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The oxygen fugacity of olivine-phyric martian basalts and the components within the mantle and crust of Mars

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Abstract–The oxygen fugacity of olivine-phyric martian basalts is estimated using olivine-pyroxene-spinel equilibria, supported by detailed petrography. Results are plotted, along with previous oxygen fugacity estimates, against La/Yb, which is used as a proxy for long-term incompatible-element depletion or enrichment in martian basalt reservoirs. In general, the correlation between oxygen fugacity and La/Yb observed by Herd et al. (2002a) holds for the olivine-phyric basalts. The implications of the correlation are re-evaluated in light of work by Borg et al. (Forthcoming), which indicates that the variations in radiogenic isotopic composition can be modeled by mixing of mantle sources established by 4.5 Ga through crystallization of a magma ocean in lieu of assimilation of crustal material. The results demonstrate that the crust-like component, interpreted as trapped liquid in a magma ocean cumulate pile, must be oxidized to explain the oxygen fugacity of the martian basalts. Consequently, the pre-eruptive water contents of the more oxidized basalts are expected to be higher, although water is not called upon as the cause of the oxidation. Unmixing of mantle components provides an important context for the interpretation of oxygen isotopes, demonstrated here, and of samples returned from the martian surface.

INTRODUCTION

Oxygen fugacity (fO_2) is an important variable in the petrogenesis of basaltic igneous rocks. On Earth, the fO_2 of a basalt is dependent on the oxidation state of the mantle source, which is modified by plate tectonic processes. In this way, the tectonic setting in which the basalt was formed has an influence on its fO_2 and is the cause of the ~7 log unit variation in fO_2 among terrestrial basalts (Carmichael and Ghiorso 1990; Carmichael 1991; Ballhaus and Frost 1994). The lack of a consistent set of rigorously-determined fO_2 estimates from mineral equilibria for shergottite meteorites (herein referred to as martian basalts) precluded any significant interpretation of this variable for Mars until recently when Herd et al. (2001) demonstrated that the fO_2 of martian basalts varies by 2 to 3 log units, a result which corroborated the range indicated by an independent method employed by Wadhwa (2001).

Several means of estimating fO_2 are now at our disposal. Herd et al. (2001) applied established Fe-Ti oxide geothermometers and oxybarometers (Ghiorso and Sack 1991; Anderson et al. 1993) to oxides in several of the martian basalts (Queen Alexandra [QUE] 94201, Elephant Moraine [EET] 79001, Zagami, Los Angeles, and Shergotty). The results corroborated and extended previous estimates that were made for Shergotty, Zagami and QUE 94201 using similar thermodynamic models (Stolper and McSween 1979; Ghosal et al. 1998; McSween et al. 1996). The drawback to the Fe-Ti oxide method is that the oxides in the martian basalts are late-crystallizing phases, and subsolidus equilibration of the oxides is known to occur if cooling rates are sufficiently slow (e.g., Lindsley and Frost 1992; Haggerty 1991). For this reason, others have questioned whether the fO_2 estimates of Herd et al. (2001) reflect the conditions under which the magma began to crystallize (Wadhwa 2001), although Herd et al. (2001) present arguments to the contrary. Wadhwa (2001) used a measure of the Eu anomaly in augite cores, expressed as D_{Eu}/D_{Gd}, as a proxy for fO_2 (Philpotts 1970; McKay 1989). Oxygen fugacity from this method should reflect magmatic conditions because the Eu and Gd measurements are made on the earliest-formed augite cores in the martian basalts. Herd et al. (2002a) demonstrated that D_{Eu}/D_{Gd} (from Wadhwa 2001) correlates with fO_2 derived from oxides (Herd et al. 2001) but that fO_2 calculated from D_{Eu}/D_{Gd} in augite is offset by 1–2 log units from the oxide-derived estimates, demonstrating that: 1) the fO_2 estimates from Fe-Ti oxides likely represent magmatic fO_2 conditions (and cooling rates were sufficiently high to preclude resetting); and 2) the Eu anomaly method required an fO_2 calibration that was more appropriate to martian basalt compositions. Since then, 2 groups have taken up the challenge and are working to recalibrate the Eu oxybarometer for martian pyroxene compositions (McCanta and Rutherford 2002; Musselwhite and Jones 2003). The preliminary estimates based on these calibrations are, in general, in better agreement with Fe-Ti oxide estimates, given uncertainties in both methods. However, the situation is not much improved, and other methods that are able to estimate magmatic fO_2 are desirable.

A third method for estimating fO_2, which uses phases considered to have formed close to the liquidus, was presented by Herd et al. (2002a) in their approach to the Dar al Gani 476 martian basalt. Noting that the Fe-Ti oxide method failed to produce reasonable estimates for this basalt, due to small oxide grain sizes and compositions that deviated from ideal Fe-Ti oxide compositions, Herd et al. (2002a) instead used the compositions of olivine, low-Ca pyroxene and chromian spinel as an oxybarometer based on the equilibrium:

$$6FeSiO_3 + 2Fe_3O_4 = 6Fe_2SiO_4 + O_2 \tag{1}$$

using the model of Wood (1991). Input to this model includes the temperature, the activity of magnetite in the spinel, pressure, mole fractions of Fe and Mg end members in olivine, and atomic fractions of Fe in the 2 orthopyroxene sites. The latter 2 parameters are easily obtained from compositional data. The temperature is derived from olivine-spinel geothermometry (Sack and Ghiorso 1991a), and the activity of magnetite in the spinel is calculated using the MELTS Supplemental Calculator (Sack and Ghiorso 1991a, b). The pressure is assumed to be 1 bar. The uncertainty on a given estimate is ±0.5 log units (Wood 1991). Careful selection of co-crystallizing olivine, pyroxene, and spinel enables an estimate of fO_2 that is presumably more representative of magmatic conditions. The limitation of this method is that equilibrium may not exist between all 3 phases. Olivine megacrysts in the olivine-phyric martian basalts may be cumulate crystals (phenocrysts) or xenocrysts. Olivine phenocrysts are cogenetic with the groundmass, while olivine xenocrysts are not. Therefore, this method may only be rigorously applied in the former case.

Herd et al. (2002a) recognized a correlation between fO_2 and certain geochemical parameters indicative of long-term incompatible-element enrichment or depletion (La/Yb, initial $^{87}Sr/^{86}Sr$, and initial ε_{Nd}), with more oxidized basalts having greater long-term incompatible-element enrichment. Wadhwa (2001) had also recognized a relationship between D_{Eu}/D_{Gd} (an fO_2 proxy) and LREE enrichment and Sr and Nd isotopic composition. Herd et al. (2002a) went further, modeling the variations in fO_2 as mixing between mantle-like and crust-like reservoirs, using geochemical parameters as constraints. The terms "mantle-like" and "crust-like" were very carefully chosen because Herd et al. (2002a) recognized that both components could be present in the mantle, where mixing during partial melting could occur, or that the crust-like component is in the martian crust, in which case, mixing would occur by assimilation. Herd et al. (2002a) favored the crustal assimilation model, in part because on Earth, the crust represents a long-term incompatible-element-enriched reservoir that is broadly complementary to the mantle. Also, the correlation between bulk oxygen isotopic composition and fO_2, in which more oxidized basalts had heavier isotopic compositions, initially suggested a crustal component. A heavier isotopic composition is consistent with communication with the martian atmosphere, as noted by Romanek et al. (1998) in their isotopic study of alteration material in the Lafayette martian meteorite.

Borg et al. (2003) demonstrate that a 2-stage model Nd isochron age of 4.51 Ga is consistent with both the short-lived ^{146}Sm-^{142}Nd and long-lived ^{147}Sm-^{143}Nd isotopic compositions of the martian meteorites, as well as the 4.5 Ga Rb-Sr whole rock isochron (Shih et al. 1982; Jagoutz 1991; Borg et al. 1997). They use this age to calculate the Rb/Sr, Sm/Nd, and Lu/Hf parent/daughter ratios of martian meteorite sources and to demonstrate that the large ranges in each correlate with oxygen fugacity. These correlations indicate that the fO_2 of martian basalts is broadly set at the time of melt extraction from their sources. Borg et al. (2003) further suggest that, because the values and ranges of parent/daughter ratios for martian meteorite sources are similar to those inferred for lunar mare basalt sources, the range in martian meteorite sources may best be explained by a magma ocean model analogous to the lunar magma ocean. In this model, the trace elements, isotopic systematics, and oxygen fugacity of a given martian basalt are constrained by its mantle source composition, inherited from magma ocean crystallization at 4.5 Ga. Major element variations are due to the mineralogy of the source at the time of partial melting and to subsequent fractionation. I will refer to this model as the Heterogenous Mantle Model. This is analogous to the lunar magma ocean (LMO) model (e.g., Snyder et al. 1992), in which the martian "crust-like" component is analogous to lunar KREEP formed during the final stages of crystallization of a magma ocean cumulate pile. In the analogous LMO model, the location of KREEP is uncertain, and its incorporation into mare basalts is likely through mixing of KREEP, through convective overturn, into mantle source regions for the mare basalts (e.g., Shearer and Papike 1999). Therefore, in the martian Heterogeneous Mantle Model, the long-term incompatible-element enriched ("crust-like") and -depleted ("mantle-like") components are considered to be located in martian basalt mantle sources similar to those considered for the Moon. However, as noted by Herd et al. (2002a), oxygen fugacity estimates for martian basalts cannot unequivocally constrain the location of the crust-like component.

Oxygen fugacity estimates from the application of the olivine-pyroxene-spinel (Ol-Px-Sp) model to some of the more recently recovered olivine-phyric martian basalts are presented here. Correlations with La/Yb, Rb-Sr, and Sm-Nd are re-evaluated in light of the Heterogeneous Mantle Model to determine the viability of this model in explaining variations in the oxygen fugacity of the martian basalts. Oxygen isotopic compositions, including those from olivine-phyric basalts, are examined in more detail to determine whether they reflect variations in mantle source composition or some interaction with a martian crustal reservoir in communication with martian atmosphere.

METHODS

Oxygen fugacity estimates were made for the EET 79001 (lithology A), Dar al Gani (DaG) 476, Sayh al Uhaymir (SaU) 005, Dhofar 019, and Northwest Africa (NWA) 1110 martian basalts. All of these are olivine-phyric basalts, following the terminology proposed by Goodrich (2002). In general, they consist of megacrystic olivine set in a groundmass of pyroxene, maskelynite, oxides, sulfides, and phosphates (e.g., Zipfel et al. 2000; Goodrich 2002). Of these, only EET 79001 lithology A contains olivine megacrysts that are generally considered to be xenocrystic, although Barrat et al. (2002b) suggest that megacrysts in NWA 1068 (tentatively paired with NWA 1110) are xenocrysts as well. Pyroxene and spinel are often included within the olivine megacrysts, as in the case of EET 79001 lithology A (Goodrich 2002; McSween and Jarosewich 1983).

Appropriate selection of olivine, pyroxene, and spinel groupings for estimation of $f\mathrm{O}_2$ is difficult at best. Herd et al. (2002a) used spatial association as an initial criterion for selection of Ol-Px-Sp groups. They verified co-crystallization of olivine and pyroxene by calculation of Mg' (molar Mg/(Mg + Fe) of coexisting melt) using Fe-Mg K_D values of 0.33 for olivine (Walker et al. 1976) and 0.28 for low-Ca pyroxene (Grove and Bence 1977). However, spatial association does not necessarily attest to co-crystallization, and subsolidus Fe-Mg exchange can occur, as evidenced by the temperatures obtained with olivine-spinel geothermometry in the case of DaG 476 (Herd et al. 2002a).

In the present case, estimates were enabled by the detailed petrography of Goodrich et al. (2003a, b), who identified early and later Ol-Px-Sp assemblages on the basis of spatial relations and composition. Textural evidence such as chromite + pyroxene included in olivine is self-evident and supports the (cautious) use of spatial association as a criterion for co-crystallization. Other cogenetic assemblages were identified by selecting the chromites with the highest Cr# (Cr/[Cr + Al]) and lowest Fe# (Fe/[Fe + Mg]), which indicate early crystallization and least re-equilibration, respectively, and by assuming that these chromites co-crystallized with the most magnesian olivine and equilibrium low-Ca pyroxene (Fe-Mg K_D (ol/px) ~1.2) (Goodrich et al. 2003a). Goodrich et al. (2003a) also identified assemblages representing a later stage of crystallization, which consists of the first Ti-bearing spinel compositions included in more Fe-rich olivine (so called Type 2 spinels; Goodrich 2003), along with equilibrium low-Ca pyroxene compositions in the groundmass.

RESULTS AND DISCUSSION

Oxygen Fugacity Estimates

Results of the $f\mathrm{O}_2$ estimates are presented in Table 1. Note that the error on the mean of each estimate is less than the error associated with the method (±0.5; Wood 1991). Therefore, I report an uncertainty of ±0.5 whenever different $f\mathrm{O}_2$ calculation methods are used, but I quote the reported error in Table 1 when comparing estimates using the same (Ol-Px-Sp) method. The estimates in Table 1 are given relative to the 3 most common $f\mathrm{O}_2$ buffers. Estimates relative to a buffer can vary depending on the specific definition used for the buffer; accordingly, sources are given in the footnotes

Table 1. Summary of $f\mathrm{O}_2$ estimates for olivine-phyric martian basalts.

Sample	Average T(°C)	Range T(°C)	No. of groups	$\mathrm{Log}_{10}(f\mathrm{O}_2)$ IW[a]	$\mathrm{Log}_{10}(f\mathrm{O}_2)$ QFM[b]	$\mathrm{Log}_{10}(f\mathrm{O}_2)$ NNO[c]	Error[d]
EET 79001 X[e]	926	854-982	5	1.0	–2.8	–3.7	0.2
EET 79001 A[f]	860	730–925	3	2.0	–1.8	–2.8	0.2
DaG 476[g]	1018	774–1186	7	1.1	–2.5	–3.4	0.4
SaU 005	1058	1017–1154	6	0.2	–3.4	–4.2	0.3
Dhofar 019	1099	n/a	1	–0.2	–3.7	–4.5	n/a
NWA 1110	1024	996–1063	9	1.9	–1.7	–2.5	0.2
NWA 1110 L[h]	796	766–836	4	4.2	0.2	–0.8	0.5

[a] Iron-wüstite as defined by O'Neill (1988).

[b] Quartz-fayalite-magnetite as defined by Wones and Gilbert (1969).

[c] Nickel-nickel oxide defined by Holloway et al. (1992) using the data of O'Neill (1987).

[d] Error = 2σ standard deviation of the mean, where n = number of groups (column 4).

[e] Refers to estimates made from Ol-Px-Sp groups in the xenocrystic assemblage of EET 79001.

[f] Refers to the lithology A groundmass of EET 79001.

[g] The average of the data presented by Herd et al. (2002a) with 2 new estimates from this study.

[h] Refers to estimates made from late-crystallizing Ol-Px-Sp groups.

of Table 1. Oxygen fugacity estimates from early assemblages are of particular interest with regard to estimating the fO_2 of the magma at the time of first crystallization. However, estimates from late assemblages can lend insight into the unique petrogenetic histories of each sample. The estimates in Table 1 are predominantly from early assemblages for 2 reasons: olivine in the olivine-phyric basalts is a liquidus phase (with the caveat that the olivine may be xenocrystic, as noted above), and establishing co-crystallization is less ambiguous if the criteria outlined above for the earliest crystallizing phases are used.

The results for EET 79001 indicate that 2 magmas having differing petrogenetic histories are represented in lithology A. The groundmass assemblage uses groundmass pigeonite, ulvöspinel rims on chromite, and rim olivine. Considerable doubt exists as to whether rim olivine should be considered a co-crystallizing phase with groundmass pigeonite and Fe-Ti-rich spinel rims. The results of Herd et al. (2002b) suggest that the olivine rims are cogenetic with the olivine cores and should be considered as part of the xenocryst assemblage. However, Goodrich (2003) suggests that some portion of the olivine rims should be considered cogenetic with the groundmass on the basis of melt inclusions within the olivine. The subsolidus chromian spinel exsolutions in olivine observed by Goodrich (2003) may have affected the Cr and V concentrations in the rim olivine measured by Herd et al. (2002b), which were used to argue for the rim olivine being xenocrystic. Regardless, the use of the rim olivine with groundmass pigeonite and ulvöspinel rims on chromite yields fO_2 = QFM −1.8 ± 0.5, which is in very good agreement with the estimate of Herd et al. (2001) of QFM −1.8 (±0.3; using the QUIlF model) from Fe-Ti oxides in the groundmass.

The megacryst assemblage yields fO_2 = QFM −2.8 ± 0.2, which is one log unit more reducing than the lithology A groundmass (QFM −1.8 ± 0.2). The difference in fO_2 between the megacrysts and groundmass supports the hypothesis that the megacrysts are xenocrysts (McSween and Jarosewich 1983). An alternative model, such as preferential subsolidus re-equilibration of the finer-grained lithology A groundmass, inadequately explains the difference: Herd et al. (2001) calculate that the fO_2 of the finer-grained (0.15 mm) lithology A groundmass is the same, within error, as that of the coarser-grained (0.30 mm) lithology B. In addition, the calculated Fe-Ti oxide temperatures for lithology A are higher than those calculated for lithology B; one would expect the opposite if lithology A had undergone subsolidus re-equilibration to a greater degree. This observation also places constraints on the impact melt model of Mittlefehldt et al. (1999), in which lithology B assimilates a hartzburgitic lithology (represented by the xenoliths) to become lithology A. If this is the case, the fO_2 of the impact melt (now represented by lithology A) was not significantly influenced by the assimilation of the more reduced (xenocryst) lithology.

Estimates for DaG 476, which are based solely on the earliest phases, yield results very similar to those of Herd et al. (2002a); specifically, 2 estimates with an average fO_2 of QFM −3.0 ± 0.4 (Table 1). The earliest assemblages in SaU 005 yield fO_2 = QFM −3.4 ± 0.3. This is the first such estimate for this meteorite, and it supports a similar petrogenesis to DaG 476 (Zipfel 2000; Gnos et al. 2002). Only one Ol-Px-Sp estimate is currently possible for Dhofar 019; however, this estimate is in good agreement with estimates of Taylor et al. (2002) from Fe-Ti oxides.

Nine distinct Ol-Px-Sp groups in NWA 1110 yield fO_2 = QFM −1.7 ± 0.2. This is the highest fO_2 estimate for the earliest assemblages in an olivine-phyric basalt, and perhaps the most robust, considering the consistency of the 9 estimates. Later assemblages, however, yield significantly higher fO_2 (Table 1). Either the selected later assemblages do not consist of coeval phases, that is, the results are an artifact of not having selected an appropriate co-crystallized assemblage, or the assemblages reflect a more oxidized melt. If the latter is true, it suggests that excursions in fO_2 are possible during the course of crystallization, an observation not yet seen in other martian basalts. Oxygen fugacity estimates from Fe-Ti oxides would be of particular interest in comparison with Fe-Ti oxide estimates for other martian basalts (Herd et al. 2001).

In general, the estimates presented here extend the range of fO_2 in the martian basalts to lower values. The total range of fO_2 observed in the martian basalts is from below IW to QFM −1, a range of 3 log units substantiated by results of Eu/Gd studies. Whether or not this range will be extended further as fO_2 estimates are made for more martian meteorites remains to be seen.

Correlations with Geochemical Parameters

Herd et al. (2002a), using fO_2 estimates from Fe-Ti oxide and Ol-Px-Sp methods, demonstrated a correlation between fO_2 and La/Yb and fO_2 and initial $^{87}Sr/^{86}Sr$, and initial ε_{Nd} (both corrected to 175 Ma). Rb-Sr and Sm-Nd isotopic measurements of martian basalts take considerable time and effort, and as a result, initial $^{87}Sr/^{86}Sr$ and initial ε_{Nd} values are not available for some of the newer olivine-phyric basalts. However, the REE are commonly measured by authors investigating new martian meteorite finds, and whole rock La/Yb ratios are readily available in the literature. The La/Yb ratio is a measure of the shape of the REE pattern—higher La/Yb indicates greater enrichment in the light rare earth elements and, therefore, in incompatible elements. Incompatible-element enrichment is reflected in initial $^{87}Sr/^{86}Sr$ and initial ε_{Nd}, but these parameters also give information about the timing and duration of the enrichment. Figure 1 is a plot of C1-normalized La/Yb versus initial $^{87}Sr/^{86}Sr$, demonstrating that the 2 parameters are correlated. The line-of-best-fit on this diagram is a polynomial with a correlation

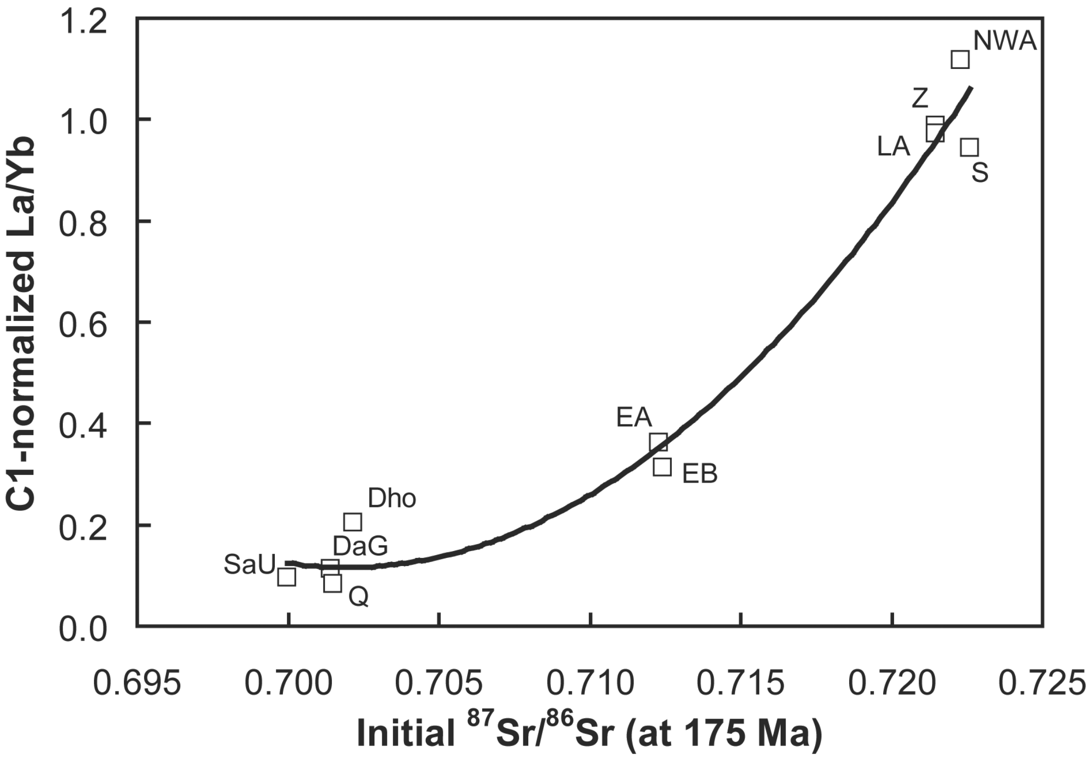

Fig. 1. C1 chondrite normalized whole rock La/Yb ratio versus initial $^{87}Sr/^{86}Sr$ isotopic composition for the martian basalts Shergotty (S), Zagami (Z), Los Angeles (LA), EET 79001 lithology A (EA), EET 79001 lithology B (EB), Dar al Gani 476 (DaG), SaU 005 (SaU), Dhofar 019 (Dho), and QUE 94201 (Q). The REE data are from sources in Meyer (1998), Rubin et al. (2000), Zipfel et al. (2000), and Taylor et al. (2002). The data for NWA 1068 (NWA) are after Barrat et al. (2002b) for REE and Nyquist (2002, personal communication) for initial $^{87}Sr/^{86}Sr$. The other initial $^{87}Sr/^{86}Sr$ isotopic compositions are after Borg et al. (1997, 2001, 2003) and Nyquist et al. (2000) for LA. The polynomial line-of-best-fit $R^2 = 0.98$.

coefficient (R^2) of 0.98. Therefore, for the purpose of this study, I will employ La/Yb as a proxy for initial $^{87}Sr/^{86}Sr$ and initial ε_{Nd} to test whether or not the correlations observed by Herd et al. (2002a) hold for the olivine-phyric martian basalts.

Figure 2 is a plot of C1-normalized La/Yb ratio versus fO_2 for the martian basalts. The oxygen fugacity estimates are taken from other sources (Herd et al. 2001, 2002a) as well as this study. Evidently, from Fig. 2, the relationship between fO_2 and incompatible-element enrichment observed by Herd et al. (2002a) generally holds for the olivine-phyric shergottites. I note that NWA 1110 and Dhofar 019 do not fall on the line-of-best-fit defined by the other samples. This may be attributable to desert weathering of these meteorites (Russell et al. 2002; Taylor et al. 2002), which contributes to uncertainty in REE analyses.

The new estimates presented here yield new information on the correlation between fO_2 and geochemistry of the martian basalts. The Ol-Px-Sp estimates made here for the lithology A xenocrysts and groundmass enables the 3 lithologies within EET 79001 to be considered separately. La/Yb ratios of the xenocrysts were obtained from the data of Wadhwa et al. (1994) for xenocrystic orthopyroxene. This value is a minimum because it may not be directly representative of the xenocryst parent magma. No constraints are on the maximum value; however, given the arguments presented by Wadhwa et al. (1994) that the ratios of REE partition coefficients are relatively constant (in spite of uncertainties in the partition coefficients themselves), the measured La/Yb ratio of the xenocryst orthopyroxene likely reflects the La/Yb ratio of the parent magma to within an order of magnitude. The point labeled “EA” represents the EET 79001 lithology A groundmass. The La/Yb ratio of groundmass whitlockite (Wadhwa et al. 1994) is taken to be representative of the groundmass La/Yb ratio. Interestingly, the trend observed in the other martian basalts appears to hold for lithologies within the EET 79001 meteorite. Although considerable uncertainty exists in the La/Yb ratio of the xenocrysts, EET 79001 may represent a case where magmas from different martian mantle sources are represented in a single sample.

Initial investigations indicate that NWA 1110 is paired with NWA 1068 on the basis of texture and mineralogy (Russell et al. 2002; Goodrich et al. 2003c). However, detailed geochemical studies of both of these meteorites are lacking. In the absence of REE data for NWA 1110, I assume that these meteorites are paired and plot the La/Yb of NWA 1068 against the fO_2 of NWA 1110 in Fig. 2. Note that NWA is one sample that does not fall on the line-of-best-fit, within uncertainties.

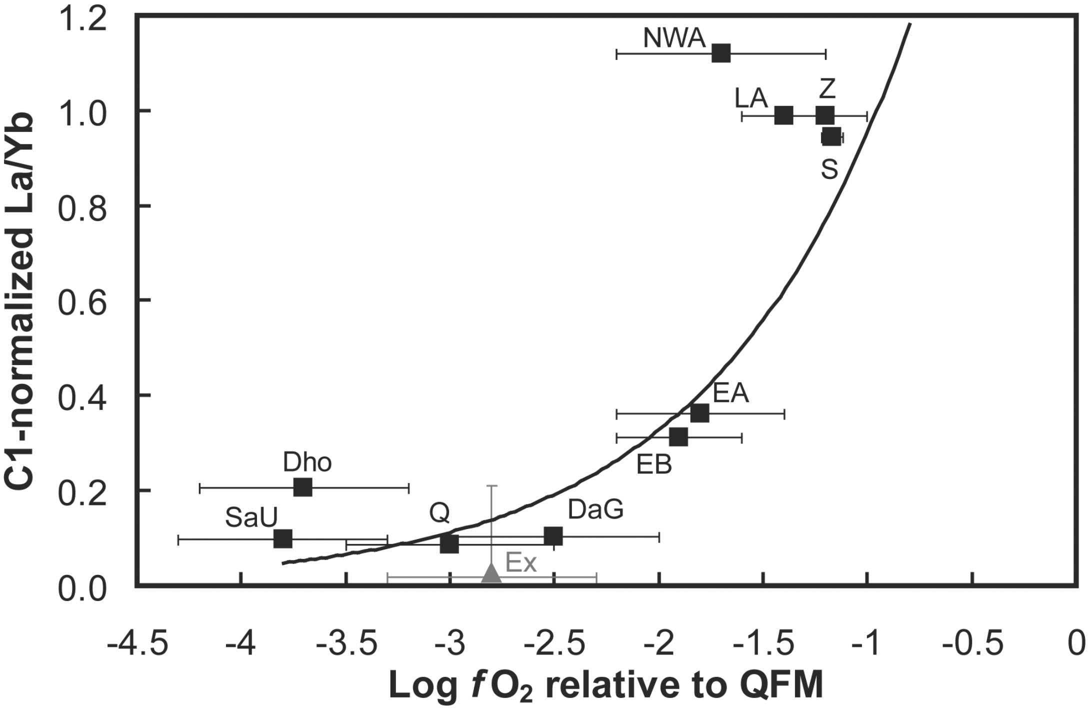

Fig. 2. C1 chondrite normalized whole rock La/Yb ratio versus oxygen fugacity for the martian basalts. The REE sources and symbols are as in Fig. 1. The oxygen fugacities for Shergotty, Zagami, Los Angeles, EET 79001 lithology B, and QUE 94201 are from Herd et al. (2001). The oxygen fugacity for EET 79001 lithology A is from Herd et al. (2001) and this study. The oxygen fugacity for Dar al Gani 476 is from Herd et al. (2002a) and this study. The oxygen fugacities for NWA 1110 (NWA), EET 79001 xenocrysts (Ex), SaU 005, and Dhofar 019 are from this study. The La/Yb of NWA 1068 (after Barrat et al. 2002b) is plotted for NWA 1110, assuming that these 2 meteorites are paired. The exponential line-of-best-fit $R^2 = 0.68$.

If the correlation between La/Yb and *f*O_2 continues to hold, then several newly recovered martian basalts are relatively oxidized, on the basis of their elevated C1-normalized La/Yb whole rock ratios, and one can estimate their oxygen fugacity using the equation for the line-of-best-fit in Fig. 2: NWA 856 (QFM −1.2), NWA 480 (QFM −1.4), and Dhofar 378 (QFM −1.3). The oxidized nature of NWA 856 is supported by Eu/Gd in pyroxene cores in this sample, which indicates an *f*O_2 similar to, or greater than, Shergotty (Wadhwa 2002, personal communication). Note that the reported mineralogy of NWA 480 indicates relatively reducing conditions of formation (Barrat et al. 2002a), but this meteorite has yet to be investigated specifically for redox conditions.

Implications for the Crustal Assimilation Model

The data shown in Fig. 2 demonstrates that the correlation between *f*O_2 and La/Yb holds, in general, for 11 different lithologies in 9 martian basalts. The lithologies represented in this diagram include both olivine-phyric and non-olivine-bearing basalts, spanning a range of ages from 165 Ma to 575 Ma (Borg et al. 1997, 2001; Nyquist et al. 1998, 2000, 2001). The range of lithologies over which the correlation holds supports the observation that whole rock major element compositions of the basalts are not correlative with REE, isotopic composition, or *f*O_2 (Herd et al. 2002a). In particular, the *f*O_2 of NWA 1110 indicates that olivine-phyric basalts are not necessarily more reduced than non-olivine bearing basalts; no textural correlation exists with *f*O_2. If the presence of olivine phenocrysts can be interpreted as reflecting greater degrees of crystallization, indicative of assimilation/fractional crystallization processes (e.g., McBirney 1979; Ussler and Glazner 1992), then this observation is less consistent with crustal assimilation than it is with partial melting of mantle sources.

Viability of the Heterogeneous (Magma Ocean) Mantle Model

Herd et al. (2002a) outlined 2 primary mechanisms of oxidation of martian basalt parental magmas: mixing with ferric iron-rich material and mixing with hydrous material. As noted, the mixing via assimilation of altered and oxidized basaltic rock that formed at ~4.5 Ga is a viable means of explaining the *f*O_2, radiogenic isotopic composition, and REE. This scenario requires several things: that the amount of assimilated ferric iron is constant for a given increase in Rb/Sr or La/Yb (or decrease in Sm/Nd) through assimilation; that the assimilated material has a relatively constant major element composition in all cases; and that the alteration of basaltic crust finished by 4.5 Ga. Given that the composition and oxidation state of alteration products depend on the composition of the fluids involved, the water/rock ratio, and temperature (e.g., Thompson and Thompson 1996), the parent magmas of the more oxidized martian basalts would be unlikely to have encountered and assimilated the same material, or at least, to have done so proportionately. In addition, hydrothermal alteration has occurred more recently than 4.5 Ga, as evidenced by iddingsite and other alteration material in the Lafayette and Nakhla martian meteorites (Treiman et al., 1993; Gooding et al. 1991). Yet Rb-Sr isotopic systematics of the martian meteorites are best explained by mixing between components formed at 4.5 Ga (Borg et al. 1997). If crustal assimilation were the process controlling the fO_2 and geochemistry of martian basalts, one would expect to find martian meteorites with Rb-Sr isotopic compositions that fall off the 4.5 Ga whole rock isochron.

An alternative to the crustal assimilation model is the mixing with hydrous material at depth (Herd et al. 2002a). In this scenario, water is imparted to the parent magma through the assimilation of hydrous minerals such as amphibole or phlogopite. The water subsequently dissociates into H_2 and O_2, and due to differences in the diffusion rates of these species, H_2 degasses preferentially from the magma while O_2 remains in the magma to cause oxidation. However, degassing is a process that depends on the ascent rate of the magma, the viscosity of the magmas, and the amount of volatiles. The amount of water imparted to the magma and the degree of degassing would be unlikely to be proportional to the radiogenic isotopic or REE composition.

Given the considerations presented here and the arguments of Borg et al. (2003) for the crust-like component being present as a mantle source formed early in Mars' history, I will outline the constraints that fO_2 estimates place on a model in which the heterogeneity of the martian mantle, consisting of the 2 geochemical components, is established through the crystallization of a magma ocean, following Borg et al. (2003). In this model, the long-term incompatible-element-enriched (crust-like) component is analogous to lunar KREEP, which has the composition of the last dregs of trapped liquid in a magma ocean cumulate pile after 99% crystallization (Borg et al. 2003). Perhaps, in contrast to the Moon, however, the trapped liquid component on Mars contains an oxidant.

The same 2 oxidation mechanisms proposed for the crustal assimilation model, ferric iron and water, are relevant to the discussion of the differences in fO_2 of the 2 components in the heterogeneous mantle model. In this case, however, the 2 components are variably involved in partial melting of mantle sources, and the presence or absence of the oxidant (ferric iron or water) is an intrinsic characteristic of each of the components. The oxidant is directly associated with the long-term incompatible-element enrichment—the more incompatible-element enrichment, the more oxidant present. This model is shown schematically in Fig. 3.

Herd et al. (2002a) modeled the mixing of the mantle-like and crust-like components and demonstrated that the crust-like component would require an fO_2 close to that of the

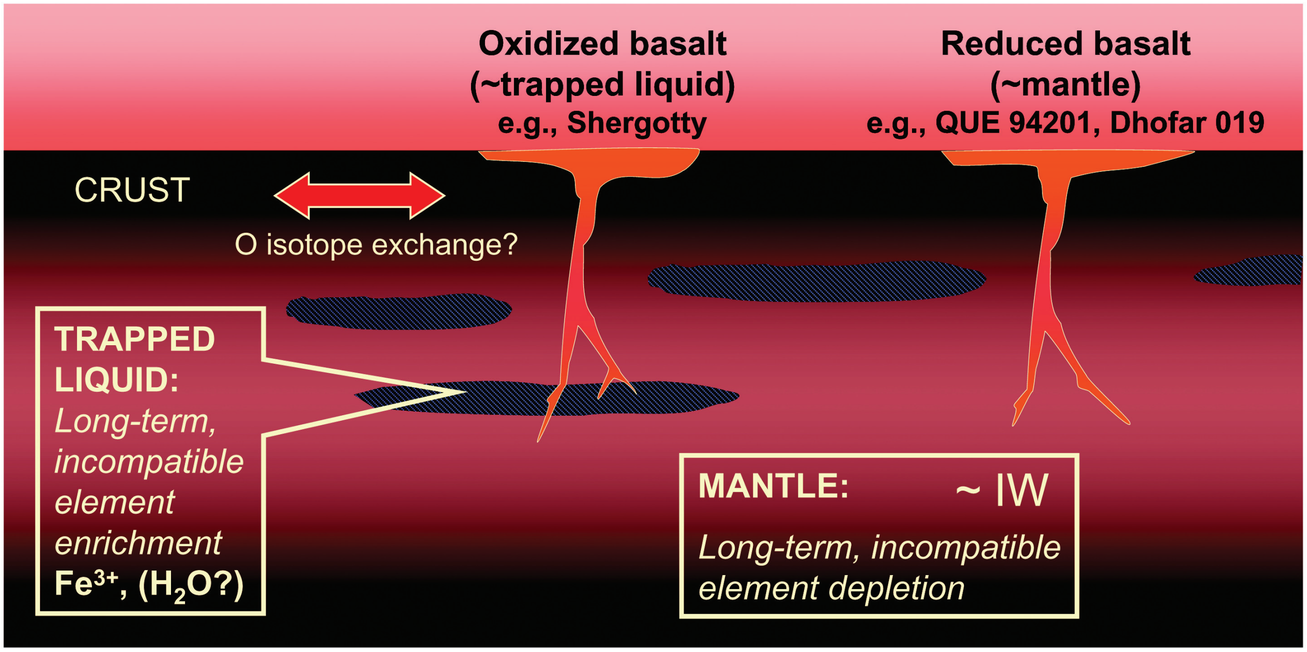

Fig. 3. Model for basalt petrogenesis on Mars showing reduced and oxidized mantle sources. Oxygen isotopic exchange is suggested for the near-surface but may be evident only in post-crystallization alteration (see text for discussion).

hematite-magnetite (HM) buffer, given a reasonable iron content (~16%; so as not to significantly change the bulk chemical composition), for reasonable proportions of mixing (10–30%). Assuming that ferric iron or water behaves incompatibly (D = 0 in all phases) during fractional crystallization of a magma ocean, then a 100-fold increase in the oxidant would be expected in the trapped liquid. Models of this increase shed light on the viability of either oxidant.

Ferric Iron in the Trapped Liquid Component

Assuming an initial fO_2 of the martian mantle of IW – 1.25 (Righter and Drake 1996) and the bulk silicate Mars composition of Longhi et al. (1992), the amount of ferric iron in the initial mantle would be about 0.06 wt%, or about 0.3% of the total.[1] At 99% fractional crystallization of a magma ocean, the amount of ferric iron in the trapped liquid would increase to about 6 wt%. Although the fO_2 of the trapped liquid is difficult to estimate (the amount of ferrous iron in the cumulate portion is poorly constrained), redox conditions equivalent to the HM buffer are easily achievable with such an increase in ferric iron. For example, if the FeO content of the trapped liquid is 33 wt%, then this represents an fO_2 of HM – 0.5 log units. In reality, some of the ferric iron may be sequestered into some of the phases (e.g., orthopyroxene, clinopyroxene, and garnet) that potentially crystallize as part of the cumulate pile, reducing the oxidation potential of the trapped liquid. But a further increase in fO_2 could occur during partial melting, in which the relative fO_2 of the magma would be greater than the source rock, due to preferential partitioning of ferric iron into the magma and/or increases during ascent due to depressurization (e.g., Ballhaus and Frost 1994).

Water in the Trapped Liquid Component

Assuming an initial water content for bulk silicate Mars of 0.004 wt% (Dreibus and Wänke 1987), which is considered to be a lower limit (Longhi et al. 1992), a trapped liquid would contain 0.4 wt% H_2O at 99% crystallization. This is not enough to stabilize a hydrous phase such as amphibole (Moore and Carmichael 1998), but partial melting of a source containing the trapped liquid could contain a significant amount of water (e.g., 30% melting of a source with 0.4 wt% H_2O would yield a magma with ~1.3 wt% H_2O). Note, however, that this scenario has the same drawbacks as the model in which magmas are oxidized by assimilation of hydrous minerals in the martian crust. Specifically, the degree of oxidation due to degassing would be unlikely to be constant for a given degree of involvement of the trapped liquid component.

Interestingly, pre-eruptive water content estimates from light lithophile elements for the more oxidized martian basalts, such as Shergotty and Zagami, appear to be consistent with water being involved in their petrogeneses (Lentz et al. 2001; McSween et al. 2001; Dann et al. 2001; Herd et al. 2003). However, the reduced basalts have yet to be examined in this way, and as such, no constraints are on whether or not the oxidized source is necessarily hydrous. Since ferric iron is almost certainly present during the formation of the martian mantle, as modeled above, ferric iron is the more likely oxidant in the martian mantle. Due to the constraints of the magma ocean model, however, if any water were present in the martian mantle at the time of its formation, it would be concentrated into the trapped liquid during magma ocean crystallization. Therefore, a correlation between oxygen fugacity and pre-eruptive water content would be expected, even if water were not the primary cause of the oxidation.

Mantle Metasomatism and Mantle Components

So far, I have only considered magma ocean crystallization as a means of establishing depleted and enriched mantle reservoirs. Early mantle metasomatism could also cause localized enrichments and differences in oxidation. Enriched metasomatic fluids or melts could be derived from enriched mantle sources or small degrees of partial melting of depleted mantle (e.g., Menzies and Hawkesworth 1987). The crystallization of a magma ocean is the simplest means of explaining the early establishment of enriched and depleted reservoirs; metasomatic fluids may be a secondary derivative from the enriched, trapped liquid component. Treiman (2003) suggests that large variations in certain trace elements in the martian basalts could be explained by the in-mixing of such metasomatic fluids at the time of partial melting. This may be the mechanism by which mixing between the components occurs in the source regions of the martian magmas, as long as the Rb-Sr and Sm-Nd isotopic compositions are not significantly disturbed in the process. The metasomatic fluids would likely be oxidizing, thus accounting for the relationship between fO_2 and enrichment. Metasomatism may also be responsible for the differences between the sources of the martian basalts (shergottite) and those of the nakhlites and Chassigny (Borg et al. 2003), although a discussion of this topic is omitted here because of the paucity of fO_2 estimates for these meteorites (Wadhwa and Grove 2002).

The Oxidation States of the Mantles of Earth, Moon, and Mars

The heterogeneous mantle model for Mars allows for some interesting comparisons between martian and lunar mantle sources and martian and terrestrial mantle sources in terms of their oxidation states.

The lunar magma ocean model has been employed as an analogy to explain the range of isotopic compositions observed in the martian basalts (Borg et al. 2003). I have argued that variations in fO_2 can be explained by the fractional crystallization of a martian magma ocean, which

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[1] The proportion of Fe_2O_3 was calculated using the MELTS Supplemental Calculator (Ghiorso and Sack 1995) at a somewhat arbitrary temperature of 1200°C and a pressure of 50 kbar.

enriched the trapped liquid in an oxidant. If the crust-like component on Mars is analogous to lunar KREEP, then it suggests that KREEP-rich basalts may be more oxidized than lunar basalts from cumulate pile sources. However, this depends on the presence of ferric iron or water in the early Moon. As such, studies of the lunar basalt oxygen fugacity may yield insights into the feasibility of the formation of geochemical reservoirs of differing redox conditions during magma ocean crystallization. Oxygen fugacity estimates for lunar basalts show that they crystallized near the IW buffer (Papike et al. 1998), but the resolution of current oxybarometers decreases significantly below IW. Proxies such as Eu/Gd or multivalent trace elements may provide further insights into this question. Regardless, in the case of Mars, the cumulate pile portion of the mantle appears to be reduced, close to the IW buffer, similar to the lunar mantle. Mars is more enriched in volatile elements than the Moon, which may explain the broad differences in the redox characteristics of lunar KREEP and the martian trapped liquid component.

On the Earth, the fO_2 of basalts is governed by the oxidation state of their mantle sources. The results of this study have demonstrated that the fO_2 of martian basalts may also be controlled in a similar manner. However, plate tectonics on the Earth continue to replenish the mantle with oxidants, altering the source regions from which basaltic magmas are derived. In contrast, the redox reservoirs on Mars were set by 4.5 Ga, and the lack of sustained plate tectonics prevents further modification of those sources. The discontinuation of plate tectonics on Mars may, therefore, cause a more restricted range of fO_2 for the martian basalts (~3 log units) compared to terrestrial basalts (~7 log units). However, the results of this study and others have already indicated a larger range than initially recognized, and future studies may further extend that range.

The Oxygen Isotopic Compositions of Martian Basalts: Evidence for Interaction with Martian Crust?

Herd et al. (2002a) noted a rough correlation between $fO2$ and oxygen isotopic composition. Figure 4a is a plot of $\delta^{18}O$ versus fO_2, and Fig. 4b a plot of $\delta^{18}O$ versus La/Yb, for all of the martian basalts for which such data exists, demonstrating that, in general, more oxidized and incompatible-element-enriched basalts have heavier oxygen isotopic compositions. The line-of-best-fit in each incorporates data from all samples except Dhofar 019 and EET 79001 lithologies A and B. EET 79001 lithologies A and B fall off the trend, but the oxygen isotopic compositions of these lithologies have yet to be investigated separately—the value plotted here represents a mixture of all 3 lithologies, measured on band saw cuttings (Franchi et al. 1999). Dhofar 019 has the heaviest isotopic composition of the martian basalts (Taylor et al. 2002), yet its fO_2 is among the lowest. However, Taylor et al. (2002) note that the $\delta^{18}O$ composition has likely been affected by the presence of terrestrial weathering products.

Romanek et al. (1998) demonstrated that the $\delta^{18}O$ of Lafayette iddingsite (~16‰) is much heavier than the igneous portions of the martian meteorites. Iddingsite in Lafayette formed as a result of alteration by low temperature (<100°C) fluids (Treiman et al. 1993), and its oxygen isotopic composition, therefore, likely represents the alteration by fluids in communication with the atmosphere (Romanek et al. 1998). A magma that assimilated, or exchanged with, alteration materials in the martian crust that are similar in oxygen isotopic composition to Lafayette iddingsite would likely have heavier oxygen isotopic composition (Herd et al. 2002a). Besides data for Dhofar 019, which can be justifiably omitted due to the presence of terrestrial weathering products, the only new $\delta^{18}O$ data available at the time of writing is SaU 005, which falls on the trend defined by the other martian basalts (Fig. 4). Therefore, oxygen isotopic composition appears to be inherited primarily from mantle components. I stress the importance of this diagram not for the data it contains but for the data to be added as more martian basalts are analyzed. Since Rb-Sr and Sm-Nd isotopic compositions, bulk REE patterns, and oxygen fugacity are inherited from mantle components, oxygen isotopic composition may be a clue to the interaction of martian basalt magmas with a crustal reservoir in communication with the martian atmosphere. The disturbance of oxygen isotopic compositions by terrestrial weathering products, especially those from hot desert environments, argues for more detailed ion probe measurements of distinct igneous phases in martian meteorites, which could, perhaps, elucidate the timing of interaction with crustal material and the degree to which the interaction occurred.

Implications for the Study of Returned Martian Samples

A Mars Sample Return (MSR) mission, although technologically challenging, is likely in the next 2 decades. However, for a variety of reasons, such a mission is unlikely to return pristine basaltic samples, opting instead for more easily obtained surface samples of martian soil or weathered rock. Such a sample would give important information about the martian atmosphere and hydrosphere but little about mantle sources. Thus, studies of martian basalts would seem to have little relevance to MSR missions. This study, and the results of the SNC workshop upon which this work is based, demonstrate otherwise—the interpretation of crustal material from a MSR mission would be impaired without knowledge of the potential variation in trace element geochemistry and oxygen fugacity that can be imparted by mantle sources, as elucidated by this study and others. A MSR mission could, in turn, greatly aid our understanding of martian meteorites, for example, by providing geochemical parameters for martian

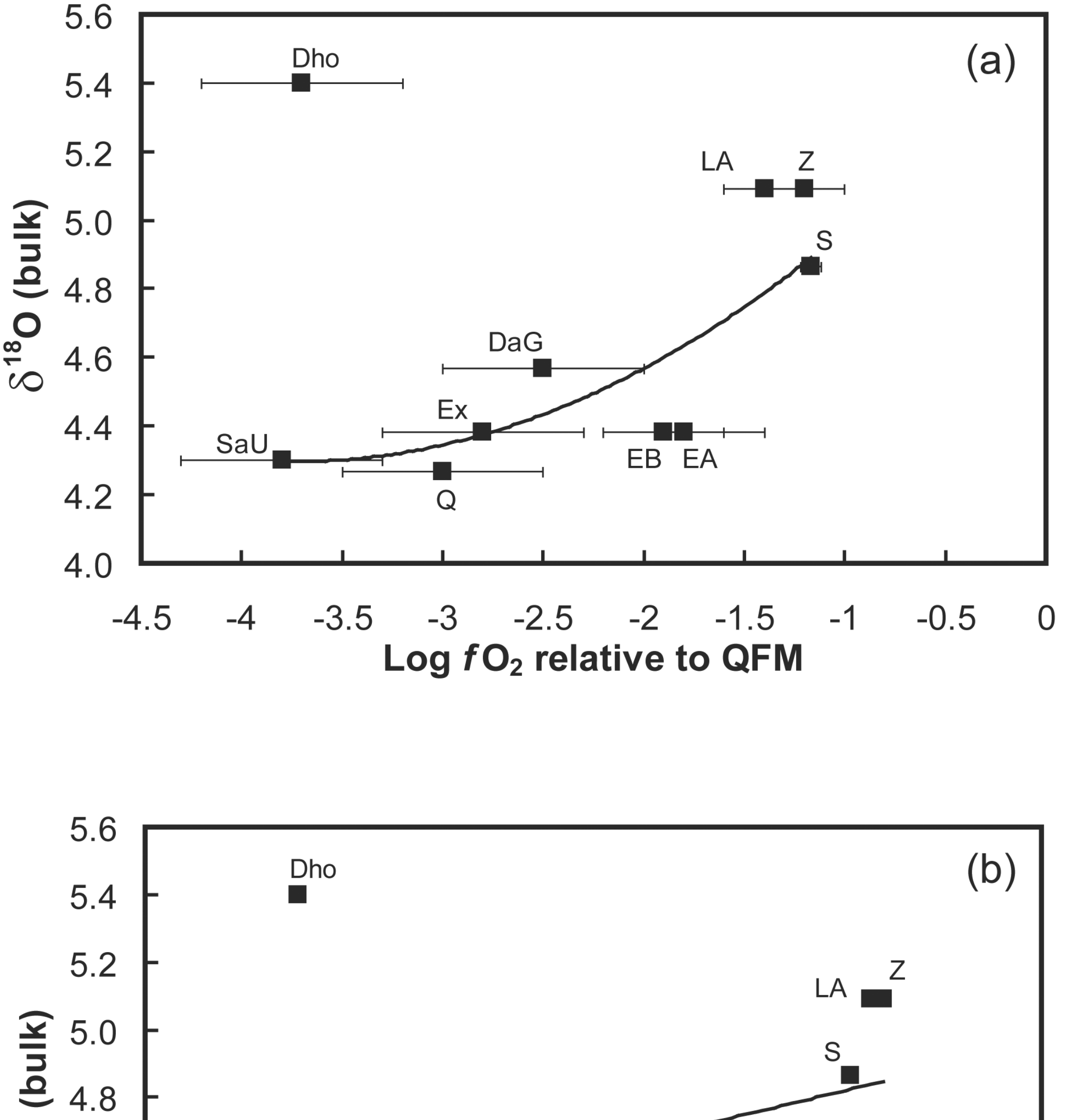

Fig. 4. Oxygen isotopic composition versus (a) oxygen fugacity and (b) C1-normalized La/Yb ratio for the martian basalts. The symbols are as in previous figures. The oxygen fugacity sources are as in Fig 2. The REE sources are as in Fig 1. The oxygen isotopic data for Shergotty, Zagami, EET 79001, and DaG 476 are from Franchi et al. (1999); the data for Los Angeles are from Rubin et al. (2000); the data for Dhofar 019 are from Taylor et al. (2002); the data for SaU 005 are from Gnos et al. (2002) for SaU 094. The polynomial line-of-best-fit in each is through all points except EET 79001 A and B and Dhofar 019; a) $R^2 = 0.75$; b) $R^2 = 0.65$.

soil and near-surface lithologies that could be used to search for evidence of crustal interaction in the martian basalts.

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REFERENCES

Anderson D. J., Lindsley D. H., and Davison P. M. 1993. QUIlF: A Pascal program to assess equilibria among Fe-Mg-Mn-Ti oxides, pyroxenes, olivine, and quartz. *Computers & Geosciences* 19: 1333–1350.

Ballhaus C. and Frost B. R. 1994. The generation of oxidized CO_2-bearing basaltic melts from reduced CH_4-bearing upper mantle sources. *Geochimica et Cosmochimica Acta* 58:4931–4940.

Barrat J. A., Gillet P. H., Sautter V., Jambon A., Javoy M., Göpel C., Lesourd M., Keller F., and Petit E. 2002a. Petrology and chemistry of the basaltic shergottite Northwest Africa 480. *Meteoritics & Planetary Science* 37:487–499.

Barrat J. A., Jambon A., Bohn M., Gillet P. H., Sautter V., Göpel C., Lesourd M., and Keller F. 2002b. The picritic shergottite Northwest Africa 1068 (NWA 1068 or "Louise Michel") (abstract #1538). 33rd Lunar and Planetary Science Conference. CD-ROM.

Borg L. E., Nyquist L. E., Taylor L. A., 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., Nyquist L. E., Reese Y., Wiesmann H., Shih C. Y., Ivanova M., Nazarov M. A., and Taylor L. A. 2001. The age of Dhofar 019 and its relationship to the other martian meteorites (abstract #1144). 32nd Lunar and Planetary Science Conference. CD-ROM.

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

Carmichael I. S. E. 1991. The redox state of basic and silicic magmas: A reflection of their source regions? *Contributions to Mineralogy and Petrology* 106:129–141.

Carmichael I. S. E. and Ghiorso M. 1990. The effect of oxygen fugacity on the redox state of natural liquids and their crystallizing phases. In *Modern methods of igneous petrology: Understanding magmatic processes,* edited by Nicholls J. and Russell J. K. Washington D.C.: Mineralogical Society of America. pp. 191–212.

Dann J. C., Holzheid A. H., Grove T. L., and McSween H. Y., Jr. 2001. Phase equilibria of the Shergotty meteorite: Constraints on pre-eruptive water contents of martian magmas and fractional crystallization under hydrous conditions. *Meteoritics & Planetary Science* 36:793–806.

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

Franchi I. A., Wright I. P., Sexton A. S., and Pillinger C. T. 1999. The oxygen isotopic composition of Earth and Mars. *Meteoritics & Planetary Science* 34:657–661.

Ghiorso M. S. and Sack R. O. 1991. Fe-Ti oxide geothermometry: Thermodynamic formulation and the estimation of intensive variables in silicic magmas. *Contributions to Mineralogy and Petrology* 108:485–510.

Ghiorso M. S. and Sack R. O. 1995. Chemical mass transfer in magmatic processes IV: A revised and internally consistent thermodynamic model for the interpretation and extrapolation of liquid-solid equilibria in magmatic systems at elevated temperatures and pressures. *Contributions to Mineralogy and Petrology* 119:197–212.

Ghosal S., Sack R. O., Ghiorso M. S., and Lipschutz M. E. 1998. Evidence for a reduced, Fe-depleted martian mantle source region of shergottites. *Contributions to Mineralogy and Petrology* 130:346–357.

Gnos E., Hofmann B., Franchi I. A., Al-Kathiri A., Hauser M., and Moser L. 2002. Sayh al Uhaymir 094: A new martian meteorite from the Oman desert. *Meteoritics & Planetary Science* 37:835–854.

Gooding J. L., Wentworth S. J., and Zolensky M. E. 1991. Aqueous alteration of the Nakhla meteorite. *Meteoritics* 26:135–143.

Goodrich C. A. 2002. Olivine-phyric martian basalts: A new type of shergottite. *Meteoritics & Planetary Science* 37:B31–B34.

Goodrich C. A. 2003. Petrogenesis of olivine-phyric shergottites Sayh al Uhaymir 005 and Elephant Moraine A79001 lithology A. *Geochimica et Cosmochimica Acta* 67:3735–3772.

Goodrich C. A., Herd C. D. K., and Taylor L. A. 2003a. Spinels and oxygen fugacity in olivine-phyric and lherzolitic shergottites (abstract #1426). 34th Lunar and Planetary Science Conference. CD-ROM.

Goodrich C. A., Herd C. D. K. and Taylor L. A. 2003b. Spinels and oxygen fugacity in olivine-phyric and lherzolitic shergottites. *Meteoritics & Planetary Science.* This issue.

Goodrich C. A., Van Niekirk D., and Morgan M. L. 2003c. Northwest Africa 1110: A new olivine-phyric shergottite possibly paired with Northwest Africa 1068 (abstract #1266). 34th Lunar and Planetary Science Conference. CD-ROM.

Grove T. L. and Bence A. E. 1977. Experimental study of pyroxene-liquid interaction in quartz-normative basalt 15597. Proceedings, 8th Lunar and Planetary Science Conference. pp. 1549–1579.

Haggerty S. E. 1991. Oxide textures—A mini-atlas. In *Oxide minerals: Petrologic and magnetic significance,* edited by Lindsley D. H. Washington D.C.: Mineralogical Society of America. pp. 129–219.

Herd C. D. K., Papike J. J., and Brearley A. J. 2001. Oxygen fugacity of martian basalts from electron microprobe oxygen and TEM-EELS analyses of Fe-Ti oxides. *American Mineralogist* 86: 1015–1024.

Herd C. D. K., Borg L. E., Jones J. H., and Papike J. J. 2002a. Oxygen fugacity and geochemical variations in the martian basalts: Implications for martian basalt petrogenesis and the oxidation state of the upper mantle of Mars. *Geochimica et Cosmochimica Acta* 66:2025–2036.

Herd C. D. K., Schwandt C. S., Jones J. H., and Papike J. J. 2002b. An experimental and petrography investigation of Elephant Moraine 79001 lithology A: Implications for its petrogenesis and the partitioning of chromium and vanadium in a martian basalt. *Meteoritics & Planetary Science* 37:987–1000.

Herd C. D. K., Treiman A. H., McKay G. A., and Shearer C. K. 2003.

Light lithophile elements in natural and experimental phases in martian basalts: Implications for the degassing of water from martian magmas (abstract #1635). 34th Lunar and Planetary Science Conference. CD-ROM.

Holloway J. R., Pan V., and Gudmundsson G. 1992. High-pressure fluid-absent melting experiments in the presence of graphite: Oxygen fugacity, ferric/ferrous ratio and dissolved CO_2. *European Journal of Mineralogy* 4:105–114.

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

Lentz R. C. F., McSween H. Y., Jr., Ryan J., and Riciputi L. R. 2001. Water in martian magmas: Clues from light lithophile elements in shergottite and nakhlite pyroxenes. *Geochimica et Cosmochimica Acta* 65:4551–4565.

Lindsley D. H. and Frost B. R. 1992. Equilibria among Fe-Ti oxides, pyroxenes, olivine, and quartz: Part I. Theory. *American Mineralogist* 77:987–1003.

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

McBirney A. R. 1979. Effects of assimilation. In *The evolution of the igneous rocks,* edited by Yoder H. S. Princeton: Princeton University Press. pp. 307–329.

McCanta M. C. and Rutherford M. J. 2002. Oxygen fugacity recorded in pigeonite: Indications of a heterogeneous martian magma source region? In *Unmixing the SNCs: Chemical, Isotopic, and Petrologic Components of Martian Meteorites.* LPI Contribution 1134. Houston: Lunar and Planetary Institute. p. 35.

McKay G. A. 1989. Partitioning of rare earth elements between major silicate minerals and basaltic melts. In *Geochemistry and mineralogy of rare earth elements,* edited by Lipin B. R. and McKay G. A. Washington D.C.: Mineralogical Society of America. pp. 45–77.

McSween H. Y., Jr. and Jarosewich E. 1983. Petrogenesis of the Elephant Moraine A79001 meteorite: Multiple magma pulses on the shergottite parent body. *Geochimica et Cosmochimica Acta* 47:1501–1513.

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* 22: 4563–4569.

McSween H. Y., Jr., Grove T. L., Lentz R. C. F., Dann J. C., Holzheid A. H., Riciputi L. R., and Ryan J. G. 2001. Geochemical evidence for magmatic water within Mars from pyroxenes in the Shergotty meteorite. *Nature* 409:487–490.

Menzies M. A. and Hawkesworth C. J. 1987. *Mantle metasomatism.* Orlando: Academic Press. 472 p.

Meyer C. 1998. *Mars meteorite compendium 1998.* Houston: NASA Johnson Space Center. 237 p.

Mittlefehldt D. W., Lindstrom D. J., Lindstrom M. M., and Martinez R. R. 1999. An impact melt origin for lithology A of martian meteorite Elephant Moraine 79001. *Meteoritics & Planetary Science* 34:357–367.

Moore G. and Carmichael I. S. E. 1998. The hydrous phase equilibria (to 3 kbar) of an andesite and basaltic andesite from western Mexico: Constraints on water content and conditions of phenocryst growth. *Contributions to Mineralogy and Petrology* 130:304–319.

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

Nyquist L. E., Bogard D. D., Garrison D. H., and Reese Y. 1998. A single-crater origin for martian shergottites: Resolution of the age paradox? (abstract #1688). 29th Lunar and Planetary Science Conference. CD-ROM.

Nyquist L. E., Reese Y. D., Weismann H., Shih C. Y., and Schwandt C. 2000. Rubidium-strontium age of the Los Angeles shergottite. *Meteoritics & Planetary Science* 35:A121.

Nyquist L. E., Reese Y. D., Weismann H., and Shih C. Y. 2001. Age of EET 79001B and implications for shergottite origins (abstract #1407). 32nd Lunar and Planetary Science Conference. CD-ROM.

O'Neill H. St. C. 1987. The free energies of formation of NiO, CoO, Ni_2SiO_4, and Co_2SiO_4. *American Mineralogist* 72:280–291.

O'Neill H. St. C. 1988. Systems Fe-O and Cu-O: Thermodynamic data for the equilibria Fe-"FeO," Fe-Fe_3O_4, "FeO"-Fe_3O_4, Fe_3O_4-Fe_2O_3, Cu-Cu_2O, and Cu-$_2$O-CuO from emf measurements. *American Mineralogist* 73:470–486.

Papike J. J., Ryder G., and Shearer C. K. 1998. Lunar samples. In *Planetary materials,* edited by Papike J. J. Washington D.C.: Mineralogical Society of America. p. 1-234.

Philpotts J. 1970. Redox estimation from a calculation of Eu^{2+} and Eu^{3+} concentrations in natural phases. *Earth and Planetary Science Letters* 9:257–268.

Righter K. and Drake M. J. 1996. Core formation in Earth's moon, Mars, and Vesta. *Icarus* 124:513–529.

Romanek C. S., Perry E. C., Treiman A. H., Socki R. A., Jones J. H., and Gibson E .K., Jr. 1998. Oxygen isotopic record of silicate alteration in the Shergotty-Nakhla-Chassigny meteorite Lafayette. *Meteoritics & Planetary Science* 33:775–784.

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.

Russell S. S., Zipfel J., Grossman J. N., and Grady M. M. 2002. The Meteoritical Bulletin, No. 86. *Meteoritics & Planetary Science* 37:A157–A184.

Sack R. O. and Ghiorso M. S. 1991a. Chromian spinels as petrogenetic indicators: Thermodynamics and petrologic applications. *American Mineralogist* 76:827–847.

Sack R. O. and Ghiorso M. S. 1991b. An internally consistent model for the thermodynamic properties of Fe-Mg-titanomagnetite-aluminate spinels. *Contributions to Mineralogy and Petrology* 106:474–505.

Shearer C. K. and Papike J. J. 1999. Magmatic evolution of the Moon. *American Mineralogist* 84:1469–1494.

Shih C. Y., Nyquist L. E., Bogard D. D., McKay G. A., Wooden J. L., Bansal B. M., and Wiesmann H. 1982. Chronology and petrogenesis of young achondrites, Shergotty, Zagami, and ALH A77005: Late magmatism on a geologically active planet. *Geochimica et Cosmochimica Acta* 46:2323–2344.

Snyder G. A., Taylor L. A., and Neal C. R. 1992. The sources of mare basalts: A model involving lunar magma ocean crystallization, plagioclase flotation and trapped instantaneous residual liquid. *Geochimica et Cosmochimica Acta* 56:3809–3823.

Stolper E. and McSween H. Y., Jr. 1979. Petrology and origin of the shergottite meteorites. *Geochimica et Cosmochimica Acta* 43: 1475–1498.

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.

Thompson A. J. B. and Thompson J. F. H. 1996. *Atlas of alteration: A field and petrographic guide to hydrothermal alteration minerals.* St. John's: Geological Association of Canada Mineral Deposits Division. 119 p.

Treiman A. H., Barrett R. A., and Gooding J. A. 1993. Preterrestrial aqueous alteration of the Lafayette (SNC) meteorite. *Meteoritics* 28:86–97.

Treiman A. H. 2003. Chemical compositions of martian basalts (shergottites): Some inferences on basalt formation, mantle metasomatism, and differentiation in Mars. *Meteoritics & Planetary Science*. This issue.

Ussler W., III and Glazner A. F. 1992. Graphical analysis of enthalpy-composition relationships in mixed magmas. *Journal of Volcanology and Geothermal Research* 51:23–40.

Wadhwa M. 2001. Redox state of Mars' upper mantle and crust from Eu anomalies in shergottite pyroxenes. *Science* 291:1527–1530.

Wadhwa M. and Grove T. L. 2002. Archean cratons on Mars?: Evidence from trace elements, isotopes, and oxidation states of SNC magmas. *Geochimica et Cosmochimica Acta* 66:A816.

Wadhwa M., McSween H. Y., Jr., and Crozaz G. 1994. Petrogenesis of the shergottite meteorites inferred from minor and trace element microdistributions. *Geochimica et Cosmochimica Acta* 58:4213–4229.

Walker D., Kirkpatrick R. J., and Hays J. F. 1976. Crystallization history of lunar picritic basalt Sample 12002: Phase-equilibria and cooling-rate studies. *Geological Society of America Bulletin* 87:646–656.

Wones D. R. and Gilbert M. C. 1969. The fayalite-magnetite-quartz assemblage between 600° and 800°C. *American Journal of Science* 267A:480–488.

Wood B. J. 1991. Oxygen barometry of spinel peridotites. In *Oxide minerals: Petrologic and magnetic significance,* edited by Lindsley D. H. Washington D.C.: Mineralogical Society of America. pp. 417–431.

Zipfel J. 2000. Sayh al Uhaymir 005/008 and its relationship to Dar al Gani 476/489 (abstract). *Meteoritics & Planetary Science* 35: A178.

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.