UNMIXING THE SNCS:
Chemical, Isotopic, and Petrologic
Components of the Martian Meteorites

October 11–13, 2002 ❖ Houston Texas

Abstract Volume

LPI

Unmixing the SNCs:
Chemical, Isotopic and Petrologic Components
of Martian Meteorites

October 11–12, 2002

Houston, Texas

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Abstracts in this volume may be cited as

Author A. B. (2002) Title of abstract. In *Unmixing the SNCs: Chemical, Isotopic, and Petrologic Components of Martian
Meteorites*, p. XX. LPI Contribution No. 1134, Lunar and Planetary Institute, Houston.

Preface

This volume contains abstracts that have been accepted for presentation at the conference on Unmixing the SNCs: Chemical, Isotopic, and Petrologic Components of Martian Meteorites, September 11–12, 2002, in Houston, Texas.

Administration and publications support for this meeting were provided by the staff of the Publications and Program Services Department at the Lunar and Planetary Institute.

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GENERAL DISCUSSION

INCOMPATIBLE TRACE ELEMENTS IN SNCs AND Li ISOTOPES SYSTEMATICS IN A SHERGOTTITE.

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In this paper, we report on two aspects of our recent investigations on Martian meteorites: 1/ Li and incompatible trace element abundances in shergottites and nakhlites and 2/ the Li isotopes systematics during the crystallization of the North West Africa 480 shergottite (NWA 480). Li is seen by many workers as a key element for tracing fluids during the genesis of nakhlites and shergottites [e.g. 1].

Li and incompatible trace-element abundances: In view of their isotopic compositions and their oxidation states, basaltic shergottites such as Zagami or Los Angeles are seen as being contaminated by a Martian crustal component [e.g. 2-6]. The isotopic compositions of shergottites are consistent with mixing between depleted and enriched components [e.g. 2, 6, 7]. Using the REE concentrations in pyroxenes, it has been shown that the patterns of parental melts of the Martian meteorites were parallel to those of the corresponding whole rocks [3, 8]. Consequently, it can be assumed that the REE ratios of these meteorites and their parental liquids are similar. This conclusion can be extended to other incompatible element ratios such as Th/Sm and Rb/Sm. The trends defined by the shergottites can be interpreted either as mixing lines between LREE- depleted and enriched melts or produced by contamination of LREE-depleted melts by an enriched component (crust?) [9]. Nakhlites are far outside the trends defined by the shergottites, implying a distinct LREE component. This interpretation is in agreement with the Li abundances determined on whole rock samples. In a Li vs. Yb diagram (fig. 1), nakhlites+Chassigny and shergottites are well distinguished: shergottites display a significant range of Li/Yb ratios (between 1.2 and 3.6); Nakhla, NWA 817 and Chassigny display similar Li/Yb ratios (about 10). In a Li/Yb vs. Be/Yb plot (Fig. 2), most of the available data for shergottites define a linear trend, indicating one more time depleted and enriched components. Two shergottites are clearly outside this trend: DaG 476 and Dhofar 019. Two hypotheses can explain these outliers: (1) these two meteorites are hot desert finds and their (yet) anomalous Li/Yb ratios were possibly produced by terrestrial weathering; (2) alternatively, other (LREE-depleted) components are possibly involved during the petro-

genesis of these two shergottites, as suggested by their unusual high Hf/Lu ratios [9,10]...

Li isotopes in the NWA 480: The Li abundances and isotopic compositions were determined in NWA 480 pyroxenes by SIMS using a procedure already described [11]. This shergottite has been chosen because: (1) its pyroxenes are large (typically 2 mm in length), and display a huge zoning (from En77 to En5); transects are easy to produce; (2) NWA 480 is more LREE-depleted than Shergotty and Zagami, which have been previously analyzed. Selected results are shown in figure 3.

Li abundances: About 30 analyses were achieved and all the results (but two) are in the range 3-4 ppm. Quite different results were obtained on Shergotty and Zagami where Li abundances decrease significantly from pyroxene cores to rims [1].

Li isotopes: δ^7Li increases systematically from core (about –9 per mil) to rim (+10 - +18 per mil).

Terrestrial weathering, closed system fractional crystallization, mixing or some kind of metasomatism failed to explain such huge isotopic variations (30 per mil) and Li behavior. In agreement with previous results obtained on Shergotty and Zagami pyroxenes [1], these results suggest a significant loss of Li (about 60 %) by the residual magma. The involvement of aqueous fluids is plausible but is not the only possibility.

References: [1] Lentz R. et al. (2001) *GCA* 65, 4551-4565, [2] Jones J. (1989) *Proc. L.P.S.C.* 19, 465-474. [3] Wadhwa M. et al. (1994) *GCA* 58, 4213-4229. [4] Wadhwa M. (2001) *Science* 291, 1527-1530. [5] Herd et al. (2001) *Am. Miner.* 86, 1015-1024. [6] Jagoutz E. (1991) *Space Sci. Rev.* 56, 13-22. [7] Borg L. et al. (1997) *GCA* 61, 4915-4931. [8] Wadhwa M. and Crozaz G. (1995) *GCA* 59, 3629-3647. [9] Barrat J.A. et al. (2002) *GCA* 66 (in press). [10] Barrat J.A. et al. (2001) *MAPS* 36, 23-29. [11] Decitre S. et al. (2002) *G³*, 3, 1, 20 p.
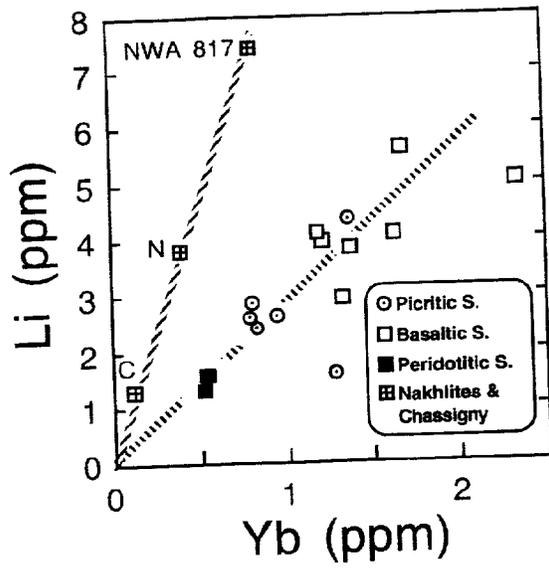
Fig. 1. Li vs. Yb for Martian meteorites. The sources of the data are too numerous to be given here.
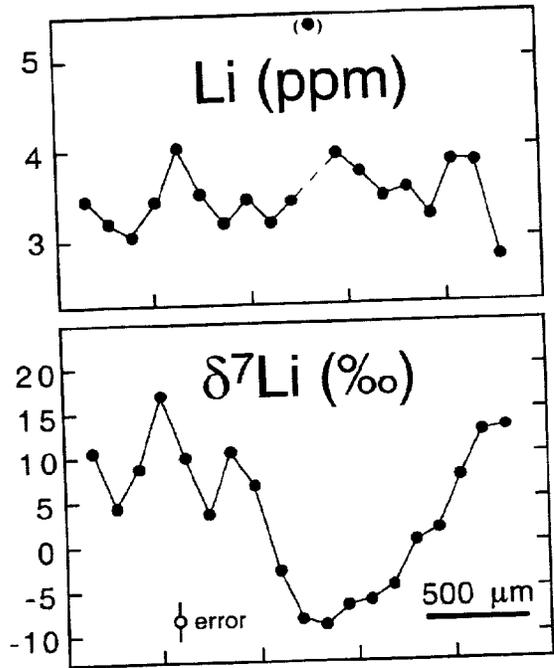
Fig. 3. Li abundances and δ^7Li profiles across a NWA 480 pyroxene.
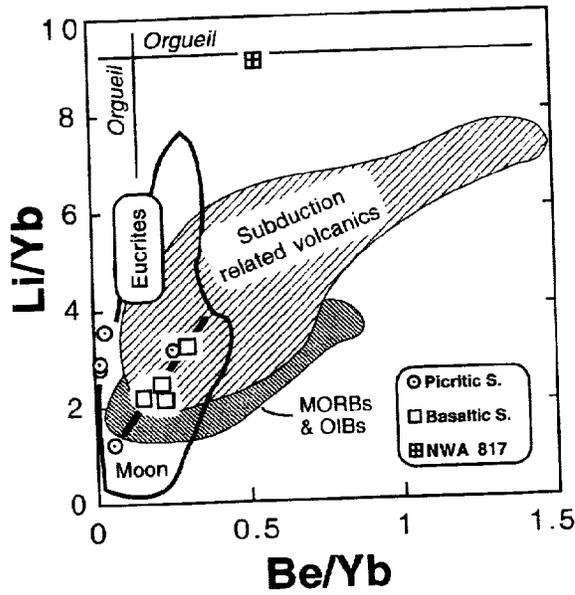
Fig. 2. Li/Yb vs. Be/Yb for Martian meteorites, lunar mare basalts and picritic glasses, non-cumulate eucrites, and terrestrial recent lavas. The sources of the data are too numerous to be given here.

EXPLORING TRACE ELEMENT AND ISOTOPIC MIXING RELATIONSHIPS IN THE MARTIAN METEORITE SUITE.

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Introduction: Variations in the incompatible trace element and isotopic systematics of the martian meteorites are consistent with mixing of compositionally distinct materials e.g., [1-3]. One end of the mixing array is defined by a component characterized by a strongly light-rare-earth-element depleted pattern, a low $^{87}Sr/^{86}Sr$ ratio, and a high ε_{Nd}^{143} value. In many ways this component is comparable to the Earth's depleted mantle. The second component is characterized by a light-rare-earth-element enriched pattern, a high $^{87}Sr/^{86}Sr$ ratio, and a low ε_{Nd}^{143} value. This component could be analogous to the Earth's crust [3], or a late stage liquid trapped in the cumulate pile of a magma ocean [2]. The nature of this "enriched" component ultimately underscores whether the compositional variations observed in the martian meteorites reflect differentiation in the crust (i.e. assimilation fractional crystallization) or are inherited from their source regions at the time of melting. Below, fundamental mixing relationships are reviewed and a mechanism to produce the compositional variations observed in the martian meteorites is proposed.

Mixing relationships: The martian meteorites display a large range of incompatible trace element and isotopic ratios. Furthermore, variations of trace element and isotopic ratios correlate and fall on calculated mixing curves defined using martian meteorites as compositional end-members [Fig. 1]. In contrast,

Shergottite mixing model
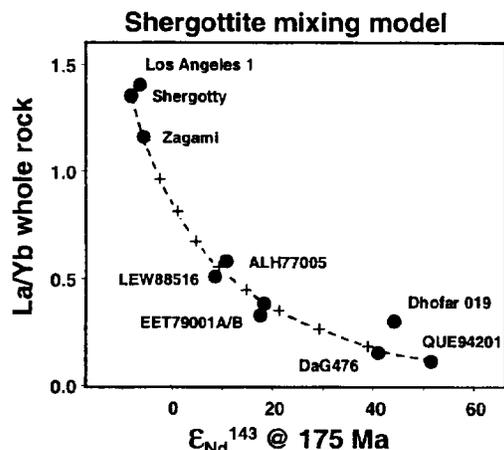
Figure 1. La/Yb vs. ε_{Nd}^{143}. Shergotty and QUE94201 define the ends of mixing line. Crosses represent 10% intervals.

major element abundances do not correlate with either incompatible trace element or isotopic systematics of the martian meteorites. This implies that variations in

incompatible trace elements and initial isotopic compositions of the shergottites are controlled by the same mixing process, whereas the major elements are not.

The whole rock isotopic systematics of the martian meteorites are also consistent with mixing processes, and in some cases offer constraints on the age of formation of the end-member components. Figure 2 is a

Rb-Sr whole rock mixing diagram
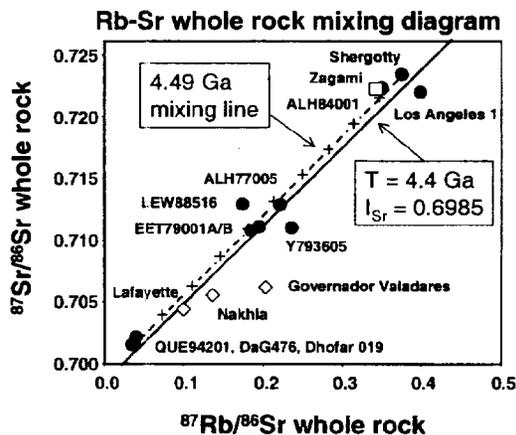
Figure 2. Whole rock Rb-Sr isochron plot of martian meteorites. The mixing line (dashed) is calculated using QUE94201 and Shergotty as end-members and has a slope corresponding to 4.49 Ga. Crosses represent 10% intervals. Solid line regressed through data represents an age of 4.4 Ga.

whole rock Rb-Sr isochron plot of the martian meteorites. The meteorites define a line with a slope corresponding to an age of 4.4 Ga. A mixing line between QUE94201 and Shergotty defines an age of 4.49 Ga, suggesting that planetary differentiation occurred near 4.4 to 4.5 Ga. A more precise age of planetary differentiation can be defined using a two-stage Nd model isochron [Fig. 3]. This chronometer is based on the ^{146}Sm - ^{142}Nd ($t_{\frac{1}{2}}$ = 103 Ma) and the ^{147}Sm - ^{143}Nd ($t_{\frac{1}{2}}$ = 106 Ga) isotopic systems and is discussed in detail by Borg et al. [4]. Although the model isochron is also a mixing line, the slope corresponds to the age of source differentiation of 4.51 Ga.

Sources of martian magmas: The $^{87}Rb/^{86}Sr$, $^{147}Sm/^{144}Nd$, and $^{176}Lu/^{177}Hf$ ratios of the martian meteorite sources can be estimated from their ages and initial and whole rock isotopic compositions by assuming they formed at 4.51 Ga. To complete this calculation, undifferentiated Mars is assumed to have chondritic $^{147}Sm/^{144}Nd$ and $^{176}Lu/^{177}Hf$ ratios, and a $^{87}Rb/^{86}Sr$ ratio of 0.16 estimated for bulk Mars [2]. The parent/daughter ratios of the martian meteorite sources correlate with one another [Fig 4a-b], La/Yb

MIXING RELATIONSHIPS IN THE MARTIAN METEORITE SUITE L. E. Borg
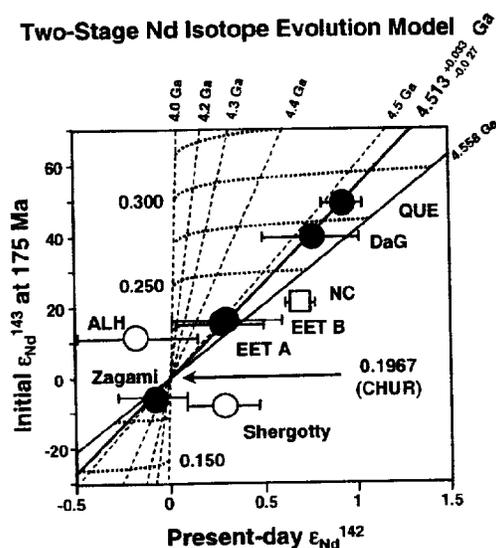
Figure 3. Two stage model isochron constraining the time of martian differentiation at ~4.51 Ga. Figure, model calculations, and data sources from Borg et al. [4].

ratios, and estimates of magmatic fO_2 [5], but not with major element abundances of the meteorites. This suggests that much of the compositional variation observed in the meteorites are inherited from their ancient sources.

Meteorite sources: The compositions of the martian meteorite sources are very similar to the compositions estimated for the sources of lunar mare basalts. For example, mafic lunar cumulate source regions for the mare basalts are estimated to have $^{147}Sm/^{144}Nd$ ratios of 0.26-0.33 and $^{176}Lu/^{177}Hf$ ratios of 0.046-0.072 [6-7] and are comparable to ratios estimated for the QUE94201 source region ($^{147}Sm/^{144}Nd$ = 0.285; $^{176}Lu/^{177}Hf$ = 0.048). Likewise, KREEP is estimated to have $^{147}Sm/^{144}Nd$ = 0.172 and $^{176}Lu/^{177}Hf$ = 0.014 [8] and is comparable to the ratios calculated for Shergotty source region ($^{147}Sm/^{144}Nd$ = 0.182; $^{176}Lu/^{177}Hf$ = 0.028). The $^{87}Rb/^{86}Sr$ ratios of lunar and martian source are difficult to compare because of different volatile element abundances on the two bodies. However, the $^{87}Rb/^{86}Sr$ ratios of the lunar sources are within ~2 of the calculated martian sources.

Mixing models produced using the compositions of lunar mafic cumulates and KREEP as end-members are presented in Figure [4a-b]. The $^{87}Rb/^{86}Sr$ ratios of the lunar sources are increased by a factor of 2 to account for different volatile element abundances on the Moon and Mars. The mixing models are able to reproduce the compositions of the martian meteorite sources suggesting that the isotopic variations observed in the martian meteorites reflect mixing of components formed by crystallization of a magma ocean. Positive correlation
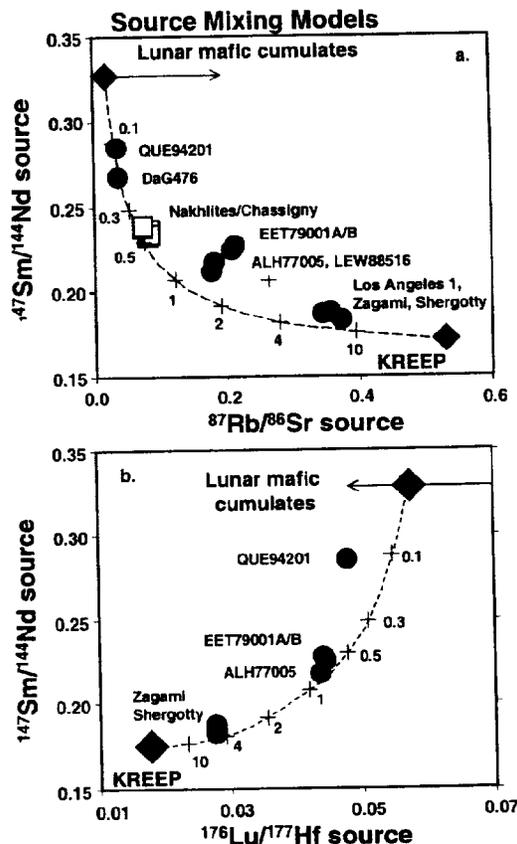
Figure 4a-b. Parent/daughter ratios of martian meteorite sources calculated assuming differentiation at 4.51 Ga. Rb-Sr and Sm-Nd data summarized in [4], Lu-Hf data from [9].

between the proportion of the KREEP-like component estimated in the meteorite source regions and estimates of fO_2 suggests that the KREEP-like component may be able to oxidize reduced martian magmas, and therefore could be hydrous. In this scenario, variations in trace element abundances, isotopic compositions, and magmatic fO_2 are produced as a result of melting compositionally diverse magma ocean cumulates. The lack of correlation of major element compositions with trace element and isotopic compositions is likely to reflect the fact that the variations in major element abundances are primarily controlled by crystallization processes after the magmas have left their source regions.

References: [1] Shih et al. (1982) *GCA* **46**, 2323-44. [2] Borg et al. (1997) *GCA* **61**, 4915-31. [3] Jones (1989) *Proc. 19th LPSC* 465-74. [4] Borg et al. (2001) *LPSC* **XXXII** #1144. [5] Herd et al. (2001) *Am. Min.* **86**, 1015-24. [6] Paces et al. (1991) *GCA* **55**, 2025-43. [7] Beard et al. (1998) *GCA* **62**, 525-44. [8] Warren & Wasson (1979) *RGSP* **17**, 73-88. [9] Blichert-Toft et al. (1999) *EPSL* **173**, 25-39.

What should we looking for in Martian meteorites? Is Evidence of Crustal process or Mantle process more important...and to whom?

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Introduction: The "sampling" of Mars, both remotely and by meteorites, provides evidence for a range of reducing and oxidizing environments. Processes that modified the crust and mantle on Mars are clearly as diverse as those on the Earth with regard to oxygen fugacity. Increasingly compelling evidence for the presence of water in the near surface regime provides a potentially oxidizing near-surface environment, especially when coupled with increasing hydrogen loss from the planet through time. Dewatering of the mantle and the purported absence of global crust-mantle recycling perhaps accounts for the apparent reducing regime that dominates the source regions of many of the meteorite samples when compared to samples of the Earth's mantle.

The meteorite samples available must however have been near the surface of the planet prior to their entrainment in impact ejecta that eventually traveled to Earth. Evidence for their interaction with that surface regime is surprisingly sparse, or perhaps has not been generally recognized. (Have we been looking for the wrong things?) Magmatic interactions with crustal material such as water and potential oxidative processes that might accompany them have not received as much attention as the search for mantle signatures of these meteorites. Crustal processes include the crystallization of the magmas, hydrothermal interaction of the solid igneous rock with its immediate environment, metamorphic modification, later weathering and erosion to form sediments, and of course impact-induced modification. All of these crustal processes have the potential to alter the redox character of the samples. Our ability to document these processes is improving rapidly. Systematic studies of elemental redox state, particularly Fe, have the promise to extract detail of the changes in oxidation history that each sample has undergone. The methodologies of these studies include both direct and indirect approaches and a corollary of these studies is the necessity that consistent results be produced by different techniques.

Crystallization Histories: Despite the broad geochemical interest in characterizing the Martian mantle, it remains obvious that the majority of the Martian meteorites represent igneous rocks that crystallized at or near the surface of the planet, i.e. in the crust. The likelihood of material, that crystallized in the Martian mantle, being emplaced in sufficient quantity to ensure their sampling by impacts capable of delivering the samples to Earth is low. In contrast, typical mafic assemblages that may be ubiquitous throughout the Martian crust should dominate the igneous meteorite suite. It is therefore imperative that we understand the crustal processes that produced the rocks we see. The phase equilibria as we know them strongly support such shallow formation histories. We must therefore ensure that our studies document that crustal history as completely as possible. (For example, the absence of identified 'sedimentary-rock' meteorites from Mars demonstrates, at best, an unknown selection process that prevents their survival as viable meteorites or at worst our inability to recognize a 'meteowrong' as an unfamiliar meteorite type.)

The Martian meteorites differ from most other igneous meteorites as they are dominated by crystalline rocks. Their histories have not been obscured by the brecciation and mixing processes that dominate both lunar and the eucrite-diogenite continuum. Shock modification, despite the general lack of brecciation, remains a definitive characteristic of these samples and must be taken into account when assessing petrologic and geochemical evidence. Their crystallization histories, began with magmatic crystallization events in some crustal chamber, proceeded through a sequence of events in the crust of Mars (about which we have little understanding) and ended with a major nearby impact event that sent the samples to Earth. The objects were recovered as stones with telltale shock indicators to alert us of their extraterrestrial provenance.

Documenting crustal processes in Martian samples: Petrological studies remain a fundamental tool for documenting the history of a sample. Extensions of those studies using powerful instrumental techniques on petrologically characterized subsamples have proven to be extremely valuable. The study of rock interaction with fluid phases that are no longer present is of course a classic problem for petrologists and Martian petrology and geochemistry is beginning to deal with this thorny problem.

Redox Exchange Processes: The oxidation or reduction of Fe in Martian near surface environments is a central issue to studies of the planet and is our focus here. Measurement of the relative abundance of ferric and ferrous iron in the phases of redox exchange reaction is one of the most direct tools for documenting the role of that reaction in the history of the sample. It is, by no means, the only approach that can be used, nor

Martian crustal processes: J.S.Delaney & M.D. Dyar

will it document all the interactions that may have taken place. Several approaches for documenting redox exchanges in the meteorites are available.

Prior to the availability of techniques for direct measurement of ferric/ferrous ratios at micro- and nano-scales, either bulk sample measurements or *very* labor intensive, mineral separation measurements were necessary. Wet chemical techniques and Mössbauer spectroscopy define the state of that art.

The advent of microanalytical tools with both the energy and spatial resolution necessary to make ferrous/ferric measurements at petrologically relevant scales (microXANES and EELS) does not reduce the importance of the bulk techniques, particularly for independent tests of instrument calibration. These micro and nanoscale methods have great potential but they suffer from the same issues that plagued other more familiar microanalytical techniques. The application of these techniques, to real problems, highlights weaknesses in their theoretical underpinning that compromise both their usefulness and acceptance of their results. In this regard, they do not differ significantly from other microbeam techniques such as secondary ion mass spectrometry for which the decades long search for fully quantitative theoretical models continues. For that matter, microanalysis techniques using the venerable electron probe continue to benefit from significant theoretical improvements even after a half-century of development. Clearly a role remains for both empirical and theoretical techniques in all these approaches. For this reason, active exchanges of results from these new techniques are critical. For example, when microXANES provides results that are the "odd man out" the challenge to find out why becomes more acute.

Indirect approaches to redox processes in the Martian meteorites cover the gamut of petrological research. Phase equilibria provide many of the basic relationships necessary for calibrating redox exchange reactions. The changes in phase assemblages as a function of oxygen fugacity provide the fundamental results against which other approaches can be compared. Fine detail of the exchanges involved is sometimes difficult to extract. Partitioning studies of redox sensitive reactions provide some of that detail. For major and some minor elements such as Fe and Cr, these studies are intimately linked to the phase equilibrium. The exchange of Fe between oxides and silicates and its change from ferric to ferrous in that context is both a phase equilibrium indicator and a sensitive redox indicator. For trace element partitioning, however, the link to phase equilibria may be less simple given the multiple possible hosts for many trace elements. Nevertheless such studies have successfully provided usable indicators for redox exchange. As the number of techniques available increases, clearly the opportunity for inconsistency among those techniques also increases.

Back to Mars! In samples that saw a variety of processes, conflict among datasets becomes more difficult to identify. No indicator of, for example, redox state will be sensitive to all crustal process and faithfully record them. This is particularly true of the direct measurements of iron redox state such as microXANES.

Ferric and ferrous contents of co-existing minerals in the Martian samples can potentially be modified during crystallization of the primary assemblage. However, later interaction with hydrothermal fluids can radically alter the magmatic signatures. For the moment, we have the luxury of ignoring large scale weathering effects in the Martian crust, as none of the meteorites presently is recognized to have a strong weathering overprint. That may change rapidly, however. Similarly, strong metamorphic overprints comparable to those on Earth are not yet part of the gamut. However, the final Martian crustal event that all these meteorites experienced was impact and ejection from Mars toward the Earth. This raises a suite of issues that will need to be explored systematically and in detail. No aspect of a shock event requires that the target experience either reduction or oxidation. However, the environment in which the shock is applied can presumably provide an impetus in either direction. Identifying and quantifying localized shock effects and relating redox modification (if any) to them, is a problem that must be addressed. When shock is accompanied, or followed by, a thermal event the potential for resetting redox indicators is high. For some indicators of redox, these late processes are irrelevant, for others they will be fundamental. At present, it is simply impossible to say which indicators will be most sensitive to each stage in the history of each meteorite sample. However, both the mantle and crustal history of these samples is probably reflected in the results of the different types of redox study.

Petrologically constrained studies that search for BOTH the effects of the mantle and crustal history of each sample remain desirable. As we look beyond the dominant magmatic signatures of the Martian meteorites, their crustal history should become clearer. While we focus on redox process here, such arguments generalize. We must begin to identify specific crustal AND explicitly surface processes so that the meteorites can continue to be useful samples of Mars when field/mission constrained samples of that planet's outermost surface begin to return to Earth.

CRUST-MANTLE RESERVOIRS OF RADIOGENIC ISOTOPES OF MARS AND EARTH: WHERE CAN WE SEE A MIXING?

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Introduction: The Earth is still a dynamic planet, with mantle convection sufficient to drive the tectonic plates and outer core convection strong enough to produce a magnetic field. Mars started its geological life almost as the Earth and had in the past a liquid core, able to generate a strong magnetic field. But today, Mars has lost this internal magnetic dynamo and its mantle is probably slowly convecting. The study of radiogenic isotopes in the Martian meteorites (SNC), reveals that their parent body "must be frozen" in its planetary evolution.

$^{129/132}$Xe systematic: From the observed higher ^{129}Xe/^{132}Xe ratio in the Martian atmosphere compared to the interior of Mars [1, 2, 3] we postulated an efficient extraction of the halogens from the interior into the crust. The enrichment of ^{129}Xe$_{rad}$ in the Martian atmosphere, produced by the decay of ^{129}I with a half-life of 15.7 Ma, points to a very early extraction of iodine into the crust; the ^{129}Xe$_{rad}$ was released into the present atmosphere over geological time. In contrast, the ^{129}Xe/^{132}Xe ratio in terrestrial rocks is equal or higher than the atmospheric ratio, because of a continuous recycling of the crust and mantle.

Rb-Sr isotopic systematic: All whole rock data of the Rb-Sr isotopes cluster in 3 groups close to the meteoritic isochron of 4.55 Ga. Starting with the Rb-Sr systematic of only 6 SNCs we postulated about 10 years ago the existence of 3 isotopically distinct reservoirs on Mars, which remained isolated for a period of 4.3 ± 0.2 Ga [4]. Since then, more than 20 SNC meteorites have been found in hot and dry deserts. New isotope data from these recently recovered SNCs confirm the three isotopically distinct reservoirs.

The first group, the basaltic shergottites Shergotty, Zagami and Los Angeles have relatively high abundances of radiogenic Sr, which might originate from a planetary crust enriched in incompatible elements. The in situ measurements of the Martian surface by Viking [5], Phobos [6], and Mars Pathfinder [7], thousands of kilometres apart, reveal similar compositions of the Martian

soils and the basaltic shergottites. Of course, we have to neglect in this comparison the extremely high S- and Cl-concentrations of the soil, which derived probably from volcanic exhalations [8]. The K contents of the soil measured by Phobos [6] and Mars Pathfinder [7], with 0.3 % and 0.55 % respectively, are higher than the 0.18 % K content in the basaltic shergottites. This higher K concentration on the Martian surface might indicate crustal reservoirs, which are more radiogenic in Sr as found in the shergottites. However, compared to the Earth's upper continental crust, with 2.8 % K [9], the Martian surface has a moderate K inventory.

A second group of Martian meteorites, characterized by non-radiogenic Sr, consists of the mafic cumulates nakhlites and Chassigny, the olivine rich shergottites DaG 476, SaU 005, Dhofar 019, and the basaltic QUE 94201 and may represent the depleted mantle. This and the first group are chemically complementary, suggesting that crust formation has caused the mantle depletion, which must have taken place during a very early process. This can be derived from the primitive Sr isotopes and the excess Nd-142, the daughter product of the extinct Sm-146, found in Chassigny, the nakhlites, SaU 005, DaG476, and QUE 94201 (E42 group). The observed correlation of ^{142}Nd with ^{182}W in SNC meteorites by Lee and Halliday [10] points to the same incompatible behaviour of Nd and W during magmatic processes and an early core formation (about 30 Ma). Core formation must have occurred concurrently with the rapid accretion of Mars, which is inferred from excess ^{182}W in Martian meteorites.

A third meteorite group with intermediate Sr isotopic composition, represented by the olivine gabbroic LEW 88516, ALHA77005, and Yamato793605, might originate from a primitive, unfractionated mantle. However a mixing process of crust and depleted mantle cannot be excluded [11].

The lack of plate tectonics can keep the obvious 3 distinct reservoirs untouched. On Earth, plate tectonics might be responsible for the homogeniza-

CRUST-MANTLE RESERVOIRS OF RADIOGENIC ISOTOPES: G. Dreibus and E. Jagoutz

tion of the terrestrial Rb-Sr reservoir. Today, only one Rb-Sr isotopic reservoir exists on Earth. The terrestrial crust and depleted mantle are developed from an isotopic homogeneous mantle at about 2 Ga while on Mars crust and depleted mantle developed at 4.3 Ga.

Sm-Nd systematic: The Sm-Nd systematic of terrestrial samples reveals also a crust-mantle differentiation from a chondritic Sm/Nd reservoir 2 Ga ago. In the terrestrial samples of crust and mantle the Sm/Nd ratio changes by a factor of 2. The SNC meteorites, however, have strongly fractionated Sm/Nd ratios and large variation of the $^{143}Nd/^{144}Nd$ ratio particularly among the rocks from a depleted mantle reservoir: Nakhla, Chassigny, DaG 487, SaU 005, Dhofar and QUE 94201. In the Sm-Nd isotope plot only the data of the minerals and the whole rock of ALHA84001 fall on the 4.55 Ga meteoritic internal isochron. All other SNCs are far away from this isochron due to their strongly fractionated Sm/Nd ratio. In the Sm-Nd system we cannot find the 3 distinct initial isotopic reservoirs as found for the case of the Rb-Sr systematic.

Pb-Pb systematic: The Pb isotopes of all measured SNCs show a similar pattern as the Sr isotopes. The present study of the Pb isotope systematic might give the strongest indication for an early differentiation of Martian mantle and crust. The initial Pb from hand-picked ultra clean plagioclase separates Los Angeles, Shergotty, Zagami, and the new shergottite Dhofar 378, from the enriched crustal reservoir, and of nakhlites and SaU 005, from the depleted mantle reservoir, plot close to the 4.5 Ga Pb-Pb isochron. The conformity of the U-Pb and Rb-Sr isotopic systematics reflects similar magmatic fractionation behaviour of Rb and U during the evolution of curst and mantle.

Summary: The ^{129}I-^{129}Xe ($T_{1/2}$ 16 Ma) and the ^{146}Sm-^{142}Nd ($T_{1/2}$ 103 Ma) isotope systems indicate a rapid accretion and a very early formation of the crust with its enrichment of volatile and highly incompatible lithophile elements. The absence or at most very limited plate tectonic activity on early Mars excludes an extensive crustal recycling back to the mantle and preserves the Rb-Sr and U-Pb isotopes systems derived from the early crustal differentiation. The observed correlation of radiogenic ^{182}W with radiogenic ^{142}Nd by [10] points also to a close relationship between core formation and mantle melting in the first ~30 Ma after formation of the Mars. Contrary to Mars. on Earth a relationship exists between the Sr- and Nd-isotope systems. Because of the remixing of the crust into the Earth's mantle and the homogenization of the isotopes through plate tectonics a "common isotopic reservoir" exists from which about 2 Ga ago crust and depleted mantle differentiated.

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MÖSSBAUER SPECTROSCOPY OF SNC METEORITES.

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Introduction: With the inclusion of Mössbauer spectrometers in the instrument payloads of both MER landers in the upcoming Athena mission, it is timely to re-examine Mössbauer data on SNC meteorites and fill the gaps in our state of knowledge. Much of this work was done by Roger Burns ten years ago on whole rock samples [1-6], but the research effort was cut short in 1993. In this project, we are summarizing existing Mössbauer spectra of SNC meteorites and showcasing new results from a state-of-the-art spectrometer customized to accommodate smaller (less than 10 mg) samples. The results demonstrate the problems inherent in drawing conclusions about individual phases chemistry on the basis of Mössbauer spectra of whole rock samples.

Previous Work: Previous work on these meteorites is summarized in Table 1. The only workers to

Table 1. Mössbauer Spectroscopy of SNC Samples

Meteorite	Analysis	%Fe^{3+}
ALHA 77005	WR[1, 2, 5]	1.7-1.8
	olivine separate [11, 12]	4.5
Chassigny	WR[3, 4, 5]	2.3
EETA 79001	WR[1, 5, 6]	0.5-1.9
Governador Valadares	WR[5, 6]	n.s.
Lafayette	WR[5, 6]	n.s.
Nakhla	WR[1, 5, 6, 8, 13]	1.6
	pyroxene separate [14]	2.0
Shergotty	WR[5, 6]	n.s.
Zagami	WR[5, 6, 7, 8, 10, 13]	n.s.
	pyroxene separate [13]	<1.0

WR = whole rock analysis, n.s. = not specified.

extract and analyze mineral separates were Ostertag et al. (olivine) [11,12], Vieira et al. [13], and Vistisen [14] (pyroxene), and these data show only very small percentages of Fe^{3+} in olivine and pyroxene. However, none of the previous workers has related the Fe^{3+}/ΣFe of the bulk separates to the Fe contents and modes of individual minerals present, so Fe^{3+}/ΣFe ratios of individual phases could not be assessed.

Methods: In the current study, roughly 200 mg samples of each of nine SNC meteorites were obtained from JSC, NMNH, and the Vatican (Table 2). Whole rock Mössbauer spectra were acquired on a 10 mg chip of each sample, and the remaining mass was crushed to allow handpicking of mineral separates for phases constituting more than 30% of the mode.

For all Mössbauer analyses, samples were then crushed under acetone to a fine powder, mixed with sucrose to avoid preferred orientation, and run on a WEB Research spectrometer at room temperature. Data were processed using the WMOSS software package, which allows use of multiple models for line shape.

Table 2. Mineral Modes (%) for Samples Studied

Meteorite	Px	Fsp*	Ol	Ox	#	Ref.
ALHA 77005	35	8	50			[15]
ALHA 84001	97	1		2		[16]
Chassigny	5	2	92	1		[17]
LEW 88516	35	8	50		5	[18]
Los Angeles	40	45	3	3	9	[19]
Nakhla	80		10		10	[20]
QUE 94201	44	46		2	8	[21]
Shergotty	70	24		2	4	[22]
Zagami	70	24		3	3	[22]

*Fsp or maskelynite, # = other phases such as glass

Results: Whole rock spectra of ALHA 84001, LEW 88516, QUE 94021, and Los Angeles have not previously been published, so they are included here as Figures 1-4. Spectra of the other five samples in Table 2 have also been acquired. The QUE 94201 spectrum is typical of orthopyroxene, with a small contribution (about 5% of the total Fe) as ilmenite. Both Los Angeles and ALHA 84001 show spectra typical of clinopyroxene, and the LEW 88516 spectrum shows a mix of Fe in olivine and pyroxene.

These spectra show good examples of how confusing the interpretation of Mössbauer spectra of mixtures can be! For example, in the spectrum of LEW 88516, 60% of the area is in the outer olivine doublet, while the remaining 40% of the area can be assigned to Cpx. Normalizing the mineral mode suggests that the sample should be 59% olivine and 41% pyroxene. The fact that these numbers match is merely coincidence because the percentage of Fe atoms in the two minerals is not the same. The olivine is 27 wt%FeO (0.60 apfu) and pyroxene is roughly 10-16 wt% FeO (0.28-0.51 apfu) [23]. The mineral modes reflect the variations in effective volume of the phases present. Thus, based on the molar volumes of the unit cell of olivine (Z=4, volume≈290 Å^3) and pyroxene (Z=4, volume≈449 Å^3), the percentage of Fe atoms based on the mineral modes should be 27% in pyroxene and 73% in olivine if all the Fe is Fe^{2+}. Thus, the predicted areas are not a bad

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match to the observed peak areas noted above, especially considering the variations in pyroxene chemistry upon which these calculations are made (and the fact that recoil-free fractions for these two minerals are similar but slightly different).

Two other examples are also useful [24]. Nahkla has a mode that is 80% cpx and 10% olivine, but these data combined with the chemical compositions suggest a Mössbauer spectrum with doublet areas of 75% cpx and 25% olivine (close to those actually observed in [1] and to our own spectrum). This change occurs because the olivine is Fe-richer than the coexisting pyroxene. ALHA 77005 has a mode with 50% olivine and 35% pyroxene, but its predicted Mössbauer spectrum has the proportions 62% olivine and 38% pyroxene.

Conclusions: If mineral modes and the Fe contents of the component phases are known, Mössbauer doublet areas can be predicted with some confidence. However, this relationship does not work in reverse because there are three variables of which two are unknown. Doublet areas in the Mössbauer spectrum of a mixture of minerals *cannot be used to estimate modal mineralogy* without known chemical compositions In cases where the bulk rock is a mixture of, say, hematite and magnetite (i.e., phases where the chemical compositions are relatively constant), modal estimates can be confidently made based on Mössbauer spectra of mixtures. Unfortunately, in cases where the bulk rock contains silicates with variable Fe contents (i.e., nearly any silicate!) it is impossible to deduce modes from Mössbauer doublet areas. Interpretation of MER data for which modes will not be known will be (regretably) complicated by this simple constraint.

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Figures 1-4 (at right). Room temperature Mössbauer spectra of SNC meteorites.
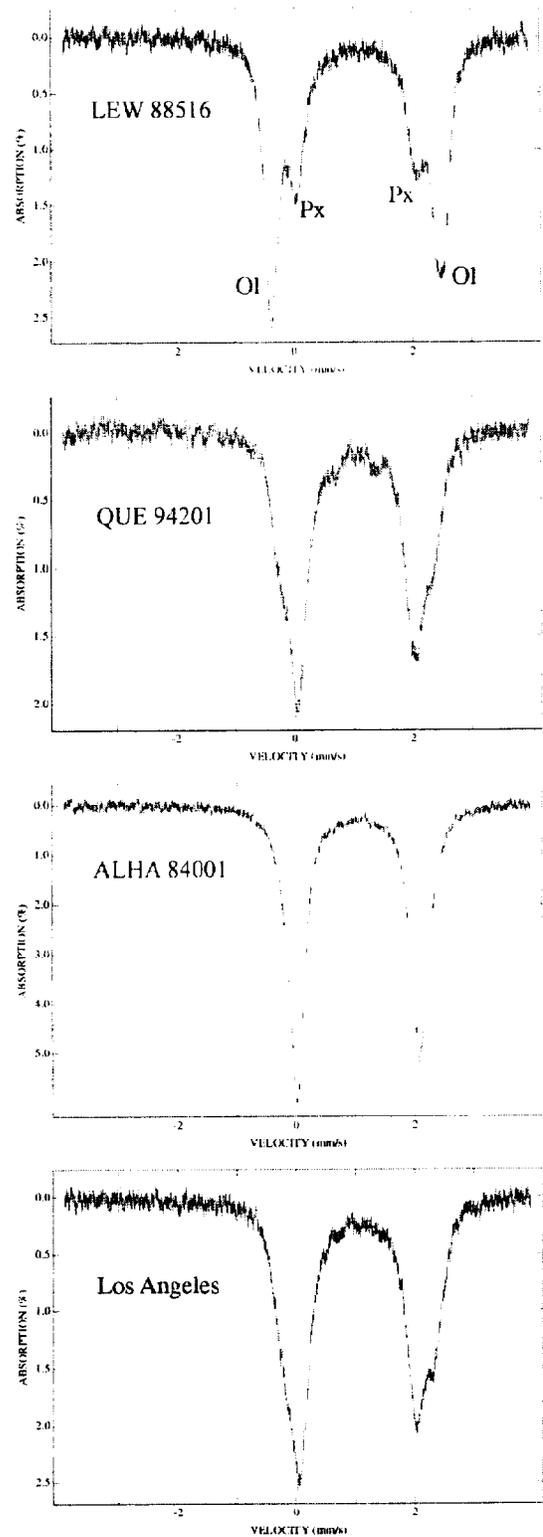
PETROGENESIS OF OLIVINE-PHYRIC SHERGOTTITES SAYH AL UHAYMIR 005 AND ELEPHANT MORAINE A79001 LITHOLOGY A.

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Introduction: Martian meteorites Sayh al Uhaymir (SaU) 005 and lithology A of EETA79001 (EET-A) belong to a newly emerging group of olivine-phyric shergottites [1]. Previous models for the origin of such shergottites have focused on mixing between basaltic shergottite-like magmas and lherzolitic shergottite-like material [2-7]. Results of this work, however, suggest that SaU 005 and EET-A formed from olivine-saturated magmas that may have been parental to basaltic shergottites.

Description: SaU 005 and EET-A have porphyritic textures of large (up to ~3 mm) olivine crystals (~25% in SaU 005; ~13% in EET-A) in finer-grained groundmasses consisting principally of pigeonite (~50% in SaU 005; ~60% in EET-A) and plagioclase (maskelynite), with <7% augite. Low-Ti chromite occurs as inclusions in the more magnesian olivine, and with chromian ulvöspinel rims in the more ferroan olivine and the groundmass. Crystallization histories for both rocks were determined from petrographic features (textures, crystal shapes and size distributions, phase associations, and modal abundances), mineral compositions, and melt compositions reconstructed from magmatic inclusions in olivine and chromite.

Results: The following observations indicate that the chromite and most magnesian olivine (Fo 74-70 in SaU 005; Fo 81-77 in EET-A) and pyroxenes (low-Ca pyroxene [Wo 4-6] of mg 77-74 and augite of mg 78 in SaU 005; orthopyroxene [Wo 3-5] of mg 84-80 in EET-A) in these rocks are xenolithic. 1) Olivine crystal size distribution (CSD) functions show excesses of the largest crystals (whose cores comprise the most magnesian compositions), indicating addition of phenocrysts or xenocrysts [8]. 2) The most magnesian low-Ca pyroxenes show near-vertical trends of mg vs. Al_2O_3 (Fig. 1) and Cr_2O_3, which suggest reaction with a magma. 3) In SaU 005, there is a gap in augite composition between mg 78 and mg 73. 4) Chromite cores of composite spinel grains are riddled with cracks, indicating that they experienced some physical stress before being overgrown with ulvöspinel. 5) Magmatic inclusions are absent in the most magnesian olivine, but abundant in the more ferroan, indicating slower growth rates for the former. 6) The predicted early crystallization sequence of the melt trapped in chromite (the earliest phase) in each rock produces its most magnesian olivine-pyroxene assemblage (Fig. 2b,d). However, in neither case is the total crystallization sequence of this melt consistent with the

overall crystallization history of the rock or its bulk modal mineralogy (Fig. 2a,c).

Further, the following observations indicate that in both SaU 005 and EET-A the fraction of solid xenolithic material is small (in contrast to previous models for EET-A [2-5]), and the bulk of the rock formed by continuous crystallization of a single magma (possibly mixed). 1) CSD functions and correlations of crystal size with composition show that most of the olivine (Fo 69-62 in SaU 005; Fo 76-53 in EET-A) formed by continuous nucleation and growth. 2) Groundmass pigeonites are in equilibrium with this olivine, and show continuous compositional trends that are typical for basalts (Fig. 1). 3) The CSD function for groundmass pigeonite in EET-A indicates continuous nucleation and growth [9]. 4) The melt trapped in olivine of Fo 76-67 in EET-A has a predicted crystallization sequence similar to that inferred for the bulk of the rock and produces an assemblage similar to its modal mineralogy. 5) Melt trapped in late olivine (Fo ~64) in SaU 005 has a composition consistent with the inferred late crystallization history of the rock.

The conclusion that only a small fraction of either SaU 005 or EET-A is xenolithic implies that both rocks lost fractionated liquids late in their crystallization. This is supported by: 1) olivine CSD functions, which show a drop in nucleation rate at high degrees of crystallization [8]; 2) high pigeonite/plagioclase ratios; and 3) low augite contents. For EET-A, this fractionated liquid may be represented by EET-B.

All magmas involved in the petrogenesis of SaU 005 and EET-A were olivine-saturated. These olivine-phyric shergottites did not form by mixing of basaltic shergottite-like magmas and lherzolitic shergottite-like material. The magmas from which they formed may, however, have been parental to basaltic shergottites.

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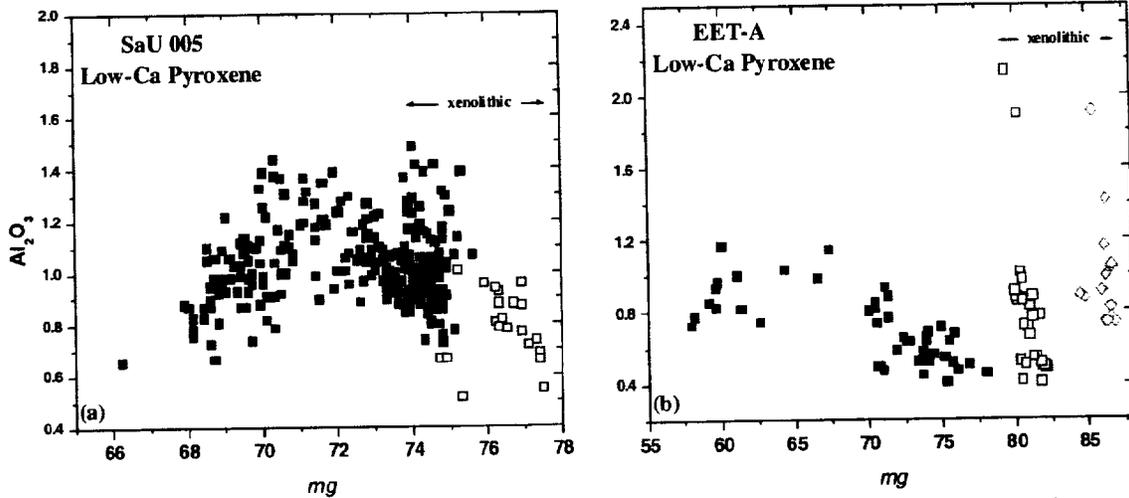
Fig. 1. Al₂O₃ content (wt.%) vs. *mg* for low-Ca pyroxenes in SaU 005 (a) and EET-A (b). For SaU 005 open red squares = opx inclusions in the most magnesian (Fo 74-70) olivine; black squares = groundmass pigeonite. For EET-A open red squares = opx cores of megacrysts; open green diamonds = opx cores in the exceptional megacryst X-14 [10, 11]; black squares = pigeonite in coronas around opx cores and groundmass. Most magnesian low-Ca pyroxenes in both rocks show near-vertical trends, which cannot be explained by closed system evolution and suggest reaction with a magma.
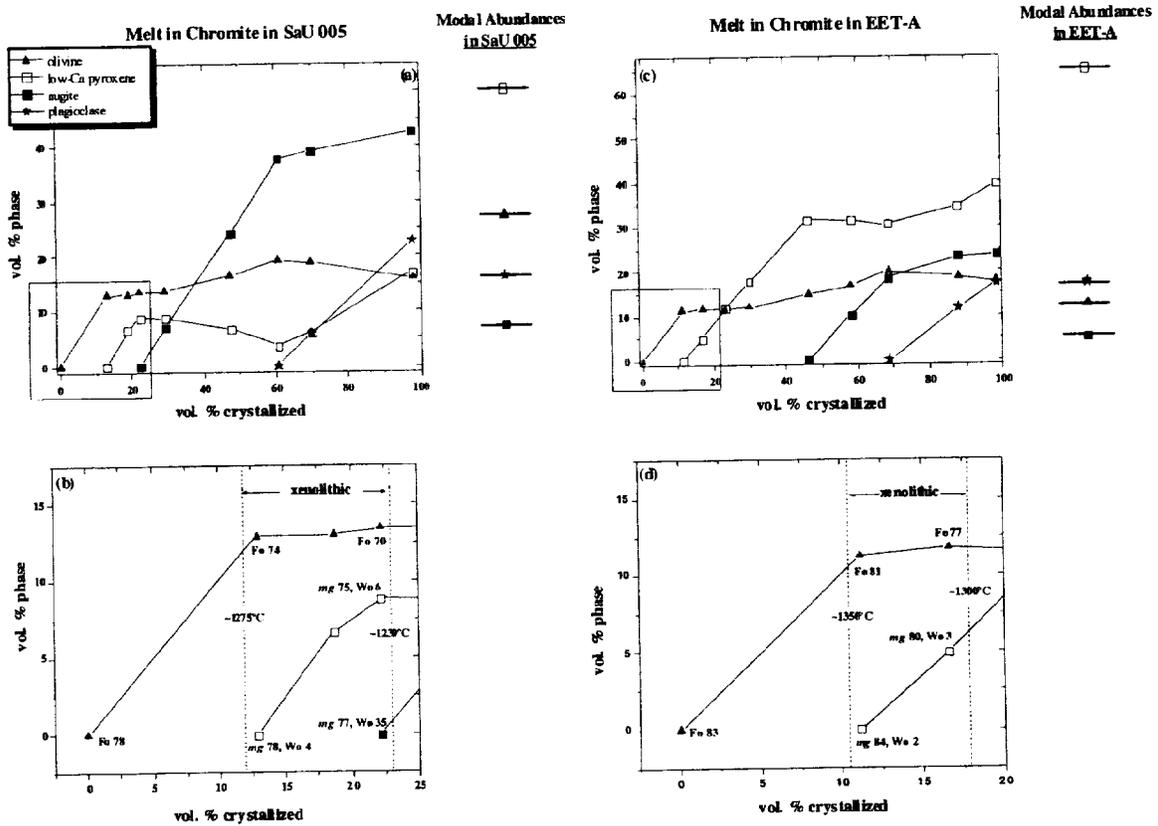
Fig. 2. Predicted crystallization sequences for melt trapped in low-Ti chromite in SaU 005 (a,b) and EET-A (c,d). In both cases, this melt produces the most magnesian phase assemblage in the rock (b,d), but is not consistent with its overall crystallization history or modal mineralogy (a,c). Areas indicated by boxes in (a,c) are shown at larger scale in (b,d).

MARS METEORITE STATISTICS AND THE MARTIAN UPLANDS.

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A significant fraction of Mars, perhaps 30-50%, is covered by heavily cratered uplands. The high crater densities constrain their ages to be >2 Gy or even 3 Gy. A somewhat smaller fraction is covered by young lava plains with crater retention ages < 1.5 Gy, and even < 0.5 Gy over wide areas of Tharsis, Amazonis, and Elysium. These young ages for basaltic lava plains agree with ages of Martian basaltic meteorites.

The problem is that all but one of the 4 to 8 sample sites of SNCs lie in the age range of 0.2 to 1.3 Gy, and the other one is a sample of primordial crust of 4.5 Gy age. These data suggest that the Martian uplands do not efficiently launch meteorites.

MGS and Odyssey data imply that the upper latitude Hesperian/Noachian Martian uplands, older than 2 to 3 Gy, are impregnated with near-surface ice. Furthermore, direct geometric considerations of crater areal coverage show that they have been pulverized into megaregolith, although that material itself may be recemented by salts, carbonates, and ice.

Thus, the Martian uplands probably do not launch meteorites as effectively as the young basaltic plains, and those that are launched may be rich in rock types that are unfamiliar as meteorites. These considerations should affect future meteorite collection strategies.

MARTIAN BASALT OXYGEN FUGACITY AND GEOCHEMISTRY: IMPLICATIONS FOR A HETEROGENEOUS MARTIAN MANTLE.

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Introduction: The oxygen fugacity (fO_2) of the martian basalts (a.k.a. basaltic shergottites) has recently been recognized as important in understanding their petrogeneses [1]. The correlation between oxygen fugacity and certain geochemical parameters (initial Sr and Nd isotopic compositions, La/Yb ratios) indicates the presence of long-term incompatible-element enriched and depleted reservoirs, which are oxidized and reduced, respectively. Oxygen fugacity variations in the martian basalts have been modeled based on assimilation of oxidized crustal ("crust-like") material by reduced, mantle-derived magmas [1]. However, there remains the possibility that the oxygen fugacity of the martian basalts is controlled by the nature of their source regions [1,2]. Here I review existing oxygen fugacity data for the martian meteorites, present some speculative estimates for newer martian basalts, and explore the heterogeneous mantle model in more detail.

Oxygen fugacity estimates: a review. Estimates based on compositions of Fe-Ti oxides are presented by [3], and an estimate for Dar al Gani 476 using olivine-pyroxene-spinel (Ol-Px-Sp) models is given by [1]. Oxygen fugacity has also been estimated by [4], using D_{Eu}/D_{Gd} ratios in pyroxene. Since this method utilizes the Eu and Gd concentrations of earliest-formed pyroxene (augite or pigeonite), it represents a better means of estimating magmatic oxygen fugacity than Fe-Ti oxides, which are subject to subsolidus equilibration. Initial estimates using this method differed greatly from the Fe-Ti oxide methods [1,4]. However, [1] and [3] demonstrated that Fe-Ti oxides in the martian basalts recorded near-magmatic fO_2 conditions, and [1] argued that the discrepancy between the methods was due to the lack of proper D_{Eu}/D_{Gd} calibration. Since then, other authors [5,6] have calibrated this model with martian basalt compositions. The estimates based on these calibrations are in better agreement with Fe-Ti oxide estimates, supporting minimal subsolidus equilibration of Fe-Ti oxides.

The observation that fO_2 in the martian basalts varies by 3 log units or more is supported by all of the available methods. General agreement between the methods suggests that the oxygen fugacity of a given martian basalt was set before crystallization, and did not change significantly over the temperature history of the rock [6].

Oxygen fugacity estimates: new. At least 7 basaltic shergottites have been described since [1,3] estimated oxygen fugacity from Fe-Ti oxides and Ol-Px-

Sp. Of the newly discovered basalts, SaU 005 (and pairs), NWA 1068/1110, NWA 1195 and Dhofar 019 are texturally the most similar to DaG 476 (and pairs) and EET 79001A; that is, characterized by olivine megacrysts in a fine-grained groundmass [7,8,9,10]. The Ol-Px-Sp method can be used to estimate the fO_2 of these samples if equilibrium between olivine, low-Ca pyroxene and Cr-spinel can be established, as was done for DaG 476 [1]. The other new basalts, namely NWA 480, NWA 856 and Dhofar 378, are texturally similar to Shergotty, Zagami, Los Angeles and QUE 94201, as noted by an absence of olivine megacrysts [11,12,13]. These contain Fe-Ti oxides, but in some cases, significant oxyexsolution has occurred (e.g., NWA 480 [11]). Regardless, the prospects are good for estimating fO_2 using the range of methods now available.

Preliminary estimates of fO_2 can be made using published data for the new martian basalts. The compositions of oxides in the SaU 094 basalt [7] (a SaU 005 pair) indicate very reduced crystallization conditions. Using the composition of the most Mg-rich pigeonite and olivine cores, and a low-Ti chromite after [7] yields (a rather rough) estimate of IW – 1.7. The compositions of oxides in Dhofar 019 suggest fO_2 near the IW buffer [10]. In contrast, the fO_2 of NWA 856 is greater than or equal to Shergotty, based on Eu/Gd ratios of pyroxene cores [14].

Oxygen fugacity and LREE enrichment: SaU 005 and Dhofar 019 appear to be reduced, like QUE 94201 or DaG 476. The LREE-depleted bulk REE pattern of SaU 005 is nearly identical to that of DaG 476 [15], and Dhofar 019 is thought to have been derived from a LREE-depleted magma [10]. In contrast, NWA 856 is oxidized, and has an accordingly LREE-enriched pattern, similar to that of Shergotty [14].

From these three examples, it appears that the relationship between LREE enrichment and oxygen fugacity [1] holds for some of the newer basalts, with more reduced basalts being LREE-depleted and more oxidized basalts being LREE-enriched. If the same relationship holds for the remaining basalts, then their relative redox conditions can be predicted based on chondrite-normalized La/Yb ratios. For example, Dhofar 378 has La/Yb ~ 0.9 [13], and would be expected to be oxidized like Shergotty or Zagami. Likewise, NWA 1068 has a REE pattern similar to Shergotty and Zagami [14], and therefore would be expected to have similar oxygen fugacity.

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NWA 480 does not appear to follow this trend. La/Yb is ~ 0.8 [11], and so the fO_2 would be expected to lie between that of EET 79001 and Shergotty/Zagami. However, the reported mineralogy of NWA 480 does not support an oxidized basalt. Oxide and Ol-Px-Sp compositions after [11] suggest fO_2 ~ IW, like QUE 94201. The bulk incompatible trace elements of NWA 480 suggest it is more like the lherzolitic shergottites, whereas the compatible trace elements suggest an affinity to Shergotty and Zagami [11].

Heterogeneous mantle model: Oxygen fugacity does not correlate with bulk composition [1], or with texture (e.g., presence/absence of olivine megacrysts). The latter apparently holds true for the new martian basalts as well as the old: the "reduced" group includes QUE 94201, as well as the olivine-bearing DaG 476, SaU 005 and Dhofar 019. The "oxidized" group includes Shergotty, Zagami, Los Angeles, and NWA 856. None of these are olivine-bearing, but NWA 1068 may belong to this group, based on its REE pattern. This decoupling of the major element compositions from trace element and isotopic compositions, along with the evidence that the oxygen fugacity of a given basalt is set before crystallization, argues for mantle source mixing to explain the variations in oxygen fugacity and geochemistry of the martian basalts.

Borg [2] argues that the Rb-Sr and Sm-Nd isotopic compositions of the martian meteorites can be used to calculate parent/daughter ratios of their sources. He demonstrates that these ratios correlate with oxygen fugacity, supporting the idea that the fO_2 of a given martian basalt is inherited from its source region.

Implicit in this model is that the long-term incompatible element enriched component in the martian basalts (the "crust-like" component of [1]) is located in a source region (possibly the mantle). Indeed, [2] models the range of parent/daughter source ratios of the martian meteorites using isotopic compositions of lunar mafic mantle and KREEP. Therefore, it is appropriate to consider the oxidizing characteristics of martian KREEP-like material, formed possibly (by analogy with the Moon) as the result of the crystallization of a martian magma ocean.

As outlined by [1], the long-term incompatible element enriched component in the martian basalts must be enriched in LREE relative to HREE, be more radiogenic in terms of Sr and less radiogenic in terms of Nd. It must have either an approximately basaltic composition, or sufficiently small volume so as not to shift the bulk composition away from basalt. Also, the Rb-Sr and Sm-Nd isotopic systematics are best explained if the enriched component is ~4.5 Ga old. All of these characteristics can be achieved by crystallization of the last dregs of a magma ocean early in Mars' history. By

analogy with lunar KREEP, the bulk major element composition of such material would not be expected to be significantly different from basaltic.

The additional observation of increasing oxygen fugacity with increasing involvement of the KREEP-like component suggests a significant difference between the martian KREEP-like component and lunar KREEP: that the martian component has higher $Fe^{3+}/\Sigma Fe$, or is hydrous.

It is difficult to envision the crystallization of highly oxidized, KREEP-like material from a magma ocean, since that material would have to have an oxygen fugacity close to that of the hematite-magnetite buffer [1], which is three orders of magnitude more oxidizing than the most oxidized basalts on Earth (Earth has the advantage of subduction). Alternatively, if the KREEP-like material is comprised of hydrous material such as amphibole or phlogopite, then it may have formed as a result of crystallization of a hydrous magma ocean. This is possible, although it is a concept not yet considered (nor modeled) for Mars. Very little water is required to oxidize a basalt from ~ IW to IW + 3 [1]. However, it is unlikely that degassing is consistent and efficient enough to cause the same amount of oxidation for a given degree of involvement of the KREEP-like material. Whether degassing occurred in the more oxidized basalts is the subject of ongoing debate [16, 17]. A combination of the two mechanisms is more likely for the heterogeneous mantle model.

Future work: Determining the fO_2 and isotopic compositions of the new martian basalts (especially the enigmatic NWA 480), as well as attempting the same for the cumulate martian meteorites will help determine if there are two or more main mantle sources. Detailed examination of correlations with stable isotopes and noble gases will further aid in discerning the multiple components that mix to make the SNCs.

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ORIGIN OF THE MARTIAN CRUST AND MANTLE.

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The existence of a planet-wide early magma ocean on Mars is supported by a growing base of petrochemical and geophysical observations 1) The parent liquids to the SNC meteorites are significantly depleted in Al_2O_3 and CaO relative to terrestrial basalts [1]. Only terrestrial komatiites, the products of more than 30% melting of the Archean mantle and boninites, wet melts of the mantle wedge in island arc regions, have similar low Al_2O_3 and CaO contents. Mare basalts and picrite glasses on the Moon have similar geochemical depletions, and the major element compositions of very low Ti mare basalts bear a striking resemblance to the Shergotty parent magmas. What these terrestrial and lunar magmas have in common is that the parent magmas last equilibrated with a mantle severely depleted in magmaphile elements. The boninites and mare basalts, in particular, last coexisted with a mantle residue of olivine and orthopyroxene. In the lunar case the mantle was a product of crystallization from a magma ocean whereas the harzburgite parent mantle for boninites was a residuum to previous melting events that eliminated diopside from the mantle. 2) ^{182}W and ^{142}Nd anomalies date the fractionation of the core and mantle, respectively, within about 50-100 million years of the origin of the solar system [2][3]. The large heavily crated Martian crust and the absence of large scale recycling suggests strongly that the crust was also a product of this ancient global differentiation and has experienced only modest volcanic activity, particularly in the southern hemisphere, in subsequent epochs. Whole rock Rb-Sr systematics appear to record this planet wide differentiation at about 4.5 Ga [4] 3) The ^{143}Nd composition of the Martian mantle is significantly more depleted than the terrestrial mantle and even the cumulate source regions of mare basalts on the Moon [5]. Only Archean lithosphere on earth has the extreme positive and negative epsilon values so characteristic of the Martian mantle [6]. Continental lithosphere, by definition, is stable and has withstood the homogenizing effects of mantle convection. The extreme epsilon values reflect ancient depletion events and subsequent metasomatic perturbations. The data is consistent with the early differentiation of a Martian magma ocean producing a buoyant crust, dense core and a complementary stratified cumulate mantle. The stratified cumulate is likely to be gravitationally unstable, at least, in the shallowmost stratigraphic levels where more iron-rich cumulates overlie dense magnesian cumulates [7]. Under these unstable conditions, solid state differentiation would have carried dense, iron-rich and relatively cool cumulates into the Martian interior ultimately resulting in a lower mantle that is denser and compositional more evolved than the upper mantle. This lower mantle would also contain varying amounts of heat producing radioactive elements.

A gravitationally stable compositionally stratified Martian mantle explains some important characteristics of Mars. 1) Mars, like the Moon, is isotopically much more heterogeneous than the Earth [3,5]. While one might argue that the small size of the Moon or the absence of water to promote solid state creep inhibits thermal convection, such arguments do not apply to Mars. 2) The presence of ^{142}Nd anomalies in some SNCs require that their source regions preserved their initial compositional heterogeneities [5]. 3) The preservation of whole rock Rb-Sr isochrons and the ancient ^{182}W and ^{142}Nd anomalies argue against crustal recycling subsequent to stabilization of the magma ocean cumulates [3]. 4) The isotopic evidence of early differentiation in the Martian mantle, in contrast to the evidence from the terrestrial mantle, indicates that the Martian mantle has successfully resisted homogenization by thermal convection. Thermal convection is inhibited by a stably compositionally zoned mantle [7].

An alternative hypothesis is that the SNC meteorites are derived from a thick and ancient lithosphere akin to the continental lithosphere on Earth. The terrestrial continental lithospheres are up to 200-300 km thick; their formation ages vary widely but generally reflect the ages of the subjacent Archean and Proterozoic cratons. The lithospheres were stabilized against thermal convection, in part, by their compositional buoyancy resulting from the extraction of basaltic and komatitic magmas in the Archean. The lithosphere is depleted in Al_2O_3 and CaO but has elevated MgO and Mg* values. The lithosphere is variably metasomatized by kimberlitic and carbonatitic magmas so that incompatible trace elements are decoupled from the more refractory major elements Because of these ancient and continuing metasomatic events, the isotopic systematics are widely varying. The ε_{Nd} values, for example, range from $\varepsilon_{Nd}+42$ to $\varepsilon_{Nd}-55$ [6]!

At first glance a "lithosphere model" would appear to explain the compositions of the SNC meteorites and the thickness of the Martian crust. A number of observations argue against this hypothesis. On earth, there is no Hadian (~4.5Ga) lithosphere as indeed there is no pervasive continental crust that dates back to the formation of the Earth [6]. Second, the existing Archean crust probably never covered the entire planet [8]. But if we allow for a planet-wide Martian crust and complementary lithosphere, the energy associated with radioactive decay in the primitive asthenosphere would gradually increase the internal temperature of the planet until thermal buoyancy of the hot interior would cause a catastrophic delamination of all or part of the crust [9]. Crustal-lithosphere foundering and widespread volcanic resurfacing of Mars would ensue. Perhaps this is the process that explains the northern hemisphere and the crustal dichotomy. The timescales of the process, however, should be over 100's of millions of years [9]. The process, moreover, probably would not be a one-time event but would repeat in some cyclic pattern as postulated for Venus [9]. While the "lithosphere" hypothesis cannot yet be totally discarded, the focus of the rest of this abstract will deal with the implications of a magma ocean on Mars.

Fractionation of a magma ocean on Mars would have important similarities and differences with the Moon. On the Moon, the crystallization sequence of the magma ocean is dominated by olivine and orthopyroxene; the progressive enrichment of FeO over MgO in these phases makes the density of the cumulates increase upward with progressive

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fractionation leading to gravitational instability [7]. The concomitant FeO enrichment in the liquid and its saturation in normative plagioclase component leads to the crystallization and flotation of plagioclase and the stabilization of an anorthosite Lunar crust.

In contrast, the liquidus phase in the Martian magma ocean is mainly garnet-majorite at depths greater than about 1000 km [10,11]. For a core radius of about 1400 km, this region will extend over the lower 1000 km of the mantle. At these depths, majorite is predicted to be only slightly negatively buoyant [12]. It is likely that crystal-liquid fractionation will be inefficient in the strongly convecting magma ocean so that the lower mantle may initially approximate the whole Mars composition. Once convection ceases the remaining intergranular liquid with the majority of the highly incompatible elements, including the heat producing ones, will migrate upwards to the still liquid magma ocean. The net effect is to sequester Al_2O_3 (as garnet-majorite) in the lower mantle. Garnet-majorite will transform to eclogite in the upper mantle so that it should remain as a stable layer in the lower mantle being less dense than only dense FeO-enriched sinking cumulates from below the crust.

This scenario has several appealing features. The fractionation of majorite will decrease the Al_2O_3/CaO ratio in the remaining cumulates, a feature characteristic of Shergotite parent liquids [1]. The remaining liquids of the magma ocean will have less normative plagioclase resulting in delayed crystallization of plagioclase. The buildup of H_2O in the residual magma ocean will also delay the onset of plagioclase crystallization. The net effect is that the anorthosite crust on Mars should be relatively thinner than that on the Moon. The progressive build up of H_2O and other fluids in the residual liquids of the magma ocean may cause plagioclase to become negatively buoyant. The anorthosite crust would no longer float resulting in the eruption of volatile-rich residual melts onto the Martian surface. The upper Martian crust, in this model, would be formed by products of the late stage magmas. The lower crust would be anorthosite-rich and would have acted as the platform on which subsequent magmatism was deposited.

Besides preserving the isotopic and compositional heterogeneity, overturning of an initially unstably stratified cumulate mantle may explain additional aspects of the evolution of Mars. After the overturn, the mantle would be stably stratified. Since thermal convection would then be inhibited by the compositional stratification, the primordial and radiogenically generated heat in the Martian interior would be slow to dissipate only by conduction. Similarly, the infertility of the cumulate mantle and the inhibition of thermal convection could limit magma production by adiabatic decompression, perhaps explaining in part the preservation of ancient crust.

The crustal dichotomy may be the product of the overturn of initially unstable magma oven cumulates. Horizontal convergence would thicken the crust above long wave-length (spherical harmonic degree one) downwelling of dense late stage cumulates. Thinning due to extension or delamination of the lithosphere in the opposing (northern) hemisphere could induce pressure-release melting and resurfacing. A similar catastrophic resurfacing model has also been suggested for the Venus [9].

Regardless of the origin of the crustal dichotomy, variations in the thickness of the Martian crust are well [13] and it is at least plausible that these variations have persisted from the very early evolution. To preserve this crustal thickness variation over a substantial fraction of Mars' evolution requires low temperatures at the base of the crust. Evolution models including heat transfer by thermal convection suggest established by gravity and topography data lower crustal temperatures high enough that crustal thickness variations may not be preserved [14]. The absence of thermal convective heat transfer due to stable compositional stratification would allow conductive cooling to result in lower crustal temperatures.

Remnant magnetism [15] in a portion of the ancient, heavily cratered Martian crust argues for the existence of an internally generated magnetic field early in the evolution. The generation of a magnetic field requires sufficiently rapid cooling of a molten metallic core. It has been argued that thermal convection beneath a cool, stagnant, conducting lithospheric lid would not cool the core rapidly enough, prompting the suggestion that the more rapid heat transfer associated with plate recycling may be required during the evolution of Mars [16]. Mantle overturn that transports relatively cool, dense cumulates to the mantle-core boundary may provide an alternative way to cool the core rapidly enough to sustain a magnetic dynamo. This cooling might induce a transient magnetic field for a part of early in Martian history, consistent with the observation that not all ancient cratered terrain is magnetized; stable mantle stratification after overturn could prevent subsequent convective heat transfer and suppress continued magnetic field generation.

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NEW ASPECTS IN THE ISOTOPE SYSTEMATICS OF SHERGOTITES.

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Introduction: Ten yeas ago we had 7 SNC meteorites while today we have 26 SNC meteorites. The newly found SNC's are essentially duplicates of the previously ones with some slight variations in their chemical composition. It seems that there are only a limited number of lithologies present on the SNC parent body, and we have already sampled the prominent lithologies.

For many years the "ages" of SNC meteorites have been under discussion. The 150 Ma to 500 Ma mineral ages for shergotites will be called the young or 180 Ma event, and will be the main focus in this contribution. Nyquist argued that the 180 Ma event might represent the age of crystallization. Indeed we have good evidence that some mineral equilibration took place at this time since in some cases Rb-Sr and Sm-Nd systematics give the same age. However, the conclusion that shergotites are magmatic rocks that were erupted at this time is not substantiated by data. To the contrary there is good evidence that a chemical fractionation, which is typical for magmatic rocks (Rb-Sr fractionation), was not associated with the young disturbance. Instead we find chemical fractionation patterns (Sm-Nd fractionation) that are not observed in any basalts.

Rb-Sr systematics:

We have good insight about the geochemical changes in the Rb/Sr during partial melting and fractional crystallization. If a reservoir is partially melted, it will be depleted in Rb compared to Sr, while the partial melt will be enriched in Rb compared to Sr. The SNC's, however, plot on the 4.5 Ga reference line in a Rb-Sr isochron diagram, implying that the Rb/Sr was unchanged for 4.5 Ga.

Partitioning of Rb in pyroxene:

Recently in a significant contribution of L. Borg et al (2002) new data on Alha77005 and Lev are reported. These authors claim that both meteorites have the same age of 175 Ma. Shih et al (1982) and Jagoutz (1989) also reported isotope data on Alha, and they found age's of 180 Ma and 165 Ma, respectively. It is interesting to compare the results of these three studies. From an in-depth investigation of mafic minerals we know that pyroxene does not accommodate Rb in the crystal structure. Clean mineral separates of pyroxene revealed that the concentration of Rb in pyroxene might be less than 1ppb (Zindler and Jagoutz 1986). Even ultra-high pressure pyroxene containing up to 1% of K2O does not have more Rb (Owen, unpublished data on diamond inclusions). Therefore, we use Rb concentration as a parameter of how clean a pyroxene mineral separate is.

A Sr versus Rb plot has been made for all published mafic minerals and whole rocks from Alha 77005. The resultant linear array is likely a mixing line caused by impact because impact glasses commonly have about whole rock chemical composition. If true, all the pyroxenes in these three studies would be dominated by impact glasses in their Rb-Sr systematic. The main difference is that Nyquist did not wash the pyroxene at all, while Borg leached the pyroxene using 2N HCl, and Jagoutz additionally removed shock glasses from the pyroxenes using 5% HF. Because the pyroxene shows a fine network of cleavages, it is unlikely that all the shock glasses was removed by leaching. Although considerable time was spend on the ion-probe to measure the Rb, efficiency of one count per second per ppm cannot measure ppb level concentrations of Rb even if all the interferences on the Rb masses are filtered out. Furthermore it is hardly possible to find areas of the pyroxene without cleavages in order to measure the intrinsic Rb concentration.

This linear array does not go thru zero and it seems there is a bias of Rb in this minerals. A similar pattern is also found in other (shocked) shergotites experiencing the young disturbance, but not in the much less shocked nakhlites where the array intersects at the intrinsic Sr concentration of pyroxene. It seems that there are two components of contamination. One component is the shock glass, which is mobilized and contains Rb and Sr in the proportions of the whole rock. The other component does not contain Sr and might be carried by a shock-related vapor phase containing only highly volatile elements like Rb.

Age significance of the Rb/Sr data:

We can assume that prior to the shock event the shergotites are well behaved magmatic rocks. Here plagioclase, the main host phase of Sr, and pyroxene both plot close to the Sr initial isotopic composition as we observe in Nakhla. Olivine might contain neither Rb nor Sr in appreciable amounts. The low alkalis in these rocks might not form an alkali rich mineral. The whole rock might have a more radiogenic Sr than any of the major phases, requiring that it was produced by interstitial Rb or the Rb in minor phases. This radiogenic Sr might then easily be equilibrated with the plagioclase during a shock event. The observation

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explaining that the plagioclase and the phosphate have different Sr isotopic composition while neither contain much Rb.

The shock essentially mobilizes Rb and produce conditions for dating the shock at least in a first order approach. We cannot expect perfect isochrones under these conditions, but there could be some age significance in these "scatter-chrones". All the Rb-Sr systematics do provide a good indication that the "180 Ma"age event may possibly represent a shock event.

Sm-Nd systematics:

Nd isotopes are much more complicated than the Sr isotopes. There are three points, which have to be considered in a genetic model.

1) The Sm-Nd fractionation of the whole rocks is very strong in shergotites, especially relative to the minor Nd-La and Sm-Yb fractionation. Even Sr-Nd and Lu-Hf are fractionated less than Sm-Nd. It seems there is a "step-function" in the REE, which cannot be explained by a simple magmatic process.

2) The high Sm/Nd in the pyroxenes and their relatively unradigenic $^{143}Nd/^{144}Nd$ may represent the same problem as observed for Sr, and be caused by incorporated shock-glass. However, even if all shock-glass is eliminated, these pyroxenes still have unradiogenic Nd and high Sm/Nd, indicating that the depletion of the LREE was caused by the young event.

3) Terrestrial weathering is a serious obstacle especially in LREE depleted shergotites. In some cases (Dhofar 019) even clean pyroxene might have been contaminated by terrestrial weathering. While we appear able to remove terrestrial contamination from pyroxene by acid leaching, we cannot use the same technique on whitlockites. In fact whitlockites are not directly measured but rather it is the acid leaches in which the whitlockites are dissolved that are taken as whitlockites. Possibly at the same time all interstitial terrestrial contamination dissolves in the same leach. This is unfortunate because the whitlocktes contain up to 90% of the Nd in shergotites. *Therefore the ages and initial Nd isotopic composition obtained by the whitlockite – pyroxene isochrones are highly questionable.* Leaches appear to form a mixing line with terrestrial sediments on an isochron plot.

U-Pb Systematics:

In SNC meteorites the U resides almost quantitatively in the whitlockites. Maskelinites, the host phase for Pb, has a very low U/Pb. We performed experiments in order to find the intrinsic Pb from the maskelinites and avoid terrestrial contamination. The Pb isotopic composition measured in clean maskelinites lines up nicely close to the Geochron.

Presumably this implies that the SNC meteorites were formed by a magmatic process at 4.55Ga, and remained undisturbed since then up to the 180 Ma event. This young disturbance increased the U/Pb drastically, which is in contrast to other meteorites, which have had their U/Pb decreased recently.

Clean pyroxene separates from Nakhla have a low U/Pb and, therefore, their Pb isotopic composition is similar to the plagioclase. Pyroxene extracted from LA, however, have U/Pb of >100 and we must assume that the U/Pb was changed by the shock event. Terrestrial magmatic pyroxenes have a low U/Pb while pyroxenes of chondrites and CAI inclusions have a very high U/Pb. Also pyroxenes from angrites have a very high U/Pb. Some pyroxene from HED meteorites have a high U/Pb and some have a low U/Pb. Our current explanation for this observation is that CAI inclusions and chondrites condensed from a hot solar nebulus; additionally, angrites may have also condensed from a hot solar nebulus. In contrast, HED meteorites and SNC meteorites are of magmatic origin and, therefore, have a low U/Pb in their pyroxenes. Some of these meteorites have increased the U/Pb of their pyroxene by a superimposed later shock event.
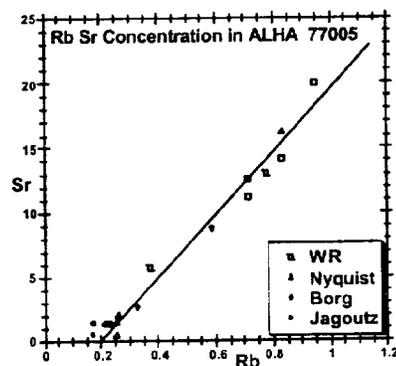
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SNC METEORITES AND MARTIAN RESERVOIRS.

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Ancient History. Jones [1] first suggested that the inverse covariation of initial $\varepsilon(^{143}Nd)$ and $^{87}Sr/^{86}Sr$ of the shergottites could be explained by interaction between mantle-derived magmas with another isotopic reservoir(s) (i.e., assimilation or contamination). In that model, magmas were generated in a source region that was isotopically similar to the Nakhla source and the second reservoir(s) was presumed to be crust. The text of [1] also permitted the second reservoir to be another type of mantle, but I can confirm that a second mantle reservoir was never seriously considered by that author. Other features of this model were that (i) it occurred at a particular time, 180 m.y. ago, and (ii) the interacting reservoirs had been separated at ~4.5 b.y. In a later paper [2], Jones explored this mixing model more quantitatively and concluded that magmas from a Nakhla-like source region at 180 m.y. would fall on or near an isotopic Nd-Sr-Pb hyperplane defined by the shergottites. This criterion was a necessary prerequisite for the parent magma(s) of the shergottites to have initially been Nakhla-like isotopically.

At this juncture, it is perhaps worthwhile to note that this mixing model was not presented to explain geochemical variations but as a justification for a 180 m.y. crystallization age for the shergottites and a 1.3 b.y. crystallization age for the nakhlites [1,2]. In the mid-1980's crystallization ages estimated for Nakhla ranged from ~1.3 b.y [3] to 4.5 b.y. [4]. Similarly, preferred crystallization ages for the shergottites ranged from 360 m.y. [5], to 1.3 b.y. [6], to 4.5 b.y. [7]. In all these models, the 180 m.y. event seen in the shergottites was deemed to be metamorphic [e.g., 6]. The fit between the Nakhla-like source region and the shergottite hyperplane was a validation both of the 1.3 b.y. igneous age of Nakhla and the 180 m.y. igneous age of the shergottites.

Less Ancient History. To some degree the original mixing model survives today [e.g., 8], but many changes have been required in the intervening decade. The original model envisioned a homogeneous mantle with a $\varepsilon(^{143}Nd)$ of ~+20 and $^{87}Sr/^{86}Sr$ of ~0.7036 at 180 m.y. The crustal contaminant had radiogenic Sr ($^{87}Sr/^{86}Sr > 0.722$) and $\varepsilon(^{143}Nd)$ of ~ -20 [9]. We now know, for example, that the mantle cannot be homogeneous because of ^{142}Nd considerations [10].

Insights from ^{142}Nd. ^{146}Sm decays to ^{142}Nd with a half life of 103 m.y. and thus records early planetary events. Borg et al. [10] have shown that, although the shergottites appear to form a mixing line on a $\varepsilon(^{142}Nd)$ vs. $\varepsilon(^{143}Nd)$ diagram, in agreement with the original

model, the nakhlites do not fall on that trend. So, ironically, one of the main premises of the orginal model cannot be true. Shergottite parent magmas must come from a distinct source region from that of the nakhlites. This, in turn, implies that the martian mantle is not homogeneous, but the scale of this heterogeneity is unknown. Another implication is that the nakhlite source region was re-fertilized (i.e., Sm/Nd decreased) early in martian history. Since the nakhlites have a very significant amount of radiogenic ^{142}Nd, this re-fertilization must be done carefully (or else the anomaly would have been diminished).

Insights from QUE94201. Another shock to the original model came with the finding of QUE94201. At 180 m.y. the QUE source region would have had an $\varepsilon(^{143}Nd)$ of ~+50 and $^{87}Sr/^{86}Sr$ of ~0.7014, significantly more depleted than the nakhlite source [11]. This raises the issue of how depleted a martian mantle can be and still produce basaltic magma at 180 m.y.

Insights from Hf-Nd isotopes. The Lu-Hf and Sm-Nd chronometer systems both indicate that large elemental fractionations occurred during SNC petrogenesis [11,12]. These are indicative of complex igneous processes that occurred during or immediately preceding the melting events that produced the SNC's (e.g., QUE94201 [11]) Even so, initial SNC Hf and Nd isotopic ratios, allow reconstruction of the Sm/Nd, Lu/Hf, and Ho/Tm ratios of the SNC source regions [13]. Comparison of lunar and martian Lu/Hf vs. Sm/Nd systematics show strong similarities [14,15]. The QUE94210 source appears similar to that of high-Ti lunar basalts; and the martian "crust" inferred from shergottites appears very similar to KREEP.

How these observations should be interpreted is not clear, but certainly, if the Moon passed through a magma ocean stage, then perhaps Mars did as well. There are other similarities between lunar and martian basalts. Both appear to come from depleted source regions (e.g., super-chondritic Sm/Nd and low Al_2O_3). The above discussion indicated that the martian mantle has not been homogenized and the same appears true for the lunar mantle.

Insights from experiments. Martian magmas tend to be hot by terrestrial standards. The liquidus temperature of the groundmass of EET79001A, with an Mg# of ~54, is ~1290°C [16]. The highly evolved composition QUE94201, with Mg# of ~38, has a liquidus temperature of ~1170°C [17] For comparison, the Kilauea tholeiitic lava that formed Makaopuhi Lava Lake, with an Mg# of ~57 had a liquidus temperature of ~1190°C [18]. These

elevated liquidus temperatures are probably a consequence of the depleted nature of the martian mantle.

Insights from oxygen fugacity. Two recent papers have emphasized the correlation of isotopic (Nd, Sr) and chemical (La/Yb) parameters with oxygen fugacity within the shergottite suite [19,20]. The greater the amount of "assimilant" or "contaminant" the higher the oxygen fugacity recorded by Eu anomalies and Fe-Ti oxide assemblages. Therefore, there is an inference that the assimilated (or contaminating) component was more oxidized than pristine basalts emanating from the martian mantle. This inference, coupled with the lack of observational evidence for subduction zones on Mars [21], suggests that the martian mantle is reduced (~IW-1) and that assimilation of crustal materials oxidizes the assimilating magmas to varying degrees. Because Shergotty and Zagami experienced the most "contamination," it was in fact an accident that early studies of the shergottites pronounced them "Earthlike" in terms of their oxygen fugacity [22].

This new presumption that the martian mantle is actually rather reduced makes sense in terms of phase equilibria. The FeO content of SNC basalts is not that different from typical lunar basalts and eucrites (~18-19 wt.%). As Stolper [23] has shown, the fo_2 at which such basalts are in equilibrium with iron metal is ~IW-1, in agreement with the fo_2 inferred for the most reduced SNC, QUE94201 [19]. Apparently, the martian mantle has remained relatively isolated over geologic time; and it maintains the redox state it had at the time of core formation, ~4.5 b.y. ago.

Discussion: From these insights an incomplete picture emerges that may nevertheless serve as a useful guide to the igneous evolution of Mars. First, if the Moon had an early magma ocean, it is likely that Mars did too. The contaminant of the shergottites is likely the solidified dregs of that magma ocean — martian KREEP. The physical location of martian KREEP is likely to be one of three regions: (i) the crust; (ii) the crust-mantle interface; or (iii) deep in the mantle (due to convective overturn). But the correlation between degree of contamination and redox state argues more for a crustal contaminant than for mixing between mantle reservoirs.

Second, it is highly unlikely that the source region of QUE94201 could represent typical martian mantle. This basalt contains so little in the way of heat-producing elements that recent (< 180 m.y.) volcanism on Mars would be highly improbable, if not impossible [24]. A more likely scenario is that QUE mantle was melted by an external heat source, perhaps at a thermal boundary layer. Because QUE mantle is so depleted, it is likely to be buoyant relative to more fertile mantle. This conjures an image of a layered martian mantle with fertile material below and convectively-isolated, less-fertile material above. Conceivably, this layering was established during or after the solidification of the magma ocean.

Third, the more complex history of the nakhlite source region is most easily achieved by an internal differentiation to avoid resetting ^{142}Nd [10]. A small degree partial melt, moving from one portion of the nakhlite source to another could lower the Sm/Nd ratio of the latter at the expense of the former without changing the $^{142}Nd/^{144}Nd$ of either. This differentiation presumably occurred fairly late (~4 b.y.), after the decay of ^{146}Sm. In principle, this differentiation event could also have resulted in additional layering.

Summary: The martian mantle is apparently heterogeneous, which opens the possibility that it is layered, with each layer convectively isolated. If this is correct, melt generation should occur either at thermal boundary layers or in plumes generated at those boundaries. Mantle layering may be a good means of slowing the planet's cooling rate, allowing young volcanism. Layering may also provide a means for keeping the crust and upper mantle cool, allowing the preservation of ancient variations in crustal thickness [25].

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MELTING THE MARTIAN MANTLE: SHERGOTTITE FORMATION AND IMPLICATIONS FOR PRESENT DAY MANTLE CONVECTION ON MARS.

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The shergottites are basaltic meteorites from Mars, many of which have igneous crystallization ages of about 180 million years ago [1,2]. The observed density of small impact craters in MOC images of Olympus Mons and Elysium Planitia indicates that some volcanic flows in these regions are just 10 to 30 million years old [3]. The existence of young volcanism on Mars implies that adiabatic decompression melting and hence mantle convection has remained an important process on Mars to the present day. Numerical simulations of mantle convection and magma production set important constraints on the current properties of the mantle of Mars, particularly the minimum abundance of radioactive elements that has been retained in the mantle.

Mantle Convection Model

The mantle convection simulations are performed using finite element methods in spherical axisymmetric geometry [4,5]. The best observational constraint on the pattern of density heterogeneities in the martian mantle is the non-hydrostatic geoid, which shows a high degree of axisymmetry about central Tharsis [6]. This indicates that the spherical axisymmetric flow model is a very good approximation for modeling present-day convection on Mars. The model includes both internal heating from mantle radioactivity and basal heating due to the heat flux out of the core. The internal heating is related to the broad Tharsis plateau, and the basal heating produces mantle plumes that feed individual shield volcanos such as Olympus Mons.

The finite element grid has a vertical resolution of 13 km and an assumed core radius of 1700 km. The model includes a 210 km thick high viscosity lid at the top of the model, with a viscosity contrast of 10^5 between the surface and the base of the lid. The characteristic flow velocity at the top of the high viscosity layer is just 0.01 mm/year, confirming that the model is in the stagnant lid convective regime [7]. In the preferred model, the heat flux is $16\ mWm^{-2}$ at the base of the crust and $22\ mWm^{-2}$ at the surface. This is consistent with flexure studies using Mars Global Surveyor gravity and topography data, which indicate that the near-surface heat flux at large, Amazonian age volcanos is $16\text{-}28\ mWm^{-2}$ [8].

Radioactivity Models

Models for the silicate composition of Mars are constrained by the chemistry of the SNC meteorites and imply present-day radioactive heating rates of $4.1\text{-}6.2 \times 10^{-12}\ Wkg^{-1}$ [9,10]. In the convection simulations, 30 to 90% of the total radioactivity is partioned into the crust. The crust is assumed to be 50 km thick [11], with radioactivity uniformly distributed within the crust. The remaining radioactive heating is assumed to be uniformly distributed throughout the mantle. Models that retain large amounts of radioactivity within the mantle have higher present-day mantle temperatures and thus produce greater amounts of magmatic activity. An important goal of this study is to determine the minimum amount of radioactivity that must have been retained in the mantle in order to permit pressure release melting to occur on present-day Mars.

Magma Production Calculations

Melting relationships are taken from the experimental work of Bertka and colleagues on a Mars-analog composition [12, 13]. These experiments cover the pressure range 1-3 GPa and 12-25 GPa. In my calculations, most melting occurs near a pressure of 5 GPa, so some interpolation of the solidus location is necessary. Recent work by Draper et al. [14] on a slightly different composition covers the pressure range 5-9 GPa. Melting calculations using this solidus will be presented at the conference. I have assumed a dry solidus based on studies indicating a low oxygen fugacity in the mantle [15-17]. Existing experimental results are for a primitive martian mantle composition. Because the present-day mantle has had its lowest melting point components removed via previous melting, the actual solidus should be somewhat higher than indicated by these experiments. A 50 km thick crust [11] constitutes only about 5% of the mantle volume, so this effect is likely to be small, but experimental melting studies of an evolved mantle composition would be helpful. Melt productivity above the solidus is assumed to be 0.4% per degree based on studies of KLB-1 [18]. Melt volumes are determined by tracing streamlines through the melting region [19]. Latent heat of melting and specific heat are taken from the compilation of Navrotsky [20].

Results

In these models, magma production is restricted to mantle plume heads, which is consistent with the localized distribution of young volcanism on Mars (Figure 1). In order for the mantle to remain warm enough to permit on-going pressure-release melting, the minimum average radioactive heating rate in the mantle must be at least $1.6 \times 10^{-12}\ Wkg^{-1}$. This corresponds to 40% of the total radioactivity in the Wanke and Dreibus model [9] or 25% of the total radioactivity in the Lodders and Fegley model [10]. The corresponding average mantle temperature and viscosity corresponds to a thermal Rayleigh number for the martian mantle that exceeds 10^6 at present. This implies that mantle convection on Mars remains relatively vigorous at present. As a corollary, the density anomalies and dynamic topography associated with this convective flow must be considered in any complete model for the long-wavelength geoid and topography of Mars. Surface volcanic loads obviously make an important contribution to the long-wavelength geoid [e.g. 21], but models that consider only surface loads are incomplete descriptions of the planet.

The best current convection simulation has a present-day, average magma production rate of $7 \times 10^{-6}\ km^3 year^{-1}$. Assuming a mean lava flow thickness of 5 meters and that 10% of total magma production is extruded on the surface, this corresponds to resurfacing $140\ km^2$ per million years. Transient periods with resurfacing rates a factor of 10 larger than this sometimes occur in the models. For comparison, the Hawaiian
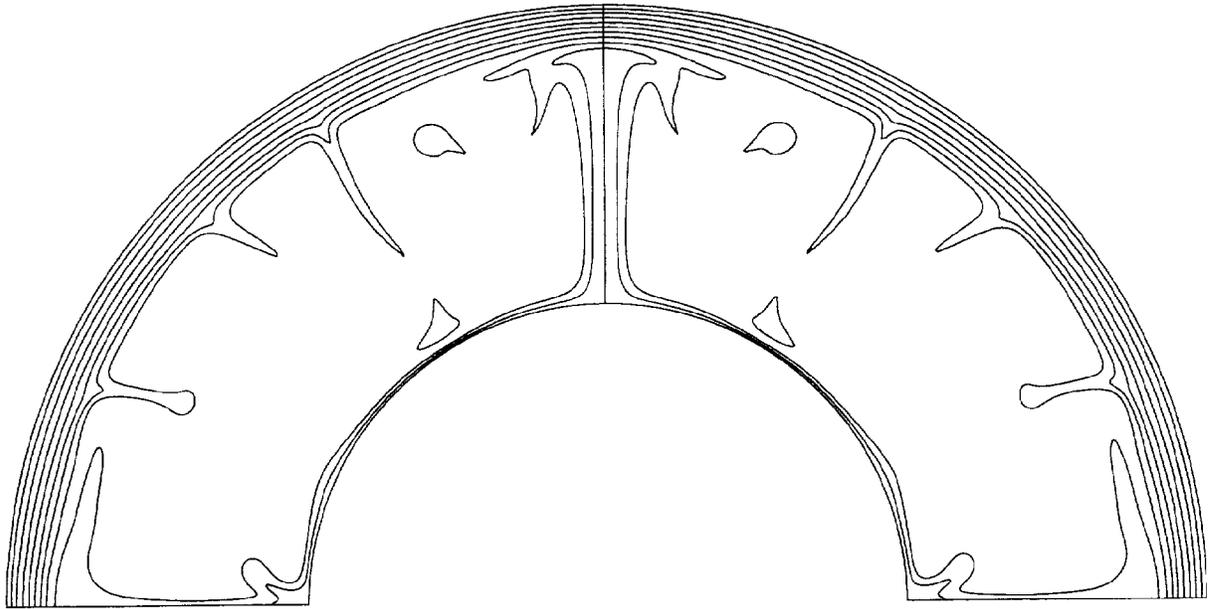
MARS MANTLE MELTING: W. S. Kiefer

Figure 1: A simulation of mantle convection on Mars. The contour interval is 160 degrees Kelvin. Melting only occurs in the mantle plume head at the center of the image. A color version of this image that explicitly shows the melting region is available at http://www.lpi.usra.edu/meetings/sncs2002/pdf/6006.pdf .

hotspot on Earth has a long-term average magma production rate of about 0.01 $km^3 year^{-1}$ [22]. The mean melt fraction in the numerical models ranges up to 8%, in very good agreement with estimates of 2-8% partial melting in the shergottites based on rare earth element concentrations [23].

The melt production rate is extremely sensitive to the precise value of the assumed solidus. Raising or lowering the solidus by 50 K can change the melt production rate by a factor of 5. The high pressure solidus measured by Draper et al. [14] is about 50 K hotter than the solidus that I have interpolated from the results of Bertka and collaborators [12, 13]. This new constraint on the high pressure solidus implies that the required amount of radioactivity retained in the mantle of Mars is somewhat higher than the value cited above. Detailed calculations of this are presently underway and will be reported at the conference. Alternatively, if a wet solidus is appropriate, the required abundance of mantle radioactivity would be reduced. The mantle radioactivity value derived here is a mantle-wide average. Some of the shergottites (notably QUE94201 and SaU005) have very low radioactivity abundances and imply source regions that are highly depleted in radioactivity. The results of this study indicate that the average martian mantle must have a much higher present-day concentration of radioactive elements. One possibility is that the martian mantle consists of blobs of both depleted and primitive compositions. At least in some cases, the low radioactivity blobs must occur in close association with high radioactivity blobs to account

for the formation of meteorites such as QUE94201.

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QUE 94201: RECONSIDERING ITS ORIGINS AS A BULK MELT FROM A VOLCANIC REGION OF

MARS. D. A. Kring, Lunar and Planetary Laboratory, University of Arizona, 1629 E. University Blvd., Tucson, AZ 85721, kring@LPL.arizona.edu.

Introduction: Shergottites from Mars, like basalts on Earth, are important because they provide an opportunity to determine the chemical and thermal evolution of the planet's mantle, relationships between the crust and mantle, and the role of crustal assimilation in the petrogenetic processes that produce surface lavas. Attempts to utilize these rocks, however, have been frustrated because they are cumulate rocks rather than bulk melt samples that lie on liquid lines of descent. To overcome this problem, estimates of bulk melt compositions have been made by trying to identify and subtract the compositions of cumulate minerals [1-5], analyzing trapped melt inclusions [6-9], interpreting phase equilibria [10], and using minor element compositions in pyroxene with equilibrium coefficients [11]. Unfortunately, these attempts have produced contradictory results.

QUE 94201: When Martian meteorite QUE 94201 was first described, it appeared to be a bulk melt rather than a cumulate fraction [12-14], thus providing our first unambiguous melt composition for modeling purposes. The evidence seemed compelling. Typically, basaltic and lherzolitic shergottites contain cumulus olivine and/or pyroxene, estimated to range from 14% to 63% of the rocks [1,5]. In contrast, there is no evidence of any xenocrystic or cumulus minerals in QUE 94201. Indeed, the mineral assemblage, mineral compositions, textures, trace elements in pyroxene, and the bulk composition of QUE 94201, suggested it fractionally crystallized in a closed system [12-15]. QUE 94201 contains numerous melt inclusions and abundant interstitial melt pockets, suggesting that most interstitial melt was trapped in the rock rather than being removed during the crystallization process. Likewise, and in contrast to other shergottites, the rock contains an unusually large amount of accessory minerals, again suggesting that lower temperature melt fractions were not separated from the higher temperature crystallization products. This can be illustrated quantitatively by comparing the compositions of pyroxene cores (the highest temperature, and thus earliest, crystalline phase in the rock) with the calculated pyroxene composition that would be in equilibrium with the bulk rock (*i.e.*, when it was initially wholly molten). Figure 1 shows the molar Mg/(Mg+Fe) across a zoned pyroxene crystal in QUE 94201. Also shown is the calculated pyroxene composition that would be in equilibrium with a melt of the bulk composition of the meteorite. Because the core pyroxene composition is identical to the equi-

librium composition, it is clear the pyroxene is not a cumulus mineral and that a fraction of the melt was not lost after pyroxene began to crystallize. In contrast, similar agreement is completely lacking in other shergottites, as illustrated for the case of Elephant Moraine (EET) 79001 (Fig. 1, right panel). Consequently, the bulk composition of QUE 94201 seems to represent a bulk melt rather than a cumulate fraction. The mineralogical evidence is similarly expressed in the chemistry of the rock. QUE 94201 is more aluminous than any other shergottite, all of which have compositions that are skewed from melt compositions by Al-poor cumulus phases. In addition, QUE 94201 has higher abundances of many other elements which are incompatible during the earliest stages of crystallization (Ti, P, and REE).
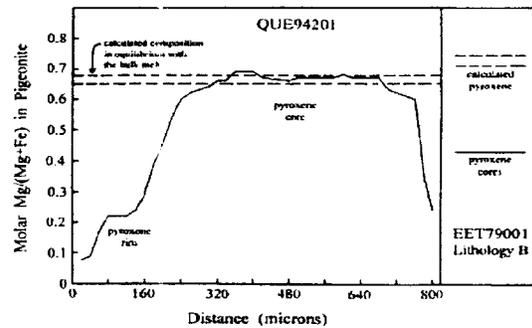
Fig. 1. Molar Mg/(Mg+Fe) in a linescan across a zoned pyroxene grain in QUE 94201. The core composition is similar to the calculated composition for a pyroxene in equilibrium with a melt with the bulk composition of QUE 94201. In contrast, core compositions of pyroxene in EET 79001 lithology B are not similar to the calculated composition for pyroxene in equilibrium with a melt with the bulk composition of that rock.

Petrogenetic Contradictions: If QUE 94201 is a bulk melt, then it can be used to investigate the petrogenetic evolution of magmas on Mars using liquidus phase diagrams. When one does so, however, it is clear that something is amiss. To illustrate the problem, Fig. 2 shows the projection of the bulk composition of QUE 94201 into an Olivine-Plagioclase-Quartz ternary in the psuedoquarternary Olivine-Plagioclase-

Wollastonite-Quartz system often used to investigate basaltic melts [16]. Mineralogically, QUE 94201 is dominated by plagioclase (now maskelynite) and pyroxene [e.g., 12]. Plagioclase is zoned from An_{57} to An_{68}. Pigeonite is also continuously zoned, from $Wo_9En_{60}Fs_{31}$ to $Wo_{16}En_1Fs_{83}$. Augite compositions are bimodal, averaging $Wo_{30}En_{45}Fs_{25}$ and $Wo_{40}En_2Fs_{58}$. This is coherent set of compositions that suggests closed system fractional crystallization. Consequently, one would expect the bulk composition of QUE 94201 to plot close to the pigeonite-augite-plagioclase boundary. Instead, the bulk composition plots in the olivine stability field, even though olivine does not appear to be an early crystallizing principal phase in QUE 94201. (The meteorite contains traces of fayalite, $Fa_{97-99.7}$ [12], but it was produced from the last vestiges of melt and is not relevant to the projected phase composition.) Consequently, while the phase diagram suggests the rock contains olivine, it does not.
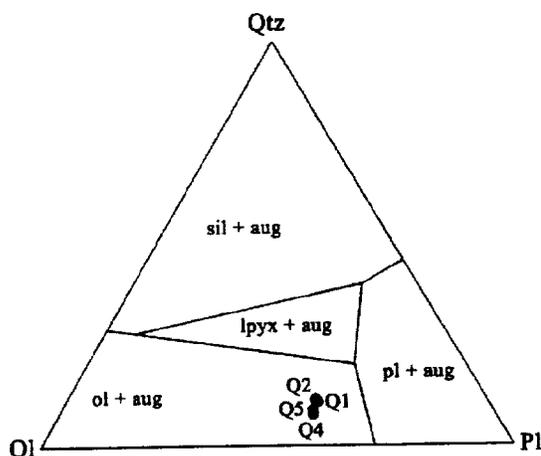

Fig. 2. Composition of QUE 94201 projected into a quartz-olivine-plagioclase liquidus ternary phase diagram in the psuedoquarternary (Quartz-Olivine-Plagioclase-Wollastonite) system (after [15] and modifications after J. Longhi, personal comm., 1996]. Compositions Q1, Q2, Q4, and Q5 represent the uncertainties among different analyses of the QUE 94201 ([12] and unpublished data; [17]). Standard abbreviations are used: Ol=olivine, Pl=plagioclase, Qtz=quartz, sil=silica, aug=augite, lpyx=low-Ca pyroxene.

A Porphyritic Olivine Basalt?: There are two ways to resolve this conundrum. The chemical composition of QUE 94201 used in the projection could be in error. If the rock contained several more weight percent SiO_2, then the composition would not plot in the

olivine stability field. The data seem robust, however, having been replicated with multiple splits in the same laboratory and in different laboratories.

The conundrum can also be resolved if the meteorite is not representative of its parent lithology. While QUE 94201 is in chemical equilibrium with olivine, it may have been physically separated from olivine. It is perhaps worth remembering that QUE 94201 is a very tiny sample, weighing only 12 grams, for a medium-grained (1 to 5 mm) rock. It is conceivable that it is not representative of the outcrop or near surface lithology from which it was excavated from Mars. In particular, it could potentially be the matrix of a porphyritic olivine basalt, rather than a representative bulk sample of the basalt. This accounts for olivine being part of the residuum in the phase space topology, but not actually part of the meteorite. While other shergottites are plagued with too many crystals (xenocrysts and cumulate phases), QUE 94201 may be plagued with having too few (the missing olivine). Unfortunately, this problem suggests QUE 94201 is not representative of a true bulk melt, nor can a true bulk melt be calculated easily because the proportion of olivine in the bulk basalt from which it came is unknown. If olivine was physically separated from QUE 94201, the meteorite's bulk composition will not lie on an equilibrium liquid line of descent. Rather, it will lie on an open system crystal fractionation line that is controlled by the loss of olivine.

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SNC METEORITES AND THEIR SOURCE COMPOSITION(S). John Longhi, Lamont-Doherty Earth Observatory, Palisades, NY 10964

Detailed chemical and isotopic measurements reveal complexities in planetary differentiation that will make any reconstruction of the SNC source region difficult. Recent age determinations of shergottites have resolved a long-standing uncertainty in their crystallization ages in favor of ages in the range of 200 to 400 Ma [1]. These young ages, together with 1.3 Ga ages of the Nahklites and Chassigny, require that the SNC source regions maintained more pronounced depletions of incompatible elements than the terrestrial MORB source since primordial differentiation (4.525 Ga) and that the parent magmas of the classical shergottites (Shergotty, Zagami) assimilated a long term light-REE enriched component (crust) [2]. The isotopic evidence indicates little or no mixing between differentiated and primitive mantle or between differentiated mantle and crust during martian history.

Estimated SNC parent magma compositions [e.g., 3] have lower Al_2O_3 concentrations than terrestrial MORB and OIB [2]. These low Al_2O_3 contents are consistent with highly depleted source regions as inferred from the isotopic data. New modeling of polybaric melting reveals that the extent of the depletion in terms of major elements is greater than expected for basalt extraction. There are two general scenarios conistent with the major elements: one is that the portion of the martian mantle from which the SNC magmas are derived is a magma ocean cumulate; the other is that initial melts in a polbaric fractional fusion event were never aggregated with later melts (possibly the inial melts were too dense). Loss of the initial melts is also consistent with the extremely high Sm/Nd ratios inferred for the parent magmas of the Antarctic shergottites. Figure 1 contrasts the results of batch and fractional fusion calculations for a martian mantle (dDW — open diamond) that is depleted relative to primitive Mars (DW [4] — open square) in a manner analogous to the MORB source (dPUM) is related to primitive upper mantle (cross — PUM [5]).source compositions with the compositions of the SNC magmas. The string of blue circles represents 10% batch melts of dDW from 35 kb to 6 kb. The string of open suares are polybaric fractional melts of the dDW source also beginning at 35 kb. The strings of triangles represents the same melting beginning at 35 kb, but from which the 35 to 26 kb melts have been removed. The string of cicles is analogous to the triangles, but in tis caseThe Al_2O_3 content of the source was arbitarily reduced by 50%. These results suggest a way to have source regions with apparently low Al without a magma ocean. However, at least two sources appear necessary to yield the nahklite and shergottite parent magmas.

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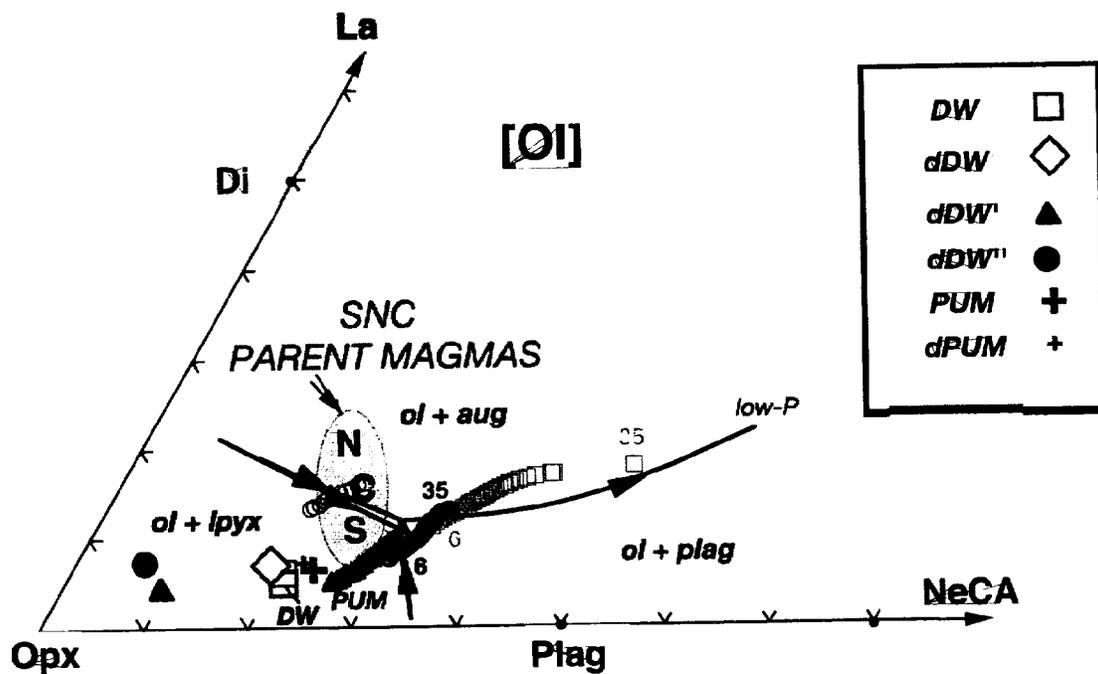
Figure 1. Olivine projection in the system larnite (La)–olivine(Ol)–nepheline + $CaAl_2O_4$ (NeCA)–quartz (Qtz). Liquidus boundaries and field of SNC parent magma compositions modified after [2,3].

OXYGEN FUGACITY RECORDED IN PIGEONITE: INDICATIONS OF A HETEROGENEOUS MARTIAN MAGMA

SOURCE REGION? M. C. McCanta and M. J. Rutherford, Brown University, Department of Geological Sciences, 324 Brook St, Providence, RI 02912, molly_mccanta@brown.edu.

Introduction: Oxygen fugacity (fO_2) is a key physical parameter which influences the crystallization sequences of magmas, as well as the composition of the resulting minerals [e.g. 1,2]. On a planet-wide basis, the distribution of elements between the metallic core and the silicate portion of the planet is influenced by the fO_2 at the time of differentiation. Additionally, if the intrinsic fO_2 of a planet is known, the processes which may change that value can be investigated. Although magmatic fO_2 can reflect the degree of oxidation of the magma source region, it can also provide insight into processes, such as metasomatism, degassing, or assimilation, which may have operated on and in the magma as it moved to the surface.

Recent work on the basaltic shergottites has provided new measurements of the fO_2 recorded in the pyroxenes of these meteorites [3,4,5]. These pyroxenes exhibit an fO_2 range of ~3-4 orders of magnitude [5]. Several processes have been proposed to explain the origin of these differences, the majority of which rely on assimilation [e.g. 6]. New data, however, is consistent with intrinsic fO_2 differences in the magma source region being responsible for the measured SNC fO_2 variations. More detailed analyses of natural SNC pyroxenes are needed in order to better understand the source of the fO_2 range recorded in the basaltic shergottites.

Determination of fO_2: Because of the cumulate nature and inferred slow cooling of the SNC's, there are difficulties in measuring fO_2 with traditional methods. Typically, fO_2 measurements are made using the Fe^{2+}/Fe^{3+} ratios of oxides. However, oxides must cool rapidly to lock in their crystallization fO_2. It has been demonstrated that oxides can reequilibrate in the subsolidus [7], leading to non-magmatic fO_2 estimates. For example, Fe-Ti oxides in the meteorite Shergotty record temperatures of 682°C, with a log fO_2 of -20 [8]. This temperature is not magmatic, implying the oxides experienced subsolidus reequilibration thereby discounting the fO_2 calculation. A new technique utilizing electron probe oxygen measurements and stoichiometric determinations has resulted in more accurate fO_2 measurements [9], although the compositions still appear to record post-magmatic conditions. Furthermore, oxides, except chromite, come on the liquidus late in most shergottite magma crystallization sequences, thereby not recording the early fO_2 history of the melt. Thus, for the currently available SNCs, Fe-Ti oxide fO_2 calculations may not reflect magmatic conditions.

Eu-oxybarometer. The fO_2 of a melt can also be calculated using the partitioning of Eu, relative to adjacent REEs, into the first crystallized minerals [10,11]. The Eu distribution coefficient between melt and mineral depends on the ratio of Eu^{3+}/Eu^{2+} in the melt, which is a function of the fO_2 conditions during crystallization [10]. Previous experimental studies have investigated the partitioning of Eu between augite and melt as a function of fO_2 in order to use this relationship to understand natural systems [10,11]. We have applied this approach to a synthetic shergottite melt and low-Ca pyroxene assemblage in order to determine the fO_2 of the resulting magmas (Figure 1) [3,5]. Since pigeonite is known to be one of the first minerals to crystallize from a shergottite melt, the pigeonite Eu-oxybarometer provides fO_2 estimates of the earliest magmatic history.
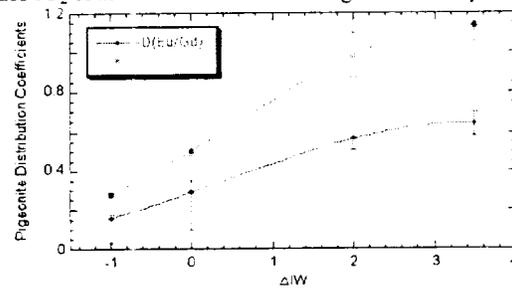
Figure 1. Distribution coefficient of Eu/Gd and Eu/Sm in pigeonite in a dry shergottite melt vs. fO_2. Error bars shown are calculated from the standard deviations between ion probe measurements of the same sample.

The Eu-oxybarometer has an important advantage over other methods which rely solely on Fe measurements. Although the Fe^{2+}/Fe^{3+} ratio of a melt or mineral phase is a function of fO_2, this ratio is known to be reset through processes such as mineral reequilibration, metasomatism, or shock [7,12]. One or more of these processes have certainly affected the SNC meteorites. This resetting of ferrous/ferric ratios can lead to erroneous fO_2 measurements as discussed above. The REEs, acting as trace elements, on the other hand, are essentially locked into a mineral during crystallization and are unlikely to be reset by later igneous or shock events. This leads to more robust crystallization fO_2 measurements made using the Eu-oxybarometer technique. Due to the small number and special nature of the SNCs (slowly cooled cumulate rocks subjected to high shock pressures), the measurement of fO_2 as re-

PIGEONITE EU-OXYBAROMETER: M. C. McCanta and M. J. Rutherford

corded in the pyroxenes provides the most accurate measurements of magmatic oxidation state.

Results: The new Eu-oxybarometer calibration for pigeonite yields refined fO_2 values for the basaltic shergottites, ranging from 1W 3.5 for Shergotty to 1W+0.2 for QUE94201. These numbers differ in value, but not trend, from those published previously [e.g. 9,11]. These fO_2 values were calculated using natural pigeonite core data from [13].

In order to better constrain small variations in fO_2 recorded in the pigeonites, new, more detailed analyses of natural phenocryst REE contents are needed. This data will be collected on the Woods Hole Oceanographic Institution 3F and 1270 ion probes. Detailed traverses of pigeonite cores will be carried out using the smallest beam diameter feasible. This will allow for a closer look into potential small-scale fO_2 variations in single meteorites and may shed light on the origin of the fO_2 differences exhibited by the SNCs.

fO_2 differences: The new results from the pigeonite Eu-oxybarometer detailed above show ~3-4 orders of magnitude difference in fO_2 between the basaltic shergottite meteorites. This variation is less than the observed terrestrial variation of ~9 orders of magnitude [14,15], but much greater than that seen on the moon. Several possibilities exist that could explain these differences. These could reflect intrinsic fO_2 differences in the magma source regions on Mars (i.e. the martian mantle or lithosphere) or they could result from interactions between the magma and an assimilant, that is as yet unsampled, either at depth or near the surface. This new fO_2 data may provide insight into which of these is the more likely explanation.

Experimental studies have shown that pigeonite is one of the first minerals to crystallize from a shergottite melt, whereas Fe-Ti oxides come on the liquidus late in the melts crystallization sequence (after 30 and 60% crystallization in hydrous and dry experiments, respectively, to possibly 95% in Los Angeles) [e.g. 16,17]. Therefore pigeonite core fO_2 values should record a different portion of magmatic history than the oxides. However, when the pigeonite fO_2 values are compared with the most recent determination of Fe-Ti oxide fO_2 values a close correlation is observed (Figure 2). This implies that the melt fO_2 for each of these meteorites was buffered internally throughout much of the crystallization sequence. That is, the early crystallizing minerals were exposed to the same relative fO_2 environment as the late crystallizing minerals. These results are consistent with the argument that the variations in fO_2 recorded in the basaltic shergottites are the result of intrinsic fO_2 differences in the magma source regions of these rocks. However, assimilation cannot be completely ruled out on this basis alone. If the assimilation

occurred before any crystallization had taken place, the primary fO_2 recorded in the phenocrysts would be that of the source region modified by the assimilant.
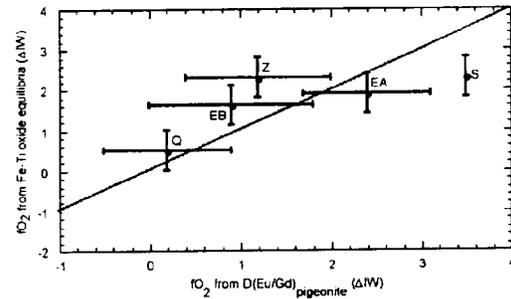
Figure 2. Comparison of fO_2 data from pigeonite Eu-oxybarometer and Fe-Ti oxide equilibria. Oxide data from [6].

Conclusions: We have presented a calibration of the pigeonite Eu-oxybarometer for the basaltic shergottites. This tool allows for the measurement of fO_2 during the earliest crystallization history of the melt. The new fO_2 values in the pigeonites correlate well with recent Fe-Ti oxide data. This apparent fO_2 buffering during crystallization is consistent with the fO_2 variations between the SNCs being the result of intrinsic fO_2 differences in the magmas' source regions, the martian mantle or lithosphere. However, an assimilation event which took place before crystallization commenced cannot be ruled out. New, more detailed REE analyses of natural pigeonite cores are being collected now in order to explore the full implications of these results.

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GEOCHEMISTRY OF MARTIAN METEORITES AND THE PETROLOGIC EVOLUTION OF MARS.

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Introduction: Mafic igneous rocks serve as probes of the interiors of their parent bodies – the compositions of the magmas contain an imprint of the source region composition and mineralogy, the melting and crystallization processes, and mixing and assimilation. Although complicated by their multifarious history, it is possible to constrain the petrologic evolution of an igneous province through compositional study of the rocks. Incompatible trace elements provide one means of doing this. I will use incompatible element ratios of martian meteorites [1] to constrain the early petrologic evolution of Mars. Incompatible elements are strongly partitioned into the melt phase during igneous processes. The degree of incompatibility will differ depending on the mineral phases in equilibrium with the melt. Most martian meteorites contain some cumulus grains, but nevertheless, incompatible element ratios of bulk meteorites will be close to those of their parent magmas. ALH 84001 is an exception, and it will not be discussed. The martian meteorites will be considered in two groups; a 1.3 Ga group composed of the clinopyroxenites and dunite, and a younger group composed of all others.

Planetary Comparisons: On Earth, P and La are highly correlated in igneous rock suites, resulting in a small range in P/La ratios for terrestrial mafic magmas (Fig. 1). Magmas with higher incompatible element contents have lower P/La, indicating La is more incompatible than P. This is also supported by various estimates of the composition of the bulk continental crust [2], which is more highly enriched in La than P compared to an estimated bulk silicate Earth [2]. Mafic rocks from the Moon follow the terrestrial example – P/La ratios exhibit a narrow range (Fig. 1). In contrast, martian meteorites show a wide range in P/La (Fig. 1). The planetary distinctions are also clearly shown on a P vs. Yb diagram (Fig. 1). The terrestrial mafic rocks show no correlation between P and Yb, lunar rocks occupy a band of increasing P and Yb, while in martian meteorites these elements are strongly correlated. This suggests a fundamental difference in the petrologic evolution of Mars as compared to the Earth or Moon. The constancy of Yb/P implies that the partitioning of these elements is governed by a single phase, or two phases either in constant proportions or with similar P/Yb partition coefficient ratios. The phase or phases would have a much lower partition coefficient for La, such that P and La are decoupled.
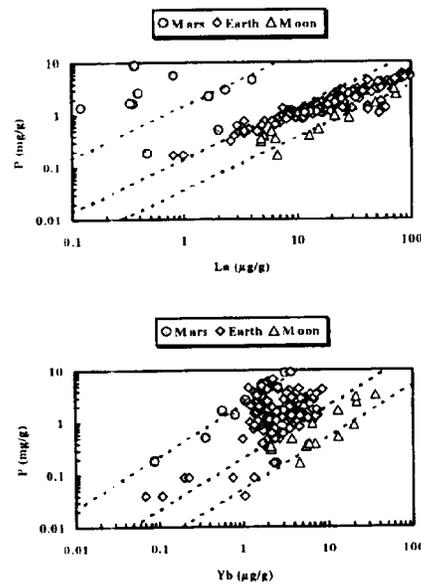

Figure 1. P-La and P-Yb plots for mafic igneous rocks from Mars, the Earth and Moon.

Crustal Assimilation: Recently, a number of geochemical characteristics of a subset of martian meteorites have been ascribed to assimilation of crustal material by mafic magmas [e.g. 3]. The P/La ratios for martian meteorites $<$1 Ga in age are positively correlated with their ϵ^{143}Nd [1] (Fig. 2), a presumed measure of crustal assimilation/contamination, indicating that this process may have contributed to the scatter in P/La. This is in general in accord with terrestrial geochemistry – the P/La ratio for the bulk continental crust is lower than that estimated for the bulk silicate Earth [2]. However, P and La are enriched in the continental crust by roughly 10× and 30×, respectively [2]. QUE 94201 has the highest ϵ^{143}Nd (Fig. 2) and the highest P content (Fig. 1). This rock is considered to have suffered minimal crustal contamination [see 3]. Hence, if basalts like Shergotty were formed by contamination of primary or evolved magmas, then these magmas, and possibly their source regions, must have had incompatible element contents different in detail from those of QUE 94201. Thus, for example, their Sm/Nd ratios may have been lower, and the source region would then have had lower ϵ^{143}Nd. Regardless of complications from possible assimilation of crust, the P/La ratios of martian mafic igneous rocks show wide ranges, while

the P/Yb ratios are roughly constant, quite unlike the cases for the Earth or Moon.
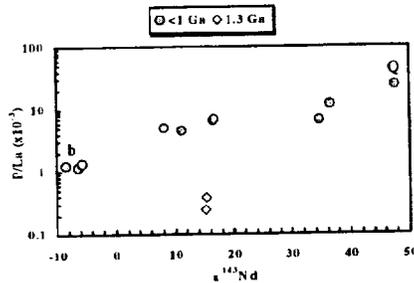

Figure 2. Correlation of P/La with ε^{143}Nd in martian meteorites. Q = QUE 94201; b = martian basalts Los Angeles, Shergotty and Zagami.

Incompatible Element Ratios: Martian meteorites 1.3 Ga in age do not follow the trend exhibited by the younger rocks (Fig. 2). These rocks have by far the lowest P/La ratios, yet intermediate ε^{143}Nd. They are also distinct in other trace element ratios (Fig. 3). These distinctions are not due to crustal assimilation – the terrestrial continental crust has CI-normalized Hf/Sm of ~1.3 and Ta/La of ~1.0 [2] and it is likely that the martian crust is also unfractionated in these ratios from the primitive Mars composition. Thus, it is unlikely that the low ratios observed for the 1.3 Ga martian meteorites could be a result of contamination by martian crustal rocks. The 1.3 Ga martian meteorites and QUE 94201 have the lowest and highest P/La ratios, respectively.
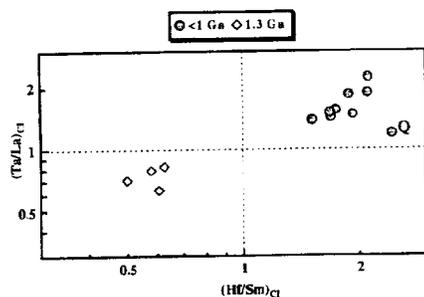

Figure 3. Ta/La vs. Hf/Sm for martian meteorites showing the distinction between the 1.3 Ga and younger rocks. Q = QUE 94201.

Modeling Mars: Using the experimental high pressure mineralogy [4] of a Dreibus-Wänke Mars composition and a variety of partition coefficients [1], I have attempted to model the martian meteorite trace element signatures as arising from a sequentially depleted primitive mantle (*i.e.* fractional fusion). Models were done for pressures in the garnet lherzolite and the majorite-clinopyroxene-β-phase stability regimes. In

no case did either QUE 94201 or the 1.3 Ga martian meteorites fall within the envelop of possible melt compositions in any of the tested models. In short, sequential melting of a Dreibus-Wänke martian mantle composition under any P-T regime will not yield melts with incompatible element ratios that come close to those of either the 1.3 Ga martian meteorites, nor of the most pristine younger volcanic rock, QUE 94201. Alternative models must be sought.

High Pressure Cumulates: I have begun evaluating high pressure magma ocean cumulates as alternative source regions for the martian meteorites. The garnet-like REE pattern of QUE 94201 suggests that cumulus garnet may be required. However, garnet *sensu stricto* is not a near-liquidus phase in ultramafic melt compositions, and thus is not likely to be a cumulus phase. At P >15 GPa, majorite does become a liquidus phase. At P >15 GPa, majorite does become a liquidus or near liquidus phase in ultramafic melts [5]. Limited partition coefficient data [1] indicate that majorite crystallizing from a martian magma ocean should have a garnet-like REE pattern, and thus could impose a garnet-like signature to the cumulates. In addition, very limited P data suggest that majorite/melt K_ds for P and Yb are similar at ~1. Thus, cumulus majorite could define the P/Yb of the martian meteorite source regions, and P and La would be decoupled. Finally, measured Hf/Sm partition coefficient ratios for majorite are >2, although Hf is incompatible in majorite (k_ds ~0.5-0.9). Hence, it appears plausible that the parent magma of QUE 94201 originated by remelting a magma-ocean-cumulate source region in which majorite was a cumulus phase. However, a serious stumbling block might be Al. Martian basalts are noted for being Al-poor [see 3], while a majorite-rich source region should be Al-rich.

The 1.3 Ga martian meteorites must have come from a different source in order to explain the different P/La, Hf/Sm and Ta/La ratios (Figs 1, 3). Other possible high P phases are Mg-perovskite, γ-spinel, β-phase and clinopyroxene. I will be evaluating these as possible cumulus phases in addition to majorite to explain the geochemical characteristics of the 1.3 Ga martian meteorites.

References: [1] References for martian meteorite data, and high P partition coefficients can be found at http://ares.jsc.nasa.gov/mittlefehldt/.
[2] http://www.earthref.org/databases/GERMRD/reservoir.htm. [3] McSween (2002) *Meteoritics & Planet. Sci., 37*, 7. [4] Bertka and Fei (1997) *J. Geophys. Res., 102*, 5251. [5] Ohtani *et al.* (1989) *Contrib. Mineral. Petrol., 103,* 263.

SILICON IN MARS' CORE: A PREDICTION BASED ON MARS MODEL USING NITROGEN AND OXYGEN ISOTOPES IN SNC METEORITES.

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Introduction: Chemical and (oxygen) isotopic compositions of SNC meteorites have been used by a number of workers to infer the nature of precursor materials for the accretion of Mars [1-4]. The idea that chondritic materials played a key role in the formation of Mars has been the central assumption in these works. Wänke and Dreibus [1] have proposed a mixture of two types of chondritic materials, differing in oxygen fugacity but having CI type bulk chemical composition for the non-volatile elements, for Mars' precursor. But a number of studies based on high pressure and temperature melting experiments do not favor a CI type bulk planet composition for Mars, as it predicts a bulk planet Fe/Si ratio much higher than that reported from the recent Pathfinder data (e.g., [5]). Oxygen forms the bulk of Mars (~40 % by wt., e.g., [1]), and might provide clues to the type of materials that formed Mars. But models based on the oxygen isotopic compositions of SNC meteorites predict three different mixtures of precursor materials for Mars: 90% H + 10% CM [2], 85% H + 11% CV + 4% CI [3] and 45% EH + 55% H [4]. As each of these models has been shown to be consistent with the bulk geophysical properties (such as mean density, and moment of inertia factor) of Mars, the nature of the material that accreted to form Mars remains ambiguous.

The N and O isotopic model: We have adopted a new approach to this study, which involves the isotopic compositions of nitrogen ($\delta^{15}N$) and oxygen ($\Delta^{17}O$) in SNC meteorites. As we have shown earlier [6], the nitrogen and oxygen isotopic systematics of Mars mantle derived from the SNC data ($\delta^{15}N = -30‰$ [6]; $\Delta^{17}O = 0.321\pm0.013‰$ [7]) are consistent with a mixture of EC and OC type precursor materials for the planet. A similar result is obtained if one considers $\Delta^{17}O$ and radiogenic chromium ($\varepsilon^{53}Cr$) data for the SNCs [8]. Moreover, such a mixture is also consistent with the bulk planet Fe/Si ratio for Mars as predicted from the moment of inertia factor obtained from the Mars Pathfinder data [5]. We would like to point out here that the relative contributions of EC and OC in our earlier calculations [6] were based the $\Delta^{17}O$ of EH and H. But as we have already pointed out, one cannot actually resolve such a mixing proportion from those involving the other types of EC and OC by the N and O isotopic systematics. Therefore we repeated the calculations by using the mean values for the EC [9] and OC [10], which suggested the EC:OC ratio to be 74:26 (Fig. 1).

We also tried to further resolve the possible mixing proportions between EC and OC by using the bulk planet Fe/Si for Mars predicted by Bertka and Fei [5] as a constraint. But such an exercise did not prove encouraging.
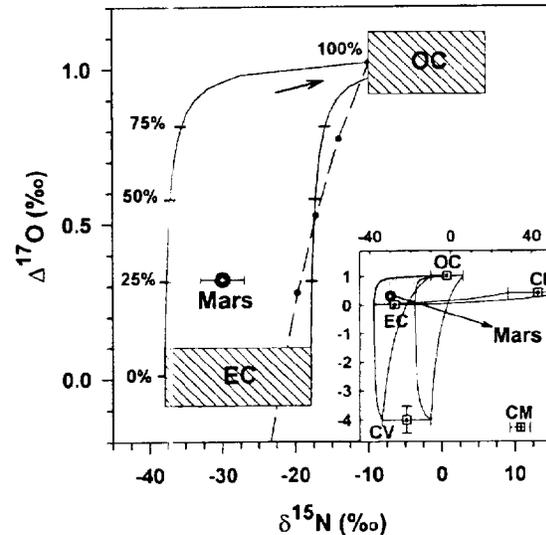
Fig. 1. The nitrogen and oxygen isotopic systematics of Mars, in relation to those of different types (inset) of chondrites (after [6]). Mars is consistent with a mixture of EC and OC in a ratio of 74:26 (main plot).

Therefore we derived the bulk chemical composition for Mars by mixing 74% EC and 26% OC, and investigated the consequences of such a model. The bulk planet Fe of 24.7 wt % and Fe/Si ratio (by wt.) of 1.39 obtained from the above mixture are consistent with the ranges given by Bertka and Fei [5]. It is possible to reproduce the bulk chemical composition (major oxides) of the martian mantle (Table 1) and its mean density as suggested by the SNCs [1] if one accommodates a small fraction (~0.08) of the planet's Si in the core. The core predicted by the present model thus has 6.7 wt % of Si. a density of 6.5 g/cc and accounts for 23 % of the planet's mass. The moment of inertia factor of 0.368 ± 0.003 calculated for Mars, by assuming a crust with thickness of 20 to 50 km and density of 2.7 to 3 g/cc, is consistent with the value predicted from the Mars Pathfinder data [11].

Si in martian core: Si has commonly not been invoked as a light element in the core of Mars [12] although its presence in the terrestrial core has often been suggested from geochemical arguments [13].

SILICON IN MARS' CORE: R. K. Mohapatra and S. V. S. Murty

Wänke and Dreibus [14] have pointed out that the de-
pletion of Si in Earth's mantle-derived rocks as com-
pared to samples from Mars can be explained by the
presence of 14.4 wt % of Si in Earth's core. Although,
the presence of significant Si in Earth below core-
mantle boundary is a matter of debate at the present,
recent results from high pressure and temperature melt-
ing studies [15] and theoretical studies based on ab
initio calculations and seismic data [16] suggest as low
as 8 mol % of Si in Earth's outer core. Iron sillicide as
a possible host phase for Si in the core has thus been
the focus of a number of experimental and theoretical
studies. The results from Guyot et al. [17], based on
both experimental and theoretical observations, show
that significant amounts of Si can be dissolved in Fe
between the pressures 8 and 15 GPa. A number of
similar studies have also shown that at pressures below
25 GPa liquid iron can accommodate significant
amounts of Si in solution, while at pressures above 25
GPa it (Si) may exsolve from the solution [13]. The
expected pressure at the core-mantle boundary of Mars
for the present model is about 20 GPa, which falls
within the regime of significant Si solubility indicated
by the above studies. Therefore, we cannot neglect the
possibility of Si being present as a light element in the
martian core. The partitioning of Si into the martian
core would require a reducing environment to prevail
during the core-mantle separation, which is supported
by the reducing nature of the martian mantle as has
been recently pointed out [18-19]. The possible
partitioning of Si into the core is also compatible with
the chemical data on the opaque phases (metal bearing)
in enstatite chondrites. A recent study [20], for
example, has shown up to 12.5 wt % of Si in such
phases.

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REE IN SHERGOTTITE AUGITES AND WHOLE ROCKS. D. S. Musselwhite[1] and M. Wadhwa[2], [1]NASA/Johnson Space Center, Mail Code SR, Houston, Texas 77058 doald.s.musselwhite1@jsc.nasa.gov, [2]Dept of Geology, The Field Museum, 1400 S. Lake Shore Dr., Chicago, IL 60605 mwdhwa@fieldmusem.org.

Introduction: Redox variations have been reported among the shergottites [1,2,3]. [1] used the Eu and Gd partitioning experiments of [4], designed for the LEW86010 angrite, to infer a range of fo_2 for the shergottites. [2,3] inferred fo_2 using equilibria between Fe-Ti oxides. There is fairly good agreement between the Fe-Ti oxide determinations [2,3] and the estimates from Eu anomalies [1] in terms of which meteorites are more or less oxidized. The Eu anomaly technique and the Fe-Ti oxide technique both essentially show the same trend, with Shergotty and Zagami being the most oxidized and QUE94201 and DaG 476 being the most reduced. Thus, the variation in fo_2 appears to be both real and substantive. However, although the redox trends indicated by the two techniques are similar, there is as much as a two log unit offset between the results of [2,3] and [1]. One explanation for this offset is that the Eu calibration used for the shergottites was actually designed for the LEW86010 angrite, a silica-undersaturated basalt whose pyroxene (diopside) compositions are rather extreme. To correct this, [5] conducted a set of experiments on the redox relationship of Eu partitioning relative to Sm and Gd for pyroxene and melt compositions more relevant to Martian meteorites. We have taken the experimentally determined relationship between $D^{Augite/melt}$ (Sm,Eu,Gd) and fO_2 of [5] and applied it to augite Eu and Gd data for the basaltic Shergottites of [1] as well as previously unreported augite Sm data (analytical methods identical to [1]).
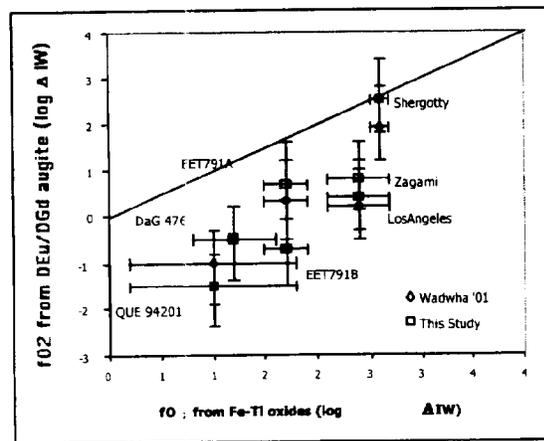
Figure 1:
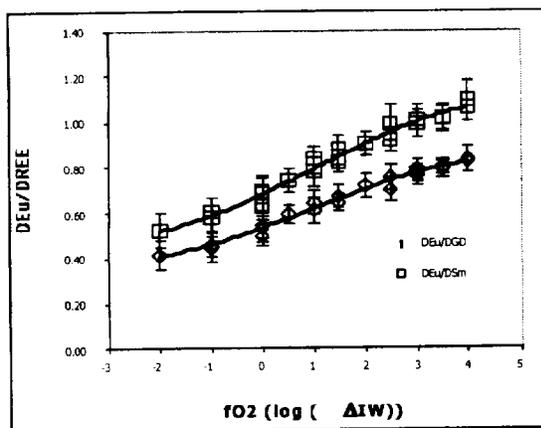
Data Set. The results of the controlled fO_2 partitioning experiments of [5] are shown in figure 1. Table 1

shows the Eu and Gd augite core data of [1] along with previously unreported Sm augite core data. Using using these data and whole-rock Sm, Eu, and Gd data [6], we have calculated the D_{Eu}/D_{Gd} and D_{Eu}/D_{Sm} ratios for selected basaltic Shergottites (also Table 1). Applying these D ratios to the curves in Figure 1, we determined the fO_2 for the meteorites. These are given in Table 2 along with fO_2's determined from Fe-Ti oxides [2,3] for comparison.

Figure 2:

Discussion and Conclusions: Figure 2 shows a plot of fO_2 for Shergottites determined from D_{Eu}/D_{Gd} both from this study and [1] *versus* fO_2 as determined from Fe-Ti oxides [2,3]. The fO_2's determined from D_{Eu}/D_{Gd} using the calibration of [5] are offset to higher values at higher fO_2's compared to those determined from D_{Eu}/D_{Gd} [1] using the calibration of [4] but to slightly lower values at the lowest fO_2's. It appears that for some of the Shergottites (Shergotty, Zagami and EET 79,1A), some of the discrepancy between fO_2's determined using the Fe-Ti method and that using the D_{Eu}/D_{Gd} method was due to the need to calibrate the relationship between D_{Eu}/D_{Gd} and fO_2 for Martian basalt and pyroxene compositions. However, for all of the Martian meteorites considered here except Shergotty, a discrepancy remains between the fO_2 determined from D_{Eu}/D_{Gd} and that determined from Fe-Ti oxides. That discrepancy may in fact be real in the sense that the two methods are recording fO_2 at different stages in the crystallization of the magma. However, before we accept this conclusion, other factors must also be con-

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sidered. In particular, two important considerations may be exemplified by Zagami and EET79,1A.

(1) How representative are the whole rocks?: In the case of Zagami, whole rock data used to estimate D_{Eu}/D_{REE} ratios [6] are highly variable. This variability is evident in separate analyses conducted in the same laboratories as well as between those performed in separate labs. These analyses are mostly INAA measurements conducted on small chips. The variability of the modal compositions of the chips (in particular, the relative phosphate and pyroxene abundances) are likely the cause of the variability of the in the REE ratios. Therefore, care needs to be taken in selecting the appropriate analyses for estimating the whole-rock REE ratios.

(2) Are the augite cores in equilibrium with the melt as represented by the whole-rock REE ratios?: This could be particularly problematic for EET79,1A. Augite may have formed quite late in the crystallization of its parent magma. In fact, equilibrium crystallization experiments conducted on the EET79,1A composition at successive temperatures between its liquidus and solidus, produce no pyroxenes of augite composition [7].
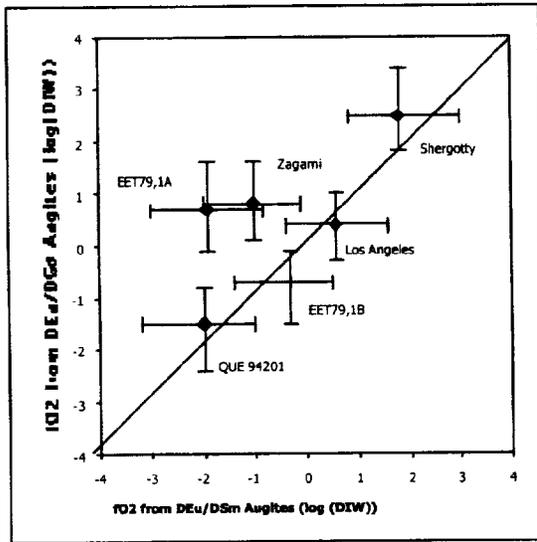
Figure 3:

fO_2 from D_{Eu}/D_{Sm} Augites (log (DTW))

D_{Eu}/D_{REE} method may be suspect for these meteorites for the reasons stated above. Agreement is seen within error for the fO_2's determined with these two ratios for Shergotty, Los Angeles, EET79,1B and QUE94201. We might, therefore, conclude that the fO_2's determined by the D_{Eu}/D_{REE} method for these rocks is the correct one for their parent magmas at the early stages of magma crystallization. However, before accepting this conclusion, further corroboration is necessary. Specifically, employment of D_{Eu}/D_{REE} for pigeonite and melt is suggested. [8] have begun to calibrate the relationship between D_{Eu}/D_{REE} and fO_2 for pigeonite/melt at Martian compositions. Up until now, however, REE abundances on pigeonite cores have not been of suitable precision to employ this method with any certainty.

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Table 1: SIMS analyses of Augite cores and calculated D				
Sm ppb	Eu ppb	Gd ppb	DEu/DSm	DEu/DGd
SHERGOTTY 164 ±14	58 ±3	315 ±16	0.88 ±0.11	0.75 ±0.0
ZAGAMI 369 ±31	103 ±8	670 ±59	0.58 ±0.15	0.60 ±0.0
LOS ANGE 456 ±35	140 ±11	946 ±79	0.75 ±0.11	0.57 ±0.0
EET 79,1(214 ±22	56 ±4	374 ±28	0.53 ±0.07	0.59 ±0.0
EET 79,1(I 240 ±27	73 ±5	630 ±47	0.65 ±0.09	0.47 ±0.0
DaG 476	62 ±5	607 ±46		0.50 ±0.0
QUE 94201 239 ±18	56 ±4	552 ±28	0.52 ±0.06	0.44 ±0.0

C. (1998) *NASA Johnson Space Center Publication* 27672, Revision A, 88. [7] Jones, J.H. personal commu-

Table 2: fO for selected Shergottites determined by various methods			
from Fe-Ti [2,3]	from Eu/Gd [1]	from Eu/Gd This Study	from Eu/Sm
Shergotty **2.6** ±0.1	**1.9** +0.9/-0.7	**2.5** +0.9/-0.7	**1.8** +1.2/-1.0
Zagami **2.4** ±0.3	**0.4** +0.8/-0.7	**0.8** +0.8/-0.7	**-1** +0.9/-1.0
Los Angel **2.4** ±0.3	**0.2** +0.6/-0.7	**0.4** +0.6/-0.7	**0.6** ±1.0
EET 79,1/ **1.7** ±0.2	**0.3** +0.9/-0.8	**0.7** +0.9/-0.8	**-1.9** ±1.1
EET 79,1B **1.7** ±0.2	**-0.7** +0.6/-0.8	**-0.7** +0.6/-0.8	**-0.3** +0.8/-1.1
DaG 476 **1.2** ±0.4	**-0.5** +0.7/-0.9	**-0.5** +0.7/-0.9	
QUE 942C **1** ±0.8	**-1.0** +0.7/-0.9	**-1.5** +0.7/-0.9	**-2** +1.0/-1.2

nication. [8] McCanta, M.C. et al. (2002) *MAPS* 37, A97.

Figure 3 shows a plot of fO_2 for shergottites determined using D_{Eu}/D_{Gd} *versus* that determined using D_{Eu}/D_{Sm} both from this study. Agreement is not found for the fO_2's determined with these two ratios for Zagami and EET79,1A. The fO_2's determined by the

AN "ANDESITIC" COMPONENT IN SHERGOTTITES WITH RESTORED LREE ABUNDANCES?

AN "ANDESITIC" COMPONENT IN SHERGOTTITES WITH RESTORED LREE ABUNDANCES? L. E. Nyquist[1], C.-Y. Shih[2], H. Wiesmann[2], and J. A. Barrat[3], [1]Mail Code SR, NASA Johnson Space Center, Houston, TX 77058, l.nyquist@jsc.nasa.gov, [2]Mail Code C23, Lockheed-Martin Space Mission Systems and Service Co., 2400 NASA Road 1, Houston, TX 77058, [3]Université d'Angers, 2 bd Lavoisier, 49045 Angers Cedex, France.

Introduction: The shergottite Martian meteorites present a variety of oft-confusing petrologic features. In particular, represented among this subgroup are basalts with very depleted LREE abundances, as well as those with nearly chondritic overall REE abundances. The LREE-depleted basalts appear to more closely record the REE and isotopic features of their mantle source regions. Those basalts with more nearly chondritic REE abunandances appear to contain an extra component often referred to as a "crustal" component. The addition of the crustal component tends to restore the overall REE abundance pattern towards chondritic relative abundances. Here we suggest that the crustal component could derive from "andesitic" rocks observed remotely to occur on the Martian surface, and which were analysed at the Pathfinder site.
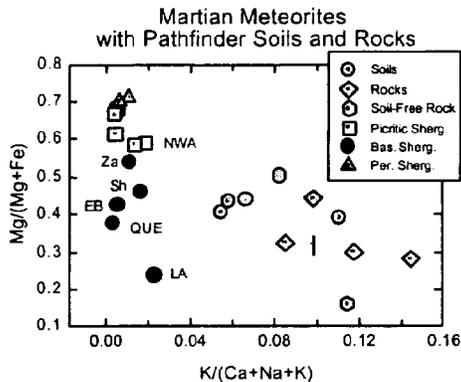
Figure 1. Mg/(Mg+Fe) vs. K/(Ca+Na+K) for Martian meteorites and Pathfinder soils and rocks.

Comparison of Martian meteorites to Pathfinder rocks and soils: Figure 1 compares Mg/(Mg+Fe), i.e., mg-values, and K/(Ca+Na+K) for Martian meteorites to those in Pathfinder rocks and soils [1]. The mg-values are related to olivine abundances in the shergottites. "Picritic basalts" and "peridotitic shergottites" are enriched in olivine compared to the "basaltic shergottites". However, it is clear that the shergottites cannot be adequately characterized by a single parameter. Also, K/(Ca+Na+K) cannot be identified with a single mineralogical feature of the samples, but was chosen partly to reflect the feldspar composition of the samples, partly to reflect the feldspar composition in possibly assimilated precursor materials, and partly because

K has geochemical affinities to both La and Rb. Thus, this parameter might be expected to correlate to the Sm-Nd and Rb-Sr isotopic systematics of the meteorites.

The meteorite and Pathfinder data fields are completely separated in Figure 1. However, the peridotitic shergottites and picritic basalts lie on the extension of the trend of Pathfinder data, and thus could be interpreted as capable of providing a mafic component to the Pathfinder soils. The need for such a component, not represented among the analysed Pathfinder rocks, was recognized by Wänke et al. [1].

Preliminary Nd and Sr isotopic data for NWA 1068: In Figure 1, the picritic basalt displaced most strongly towards the pathfinder data is NWA 1068. It contains large olivine megacrysts characteristic of strongly LREE-depleted picritic basalts like DaG 476 and 489, SaU 005, and EET79001, but it has nearly chondritic relative REE abundances like basaltic shergottites, Shergotty, Zagami, and Los Angeles [2]. We have begun Sr and Nd isotopic investigations of NWA 1068. Comparing preliminary Sm-Nd data to that of Los Angeles (LA), another hot-desert meteorite, shows the effect of terrestrial contamination on analyses of an unleached whole rock (WR) and a leachate from a second whole rock (WR(l)). Sm-Nd of the leach residue, WR(r), are very similar to leach-residue data for LA, and lie on the ~172 Ma isochron determined for LA [3]. The WR and WR(l) data are displaced from WR(r) along a mixing line terminating at the isotopic data for caliche physcially removed from LA. The slope of this mixing line corresponds to a maximum apparent age of 245 Ma. The initial Rb-Sr isotopic data show analogous relationships, with the WR(r) datum falling in the range of values for ~170 Ma isochrons for Shergotty, Zagami, and Los Angeles. Again, the WR and WR(l) data are displaced along a mixing line terminating at the caliche datum. For this discussion, we assume an age of 173 Ma for NWA 1068, characteristic of shergottites with similar REE abundances [4], and calculate initial $^{143}Nd/^{144}Nd$ and $^{87}Sr/^{86}Sr$ ratios from the WR(r) data. Additonal isotopic data will be presented at the workshop.

Olivine accumulation and fractional crystallization in shergottites: Figure 2 shows that magma-chamber and/or near-surface processes of olivine accumulation and fractional crystallization have been operative on shergottite magmas of differing isotopic compositions. These effects have operated independently of whether

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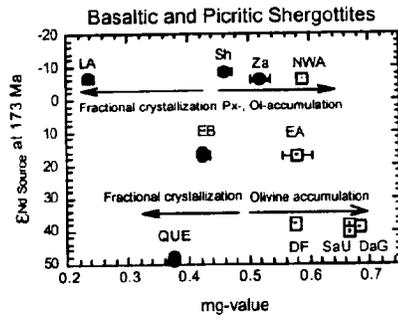
Figure 2. Illustrating the effect of olivine accumulation and fractional crystallization, resp., on shergottite magmas.

Figure 3. Isotopic binary mixing models for mantle and crustal components of fixed isotopic composition present in differing abundances.

the isotopic systematics were inherited from the Martian mantle directly (meteorites with large, positive values of ε_{Nd}), or likely represent mixing of mantle and crustal components (meteorites with negative ε_{Nd}). Olivine accumulation is manifest in the presence of large megacrysts of olivine in the picritic basalts NWA 1068, EET79001A, Dhofar 019, SaU 005, and DaG 476, 489. The effect of fractional crystallization is manifested in low Mg/(Mg+Fe) for several of the basaltic shergottites, including especially Los Angeles and QUE94201 (Figure 1). Los Angeles has "crustal" isotopic systematics, whereas QUE94201 has "mantle" isotopic systematics (Figure 3). Olivine fractionation clearly occurred after the isotopic and REE characteristics of the magmas were established.

Isotopic mixing relationships: We presented two component isotopic mixing models for the initial Nd- and Sr-isotopic composition in EET79001 and Los Angeles [5]. The simplest scenario, binary mixing, is illustrated in Figure 3, updated from [5].

Because late-stage magma-chamber and near-surface fractionation processes affect the abundances of Sr and Nd in the basalts, but not their isotopic compositions, we allow the abundances of Sr and Nd in the mixing endmembers to vary within reasonable limits. The assumed isotopic characteristics of the crust are fixed by requiring the crustal component in LA to be <20%. To match the isotopic characteristics of LA, a highly fractionated basalt, we use the relatively high Sr and Nd abundances in QUE94201 for the "mantle-derived" basalt mixed with a crustal component with ~30X higher Nd, and 4.4X higher Sr abundances. The parameter K/(Ca+Na+K) = 0.0033 for QUE, ~30X less than for the Pathfinder soils and rocks, so the required level of Nd enrichment (~117 X CI) may be readily available in Martian crustal rocks.

Figure 4 shows the results of an AFC model using the same endmembers as for Figure 3. A high ratio of
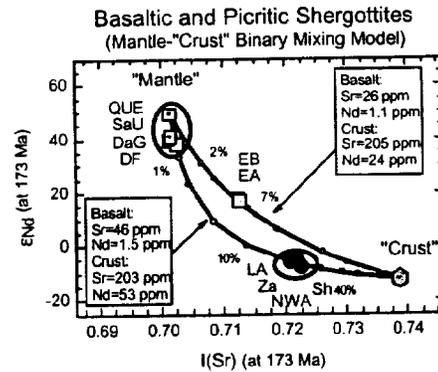
the rate of assimilation to the rate of crystallization, r = 0.3, is shown for illustration. The amount of assimilant is ~3X higher than for the binary mixing model. The resultant is enriched in Nd and Sr by ~3X for LA, but by only ~20% for EET79001B. Thus, the models are equivalent for EET79001B, not for LA.
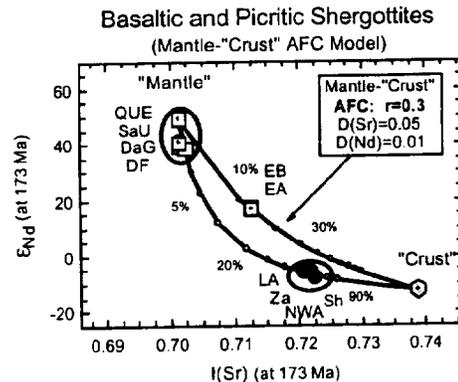
Figure 4. AFC models for the same mantle and crustal components as for Figure 3.

References: [1] Wänke H. et al. (2001), *Chron. & Ev. Mars*, ISSI, 317-330. [2] Barrat J. A. et al. (2002) *Geochim. Cosmochim. Acta (submitted)*. [3] Nyquist L. E and Reese Y. D. (2001) *Eos Trans. AGU, 82 (47), Fall Mtg.* abs. P51A-02 [4] Nyquist L. E. et al. (2001) *Chron. & Ev. Mars*, ISSI, 105-164. [5] Nyquist L. E. et al. (2001) *LPS XXXII*, abs. #1407.

EVOLUTION OF MARTIAN ATMOSPHERIC, CRUSTAL, AND MANTLE XENON COMPONENTS IN BASALTIC SHERGOTTITES.

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Introduction: As part of an ongoing study of the shergottites [1-3], we have measured the isotopic signature and concentration of xenon in mineral separates of Shergotty and EET79001 Lithology-B. Similarities between the meteorites include the enhanced concentration of martian atmospheric xenon in opaque and maskelynite minerals relative to pyroxene [2]. The interior component appears to be present in all minerals but is best defined in pyroxene separates. This component consists of isotopically solar xenon with a significant contribution from fission xenon and is similar to those observed in Chassigny, ALH84001 and Nakhla [4]. The proportion of fission xenon in the pyroxene separate of EET79001 is lower than that in Shergotty. Pyroxene separates from Shergotty also have a well defined $^{129}Xe/^{132}Xe$ ratio higher than solar.

One explanation for these variations and which we were seeking the effects of in this study, is that they reflect the degree of incorporation of 'crustal' material into the parent melt of the shergottites. The covariation of oxygen fugacity and ε_{Nd} among the Shergottites has been argued to reflect different degrees of assimilation of crustal material (or other material with similar geochemical properties) in the parent melt. Geochemical, both plutonium (the most strongly implicated precursor of fission xenon in the martian meteorites) and uranium would be expected to be associated with the high ε_{Nd} endmember, and so $^{136}Xe/^{132}Xe$ might be expected to be higher in Shergotty than in EET79001, as observed.

Here we present preliminary results from a simple model tracking xenon isotopically through differentiation, outgassing and atmospheric loss of Mars. We require an atmosphere with elevated $^{129}Xe_{xs}/^{130}Xe$ and low $^{136}Xe*/^{129}Xe_{xs}$; in addition, we attempt to produce two interior reservoirs, one consisting of solar xenon with no radiogenic xenon and one with a high ratio of fissiogenic $^{136}Xe*/^{130}Xe$ and a low $^{129}Xe_{xs}/^{136}Xe*$ ratio to account for the variable interior component.

Model of Martian Xenon Reservoir Evolution: The model uses a simple rate equation approach to trace the passage of xenon and its parent radiogenic isotopes ^{129}I ($t_{1/2}$ = 17 Myr), ^{244}Pu ($t_{1/2}$ = 82 Myr), and ^{238}U ($t_{1/2}$ = 4.468 Gyr) between reservoirs and radioactive decay. Rates of differentiation, degassing and atmospheric loss can be varied as free parameters to investigate under what circumstances reservoirs are qualitatively similar to those necessary to explain martian meteorite xenon components. Initial concentrations and ratios are similar to those of Swindle and Jones [5]. Xe, I and Pu are assumed to have behaved as incompatible elements during differentiation, with the exception that xenon could also be degassed from the crust – xenon appears to have behaved as an incompatible element during the formation of the nakhlites [6, 7].

Results and Discussion As expected, the requirement to produce a crust with high $^{136}Xe/^{130}Xe$ and low $^{129}Xe/^{130}Xe$, and with significant concentrations of $^{136}Xe*$ imposes quite stringent constraints on its degassing history. Early major loss of ^{130}Xe is required to allow the $^{136}Xe/^{130}Xe$ ratio to evolve upwards subsequently. This loss must have continued on timescales long compared to that characteristic of

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^{129}I decay (>~100Ma) to allow high ^{136}Xe*/^{129}Xe$_{xs}$ ratios. In order to preserve significant concentrations of ^{136}Xe*, this degassing rate must have declined drastically on time-scales short compared to that characteristic of ^{244}Pu decay (<~800 Ma). The broad characteristics of the martian atmospheric xenon isotopic composition can also be reproduced within this model, using the atmospheric loss history proposed by Pepin [8, 9].

The identification of a pure solar component in the Chassigny meteorite argues that, if anything, our model underestimates the initial xenon to iodine/plutonium ratio. Since degassing of the source region rich in plutonium is thus crucial to the model's success (decay of Pu can only increase ^{136}Xe/^{130}Xe once the original complement of solar xenon has been effectively removed), should our interpretation withstand further tests constraints are imposed on the location of this reservoir. Although labeled 'crustal', its identification with the martian crust remains controversial – a mantle reservoir rich in incompatible elements is also a candidate source region. However, the requirement for the source region to be degassed argues in favor of a location close to the surface, in effect strengthening the case for identification with the crust itself.

Extending the model to the other major radiogenic rare gas component has presented some problems. In our model, the same properties that lead to elevated ^{136}Xe* in the crust lead to elevated ^{40}Ar* excesses. As yet, no interior component enriched in ^{40}Ar from ^{40}K decay has been identified. Notably, K-Ar (total ^{40}Ar/K) ages of the nakhlites are virtually identical to Ar-Ar ages and crystallization ages in other systems (1.3 Ga) [10] arguing for complete degassing of argon from the parent melt or its source shortly before formation of the meteorites. This is consistent with the proposal that they formed in a near-surface flow, but is diffi-

cult to reconcile with the presence of inherited ^{136}Xe*. We note in passing that this must cast some doubt on models relying on the total retention of xenon during formation of the nakhlites [7]. The resolution of this conundrum remains unclear.

Summary: Although work is at an early stage, our model seems capable of qualitatively accounting for the evolution of xenon isotopes in the martian interior and atmosphere provided degassing of the crust is limited to an early period of martian history. It produces ^{136}Xe*/^{129}Xe$_{xs}$ ratios low in the atmosphere and high in the crust and a source of gas close to solar in the mantle, as required by our present understanding of the components. This can be seen as a consequence of the concentration of incompatible elements in the crust during differentiation, supporting the argument for crustal assimilation.

We plan further work on the basaltic shergottites to establish whether the variation between Shergotty and EET79001 Lithology-B represents a wider trend, and hope to present data from DaG489 at the meeting.

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NOBLE GASES IN THE TERRESTRIAL PLANETS, WITH FOCUS ON WHAT THE SNC METEORITES TELL US ABOUT MARS.

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Introduction: Noble gases in the solar wind and giant-planet atmospheres are generally assumed to be the best —perhaps the only— available proxies for isotopic distributions in the early solar nebula. Both, however, may be isotopically fractionated to some degree from their source composition, the wind in processes that transport solar plasma to and release it from the corona [1], and giant-planet Ar, Kr and Xe by trapping in icy planetesimals if these were indeed the principal suppliers of heavy noble gases to their present atmospheres [2]. Noble gas isotopic ratios in the solar wind are reasonably well established from lunar and asteroidal regolith studies [3,4] and the Galileo Probe mass spectrometer has given us our first look at compositions in Jupiter's atmosphere [2].

Modern theories of atmospheric evolution on the terrestrial planets are focused on the nebula as the primary supplier of primordial planetary volatiles, either directly —i.e., in ways that do not fractionate isotopes (by adsorption on planetary embryos or "ingassing" from dense, gravitationally condensed atmospheres)— or by accretion of cometary ices carrying noble gases that could have been either isotopically solar or mildly fractionated during trapping from the ambient nebula [5]. The observation that nonradiogenic Ne, Ar, Kr and Xe in Earth's current atmosphere are all isotopically heavier than their solar counterparts is an important clue to the nature of the processes that subsequently acted on these primordial planetary reservoirs. This is also the case on Mars, except for Kr which is isotopically near-solar (and therefore an interesting challenge for evolutionary modeling), and on Venus as well, as far as one can tell from the limited data on hand [1,5].

Much of the evolutionary modeling over the past 15 years or so has focused on fractionation from primordial source compositions during thermally-driven, hydrodynamic atmospheric escape (reviewed in [5]). Hydrogen-rich primordial atmospheres on partially or fully accreted planets are heated at high altitudes by intense ultraviolet radiation from the young sun or alternatively, in the case of the Earth, by energy deposited in a large Moon-forming impact. Under these conditions hydrogen escape fluxes can be large enough to exert upward drag forces on heavier atmospheric constituents sufficient to lift them out of the atmosphere. Lighter species are entrained with the outflowing hydrogen and lost more readily than heavier ones, leading to mass fractionation of the residual atmosphere.

Models in which a planetary atmosphere is driven from isotopically solar-like progenitors to its present compositional state by energetic hydrodynamic escape of the primary atmosphere, followed by mixing of the isotopically fractionated atmospheric residue with solar gases evolved from the interior, are able to account for many of the details of contemporary noble gas isotopic distributions on Earth [5-7]. The one glaring exception is Xe. Isotope ratios of terrestrial nonradiogenic Xe cannot be generated by hydrodynamic escape fractionation of the measured solar-wind Xe composition. An initial composition called U-Xe, which appears to be isotopically identical to solar-wind-Xe except for sharply lower abundances of the two heaviest isotopes, is required [8]. There is some evidence that a U-Xe-like composition may have been present in the presolar molecular cloud and at some stage in the history of the solar nebula. But if so, we are still left with the puzzling question of why it differs isotopically from the Xe composition in the solar wind and presumably also in the sun.

Applied to Venus, the hydrodynamic escape model makes specific predictions for the currently unknown Kr and Xe isotopic distributions in its contemporary atmosphere [7]. This opportunity for an observational test of the modeling assumptions is one of the primary scientific drivers in current proposals for a suitably instrumented Discovery mission to the planet.

Mars: Mars. as usual, is interestingly different. Atmospheric Kr is isotopically similar to solar-wind Kr, as noted above, and so is evidently largely unfractionated. Severe fractionation, however, is needed to establish present Xe isotope ratios, and here the composition of its primordial progenitor is completely consistent with solar-wind Xe, not U-Xe. Current Ar and Ne isotopic compositions appear to result from interplay of planetary degassing and fractionating sputtering loss from the exosphere over the past several Ga.

Current modeling divides Martian atmospheric history into early and late evolutionary periods (e.g. [9-14]). The first is characterized by an initial episode of hydrodynamic escape that sets the Martian Xe inventory, followed by high CO_2 pressures and a possible greenhouse, and the second by either a sudden transition to a low pressure environment similar to present-day conditions on the planet —perhaps initiated by abrupt polar CO_2 condensation ~3.7 Ga ago [9]—or by a more uniform decline to present pressure.

The early atmosphere. Early in the pre-3.7 Ga epoch, nonradiogenic Xe isotopes are assumed to be hydrodynamically fractionated to their present composition, with corresponding depletions and fractionations of lighter primordial atmospheric species [11]. Subsequent CO_2 pressure and isotopic history is dictated by the interplay of estimated losses to impact erosion, sputtering, and carbonate precipitation, additions by

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outgassing and carbonate recycling, and perhaps also by feedback stabilization under greenhouse conditions [11,14]. It should be stressed, however, that little is actually known about the values of the parameters governing these various processes. Models of this epoch are no more than qualitative illustrations of how they might have driven early atmospheric behavior.

Later atmospheric evolution: Sputtering loss. Probable operation, on Mars, of a sputtering loss mechanism that results in fractionation of elements and isotopes in the residual atmosphere was demonstrated by [15]. Oxygen atoms in the Martian exosphere, ionized by solar ultraviolet radiation and accelerated in the motional vxB electric field of the solar wind, can impact species near the top of the atmosphere with enough energy transfer to eject them from the planet's gravitational field. Fractionations are governed primarily by diffusive mass separation in the upper atmosphere, which enhances the relative abundances of light to heavy species. Sputtering loss therefore preferentially removes lighter masses, leaving the atmosphere enriched in heavier constituents [5,10,11].

CO_2 pressure collapse on Mars near 3.7 Ga would have triggered the rapid sputtering removal of pre-existing Ne and Ar from the atmosphere (Kr and Xe are too heavy to be affected) [11]. This has the interesting consequence that no isotopic memory of their earlier processing survives. Current abundances and isotopic compositions are entirely determined by the action of sputtering on gases supplied by outgassing during the late evolutionary epoch, and final distributions of the light noble gases are therefore decoupled from whatever their elemental and isotopic inventories might have been in the pre-3.7 Ga atmosphere. The issue of how much Ne and Ar degassing was required to prevent their complete sputtering annihilation from the atmosphere during this epoch is unresolved. One study concluded that the Ne-Ar outgassing flux attributable to degassing during major episodes of volcanic activity would have been ~1-3 orders of magnitude too low to balance sputtering losses, and thus another major source of juvenile volatiles must have contributed to the atmosphere over geologic time, perhaps via input from gas-enriched hydrothermal systems [12].

Sputtering is greatly attenuated by the presence of a planetary magnetic field [13]. Efficient operation of this fractionating loss mechanism over time on Mars is thus centrally linked to the timing of the disappearance of the Martian paleomagnetic field [13,16].

Atmospheric Xe and the ^{244}Pu problem. The isotopic composition of Martian atmospheric Xe most recently derived from Xe trapped in the shock-glass phases of shergottites [17] is almost perfectly consistent (except for ^{129}Xe) with a composition generated entirely by fractionation of solar-wind Xe [8]. This has the interesting consequence that additional contributions to the Xe inventory from degassed fission Xe are either very minor or absent altogether. And yet the pre-

sent atmosphere is clearly heavily enriched in ^{129}Xe from extinct ^{129}I decay. The presence of radiogenic ^{129}Xe but apparently little if any ^{244}Pu fission Xe, a situation quite unlike that on Earth, has been awkward to reconcile with models of Martian geochemical evolution and degassing history. A less severe fractionation of SW-Xe does allow the presence of an additional component with Pu-Xe fission yield ratios, amounting to ~5% of total ^{136}Xe [18] —similar to the fraction on Earth. At the moment the central question of the presence or absence of Pu-Xe is plagued by apparent coincidences. The excellent match of fractionated SW-Xe alone to the atmospheric data is presumably fortuitous if Pu-Xe is present; and if it is absent, the fact that a weaker fractionation generates a pattern in good accord with ^{244}Pu fission yields must likewise be accidental.

Interior Xe. The nonradiogenic Xe isotope ratios found in Chassigny appear to be indistinguishable from solar values [19]. The relative abundances of ^{129}Xe and ^{136}Xe are also close to solar, and so there is little scope for radiogenic additions. Data from Nakhla [20] indicate that there are other interior Martian reservoirs that contain solar Xe but with resolvable fissiogenic contributions, and so have had lower Xe/Pu ratios. It seems likely that the interior is relatively undegassed, with high ratios of primordial Xe to parent elements.

Degassing history. Viking measurements of atmospheric ^{40}Ar and estimates of ^{40}K in the mantle from the SNCs suggest that only ~2% of the ^{40}Ar generated in the planet has degassed. Atmospheric ^{129}Xe from extinct ^{129}I decay is consistent with ~2% degassing if the closure age of Mars against gas loss during accretion was ~70 Ma; the same closure age and degassed fraction would be indicated by the atmospheric ^{136}Xe inventory if ~5% of it derives from ^{244}Pu decay [5] — currently an open issue, as noted above.

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SHERGOTTITE IMPACT MELT GLASSES CONTAIN SOIL FROM MARTIAN UPLANDS.

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Introduction: Martian meteorite (shergottite) impact melt glasses that contain high concentrations of martian atmospheric noble gases [1] and show significant variations in $^{87}Sr/^{86}Sr$ istopic ratios [2] are likely to contain Martian surface fines mixed with coarser regolith materials. The mixed soil constituents were molten due to shock at the time of meteoroid impact near the Martian surface and the molten glass got incorporated into the voids and cracks in some shergottite meteorites. Earlier, Rao et al. [3] found large enrichments of sulfur (sulfate) during an electron-microprobe study of several impact melt glass veins and pods in EET79001,LithC thin sections. As sulfur is very abundant in Martian soil, these S excesses were attributed to the mixing of a soil component containing aqueously-altered secondary minerals with the LithC precursor materials prior to impact melt generation. Recently, we studied additional impact melt glasses in two basaltic shergottites, Zagami and Shergotty using procedures similar to those described in [3]. Significant S enrichments in Zagami and Shergotty impact melt glass veins similar to the EET79001, LithC glasses were found. In addition, we noticed the depletion of the mafic component accompanied by the enrichment of felsic component in these impact melt glass veins relative to the bulk host rock in the shergottites. To explain these observations, we present a model based on comminution of basaltic rocks due to meteroid bombardment on martian regolith and mechanical fractionation leading to enrichemnt of felsics and depletion of mafics in the fine grained dust which is locally mobilized as a result of saltation and deflation due to the pervasive aeolian activty on Mars.

Methods and Results: Several impact melt glass veins and pods in EET79001, LithC (,77 ,78 ,18, 20A and ,506) sections ; Zagami (,992 a2 & c2) and Shergotty (dbs) glasses were studied using a Cameca SX100 microbeam automated electron microprobe equipped with standard Cameca instrument controls and PAP data reduction software. Standard analytical methods and calibration procedures were used. The elemental abundance data obtained by raster scans along different line traverses at homogeneous sites in the veins and pods are averaged and normalized to the bulk composition of the host rock. Typical results (average) for EET79001,LithC are shown in Fig 1. In these shergottite glass veins, the maximum enrichment of Al_2O_3 is upto ~60%; CaO is upto ~20%; and Na_2O, upto ~60%. On the otherhand, the maximum depletion of FeO is upto

~15%; MgO is upto ~36% and TiO_2 upto ~36%. Also, the volatile element, S showed large SO_3 excesses (upto a maximum of ~300%) in these shergottite glasses over the host rock. Further, sulfur was shown to be present predominantly as sulfate (oxidized S / reduced S = 1.83) in LithC glass veins by [4]. However, the Cl abundance in the LithC glasses is very low (<0.05%) compared to the Cl abundance estimated from the Cl/S ratio of the Viking and Pathfinder soils [5,6]. Note that precautions were taken to avoid heating losses during measurement of alkalies and halogens by using defocussed beam, low current and long counting rates. The results suggest that the impact melt glass veins in shergottites are enriched in felsics (Al & Ca) and depleted in mafics (Fe & Mg) compared to the host rock. Further, S which is an index element for Martian soil is enriched in these glass veins, whereas Cl (also a volatile) is depleted in these veins. These results suggest that the martian soil in the shergottite glass veins is different from the Viking and Pathfinder soils.

Discussion and the Model: During the study of glass veins in Zagami, [7] noted "slight enrichments of SiO_2, Al_2O_3 and Na_2O along with depletions of FeO and MgO relative to the bulk". Similar observations were made by [8] in the case of EET79001, LithC glasses. Further, [9] noted large enrichment of LREE in EET79001, LithC glass during an ion-microprobe study.

Felsic enrichment and mafic depletion. Modest-sized rocks in Martian regolith undergo collissional destruction by multiple impacts due to meteoroid bombardment. It was shown by [10] and [11] that small-sized meteoroids survive passage through martian atmosphere and encounter the surface with few km/sec velocity. As a result, the unconsolidated materials will be incresingly fractured and shock-processed with time into fine-grained soil. This bombardment causes extensive regolith production and redistribution of dust and rubble on Mars surface[12]. From the impact-gardened regolith on Mars, finer material is mobilized and redistributed locally by deflation and saltation processes due to aeolian activity.

Hoerz and Cintala [13] carried out a series of lab experiments using the high velocity impactor machine at JSC to simulate the conditions of bombardment of basaltic roks in space using gabbro target. The results indicate that in the fine-grained comminution products, plagioclase (Al and Ca) is enriched as it comminutes easily whereas mafic materials (Fe and Mg) which are hard are depleted relative to the starting materials. This

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mechanical fractionation was found to be most severe in fine grain sizes (<20 um). Further, in thencase of lunar soils, [14] showed that the <10 um fraction of lunar soils is enriched in felsics (Al_2O_3, CaO, Na_2O, K_2O and LREE) and depleted in mafics (FeO, MgO, MnO) relative to the bulk lunar soil. These results are consistent with those obtained for shergottite glasses, indicating that their precursor materials were similarly produced on Mars surface.

S and Cl in shergottite glasses: Secondary sulfate and chloride minerals in Martian soil result from the volatiles entring into the atmosphere through volcanic emnations and subsequently interacting with aqueous media on Mars surface. S is enriched in EET79001, Lith C glasses compared to Lith A. Elemental correlation diagrams indicate that Al_2O_3 and CaO correlate positively with SO_3 whereas MgO correlates negatively with SO_3. In contrast, the Cl abumdance in LithC samples is very low. Halite was never found during SEM studies in these glasses. The S/Cl ratio in the shergottite glasses is >50 whereas the same ratio in Viking and Pathfinder soils is 5. These results suggest that insoluble Al & Ca rich sulfates are decoupled and mobilized from soluble sulfates of Mg and chlorides of Na & K by local aqueous activity near the source regions of the precursorr materials on Mars regolith.

Conclusion: The shergottite impact glasses contain fine-grained soil, which was exposed to local fluid activity in the subsurface regolith associated with young volcanic upland regions (Olympus Mons or Elysium) on Mars.

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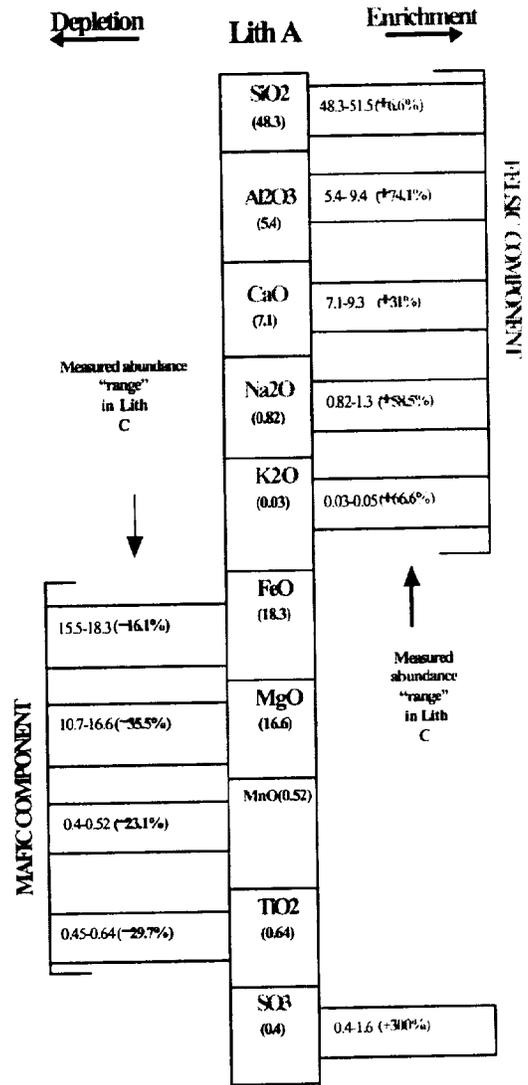

Fig.1. Depletion & enrichment in LithC relative to LithA

Is olivine speedometer a reliable tool to constrain thermal story of SNC meteorite ?

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Several quantitative studies on thermal stories of SNC meteorites have been carried out to infer burial depth. Two approaches are generally used: (i) indirect estimation based on textural observation compared with products from controlled cooling crystallization experiment (ii) direct quantitative cooling rate calculation from diffusion zoning in mineral. The first method, applied on basaltic shergottite, is largely based on textures and compositions of pyroxene and/ or maskelinite. The second one, performed on picritic shergottite (EET79001 and Dar al Gani 476) and the nakhlite NWA 817, uses zoning of olivine to extract cooling rate. At the onset of cooling, olivine was homogeneous and was then modified by atomic diffusion due to contact with Fe-rich surrounding melt when olivine was incorporated as a xenocryst.

It had long been argued that olivine speedometer, giving absolute cooling rate, was the reliable method compared to the first one which bears large uncertainties. Unfortunately any contribution using olivine as a speedometer in meteorites are negligent (or at least optimistic) about the assignment of uncertainties to cooling rate estimate. In such studies numerical procedures, where diffusion equation is solved by finite difference approximation, are generally preferred to analytical one. However error propagation becomes obvious when using analytical methods in as much they allow the dependence of cooling rate results on input parameter to be clearly seen. For instance temperature To and diffusion data (E the activation energy and Do the preexponential term of diffusion coefficient D expressed through the Arrhenius law) are first order parameters in cooling rate equation. Small errors on temperature and diffusion data are magnified due to the logarithmic relation ship between input T and cooling rate S.

Reading the literature on SNC meteorites, uncertainties on To, temperature at which cooling started, are at least of ± 50°C. In NWA 817, for a given D (Buning & Buseck 74 for T< 1125 °C), S is 0.41 K/h for To = 1100°C and 0.043 K/h for To = 1200°C (B & B 74 T>1125°C).

Uncertainties on input diffusion parameters are worst compared to temperature one, as diffusivity of a given element (Fe-Mg) in a given mineral (olivine) is highly variable due to different laboratory experimental conditions and crystal impurities. For sake of demonstration let's used two extreme values of D_{Fe-Mg} given respectively by **B & B 74** and Chakraborty **97**. In NWA 817, for a given To of 1100°C, **B&B 74** diffusion coefficient gives S of 0.41 K/h and **C.97** 's one gives $2.66 \ 10^{-3}$ K/h i.e. 2 orders of magnitude difference in the cooling rate estimate.

To conclude, cooling rate quantification of SNC meteorites using olivine speedometer is a perilous exercise as such a method bears itself large uncertainties. Those results should be cross-calibrated with data obtained from controlled cooling crystallization experiments. However it should be noted that fast crystallization rate does not always relate to fast cooling and may be rather due to supersaturation phenomenon.

NITROGEN AND NOBLE GASES IN MINERAL SEPARATES FROM ZAGAMI.

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Introduction: Isotopic compositions of nitrogen and noble gases have played a key role in understanding SNC meteorites and Mars. For example nitrogen and argon data from the glass of EET 79001 were one of the convincing evidences that linked these meteorites to Mars [1]. Similarly, the observation of components with largely different isotopic compositions (of both nitrogen [2, 3] and noble gases [4]) in these meteorites has led to the realization that the martian atmosphere (as measured by Viking) is quite different from the martian interior (as pictured from data from these meteorites). But at the same time we have not yet been able to clearly define the (interior) mantle end member and reduce the uncertainties presented by the Viking data for the martian atmosphere. Similarly we do not know for sure the $^{20}Ne/^{22}Ne$ signature of Mars. It is clear that many of these ambiguities as to the indigenous martian components result from interferences from cosmogenic contributions and terrestrial contamination, which are impossible to avoid. But they can be minimized by step temperature heating, and selection of mineral phases rather than bulk samples. We have initiated a simultaneous nitrogen and noble gas isotopic study of mineral separates and a few bulk samples from martian meteorites with the newly set up experimental facility at Mainz [5]. Here we report data for maskelynite and pyroxene separates from Zagami.

Experimental: Gases were extracted by vacuum pyrolysis in an iridium crucible in temperature steps, while simultaneously adsorbing them on a stainless-steel-mesh (SSM) finger (at -196 °C) near the crucible. A split of ~5 % of the sample gas was processed for the analysis of nitrogen, while the rest was processed for the noble gases using standard procedures [6]. The nitrogen fraction, prior to analysis, was cleaned by oxygen generated by an in-line copper oxide finger in a line made of quartz and pyrex. Pipettes of Air standard were run similar to the sample steps to calibrate the experiment, which were consistent with a sensitivity of 4×10^{-7} μg/mV (±10 %). The nitrogen isotopic composi-

Table 1. Nitrogen and selected noble gas data.

	N (ppm)	$\delta^{15}N$ (‰)	$^{40}Ar/^{36}Ar$	$^{129}Xe/^{132}Xe$
Mask.	25	23	3600	1.20
Px.	10	13	2160	1.09

tion ($\delta^{15}N$) of the standards was up to 2 ‰ heavier than that of air. A typical blank for nitrogen at 1600 °C was 60 picograms, with a $\delta^{15}N$ of +2 ‰. The noble gas

blanks and calibration parameters were similar to those of [6]. The nitrogen data have additionally been corrected for background contributions from CO using the procedure of [7].

Discussion: The concentrations of nitrogen and $\delta^{15}N$ in the maskelynite sample are about 2 times higher as compared to that in pyroxene (Table 1). Although one expects the low temperature extraction (at 400 °C) to have significant contribution from terrestrial contamination (as seen in the $^{40}Ar/^{36}Ar$ and $^{129}Xe/^{132}Xe$ ratios), the $\delta^{15}N$ (+22 ‰ in maskelynite and +13 ‰ in pyroxene) are much different from that of terrestrial atmosphere. The high temperature release (accounting for ~85 % of nitrogen) in maskelynite shows a variation from +15 to +25 ‰ in $\delta^{15}N$ (Fig. 1). Nitrogen in pyroxene is dominated by the release (accounting for ~70 %) at 1200 °C which has a $\delta^{15}N$ of +10 ‰. $\delta^{15}N$ of the 800 and 1600 °C steps of this sample are similar to those of maskelynite. Marti et al. [8] have shown the presence of a martian atmospheric component (for nitrogen and noble gases) in glass samples of Zagami. A heavy $\delta^{15}N$ of +147 ‰ observed by Mathew et al. [9] in a bulk sample of Zagami also suggests the presence of a martian atmospheric component in this meteorite. While the present nitrogen concentrations are at least an order of magnitude higher than those in the Zagami glass [8], the $\delta^{15}N$ show significant contribution from a component with lighter $\delta^{15}N$.
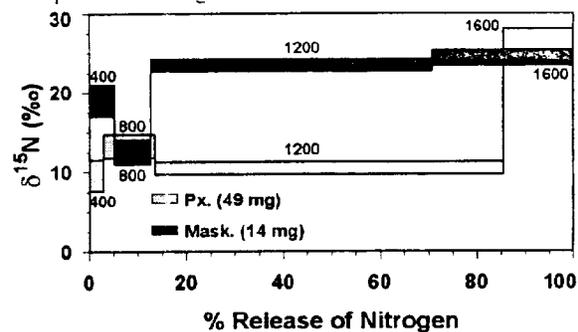

Fig. 1. Stepped temperature release of nitrogen.

Similar to nitrogen, concentrations of trapped Ar, Kr and Xe in maskelynite are a factor of two higher as compared to those in pyroxene. A considerable fraction (Figs. 2 and 3) of these gases released in the 400 °C step, could have been contributed by terrestrial contamination, as suggested by the $^{40}Ar/^{36}Ar$ and $^{129}Xe/^{132}Xe$ signatures. But the gases released in the high temperature (>400 °C) extractions are clearly different. Neon and argon in the present samples are

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dominated by the cosmogenic component (up to 90 % for Ne and 79 % for Ar). We have corrected the nitrogen data for cosmogenic contributions using the $^{21}Ne_{cosm}$ following [10]. The corrections amount to less than 1 ‰. Similarly, the measured $^{40}Ar/^{36}Ar$ ratios have been corrected for the cosmogenic contributions following [4].
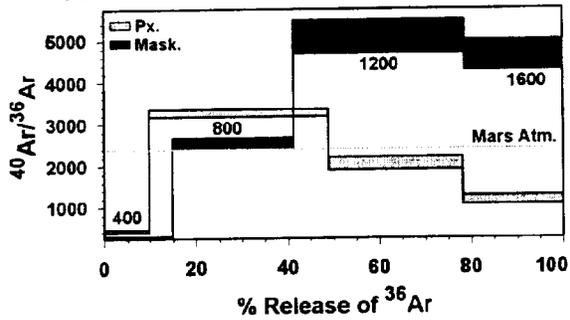

Fig. 2. Stepped temperature release of trapped argon.

Although $^{40}Ar/^{36}Ar$ of the low temperature extraction in these samples shows a contribution from terrestrial atmospheric argon, that in the high temperatures shows the presence of contributions from an end-member similar to martian atmosphere (as shown by the release in 800 °C in pyroxene) and radiogenic argon (as shown by the elevated signatures in 1200 and 1600 °C releases of maskelynite). The higher contribution from the radiogenic component in maskelynite compared to pyroxene can be explained by the higher K content of maskelynite. $^{40}Ar/^{36}Ar$ in the 1200 and 1600 °C extractions of pyroxene, contrary to maskelynite, indicates contributions from a component with low $^{40}Ar/^{36}Ar$ (<1000), which can be explained by the martian mantle (e.g., [11]). $^{129}Xe/^{132}Xe$ in the present samples varies from an air-like signature (in the 400 °C extractions) to 1.3 (in 1600 °C extraction of maskelynite), and is smaller than the signatures observed in the Zagami glass [8].
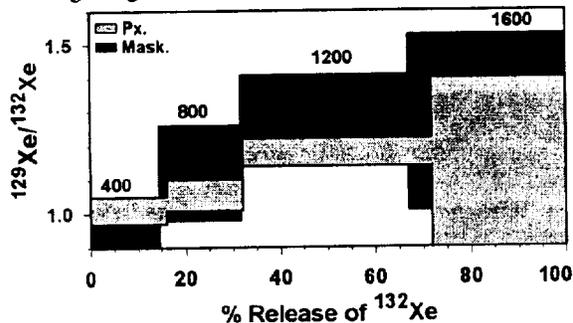

Fig. 3. Stepped temperature release of trapped xenon.

The higher gas (apparently from martian atmosphere) concentrations in maskelynite as comapraed to

pyroxene may be explained by the fact that the former is a result of shock metamosphism which has been shown to be efficient in implanting ambient atmospheric gases into shock-produced phases [12]. However, it should be noted that maskelynite (+mesostasis) and pyroxene from Shergotty [11] do not show any significant differences in their trapped gas concentrations (except for He).

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CHEMICAL COMPOSITION OF NEWLY COLLECTED ANTARCTIC NAKHLITES, Y000593 AND Y000749.

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Introduction: Y000593 and a possibly paired meteorite Y000749 are grouped into nakhlites, a group of SNC meteorites, by their noble gas compositions [1] They are the first nakhlite recovered on Antarctica. So far about 30 SNC meteorites (shergottite, nakhlite and chassignite) have been identified, most of which are classified into shergottites. Nakhlites are rare, to which 6 meteorites including Y000593 and Y000749 belong. In this study, we have analyzed Y000593, Y000749 and Nakhla for their bulk chemical compositions by nuclear analytical methods. At the Antarctic meteorite symposium at NIPR of this year, we l reported some preliminary results [2]. We have being continuing a suit of analyses and their results are presented in this workshop.

Experimental: We first performed neutron-induced prompt gamma-ray analysis (PGA). For PGA, lump samples of Y000593,66 (1.2 g), Y000749,46 (3.6 g) and Nakhla (0.88 g) were used. PGA was conducted by using cold neutron beam at JRR-3M, Japan Atomic Energy Research Institute. The specimens of Y000593 and Y000749 were loaned from NIPR and were subjected to PGA without any additional sample preparation at our side. Because the size of the Y000749 specimen is larger than the neutron beam size used in PGA, only content ratios normalized to Si content were determined for Y000749 and the other samples by the internal mono-standard method developed by our group. Absolute contents were also obtained for Y000593 and Nakhla by conventional comparison method using JB-1 (a basaltic geological reference sample issued by GSJ) and chemicals of analytical grade as reference standards for quantification. For instrumental neutron activation analysis (INAA) and instrumental photon activation analysis (IPAA), powdered samples were prepared for Y000593 and Nakhla. Six chunks weighing about 2 g each, which are located at different position from each other, were sampled from the interior of Y000593 and powdered at NIPR. About 100 mg of each powdered sample was used for INAA and IPAA.

Results and Discussion: Since Si-normalized contents for major elements obtained by PGA using the internal mono-standard method are almost the same for three nakhlites analyzed, it is inferred that their absolute elemental abundances are also similar. Our absolute content values for Y000593 and Nakhla obtained by PGA are shown in Table 1 with contents in Nakhla compiled by Lodders [3]. All major elements and several minor and trace elements can be determined by PGA. It is seen in Table 1 that there is no apparent difference in contents of

analyzed elements between Y000593 and Nakhla except for H and Cl and that our PGA results for Nakhla are also consistent with compilation data [3]. There appear clear boundaries in Mg/Si, Al/Si, Ca/Si, and/or Ti/Si weight ratios among SNC groups; for example, Mg/Si - Ca/Si diagram is shown in Fig.1. These ratios for Y000593 and Y000749 are different from those for Shergotty and Chassigny but consistent with those for Nakhla. Therefore it is confirmed based on chemical composition that Y000593 is a nakhlite. Our determination of Cl in Nahkla is about 16 times higher than the compilation data. As our sample of Nakhla was sampled from the interior of a large mass at the lunar sample processing room at JSC, NASA and no additional treatment was given for PGA, a high content of Cl cannot be attributed to experimental contamination. It must be highly probable that Cl is heterogeneously distributed in nakhlite, just like the case for chondrites [4]. As only one value has been reported for Cl content in Nakhla, additional analyses are desired for Cl (and other halogens) in future. INAA and IPAA data are under examination, and their results and discussion will be presented at the workshop.

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Chemical composition of Y000593 and Y000749: N. Shirai *et al.*

Table 1. PGA results for Y000593 and Nakhla*

Element	Y000593	Nakhla	*Nakhla*[S]
H[#], ppm	541 (14)	252 (10)	
B, ppm	3.47 (6)	3.02 (7)	*4.6*
Na, %	0.432 (3)	0.447 (25)	*0.34 (5)*
Mg, %	6.26 (26)	6.93 (29)	*7.3 (0.2)*
Al, %	0.999 (30)	0.974 (33)	*0.89 (11)*
Si, %	22.2 (4)	23.5 (4)	*22.7 (8)*
Cl, ppm	52.9 (6.1)	872 (13)	*80*
K, %	0.119 (7)	0.117 (7)	*0.107 (19)*
Ca, %	10.2 (0.3)	10.8 (0.5)	*10.5 (0.5)*
Ti, %	0.218 (4)	0.208 (4)	*0.202 (25)*
Cr, %	0,179 (6)	0.208 (7)	*0.177 (28)*
Mn, %	0.398 (27)	0.388 (30)	*0.382 (31)*
Fe, %	15.3 (5)	14.5 (4)	*16.0 (1.2)*
Co, ppm	91 (11)	79 (12)	*48 (5)*
Ni, ppm	179 (48)	191 (55)	*90*
Sm, ppm	1.46 (9)	1.01 (7)	*0.77 (8)*
Gd, ppm	1.17 (9)	1.08 (7)	*0.86 (8)*

*Values in parentheses are errors due to errors (1σ),
These values correspond to last digit(s) of the preceding
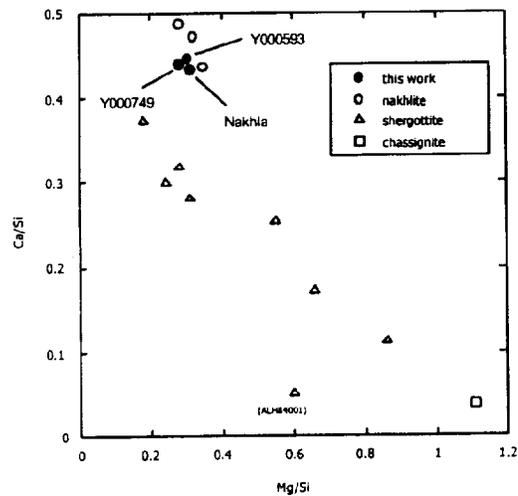figures.
[#]Information values.
[S][3].

Figure 1. Elemental abundance ratios of Mg/Si vs. Ca/Si
for SNC meteorites.

SOME PUZZLES ABOUT WHAT NOBLE GAS COMPONENTS WERE MIXED INTO THE NAKHLITES, AND

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Introduction: Nakhlites, the intermediate-aged (~1300 Ma) Martian meteorites, are similar to one another in noble gas characteristics, as well as mineralogy, but distinct from other Martian meteorites. There are also are subtle differences among the well-studied nakhlites (Nakhla, Lafayette, and Govemador Valadares), which may be important in understanding the processes affecting Martian volatiles. This abstract will summarize some noble gases properties of Martian meteorites, particularly nakhlites, and then highlight five unanswered questions.

To first order, Xe in these meteorites appears to be a mixture of an interior component, seen mostly clearly in Chassigny, and an atmospheric component seen mostly clearly in shergottites like EETA 79001 [1, 2]. Nakhlites are rich in the atmospheric component (Nakhla being the richest), but the component appears to be elementally fractionated, with a higher Xe/Kr ratio than the (atmospheric) component seen in EETA 79001. Nakhlite Ar has been studied most in the context of Ar-Ar age experiments. All three appear to be about 1300 Ma old, but with some disturbances to the system, most noticeable in Nakhla. Shergottites all appear to have either incorporated variable amounts of two different Ar components (interior and atmosphere?), to have incorporated different components from one another, or to have incompletely degassed upon formation.

Question 1: How did atmospheric (?) Xe get trapped in the nakhlites? This topic has been intensively investigated, and several different scenarios have been suggested, each of which has advantages and drawbacks. The basic problem is that while most of the Xe is isotopically indistinguishable from the Martian atmosphere [3], the Kr/Xe elemental ratio is very distinct: it appears that atmospheric gas has been fractionated in favor of the heavier gas. ALH84001 shows a very similar effect although, unlike Nakhla, there may be some isotopic differences [4].

a. Incorporation related to liquid water: Liquid water will produce elemental fractionation of the right magnitude and direction. Since the nakhlites contain the strongest evidence for interaction with liquid water [5], Drake et al. [6] suggested that nakhlites contain atmospheric gas that was elementally fractionated by water. A similar scenario was suggested for ALH84001 [7, 8]. In this scenario, the gas would be in the aqueous alteration products, iddingsite for the nakhlites, carbonate for ALH84001. One problem with this scenario

is that Nakhla has more Xe than Lafayette, although Lafayette has been more heavily altered. Most seriously, two sets of experiments on mineral separates have now shown that the bulk of the gas in the nakhlites is in the major minerals, not alteration products [9, 10]. The gas in ALH84001 is also in pyroxene, not carbonate [11].

b. Magmatic Incorporation: Gilmour et al [9] proposed that the gas was incorporated during crystallization, perhaps from soil degassing as the rock crystallized. It is not clear whether the outgassed material could be incorporated that efficiently. More recently, the same group suggested the next scenario [12].

c. Shock implantation of adsorbed gas: Adsorption will also produce elemental fractionation in favor of the heavy gas, but little or no isotopic fractionation. If shock can implant gas without further fractionation, this process could work. Gilmour et al. originally suggested this for ALH84001 [11], and later suggested it for nakhlites as well [12]. This is probably the leading candidate at the moment, but it has some problems that will be discussed below.

d. Changing atmospheric elemental composition: Musselwhite and Swindle [13] pointed out that Xe could be preferentially incorporated into polar clathrates under certain climate conditions, which would lead to an elemental fractionation in the atmosphere, which could have been implanted without any elemental fractionation (as appears to have happened with the shergottites). Then, the differences between ALH84001 and the nakhlites, on the one hand, and the shergottites on the other could be because of different climate conditions. Since ALH84001 and the nakhlites were all ejected from Mars >10 Ma ago, and the shergottites were all ejected <5 Ma ago, this is at least plausible.

e. Recent addition of a cometary component to the Martian atmosphere: Owen and Bar-Nun [14] also suggested that the Martian atmosphere may suffer elemental changes over millions of years, but suggested that it could be the result of input of cometary gas.

Question 2: Why did the nakhlites and ALH84001 trap elementally fractionated atmosphere, when shergottites and Chassigny didn't? Attributing the effect to aqueous alteration, would have explained this naturally for the nakhlites, but has been ruled out by further experiments. Invoking shock implantation of adsorbed atmosphere is logical, but any shock scenario requires some special pleading.

NAKHLITE NOBLE GAS PUZZLES: T. D. Swindle

The nakhlites have experienced the least shock of any of the Martian meteorites [e.g., Table 1 in [15]], yet have abundant elementally fractionated atmosphere. One possibility is that different amounts of gas were adsorbed, presumably because of temperature. If the nakhlites and ALH84001 were ejected when the atmosphere was colder (because of season, latitude, altitude, or some combination), they might have had more adsorbed atmosphere available for incorporation. Meanwhile, the shergottites experienced higher shock pressures, high enough to produce melt glass that incorporated unfractionated atmosphere. But what about Chassigny, which very possibly was ejected in the same event as the nakhlites[15]? Also, EETA79001, ALH84001, and Chassigny experienced comparable shock pressures [15], but the first incorporated copious quantities of unfractionated atmosphere, the second incorporated elementally fractionated atmosphere, and the third incorporated no atmosphere at all. Other differences (e.g., the presence of vesicles or the time of incorporation) could explain at least some of the difference, but could such differences explain everything?

Question 3: Why did Chassigny incorporate so much more interior Kr and Xe than any other Martian meteorite? By far the best sample of Kr and Xe from a component that appears to represent the Martian interior comes from Chassigny [1, 2, 4], although this component is apparently present in Nakhla as well [3]. On Earth, the best samples of mantle noble gases come from quickly cooled undersea basalts [16]. Although it is a dunite, a reasonable choice for a mantle-derived rock, Chassigny is definitely not a chilled basalt.

Question 4: Why do shergottites show signs of interior-derived Ar, when the nakhlites and Chassigny do not? Shergottites are notorious for having one or more trapped argon components that make it virtually impossible to perform ^{40}Ar-^{39}Ar dating [17]. This would be relatively easy to understand if it were merely because of the presence of atmospheric Ar associated with the elemental unfractionated (i.e., high Ar/Xe) atmosphere trapped in impact glasses. However, a simple correction for Martian atmosphere still does not yield interpretable results [17]. Rather, the "trapped" argon seems to be a mixture of Martian atmosphere and a component with a lower $^{40}Ar/^{36}Ar$ ratio, presumably from the crust or mantle [17, 18]. Chassigny and the nakhlites, on the other hand, seem to have much simpler Ar-Ar systems [17, 19, 20]. Yet in Xe, the shergottites seem to have less evidence for any interior component. An obvious source for the interior-derived Ar in shergottites is crustal material that may have been assimilated. However, shergottite QUE94201 has one of the lowest $^{40}Ar/^{36}Ar$ ratios [18] (implying the most

crustal material), but it seems to have assimilated the least material, based on other criteria

Question 5: Why does the Ar-Ar pattern in Nakhla the most disturbed of the nakhlites, when Lafayette has the most evidence for aqueous alteration? Both Lafayette and Governador Valadares have relatively simple Ar-Ar patterns, suggesting crystallization ~1300Ma ago, with only a little evidence for loss of radiogenic ^{40}Ar since [19, 20]. Nakhla shows much more evidence of later disturbance than Lafayette or Governador Valadares [19, 20], and also gives an Ar-Ar age that is the same or older, even though it gives slightly younger ages in other systems [15]. A quick answer to part of the question is that the products of aqueous alteration must not be affecting the Ar-Ar systematics much. While that must be true, it still doesn't explain what the source of disturbance in Nakhla is. The key to the answer may be that while the nakhlites are all similar, they are not identical. For example, Nakhla's Sm-Nd systematic is also distinct from the other two [21, 22]. Remember that in the Kr/Xe system, Nakhla is again slightly, but distinctly, different as well. The distinction in histories may be sufficient to explain the noble gases.

To solve these noble gas puzzles, we may ultimately have to understand more details about the magmatic, eruption, and even climate history of these meteorites than we currently do.

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ELEMENT-ELEMENT CORRELATIONS AMONG MARTIAN METEORITE BULK COMPOSITIONS: PECULIARITIES EXPLAINED(?) BY MIXING, WITH IMPLICATIONS FOR THE COMPOSITION OF MARS.

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Correlations of elements abundances among the Martian meteorites have been used to infer the bulk composition of the Martian mantle [1-3], and thence the broad petrogenesis of the planet. It has been assumed that the correlations represent igneous fractionations. However, the correlations are also consistent with mixing, broadly similar to that inferred from radio-isotope data. If the correlations represent mixing of geochemical components, it is not clear that they represent Mars' mantle or bulk composition.

Introduction: Most estimates of the chemical composition of Mars' mantle and core derive from element-element correlations bulk analyses of Martian meteorites [1-3]. To use the correlations in this manner assumes implicitly that they reflect mineral/melt fractionations (e.g., partial melting, fractional crystallization, accumulation) among a cogenetic suite of igneous rocks. However, similar correlations can appear from mixing of chemical components, and need not imply that the components were cogenetic nor that they had an igneous origin.

Several aspects of the elemental and isotopic chemistries of the Martian meteorites can be explained by mixing of geochemical components (mantle or crustal), e.g. [5,6]. Thus, it is worth asking whether mixing relations might be seen in bulk chemical data, and (if so) whether the mixing components can be used to infer average planet or mantle compositions.

Data: Data are from compilations [2, 7]. Where many analyses were available, a single average value was used. Where there were few or discrepant analyses, judgment favored large samples and recent results. Considerable scatter is expected for elements (S, Se) that are concentrated in minor or trace phases.

Results: For the most part, new analyses confirm the correlations noted >20 years ago. Treiman et al. [2] found that nominally incompatible elements could be divided into two groups that covaried coherently (Figure 1). Group 1 elements (highly incompatible) include: La, Ag, As, Au, Ba, Br, Cl, Cs, K, Li, Rb, Sb, Ta, Th, U, and W. Group 2 elements (moderately incompatible) include: Ti, Al, Cu, Eu, Ga, Hf, the HREE, In, Na, P, S, Sc, Se, Tl, and V. Elements in one group did not covary cleanly with those of the other group (Figure 1). Most of these correlations are as expected for basaltic systems; e.g., highly incompatible elements do not enter solid phases, and so become equally concentrated in progressive melt fractions. Correlations of
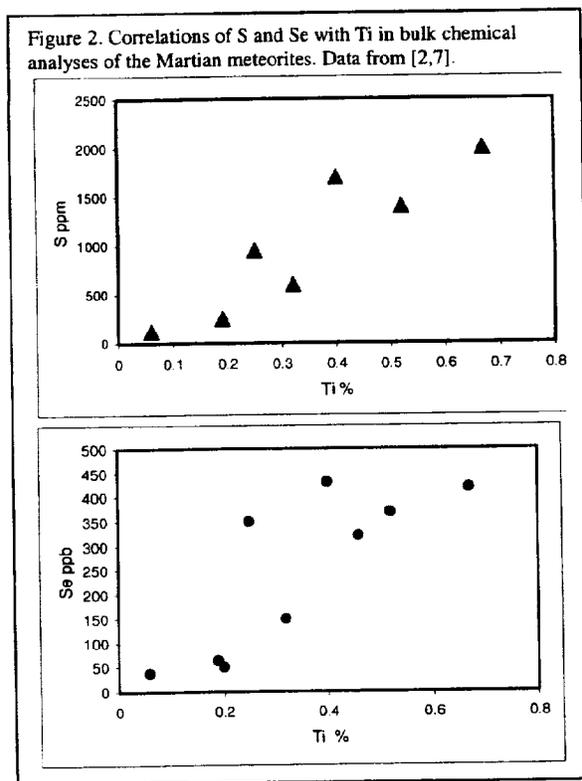
Ti with Na, Al, and Ga are also expected for Martian basalts, where plagioclase is not a liquidus phase. A few elements were found to behave compatibly (Ni, Cr), and a few 'indifferent' elements had constant abundances across the whole sample suite (e.g., Co, Re).

Figure 1. Correlations of P with La and Ti in bulk chemical analyses of the Martian meteorites. Data from [2,7].
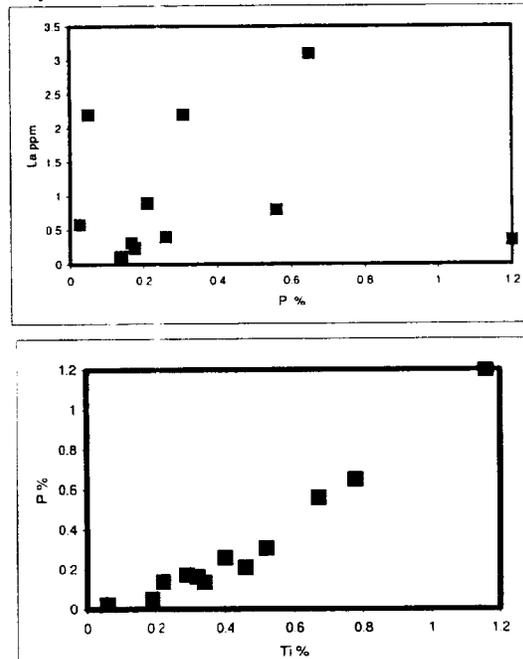
Unexpected Results. The behaviors of a few elements are unexpected or bizarre. Abundances of phosphorus closely track those of other moderately compatible elements (Fig. 1b), whereas in most cases P tracks highly incompatible elements like La (Fig. 1a). Second, abundances of the chalcogenides S and Se also track those of Ti and other moderately compatible elements (Fig. 2). In terrestrial basalts and mantle rocks, S and Se are not correlated with any lithophile elements but track other chalcogenides (Re, Ag) so to suggest a separate sulfide phase in the source [2].

Interpretations: The element-element correlations listed above have been interpreted as products of igneous fractionation, but might also represent mixing lines.

Figure 2. Correlations of S and Se with Ti in bulk chemical analyses of the Martian meteorites. Data from [2,7].

The correlation of P with other moderately incompatible elements is a problem – it requires that P the average bulk $^PD_{solids/basalt}$ be > 0.1, significantly higher than in typical terrestrial petrogenesis. This can perhaps be justified by invoking high P-T fractionation with olivine ($^PD_{ol/basalt}$ ~0.1) and/or garnet ($^PD_{gar/basalt}$ ~ 0.3) [8,9]. Even higher bulk D values may be required by the fractionation of HREE from LREE [10].

The correlation of S and Se with moderately incompatible lithophile elements is difficult to explain by igneous processes. Neither sulfide nor sulfate (nor selenide nor selenate) has is significantly soluble in common rock-forming minerals. Igneous sulfide is common but minor in the Martian meteorites, and there is no reason to expect that it would fractionate coherently with silicate minerals (e.g., pyroxene). The Martian meteorites contain no igneous sulfate minerals. They do contain rare secondary sulfate minerals but there is no obvious reason that the abundance of secondary sulfates should follow those of Ti, HREE, Al, etc.

Mixing as an Explanation (?): In a formal sense, the co-linearities seen in bulk chemical data can be explained by mixing of at least three components: **a** – a reservoir rich in highly incompatible (Group 1) elements; **b** – a reservoir rich in moderately incompatible (Group 2) elements; and **c** – a reservoir strongly depleted in all incompatible elements and so presumably rich in ferromagnesian and compatible elements. The

meteorite richest in component **a** would be Nakhla, which has high La and low Ti and P. This assignment is stronger for Nakhla's parent magma, which is inferred to contain Ti=0.46%, P=0.26%, La~6ppm [10,11]. The meteorite richest in component **b** would be QUE94201, which in has the highest abundances of P and Ti, but low La etc. The meteorites seemingly richest in component **c** are the olivine-phyric basalts like DaG and SaU, which have low abundances of elements in both Groups 1 and 2 (e.g., La and Ti).

These bulk-chemical components have some correspondence with components derived from isotopic systematics [5,6,12]. It may be possible to "flesh out" the isotopically defined components into estimates of rock compositions, and thus better constrain their origins.

Estimates of the bulk composition of Mars are thrown in some doubt if the element-element correlations are mixing lines. Then, one has to ask if the mixing components represent only products of an igneous event (e.g., magma ocean differentiation). If so, then the element-element correlations may reflect planetary compositions. If not, or if the components have been affected by other processes (e.g. aqueous alteration of crust with introduction of sulfur), then all bets are off.

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CHEMISTRY AND MICROTEXTURES OF MELT POCKETS IN THE LOS ANGELES BASALTIC SHERGOTTITE.

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Introduction: Los Angeles is a non-brecciated, highly shocked basaltic shergottite. The shock effects in Los Angeles can be classified into two basic types: (1) mechanical deformations and transformations that take place essentially in the solid state; and (2) localized regions of shock melting forming glassy to microcrystalline enclaves. A brief description of the former type, based largely on optical observations, is given by [1]. They describe the complete transformation of plagioclase to maskelynite, mosaicism and planar fracturing of clinopyroxenes, pyrrhotite veins within clinopyroxene, polycrystallinity of some pyrrhotite grains, and a 350 μm-long fault with ≈ 15-μm displacement. These results are in agreement with this study.

This work presents a detailed description of the shock-related microtexture and mineralogy of the localized melt pockets which have formed by *in situ* melting of local mineral phases. The melt pockets range from 3 mm $\times$ 3 mm – 0.07 mm $\times$ 1.25 mm, in direct contact with the host matrix. Two polished thin sections of stone 1 (1.3 cm $\times$ 1 cm, 2.1 cm $\times$ 1.2 cm) have been investigated to determine the mineralogy and microtextures of the shock-induced melt pockets using a JEOL 6400 digital scanning electron microscope equipped with a Link Analytical eXL energy dispersive spectrometer (EDS) fitted with a Si (Li) LZ-4 Pentafet detector, and a FEG-SEM equipped with the In-Lens Thermal FEG which produces high probe current sufficient for EBSP, WDS, and EDS. These instruments are capable of characterizing compositional variations and microtextures of the melt pockets that are unresolvable using optical techniques.

Melt pockets — an overview: Los Angeles stone 1 contains several unusual localized regions of shock melting which are texturally very different from typical melt veins observed in other SNC meteorites (e.g., Zagami) and ordinary chondrites. Melt pockets are contained within the two dimensions of the thin sections. Optically the melt pockets appear as irregularly-shaped dark brown to black coloured areas which are often observed to be spatially related to large, open fractures infilled with calcite. Three texturally distinguishable types have been observed: (1) Small (0.5 mm $\times$ 0.70 mm; 0.07 mm $\times$ 1.25 mm) vesiculated, clast-rich melt pockets with abundant crystallites indicative of quenching. Entrained clasts have subangular morphologies and consist of isotropic whitlockite, isotropic plagioclase significantly enriched in K_2O (Or_{19-28}) compared to maskelynite in the adjacent host rock ($An_{40}Or_{4-11}$), and SiO_2 clasts (95.02–98.35 wt% SiO_2 with variable amounts of Al_2O_3). Clast size ranges from 200 μm to 0.5 μm; avg. = 39 μm (n = 100). The contact with adjacent host rock minerals varies from smooth boundaries to intrusive stringers and veins of shock-induced melt material One such melt pocket contains clasts which display interior quench textures, possibly inherited from a previous impact event. (2) Small (0.03 $\times$ 0.04 mm) vesiculated, clast-poor (relatively) melt pockets with abundant crystallites of hollow SiO_2 rods (with minor

amounts of Al_2O_3). (3) With increasing volume of melt (3.5 mm $\times$ 3.0 mm) textures are dominantly vesicular, clast-poor (relatively) with flow textures and abundant spheres/blebs of immiscible Fe-sulphides. These range in size from 20 μm to >0.1 μm and comprise mono- and poly-crystalline pyrrhotite. Most vesicles are spherical, indicative of quenching at low confining pressure, however, some are elongated with their c-axis parallel to the direction of flow. Opaques within these shock-produced glasses are perfectly spherical. It is interpreted that the vesicles were elongated by fluidal flow in the molten host, followed by quenching to produce glass, and spherical globules of sulphides. Vesicles range from 0.5 mm to ≥ 1 μm apparent diameter.

Quench Textures: The crystals formed during quenching have a variety of distinctive shapes (skeletal, dendritic, feathery) and comprise a variety of minerals (olivine, whitlockite, ulvospinel, plagioclase). Quench crystals are invariably microscopic (microlites, crystallites). The groundmass consists of glassy material rich in Fe, Mg and Ca and is relatively pristine showing no signs of devitrification or alteration to aggregates of new phases (e.g., clays, iddingsite).

Severely fractured, melt intruded clinopyroxenes adjacent to the melt pockets allow for preferential nucleation of dendritic crystals that extend from the contact into glasses. These consist of intimate intergrowths of pigeonite and orthopyroxene with dendritic textures. In addition, clasts within melt pockets serve as nucleation sites for dendritic growth. These textures are consistent with rapid crystallization of the melt.

Discussion: Remobilization and injection of opaques and melt from the melt region into pre-existing fractures in adjacent pyroxene in the host rock could have occurred during compression and subsequent stress relaxation. Although the contact between the melt pockets and adjacent host rocks is observed to be smooth to arcuate, it is also intrusive in areas, it is thought that these could have formed by pressure generated by a volume increase associated with the melting event, and that the melt pockets have formed *in situ*. With increasing volume the melt pockets comprise texturally heterogeneous (flow-structured and meandering) schlieren-rich glasses. These show compositional variability related to the melting of variable proportions of the major rock-forming minerals (plagioclase and pyroxenes) of the host meteorite and incomplete mixing of melt. Abundant quench textures attest to rapid cooling of the shock-induced melt. The high abundance of relatively cold clasts in the smaller melt pockets probably contributed to the quenching of the melt to generate abundant crystallites and an absence of flow textures.

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