Chemical compositions of martian basalts (shergottites): Some inferences on basalt formation, mantle metasomatism, and differentiation in Mars

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Abstract–Bulk chemical compositions of the shergottite basalts provide important constraints on magma genesis and mantle processes in Mars. Abundances of many major and trace elements in the shergottites covary in 2 distinct groups: Group 1 (G1) includes mostly highly incompatible elements (e.g., La, Th), and Group 2 (G2) includes mostly moderately incompatible elements (e.g., Ti, Lu, Al, Hf). Covariations of G2 elements (not necessarily linear) are consistent with partitioning between basalt magma and orthopyroxene + olivine. This fractionation represents partial melting to form the shergottites and their crystallization; the restite minerals cannot include aluminous phase(s), phosphate, ilmenite, zircon, or sulfides.

Overall, abundances of G1 elements are decoupled from those of G2. In graphing abundances of a G1 element against those of a G2 element, G1/G2 abundance ratios do not appear to be random but are restricted to 4 values. Shergottites with a given G1/G2 value need not have the same crystallization age and need not fall on a single fractionation trajectory involving compatible elements (e.g., Ti versus Fe*). These observations imply that the G1/G2 families were established before basalt formation and suggest metasomatic enrichment of their source region (major carrier of G2 elements) by a component rich in G1 elements.

Group 1 elements were efficiently separated from G2 elements very early in Mars' history. Such efficient fractionation is not consistent with simple petrogenesis; it requires multiple fractionations, "complex" petrogenetic processes, or minerals with unusual geochemistry. The behavior of phosphorus in this early fractionation event is inexplicable by normal petrogenetic processes and minerals. Several explanations are possible, including significant compatibility of P in majoritic garnet and the presence of P-bearing iron metal (or a phosphide phase) in the residual solid assemblage (carrier of G2 elements). If the latter, Mars' mantle is more oxidized now than during the ancient fractionation event.

INTRODUCTION

Twenty years ago, Bogard and Johnson (1983) presented the first solid evidence that the "SNC" meteorites, including the shergottites, formed on Mars. Since then, the meteorites have been studied intensely for insights into martian volcanism, mantle chemistry, and differentiation history (e.g., McSween 1994). One of the most valuable approaches has been interpretation of their bulk chemical compositions using methods established in studies of the Earth's basalts and mantle (e.g., Wänke 1981; Drake 2000). Applied to Mars, those methods have yielded estimates of the bulk composition of the planet, its mantle, and its core (e.g., Treiman et al. 1986, 1987; Longhi et al. 1992) and constraints on its differentiation history (e.g., Treiman et al. 1986).

Two recent developments make revisiting older inquiries into the bulk compositions of shergottites worthwhile. First, many new and varied shergottites have been discovered, including the critical samples Queen Alexandra Range (QUE) 94201, Los Angeles, and Dar al Gani (DaG) 476. These meteorites, in particular, have increased the known chemical diversity of the shergottites and, thus, allow new insights into the processes responsible for that diversity. Second, new radioisotopic data on the shergottites, especially on those critical samples, have resolved several uncertainties in their petrogenesis. Since the definitive works listed above, the crystallization ages of the shergottites have been firmly established: most at ~180 Ma, QUE 94201 at 327 Ma, and DaG 476 at 474 Ma (Borg et al. 1997, 2003). Consideration of initial radioisotopic ratios has led to the recognition that Mars

underwent an extreme geochemical fractionation very early in its history and, thus, that the chemical compositions of the shergottites need not represent only recent fractionations.

In light of these new developments, I have revisited my early work (Treiman et al. 1986) to see if the regularities established then are still valid and to interpret them in terms of geochemical processes. In this work, the sources of data and their uncertainties are described first. Then, the incompatible element groups of Treiman et al. (1986) are revisited and revised. Abundances of the Group 2 elements (moderately incompatible) are explained in terms of recent basalt/mineral fractionations. The separation of Group 1 (highly incompatible) and Group 2 elements is shown to have occurred early in Mars' history, and several elements (notably phosphorus) behaved differently then than in more recent fractionations.

DATA SOURCES

Many chemical analyses of shergottite meteorites are available (e.g., Treiman et al. 1986; Lodders 1998; Meyer 2003). Those used here, Table 1, emphasize average or "best estimate" analyses and recent data. In several cases, duplicate analyses are included, e.g., 3 separate analyses of Los Angeles and 2 each of Shergotty and Zagami. Additional analyses not in the compilations are from Wang et al. (1998), Rubin et al. (2000), Barrat et al. (2001, 2002a, b), Jambon et al. (2002), and others listed in the figure captions.

Uncertainties in these chemical data are considerable, derive from several causes, and cannot be adequately quantified. Thus, the following figures do not show "error bars," and the quality of the correlations must be viewed skeptically. Analytical uncertainties for each individual data point depend on the usual factors (see original papers for discussions) and vary by element, analytical method, and element abundance.

More critical is the issue of unrepresentative sampling— are the analyzed aliquots statistically representative of the bulk rock? Sample masses for chemical analyses of martian meteorites (when given) are typically 100–500 mg, and this is generally too small to yield representative analyses of crystalline basalt rocks (Ryder and Schuraytz 2001). This problem is exacerbated for the most incompatible trace elements, which are concentrated in small, dispersed mineral grains or melt pockets. The problem of nonrepresentative analyses is most acute where the elements are carried by different phases (e.g., La and K). Thus, analyses of small samples tend to show wide ranges in abundances of

incompatible elements and in element abundance ratios if the elements are carried in different minerals (Fig. 1).

A third cause of uncertainty in the chemical data is sample variability. Several shergottites are not homogeneous: Elephant Moraine (EET) A79001 has 2 lithologies, 1 with xenoliths; Zagami has multiple lithologies; Allan Hills (ALH) A77005 and Lewis Cliff (LEW) 88516 have domains of different textures; and the 2 Los Angeles stones may be chemically distinct (Steele and Smith 1982; Treiman et al. 1994; McCoy et al. 1999; Rubin et al. 2000). In such cases, which lithology is represented by a given analysis may not be clear, nor whether it corresponds to a recognized lithology.

RATIONALE AND ELEMENT GROUPS

In the last 20 years, bulk compositions of martian basalts have been used to constrain the composition of Mars' mantle and the petrogenesis of its basalt (e.g., Treiman et al. 1986; Longhi et al. 1992). The composition of a basalt reflects (to greater or lesser extent) the composition of its mantle source, as modified by element distributions during melting and crystallization. The basalt's mantle source is related to the bulk composition of the planet and of the solar nebula (i.e., CI chondrites) by known processes of accretion, volatile loss,
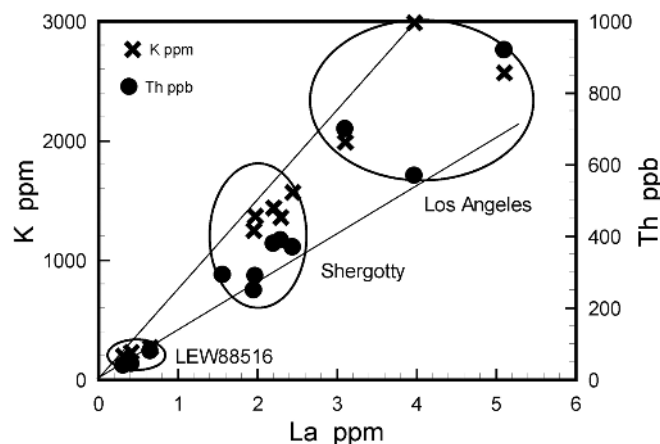

Fig. 1. Abundances of La, Th, and K (G1 elements, Table 1) from individual analyses of shergottite meteorites LEW 88516, Shergotty, and Los Angeles. Among the analyses of each meteorite, abundances of an element can vary by a factor of ~1.5. Abundance ratios may be relatively constant (e.g., K/La in Shergotty ranges only from ~600 to ~700) or highly discordant (Th/La in Los Angeles ranges from ~140 to ~225). The straight lines encompass all K/La ratios for these analyses. The data are from Dreibus et al. (1982, 1992), Laul et al. (1986), Treiman et al. (1986, 1994), Rubin et al. (2000), and Jambon et al. (2002).

Table 1. Element Groups 1 and 2 in shergottites (modified from Treiman et al. [1986]).

Group 1 elements	Geochemistry	Group 2 elements	Geochemistry
La, Ce, Nd	Light REE	Sm, Du, HREE	Middle and heavy REE
Th, U, Ta, Nb, W	Hight field strength	Ti, Sc, Zr, Hf, In, P	High field strength
K, Rb, Cs, Ba, Pb	Large ion lithophile	Al, Ga, Na, Eu, Sr	"Plagiophile"
Cl, Br	Halogens		

and core formation. Thus, if 2 elements have identical behaviors in basalt melting and element partitioning, their abundance ratio in the basalt should be identical to that in the source mantle (see Drake 2000; but, see Sims and DePaolo 1997). Further, that mantle composition deviates from CI chondritic by the actions of igneous processes (e.g., partial melting), metal loss during core formation, and failure of volatile elements to accrete fully to a planet during its formation.

An implicit assumption in this scheme is that the processes of basalt melting and diversification cleave closely to the simple models of partial melting and fractional crystallization (e.g., Basaltic Volcanism Study Project 1981). Increasingly, workers find that igneous processes can be complex and produce basalts with compositions far removed from those of their source mantles or of the partial melts of those sources (e.g., O'Hara and Mathews 1981). Those mantle sources may have been modified away from "average mantle" by metasomatic fluids and processes (e.g., Ionov et al. 2002). And, once basalts are created, they can be modified by reactive flow in transit (e.g., Braun and Kelemen 2002), assimilation of crustal material (e.g., Reiners et al. 1995), or magma-chamber processes (e.g., O'Hara and Mathews 1981).

Incompatible Element Groups in Martian Meteorites

Seeking regularities in the geochemistry of the martian basalts, Treiman et al. (1986) delineated several groups of elements that behaved similarly in their genesis and fractionation. Within each group, element abundances are strongly correlated. But abundances of an element in 1 group were effectively uncorrelated with abundances of an element in another group (Fig. 2). Here, I revisit two of these groups, "Group 1: Highly Incompatible" and "Group 2: Moderately Incompatible" (Treiman et al. 1986), referring to their behavior in fractionations between silicate minerals and basalt magma. The behavior of Groups 1 and 2 is exemplified in Fig. 2. Groups 1 and 2 include nearly all of the usually analyzed lithophile elements of igneous rocks. Strongly siderophile and chalcophile elements behave otherwise, and a few elements do not show obvious chemical regularities (e.g., Fig. 2d) The division of elements into these groups (with modifications) has been confirmed by additional analyses of old meteorites and by analyses of new meteorites, as shown below.

However, Treiman et al. (1986) did not explain several peculiar element assignments. Most distressing is that phosphorus (P) belongs to Group 2, i.e., P is inferred to fractionate as a moderately incompatible element like Ti (Fig. 3c). In terrestrial petrogenesis, phosphorus is highly incompatible in basalt petrogenesis on Earth, and the reason that it should behave otherwise on Mars is not obvious. Similarly, abundances of S, Se, and Cu covary closely with those of Ti in the shergottites (Figs. 3f and 3g). In sulfur-poor systems, these elements would dissolve completely in silicate melt, be excluded completely from silicate phases, and behave as Group 1 (highly incompatible). In sulfur-rich systems, these elements should enter sulfide phases and be relatively decoupled from silicate fractionations (e.g., earth basalts and mantle rocks; Treiman et al. 1986). Behavior like Ti and other Group 2 lithophile elements is unexpected.

Group 2 Elements

Group 2 (G2) elements are given in Table 1, and covariations among the abundances of several are shown in Figs. 2b and 3. Within G2, element abundances covary closely, indicating that they behaved coherently in the formation of martian basalts. Most G2 elements are moderately incompatible in basalt petrogenesis, with $D_{pyroxene/basalt}$ values in the range of ~0.1–0.7 and low $D_{olivine/basalt}$ values (see Irving 1978; Jones 1995).

A few differences exist between the G2 elements of Treiman et al. (1986) and those of Table 1. With newly available data, Zr and Sr (which had previously been unassigned) are placed in G2 (Fig. 3e). Because of its importance in radioisotope chronology, Sr is discussed separately below. New data, however, have not confirmed the assignment of V to G2 (Fig. 2d).

Middle and Heavy REE and High Field Strength Elements (HFSE)

The geochemical coherence of the middle REE, heavy REE, and many HFSE is expected because they have similar compatibilities between basaltic magma and common igneous minerals (Irving 1978; Jones 1995). The coherence of middle and heavy rare earth elements among the martian meteorites has been recognized since very early in their study (e.g., Ma et al. 1981). Recent analyses have confirmed the coherence, mostly through CI-normalized REE plots (e.g., Fig. 8 of Zipfel et al. 2000; Fig. 12 of Barrat et al. 2002b; Fig. 13 of Jambon et al. 2002).

Beyond the REE as a group, only the coherence of Lu and Hf has been noted to any effect (compare Figs. 3a and 3b). Blichert-Toft et al. (1999) found that Lu/Hf abundance ratios hardly vary among the shergottites: "One of the more remarkable aspects of the present study is the relatively narrow range of Lu/Hf ratios among the shergottites." Interestingly, the Lu/Hf ratio for the shergottites, 0.1230–0.1440, is significantly lower than the chondritic value of 0.23 (Anders and Grevesse 1989). Zr and Hf covary nearly exactly, with Zr/Hf at nearly exactly the chondritic abundance ratio.

The behavior of phosphorus, P, among the martian meteorites is most puzzling (Fig. 3c) and was the original anomaly that inspired this line of inquiry (Treiman et al. 1984). In typical basaltic systems, P is highly incompatible and follows the light rare earth elements. Its presence in G2 means that the group is not defined entirely by typical
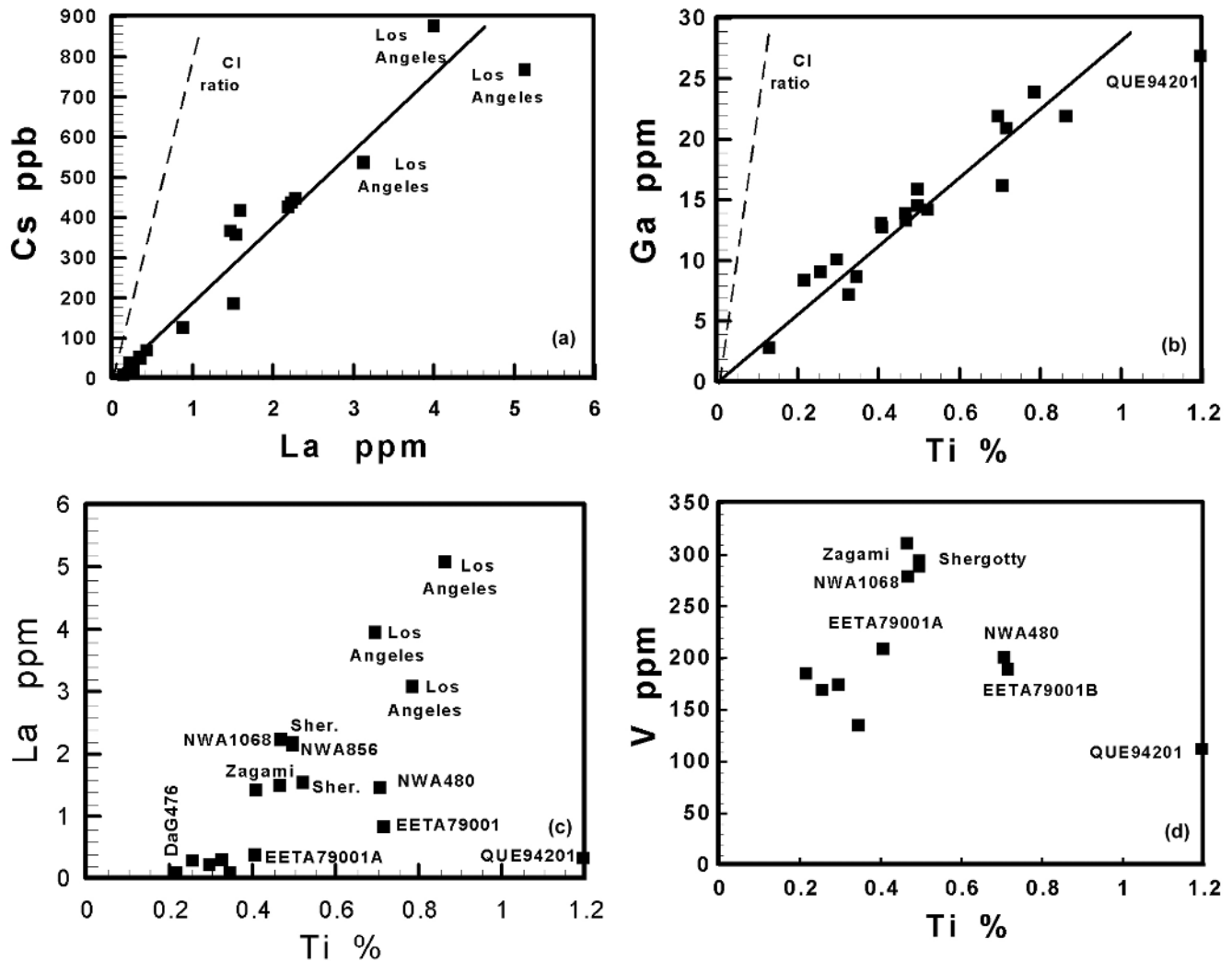
Fig. 2. Definitions of the 2 element groups: a) abundances of G1 elements like Cs (Table 1) covary closely with abundances of La; b) abundances of G2 elements like Ga (Table 1) covary closely with abundances of Ti; c) abundances of G1 elements (like La, Table 1) do not covary closely with abundances of G2 elements (Ti) but show a broad scatter; d) vanadium does not fall cleanly into G1 or G2. V versus Ti shows broad scatter. V versus La is worse.

mineral/melt partitioning, because no indication exists that P can act as a moderately incompatible element (like Ti or Al) in typical basalt petrogenesis. Similarly, the decoupling of P and the light REE (G1) is unusual and troubling and is considered below.

Plagiophile Elements

"Plagiophile" elements, such as Al, Ga, Na, and Sr, covary closely with Ti for all shergottites and so belong in G2 (Figs. 2b, 3d, and 3e). Only for the Los Angeles shergottite (1.2% Ti) does this covariation fail—in it, abundances of these elements fall lower than expected from the other meteorites. This "deficiency" in plagiophile elements in Los Angeles suggests that its magma had fractionated plagioclase, consistent with its highly evolved character (Fe* = molar Fe/ (Mg + Fe) = 77; Rubin et al. 2000).

Strontium should act as a plagiophile element in G2 because of its affinity for plagioclase and incompatibility in olivine and pyroxene (Irving 1978; Jones 1995). Jambon et al. (2002) confirm this behavior in their Fig. 11, and I concur here in Fig. 3e. However, that figure requires some explanation. First, most Sr analyses in the literature are by INAA and, so, are rather imprecise. One might expect, and does find, widely divergent Sr values from different INAA analyses, the most extreme being for EET A79001 A and B and QUE 94201 (in Fig. 3e, several individual analyses are shown). In such cases, average values (e.g., in Lodders 1998) are uninformative. Second, most analyses for Sr by more precise methods (e.g., ICP-MS or ICP-AES) are on desert meteorites, which are commonly contaminated with terrestrial Sr in carbonate deposits. Thus, the Sr analysis for Dhofar 019 is not useful and those for DaG 476 and
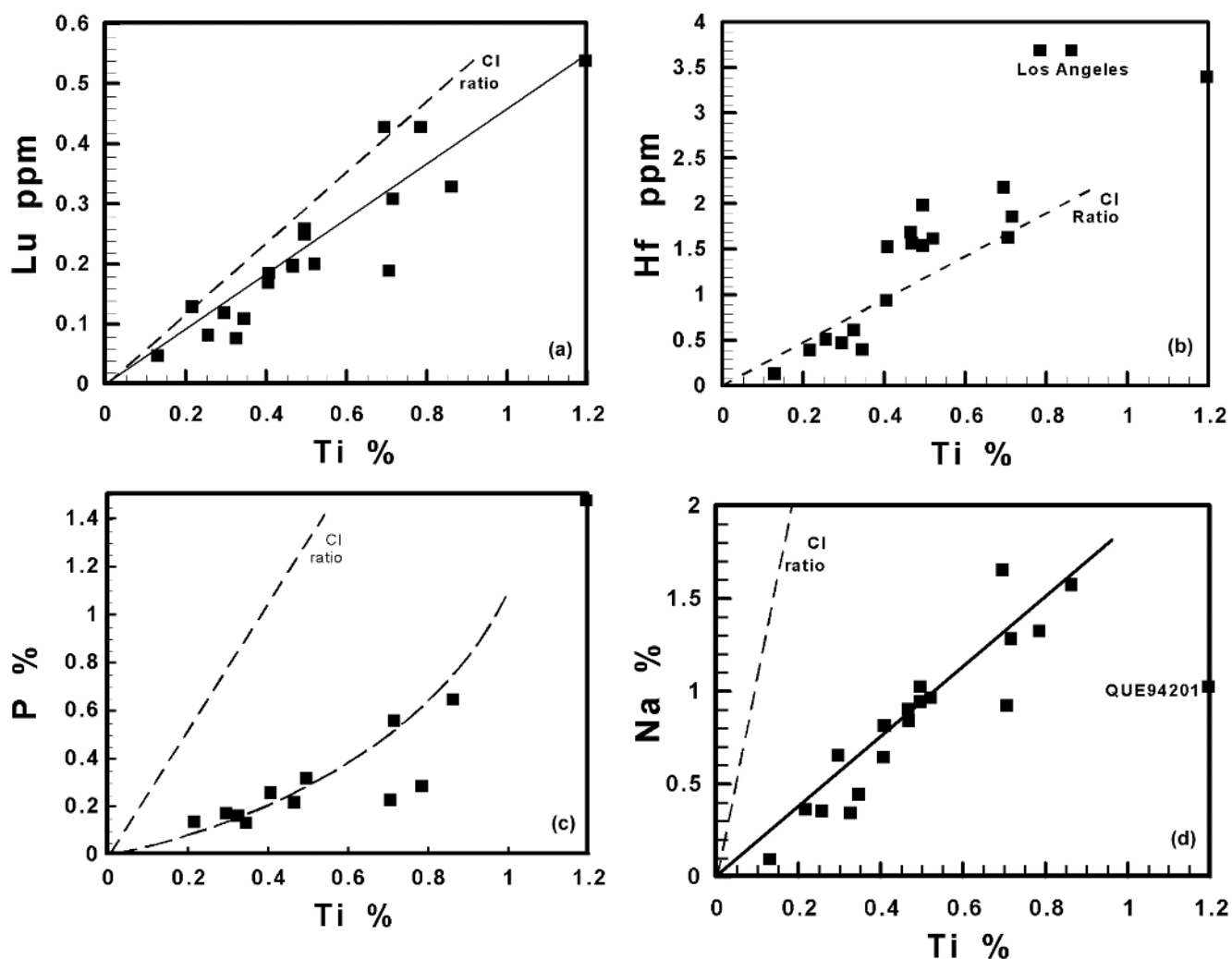
Fig. 3. Abundances of G2 elements: a) Lu versus Ti. The Lu/Ti abundance ratio is close to chondritic; b) Hf versus Ti. The trend is convex upward, not linear. Hf is anomalously low in QUE 94201—it is the only shergottite with a Hf/Zr ratio that is significantly sub-chondritic; c) P versus Ti. This trend is concave upward, not linear. The heavy dashed curve is calculated for basalt formation by partial melting, with bulk basalt/mineral partitioning of $^PD = 0$ and $^{Ti}D = 0.1$; d) Na versus Ti. The Na/Ti abundance ratio is constant and distinctly sub-chondritic, ascribed by Treiman et al. (1986) to the volatility of Na.

NWA 1068 can be viewed skeptically (Fig. 3e; Crozaz and Wadwha 2001; Taylor et al. 2002; Barrat et al. 2002a; Borg et al. 2002; Jambon et al. 2002). With those caveats, the covariance between Sr and Al (or Ti, etc.) is strong enough to assign Sr to G2.

Chalcophile Elements

The chalcophile elements S, Se, Cu, and Tl also covary with G2 elements like Ti (Figs. 3f and 3g), although with significant scatter. Much of this scatter may represent alteration on Earth: either oxidation of primary sulfide minerals or addition of alkaline earth sulfate minerals (e.g., Taylor et al. 2002). In particular, DaG 467 has excess Ba, Sr, S, and Se compared to similar non-desert shergottites (Figs. 3e and 3f; Crozaz and Wadhwa 2001; compare Barrat et al. 1999). The Se value for QUE 94201 falls below the

covariation marked by the other SNC meteorites, which could be ascribed to fractionation of a sulfide phase; this behavior is similar to that of Al in QUE 94201, which is ascribed to fractionation of plagioclase. Abundances of As and Sb do not show clear covariations with G2 elements.

Group 1 Elements

Group 1 elements (Table 1) include most of those considered to be highly incompatible in basalt petrogenesis (Figs. 1, 2a, and 4). These include the light REE (Nd; Fig 4a), high-field strength ions (HFSE; Th, Nb; Figs. 4b and 4c), large ion lithophile elements (LIL; K, Cs, Rb, Pb; Figs. 1, 2a, 4d, and 4e), light lithophiles (LLE; Be, Li; Figs. 4f and 4g), and halogens (Cl, Br; Fig. 4h). The G1 elements include the most important sources of radioactive heating (K, Th, U) and
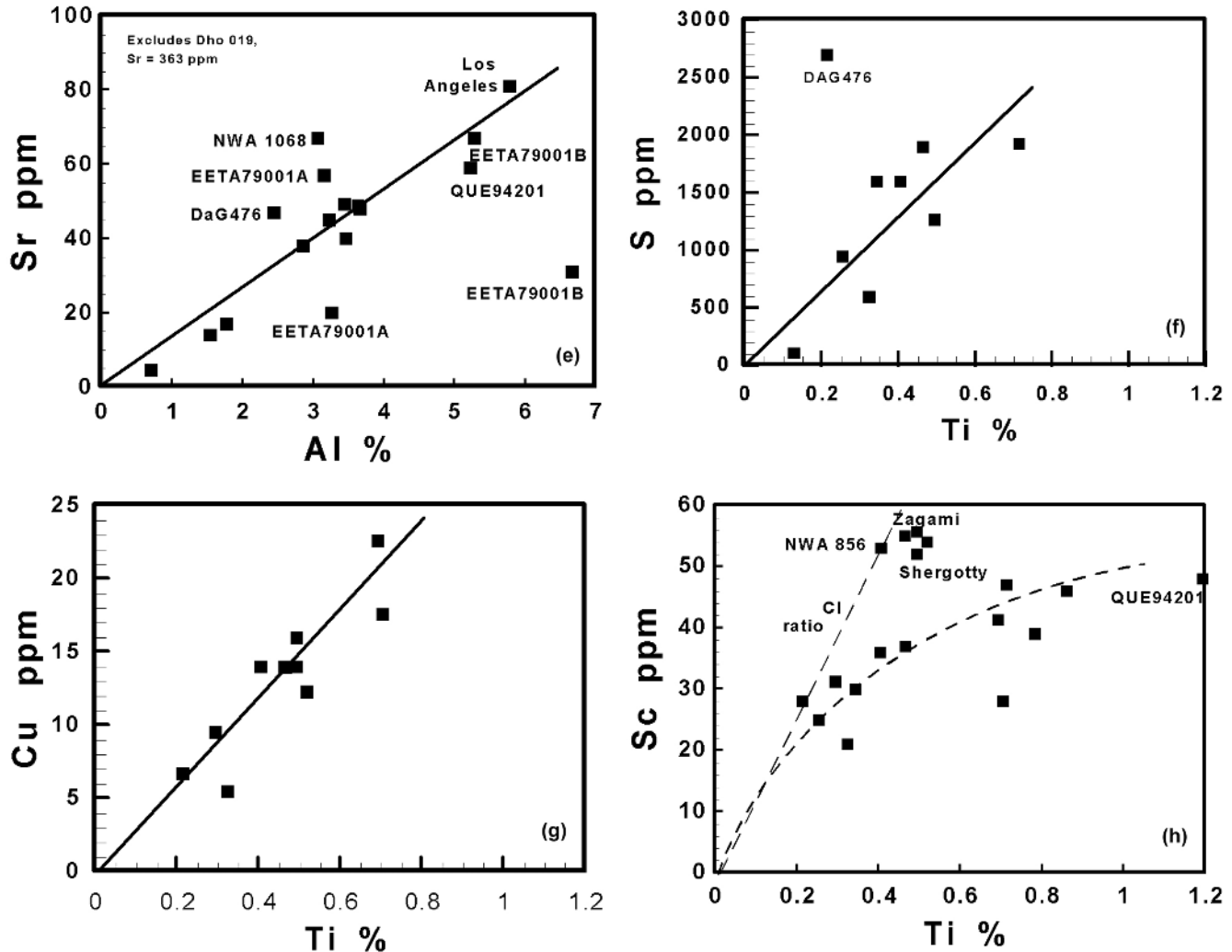
Fig. 3. Abundances of G2 elements: e) Sr versus Al, a G2 element. Most Sr analyses, being by INAA, are relatively imprecise. Sr abundances in DaG 476, NWA 1068, and Dho 019 are affected by terrestrial contamination (see text); f) S versus Ti. The S/Ti ratio is approximately constant at $\sim10^{-3} \times$ CI, with significant scatter. The high S in DaG 476 probably reflects significant terrestrial contamination (Crozaz and Wadhwa 2001); g) Cu versus Ti. This correlation is surprisingly good as most Ti is in pyroxene and oxide minerals, and most Cu is likely in sulfide minerals; h) Sc versus Ti. The trend is convex upward, not linear. The heavy dashed curve is calculated for basalt formation by partial melting, with bulk basalt/mineral partitioning of $^{Sc}D = 0.3$ and $^{Ti}D = 0.1$.

are critically important for understanding Mars' thermal structure and the formation of martian basalts (Kiefer 2003). A few differences exist between the G1 assignments here and in Treiman et al. (1986). Sufficient data are now available for Nb, Pb, and Be to assign them to G1 (Figs. 4c, 4e, and 4f). On the other hand, data for Ag, As, and Au were quite scattered (Treiman et al. 1986) and are now considered too scattered for assignment to G1.

Figure 4 shows selected covariations among G1 element abundances. As noted above, covariations of pairs of elements hosted in the same mineral (e.g., Nb and Ta) are considerably tighter than those hosted in different minerals (e.g., K and La). Abundance ratios of the most refractory, lithophile, and incompatible elements are near the CI ratio

(Anders and Grevesse 1989), including Th, U, Ta, Nb, and Ba (Fig. 4; Wänke 1981; Treiman et al. 1986). Small but significant differences in Th/U ratios (e.g., Fig. 3 of Blichert-Toft et al. 1999) are not readily resolved here. Elements with significant volatile or siderophile characters are depleted relative to refractory lithophlile elements (U, Th, etc.) including K, Rb, Cs, Pb, Li, Cl, and Br (Figs. 2a and 4).

Mixed Behavior

The division of elements into groups is a convenient but imperfect construct. One cannot expect a real chemical process to produce a complete separation of elements. In fact, the separation of elements between G1 and G2 is

Fig. 4. Abundances of G1 elements: a) Nd versus La; linear variation, nearly at the CI ratio. Note that several shergottites fall off the linear trend in a sense comparable to that of G2 elements (Figs. 2c and 5). See the text for further discussion; b) Th versus La; linear variation, nearly at chondritic ratio. The Th values for Los Angeles are widely scattered (see Fig. 1), reflecting inhomogeneity on the scale of the analyzed aliquots; c) Nb versus Ta is at the CI ratio; d) Rb versus La. This correlation is surprisingly close, considering the ease of Rb exchange with the terrestrial environment.

astonishingly good (e.g., Borg et al. 1997). In the real world of the shergottites, one should expect to see "mixed" behavior for some elements. For instance, an element that is nominally G1 would behave as a G2 element in meteorites where G1 abundances are very low.

Neodymium is the clearest example of this mixed behavior, as shown in Fig. 4a. In shergottites that are rich in La and the other G1 elements, the Nd/La ratio is nearly constant. Shergottites that are very poor in La and other G1 elements have higher Nd/La ratios. This implies another carrier for Nd, which is noticeable only at small proportions of La. That Nd carrier follows the same pattern as G2 elements (compare Figs. 2c, 4a, and 5a) and can be ascribed to the G2 element reservoir. Presumably, the G2 element reservoir has small proportions of G1 elements, which are

detectable only in samples with very little contribution from the G1 reservoir.

INTERPRETATION: SHERGOTTITE ORIGINS

Recognition of these 2 groups of elements in the shergottites has potential to provide additional insights into the origins of those basalts and, thus, into mantle and magmatic processes in Mars. Abundances of G2 elements appear to reflect fractionation between basalt magma and orthopyroxene + olivine (without other phases). This is interpreted to represent "recent" partial melting and crystallization of shergottite magmas.

The shergottites now contain variable proportions of G1 and G2 elements. This observation is interpreted to represent
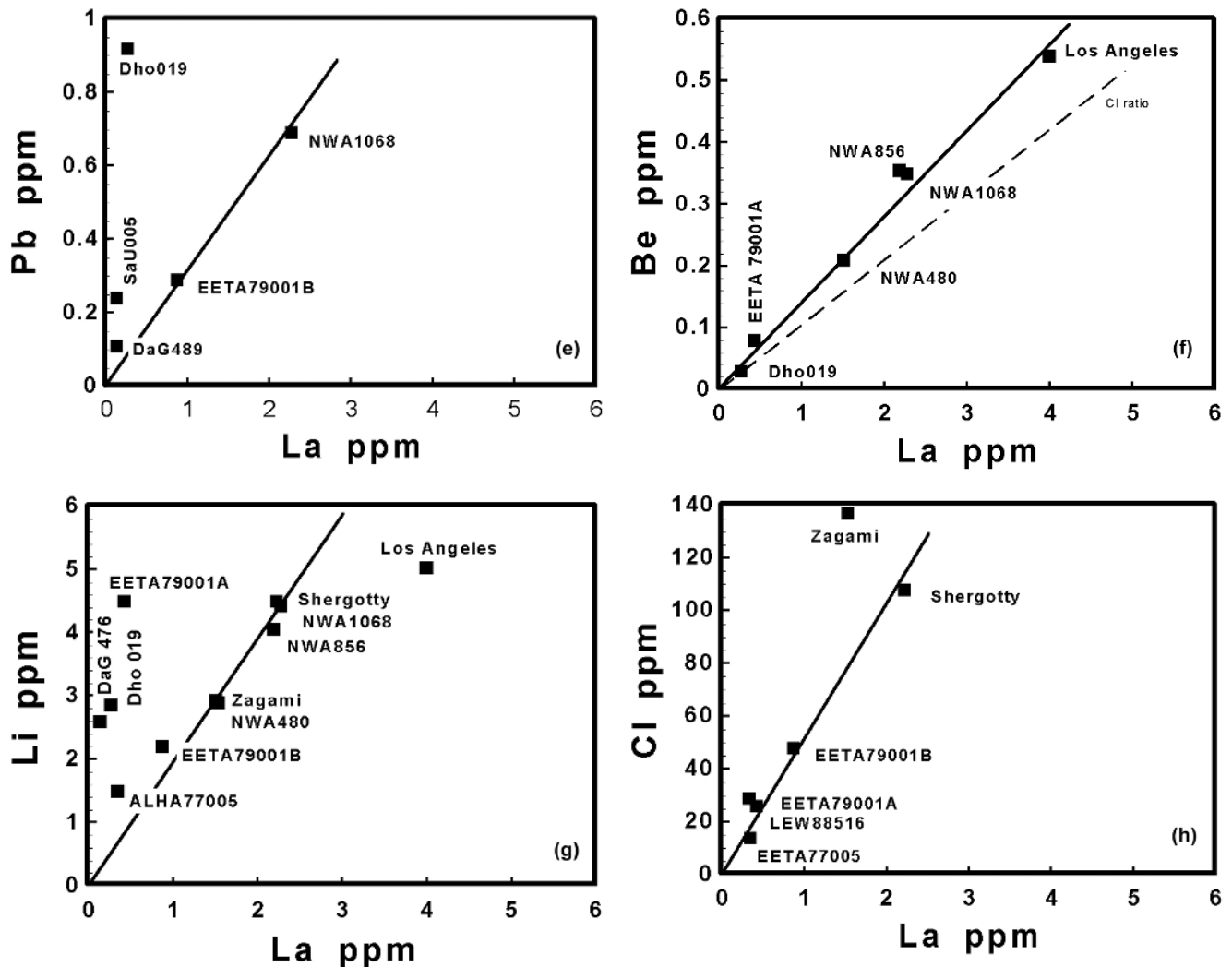
Fig. 4. Abundances of G1 elements: e) Pb versus La. Of the 6 available Pb analyses, 4 fall on or close to a line through the origin, suggesting that Pb behaves like La in shergottite petrogenesis; f) Be versus La; g) Li versus La; h) Cl versus La. This correlation is surprisingly close, considering the ease of Cl gain from the terrestrial and antarctic environment.

mixing of 2 physical substances, enriched respectively in G1 and G2 elements. Relative abundances of G1 and G2 elements in the shergottites suggest that G1/G2 abundance ratios were established before the fractionations that produced the range of G2 element abundances. This observation suggests that G1/G2 ratios were established before the fractionations of partial melting and crystallization and, thus, is consistent with mixing in the shergottites sources (i.e., mantle metasomatism) rather than mixing after basalt formation (i.e., assimilation).

The differentiation between G1 and G2 elements occurred in Mars' distant past, as shown by radioisotope systematics. This differentiation did not follow the same "rules" of element fractionation as did the later (G2) differentiation; i.e., P was decoupled from La, and S was not highly incompatible. This differentiation was also extreme (see Borg et al. 1997). That this early differentiation event involved unusual minerals and uncommon processes seems likely.

Element Groups as Physical Entities

The simplest physical interpretation of G1 and G2 elements in shergottite genesis is that they refer to substances enriched respectively in those elements. This inference is proven by radioisotope data, most convincingly by ε_{Nd}^{142} and ε_{Nd}^{143} data that show great separation of Nd (G1) and Sm (G2) at 4.513 Ga (Borg et al. 1997, 2003) long before shergottite formation at 474–180 Ma. The origins of the 2 groups and their physical substances are considered later.

Group 2 Fractionation

Group 2 includes elements that are moderately incompatible in basalt petrogenesis and several that are typically highly incompatible (Table 1; Figs. 2b and 3). Here, the focus is on how abundances of G2 elements vary.
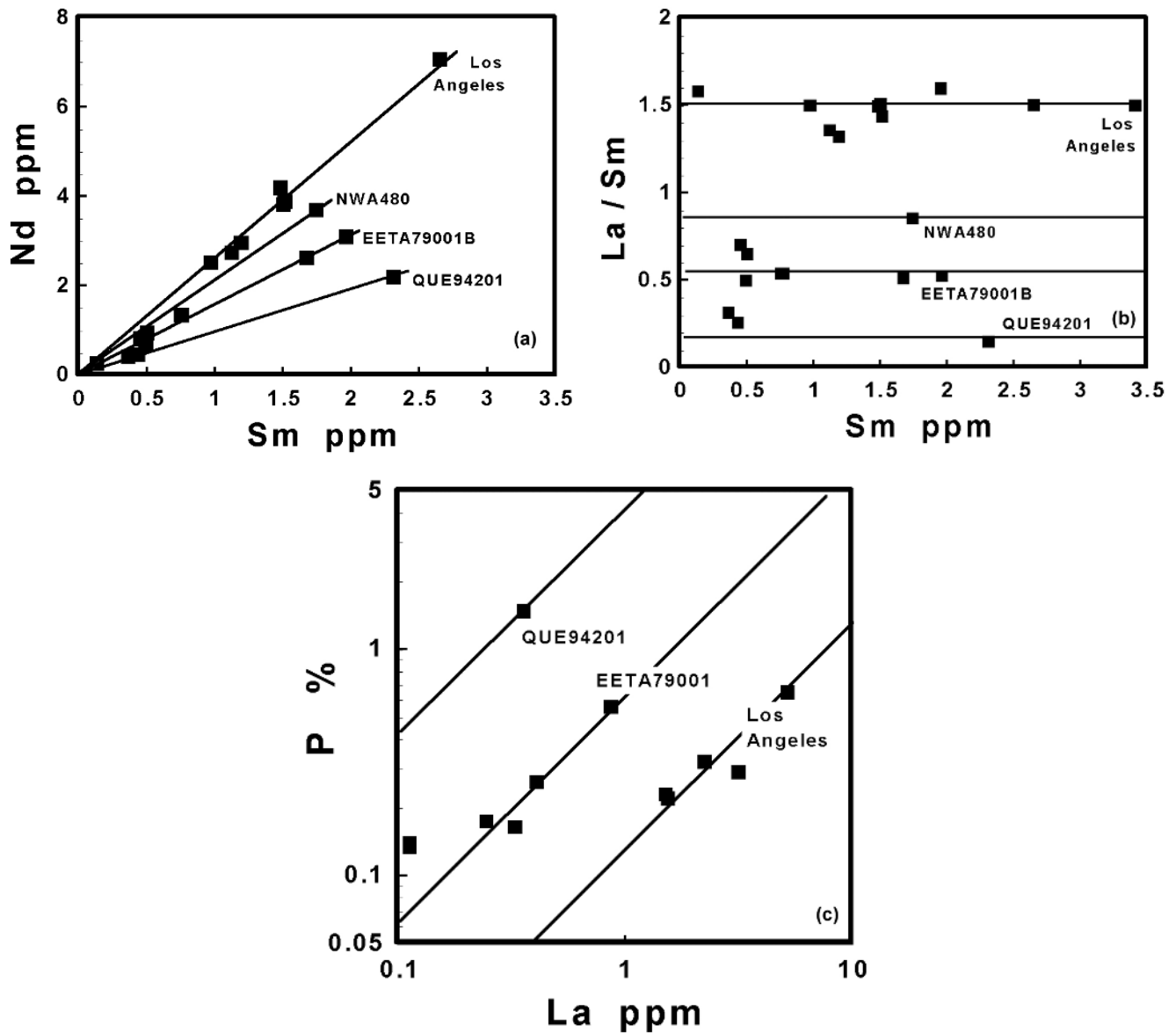
Fig. 5. Definition of the families of shergottites based on G1/G2 ratios, shown in several presentations and element groupings: a) Nd versus Sm; Sm is G2, Nd is G1 (but, see text; Fig. 4a). The QUE 94201 family includes DaG 476 and Dho 019. The EET A79001 family includes the lherzolites ALH A77005 and LEW 88516. NWA 480 appears unique. The Los Angeles family includes Shergotty, Zagami, NWA 856, and NWA 1068; b) La/Sm versus Sm shows the same families and emphasizes the low-abundance end of the graphs. Terrestrial contamination increases the La/Sm ratio, as average crust and desert alterations are LREE-enriched (Crozaz and Wadhwa 2001; c) logarithmic presentation of abundances of P and La. In this plot, NWA 480 falls close to the Los Angeles line, and DaG 476 and Dho 019 fall closer to the EET A79001 ratio than that of QUE 94201. These all may reflect addition of La to the samples via desert weathering (Crozaz and Wadhwa 2001).

A critical new observation is that not all covariations among G2 elements are linear and that the non-linearities are consistent with silicate mineral/melt fractionations. When plotted against Ti (Fig. 3), other G2 elements describe convex-up trajectories (humped, like Sc; Fig. 3h), linear trajectories (like Na; Fig 3d) or convex-down trajectories (bowl-shaped, like Lu and P; Figs. 3a and 3c). These trajectories can be interpreted as mineral-melt fractionation trends: elements with convex-up trajectories have $^{El}D >^{Ti}D$; elements with linear trajectories have $^{El}D \approx ^{Ti}D$; and elements with convex-

down trajectories have $^{El}D <^{Ti}D$. Together, the G2 elements imply D values in this order, $^{Sc}D > ^{Al}D \approx ^{Ti}D \approx ^{Na}D > ^{Lu}D > ^{Hf}D > ^{P}D$, which is consistent with pyroxene-basalt fractionations. Note that Sc is noticeably elevated in Shergotty, Zagami, and NWA 856 because they contain cumulus pyroxene (Fig. 3h; e.g., Stolper and McSween 1979; McCoy et al. 1992; Treiman and Sutton 1993; Jambon et al. 2002).

These partitioning relationships are consistent with mantle partial melting, leaving a restite of olivine and low-Ca pyroxene. Partial melting seems an appropriate starting model
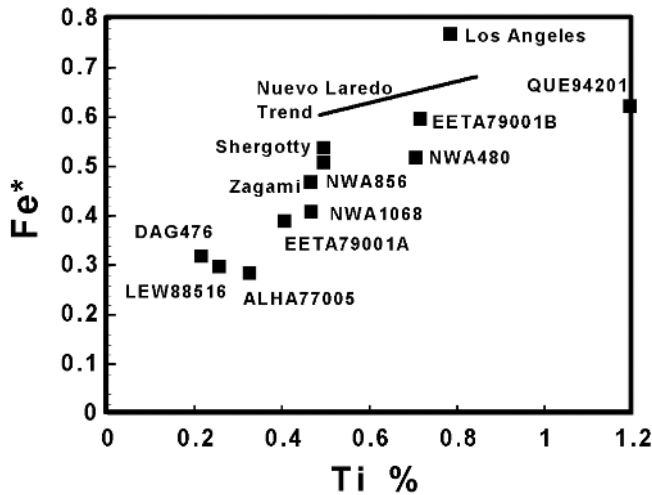
Figure 6. Comparison of Ti content and Fe* [= molar Fe/(Fe + Mg)] among shergottites. A trajectory for magma evolution by fractional crystallization is shown as the "Nuevo Laredo Trend," based on the eucrite meteorite basalts (Warren and Jerde 1987). Because of their dispersion on this graph, the shergottites clearly cannot all belong to a single fractionation trend. The clearest evidence is the true basalts Los Angeles, QUE 94201, and EET A79001 B, which do not fall on lines parallel to the Nuevo Laredo Trend line. Thus, they cannot be related by simple fractional crystallization of pyroxene + plagioclase. Plotting along a fractionation trajectory here is permissive but not conclusive proof of a fractionation relationship; for instance, NWA 480 and QUE 94201 plot along a fractionation trajectory, but their REE contents preclude close kinship (Barrat et al. 2002a; Kring et al. 2003). Cumulate rocks, like the lherzolite ALH A77005, fall closer to the origin, as their low magma content implies low Ti, and their cumulate crystals have low Fe*.

for genesis of the martian basalts, but fractional crystallization gives similar results. If one assumes a mantle dominated by olivine, augite, and low-Ca pyroxene, one can take $^P D_{solids/basalt} = 0$. Then, the trends for Ti and Sc can be modeled by partial melting with bulk partition coefficients of $^{Ti}D \approx 0.1$ (± 0.05) and $^{Sc}D \approx 0.3$ (± 0.1) (Figs. 3c and 3h). For a relatively magnesian mantle, such as might produce "primitive" basalt like EET A79001 A (Herd et al. 2002), $^{Sc}D_{augite/basalt} \approx 3$ (Irving 1978; Jones 1995), $^{Sc}D_{opx/basalt} \approx 0.75$, and $^{Sc}D_{olivine/basalt} \approx 0.17$; the latter 2 Ds are calculated following Jones (1995) for EET A-like basalt composition (examples: EA Wo_{0-4} and Wo_{0-3} of Longhi and Pan [1989]). From these values, the restite assemblage can contain at most ~7.5% augite to give the proper bulk ^{Sc}D and then only if it contains little low-Ca pyroxene. A more reasonable restite to give $^{Sc}D \approx 0.3$ would be about 25% low-Ca pyroxene and 75% olivine. Given the uncertainties in assigning bulk D values, this assemblage seems marginally consistent with the bulk $^{Ti}D \approx 0.1$ in partial melting; laboratory experiments (Longhi and Pan 1989; Dann et al. 2002) give $^{Ti}D_{pigeonite/basalt} \approx 0.08-0.14$.

The scope of elements that covary in G2 implies that the restite from this partial melting contained no minerals besides olivine and pyroxene. The restite cannot contain an aluminous phase (garnet, spinel, or plagioclase) because Al abundances covary with the other G2 elements. If the restite had contained an aluminous phase, it would have buffered Al abundances in the magmas to a relatively constant value. By similar arguments, the mantle residua after shergottite formation cannot contain ilmenite (Ti and Hf vary), any phosphate (P varies), zircon (Zr and Hf vary), or any sulfides (S, Se, and Cu vary).

The absence of an aluminous phase in the mantle residua is surprising, at least compared to terrestrial magma genesis. The Al content of terrestrial basalts is nearly constant, which is consistent with partial melting that leaves behind an aluminous phase and/or saturation in plagioclase. Only in some komatiite suites does Al content covary with Ti content or other measures of fractionation. Similarly, nearly all mantle peridotites, xenoliths, and ophiolites contain either garnet or chrome spinel. This absence of a residual aluminous phase is consistent with the low alumina in the SNC basalts and their sub-chondritic Al/Ti ratios (Treiman et al. 1986), which were inferred to reflect an early mantle depletion event.

G1 Diversification: Assimilation Versus Metasomatism

The shergottites show an enormous range of G1 element abundances. For instance, Los Angeles contains La at ~20 × CI chondritic, and DaG 467 contains La at only ~0.2 × CI (Fig. 4). Abundances of G1 elements are decoupled from those of G2; given the abundance of a G2 element in a shergottite, one can predict the abundances of other G2 elements but not those of G1 elements. So, how and when did the range in G1 element abundances arise?

G1/G2 Abundance Ratio Families

The key to understanding the abundances of G1 elements is that G1/G2 abundance ratios are restricted to only a few values, as shown in Fig. 5 (Treiman 2002, 2003). It can be seen that the shergottites fall into several distinct families of G1/G2 abundance ratios: QUE 94201 and others at the lowest ratios; then EET A79001 and the lherzolites; then NWA 480 alone; and then Los Angeles, Shergotty, and others with the highest ratios.

The families are best defined for the meteorites richest in the G2 elements (like QUE 94201 and Los Angeles) because uncertainties on those analyses are small. The ratio families are less clearly separated for meteorites with low abundances of La, Lu, and Sm because of greater analytical uncertainties, small proportions of G1 elements in the G2 element carrier (see above concerning Nd), and terrestrial contamination. Terrestrial contamination, most significant for desert meteorites, will tend to increase La/Sm and La/Lu ratios because the Earth's continental crust is LREE-enriched.

These trace element families have been noted in the last few years with the many new shergottite finds in deserts, both in the context of REE patterns (e.g., Rubin et al. 2000; Zipfel

et al. 2000) and in consideration of La/Sm ratios as an index of fractionation (Fig. 12 of Jambon et al. 2002). Here, these groupings by REE patterns are generalized to the whole of G1 and G2 elements—regularities in the REE patterns of shergottites must be seen in light of the broad scope of G1 and G2 element groups. These shergottite families are also evident in Sm-Nd isotopic ratios and in oxygen fugacities (Borg et al. 2002, 2003; Herd et al. 2002).

Source Metasomatism Versus Assimilation

Why do the shergottites fall into a limited number of chemical families, marked by G1/G2 ratios, radioisotope ratios, and oxygen fugacities? The variability in these chemical parameters has been ascribed to assimilation of enriched materials (i.e., crust) or to fluid-caused metasomatic enrichment of the basalts' source regions (i.e., mantle metasomatism). The data here are more consistent with metasomatism.

As a prelude, the G1/G2 element abundance ratios would be changed little by the fractionations implicated in diversification of G2 element abundances. Relative abundances of G2 elements in the shergottites are consistent with partitioning between the basalt magmas and orthopyroxene + olivine (as shown above). In these fractionations, G1 elements would be strongly partitioned into the basalt magma. Thus, the fractionations would have affected G1 and G2 elements similarly and changed G1/G2 abundance ratios only slightly. Because G1/G2 element ratios are unaffected by these fractionations, the ratios must have been set prior to the fractionations. Is it more reasonable that these G1 elements were added into shergottite magmas by assimilation or into the magmas' source regions by metasomatism?

Enrichment by assimilation is not the favored model for formation of the G1/G2 families of shergottites. If enrichment was by assimilation, each G1/G2 family must represent a single batch of magma because no reason exists for the different batches having assimilated identical proportions of G1-rich material. Further, each family should have the same crystallization age and should trace a single trajectory in Fe* versus some other measure of fractionation, like Ti content (Fig. 6). Neither of these inferences is validated. The age inference is not consistent with QUE 94201 and DaG 476, which appear to be in the same G1/G2 family but crystallized at significantly different times (327 and 474 Ma; Borg et al. 1997, 2003). The Fe* inference is not consistent with Los Angeles, Shergotty, and Zagami. Los Angeles belongs to the high-G1/G2 family with Shergotty and Zagami, but the Fe* of the former is too high to fall on the Fe*-Ti trajectory of the latter. "For most major and minor elements, the intercumulus compositions inferred by Stolper and McSween (1979) [for Shergotty and Zagami] match Los Angeles well. However, [they] are appreciably less ferran . . . than the analyzed samples of Los Angeles" (Rubin et al. 2000).

On the other hand, if the enrichment were source metasomatism, each G1/G2 family would represent magmas drawn from a source region (i.e., a portion of the mantle) that had been enriched to some degree in G1 elements. Magmas in a G1/G2 family could be related by fractional crystallization, but need not be. Similarly, magmas in a single G1/G2 family need not have formed simultaneously—they could represent temporally distinct melting events from the same source region. The source metasomatism model allows more latitude in the compositions and ages of magmas than does the assimilation model and so is better able to accommodate the complexities of the shergottites.

INTERPRETATION: ANCIENT DIFFERENTIATION

When and how did the elements of G1 and G2 become separated so cleanly? This question is significant because it encompasses that of the extreme fractionation of Nd from Sm seen in QUE 94201 and DaG 476 (Borg et al. 1997; Lodders 1998; Barrat et al. 2002; Kring et al. 2003). The "when" is known precisely, but the "how" is not; at this point, one can offer broad constraints on this early differentiation event, extending the knowledge already gleaned from radioisotope systematics.

The timing of this extreme fractionation is known precisely. Neodymium isotope ratios, ε_{Nd}^{142} and ε_{Nd}^{143}, in QUE 94201 and other shergottites fix the time of Sm-Nd fractionation as ~4.513 Ga (Borg et al. 1997, 2003). Given the geochemical coherence of elements within each element group, one can reasonably infer that all elements in G1 and G2 were separated at the same time, ~4.513 Ga. Initially, the martian mantle probably had chondritic relative proportions of refractory lithophile elements (e.g., Treiman et al. 1986; Longhi et al. 1992; Fig. 7 of Blichert-Toft et al. 1999). From that chondritic material, G1 elements (including Nd) were removed nearly quantitatively (Blichert-Toft et al. 1999), leaving a residue relatively enriched in G2 elements (including Sm). These fractionations may have happened in a magma ocean and during crystallization of its cumulates (Borg et al. 1997; Brandon et al. 2000), which may have been simultaneous with core formation (Lee and Halliday 1997; Kleine et al. 2002).

Two particular aspects of this early differentiation event can be addressed via the bulk compositions. First, how could this early fractionation be so extreme? And, second, why do some elements appear to have behaved weirdly (i.e., with the wrong element group)?

Extreme Fractionation

The extreme fractionation of G1 from G2 is best exemplified by the separation of Sm from Nd, as modeled for radioisotope chronology and tracking (Borg et al. 1997, 2003). The Sm/Nd ratio in QUE 94201 is approximately 2.5

times that of chondrites (Borg et al. 1997; Kring et al. 2003)—a huge fractionation between two nearly adjacent rare earth elements. This degree of fractionation cannot be modeled by a few simple events (e.g., partial melting, fractional crystallization) involving common mantle minerals. Borg et al. (1997) found that they required 4 or 5 successive partial melting events, with low melt proportions, leaving a garnet-bearing residue. Similarly complex schemes are required by the less-extreme shergottites like EET A79001 (e.g., Smith et al. 1984).

Such multi-stage fractionation schemes are possible, even likely, in a long-lived magmatic system like the planet Mars. However, constraining the minerals involved in the multi-stage fractionations would be helpful: whether "complex" magmatic processes might be possible or whether unusual minerals might permit simpler fractionation schemes.

First, the mineralogy of multi-stage fractionation must involve a phase (or phases) that discriminates greatly between the light rare earth elements (La, Ce, Nd) and the heavier rare earths (e.g., Borg et al. 1997). This solid assemblage must also permit the fractionations that separate the other G1 and G2 elements. Garnet has generally been identified as the phase responsible for Sm-Nd fractionation, and it is consistent with many of the fractionations between G1 and G2. For instance, garnet can contain Al as an essential constituent and has D values for G2 HFSE (except P; Table 1) similar to those of heavy REE, so a garnet-bearing assemblage would be a reasonable sink for these elements as G1 elements were removed. However, garnet alone could not sequester the plagiophile elements Na and Sr (Table 1). A garnet-augite assemblage (i.e., eclogite) could be adequate, as those elements' partition coefficients $D_{basalt/augite}$ are similar enough to those of $^{Sm}D_{basalt/garnet}$ to expect that they might behave with Sm during fractionations. Scenarios like this await detailed modeling. In any case, the multi-stage fractionation scheme must satisfy distributions of more elements than the REE.

Few minerals besides garnet (normal or majoritic) can fractionate the LREE (G1) from the HREE (G2) with any efficiency. Allanite (an epidote-group mineral) has been suggested (Beard et al. 2002) but is unlikely in basaltic systems. Amphibole is approximately as efficient as augite in fractionating LREE from HREE (Jones 1995), but it is unlikely to be a residual mantle phase in basalt petrogenesis.

In another view, the separation of G1 and G2 elements can be seen as a gross amplification of normal basalt-mineral fractionations (except for a few elements). Group 1 elements are strongly partitioned into basalt magma relative to common silicates, and G2 elements are partitioned similarly but less intensely (Irving 1978; Jones 1995). Multi-process petrogenetic schemes like that of Borg et al. (1997) work by amplifying normal fractionations, but other processes are possible.

In fact, many processes undreamt of by Wager and Brown

(1967) can operate in large magmatic systems (presumably including magma oceans) and produce highly differentiated rocks. Zone refining can produce magmas highly enriched in G1 elements and residual solids grossly depleted in those elements (e.g., McBirney 1987; Neal and Davidson 1989). Magmas can convect into and through a pile of cumulus crystals, strongly modifying the compositions of both, even to the point of producing monomineralic rocks (e.g., Kelemen et al. 1992; Meurer and Boudreau 1998; Braun and Kelemen 2002). In brief, large magmatic systems (including planets) need not only rely on simply modeled processes to produce highly enriched or depleted sources for magmas.

Weird Fractionations

Chalcogenides

Why should sulfur, selenium, and copper behave similarly to titanium and aluminum (etc.), as G2 elements, in Mars' early differentiation? For sulfur and selenium, at least, no evidence exists of significant compatibility into silicate or oxide minerals of basalt petrogenesis, so the mineral assemblage that carries G2 elements must include a sulfur-bearing phase. That phase is probably an iron sulfide, like troilite or pyrrhotite, that accompanies the garnet and augite hypothesized above.

Phosphorus

Why should phosphorus have behaved as a G2 element in Mars' early fractionation? Phosphate is highly soluble in basalt magmas (Watson 1980); QUE 94201-like magma can contain ~7% P_2O_5 by weight before Ca-phosphate appears on its liquidus (C. Herd, personal communication). Yet, P is nearly insoluble in common silicates, like olivine and pyroxene, and in less abundant mantle minerals, like spinel and garnet. Thus, phosphorus should behave as a highly incompatible element, G1, and does so in most basalt petrogenesis.

The clearest manifestation of P's anomalous behavior is the decoupling of P and light rare earth elements like La. In most basalt genesis, P and La covary closely (e.g., Fig. 2 of Newsom and Drake 1983) because both are (as above) nearly insoluble in common silicate and oxide minerals, and because the principal La-bearing solid in basaltic systems is Ca phosphate. So, how can the anomalous behavior of phosphorus be rationalized? The data here provide no unique solution but suggest some possibilities.

One possible way to decouple P from La is to invoke the distillation or zone melting model suggested above for the extreme fractionations of REE. This scenario would require that the residual solids have $^{P}D_{fluid/solids}$ comparable to that of Ti or Al, ~0.1. What phase(s) might allow such a moderate ^{P}D is not clear. Majoritic garnet is possible because it can accept significant phosphorus (Berlin and Xirouchakis 2002), but it is only stable very deep in the martian mantle (Bertka and Fei

1997). Further experiments will be needed to test this possibility.

Another possibility is that the solid assemblage included a relatively insoluble phosphate phase that accepts little La. What such a phase might be is not clear—merrillite and apatite are unsuitable. The light REE are strongly partitioned into merrillite (whitlockite) from basalt magma with D values near 25 (e.g., Lundberg et al. 1990; Jones 1995). Fluorapatite has D values for LREE an order of magnitude smaller than merrillite, but these $D_{fluorapatite/basalt}$ are either greater than unity or slightly smaller (Murrell et al. 1984; Lundberg et al. 1988; Joliff et al. 1993; Jones 1995; McSween et al. 1996). Similarly, $^{LREE}D_{chlorapatite/basalt}$ are less than unity but not low enough to produce significant fractionation of La from P (Fleet et al. 2000). Perhaps some other phosphate phase occurs at high pressure, such as $\gamma-Ca_3(PO_4)_2$ (Xie et al. 2002). Conceivably, such a phase in Mars' deep mantle might not accept LREE as substituents. Again, further experiments would be needed.

Finally, P could be completely decoupled from La (and most other elements) if it were not present as phosphate but as a reduced species such as a solute in iron metal or as a phosphide. One could imagine that P-bearing metal or a phosphide would be minimally soluble in the fluid that mobilized G1 elements, so P would remain with the solid assemblage. This scheme could be reasonable if the martian mantle were at an oxidation state at or below the IW buffer (e.g., Herd et al. 2002; McCanta et al. 2003; Musselwhite et al. 2003) so that iron metal could form (perhaps these constraints would be ameliorated if significant water were available; Righter and Drake 1999). In that case, significant P could enter the solid metal (Jones 1995).

If a phosphide or P-bearing metal were stable during this early differentiation event and insoluble in basalt magma, it cannot now be present in Mars' mantle. This follows from 2 facts: the P content of the shergottites is not buffered (Fig. 3c), so a residual P-bearing phase cannot exist; and the oxidation state of the martian mantle (Herd et al. 2002) is now far too oxidizing to permit phosphides.

CONCLUSIONS

The chemical compositions of the shergottite martian meteorites are complex but show enough regularity to constrain their formation processes. From the element-element correlations described here, 4 broad conclusions are inferred.

1. The most recent fractionation that affected the shergottites, evident in abundances of G2 elements, is consistent with partial melting of lherzolitic material leaving a restite of opx + ol. Significantly, the restite cannot contain aluminous phases, ilmenite, zircon, phosphates, or sulfides.
2. Abundances of highly incompatible elements in G1 are

decoupled from those of G2. Abundance ratios of G1/G2 elements are not randomly dispersed but fall into ~4 separate families. Shergottites in a G1/G2 family do not necessarily have the same crystallization age nor do they necessarily fall on the same fractionation trajectory involving compatible elements (e.g., Ti versus Fe*). These observations imply that the G1/G2 families were established before basalt formation and, thus, are more consistent with metasomatic enrichment (in G1) of their source rather than with assimilation after basalt formation.
3. The distinction between G1 and G2 elements was established very early in Mars' history and was extreme (as known from radioisotope studies). The extreme fractionations are not consistent with simple petrogenesis and require either multiple fractionations or "complex" petrogenetic processes.
4. The behavior of phosphorus in this early fractionation event is inexplicable by normal petrogenetic processes and minerals. Several explanations are possible; the simplest mineralogically is that the residual solid assemblage (carrier of G2 elements) included a phosphide or P-bearing metal. If so, this suggests that Mars' mantle is much more oxidized now than during the ancient fractionation event. On the other hand, P may be partitioned significantly into garnet or another silicate phase at high pressure (e.g., Berlin and Xirouchakis 2002).

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REFERENCES

Anders E. and Grevesse N. 1989. Abundances of elements: Meteoritic and solar. *Geochimica et Cosmochimica Acta* 53:197–214.

Barrat J. A., Gillet P., Lesourd M., Blichert-Toft J., and Poupeau G. R. 1999. The Tatahouine diogenite: Mineralogical and chemical effects of sixty-three years of terrestrial residence. *Meteoritics & Planetary Science* 34:91–97.

Barrat J. A., Blichert-Toft J., Nesbitt R. W., and Keller F. 2001. Bulk chemistry of Saharan shergottite Dar al Gani 476. *Meteoritics & Planetary Science* 26:23–29.

Barrat J. A., Gillet P., Sautter V., Jambon A., Javoy M., Gpel C., Lesourd M., Keller F., and Petit E. 2002a. Petrology and

geochemistry of the basaltic shergottite Northwest Africa 480. *Meteoritics & Planetary Science* 37:478–500.

Barrat J. A., Jambon A., Bohn M., Gillet P., Sautter V., Gpel C., Lesourd M., and Keller F. 2002b. Petrology and chemistry of the picritic shergottite Northwest Africa 1068 (NWA 1068). *Geochimica et Cosmochimica Acta* 66:3505–3518.

Basaltic Volcanism Study Project. 1981. *Basaltic volcanism on the terrestrial planets.* New York: Pergamon. 1286 p.

Berlin J. and Xirouchakis D. 2002. Phosphorus equilibria among mafic silicate phases (abstract #234-4). *Geological Society of America Abstracts with Programs.*

Bertka C. M. and Fei Y. 1997. Mineralogy of the martian interior up to core-mantle boundary pressures. *Journal of Geophysical Research* 102:5251–5264.

Blichert-Toft J., Gleason J. D., Telouk P., and Albarede 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.

Bogard D. D. and Johnson P. 1983. Martian gases in an Antarctic meteorite? *Science* 221:651–654.

Borg L. E., Nyquist L. E., Wiesmann H., and Shih C. Y. 1997. Constraints on martian differentiation processes from Rb-Sr and Sm-Nd isotopic analyses of the basaltic shergottite QUE 94201. *Geochimica et Cosmochimica Acta* 61:4915–4931.

Borg L. E. 2002. Exploring trace element and isotopic mixing relationships in the martian meteorite suite (abstract). In *Unmixing the SNCs: Chemical, isotopic, and petrologic components of the martian meteorites,* edited by Treiman A. H. and Herd C. D. K. LPI Contribution 1134. Houston: Lunar and Planetary Institute. p. 9.

Borg L. E., Nyquist L. E., Wiesmann H., Shih C. Y., and Reese Y. 2003. The age of Dar al Gani 476 and the differentiation history of the martian meteorites inferred from their radiogenic isotopic systematics. *Geochimica et Cosmochimica Acta* 67:3519–3536.

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

Braun M. G. and Kelemen P. B. 2002. Dunite distribution in the Oman Ophiolite: Implications for melt flux through porous dunite conduits. *Geochemistry, Geophysics, Geosystems* 3:11.

Crozaz G. and Wadhwa M. 2001. The terrestrial alteration of Saharan shergottites Dar al Gani 476 and 489: A case study of weathering in a hot desert environment. *Geochimica et Cosmochimica Acta* 65:971–978.

Drake M. J. 2000. Accretion and primary differentiation of the Earth: A personal journey. *Geochimica et Cosmochimica Acta* 64: 2363–2370.

Dreibus G., Palme H., Rammensee W., Spettel B., Weckwerth G., and Wänke H., 1982. Composition of the Shergotty parent body: Further evidence of a two-component model for planet formation (abstract). 13th Lunar and Planetary Science Conference. pp. 196–187.

Dreibus G., Jochum K., Palme H., Spettel B., Wlotzka F., and Wänke H. 1992. LEW 88516: A meteorite compositionally close to the "martian mantle" (abstract). *Meteoritics* 27:216–217.

Dreibus G., Spettel B., Wlotzka F., Schulz L., Weber H. W., Jochum K. P., and Wänke H. 1996. QUE 94201: An unusual martian basalt (abstract). *Meteoritics & Planetary Science* 31:A39–A40.

Fleet M. E., Liu S., and Pan Y. 2000. Rare earth elements in chlorapatite $[Ca_5(PO_4)_3Cl]$: Uptake, site preference and degradation of the monoclinic structure. *American Mineralogist* 85:1437–1446.

Herd C. D. K., Borg L. E., Jones J. H., and Papike J. J. 2002. Oxygen fugacity and geochemical variation in the martian basalts:

Implications for martian basalt petrogenesis and the oxidation state of the upper mantle of Mars. *Geochimica et Cosmochimica Acta* 66:2025–2036.

Ionov D. A., Bodinier J. L., Mukasa S. B., and Zanetti A. 2002. Mechanisms and sources of mantle metasomatism: Major and trace element compositions of peridotite xenoliths from Spitsbergen in the context of numerical modeling. *Journal of Petrology* 43:2261–2278.

Irving A. J. 1978. A review of experimental studies of crystal/liquid trace element partitioning. *Geochimica et Cosmochimica Acta* 42:743–770.

Jambon A., Barrat J. A., Sautter V., Gillet P., Gpel C., Javoy M., Joron J. L., and Lesourd M. 2002. The basaltic shergottite Northwest Africa 856: Petrology and chemistry. *Meteoritics & Planetary Science* 37:1147–1164.

Jolliff B. L., Haskin L. A., Colson R. O., and Wadhwa M. 1993. Partitioning in REE-saturated minerals: Theory, experiment and modelling of whitlockite, apatite, and evolution of lunar residual magmas. *Geochimica et Cosmochimica Acta* 57:4069–4094.

Jones J. H. 1989. Isotopic relationships among the shergottite, the nakhlites, and Chassigny. Proceedings, 19th Lunar and Planetary Science Conference. pp. 465–474.

Jones J. H. 1995. Experimental trace element partitioning. In *Rock physics and phase relations; vol. 3,* edited by Ahrens T. J. Washington D.C.: American Geophysical Union. pp. 73–104.

Kelemen P. B., Dick H. J., and Quick J. E. 1992. Formation of harzburgite by pervasive melt-rock reaction in the upper mantle. *Nature* 358:635–641.

Kiefer W. 2002. Melting the martian mantle: Shergottite formation and implications for present-day mantle convection on Mars (abstract). In *Unmixing the SNCs: Chemical, isotopic, and petrologic components of the martian meteorites,* edited by Treiman A. H. and Herd C. D. K. LPI Contribution 1134. Houston: Lunar and Planetary Institute. pp. 29–30.

Kiefer W. 2003. Melting in the martian mantle: Shergottite formation and implications for present-day mantle convection on Mars. *Meteoritics & Planetary Science.* This issue.

Kleine T., Munker C., Mezger K., Palme H., and Bischoff A. 2002. Revised Hf-W ages for core formation in planetary bodies (abstract). 12th Annual V. M. Goldschmidt Conference. pp. A404.

Kring D. A., Hill D. H., and Boynton W. V. 2003. Geochemistry of QUE 94201. *Meteoritics & Planetary Science.* This issue.

Laul J. C., Smith M. R., Wänke H., Jagoutz E., Dreibus G., Palmen H., Spettel B., Burghele A., Lipschutz M. E., and Verkouteren R. M. 1986. Chemical systematics of the Shergotty meteorite and the composition of its parent body (Mars). *Geochimica et Cosmochimica Acta* 50:909–926.

Lee D. C. and Halliday A. N. 1997. Core formation in Mars and differentiated asteroids. *Nature* 388:854–857.

Lodders K. 1998. A survey of shergottite, nakhlite, and chassignite meteorites' whole rock compositions. *Meteoritics & Planetary Science* 33:A183–A190.

Longhi J. and Pan V. 1989. The parent magmas of the SNC meteorites. Proceedings, 19th Lunar and Planetary Science Conference. pp. 451–464.

Longhi J., Knittle E., Holloway J., and Wänke H. 1992. The bulk composition, mineralogy, and internal structure of Mars. In *Mars,* edited by Kieffer H. H., Jakosky B. M., Snyder C. W., Matthews M. S. Tucson: University of Arizona Press. pp. 184–208.

Lundberg L. L., Crozaz G., McKay G. A., and Zinner E. 1988. Rare earth element carriers in the Shergotty meteorite and implications for its chronology. *Geochimica et Cosmochimica Acta* 52:2147–2163.

Lundberg L. L., Crozaz G., and McSween H. Y., Jr. 1990. Rare earth

elements in minerals of the ALH A77005 shergottite and implications for its parent magma and crystallization history. *Geochimica et Cosmochimica Acta* 54:2535–2547.

Ma M. S., Laul J. C., and Schmitt R. A. 1981. Complementary rare earth patterns in unique achondrites, such as ALH A77005 and shergottites, and in the Earth. Proceedings, 12th Lunar and Planetary Science Conference. pp. 1349–1358.

McBirney A. R. 1987. Constitutional zone refining of layered intrusions. In *Origins of igneous layering,* edited by Parsons I. Dordrecht: D. Reidel. pp. 437–452.

McCanta M. C., Rutherford M. J., Dyar M. D., and Delaney J. S. 2003. *Oxygen fugacity of the martian mantle from pyroxene/melt partitoning of REE* (abstract #1361). 34th Lunar and Planetary Science Conference. CD-ROM.

McCoy T. J., Taylor G. J., and Keil K. 1992. Zagami: Product of a two-stage history. *Geochimica et Cosmochimica Acta* 56:3571–3582.

McCoy T. J., Wadhwa M., and Keil K. 1999. New lithologies in the Zagami meteorite: Evidence for fractional crystallization of a single magma unit on Mars. *Geochimica et Cosmochimica Acta* 63:1249–1262.

McSween H. Y., Jr. 1994. What we have learned about Mars from SNC meteorites. *Meteoritics* 29:757–779.

McSween H. Y., Jr., Eisenhour D. D., Taylor L. A., Wadhwa M., and Crozaz G. 1996. QUE 94201 shergottite: Crystallization of a martian basaltic magma. *Geochimica et Cosmochimica Acta* 60: 4562–4569.

Meurer W. P. and Boudreau A. E. 1998. Compaction of igneous cumulates Part I: Geochemical consequences for cumulates and liquid fractionation trends. *Journal of Geophysical Research* 106:281–292.

Meyer C. 2003. Mars Meteorite Compendium 2003. Johnson Space Center, JSC #27672 Rev. B. http://curator.jsc.nasa.gov/antmet/mmc/mmc.htm.

Mikouchi T., Miyamoto M., and McKay G. A. 1998. Mineralogy of basaltic shergottite Queen Alexandra Range 94201: Similarities to Elephant Moraine A79001 (Lithology B) martian meteorite. *Meteoritics & Planetary Science* 33:181–189.

Mikouchi T., Miyamoto M., and McKay G. A. 2001. Experimental crystallization of the QUE 94201 basaltic shergottite (abstract #2100). 32nd Lunar and Planetary Science Conference. CD-ROM.

Murrell M. T., Brandriss M., Wollum D. S., and Burnett D. S. 1984. Pu-REE-Y partitioning between apatite and whitlockite (abstract). 15th Lunar and Planetary Science Conference. pp. 579–580.

Musselwhite D. S. and Jones J. H. 2003. Oxygen fugacity of the martian mantle from pyroxene/melt partitoning of REE (abstract #2032). 34th Lunar and Planetary Science Conference. CD-ROM.

Neal C. R. and Davidson J. P. 1989. An unmetasomatized source for the Malaitan alnite (Solomon Islands): Petrogenesis involving zone refining, megacryst fractionation, and oceanic crustal assimilation. *Geochimica et Cosmochimica Acta* 53:1975–1990.

Newsom H. E. and Drake M. J. 1983. Experimental investigation of the partitioning of phosphorus between metal and silicate phases: Implications for the Earth, Moon, and eucrite parent body. *Geochimica et Cosmochimica Acta* 47:93–100.

O'Hara M. J. and Mathews R. E. 1981. Geochemical evolution in an advancing, periodically replenished, periodically tapped, continuously fractionating magma chamber. *Journal of the Geological Society, London* 138:237–277.

Reiners P. W., Nelson B. K., and Ghiorso M. S. 1995. Assimilation of felsic crust by basaltic magma: Thermal limits and extents of crustal contamination of mantle-derived magmas. *Geology* 23: 563–566.

Righter K. and Drake M. J. 1999. Effect of water on metal-silicate partitioning of siderophile elements: A high pressure and temperature terrestrial magma ocean and core formation. *Earth and Planetary Science Letters* 171:383–399.

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.

Ryder G. and Schuraytz B. C. 2001. Chemical variation of the large Apollo 15 olivine-normative basalt rock samples. *Journal of Geophysical Research* 106:1435–1451.

Sims K. W. W. and DePaolo D. J. 1997. Inferences about mantle magma sources from incompatible element concentration ratios in oceanic basalts. *Geochimica et Cosmochimica Acta* 61:765–784.

Steele I. M. and Smith J. V. 1982. Petrography and mineral chemistry of two basalts and olivine-pyroxene-spinel fragments in achondrite EET A79001. Proceedings, 13th Lunar and Planetary Science Conference. *Journal of Geophysical Research* 87:A375–A384.

Stolper E. and McSween H. Y., Jr. 1979. Petrology and origin of the shergottite meteorites. *Geochimica et Cosmochimica Acta* 43: 589–602.

Smith M. R., Laul J. C., Ma M. S., Huston T., Verkouteren R. M., Lipschutz M. E., and Schmitt R. A. 1984. Petrogenesis of the SNC (shergottites, nakhlites, chassignites) meteorites: Implications for their origin from a large dynamic planet, possibly Mars. Proceedings, 14th Lunar and Planetary Secience Conference. *Journal of Geophysical Research* 89:B612–B630.

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.

Treiman A. H. 2002. Element-element correlations among martian meteorite bulk compositions: Peculiaritites explained (?) by mixing, with implications for the composition of Mars (abstract). In *Unmixing the SNCs: Chemical, isotopic, and petrologic components of the martian meteorites,* edited by Treiman A. H. and Herd C. D. K. LPI Contribution 1134. Houston: Lunar and Planetary Science Institute. pp. 59–60.

Treiman A. H. 2003. Mantle metasomatism in Mars: Evidence from bulk chemical compositions of martian basalts (abstract #1413). 34th Lunar and Planetary Science Conference. CD-ROM.

Treiman A. H. and Sutton S. R. 1992. Petrogenesis of the Zagami meteorite: Inferences from synchrotron X-ray (SXRF) microprobe and electron microprobe analyses of pyroxenes. *Geochimica et Cosmochimica Acta* 56:4059–4074.

Treiman A. H., Jones J. H., and Drake M. J. 1984. The SNC/Mars connection: Geochemical inconsistencies (abstract). 15th Lunar and Planetary Science Conference. pp. 864–865.

Treiman A. H., Jones J. H., and Drake M. J. 1987. Core formation in the shergottite parent body: A chemical model. *Journal of Geophysical Research* 92:E627–E632.

Treiman A. H., Drake M. J., Janssens M. J., Wolf R., and Ebihara M. 1986. Core formation in the Earth and shergottite parent body (SPB): Chemical evidence from basalts. *Geochimica et Cosmochimica Acta* 50:1071–1091.

Treiman A. H., McKay G. A., Bogard D. D., Mittlefehldt D. W., Wang M. S., Keller L., Lipschutz M. E., Lindstrom M. M., and Garrison D. 1994. Comparison of the LEW 88516 and ALH A77005 martian meteorites: Similar but distinct. *Meteoritics* 29:581–592.

Wager L. R. and Brown G. M. 1967. *Layered igneous rocks.* San Francisco: W. H. Freeman. 588 p.

Wang M. S., Mokos J. A., and Lipschutz M. E. 1998. Martian

meteorites: Volatile trace elements and cluster analyses. *Meteoritics & Planetary Science* 33:671–675.

Wänke H. 1981. Constitution of the terrestrial planets. *Philosophical Transactions of the Royal Society of London A* 303:287–302.

Warren P. H. and Jerde E. A. 1987. Composition and origin of Nuevo Laredo trend eucrites. *Geochimica et Cosmochimica Acta* 51: 713–725.

Warren P. H. and Kallemeyn G. W. 1997. Yanati 793605, EET 79001, and other presumed martian meteorites: Compositional clues to their origins. *Antarctic Meteorite Research* 10:61–81.

Watson E. B. 1980. Apatite and phosphorus in mantle source regions: An experimental study of apatite-melt equilibria at pressures to 25 kbar. *Earth and Planetary Science Letters* 51:322–335.

Xie X., Chen M., and Wang D. 2002. Comparison of shock-induced phase transition of phosphates between the Suizhou and Sixiangkou meteorites (abstract). *Meteoritics & Planetary Science* 37:A151.

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

APPENDIX

Sources of bulk chemical data.

Data source	Meteorite(s)
Lodders (1998)	Shergotty, Zagami, ALH A77005, LEW 88516, EET A79001 A, EET A79001 B, Nakhla, Chassigny, Lafayette
Barrat et al. (2002a)	DaG 476, Shergotty, Zagami
Rubin et al. (2000)	Los Angeles
Mikouchi et al. (1996), Dreibus et al. (1996), Warren and Kallemeyn (1997), Kring et al. (2003)	QUE 94201
Barrat et al. (2002b)	NWA 1068
Jambon et al. (2002)	NWA 856, Los Angeles
Dreibus et al. (2002)	SaU 005
Taylor et al. (2002)	Dhofar 019