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EXCHANGE BETWEEN THE ATMOSPHERE AND THE REGOLITH OF MARS: DISCUSSION OF OXYGEN AND SULFUR ISOTOPE EVIDENCE. J. Farquhar ESSIC and Department of Geology, University of Maryland, College Park, Maryland, 20742 (jfarquha@essic.umd.edu).

Introduction: Mass-independent fractionations for oxygen isotopes and sulfur isotopes between secondary phases and primary igneous phases in SNC meteorites have been interpreted to reflect a difference between surface and deep oxygen and sulfur reservoirs on Mars [1-6]. Several hypotheses have been proposed to explain this observation such as fractionation by escape processes (in the case of oxygen), addition of a late veneer of anomalous oxygen and sulfur, and mass-independent atmospheric chemistry [1, 4, 5, 7, 8]. The observation of a variable magnitude mass-independent oxygen isotope signature for carbonate and water among different meteorites, and for carbonate and sulfate from the same meteorite (Nakhla) is most consistent with the latter interpretation.

Narrowing the source of the sulfur isotope data is less straightforward but bears on the question atmosphere-surface oxygen exchange because it may reflect a similar process. The magnitude of the mass-independent fractionations for sulfate sulfur from Nakhla and for isolated grains in ALH84001 [1, 3] are larger than those seen for all analyses of whole rock sulfide and sulfate from other meteorite groups (e.g., [9-11]). This argues against an origin associated with addition of a late veneer of exotic sulfur. Experimental and theoretical evidence allows a gas-phase (atmospheric) origin for these mass-independent sulfur and oxygen isotope signals [12], and the observation of mass-independent sulfur isotope signatures in atmospheric and atmospheric-derived species on Earth [13] provides a consistency argument in favor of similar processes operating on Mars. Mass-independent oxygen and/or sulfur isotope signatures have been observed in terrestrial sulfate aerosols, ice core sulfate from stratosphere-piercing volcanic eruptions, and terrestrial rock samples older than 2.0-2.5 billion years old [3, 12, 14, 15]. For sulfur, these signatures are larger than the largest that have been identified in the meteoritic record and direct transfer of atmospheric sulfur species such as sulfate to the surface has been suggested as the source for the SNC signature. (Minor components of some carbonaceous chondrites have been shown to possess mass-independent signatures up to a few permil.)

The Earth-centered perspective also tells us that the exchange pathways and local reservoir sizes for oxygen and sulfur can play a significant role in the transfer and preservation of these signals in the rock record leading to the interpretation that the sulfur and oxygen isotope signature in sulfate sulfur may reflect direct

transfer of the sulfate from the atmosphere to the surface, but that the oxygen isotope signatures for carbonate and water may reflect the transfer of oxygen from another species that itself acquired a mass-independent oxygen isotopic composition from the atmosphere.

Consideration of the amounts of oxygen in the carbonate and water, leads to the suggestion that the isotopic composition of both species was buffered by an oxidized species in the regolith that itself had a mass-independent oxygen isotopic composition. This oxidized species may have been directly deposited to the regolith, or formed by oxidation of another species by reaction with a mass-independent species like ozone. The signature would then be transferred from the water to the carbonate during carbonate formation. In the case of SNC carbonate, this interpretation would imply that the amounts of aqueous phase were limited, or at least comparable to the amounts of the phases in the regolith with which they exchanged oxygen. The significance of this observation for the Martian surface oxygen reservoirs is that it suggests the absolute amounts of oxygen stored in liquid phase water may have been small, and that transfer of oxygen between phases in the regolith and the martian atmosphere is a common phenomenon. The observation of this signature in carbonate from ALH84001 suggests that the conditions required for the production and preservation of these signals in the SNC record extend were established early in Mars's history.

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OXYGEN AND HYDROGEN ISOTOPE SYSTEMATICS OF ATMOSPHERIC WATER VAPOR AND METEORIC WATERS: EVIDENCE FROM NORTH TEXAS . K. M. Ferguson¹ and R. T. Gregory¹, ¹Stable Isotope Laboratory, Department of Geological Sciences, SMU PO Box 750395, Dallas TX 75275; kferg@smu.edu

Introduction: Understanding the relationship between surface temperature and the oxygen and hydrogen isotopic composition of meteoric water is critical for unraveling the climate history of the Earth. The correlation between mean annual temperature and the isotopic composition of precipitation forms the basis of interpretation of temperature fluctuations in ice core data and hence some similar relationship may obtain for a planet like Mars. The signal inferred from ice measurements correlates with oxygen isotope ratios determined from marine sediments that documents 450,000 years of glacial-interglacial cycles [1].

Why Dallas?: Dallas, Texas, sits in the pathway of Polar, Pacific, and Gulf of Mexico air masses. Stable isotopes being a conservative tracer provide an opportunity to track the time integrated history of air masses interacting over Dallas. Isotopic concentration data provide hard constraints on storm and air mass evolution currently modeled by weather forecasting programs and global circulation models.

Methodology: For the years 2001-2003, we sampled individual precipitation events over periods lasting between minutes to hours to examine intrastorm isotopic ratio variability in the context of satellite and radar images taken over the same time intervals. In order to gain a more continuous record, we began monitoring the isotopic composition of the atmospheric water vapor at approximately 30 m above the ground on a daily basis.

Results: Over the 2+ year period, our data capture a good portion of the temperature-water isotope variability of the International Atomic Energy Agency data set, e.g., [2]. Despite ¹⁸O values ranging from +8 to -18 permil, there is only a weak correlation with temperature for most storms, or for longer term time averages. Meteoric waters define meteoric water lines of:

$$D = 7.01 \text{ }^{18}\text{O} + 8.29 \quad R^2 = 0.90 \quad 2001$$

$$D = 7.13 \text{ }^{18}\text{O} + 7.61 \quad R^2 = 0.93 \quad 2002$$

Distribution diagrams for isotope data for these two years show slightly different means (2001 mean ¹⁸O = -4.0, n = 433; 2002 mean ¹⁸O = -5.0, n = 517), suggesting different proportions of Gulf moisture (the dominant source) and more ¹⁸O-depleted Polar or Pacific sourced moisture. In D-¹⁸O plots, cloud bands exhibit distinctive isotopic evolution suggesting that water vapor maintains isotopic heterogeneities over significant distances and further suggesting stirring without homogenization by mixing. Comparison of the values of the water vapor against 1/concentration

suggests two end-member behaviors: 1) isotopic depletion by advection between air masses of different provenance and 2) isotopic depletion by distillation (rain-out effect). Comparison of isotopic data from storm events with satellite imagery provides evidence of the relative importance of the two end-member processes. An example is shown in Figure 1 for February 15-16, 2001. The 4.5 permil oxygen isotope depletion in the early morning of Feb., 16 occurred over approximately 2 hours, with no correlation between surface air temperature and ¹⁸O. Satellite imagery of the storm suggests at least part of the depletion event may result from advection of higher altitude, isotopically depleted air towards the surface.

The dominant source of moisture for Dallas meteoric water is from the Gulf of Mexico, not necessarily clear from examination of satellite images. During intense rainout events, on rare occasions, evidence of mixing with supercooled or ¹⁸O-depleted upper air masses is inferred by changes in the slope and intercept of the meteoric water line during huge collapses of the unstable air mass.

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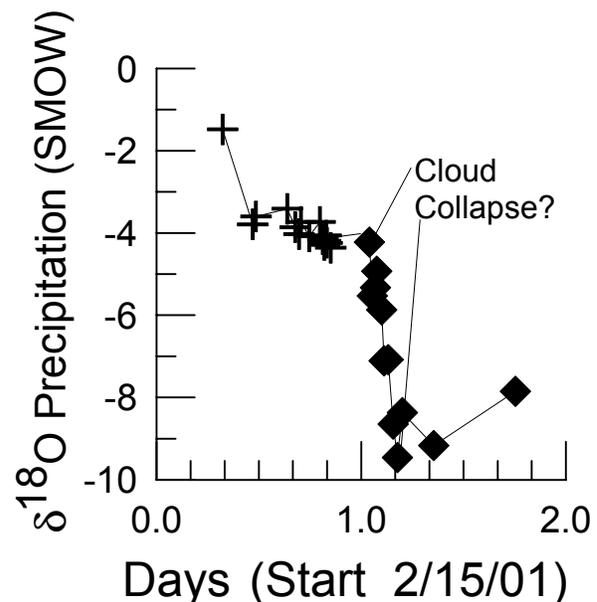


Figure 1. ¹⁸O-time graph for storm of February 15-16, 2001. Crosses represent meteoric water samples from Feb. 15, filled diamonds samples from Feb. 16.

IMPLICATIONS OF ISOTOPIC AND REDOX HETEROGENEITIES IN SILICATE RESERVOIRS ON MARS. C. N. Foley¹, M. Wadhwa¹, L. Borg², and P. E. Janney¹, ¹ Isotope Geochemistry Laboratory, Department of Geology, The Field Museum, 1400 S. Lake Shore Dr., Chicago, IL 60605, nfoley@fmnh.org, ²Institute of Meteoritics, University of New Mexico, Albuquerque, NM 87131.

Introduction: New constraints on Nd and W isotopic systematics [1] show that there is no simple linear relationship between $\epsilon^{142}\text{Nd}$ and $\epsilon^{182}\text{W}$ values in the Martian meteorites as was suggested by [2] based on earlier data [2, 3]. Instead, three distinct end-members are apparent: LREE-enriched shergottites, such as Shergotty and Zagami, which have chondritic $\epsilon^{142}\text{Nd}$ and superchondritic $\epsilon^{182}\text{W}$ ($\sim 0\epsilon$ and $\sim 0.5\epsilon$, respectively, relative to terrestrial); LREE-depleted shergottites, such as DaG 476, with superchondritic $\epsilon^{142}\text{Nd}$ and $\epsilon^{182}\text{W}$ ($\sim 0.9\epsilon$ and $\sim 0.5\epsilon$, respectively, relative to terrestrial); and the nakhlites-chassignite (NC) with superchondritic $\epsilon^{142}\text{Nd}$ and $\epsilon^{182}\text{W}$ ($\sim 0.7\epsilon$ and $\sim 3\epsilon$, respectively, relative to terrestrial). These systematics reveal that early differentiation events on Mars resulted in the formation of at least three distinct silicate reservoirs which have subsequently remained unaffected by global convective mixing. In particular, as discussed in [1], core formation occurred early (within ~ 12 Ma from the beginning of the solar system) followed by a silicate differentiation event (~ 20 - 25 Ma after solar system formation) which established a mantle reservoir with the unique NC source characteristics; continued silicate differentiation (extending >45 Ma after solar system formation, when ^{182}Hf was extinct but ^{146}Sm was extant) resulted in the formation of two end-member silicate reservoirs involved in shergottite petrogenesis, i.e., a depleted mantle reservoir and an enriched (mantle or crustal) reservoir. Here we will discuss the constraints on the redox conditions in these three isotopically distinctive silicate reservoirs and how they may relate to their isotopic characteristics.

Shergottite isotopic and redox systematics: The basaltic shergottites record a range of magmatic redox conditions [4, 5, 6]. It has been suggested that the apparent correlation of magmatic redox conditions with other geochemical and isotopic parameters (such as initial $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ ratios and the degree of LREE-enrichment in the shergottite whole rocks) indicates that this range may result from the assimilation of varying amounts of an oxidized crust-like component by melts derived from a depleted, reduced mantle reservoir [4, 6]. In this scenario, the oxidation of the crust-like component may have occurred *at any time* prior to its assimilation into the mantle derived melts.

Alternatively, variations in the oxygen fugacities of shergottite magmas may reflect the mixing of melts derived from depleted and enriched mantle sources that were the crystallization products of an ancient magma ocean [7]. In this scenario, the redox conditions in the depleted (reduced) and enriched (KREEP-like, hydrous and oxidized) sources were established *early*, at the

time of magma ocean crystallization. These two alternatives have implications for the timing at which redox heterogeneities in silicate reservoirs on Mars were established. As discussed by [7], the decoupling of major element and trace element-isotopic systematics in the shergottites supports the latter scenario, and could indicate that isotopic and redox heterogeneities in the two shergottite end-member sources are causally related and were established early.

Nakhlite isotopic and redox systematics: The nakhlites show isotopic and redox systematics that are quite distinct from the shergottites. As mentioned earlier, $^{147,146}\text{Sm}$ - $^{143,142}\text{Nd}$ and ^{182}Hf - ^{182}W isotope systematics in the nakhlites indicate that their source was established prior to the two shergottite end-member sources discussed above [1]. Moreover, while the initial $\epsilon^{143}\text{Nd}$ values for the nakhlites suggest a long-term depletion in the nakhlite source [8], the estimated parent melt compositions for these pyroxenites are LREE-enriched [9,10]. Finally, estimations of magmatic redox conditions for the nakhlites indicate that they originated from an oxidized source (close to $\sim\text{QFM}$) [10,11].

Therefore, while the depleted shergottite end-member mantle source was highly reduced, the depleted (and isotopically distinct) nakhlite source was relatively oxidized. It has been suggested that the decoupling of the isotope and trace element systematics in the nakhlites may be accounted for by late metasomatism of the nakhlite source by an LREE-enriched fluid [7,10]. Late mantle metasomatism by an LREE-enriched, oxidizing (possibly hydrous) fluid could also account for the oxidation of the nakhlite source.

Implications: The main implication from the above discussion is that redox conditions of mantle sources on Mars may largely have been established early (most likely during crystallization of the ancient magma ocean). However, late mantle metasomatism may have subsequently modified the redox conditions in some of the early established mantle reservoirs.

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OXYGEN ISOTOPIC VARIATION OF THE TERRESTRIAL PLANETS. I. A. Franchi and R. C. Greenwood, Planetary and Space Sciences Research Institute, Open University, Walton Hall, Milton Keynes, MK7 6AA, UK (i.a.franchi@open.ac.uk)

Introduction: Since the seminal work of Clayton and co-workers [1] it has been clear that there was oxygen isotopic heterogeneity in the most primitive materials in the solar nebula, with variations of up to 50‰ in $\delta^{18}\text{O}$ and over 25‰ in $\Delta^{17}\text{O}^1$ in materials formed or at least heavily processed within the nebula. In the terrestrial planets (Earth, Moon, Mars and the HED parent body (possibly Vesta)) the range in $\delta^{18}\text{O}$ values can remain very large, especially on geologically active bodies, particularly the Earth where low temperature reactions with water can play an important role in developing large isotopic variations. However, the variation that is now seen in $\Delta^{17}\text{O}$ is <1‰ [e.g. 3], with the variation from each body generally much less. This limited range in the $\Delta^{17}\text{O}$ values is generally believed to be the result of large volume homogenization during widespread heating/melting events during the history of these planets and large asteroids. However, variation still exists within and between the suites of rocks from each of the terrestrial planets, and this can provide valuable information on their origin, inter-relationship and evolution. In order to extract this information it is necessary to measure the oxygen isotopic composition of clean, well characterised materials to very high precision.

We have undertaken a number of studies covering most the main sample suites from evolved planets or asteroids using a technique of laser (CO_2 laser @ 10.6 μm) assisted fluorination (BrF_3) coupled to a high dispersion, high precision mass spectrometer (VG PRISM III). This offers analytical precision for $\delta^{18}\text{O}$ and $\delta^{17}\text{O}$ of 0.08 and 0.04‰ respectively, but as much of this uncertainty is related to gas handling fractionation the $\Delta^{17}\text{O}$ uncertainty is <0.025‰ [4] and allows us to determine mass fractionation lines with uncertainties down to ± 0.013 ‰ [e.g. 5] –

approximately 50 times smaller than the variation displayed by the terrestrial planets/asteroids.

Oxygen Isotope Variation: Within the limited range of $\Delta^{17}\text{O}$ values displayed by samples of the terrestrial planets three broad grouping could readily be discerned – Mars, the Earth/Moon and the basaltic meteorites (HEDs, angrites, plus various other meteorite types) [3] allowing discrimination of the groups, useful in the classification of new meteorites, and offering insight into the degree of homogenization and into the identification of the relative contributions of possible primitive precursors. High precision analyses have revealed considerable more detail to this initial picture. The SNC meteorites define a martian fractionation line with a $\Delta^{17}\text{O}$ value of $+0.032 \pm 0.01$ [5]. The basaltic meteorites (HEDs and angrites) previously defined what appeared to be a single, albeit relatively poorly defined mass fractionation line. However, as shown in Figure 1 the HEDs define what appears to be a well defined fractionation line ($\Delta^{17}\text{O} = -0.24 \pm 0.007$) with the angrites ($\Delta^{17}\text{O} = -0.072 \pm 0.007$) now clearly resolved. In contrast, high precision measurements of lunar rocks by Wiechert et al [6] shows that there is no isotopic difference between the Earth and the Moon.

Discussion: While the oldest, and possibly least precise of the high precision data the SNC meteorites clearly define a single martian fractionation line. Virtually all martian meteorites have relatively young crystallization ages but the data set includes ALH 84001, a sample of ancient crust with a crystallization age of approx 4.5Ga. As such it is clear that homogenisation of any initial isotopic heterogeneity occurred within the first few tens of millions of years after formation [5]. Even more rapid melting and homogenization may be required for 4 Vesta (HEDs) as all but one (Pasamonte) of the eucrites and diogenites fall on a single mass fractionation line, despite the fact that there are several geologically distinct groups with different histories within the eucrites. The anomalous nature of Pasamonte was also detected by [7] who also reported two other meteorites with similar $\Delta^{17}\text{O}$ values – suggesting that in fact some isotopic heterogeneity was retained within Vesta as cooling progressed. It may be that these anomalous eucrites are not from the same parent body, or were contaminated by impactor material or that homogenization was not complete.

¹ Virtually all physical processes acting upon any homogeneous reservoir of oxygen, will have an impact on the $^{16}\text{O}/^{17}\text{O}$ ratio approximately 0.52 times that of the effect on the $^{16}\text{O}/^{18}\text{O}$ ratio – such that on a three isotope plot ($\delta^{17}\text{O}$ vs $\delta^{18}\text{O}$) any such suite of samples resulting from this reservoir would plot upon a line of slope 0.52 [2]. The $\Delta^{17}\text{O}$ value is defined as the offset from such a line defined by crustal and mantle rocks from Earth ($\Delta^{17}\text{O} = \delta^{17}\text{O} - (0.52 * \delta^{18}\text{O})$)

Further detail on the geochemical similarities and differences between the oxygen isotope populations within suites of similar basaltic rocks will go a long way to helping to resolve this problem, but will also shed considerable light on the structure of this body as it formed.

The angrite meteorites are another suite of ancient basaltic meteorites. Geochemically distinct from the HEDs, they are now clearly resolved on the basis of oxygen isotopes as well. With very ancient crystallization ages homogenisation of the angrite parent body must have been very rapid. It should be noted that a fairly typical eucrite (Ibitira) has a $\Delta^{17}\text{O}$ value indistinguishable from the angrites – which raises the question as to whether a geological relationship exists between the angrites and (at least) some of the eucrites.

Other examples of the use of high precision oxygen isotope analysis includes the complete similarity in the $\Delta^{17}\text{O}$ value of the Moon and the Earth which has been taken to show that the Earth and Theia (putative Moon-forming Earth impactor) were formed from the same material, presumably at a similar heliocentric distance [6].

High precision oxygen isotopic measurements are required on a number of other groups with close associations with the basaltic meteorites (e.g. the mesosiderites) in order to determine if they have distinguishable isotopic reservoirs, and in combination with detailed geochemical data determine if these reservoirs originate on a single or discrete parent bodies.

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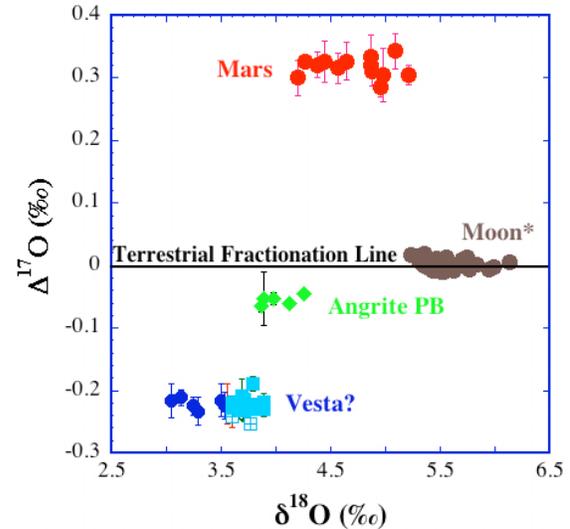


Figure 1 – Oxygen isotopic variation of the terrestrial planets. On this modified version of a three isotope plot mass fractionation lines (constant $\Delta^{17}\text{O}$) plot as horizontal lines. Terrestrial data not shown as this spans a very large range in $\delta^{18}\text{O}$ but has a similar scatter to lunar and martian data sets [e.g. 5,7]. Lunar data from [6].

REDOX EXCHANGES IN HYDROUS MAGMA. F. Gaillard¹, B.C. Schmidt¹, C. A. MacCammon¹, M. Pichavant², B. Scaillet² and S.J. Mackwell³. ¹Bayerisches Geoinstitut, Universitt Bayreuth, D-95440, Bayreuth, Germany; ²ISTO, 1A rue de la Ferrollerie, 45071 Orleans cedex 2, Orléans, France; ³Lunar and Planetary Institute, 3600 Bay Area Boulevard, Houston, TX 77058.

Abstract: Contrasts in redox conditions prevailing in magma within the Earth have been and are still responsible for extensive large-scale chemical differentiation during the past 4.6 billion years. The formation of the core is likely attributable to a primary magma ocean in equilibrium with Fe-metal in the early age of the Earth [1]; the oceanic crust is constructed by accretion of mid-ocean-ridge-basalt containing dominantly ferrous iron [2]; and the continental crust probably derives from subduction-related arc-magmas that contain ~20-60% of iron in the ferric form [3]. These redox controls on the magma-derived stratification of the Earth underline the need for a fundamental understanding of mechanisms and rate of redox exchanges in natural silicate melts.

The redox state of a melt is commonly associated with its iron redox ratio $\text{Fe}^{3+}/\text{Fe}^{2+}$ and correlated to the intensive parameter oxygen fugacity, $f\text{O}_2$. Since the 1960s, numerous experimental studies have contributed to the calibration of the thermodynamic relationship between $f\text{O}_2$, $\text{Fe}^{3+}/\text{Fe}^{2+}$, T , and chemical composition of the silicate liquid [4-5]. In contrast, the nature of the rate and mechanisms of acquisition of redox state in anhydrous melts has only been recently elucidated and it has been shown that migration of both monovalent and divalent cations rate-limits the kinetics of iron oxidation-reduction in silicate melts [6]. However, natural silicate melts contain water in the range of hundred of ppm to several wt% [7], which contribute, in comparison to anhydrous systems, an additional redox couple, $\text{H}_2 / \text{H}_2\text{O}$. Due to the great mobility of both H_2 and H_2O species, the application of the reaction mechanisms indentified in dry melt is questionable in the case of water-bearing melts.

Cylinders of crystal free glasses were exposed, at high temperature (and pressure), to atmospheres containing $\text{H}_2\text{-H}_2\text{O-Ar-CO}_2\text{-CO}$. The progression of a redox front within the glass was optically monitored and the associated chemical migrations were characterized using electron microprobe, infrared and Mössbauer spectroscopies. The advancement of the redox front was shown to be proportional to the square-root of time, revealing the overall reaction as a diffusion-limited process. Iso- $f\text{O}_2$ experiments performed with different gas mixtures, $\text{CO}_2\text{-CO}$, Ar-H_2 , and $\text{CO}_2\text{-H}_2$, have shown that the hydrogen fugacity, $f\text{H}_2$, rather than $f\text{O}_2$ is the dominant parameter controlling the reaction rate. The $f\text{H}_2$ dependence of the reaction rate

was then characterized in the range 0.02 to 70 bar of $f\text{H}_2$. The growth rate of the redox front, which is accompanied by changes in the quantity of reaction-derived OH-groups, was successfully fitted considering that the reduction rate is controlled by the migration through the melt of a free mobile species (H_2) immobilized in the form of OH subsequent to reaction with ferric iron. The extremely weak temperature dependence of the reaction rate was shown to be consistent with the activation energy for molecular H_2 migration in silicate melt (~40 kJ/mol). Furthermore, we extracted a solubility law for molecular H_2 in silicate melts that matches well the results of previous studies. Probably due to its small size, we found that both solubility and mobility of H_2 in melt is almost insensitive to the structure of the melt [8].

We therefore provide a model that allows the prediction of oxidation-reduction rates in the presence of hydrogen for a wide range of melt compositions. Comparisons with previous work elucidating the rate of redox exchange in dry systems allow us to anticipate the $f\text{H}_2\text{-T}$ domains where different redox mechanisms may apply. We conclude that equilibration of redox potential in nature should be dominated by H_2 transfer at a rate controlled by both H_2 solubility and diffusion in melt. Therefore, changes in the redox state of magmas are intimately related to changes in the concentration of water-derived species. Several consequences of these findings are proposed.

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HYDROTHERMAL SYSTEMS ON TERRESTRIAL PLANETS: LESSONS FROM EARTH. R. T. Gregory¹ Stable Isotope Laboratory, Department of Geological Sciences, SMU, PO Box 750395, Dallas TX 75275; bgregory@smu.edu

Introduction: Stable isotopic measurements have been instrumental in elucidating the role of fluid-rock interaction in the lithosphere of the Earth; e.g. [1]. Analyses of geothermal fluids [2] and subsurface formation waters [3] provide direct evidence of penetration of surface waters into the crust. Oxygen isotope determinations of whole rocks and their coexisting minerals, e.g. [4,5], provided evidence for the depth of penetration of hydrothermal fluids and mechanisms of isotopic exchange necessary to explain the variations of observed in the water studies. Earth, with water near its triple point at the surface and with silicates near their solidus in the mantle at the base of the lithosphere, provides tremendous opportunities for generating oxygen isotopic heterogeneities in the lithosphere.

Isotopic Impact of Fluid Rock Interaction: The temperature dependence of oxygen isotopic fractionations between silicates varies from approximately +40‰ at surface temperatures (e.g. quartz-water) to \approx -2‰ (magma-water) at magmatic temperatures. The temperature dependence of the solid-water isotope fractionation along with the high thermal gradient at midocean ridges generates the conditions for exchange between dominant silicate (the mantle) and water (the ocean) reservoirs. The time scale for this exchange is approximately 100 Myr, e.g. [6]; this buffers the oxygen isotopic composition of the oceans. The isotopic composition of the ocean anchors the meteoric water cycle, which in turn determines the range of possible fractionations with the crust at near surface conditions. The net result is that the lithosphere exhibits a \approx 50‰ spread in $\delta^{18}\text{O}$ values; in contrast to homogeneous post-accretion, differentiated Earth-Moon system at +6‰.

δ - δ Representation: The natural coordinate system for representing stable isotopic variations is the δ - δ plot that simultaneously portrays the effects of temperature and mass balance on stable isotope distributions. In a fluid + rock binary system, any natural system generates a spectrum of fluid compositions ranging from fluid-buffered to rock-buffered; this is controlled by the dimensionless ratio of the fluid flux rate to the reaction rate (u/k). The primary controls on this critical ratio are permeability (for u) and temperature (for k). Mechanical limits on permeability at depth allow the preservation of surface-derived isotopic heterogeneities to great depths and for geologically long time scales. When $u/k \ll 1$, the fluid isotopic composi-

tion is buffered by the local host rocks on time scales of 1000's of years while mineral heterogeneities will persist for millions of years. Secondary phases grown in the presence of this buffered fluid will reflect isotopic equilibrium with the local fluid environment and exhibit non-equilibrium fractionations with the remaining partially-exchanged phases. The time scales for this type of fluid-rock interaction are comparable to time scales for assembly for meteoritic parent bodies.

Implications for ^{17}O - ^{18}O Plots. Translating complete open system behavior into the $\delta^{17}\text{O}$ - $\delta^{18}\text{O}$ coordinate system shows that exchange between a "terrestrial-like" oxygen reservoir and a low $\Delta^{17}\text{O}$ reservoir generates an array of slope 1 for systems whose end members are initially far from isotopic equilibrium; this is similar to the observed chondritic arrays [e.g. 7].

For most achondrites, magmatic differentiation and subsolidus exchange generates arrays that follow mass dependent arrays whose isotopic ranges along the arrays are consistent with high-T exchange [e.g. 8]. Secondary carbonates in some CM2 chondrites exhibit behaviors consistent with an intermediate behavior, probably very locally-buffered, exhibiting 1) large fractionations between the carbonate phases and coexisting matrix and 2) approach to a mass dependent fractionation line while 3) exhibiting non-equilibrium, reversed $\Delta^{18}\text{O}$ values between dolomite and calcite [9].

Extrapolation of these types of results to the hydrology of meteoritic parent bodies, e.g. [10], depends upon the phase diagram for water and whether liquid-water can survive where hydrostatic pressures would be well below 1 bar. The water vapor-liquid transition also would have important consequences for the evolution of the shallow crust of Mars.

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Oxygen in martian meteorites: A review of results from mineral equilibria oxybarometers. C. D. K. Herd¹,
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Introduction: Two oxybarometers based on mineral equilibria have been used to determine oxygen fugacity (fO_2) in the martian meteorites: the Fe-Ti oxide and olivine-pyroxene-spinel (Ol-Px-Sp) methods. The details of these methods and a review of their application to martian basalts (i.e., basaltic and olivine-phyric shergottites) is provided in [1]. The purpose of this abstract is to summarize results for martian basalts (Table 1) and to provide details that elucidate the advantages and potential pitfalls of these methods.

Fe-Ti oxides method: This method is based on the compositions of co-existing titanomagnetite (spinel) and ilmenite. These are common accessory minerals in basaltic shergottites such as Shergotty, Zagami, Los Angeles, and QUE 94201.

Any thermodynamic model is limited by the data used in its construction. Such is the case with the Fe-Ti oxide oxybarometer models [2, 3] – significant deviation in composition of the oxides from “ideal” Fe-Ti endmembers results in greater uncertainty. As noted by [4, 5], its application to certain oxides is problematic. For example, in Dar al Gani 476, spinel contains up to 20 wt% Cr_2O_3 and ilmenite 5 wt% MgO. The Ol-Px-Sp method (see below) presents a more suitable alternative in such cases [5].

Subsolidus diffusion presents an additional complication. Oxyexsolution of titanomagnetite results in lamellae of ilmenite in the spinel host, as seen in QUE 94201 [4], NWA 480 [6], and the Ti-rich rims of chromite in NWA 1110 [7] and Dhofar 019 [8], among others. Although the lamellae are typically less than 1 μm in width, their presence results in increased uncertainty in fO_2 (e.g., compare the range of fO_2 for QUE 94201 with that of other samples in Table 1). Whether the oxyexsolution occurred as a result of an increase in fO_2 (open-system) or under ambient fO_2 (closed-system) conditions is unclear. Open-system conditions imply that the titanomagnetite in QUE 94201 has been oxidized; therefore, the Fe-Ti oxide results should be considered an upper limit on the fO_2 .

Ol-Px-Sp method: This method is based on the compositions of co-existing olivine, pyroxene and Cr-spinel. These assemblages are common in the olivine-phyric shergottites such as DaG 476, SaU 005, Dhofar 019, NWA 1110 and Y980459. Careful petrographic observations are required to select equilibrium assemblages for fO_2 calculation [7, 9]. In some cases, fO_2 can be estimated for different generations of assemblages, allowing evaluation of fO_2 changes with cooling.

Table 1: Summary of fO_2 results for martian basalts.

Sample	T (°C)	fO_2 range ^a	Comments ^b
Zagami	756 – 816	-1.0 to -1.5	FeTi, [4]
Shergotty	759 – 793	-1.1 to -1.2	FeTi, [4]
QUE94201	624 – 794	-2.4 to -3.8	FeTi, [4]
Los Angeles	748 – 832	-1.0 to -1.6	FeTi, [4]
NWA 3171 ^c	761 – 782	-1.3 to -1.4	FeTi [10]
Y980459 ^c	1400 ^d	-2.7 to -3.5	OPS
Dhofar 019	1099	-3.7	OPS, [7, 9]
	650 – 800	-3.8 to -4.3	FeTi, [8]
EET79001B	712 – 848	-1.3 to -2.4	FeTi, [4]
EET79001A	794 – 1009	-1.1 to -1.9	FeTi, [4]
groundmass	730 – 925	-1.7 to -1.9	OPS, [7, 9]
EET79001A	854 – 982	-2.5 to -3.0	OPS, [7, 9]
xenocrysts			
DaG 476	774 – 1186	-1.9 to -3.3	OPS, [7, 9]
SaU 005	1017-1154	-3.0 to -3.8	OPS, [7, 9]
SaU 005 L ^e	1047-1093	-3.0 to -3.4	
NWA 1110	996 – 1063	-1.2 to -2.0	OPS, [7, 9]
NWA 1110 L ^e	766 – 836	-0.5 to 0.5	
ALH77005	1273	-2.6	OPS, [7]

Notes: ^a fO_2 relative to QFM [11]; ^bFeTi = Fe-Ti oxide method of [2], OPS = Ol-Px-Sp method [5, 9]; ^cpreliminary results; ^dEstimate; ^eL = late assemblage [7, 9].

Comparison of the methods: The criticism that the results of these methods, especially Fe-Ti oxides, do not represent magmatic fO_2 conditions has been addressed [4, 7]. In sum, the T- fO_2 trends recorded by either method indicate that fO_2 changes very little with cooling and crystallization in most cases: the spread of estimates in a given sample run parallel to the QFM buffer in T- fO_2 space. The notable exceptions are EET 79001 lithology A and NWA 1110 (Table 1); in these cases, variations are attributable to processes in the magma [e.g., 7], as opposed to errors in fO_2 .

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NON-LINEAR FRACTIONATION OF OXYGEN ISOTOPES IMPLANTED IN LUNAR METAL GRAINS: SOLAR, LUNAR OR TERRESTRIAL ORIGIN?; T. R. Ireland, P. Holden, M. Norman, and J. Clarke, Research School of Earth Sciences, The Australian National University, Canberra ACT 0200, Australia <Trevor.Ireland@anu.edu.au>

Introduction: The imminent return of the Genesis experiment motivated us to look for natural analogs. The occurrence of metal grains in lunar soil offers such a possibility. The metal, probably splash droplets from meteorite impacts, offer a robust medium with low intrinsic concentrations of oxygen. These grains have been exposed to surface conditions and effects, most notably to the solar wind for a much longer time than the Genesis materials and hence signals should be larger, making for easier analytical conditions.

Analytical: The analyses were carried out on SHRIMP II in multiple collection mode. A 1 nA Cs⁺ beam was used to sputter oxide and metal grains and all samples were analyzed with a faraday cup for ¹⁶O⁻ and CDEM for ¹⁷O⁻ and ¹⁸O⁻. Terrestrial magnetite and ilmenite analyses were interspersed with analyses of the metal grains. Preliminary results were presented previously [1].

Results: The results of the analyses are shown in Figure 1. One spherical grain (α) shows highly anomalous compositions. The most anomalous compositions are in the first analyses of the surface with progressively lower anomalies and ¹⁶O⁻ count rates as the ion beam sputters deeper into the grain. These compositions lie on a non-linear mass fractionation line of approximately unit slope with relative depletion of ¹⁶O (or ¹⁷O, ¹⁸O enrichment) of up to 100 ‰. One analysis (1b) of grain α , and the analyses of another grain (ν) are dominated by contamination (non-decaying depth profiles) and lie on or close to the terrestrial mass fractionation line at about -50 ‰. The lunar ilmenites are corrected for temporal variations in the counting system, but this correction is highly correlated with total counts, and it would not produce the magnitude of the effects measured.

Discussion: The lunar metal grains provide an isotopic composition that has not been seen previously beyond the terrestrial atmosphere. Is this the composition of solar wind, is it a surface effect on the Moon, can Earth atmosphere oxygen interact with the Moon?

Decaying depth profiles make it tempting to consider that the ¹⁶O-depleted composition is that of the solar wind. Then the question will remain as to whether this is the composition of the Sun, or a composition formed by the processes responsible for solar wind acceleration.

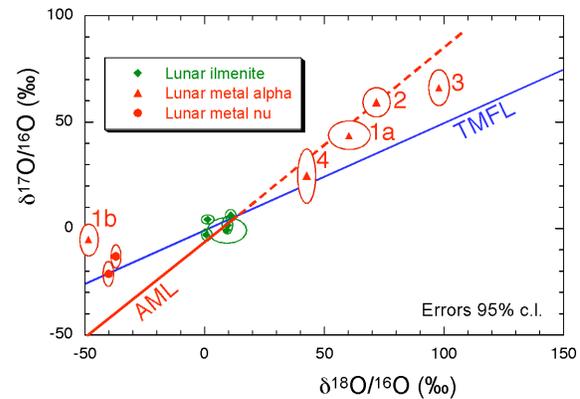


Figure 1. Oxygen isotopic compositions in lunar metal grains. Grain alpha has a highly anomalous surface composition depleted in ¹⁶O relative to terrestrial (+lunar). Analysis 1b and grain ν are dominated by contamination.

Isotopic mass fractionation is well known from lunar soils but this is mass dependent (linear) mass fractionation enriching the heavy isotopes in the grain surfaces as a result of grain sputtering [2].

The extreme depletion of ¹⁶O (or ¹⁷O, ¹⁸O enrichment) in the lunar metal is a factor of two larger than the CWAS samples of Earth's stratosphere (e.g. [3]). Coincidentally, it has been postulated that Earth atmosphere components (N, noble gases) could be transported (as ions) to the Moon when the geomagnetic field was weaker during the early Earth [4].

The metal grains lack intrinsic oxygen requiring that any oxygen be surface related. At this stage, it is unclear whether the oxygen is implanted below the surface (as for solar wind) or present at the surface. Resolution of this issue will help establish the source of this exotic oxygen. The Genesis experiment will resolve the issue of a solar origin. If Genesis returns a composition markedly different than the composition measured here (viz. close to refractory inclusions or meteorites/terrestrial planets), then a hitherto unknown mechanism is responsible for a high degree of non-linear O isotope fractionation.

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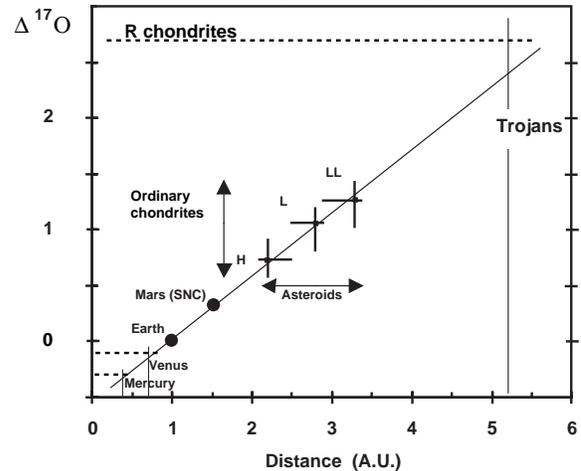
ISOTOPIC ZONING IN THE INNER SOLAR SYSTEM. A. Jambon¹, Laboratoire MAGIE, Université Pierre et Maris Curie Case 110, 4 place Jussieu, 75252 Paris cedex 05, France. jambon@ccr.jussieu.fr

Introduction: The main lines of meteorite classification rest upon chemical criteria. Primitive meteorites or chondrites derive their composition directly from the solar nebula without differentiation processes in their parent body (e.g. no core extraction). Chondrites are distinguished from differentiated meteorites (achondrites and siderites). More detailed studies of chondrites showed they could be separated into a number of classes, the most effective criterion for that being the oxidation state of iron, which can be either combined as a metal alloy (with Ni) or with sulfur or oxygen. In this latter case it enters the constitution of Fe-Mg silicates, like olivine. The following major groups are distinguished: carbonaceous chondrites wherein Fe is completely oxidized or nearly so, ordinary chondrites which are intermediate and enstatite chondrites in which Fe is not combined to oxygen. These wide groups are further divided into classes using more subtle criteria, specific to each group. The most abundant meteorites by far, are the ordinary chondrites. Enstatite chondrites are least frequent but statistical considerations lead to conflicting views: If one class is poorly populated, one may argue that it is a curiosity, not an important one. Conversely one can say that this results from their great success in forming larger parent bodies and their study is therefore of utmost importance to the understanding of planetary bodies. According to this view, ordinary chondrites are expected to stem from the main asteroid belts. Accretion in this region has been highly perturbed by the vicinity of Jupiter so that no massive planet could emerge. Chondrites from this region can therefore be viewed as leftover from the planetary formation.

This discussion is supported by prejudices on the way the solar system evolved and planets formed; it is established on chemical and mineralogical criteria. For a few decades, oxygen isotopes have been used and confirmed the rationality of this classification since a new criterion independent from the chemical composition permitted to separate the same classes but the rationale behind it is not well understood.

Facts: After a rapid review of relevant isotopic data [1-4], especially the new data on achondrites [1,2], a strong correlation of $\Delta^{17}\text{O}$ with distance from the sun appears. Zoning of the present day solar system is established and discussed. Oxygen isotopic compositions are fundamental data which permit to establish that the primitive solar system was isotopically zoned as a result of binary mixing. This is still visible in the present day planetary

compositions from Mercury to Mars and the asteroid belt. This observation leads to the



question of how did this zoning originate? The other question is how do carbonaceous chondrites fit in this picture?

Conclusions: According to this solar system zonation model we have to admit that our speculations on parent bodies of achondrites have to be revised: HED are from Mercury and angrites from Venus.

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REDOX CONDITIONS ON SMALL BODIES.
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The Eucrite Parent Body (4 Vesta). The eucrites are basalts that contain ~18 wt% FeO and contain trace metal. The eucrites are very depleted in siderophile elements, so it appears that the source regions of these basalts once equilibrated with Fe-Ni metal [1]. Therefore, it is of interest to ask what f_{O_2} is required to precipitate metal from a liquid of eucrite composition. Or in other words, what f_{O_2} did eucrites form under? This f_{O_2} has been determined experimentally by [2] and was found to be IW-1. Therefore, eucrites formed at about IW-1. In addition, it is interesting to note that assuming $X_{FeO} = a_{FeO}$ allows calculation of eucrite f_{O_2} (assuming equilibrium with Fe metal). This calculation yields the same result as the experiments to within ~0.25 log units, reinforcing this result.

Approaching this problem a third way, Jurewicz et al. [3] noted that partial melts of the Murchison (CM) chondrite at 1180-1200°C and IW-1 were virtually identical in their major element concentrations to those of eucrites.

Thus, several lines of evidence conspire to convince us that eucrites formed near IW-1. Further, we anticipate that basalts having ~18 wt.% FeO and coming from planetary mantles that experienced core formation should also have f_{O_2} 's near IW-1. This is true for the Moon [4] and now appears to be approximately true for Mars [5].

Ordinary Chondrites. In addition to experiments on eucrites themselves, we may approach the problem from another direction. Larimer [6] noted that an assemblage of olivine, low-Ca pyroxene and metal can be used to evaluate redox conditions:



a variant of the QFI buffer, which is about IW-0.5. To the extent that FeO does not fractionate greatly between olivine and pyroxene and that the Fe-Ni metal is mostly Fe, then the above reaction will also not stray greatly from the QFI buffer, as long as non-idealities are not large. Therefore, we anticipate that ordinary chondrites and their achondritic relatives, lodranites and acapulcoites, will also have redox states in the vicinity of IW-0.5 to IW-1.

Thus, from our experience with eucrites, lunar mare basalts, and ordinary chondrites, a picture emerges that small bodies whose mantles initially contained olivine, low-Ca pyroxene and Fe-Ni metal will, upon partial melting, produce basalts that contain ~18

wt.% FeO and that this process will take place at oxygen fugacities near IW-1. Therefore, ~18 wt% FeO in a basalt is an easily recognizable signature of a particular f_{O_2} .

Exceptions to the Rule. Not all chondrites and asteroids are as reduced as ordinary. The enstatite chondrites and their achondritic associates (aubrites) are much more reduced and contain little or no FeO. And some bodies are more oxidized than the ordinary chondrites. This is emphasized by the observation that some asteroids have a small Fe^{3+} absorption feature [7]. Do we see any igneous meteorites that appear to have come from more oxidized bodies. As a matter of fact we do.

One class of igneous meteorites that does not easily fit into normal categories is the angrites. They are critically silica undersaturated and have unusual mineralogies. Experimental melts of Allende (CV) performed at IW+1 and IW+2 are the best matches to the most primitive angrites [8]. So it appears that we now have samples from oxidized mantles other than the Earth's.

Even though the angrites are more oxidized than the eucrites, their source region probably contained metal. We infer this because siderophile elements are depleted in the angrites [e.g., 9]. The reason metal can remain stable above the IW buffer is because of the presence of Ni. Since the Ni-NiO buffer is about 4.5 log units above IW, Ni can expand the Fe-Ni metal stability field; and Ni-rich metal is observed in Angritos Reis. Thus, the uncommon mineralogies observed in the angrites is directly attributable to the redox conditions during the partial melting of the angrite source regions.

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DETERMINING THE OXYGEN FUGACITY OF LUNAR PYROCLASTIC GLASSES USING VANADIUM VALENCE-AN UPDATE J.M. Karner¹ (jkarner@unm.edu), S.R. Sutton^{2,3}, J.J. Papike¹, C.K. Shearer¹, J.H. Jones⁴, and M. Newville³. ¹Institute of Meteoritics, Dept. of Earth and Planetary Sciences, University of New Mexico, Albuquerque, NM 87131-1126; ²Dept. of Geophysical Sciences and ³Consortium for Advanced Radiation Sources, University of Chicago, Chicago, IL 60637, ⁴SR NASA/JSC, Houston, TX 77058

INTRODUCTION We have been developing an oxygen barometer based on the valence state of V (V^{2+} , V^{3+} , V^{4+} , and V^{5+}) in solar system basaltic glasses. The V valence is determined by synchrotron micro x-ray absorption near edge structure (XANES), which uses x-ray absorption associated with core-electronic transitions (absorption edges) to reveal a pre-edge peak whose intensity is directly proportional to the valence state of an element [1]. XANES has advantages over other techniques that determine elemental valence because measurements can be made non-destructively in air and *in situ* on conventional thin sections at a micrometer spatial resolution with elemental sensitivities of ~ 100 ppm. Recent results show that fO_2 values derived from the V valence technique are consistent with fO_2 estimates determined by other techniques for materials that crystallized above the IW buffer [2]. The fO_2 's determined by V valence (IW-3.8 to IW-2) for the lunar pyroclastic glasses, however, are on the order of 1 to 2.8 log units below previous estimates [3,4]. Furthermore, the calculated fO_2 s decrease with increasing TiO_2 contents from the A17 VLT to the A17 Orange glasses. In order to investigate these results further, we have synthesized lunar green and orange glasses and examined them by XANES.

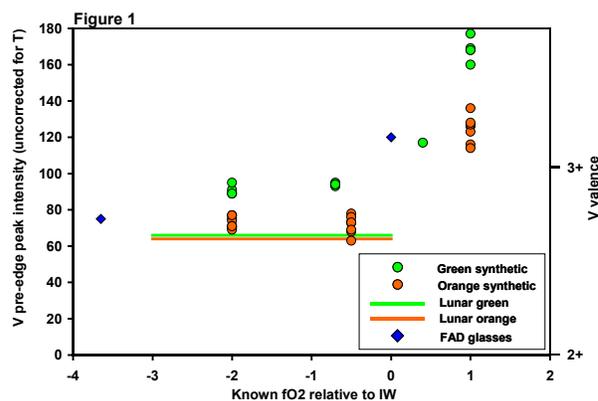
EXPERIMENTAL Lunar green and orange glass compositions were synthesized at several different fO_2 conditions in the 1 atm gas-mixing furnaces at NASA JSC. The starting compositions were Apollo 15 Green C, containing about 16 wt.% FeO, 0.2 wt.% TiO_2 , 0.6 wt.% Cr_2O_3 , and Apollo 17 Orange, containing 26 wt.% FeO, 9 wt.% TiO_2 , 0.7 wt.% Cr_2O_3 ; both compositions were doped with 5000 ppm V. The glasses were produced by drop quenching into water after equilibrating at imposed fO_2 conditions of approximately IW+1, IW, IW-1, and IW-2 at 1430 °C. The glasses were then examined by electron microbeam techniques and found to be homogenous and free of crystals, although there was systematic FeO loss with decreasing fO_2 , presumably to the Re-wire used to suspend the samples in the furnace.

RESULTS AND DISCUSSION Figure 1 shows the V pre-edge peak intensities for synthetic glasses against the fO_2 values at which they were produced, as well as the intensities for the natural lunar green and orange glasses (lines). The plot shows a plateauing of V pre-edge peak intensity (i.e. V valence) independent of fO_2 below approximately IW-0.5. The plateauing, or

stabilization of V^{2+}/V^{3+} suggests it may be difficult to quench V^{2+} , an effect that has been documented for Cr^{2+} in basaltic glasses [5]. The inability to quench reduced Cr in glasses is attributed to the oxidation of Cr^{2+} to Cr^{3+} on cooling in the presence of Fe^{3+} by electron exchange. Here we could be seeing the oxidation of V^{2+} to V^{3+} by either Cr^{3+} or Ti^{4+} . Another explanation could be that V^{2+} does not exist in our samples, and the transition from V^{3+} to V^{2+} occurs at much lower fO_2 conditions than previously expected. Figure 1 also shows the effect of composition on V valence. The orange synthetic glasses (9 wt.% TiO_2) show a lower valence than the green synthetic glasses (0.2 wt.% TiO_2), even though they were produced at the same fO_2 . This compositional effect is not seen in the natural orange and green glasses however, and leads us to believe that doping the green synthetic mix with V resulted in a greatly increased V/Ti ratio compared with the natural samples, and in turn this has affected the V valence. The final observation from Figure 1 is that the lunar green and orange glasses plot at essentially the same V valence, which also corresponds to the V valence of the IW-0.7 and IW-2 orange synthetic samples. From these observations, we conclude that our best estimate of the fO_2 for the lunar glass beads is IW-1, with an uncertainty of about 1 log unit.

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MANTLE REDOX EVOLUTION AND THE RISE OF ATMOSPHERIC O₂. J. F. Kasting, Department of Geosciences, 443 Deike, Penn State University, University Park, PA 16802; kasting@essc.psu.edu.

Why did atmospheric O₂ rise around 2.3 Ga [1,2] when photosynthetic cyanobacteria appear to have arisen at least 400 m.y. earlier [3]? Either cyanobacterial productivity was lower for some reason during the Archean, or else the volcanic sink for O₂ must have been larger. The relative constancy of the $\delta^{13}\text{C}$ values of carbonates at $\sim 0\text{‰}$ both before and after the initial rise of O₂ implies that organic carbon burial rates did not change and, hence, that the volcanic sink for O₂ must have decreased with time. Kasting et al. [4] suggested that this happened because the upper mantle became progressively oxidized during the Archean as hydrogen escaped to space. The hydrogen came from water originally, so this process would have oxidized the Earth. In their model, it was Earth's upper mantle that was oxidized by subduction of water and carbonates, followed by outgassing of H₂ and CO. Subduction of ferric iron may also have been important [5]. As the upper mantle became more oxidized, the volcanic gases would have become less reduced, until eventually they were overwhelmed by photosynthetically produced O₂.

This hypothesis, while attractive in many respects, is in apparent disagreement with observations. Data on the Cr and V content of ancient basalts and komatiites [6-8] indicate that upper mantle $f\text{O}_2$ has changed very little since at least 3.5 Ga. A recent reanalysis of volcanic gas oxidation states by Holland [9] shows that only a small change (<1 log unit) in $f\text{O}_2$ may be required in order to get the atmospheric oxidation state to flip, but even this small change may be ruled out. Thus, the question of why atmospheric O₂ rose when it did remains a mystery.

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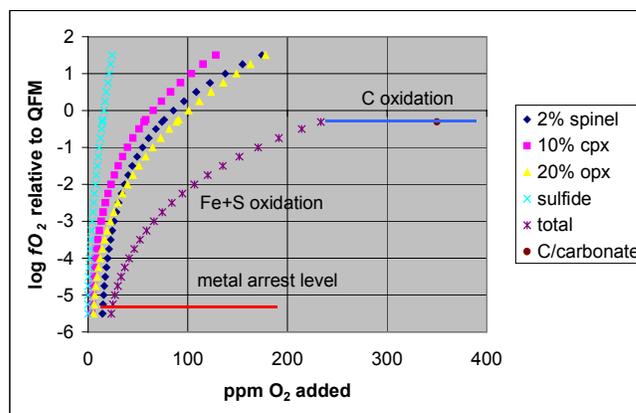


Fig. 1 Diagram showing how many ppm (by weight) of O₂ must be added to the upper mantle in order to increase its oxidation state from iron-wüstite (IW) to quartz-fayalite-magnetite (QFM). This estimate assumes 10^{24} kg of material above 700 km depth and ~ 6 wt. percent Fe. The total O₂ added is $\sim 7 \times 10^{21}$ mol. By comparison, the present rate of volcanic input of H₂ is 5×10^{12} mol/yr, and the Archean volcanic input rate was probably several times higher. Escape of a significant fraction of this H₂ prior to 2.3 Ga could have led to progressive mantle oxidation.

Variation Of Kd For Fe-Mg Exchange Between Olivine And Melt For Compositions Ranging From Alkaline Basalt To Rhyolite

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Analysis of more than 200 olivine-melt pairs in terms of Fe-Mg exchange between olivine and coexisting melt indicates that Kd varies with bulk composition and oxygen fugacity. For tholeiitic basalts Kd value is 0.3 ± 0.03 ; however, as the composition changes from tholeiitic to alkaline the Kd decreases to as low as 0.18. On the other end of the compositional spectrum as the silica content of melts increase to rhyolitic composition Kd increases up to 0.68.

Our calculations of Kd using Sack et al. (1980), Kilinc et al. (1983) and Kress and Carmichael (1988) equations relating Fe⁺³/Fe⁺² to temperature, oxygen fugacity and compositional parameters shows that Kd is a function of composition. Using S/SCAM as the differentiation index a third degree polynomial equation value of Kd can be calculated for any bulk composition.

$$\ln K_D = 24.937 \cdot (S/SCAM)^3 - 27.769 \cdot (S/SCAM)^2 + 9.9783 \cdot (S/SCAM) - 2.4363$$

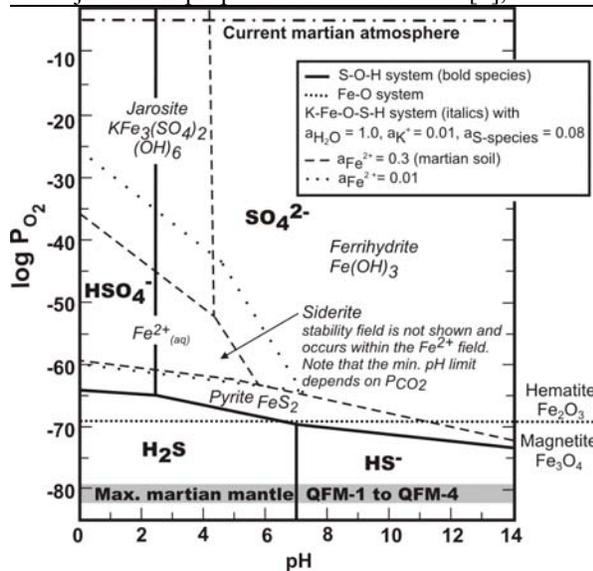
DETERMINING THE PARTIAL PRESSURE OF OXYGEN (P_{O_2}) IN SOLUTIONS ON MARS. P. L. King
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The current martian atmosphere has $\log(P_{O_2}) = -5$, but martian mantle estimates are below the quartz-fayalite-magnetite (QFM) buffer ([1,2]; recalculated as $\log(P_{O_2}) < -79$ at 25°C using data from [3]). Also, it is likely that early Mars had relatively low P_{O_2} conditions, analogous with those proposed for the early Earth [4]. Here, I examine the martian P_{O_2} evolution using phase equilibria, S^{2-}/S^{6+} and Fe^{3+}/Fe^{2+} minerals or species in surface solutions on Mars.

P_{O_2} of martian solutions

The primordial solutions on Mars likely contained C-O-H-S-N-halogen species (similar to Earth [4]). Such reactive solutions may have leached the martian surface materials (sulfides-Fe-Mg minerals-plagioclase±glass) to produce saline solutions [5]. Since pyrite is the most easily leached mineral, we can model the leaching solutions in the Fe-O-S-H system. At low P_{O_2} H_2S and HS^- -bearing solutions are predicted as a function of pH (Fig.). It is probable that $\log(P_{O_2}) > -69$ because Fe^{3+} (hydrated) oxides, (e.g. hematite) are found on the martian surface [6] (Fig.).

To further constrain P_{O_2} on the martian surface it is possible to examine the stability of phases in the K-Fe-C-O-S-H system. This system is chosen because jarosite is proposed to exist on Mars [7],



Stability limits of Fe-bearing phases relative to pH and P_{O_2} in the K-Fe-O-S-H system at 25°C and $\sim 10^5$ Pa. At lower martian temperatures the P_{O_2} values will be lowered [9,15] and there may be effects due to the anion content [15], therefore the data should be assessed with reference to displacement from the buffer reactions.

siderite and ferrihydrite are observed in martian meteorites [8] (where ferrihydrite is used as a proxy for goethite and magnetite following [9]).

The figure shows stability limits for model martian surface compositions calculated using the Viking and Pathfinder soils [10-12] ($a_{K^+}=0.01$, $a_{S-species}=0.08$, $a_{Fe^{2+}}=0.3$), using equilibrium constants from [13-14], assuming that activity coefficients and the activity of water are unity (see [9] and [15] for a discussion of assumptions).

At near-neutral to acidic conditions, pyrite weathers to either Fe^{2+}_{aq} or siderite (Fig.). Siderite stability depends on P_{CO_2} , with a lower limit of $pH \sim 3.9$ for $P_{CO_2} = 2$ and $pH \sim 4.7$ for $P_{CO_2} = 0.05$. If conditions are acidic and P_{O_2} is higher then jarosite precipitates. If K is a limiting component, then other ferric hydroxy-sulfate minerals may precipitate. If jarosite is present on the martian surface, then the solutions contain SO_4^{2-} or HSO_4^- , dependent on pH. If conditions are near-neutral to basic, then ferrihydrite (or other Fe-(hydr)oxides) precipitate. If $a_{Fe^{2+}}$ is lower (due to precipitation of Fe-minerals), then higher P_{O_2} is required to form jarosite and ferrihydrite (Fig.).

Possible method to increase P_{O_2} on Mars

On Mars, H_2 -loss is indicated by the high D/H value of the martian atmosphere relative to the martian mantle [16]. Hydrogen-loss may drive up oxygen fugacity [17] via reactions such as dehydrogenation of the atmosphere ($H_2O = H_2 + 0.5O_2$), which in turn may promote oxidation of Fe in solids (e.g., martian amphiboles [18]).

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THE INFLUENCE OF OXYGEN ENVIRONMENT ON KINETIC PROPERTIES OF SILICATE ROCKS AND MINERALS. D. L. Kohlstedt¹, S. Hier-Majumder¹, and S. J. Mackwell, ¹Department of Geology and Geophysics, University of Minnesota, Pillsbury Hall, Minneapolis, MN 55455, ²Lunar and Planetary Institute, 3600 Bay Area Boulevard, Houston, TX 77058.

Abstract: The oxygen content in a geologic environment, expressed as oxygen partial pressure or oxygen fugacity, has a direct effect on the kinetic properties of rocks composed of minerals that contain a significant concentration of transition metal cations. In this context, the most extensively studied mineral is Fe-Mg olivine. Experimental investigations demonstrated that the rates of cation diffusion, electrical conductivity, and creep all increase systematically with increasing oxygen partial pressure. The measured dependencies of such physical properties on oxygen partial pressure provide insight into the mechanisms by which ionic and electronic transport proceed as well as constraints on the variation of these properties from one environment to the next.

Investigations of cation diffusion in olivine all yield a power law relation between diffusivity, D_{Me} , and oxygen partial pressure, p_{O_2} , with D_{Me} increasing as p_{O_2} to the 1/7 to 1/5 power [1-4]. Related thermogravimetry experiments yield the same dependence for cation vacancy concentration, X_V , on p_{O_2} [5,6]. Therefore, the authors of [3] have concluded that cation diffusion takes place by a vacancy mechanism, since D_{Me} is directly expressed in terms of the cation vacancy concentration and the vacancy diffusivity, D_V , through the relation $D_{Me} = X_V \times D_V$.

Measurements of the dependence of electrical conductivity on p_{O_2} in olivine provide related constraints on the mechanisms of charge transport. In the case of electrical conductivity, the analysis is somewhat more complicated than for cation diffusion because multiple electronic and ionic species can contribute. For olivine, a transition occurs from conduction primarily by electron holes (polarons) below 1100-1300°C to conduction by octahedral cations at higher temperatures [7-8]. Again, a key observation in identifying the mechanism of electrical conduction is the dependence of conductivity on oxygen fugacity, here combined with the activation energy.

Finally, studies of creep of olivine single crystals reveal a clear increase in creep rate with increasing p_{O_2} [10,11]. Because creep involves not only ionic diffusion but also dislocation motion, the results are more difficult to interpret in terms of fundamental mechanisms. The dependence of creep rate on p_{O_2} and temperature is more complex than in the case of cation diffusion or electrical conductivity. Both the p_{O_2} dependence and the T dependence of creep rate varying with the slip system activated as well as the ranges of

p_{O_2} and temperature investigated. The dislocation microstructure also changes from one p_{O_2} - T regime to the next, indicating transitions from glide-dominated to climb-dominated to cross slip-dominated dislocation processes [12].

Each of these kinetic properties plays an important role in mantle processes of the terrestrial planets. Cation diffusion controls the rate of chemical exchange and degree of zoning observed in olivine grains transported in basaltic magmas. Magnetotelluric observations provide constraints on the temperature distribution and composition of Earth's deep interior. Viscosity is a critical parameter for understanding convection in the mantle. While variations in oxygen fugacity produce only moderate changes in these important physical properties, analysis of the dependence of these properties on oxygen partial pressure provide critical insights into the fundamental mechanisms of transport. With this basis, a robust physical framework can be developed for extrapolating kinetic properties from the thermodynamic conditions imposed in laboratory experiments to those experienced by rocks in the mantle.

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REDOX EVOLUTION OF MAGMATIC SYSTEMS. V.C. Kress, Earth and Space Sciences, University of Washington, Box 351310, Seattle, WA, 98195. kress@u.washington.edu

Introduction: Iron is the most abundant of the elements that exist in multiple redox states under typical terrestrial planetary conditions. Fe can exist in ferric, ferrous and metallic states under planetary conditions in percent to tens of percent concentrations. For this reason, iron-bearing phases will tend to be the principle buffers of redox variation in the terrestrial planets. Because of the relatively low chemical diffusivity of oxygen in solid phases, transfer and modification of relative redox potential in planetary bodies is primarily mediated by a melt or vapor phase [e.g. 1].

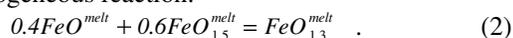
Redox chemistry in silicate melts: To a first approximation, ferric-ferrous equilibrium in silicate melts can be represented by the equation:

$$\ln \left(\frac{X_{Fe_2O_3}}{X_{FeO}} \right) = a \ln (f_{O_2}) + \frac{b}{T} + c + \sum X_i d_i \quad (1)$$

[2], where a, b, c and d's are empirically determined variables. Eq. 1 resembles a thermodynamic form, but differs in several important respects. Despite its thermodynamic shortcomings, Eq 1 has repeatedly been found to be the simplest functional form to adequately represent Fe-redox chemistry at 1 bar pressure in a remarkable variety of silicate melts.

Kress and Carmichael [3] used one-bar volume and compressibility data to extend Eq. 1 to allow calculation of redox equilibrium as a function of pressure. The resulting model suggested that a closed-system silicate melt at fixed redox state (closed system) will define an oxygen fugacity that roughly parallels solid oxygen buffers, such as the FMQ, as a function of both pressure and temperature. This would imply that adiabatically rising melts should not change their relative oxidation state unless they interact chemically with a contrasting redox reservoir.

[3] also pointed out that the apparently non-thermodynamic behavior of the Fe-redox behavior can be explained simply if one assumes that ferric and ferrous iron react to form an associated melt species by the homogeneous reaction:



The possible presence of such a mixed-valence melt species in silicate melts has been independently suggested based on spectroscopic data [4][5].

One bar experimental redox data suggests an equilibrium constant for reaction 2 of 0.4. a recent re-analysis of available silicate liquid density data [6] suggest that the volume of reaction for reaction 2 is not zero, as was assumed by [3], but must be on the order of -2.2 cc/mole. A non-zero ΔV for reaction 2 implies

that the equilibrium constant is not independent of pressure.

A negative ΔV for reaction 2 makes the predicted oxygen fugacity of an ascending closed-system melt parallel fugacities defined by typical solid oxygen buffers more closely than earlier models had suggested. This amplifies our previous conclusion that the relative redox state of silicate melts will reflect that of the host they most recently interacted with chemically.

Formation of an associated mixed-valence iron species will have significant effect on the activity coefficient of ferrous and ferric iron in silicate melts. At one-bar pressure, reaction 2 is responsible for decreasing the response of ferric/ferrous ratio in silicate melt to variations in oxygen fugacity relative to the effect expected if mixing were ideal. The negative volume of reaction for reaction 2 suggests that the slope of this response will decrease still further with increasing pressure. With increasing pressure, this volume term will decrease the activity coefficients for both ferrous and ferric components in the silicate melt.

Sulfide phases: Though sulfur is present in much lower concentrations than iron in the silicate Earth. Nevertheless, the large oxidation state change between sulfide (S^{2-}), and sulfate (S^{6+}) along with the fact that sulfur is important in solid, liquid and vapor phases leads to a disproportionately large influence of sulfur-bearing phases on redox chemistry in mantle and crustal systems. Because sulfur complexes with hydrogen, oxygen and carbon in the vapor phase, and with iron in the sulfide liquid and solid phases, the chemistry of sulfur in terrestrial planets is intimately tied to redox chemistry in subtle and complicated ways. Most experiments suggest that the solubility of sulfur in silicate melts decreases with increasing depth [e.g. 7]. This experimental pressure/solubility trend may be an oversimplification of the behavior of sulfur in natural magmatic systems.

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