plot above the K/La ratio of 635, while those with higher abundances tend to plot below the K/La = 635 line.

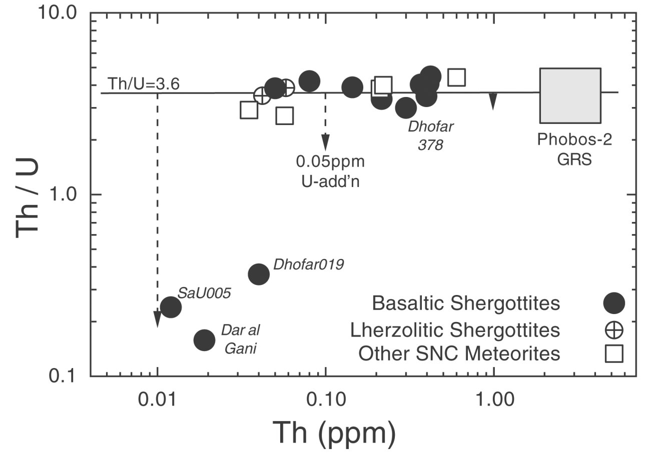

Fig. 4. Plot of Th/U versus Th for SNC meteorites. A line representing the chondritic Th/U ratio of 3.6 and the field encompassing orbital gamma ray spectrometric measurements from Phobos-2 (Surkov et al. 1994) is shown for reference. The effects on the Th/U ratio of adding 0.05 ppm uranium to samples with 0.01, 0.10, and 1.00 ppm Th is also shown. Most SNC meteorites scatter about the chondritic Th/U ratio. Several low Th SNC meteorites have anomalously low Th/U, consistent with U addition during terrestrial weathering.

processes (Dreibus et al. 2000, 2001, 2002). Among the most important chemical changes that have been noted are increases in K and U. Accordingly, one must evaluate meteorite samples individually for such processes. Thorium and uranium are both refractory elements with similar levels of incompatibility, however, redox sensitive uranium is far more prone to secondary mobility during terrestrial weathering than is Th (Taylor and McLennan 1985). On Fig. 4, most SNC meteorites plot along a line corresponding to a chondritic Th/U ratio of about 3.6. On the other hand, a number of shergottites from desert environments (Dar al Gani, SaU 005, Dhofar 019) have much lower Th/U ratios corresponding to an addition of about 0.05–0.15 ppm of uranium. Accordingly, this diagram provides a useful filter for evaluating the effects of terrestrial weathering on low Th and U SNC meteorites.

An additional basaltic shergottite, Dhofar 378, also has been interpreted to have been affected by terrestrial weathering processes but has a Th/U ratio of 3, much closer to the chondritic value (Dreibus et al. 2002). Dhofar 378 also has much higher Th abundances than do Dar al Gani, Dhofar 019, and SaU 005 and the addition of 20–30% U would be difficult to distinguish on such a diagram. On the other hand, this sample does plot an anomalously high K/La ratio (see above and Fig. 3), consistent with the effects of terrestrial weathering.

Because of these effects, a number of the SNC meteorites found in desert environments (Dhofar 378, Dhofar 019, Dar al Gani, and SaU 005) are considered to have K and U abundances that are not representative of their igneous origin. Accordingly, these elements in these samples are not further considered in this study. On the other hand, one has less of a reason to suspect that REE (particularly La) and Th distributions have been altered significantly by terrestrial weathering effects (e.g., Dreibus et al. 2001) and so these elements are considered more reliable for these samples. One caveat is the possible occurrence of small Ce anomalies (e.g., in Dhofar 019) suggestive of terrestrial weathering effects (Taylor et al. 2002).

Moderately Volatile Refractory Element Relationships

Careful examination of Fig. 3 shows that low abundance SNCs plot mostly above the K/La = 635 ratio line while the higher abundance samples plot mostly below the line, suggesting that systematic variations in the K/La ratio as a function of absolute abundances may exist. This is confirmed in Fig. 5, which plots the ratios of K/Th, K/U, and K/La for SNC meteorites as a function of K content. In each of these cases, the basaltic shergottites form a clear negative correlation between the various ratios and K content. For the K/Th and K/U diagrams (Figs. 5a and 5b), fields representing the Mars surface from Phobos-2 gamma ray spectrometric analyses (and the range of K abundances in Pathfinder soils and rocks) are also shown. In both cases, these fields plot on the extrapolated trend of the basaltic shergottites. The trend for K/La (Fig. 5c) is less well-defined and more scattered. The

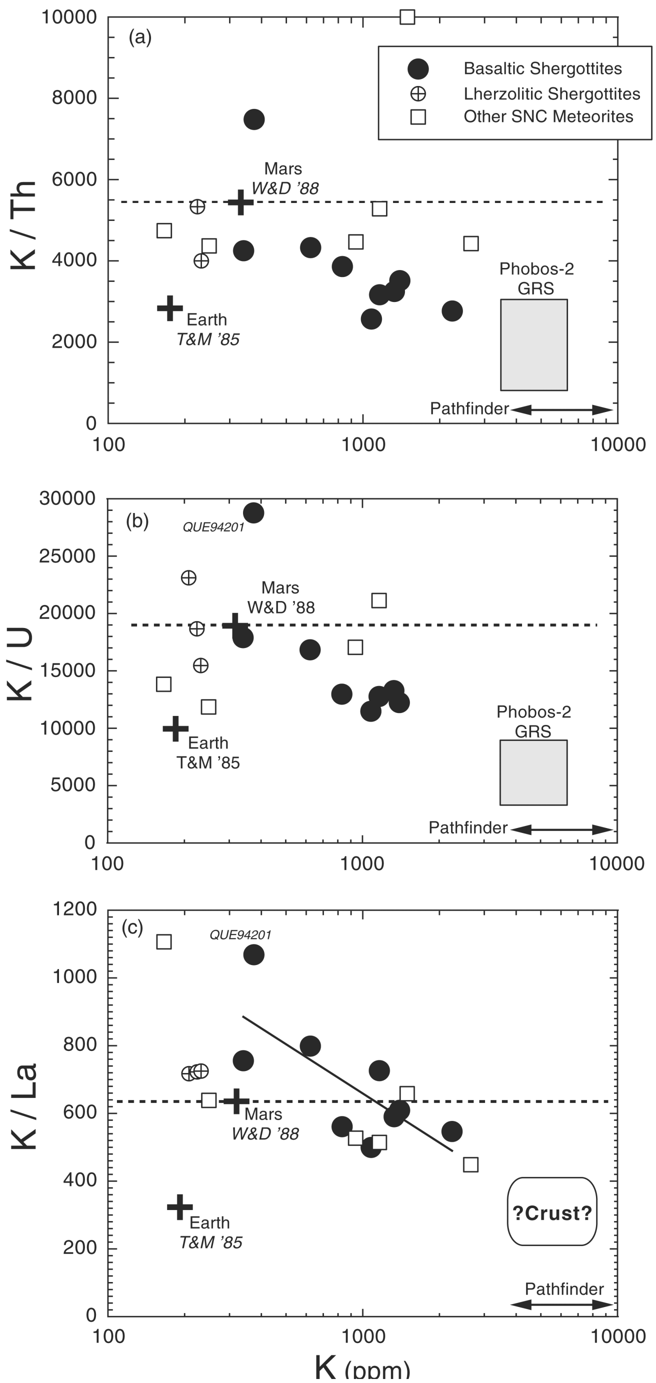

Fig. 5. Plots of K/Th, K/U, and K/La ratios versus K content for SNC meteorites. The range of compositions measured for the martian surface by Phobos-2 gamma ray spectroscopy (in Figs. 5a and 5b) and the range of K content from rocks and soils at the Mars Pathfinder site are also plotted. The bulk compositions of Earth's primitive mantle from Taylor and McLennan (1985), the Mars primitive mantle from Wänke and Dreibus (1988), and dashed lines representing the K/Th, K/U, and K/La ratios in the Wänke and Dreibus (1988) martian primitive mantle are shown for reference. Note that the basaltic shergottites form linear trends with low K meteorites having high K/Th, K/U, and K/La ratios and high K meteorites having low values of these ratios. These trends are interpreted to represent mixing between magmas derived from depleted mantle sources and enriched crustal sources.

fact that the trends for K/Th and K/U intersect the Wänke and Dreibus (1988) primitive mantle values near the highest ratios seen for basaltic shergottites is also notable, while the K/La trend intersects the Wänke and Dreibus (1988) primitive mantle K/La ratio mid-way through the trend.

Variations in K/Th, K/U, and K/La for basaltic shergottites also appear to correlate generally with the degree of LREE-depletion. Figure 6 plots the K/Th, K/U, and K/La ratios against the La/Sm ratio for basaltic shergottites. Lherzolitic shergottites are also plotted for comparison. The variations in these ratios exhibit a clear, though somewhat scattered, negative correlation with the degree of LREE-depletion, as indicated by the La/Sm ratio.

The lherzolitic shergottites and other SNC meteorites, mainly ultramafic cumulates, are highly scattered on the diagrams in Fig. 5, although the lherzolitic shergottites generally plot on or slightly below the trends defined by the basaltic shergottites. On average, they have relatively high K/Th ratios compared to basaltic shergottites, but no correlation with K content exists. On the other hand, the K/U and K/La ratios cover approximately the same range as the basaltic shergottites. In the case of K/La, a scattered negative correlation with K content exists, but in the case of K/U, a scattered positive correlation with K content may even exist. Given the ultramafic compositions and cumulate origin for most of the other SNC meteorites, that the relationships among the LIL elements are complex is not surprising.

DISCUSSION

Volatile Depletion in the Mars Primitive Mantle

The most likely explanation of the relationships seen in Fig. 5 is that they represent mixing between basaltic melts derived from highly depleted mantle sources and an enriched crustal component, consistent with the model of Norman (1999, 2002). This interpretation is consistent with the isotopic evidence suggesting that SNC meteorites contain components of both LIL-depleted and ancient LIL-enriched sources.

However, an important implication of these trends is that a significant fractionation of critical element ratios exists, which is generally thought to be representative of the degree of planetary volatile depletion. Extrapolating the trends, the LIL element-depleted mantle component possesses K/Th >5,000, K/U >20,000, and K/La >800, and the enriched (crustal) component has K/Th <2,000, K/U <11,000, and K/La <500. This suggests that a fractionation on the order of a factor of 2 or more exists in these critical ratios between depleted mantle and enriched crust. Preliminary GRS data from Mars Odyssey also appear to confirm this finding (Taylor et al. 2003).

Because of the very low K and other LIL element concentrations in most SNC meteorites, such fractionation of highly incompatible elements is perhaps not especially

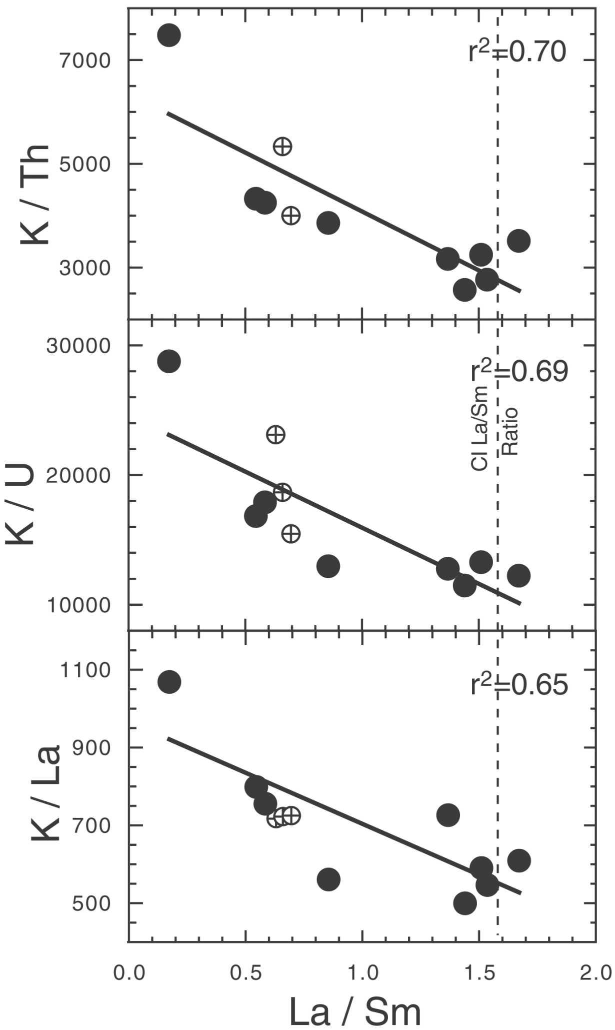

Fig. 6. Plots of K/Th, K/U, and K/La ratios versus La/Sm ratio for basaltic shergottites (filled circles). Although somewhat scattered, a negative linear trend with high K/Th, K/U, and K/La ratios exists corresponding with low La/Sm (i.e., most LREE-depleted) ratios. Lherzolitic shergottites (crossed circles) and the chondritic (CI) La/Sm ratio are shown for reference.

surprising. In terrestrial environments, many magmatic rocks with very low K content (e.g., mid-ocean ridge basalts, low-K island arc basalts) are well-known to have highly fractionated K/Rb ratios (Shaw 1968; Rudnick et al. 1985). Mid-ocean ridge basalts are also known to have low Th/U ratios that correlate with Th abundances and relatively high K/U ratios (e.g., Jochum et al. 1983). These variations are likely the result of subtle differences in the level of incompatibility among these elements coupled with complex magmatic histories.

In estimating the moderately volatile element content of the martian primitive mantle, Wänke and coworkers effectively averaged all available SNC meteorites. However, that implicitly assumes that the average of available SNC meteorites just happens to mimic the appropriate proportions of the 2 end members, which is possible but unlikely. Assuming a 3 component model (primitive mantle, depleted mantle, enriched crust), the primitive mantle ratios will lie somewhere along the trends shown in Fig. 5, the exact position depending on the composition and relative mass of the end members. (The possibility of an additional LIL-bearing mantle reservoir is discussed below.)

Although the composition of the martian crust is not well constrained, data from Pathfinder soils and rocks (Rieder et al. 1997; Brückner et al. 2001; Foley et al. 2001) and orbital gamma ray spectroscopy (Surkov et al. 1994; also see Taylor et al. 2003) are consistent with the enriched portion of the crust having on the order of 5,000 ppm K (McLennan 2001; see Fig. 5). For a crust on the order of 50 km thick (e.g., Zuber et al. 2000), this would imply that >50% of the LIL element complement of Mars is in the crust. Accordingly, the K/Th, K/U, and K/La ratios of the martian primitive mantle are likely to be significantly below the values obtained from simply averaging all SNC meteorites. On the other hand, the composition of the enriched crustal end member on Mars cannot be distinguished, within uncertainty, from the primitive mantle values of the Earth (Fig. 5). This suggests that the K/Th, K/U, and K/La ratios of the martian primitive mantle most likely lie somewhere between the values of Earth's primitive mantle and the martian depleted-mantle end member. Accordingly, Mars would appear to be a volatile-rich planet compared to Earth but not to the degree previously thought. Nevertheless, given the uncertainties in the exact composition of the depleted and enriched end members, the relative sizes of these reservoirs and the possibility of additional LIL-bearing mantle reservoirs (see below), one cannot entirely discount the possibility that Mars and Earth have comparable levels of moderately volatile element depletion.

A Previously Unrecognized LIL Reservoir on Mars?

A fundamental assumption in estimating planetary bulk compositions is that refractory elements exist in chondritic proportions (e.g., Taylor 2001). Thus, the La/Th ratio should be about 8.6 for both Earth and Mars, and this is reflected in most models for the compositions of terrestrial planets (see Taylor [2001] for a recent review). However, the La/Th ratios of SNC meteorites, with few exceptions, are subchondritic with values mostly in the range of about 4–9 (Fig. 7). Slight variations in the levels of incompatibility could cause fractionation in this ratio during magmatic differentiation (e.g., McLennan et al. 1980), but the depleted mantle and enriched crustal components should have complementary values relative to the primitive mantle. This is the case for Earth, where typical LREE-depleted mid-ocean ridge basalts, representative of depleted mantle, have La/Th ratios averaging about 17, while average continental crust has a La/Th ratio of about 4.6 (Taylor and McLennan 1985; see Fig. 7).

For the SNC meteorites, the trends for La/Th are very different. Basaltic and lherzolitic shergottites appear to form a shallow trend with a negative slope on Fig. 7. Only one of the

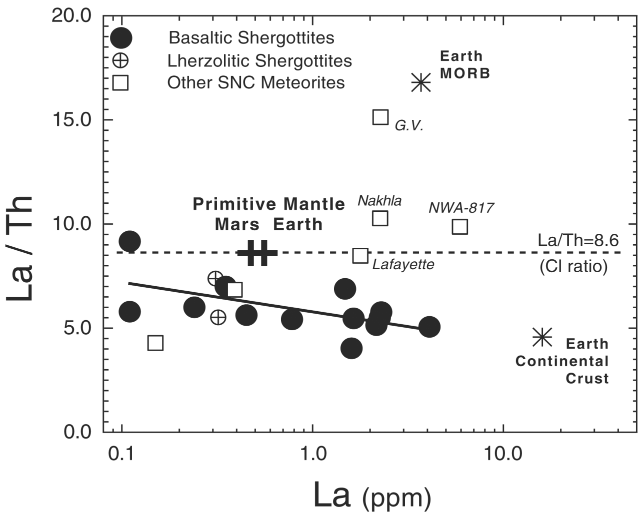

Fig. 7. Plot of La/Th versus La for SNC meteorites. Shown for reference are a line corresponding to the CI ratio, estimates of the martian and terrestrial primitive mantle compositions (Wänke and Dreibus 1988; Taylor and McLennan 1985), and average terrestrial MORB and continental crust compositions (Taylor and McLennan 1985). Note that the basaltic shergottites that are thought to have been affected by terrestrial weathering effects are included since La and Th are much less likely to be significantly disturbed by such processes. Most SNC meteorites and all but one basaltic shergottites have subchondritic La/Th ratios indicating that these refractory lithophile elements fractionate from each other during magmatic differentiation of Mars and that there must be a complementary high La/Th mantle reservoir, possibly sampled by the nakhlites. See text for further discussion.

most depleted samples, with the lowest La content (~0.1 ppm), has a La/Th ratio comparable to the chondritic value. Samples with high La (>1.0 ppm) have even lower La/Th ratios, in some cases similar to that seen for the terrestrial continental crust (McLennan et al. 1980; Taylor and McLennan 1985). Accepting that basaltic shergottites represent a mixture of depleted mantle and enriched crustal end members, extrapolation of the La/Th versus La relationships (Fig. 7) indicates that any reasonable mix of depleted (low La/Th) and enriched (high La/Th) end members results in a La/Th ratio well below the chondritic value of 8.6.

Assuming that Mars does indeed have a chondritic La/Th ratio, one implication of these relationships is the presence of an additional geochemical reservoir on Mars, likely in the mantle, characterized by high La/Th ratios. To date, no such reservoir has been unambiguously identified in the isotopic data. Although complex in detail, the long-lived radiogenic isotope systems appear to be reasonably well-explained by a 3 reservoir model including primitive mantle, depleted mantle, and enriched crust (e.g., Dreibus and Jagoutz 2002). The La/Th systematics suggest at least one additional reservoir.

Although involving different elements, a similar case for a distinctive mantle reservoir has been made for the Earth's mantle (Rudnick et al. 2000). In that case, the distinctive mantle reservoir is characterized by high Nb/Ta, Nb/La, and Ti/Zr ratios.

The size of the additional reservoir on Mars depends on trace element concentrations and La/Th ratios. However, assuming that the reservoir is characterized by very high La/Th (i.e., negligible Th content), approximately 20–30% of the primitive mantle La budget would be required. The physical character is highly uncertain and much work remains to be done to characterize this. The REE budget of the SNC meteorites is mainly controlled by trace phosphatic phases (e.g., whitlokite) consistent with the P-rich character of Mars (e.g., Halliday et al. 2001). The REE budget of the nakhlites is dominated by the trace mineral chlorapatite (Wadhwa and Crozaz 1995). Accordingly, fractionation of trace phosphatic phases could control the La/Th systematics and the additional reservoir certainly need not have a large physical size (see Rudnick et al. [2000] for an analogous example on Earth).

Of the remaining SNC meteorites, only the nakhlites may provide a possible sampling of this geochemical reservoir. These 1.3 Ga meteorites (Governador Valadares, Nakhla, Lafayette, NWA 817) are characterized by relatively high La content, LREE-enrichment (see Fig. 2), and relatively high La/Th ratios, although only Governador Valadares has a La/Th ratio that exceeds the chondritic value by a substantial amount. (This contrasts fundamentally with the complementary MORB mantle source reservoir on Earth that is characterized by relatively low La content and LREE-depletion.) These meteorites are cumulate clinopyroxenites and, accordingly, some care is required in interpreting trace element relationships, but careful examination of the trace element content of the constituent minerals indicates that the parent magmas were also LREE-enriched (e.g., Wadhwa and Crozaz 1995). Isotopic data for the nakhlites suggest that they were part of an early differentiation event, similar to the other SNC meteorites (e.g., Jagoutz 1991; Harper et al. 1995; Halliday et al. 2001), and so no obvious fundamental isotopic characteristic separates the nakhlites from the other SNC meteorites. On the other hand, the possibility that nakhlites form a distinctive geochemical reservoir has also been suggested by McSween (2002) on the basis of Nb/Y relationships. In any case, more careful trace element and isotopic studies of the nakhlites (especially Governador Valadares and NWA 817) are warranted.

CONCLUSIONS

The increasing numbers of SNC meteorites that are becoming available provide greater understanding of the detailed geochemical relationships among these meteorites. In turn, this allows for greater refinement of models for the composition of Mars and its various geochemical reservoirs (core, mantle, crust). This evaluation of the LIL element relationships among the SNC meteorites leads to the following conclusions:

1. High Th/U ratios of SNC meteorites with low LIL content appears to provide a good filter for identifying U-addition during terrestrial weathering

processes. The degree of U-addition is too slight to substantially change the Th/U ratios of SNC meteorites with Th greater than about 0.5 ppm.

2. Negative correlations exist between K/Th, K/U, and K/La ratios and K content for basaltic shergottites and are interpreted to result from the mixing of depleted (high K/Th, K/U, K/La) mantle and enriched (low K/Th, K/U, K/La) crustal reservoirs. A major implication of this observation is that the martian primitive mantle is less volatile-enriched than previously thought but probably (though not necessarily) still more volatile-enriched than the terrestrial primitive mantle.
3. The La/Th ratios of nearly all SNC meteorites are subchondritic and any reasonable extrapolations of the La/Th ratios lead to the conclusion that both the depleted mantle and enriched crustal reservoirs are also characterized by subchondritic La/Th ratios. Assuming that the primitive mantle of Mars has chondritic proportions of refractory elements implies that there is an additional, previously unrecognized, geochemical reservoir on Mars that is characterized by a high La/Th ratio. Assuming that this reservoir has very high La/Th, about 25% of the La from the primitive mantle must reside in this reservoir.

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REFERENCES

Barrat J. A., Gillet P. H., Sautter V., Jambon A., Javoy M., Göpel C., Lesourd M., Keller F., and Petit E. 2001a. The basaltic shergottite North West Africa 480: Petrology and geochemistry (abstract). *Meteoritics & Planetary Science* 36:A14.

Barrat J. A., Blichert-Toft J., Nesbitt R. W., and Keller F. 2001b. Bulk chemistry of Saharan shergottite Dar Al Gani 476. *Meteoritics & Planetary Science* 36:23–29.

Bertka C. M. and Fei Y. 1998a. Density profile of an SNC model martian interior and the moment-of-inertia factor of Mars. *Earth and Planetary Science Letters* 157:79–88.

Bertka C. M. and Fei Y. 1998b. Implications of Mars Pathfinder data for the accretion history of the terrestrial planets. *Science* 281: 1838–1840.

Blichert-Toft J., Gleason J. D., Télouk P., and Albarède F. 1999. The Lu-Hf isotope geochemistry of shergottites and the evolution of the martian mantle-crust system. *Earth and Planetary Science Letters* 173:25–39.

Brandon A. D., Walker R. J., Morgan J. W., and Goles G. G. 2000. Re-Os istopic evidence for early differentiation of the martian mantle. *Geochimica et Cosmochimica Acta* 64:4083–4095.

Brückner J., Dreibus G., Rieder R., and Wänke H. 2001. Revised data of the Mars Pathfinder alpha proton X-ray spectrometer: Geochemical behavior of major and minor elements (abstract #1293). 32nd Lunar and Planetary Science Conference. CD-ROM.

Chen J. H. and Wasserburg G. J. 1986. Formation ages and evolution of Shergotty and its parent planet from U-Th-Pb sytematics. *Geochimica et Cosmochimica Acta* 50:955–968.

Dreibus G. and Jagoutz E. 2002. Radiogenic isotopes and bulk composition of Mars (abstract #1040). 33rd Lunar and Planetary Science Conference. CD-ROM.

Dreibus G. and Wänke H. 1985. Mars: A volatile rich planet. *Meteoritics* 20:367–382.

Dreibus G., Spettel B., Haubold R., Jochum K. P., Palme H., Wolf D. and Zipfel J. 2000. Chemistry of a new shergottite: Sayh al Uhaymir 005 (abstract). *Meteoritics & Planetary Science* 35: A49.

Dreibus G., Huisl W., Haubold R., and Jagoutz E. 2001. Influence of terrestrial desert weathering in martian meteorites (abstract). *Meteoritics & Planetary Science* 36:A50–A51.

Dreibus G., Wlotzka W., Jagoutz E., Kubny A., and Spettel B. 2002. Chemistry and petrology of the most feldspathic shergottite: Dhofar 378 (abstract). *Meteoritics & Planetary Science* 37:A43.

Folco L., Franchi I. A., D'Orazio M., Rocchi S., and Schultz L. 2000. A new martian meteorite from the Sahara: The shergottite Dar al Gani 489. *Meteoritics & Planetary Science* 35:827–839.

Foley C. N., Economou T., and Clayton R. N. 2001. Chemistry of Mars Pathfinder samples determined by the APXS (abstract #1979). 32nd Lunar and Planetary Science Conference. CD-ROM.

Folkner W. M., Yoder C. F., Yuan D. N., Standish E. M., and Preston R. A. 1997. Interior structure and seasonal mass redistribution of Mars from radio tracking of Mars Pathfinder. *Science* 278:1749–1752.

Halliday A. N., Wänke H., Birck J. L., and Clayton R. N. 2001. The accretion, composition and early differentiation of Mars. *Space Science Reviews* 96:197–230.

Harper C. L., Nyquist L. E., Bansal B., Wiesmann H., and Shih C. Y. 1995. Rapid accretion and early differentiation of Mars indicated by ^{142}Nd/^{144}Nd in SNC meteorites. *Science* 267:213–217.

Hauck S. A., II and Phillips R. J. 2002. Thermal and crustal evolution of Mars. *Journal of Geophysical Research* 107(E7), doi: 10.1029/2001JE001801.

Jacobsen S. B. and Yin Q. Z. 2002. The mean age of mantle and crustal reservoirs for the planet Mars (abstract #1940). 33rd Lunar and Planetary Science Conference. CD-ROM.

Jagoutz E. 1991. Chronology of SNC meteorites. *Space Science Reviews* 56:13–22.

Jambon A., Barrat J. A., Gillet P., Göpel C., Javoy M., Joron J. L., and Sautter V. 2001. One more shergottite from Northwestern Sahara (abstract). *Meteoritics & Planetary Science* 36:A90.

Jochum K. P., Hofmann A. W., Ito E., Seufert H. M., and White W. M. 1983. K, U, and Th in mid-ocean ridge basalt glasses and heat production, K/U, and K/Rb in the mantle. *Nature* 306:431–436.

Lodders K. 2000. An oxygen isotope mixing model for the accretion and composition of rocky planets. *Space Science Reviews* 92: 341–354.

Lodders K. and Fegley B. 1997. An oxygen isotope model for the composition of Mars. *Icarus* 126:373–394.

Lodders K. and Fegley B. 1998. *The planetary scientist's companion.* Oxford: Oxford University Press. 371 p.

McLennan S. M. 2001. Crustal heat production and the thermal evolution of Mars. *Geophysical Research Letters* 28:4019–4022.

McLennan S. M., Nance W. B., and Taylor S. R. 1980. Rare earth element—Thorium correlations in sedimentary rocks, and the composition of the continental crust. *Geochimica et Cosmochimica Acta* 44:1833–1839.

McSween H. Y., Jr. 1985. SNC Meteorites: Clues to martian petrologic evolution? *Reviews of Geophysics* 23:391–416.

McSween H. Y., Jr. 2002. The rocks of Mars, from far and near. *Meteoritics & Planetary Science* 37:7–25.

McSween H. Y., Jr. and Treiman A. H. 1998. Martian meteorites. *Reviews in Mineralogy* 36:6-1–6-53.

Meyer C., compiler. 2002. *Mars Meteorite Compendium—2001*. Houston: Johnson Space Center.

Morgan J. W. and Anders E. 1979. Chemical composition of Mars. *Geochimica et Cosmochimica Acta* 43:1601–1610.

Nimmo F. and Stevenson D. J. 2001. Estimates of martian crustal thickness from viscous relaxation topography. *Journal of Geophysical Research* 106:5085–5098.

Norman M. D. 1999. The composition and thickness of the crust of Mars estimated from rare earth elements and neodymium-isotopic composition of martian meteorites. *Meteoritics & Planetary Science* 34:439–449.

Norman M. D. 2002. Thickness and composition of the martian crust revisited: Implications of an ultradepleted mantle with a Nd isotopic composition like that of QUE 94201 (abstract #1175). 33rd Lunar and Planetary Science Conference. CD-ROM.

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.

Rieder R., Economou T., Wänke H., Turkevich A., Crisp J., Brückner J., Dreibus G., and McSween H. Y., Jr.1997. The chemical composition of martian soil and rocks returned by the mobile alpha proton X-ray spectrometer: Preliminary results from the X-ray mode. *Science* 278:1771–1774.

Rubin A. E., Warren P. H., Greenwood J. P., Verish R. S., Leshin L. A., Hervig R. L., Clayton R. N., and Mayeda T. K. 2000. Los Angeles: The most differentiated basaltic martian meteorite. *Geology* 28:1011–1014.

Rudnick R. L., McLennan S. M., and Taylor S. R. 1985. Large ion lithophile elements in rocks from high-pressure granulite facies terrains. *Geochimica et Cosmochimica Acta* 49:1645–1655.

Rudnick R. L., Barth M., Horn I., and McDonough W. F. 2000. Rutile-bearing refractory eclogites: Missing link between continents and depleted mantle. *Science* 287:278–281.

Sanloup C., Jambon A., and Gillet P. 1999. A simple chondritic model of Mars. *Physics of the Earth and Planetary Interiors* 112: 43–54.

Shaw D. M. 1968. A review of K-Rb fractionation trends by covariance analysis. *Geochimica et Cosmochimica Acta* 32:573–601.

Spohn T., Acuña M. H., Breuer D., Golombek M., Greeley R., Halliday A., Hauber E., Jaumann R., and Sohl F. 2001. Geophysical constraints on the evolution of Mars. *Space Science Reviews* 96:231–262.

Surkov Y. A., Moskaleva L. P., Zolotov M. Y., Kharynkova V. P., Manvelyan O. S., Smimov G. G., and Golovin A. V. 1994. Phobos-2 data on martian surface geochemistry. *Geochemistry International* 31:50–58.

Taylor G. J., Boynton W., Hamara D., Kerry K., Janes D., Keller J., Feldman W., Prettyman T., Reedy R., Brückner J., Wänke H., Evans L., Starr R., Squyres S., Karunatillake S., and Gasnault O. 2003. Evolution of the martian crust: Evidence from preliminary potassium and thorium measurements by Mars Odyssey gamma-ray spectrometer (abstract #2004). 34th Lunar and Planetary Science Conference. CD-ROM.

Taylor L. A., Nazarov M. A., Shearer C. K., McSween H. Y., Jr., Cahill J., Neal C. R., Ivanova M. A., Barsukova L. D., Lentz R. C., Clayton R. N., and Mayeda T. K. 2002. Martian meteorite Dhofar 019: A new shergottite. *Meteoritics & Planetary Science* 37:1107–1128.

Taylor S. R. 2001. Solar system evolution: A new perspective, 2nd Ed. Cambridge: Cambridge University Press. 460 p.

Taylor S. R. and McLennan S. M. 1985. *The continental crust: Its composition and evolution.* Oxford: Blackwell. 312 p.

Treiman A. H., Gleason J. D., and Bogard D. D. 2000. The SNC meteorites are from Mars. *Planetary and Space Science* 48: 1213–1230.

Turcotte D. L., Shchervakov R., Malamud B. D., and Kucinskas A. B. 2001. Analyses of Mars topography, gravity and aroid: Implications for Tharsis and Hellas (abstract #1006). 32nd Lunar and Planetary Science Conference. CD-ROM.

Wadhwa M. and Crozaz G. 1995. Trace and minor elements in minerals of nakhlites and chassigny—clues to their petrogenesis. *Geochimica et Cosmochimica Acta* 59:3629–3645.

Wänke H. 1991. Chemistry, accretion, and evolution of Mars. *Space Science Reviews* 56:108.

Wänke H. and Dreibus G. 1988. Chemical composition and accretion history of terrestrial planets. *Philosophical Transactions of the Royal Society of London A* 325:545–557.

Zipfel J., Scherer P., Spettel B., Dreibus G., and Schultz L. 2000. Petrology and chemistry of the new shergottite Dar al Gani 476. *Meteoritics & Planetary Science* 35:95–106.

Zuber M. T., Solomon S. C., Phillips R. J., Smith D. E., Tyler G. L., Aharonson O., Balmino G., Banerdt W. B., Head J. W., Johnson C. L., Lemoine F. G., McGovern P. J., Neumann G. A., Rowlands D. D., and Zhong S. 2000. Internal structure and early thermal evolution of Mars from Mars Global Surveyor topography and gravity. *Science* 287:1788–1793.