

Oxygen fugacity in the Martian mantle controlled by carbon: New constraints from the nakhlite MIL 03346

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Abstract—Pyroxene structural data, along with analyses of titanomagnetite, fayalite and mesostasis of the new nakhlite Miller Range (MIL) 03346, define equilibration near 1 bar, 1100 °C, and oxygen fugacity near the FMQ buffer. There is a clear progression of oxygen fugacity (f_{O_2}) in Martian meteorites from reduced Allan Hills (ALH) 84001 to intermediate shergottites to oxidized nakhlites. This trend can be explained by polybaric graphite-CO-CO₂ equilibria in the Martian mantle. Shergottites would have formed at pressures between 1.2 and 3.0 GPa, and nakhlite parent liquids formed at pressures >3.0 GPa, consistent with geochemical and petrologic data for the shergottites and nakhlites. Carbon buffering in the Martian mantle could be responsible for variation in f_{O_2} in Martian meteorites (rather than assimilation or crustal interaction), as well as C-H-O fluids that could be the source of ~30 ppb CH₄ detected by recent spacecraft missions. The conundrum of an oxidized current mantle and basalts, but reduced early mantle during core-mantle equilibrium exists for both the Earth and Mars. A polybaric buffering role for graphite can explain this discrepancy for Mars, and thus it may not be necessary to have an oxidation mechanism like the dissociation of MgFe-perovskite to account for the oxidized terrestrial mantle.

INTRODUCTION

Abundant volatile-bearing phases on the surface of Mars have been recognized by many missions to Mars including Viking (Clark and Baird 1979; Clark and van Hart 1981), the Mars Global Surveyor Gamma Ray Experiment, Mars Express, and Mars Exploration Rovers (Squyres et al. 2004). Sulfur, chlorine, oxygen, carbon, and hydrogen are found in ices, sulfates, hydrates, carbonates, and oxides. The source of these volatiles could be indigenous or exogenous, but few quantitative constraints have been placed on either. However, much of what we know about the Martian interior comes from studies of Martian meteorites. Some shergottites are basaltic rocks that appear to represent melts of the Martian mantle, whereas lherzolitic shergottites, nakhlites, Chassignites and Allan Hills (ALH) 84001 are most likely cumulate magmatic rocks (McSween 2002). Oxygen fugacity (f_{O_2}) recorded in Martian meteorites is variable, and has been attributed to both crustal assimilation processes and mantle source region characteristics (Borg and Draper 2003; Herd 2003; Jones 2003). Correlations between f_{O_2} and incompatible elements (or La/Yb) led some to propose two component mixing models (Fig. 1). However, more recent data shows a possible

decoupling of f_{O_2} and enrichment processes (Wadhwa and Grove 2002; Herd 2006), suggesting that these two are decoupled and that a different explanation is required.

This paper reports new mineral compositional and clinopyroxene X-ray diffraction data for the nakhlite Miller Range (MIL) 03346 and calculations of f_{O_2} based on mineral—melt equilibria within the rock. The new calculations will be compared to those for other nakhlites and Martian meteorites. Also, the question is addressed whether the range of f_{O_2} 's recorded in Martian meteorites can be produced by melting of graphite-bearing mantle at different pressures. Comparison of f_{O_2} recorded in basalts from Mars and Earth reveals a similar range suggesting magmatic volatiles control the range of f_{O_2} recorded in magmatic rocks from both planets.

SAMPLES AND TECHNIQUES

A small chip (, 27) (40 mg) and a standard thin section (,129) of MIL 03346 were used for this study. Scanning electron microscopy and imaging were carried out with a JEOL 5910 LV at NASA-JSC. All major elements in pyroxene, olivine, and mesostasis phases were analyzed

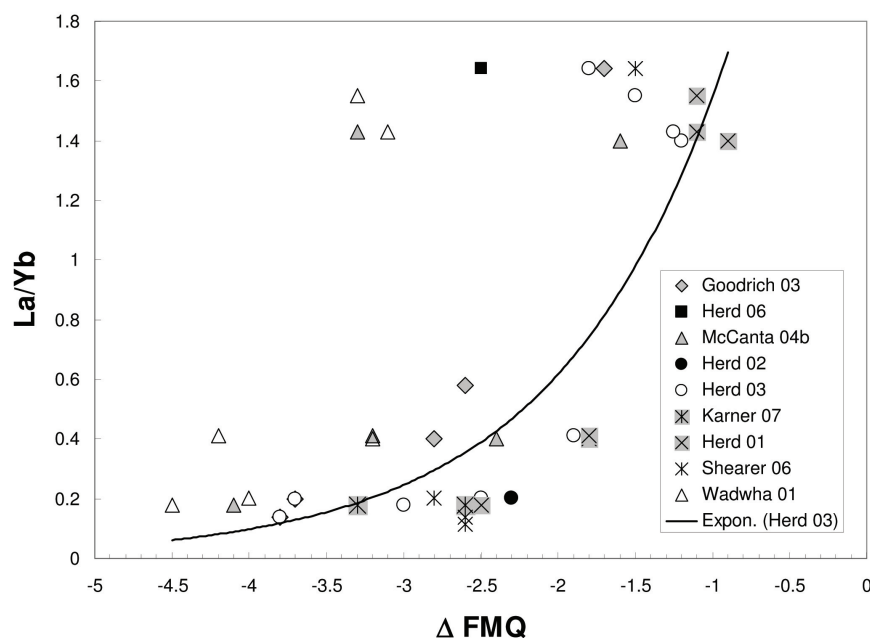


Fig. 1. fO_2 versus La/Yb for Martian basaltic meteorites illustrating the correlation that many have attributed to mixing between two mantle components, or mantle and crustal assimilation processes. Line is the fit to dataset of Herd (2003) but more recent additions show that this is more complicated. Oxygen fugacity data are from Goodrich et al. 2003; Herd et al. 2001, 2002; Herd 2003, 2006; McCanta et al. (2004b); Wadhwa 2001; Karner et al. 2007; Shearer et al. 2006; La and Yb data are from references compiled by C. Meyer, Mars Meteorite Compendium 2008 webpage). Conversion between IW and FMQ buffers was done using calibration of O'Neill (1988) for IW and O'Neill (1987) for FMQ; at magmatic temperatures the relative difference is $\sim 3.5 \log fO_2$ units.

with a CAMECA SX100 electron microprobe, using an accelerating voltage of 20 kV and sample current of 20 nA. Standards include both natural (kaersutite, wollastonite, chromite, rutile, olivine, rhodonite, potassium feldspar, albite) and synthetic (V metal, NiO) standard materials. Counting times for major elements were typically 20 s. Interference of Ti $K\beta$ on V $K\alpha$ peaks (Snetsinger et al. 1968) were avoided by counting Ti on PET using integral mode, and V on LiF in differential mode. PAP ϕ - ρ - Z corrections were used in the data reduction (Pouchou and Pichoir 1991). FeO and Fe₂O₃ in titanomagnetite were calculated by charge balance and stoichiometry, and analyses are reported in Table 1.

For the structure refinements, two nearly equidimensional augite single crystals, designated as augite 1 and augite 2, were selected from MIL 03346 ,27 based on optical examination. They were mounted on a Bruker X8 APEX2 CCD X-ray diffractometer equipped with graphite-monochromatized Mo $K\alpha$ radiation. X-ray diffraction data were collected with frame widths of 0.5° in ω and 30 s counting time per frame. For each crystal, all reflections were indexed on the basis of a monoclinic unit-cell (Tables 2 and 3). The intensity data were corrected for X-ray absorption using the Bruker program SADABS. The structures of both crystals were refined with space group $C2/c$ and anisotropic displacement parameters for all atoms using SHELX97 (Sheldrick 2007). According to previous studies, the following assumptions were made during the

refinements: (1) The total amounts of Mg²⁺ and Fe²⁺ were constrained to those determined from the microprobe analyses (see below), but their relative ratios between the M1 and M2 sites were allowed to vary; (2) All Fe³⁺, Cr³⁺, and Ti⁴⁺ were assigned to the M1 site, with (Mg²⁺ + Fe²⁺ + Fe³⁺ + Cr³⁺ + Ti⁴⁺) = 1.0; (3) (Ca²⁺ + Na⁺) was assigned into the M2 site and (Fe + Mg) into the M2' site, with (Ca + Na + Fe + Mg) = 1.0; (4) The small amount of Al³⁺ was treated as Si⁴⁺ in the tetrahedral site; (5) The small amount of Mn²⁺ was treated as Fe²⁺. The final refined site occupancies of Mg²⁺ and Fe²⁺ in M1 and M2 are listed in Table 2. The chemical compositions of augite 1 and augite 2 (Table 1) were determined from the same crystals used for the X-ray intensity data collections, using a CAMECA SX100 electron microprobe at the University of Arizona. The detailed procedures for the chemical analysis can be found at <http://rruff.info>.

RESULTS

Mineral Composition and Structure

The augite studied here has very small Na components in general, with augite 2 having slightly higher Na₂O than augite 1. Both augites also exhibit low Al, Ti, and Cr contents. Cations calculated for augite 1 indicate the presence of a small amount of Fe³⁺ on the M1 site. Both augites exhibit very small amounts of tetrahedral Al (Table 1).

Table 1. Electron microprobe data and structural formulae for mineral phases in MIL 03346.

Oxide split	Augite 129	Olivine 129	Augite 1 27	Augite 2 27	Ti-magnetite 129	Mesostasis ¹
SiO ₂	52.15	33.75	50.21	51.33	0.36	49.34
TiO ₂	0.32	0.02	0.28	0.23	16.06	1.35
Al ₂ O ₃	0.89	0.02	0.94	0.91	2.69	9.20
Cr ₂ O ₃	0.34	0.01	0.60	0.46	0.01	–
V ₂ O ₃	0.03	–	–	–	0.32	–
FeO	13.90	46.21	13.89	12.84	75.3	22.90
MnO	0.43	0.93	0.44	0.44	0.52	0.44
NiO	0.02	–	–	–	0.01	–
MgO	12.80	18.96	12.89	12.44	0.14	3.51
CaO	19.46	0.55	19.20	18.95	0.05	9.35
Na ₂ O	0.26	–	0.42	1.76	–	2.58
K ₂ O	–	–	0.02	0.00	–	0.73
P ₂ O ₅	0.38	–	–	–	–	0.60
FeO	11.34	–	11.10	9.87	47.29	19.70
Fe ₂ O ₃	3.27	–	3.20	3.20	31.13	3.56
Total	101.28	100.45	99.29	99.36	98.58	100.00
Pyroxene cations normalized to 6O						
Si	1.97		1.94	1.96		
Al	0.03		0.04	0.04		
Fe ³⁺	–		0.02	–		
Mg	0.57		0.56	0.59		
Fe	0.36		0.36	0.32		
Fe	0.05		0.05	0.07		
Cr	0.01		0.02	0.01		
Ti	0.01		0.01	0.01		
Ca	0.79		0.79	0.78		
Mg	0.16		0.17	0.13		
Na	0.01		0.03	0.08		
Mn	0.01		0.01	0.01		
Total	3.98		4.00	4.00		

¹From Rutherford et al. (2005), with FeO and Fe₂O₃ for the FMQ buffer (see text) calculated using Kress and Carmichael (1991).

For both pyroxenes, the unit cells are large for clinopyroxenes, close to 440 Å³. The titanomagnetite is similar in composition to those analyzed by Day et al. (2006) except our analytical totals are higher; overall however, the analyses are similar. The titanomagnetite contains very small amounts of Cr₂O₃, V₂O₃, NiO, and MgO (all <0.35 wt%), and ~3.7 wt% Al₂O₃.

Pressure-Temperature-Oxygen Fugacity Calculations

Pressure and temperature for MIL 03346 can be estimated three different ways, and are summarized in Fig. 2. First, the clinopyroxene unit cell barometer (Nimis and Ulmer 1998; Nimis 1999) suggests that the clinopyroxene, with a unit cell of 440.3 Å³, crystallized at pressures close to 1 bar. Furthermore application of the barometer calibrated for tholeiitic (sub-alkaline) magmas results in very low pressures, with temperature limited by the resulting negative pressures at T > ~1100 °C. This estimate is based on Fe³⁺/ΣFe ratio for the clinopyroxene of 0.15, consistent with those measured by Dyar et al. (2005) and slightly higher than those of Domeneghetti et al. (2006). Second, the

melting point of the bulk composition of the mesostasis can be calculated as a function of pressure using the MELTS algorithm (Ghiorso and Sack 1995). The resulting curve intersects the clinopyroxene results of Nimis (1999) close to 1 bar. The liquidus can be calculated utilizing either all iron as FeO, or with Fe₂O₃ calculated as appropriate for the FMQ buffer (using Kress and Carmichael 1991), but the results are nearly independent of Fe³⁺/Fe²⁺, as the differences are on the order of ~20 °C up to 0.5 GPa. And third, using nakhlite parent melt compositions (Treiman and Goodrich 2001; Stockstill et al. 2005), the P and T at which olivine and clinopyroxene of similar composition to that in the nakhlites can be calculated, again using the MELTS algorithm. The results are very similar to the previous assessment, and all three approaches combined indicate that nakhlites equilibrated at low pressures (1 bar) and temperatures near 1100 °C.

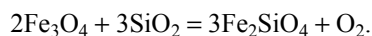
Among the nakhlites, MIL 03346 is thought to represent the uppermost unit in an augite and olivine cumulate igneous sequence, with 15 to 20% mesostasis (Treiman 2005). The mesostasis contains fine grained quenched feldspathic and glassy material, skeletal textured fayalitic

Table 2. Structural refinement data for two MIL 03346 clinopyroxenes.

Parameter	Augite 1	Augite 2
a (Å)	9.7547(6)	9.7552(6)
b (Å)	8.9456(6)	8.9456(6)
c (Å)	5.2537(3)	5.2527(4)
α (deg)	90.0000	90.0000
β (deg)	106.183(1)	106.205(2)
γ (deg)	90.0000	90.0000
V (Å ³)	440.29(8)	440.23(9)
V M1 ¹	12.13	12.02
VM1obs.	12.098	12.103
Mg ^{M1}	0.717(1)	0.670(1)
Fe ^{M1}	0.203(1)	0.240(1)
Mg ^{M2}	0.013(1)	0.000(1)
Fe ^{M2}	0.167(1)	0.090(1)
Total reflections collected	3086	3225
Unique reflections	1031	1087
Unique refl. >2 σ (I)	920	955
R_{int}	0.015	0.018
R1	0.021	0.026
wR2	0.063	0.072
Goodness of fit	1.136	1.223

¹Calculated after Nimis (1999).

olivine and titanomagnetite (Fig. 3, Table 1). The phases in the mesostasis record $f\text{O}_2$ which can be calculated based on the equilibrium:



Spinel melt olivine gas

The activities of Fe_3O_4 in spinel (Sack and Ghiorso 1991), Fe_2SiO_4 in olivine (Wiser and Wood 1991), and SiO_2 in melt (calculated using the mesostasis bulk composition as the melt and Ghiorso and Sack 1995) were combined with Gibbs free energy data (Robie and Hemingway 1995), to calculate $f\text{O}_2$ as a function of temperature:

$$f\text{O}_2 = \frac{\left(\exp^{-\Delta G_r/RT}\right) * \left(a_{\text{Fe}_3\text{O}_4}^{\text{spinel}}\right)^3 * \left(a_{\text{SiO}_2}^{\text{melt}}\right)^3}{\left(a_{\text{Fe}_2\text{SiO}_4}^{\text{olivine}}\right)^3}$$

Given the phase compositions in the mesostasis, this sample equilibrated just above the FMQ buffer at FMQ + 0.40 ($\log f\text{O}_2 = -9.11$ at 1100 °C). This oxygen fugacity is higher than basaltic rocks from Mars, but similar to previous estimates from Chassigny and nakhlites, as will be discussed below.

DISCUSSION

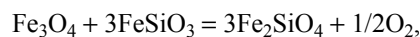
Oxygen Fugacity Estimates—Martian Meteorites

A variety of techniques and approaches have been used to constrain, measure or calculate $f\text{O}_2$ for Martian meteorites.

The range of oxygen fugacities determined in all these studies spans almost 6 $\log f\text{O}_2$ units (Fig. 4a). Nakhlites and Chassigny are most oxidized (also recognized by Delano and Arculus 1980), followed by shergottites and ALH 84001.

ALH 84001

The $f\text{O}_2$ of ALH 84001 has been estimated a number of different ways, with almost all suggesting a somewhat reduced value, despite the fact that one of the distinguishing characteristics of this sample (relative to diogenites) was the need for Fe_2O_3 to charge balance for chromite analyses; Mittlefehldt 1994). For example, Righter and Drake (1996) calculated $f\text{O}_2$ from spinel-olivine-opx equilibrium:



Spinel pyroxene olivine gas

using the chromite analysis of Mittlefehldt (1994) with 7.69 wt% Fe_2O_3 , olivine and orthopyroxene compositions from Mittlefehldt (1994) and Harvey and McSween (1994), respectively, activities of Fe_3O_4 , FeSiO_3 and Fe_2SiO_4 from Sack and Ghiorso (1989, 1991), and thermodynamic data from Berman (1988) and Knacke et al. (1991). The resulting value is FMQ-2.7, with little to no difference in relative $f\text{O}_2$ when calculated at several different temperatures. Such a reduced value is consistent with low Re contents of the bulk rock (Warren and Kallemeyn 1999), the Eu content of the pyroxene (Wadhwa 2008), and the fact that the orthopyroxene contains no Fe^{3+} (Delaney and Dyar 2001, 2003; Dyar et al. 2004). Variable chromite compositions reported by Herd and Papike (1999) and also noted by Gleason et al. (1997) are likely due to proximity to melt veins.

The crystallization pressure of ALH 84001 is not well constrained, but for an opx-saturated magma (implying high SiO_2 activity) the Al_2O_3 and TiO_2 contents of the orthopyroxene are very low and consistent with a low pressure (<0.5 GPa) origin (e.g., Sack et al. 1987), rather than those expected in a high pressure cumulate (e.g., McGregor 1974).

Nakhlites

The $f\text{O}_2$ under which the nakhlites crystallized has been somewhat controversial, with estimates between FMQ + 1 to FMQ-2. Co-existing spinel (titanomagnetite) and rhombohedral (hematite-ilmenite) oxide pairs in a number of nakhlites have yielded $f\text{O}_2$ near the FMQ buffer (Bunch and Reid 1975; Boctor et al. 1976; Sautter et al. 2002; Szymanski et al. 2003; Table 4). Fe_2O_3 content of augite is high (10–25% of total Fe; Dyar et al. 2005; this study), indicating $f\text{O}_2$ near or above the FMQ buffer based on the experimental studies of McCanta et al. (2004a). Calculations of the equilibria $3\text{Fe}_2\text{SiO}_4 + \text{O}_2 = 2\text{Fe}_3\text{O}_4 + 3\text{SiO}_2$ have yielded values near FMQ (this study). Some experimental studies have best duplicated textures at conditions near or even above FMQ (Hammer and

Table 3. Atomic coordinates and displacement parameters for two augite crystals from the nakhlite MIL 03346.

Atom	x	y	z	U11	U22	U33	U23	U13	U12	Ueq
Augite 1										
M2	0	0.3002(1)	1/4	0.0113(2)	0.0079(4)	0.0074(2)	0	-0.0001(2)	0	0.0094(2)
M2'	0	0.2639(4)	1/4	0.0118(8)	0.011(2)	0.0087(8)	0	0.0007(6)	0	0.0108(7)
M1	0	0.9067(1)	1/4	0.0076(2)	0.0073(2)	0.0063(2)	0	0.0017(1)	0	0.0071(1)
Si	0.2113(1)	0.5922(1)	0.2656(1)	0.0067(1)	0.0067(2)	0.0074(2)	0.0008(1)	0.0027(1)	0.0005(1)	0.0068(1)
O1	0.1174(1)	0.0878(1)	0.1451(2)	0.0071(3)	0.0105(4)	0.0085(3)	0.0001(3)	0.0022(3)	0.0008(2)	0.0087(2)
O2	0.3639(1)	0.2485(1)	0.3268(2)	0.0154(4)	0.0100(4)	0.0174(4)	-0.0034(3)	0.0079(3)	-0.0042(3)	0.0136(2)
O3	-0.1487(1)	0.5196(1)	-0.0025(2)	0.0083(3)	0.0151(4)	0.0085(3)	-0.0031(3)	0.0026(3)	0.0003(3)	0.0106(2)
Augite 2										
M2	0	0.2991(1)	1/4	0.0108(3)	0.0089(5)	0.0070(2)	0	-0.0002(2)	0	0.0094(2)
M2'	0	0.2597(4)	1/4	0.013(1)	0.006(2)	0.0089(9)	0	0.0006(7)	0	0.0095(8)
M1	0	0.9081(1)	1/4	0.0085(2)	0.0063(2)	0.0066(3)	0	0.0018(2)	0	0.0072(2)
Si	0.2112(1)	0.5923(1)	0.2654(1)	0.0067(2)	0.0066(2)	0.0073(2)	0.0008(1)	0.0028(1)	0.0006(1)	0.0067(1)
O1	0.1174(1)	0.0879(1)	0.1451(2)	0.0072(4)	0.0104(4)	0.0087(3)	0.0004(3)	0.0023(3)	0.0010(3)	0.0087(2)
O2	0.3639(1)	0.2486(1)	0.3270(2)	0.0149(5)	0.0097(4)	0.0176(4)	-0.0034(3)	0.0076(3)	-0.0038(3)	0.0135(2)
O3	-0.1488(1)	0.5197(1)	-0.0026(2)	0.0085(4)	0.0138(5)	0.0085(4)	-0.0033(3)	0.0025(3)	0.0007(3)	0.0103(2)

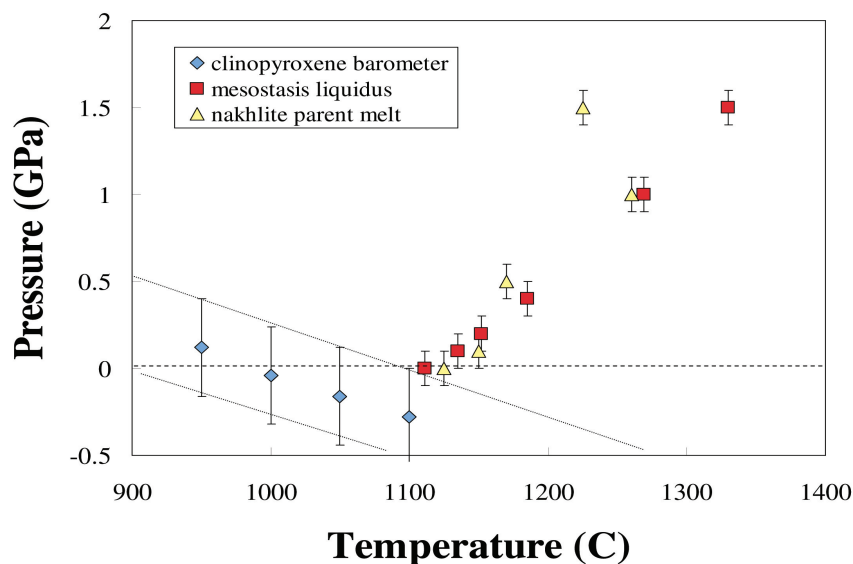


Fig. 2. Pressure and temperature estimates for the MIL 03346 nakhlite, based on three different approaches: a) clinopyroxene structural data (Nimis and Ulmer 1998; Nimis 1999), b) MELTS calculations of the liquidus of the mesostasis assuming $\text{Fe}^{3+}/\text{Fe}^{2+}$ = appropriate at FMQ buffer, and c) calculated P-T conditions where parent melt of Treiman and Goodrich (2001) stabilizes olivine and clinopyroxene similar in composition to that of the nakhlites. Note the intersection of all three equilibria near 1 bar and 1100 °C.

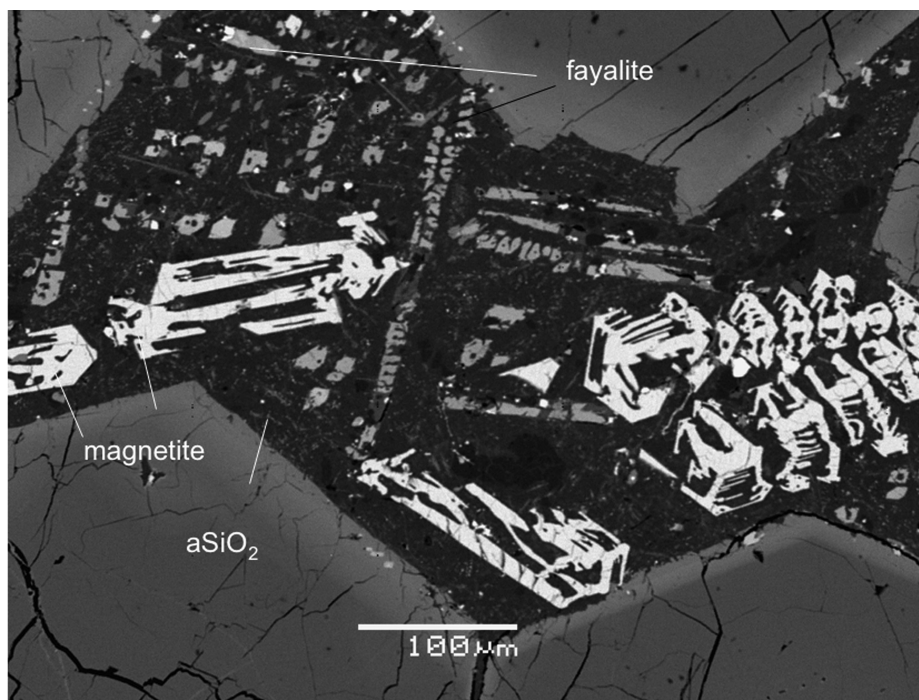


Fig. 3. Backscattered electron (BSE) image of titanomagnetite (white), fayalite (light gray), and quenched (including glass and feldspathic phases) assemblage in the mesostasis of MIL 03346. The coarse-grained enclosing crystals are augite that is unzoned except for the thin ($\sim 50 \mu\text{m}$) FeO -rich rim.

Rutherford 2005; Rutherford et al. 2005; Herd and Walton 2008). Other approaches have suggested more reduced conditions (Rutherford and Hammer 2008) even as low as FMQ–2. It has been suggested that the mesostasis of nakhlites has been oxidized relative to the conditions of crystallization, but this would not be consistent with the high amount of Fe_2O_3

measured in some nakhlite clinopyroxenes (e.g., Dyar et al. 2005). It seems that an origin near FMQ satisfies the bulk of the data currently available, and the reduced results are still being assessed. Estimates for Chassigny (Delaney and Dyar 2001) and Northwest Africa (NWA) 2737 (Treiman et al. 2007) indicate similarly oxidizing conditions (Fig. 4).

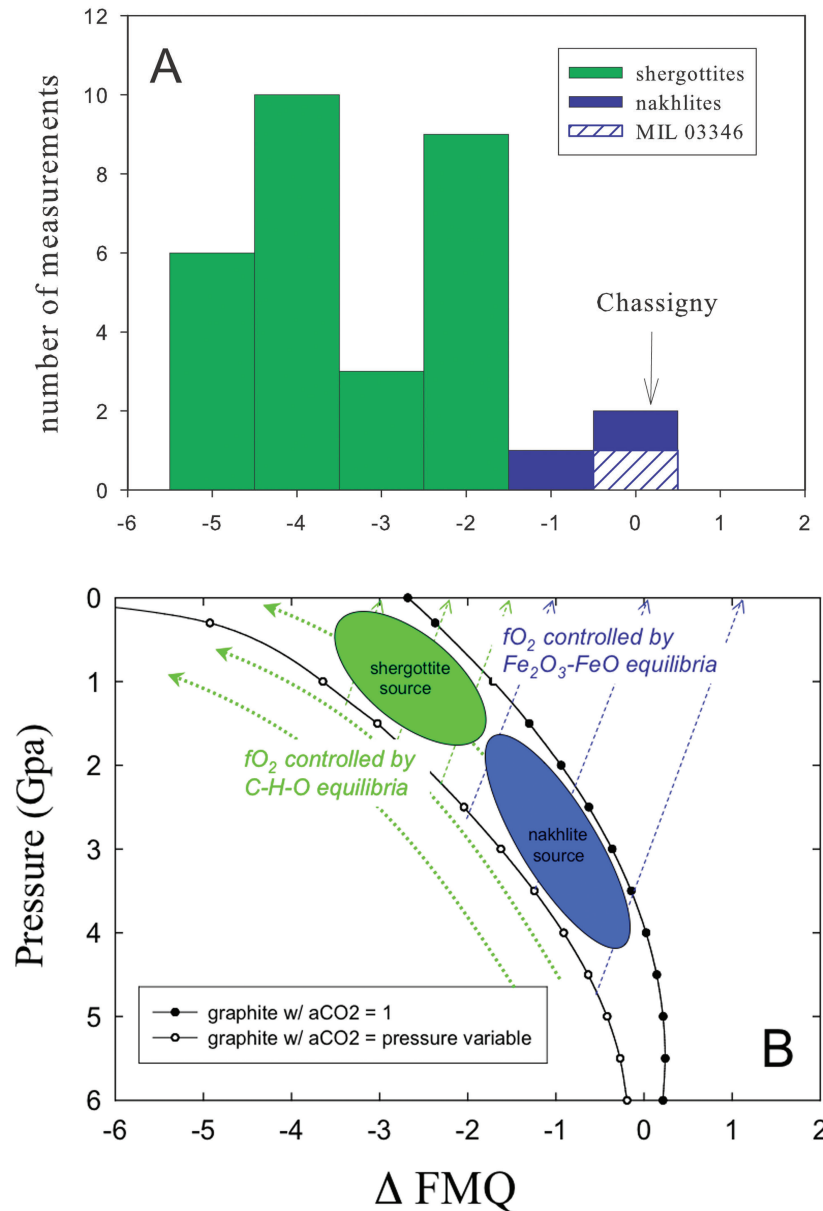


Fig. 4. a) Summary of fO_2 determinations for Martian meteorites, relative to the fayalite-magnetite-quartz oxygen buffer. Shergottite values from Wadhwa (2001); McCanta et al. (2004b), Herd et al. (2001, 2002), Goodrich et al. (2003), Herd (2003) and nakhrite and Chassigny values from Sautter et al. (2002), Bunch and Reid (1975), Szymanski et al. (2003), Delaney and Dyar (2001), and this study. b) Pressure versus FMQ for paths of ascent of magma along the graphite surface (after Ballhaus and Frost 1994; Frost and Wood 1997) and in an unbuffered system (FeO - Fe_2O_3 in melt). Solid graphite surface curves shown for Mars are for $XCO_2 = 1$, and $XCO_2 = \text{variable}$ with pressure, as is appropriate for Mars given that CO_2 solubility is pressure dependent (Pan et al. 1991), and also consistent with melt speciation calculations (Holloway and Jakobsen 1986; Holloway and Blank 1994) for the C-O-H-S system at oxygen fugacities between FMQ and IW.

Shergottites

The fO_2 of shergottites has been determined using a number of different approaches including Eu/Gd partitioning between augite and melt (Wadhwa 2001) and pigeonite and melt (McCanta et al. 2004b), and olivine-orthopyroxene-spinel equilibria (Goodrich et al. 2003; Richter and Drake 1996). In addition to these studies which report specific fO_2

calculations, several studies have shown a large variation in ferric iron and V contents in ferromagnesian silicates and spinels (Delaney and Dyar 2003; Papike et al. 2004; Karner et al. 2006). The total range of oxygen fugacities calculated for shergottites ranges from the reduced end of the spectrum FMQ-3.5 (Queen Alexandra Range [QUE] 94201 and Dhofar [Dho] 019) to the oxidized end near FMQ-0.5 (Shergotty, Zagami; Table 4 and Fig. 4).

Oxygen Fugacity Variations in the Martian Mantle—Buffering by Carbon

As summarized in the previous section, the range of oxygen fugacities recorded in shergottites, nakhlites, Chassigny, and ALH 84001 spans almost 6 log f_{O_2} units (Fig. 4A). A viable mechanism for oxidation in the Martian mantle remains elusive; water as an oxidant is possible, but there is not much water available from the interior given what we know from Martian meteorite samples, and the stability of hydrous phases (King et al. 1999; Righter et al. 2002). Furthermore, the presence of water in magmas is not automatically correlated with oxidation (Moore et al. 1995). Variations ascribed to crustal mixing, water-bearing mantle, or hydrous mineral components are interesting possibilities, but recent work shows possible decoupling between isotopes, trace elements and f_{O_2} , suggesting an alternative hypothesis is required (e.g., Herd 2006).

An idea proposed by Righter (2004, 2007) is that f_{O_2} variations are controlled by carbon (graphite) in the Martian mantle. The importance of carbon in planetary mantles has been emphasized by Sato and colleagues (e.g., Sato 1978). Specifically, if graphite is present in a planetary body, it can equilibrate with CO-CO₂-CH₄-bearing gas or melt. The effect of pressure on graphite-gas or graphite-melt equilibria is such that f_{O_2} would become very high as pressure increases. There are several reasons why carbon could be a significant phase in the Martian mantle. First, studies of Martian meteorites have shown that Mars is a volatile-rich planet, and C may be an important constituent of the volatile budget (Dreibus and Wanke 1985). Second, only 40–80 ppm C is required to keep peridotite mantle buffered at the C-O surface (Holloway 1998; for fluid absent conditions). And third, models for Mars bulk composition have included H, E, and C chondrite mixtures which include 2700 to 2831 ppm C (Lodders and Fegley 1997; Sanloup et al. 1998). Even if 1 wt% of the C partitioned into the core, there would be 1000 ppm left in the mantle; only after 1.42 wt% C went into the core would the mantle C content be zero. Finally, and most compellingly, high temperature C contents between 20 and 200 ppm have been reported in Martian meteorites (Wright et al. 1986; Grady et al. 2004).

Given the range of f_{O_2} estimates for Martian meteorites demonstrated in Fig. 4A, it is worthwhile investigating whether this could be controlled by graphite-melt or graphite-gas (CO-CO₂-CH₄) equilibria in the Martian mantle. Because shergottites and nakhlites do not record evidence for fluid-saturated conditions (such as gas-rich melt inclusions or highly vesicular lavas) it is likely that these magmas were generated under fluid absent conditions. More likely is the case of buffering by graphite-melt equilibria, where CO, CO₂ and CH₄ species are dissolved in the melt. For example, the C-saturation surface will move to higher relative f_{O_2} 's at depth (Ballhaus and Frost 1994; Frost and Wood 1997) (Fig. 4B). Once magma separates from a graphite bearing source, it will

ascend along a path in P- f_{O_2} space that is controlled by Fe²⁺/Fe³⁺ equilibria in the liquid (Fig. 4B), and thus be steeper than the path controlled by the pressure sensitive C-CO-CO₂ equilibria. Because CO₂ solubility in basaltic melt is pressure dependent, there will be a change in a CO₂ that shifts the equilibrium to more reducing conditions (Pan et al. 1991; Holloway et al. 1992).

If C buffering at variable pressure is controlling f_{O_2} in the Martian mantle, it would require formation of ALH 84001 at lowest pressures, shergottites at intermediate pressures, and nakhlite and Chassigny parent melt formation at high pressures. Estimates of the pressure of ALH 84001 are very low—<0.5 GPa, based on the low non-quadrilateral components of the orthopyroxene (see discussion section 1 regarding ALH 84001).

The pressures at which some shergottites were derived can be estimated using phase equilibria (Falloon et al. 1988), because liquid compositions from the oliv-opx cotectic become more olivine rich with pressure. The olivine-phyric shergottite, Yamato (Y-) 980459, contains olivine that is in equilibrium with the groundmass, and falls between 1.5 and 3.0 GPa on the oliv-opx cotectic in the Ol-(Jd + CaTs) + Qz system. In addition, experimental studies have demonstrated that two different candidates for primitive Martian mantle melts—Y-980459 and Humphrey—may have equilibrated with mantle phases (multiple saturation) at 1.0 to 1.5 GPa (Musselwhite et al. 2006; Monders et al. 2007; Filiberto et al. 2008). Additional experimental work on different primitive mantle melts may shed light on the issue of pressure or depth of shergottite magma genesis.

The depth of generation of the nakhlite parent magmas are less certain. However, based on trace element partitioning (Treiman 1993), and some phase equilibria constraints (Longhi and Pan 1989), nakhlites could have come from a deep source, perhaps in equilibrium with garnet. High pressure, low degree melts will be more CaO and FeO rich, similar to nakhlite parent magmas (Kushiro 1998). Zr/Hf ratios in some nakhlites are high, indicating the possible involvement of garnet in melting (Shirai and Ebihara 2008), since Zr becomes much more incompatible in garnet than Hf at high pressure (Draper et al. 2003). Similarly, a variety of geochemical information (Jones 2003) has been interpreted in terms of a deeper nakhlite source than that for shergottites. All of these constraints are consistent with nakhlite parent magma generation at >3.0 GPa.

Carbon buffering is thus a simpler explanation for f_{O_2} variations in the Martian mantle and crust, than by hydrous reservoirs (Herd et al. 2002) or by crustal assimilation (Jones 2003). Such a scenario is also consistent with small water contents inferred for the Martian mantle, which could have been dissolved in mantle minerals. Such small water contents could provide enough water upon melting to also hydrate otherwise dry Martian magmas (e.g., Hauri et al. 2006).

Table 4. Summary of calculated oxygen fugacities for Martian meteorites in FMQ.

Sample	Goodrich (2003)	Herd (2006)	McCanta (2004b)	Herd (2002)	Herd (2003)	Karner (2007)	Herd (2001)	Shearer (2006)	Wadhwa (2001)	This study	Bunch (1975)	Sautter (2002)	Szymanski (2003)
<i>Shergottites</i>													
Y98													
Sau 005	-3.8				-3.8			-2.6					
NWA 1068		-2.5			-1.8			-2.6					
NWA 1110	-1.7				-1.8			-1.5					
EET A	-2.8		-2.4		-1.8		-1.8		-3.2				
Dho 019	-3.7				-3.7								
DaG 476				-2.3	-2.5				-4				
				-2.5									
Shergotty			-1.6		-1.2		-0.9		-1.6				
Zagami			-3.3		-1.25		-1.1		-3.1				
Los Angeles					-1.5		-1.1		-3.3				
EET B			-3.2		-1.9		-1.8		-4.2				
QUE 94201			-4.1		-3	-3.3	-2.5		-4.5				
						-2.6							
DaG 489								-2.8					
ALH 77005	-2.6												
<i>Nakhlites</i>													
MIL 03346										+0.40		+0.65	-0.2
Nakhla											+0.40		
Lafayette													
Governador													
Valadares													
Yamato-000593													-0.46

Conversion between FMQ and IW buffers from values in the original papers was done using O'Neill (1987, 1988) values.

Implications for the Martian Mantle

Our results indicate that the nakhlites must have crystallized at low pressure conditions, but are derivatives from high pressure melts. Two scenarios are possible, each with separate implications for the Martian mantle. And both involve primary parental liquids that are not yet recognized in the Martian meteorite collection; the only commonly regarded primitive mantle melt among the Martian meteorites is the Y-980459 shergottite.

First, nakhlite parent melts ($Mg\# = 0.27$; Treiman and Goodrich 2001) could be primary and generated by melting of a mantle with $Mg\# \sim 0.6$; this is a much lower $Mg\#$ than that of the shergottite sources that could have produced Y-980459 ($Mg\# \sim 0.8$). If there was FeO-rich mantle at pressures >3 GPa a possible mechanism for production is density driven overturn in the aftermath of a magma ocean crystallization (Elkins-Tanton et al. 2003, 2005). Such a mechanism would deliver material from the deep mantle to the shallower mantle (3 to 5 GPa) where it would melt and move to the surface. This may be a way to produce nakhlite parent melts and move them to the surface where they fractionate and crystallize to form nakhlites.

Alternatively, the nakhlite parent melts may represent fractionated derivatives from a primary mantle melt. It is relatively easy to produce a FeO-rich and MgO-poor liquid by fractionation of a primitive melt such as Y-980459. For example, calculations presented by Symes et al. (2008) show that a liquid with $Mg\# = 0.3$, FeO $\sim 21\%$, and MgO $\sim 4.5\%$ can be generated by fractional crystallization of a relatively high $Mg\#$ melt. Therefore, the nakhlite parental melts may have been derived by fractionation of a melt with $Mg\#$ in the range of 0.75 to 0.8, not very different from the shergottite sources (but nonetheless still distinct). Given the isotopic similarity between nakhlites and highly depleted shergottites, this could be a way to link these two. Nakhlites could have formed by deep melting of depleted mantle, followed by fractionation to a low $Mg\#$ melt. Melting of the same depleted mantle at shallower depths will produce more reduced (but still depleted) shergottites. Therefore in this scenario, isotopes and fO_2 are decoupled, since the same depleted mantle produces both reduced and oxidized basalt.

Significance of Mars Mantle Oxidation and Compared to Earth

A classic problem in terrestrial petrology has been the oxidized state of the mantle (near FMQ; Arculus 1985) relative to the redox conditions required during core formation (IW-2; Palme and O'Neill 2004). No secular changes in mantle redox state have been detected since 3.3 Ga (Delano 2001; Li and Lee 2004), but there are records of more reduced portions of the Archean mantle (Eggler and Lorand

1994). Also, there is ~ 300 Ma of missing rock record for the earliest Earth, so it is not clear on what timeframe mantle oxidation could have occurred during the early stages. A recent suggestion that Earth's mantle was oxidized by the breakdown of MgFe perovskite to Fe^{3+} and Fe metal (Frost et al. 2004; Wood et al. 2006) is an interesting solution to this old problem, but is not without additional questions, as discussed below.

Models for early Mars differentiation conclude that the Martian mantle equilibrated with core-forming metal at reduced conditions, approximately 1.5 $\log fO_2$ units below the IW buffer (or FMQ-5; Dreibus and Wanke 1987; Treiman et al. 1987; Righter et al. 1998; Righter 2007). In comparison, the Martian meteorites record a range of fugacities above the IW buffer, indicating more oxidizing conditions than the early mantle (Fig. 5). The explanation proposed here—that the Martian mantle is buffered by graphite-gas or graphite-melt equilibria—suggests the broad range is caused by normal magmatic polybaric processes in the deep and shallow mantle. Additionally, some Martian basalts and cumulates are just as oxidized as primary terrestrial basalt and mantle (maybe even more so), but MgFe perovskite (small or non-existent in the Martian mantle; Longhi et al. 1992; Bertka and Fei 1997) is not available for oxidation of the comparatively poorly stirred Martian mantle (Kiefer 2003; Li and Kiefer 2007). The special mechanism for the Earth does not appear to be necessary since the same range of fO_2 has been generated in plate tectonics-free and MgFe-perovskite-free Mars. In summary, the range of fO_2 in Earth and Mars could be due simply to polybaric buffering by carbon and C-H-O fluids and magmatism, and not by any special or unique mechanism such as Mg-perovskite dissociation.

Implications for Atmosphere

The presence of carbon and buffering of mantle fO_2 is an important point to understand not only from the perspective of magmatic processes, and volatile contents of magmas, but it also affects issues that relate to atmospheric evolution, the carbon cycle on Mars, and organic geochemistry. Whether Martian C as measured in Martian meteorites is indigenous or exogenous, or even introduced after residence on the Earth's surface, has been the focus of isotopic studies (Jull et al. 1998). A small activity of CH_4 would be associated with a C-CO-CO₂-CH₄ gas in the Martian mantle (e.g., $X = 0.15$ – 0.30 at 1.0–2.0 GPa, 1200–1400 °C; [Holloway and Jakobsson 1986; Holloway and Blank 1994]), and degassing of this species could account for the small amount of methane detected recently at the surface of Mars. The Mars Express craft has detected evidence for a small amount of methane at the surface of Mars (Formisano et al. 2004), as have others using independent data sets (Krasnoplosky et al. 2004;

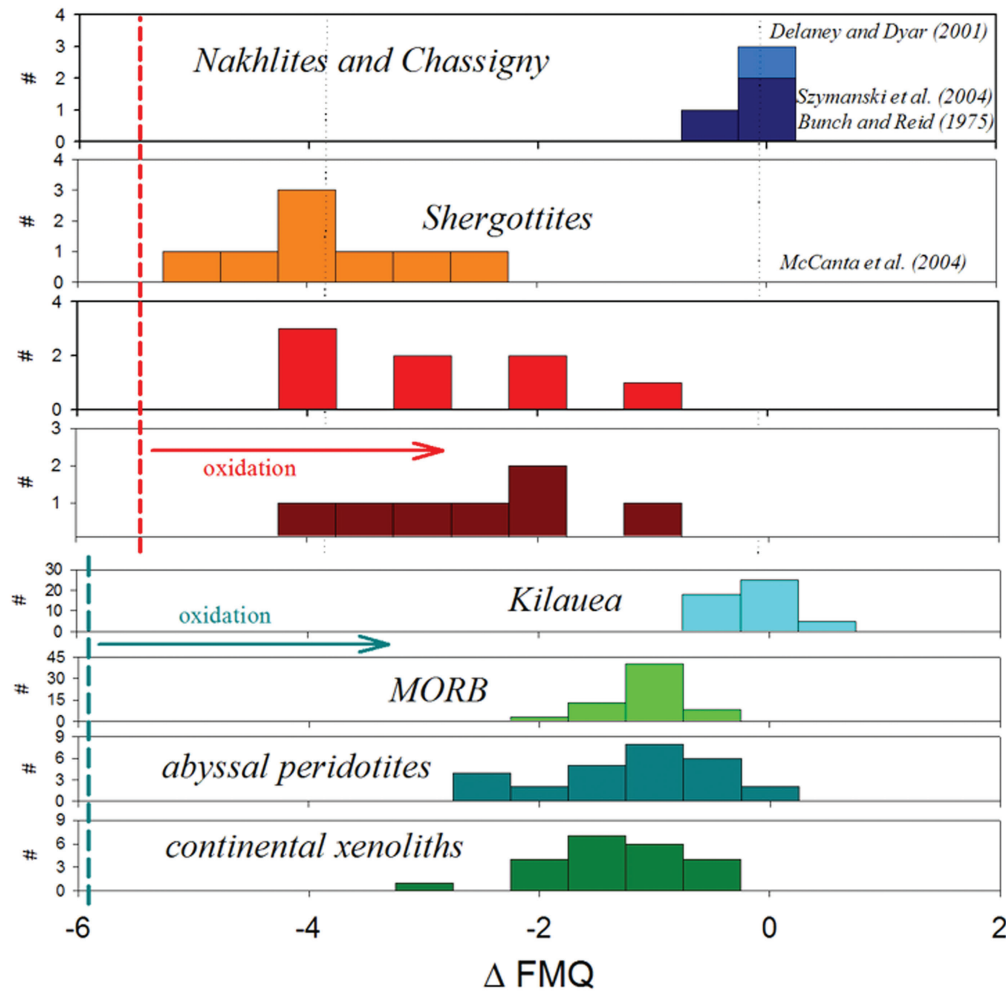


Fig. 5. (Top) Histogram of Martian meteorite values of oxygen fugacity (from Fig. 4a) compared to the conditions proposed for Martian core formation (Richter et al. 1998; Richter 2006; dashed red vertical line); shergottite values are separated into McCanta et al. (2004b) (orange), Goodrich et al. (2003) (red), and Herd et al. (2002, 2003) (brown). (Bottom) Histogram of terrestrial sample values of oxygen fugacity (from Richter et al. 2006) compared to the conditions proposed for terrestrial core formation (from Palme and O'Neill 2004; dashed vertical green line). For both the Earth and Mars, the "oxidation" line shows that the shallow mantle and basalts have become oxidized relative to conditions during early differentiation and core formation.

Mumma et al. 2004). CH_4 is also a greenhouse gas and this may have implications for evolution of thermal aspects of atmosphere over the last 4 Ga. In more oxidized gases, CO_2 will be stable and this has implications for crust formation and atmospheric evolution (Hirschmann and Withers 2008).

CONCLUSIONS

It is likely that carbon is present in the mantle of Mars. Its presence could explain sizable $f\text{O}_2$ variations observed in the Martian meteorite suite from near IW to near FMQ. Forcing an explanation for the correlations between $f\text{O}_2$ and La/Yb data into a simple two component model is not necessary. In addition, the possibility to degas reduced species such as methane has implications for the evolution of the Martian atmosphere over time,

(and also recent measurements), as well as the possible existence of life on the surface. This idea is furthermore intriguing because it is testable, and leaves some specific issues open for exploration. First, additional phase equilibria studies of primitive Martian magmas may allow determination of depths of melting in the Martian mantle. Second, isotopic and trace element modeling of Martian basalts, cumulates, and associated mantle reservoirs may also provide pressure constraints. Third, the possibility that nakhlite parent melts are from the deep or shallow mantle, or high or low FeO mantle, will ultimately relate to the number of Martian mantle reservoirs. And finally, substantial S and Cl on the Martian surface indicate that they may have also been involved with any C-H-O fluids, making imperative additional studies of more relevant volatile compositions.

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