**The unique NWA 7034 martian meteorite: evidence for multiple oxygen isotope reservoirs.** K. Ziegler[1], Z. D. Sharp[2], and C. B. Agee[1, 2], [1]Institute of Meteoritics, and [2]Department of Earth and Planetary Sciences, University of New Mexico, Albuquerque, NM 87131, USA, kziegler@unm.edu.

**Introduction:** The recently described martian meteorite NWA 7034 [1] from the early Amazonian is a geochemically enriched crustal rock, and the first meteorite that compositionally matches basalts and martian crust analyzed by NASA lander and orbiter missions. It has bulk oxygen isotope values of $\delta^{18}O \approx 5.5$ to 7.5‰ and $\Delta^{17}O = 0.58 \pm 0.05$‰, values that are, respectively, about 2‰ and 0.3‰ more positive than those of other known martian meteorites (SNCs). This suggests the existence of multiple oxygen reservoirs on Mars. Water released from this extremely water-rich meteorite has lower $\Delta^{17}O = 0.33 \pm 0.01$‰, indicating multiple reservoirs co-existing in a single rock.

Distinct $\Delta^{17}O$ and $\delta^{18}O$ reservoirs may exist either in a poorly mixed martian lithosphere, between the lithosphere and a surficial (atmospheric) component, or by incorporation of exotic material. The implications of distinct lithospheric reservoirs are consistent with a lack of initial planet-wide mantle homogenization and an absence of plate tectonics [2], whereas those attributed to a different surficial reservoir could indicate photochemical-induced isotope fractionation.

A surficial, high-$\Delta^{17}O$ component has been proposed for Mars based on low temperature alteration products [2-4], and this may explain the $\Delta^{17}O$ differences between bulk and 'water-derived' components of NWA 7034. If the bulk $\Delta^{17}O$ value of 0.58‰ is attributed to surficial components, then the rock would have to have had undergone extensive exchange with near-surface reservoirs. Given the high abundance (~10 wt.%) of low-temperature iron oxides (magnetite, maghemite) in NWA 7034, this is a possibility.

Here, we further explore the existence and nature of possible multiple martian oxygen isotope reservoirs.

**Results:** Measurements of oxygen isotopic composition ($\delta^{18}O$, $\delta^{17}O$) were made using laser fluorination at UNM on bulk and various mineral samples. $\Delta^{17}O$ values were calculated from $\Delta^{17}O = \delta^{17}O - 0.528 \times \delta^{18}O$.

*Magnetic minerals:* Separates of magnetic, dark minerals (iron oxides and pyroxenes*)* were obtained by handpicking and magnetic separation, and fall in the same $\delta^{18}O/\delta^{17}O$ space ($\delta^{18}O = 5.62$ to 7.36‰) as bulk rocks ($\delta^{18}O = 5.81$ to 7.52‰), with only a very slightly more positive $\Delta^{17}O$ value of $0.63 \pm 0.02$‰, $n=6$ (*c.f.* mean bulk $\Delta^{17}O = 0.58 \pm 0.05$‰, $n =21$) (Fig. 1). In contrast, a pure magnetite/maghemite separate performed by C-Y. Shih and L. Nyquist at JSC (Clerici solution, $\rho > 3.55 g/cm^3$) yielded $\Delta^{17}O = 0.59$‰, $n=1$, and a $\delta^{18}O$

value of 4.18‰, consistent with the preferential incorporation of $^{16}O$ by iron oxides. Handpicked orthopyroxene separates have similarly low $\delta^{18}O$ values (4.31‰) as the pure oxide, but average a lower $\Delta^{17}O = 0.33$‰, $n=2$. (Fig. 1). The pyroxene and magnetite are clearly out of oxygen isotope equilibrium with each other for both $^{18}O/^{16}O$ and $^{17}O/^{16}O$ ratios, and the $\delta^{18}O$ and $\Delta^{17}O$ values for the pyroxene fall exactly in the range of typical SNC pyroxenes [4-8]. These results suggest two oxygen isotope reservoirs, one equal to unaltered SNC and the other one the more oxidized component of the oxides. Surprisingly, the $\Delta^{17}O$ value of water released from NWA 7034 is the same as the pyroxene/SNC value of 0.3‰, suggesting either that the water responsible for the formation of the late oxides has since equilibrated with the more abundant mantle-derived pyroxene $\Delta^{17}O$ value, or that a different 'crustal/water' source is responsible for the formation of the iron oxides.
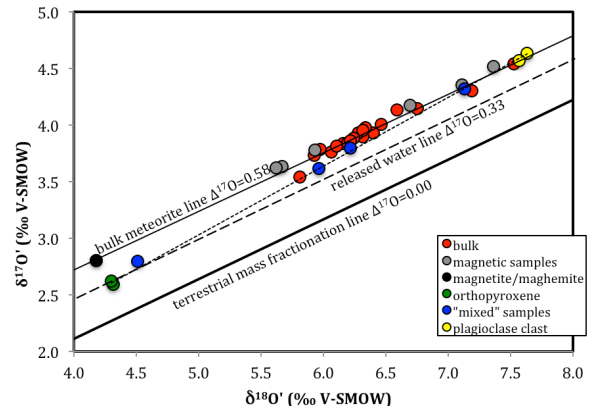


*Figure 1*: Oxygen 3-isotope plot of NWA 7034. Short dotted line is pyroxene/plagioclase mixing line (see text).

*Feldspars:* A separated plagioclase ($An_{44}$) clast has a $\Delta^{17}O$ value of 0.59‰, $n=2$, and is identical to the bulk rock $\Delta^{17}O$ value. Its $\delta^{18}O$ value of 7.60‰ is the most positive of all NWA 7034 oxygen isotope data (Fig. 1), a relationship that is consistent with equilibrium fractionation between feldspar and magnetite. This suggests that plagioclase is the positive $\delta^{18}O$ endmember of the oxygen isotope range seen in NWA 7034.

*Mixed samples:* Four "light-colored" samples consisting of a range of mixtures of various plagioclases, alkali feldspar ($Or_{50}$), pyroxene (cpx, opx, Al-px), and calcite fall on a mixing line ($r^2 = 0.99955$) between the endmembers pyroxene and plagioclase (Fig. 1). All data can be explained by mixing between a 'mantle'

$\Delta^{17}O$ value of ~0.3‰ and a 'near-surface' component of ~0.6‰, with variable fluid/rock ratios.

**Discussion:** The large range of $\Delta^{17}O$ value observed in NWA 7034 (0.31 to 0.65‰), and the non-equilibrium plagioclase-pyroxene and plagioclase-magnetite fractionations indicate that oxygen isotopes are not in equilibrium. In addition, bulk rock, iron oxide, and feldspar oxygen isotope values of NWA 7034 are anomalous compared to SNCs.

Previously observed differences in oxygen isotope compositions in SNCs were explained by lack of equilibrium between water and host rock with the lithosphere and hydrosphere having distinct oxygen reservoirs [3, 4], crustal assimilation [5-8], magmatic differentiation [9, 10], or by aqueous alteration [3, 4].

With magmatic differentiation, feldspar is expected to be more positive in $\delta^{18}O$ than pyroxenes [11] – a relationship that is observed in NWA 7034. However, the degree of feldspar-pyroxene fractionation in NWA 7034 indicates that the two minerals are out of (magmatic) equilibrium, and, therefore, we advocate that the feldspar has acquired higher $\delta^{18}O$ values during low-temperature aqueous alteration processes operating on the martian surface. Alternatively, the feldspars may have been incorporated into ascending magma during assimilation of crustally-altered material. Based on oxygen isotopes of SNC mineral separates, crustal assimilation has been hinted at before [7, 8, 12]. If this is also true for NWA 7034, we should see more signs of low-temperature, near-surface reactions.

Oxygen isotope exchange with mass independently fractionated oxygen from the martian atmosphere (photolytic reactions involving $O_3$) has been previously implicated for anomalous oxygen-isotope values of carbonates, sulfates, and water in SNCs [2-4]. Approximately 15 wt.% of NWA 7034 is composed of Fe-bearing oxides that have significant ferric iron components and a low-T stability range; much of this oxidation must have occurred in the near-surface environment, incorporating mass independently fractionated, high-$\Delta^{17}O$-oxygen from the martian litho-/hydro-/atmosphere. Noble gas analyses of NWA 7034 support a martian atmospheric component [13].

NWA 7034 data suggest that multiple processes have affected this rock. The low-temperature weathering product iddingsite in Lafayette has very positive $\delta^{18}O$ and $\Delta^{17}O$ values [3] (Fig. 2), suggesting aqueous interactions with $\Delta^{17}O$ >0.6‰ solutions. Extending the NWA 7034 pyroxene-plagioclase mixing-line (above), shows that the iddingsite falls on this line (Fig. 2).

We propose that, in addition to high-$\Delta^{17}O$-oxygen from the martian atmosphere, martian surficial aqueous alteration with a high-$\Delta^{17}O$ solution played a significant role during the formation of NWA 7034.
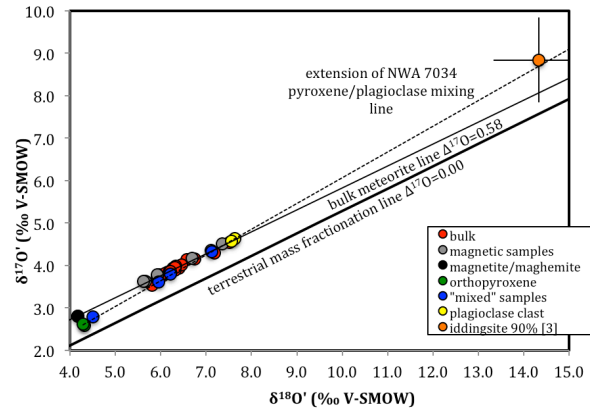


*Figure 2*: Oxygen 3-isotope plot of NWA 7034 and iddingsite separate from Lafayette [3]: NWA 7034 mixing line (short dotted line, see text) extends to iddingsite.

**Conclusions:** We conclude that this martian meteorite has multiple oxygen sources and has experienced several processes that have been preserved.

Its pyroxenes are in oxygen isotopic agreement with SNCs, and we believe they constitute initial deep mantle sources. During the early Amazonian, the martian atmosphere appears to have had a more positive $\Delta^{17}O$ value of >0.6‰ (photolytic reactions) that was imprinted, in particular, onto the easily exchangeable feldspars in the crust during low-temperature weathering. Ascending mantle magma assimilated such crustal minerals and oxygen isotopic signatures. The iron oxides magnetite/maghemite likely formed in direct contact with fluids equilibrated with the martian high-$\Delta^{17}O$ (~0.6‰) atmosphere through partial exchange. Extensive aqueous alteration, such as seen in Lafayette [3], is not observed in NWA 7034, but is consistent with it in terms of oxygen isotopes (extension of NWA 7034 mixing line to Lafayette's iddingsite).

The fact that NWA 7034 water retains the presumably martian mantle 0.3‰ $\Delta^{17}O$-signature, might testify to the fact that surficial, hydro-/atmospheric oxygen isotopes were a (transient?) major control on NWA 7034 minerals during the early Amazonian, but that hydrothermal fluid circulation and a high fluid/rock ratio probably did not permanently perturb the oxygen isotope system of the fluid.

**References:** [1] Agee, C.B. et al. (2013) *ScienceExpress* DOI: **10.1126/science.1228858**. [2] Karlsson, H.R. et al. (1992) *Science* **255**, 1409-1411. [3] Romanek C.S. et al. (1998) *Meteorit. Planet. Sci.*, **33**, 775-xxx. [4] Farquhar, J. et al. (1998) *Science* **280**, 1580-1582. [5] Slater, V.P. and McSween, H.Y. (2002) *Meteoritics & Planet. Sci.*, **37,** A5107. [6] Channon, M.B. et al. (2009) *LPS **XXXX,*** Abstract #2450. [7] Channon, M.B. et al. (2010) *LPS **XXXXI,*** Abstract #2212. [8] Rumble, D. III and Irving, A.J. (2009) *LPS **XXXX,*** Abstract #2293. [9] Lee, D.-C. and Halliday, A.N. (1997) *Nature* **338**, 854-857. [10] Kleine, T. et al. (2003) *Geophys. Res. Abstr.* **5**, 11656. [11] O'Neil, J.R. (1986) *Rev. Mineral.* **16**, 1–40. [12] Herd, C.D.K. (2003) *Meteoritics & Planet. Sci.,* **38,** 1793-1805. [13] Cartwright, J.A. et al. (2013) *this conference*.