

## Oxygen Isotope Anomalies of Primary and Secondary Minerals Reveal Past and Present History of Mars Atmosphere and Implications for the Mars Sample Return

Robina Shaheen<sup>1</sup>, V. Smirnova, T. Jackson, M. H. Thiemens,

<sup>1</sup>Department of Chemistry and Biochemistry, University of California, San Diego, La Jolla, California, 92093 USA .

[Robina@ucsd.edu](mailto:Robina@ucsd.edu) and [mthiemens@ucsd.edu](mailto:mthiemens@ucsd.edu)

**Introduction:** Oxygen with its three stable isotopes is unique in the solar system as a compound it coexists in all three phases, (gas, liquid and solid). The oxygen triple isotopes of these compounds are ideal to study interactions between the atmosphere-hydrosphere-geosphere systems. The oxygen isotopic composition of silicate minerals and water on earth follow a distinct pattern termed mass dependent fractionation. Most of the physical and equilibrium processes fractionate oxygen triple isotopes proportional to the relative mass difference between isotope pairs such as ( $^{18}\text{O}/^{16}\text{O} \sim 0.5 * ^{17}\text{O}/^{16}\text{O}$ ). The oxygen isotopic composition of silicate minerals generally follow mass dependent fractionation line and variations may quantify temperature of equilibrium ( $\delta^{18}\text{O} = 5.2$  to  $6.0$  permil and  $\delta^{17}\text{O} = 2.6$ - $3.0$  permil). The oxygen triple isotopic composition of silicate minerals in SNC (Shergotty-Nakhla-Chassigny) meteorites from Mars do not follow this mass fractionation line ( $\Delta ^{17}\text{O} = 0.3$  ‰;  $\delta^{18}\text{O} = 3.5$ - $5.0$  ‰). The deviation from this mass fractionation line is referred to as an O-isotope anomaly and quantified as  $\Delta ^{17}\text{O} = \delta^{17}\text{O} - 0.52 * \delta^{18}\text{O}$ . Meteoritic parent bodies may be identified on the basis of the  $\Delta ^{17}\text{O}$  values. NWA 7034, a newly found meteorite from Mars not only showed higher enrichment in heavier isotopes  $\delta^{18}\text{O} = 5.5$ - $6.6$  ‰ but also twice the normal anomaly;  $\Delta ^{17}\text{O} = 0.6$  ‰ (Agee et al., 2013) compared to other meteorites from Mars. The higher anomaly observed in NWA 7034 is puzzling and begs for a plausible explanation beyond simply heterogeneity in the planetesimal material.

We have observed that in the present day atmosphere carbonate minerals acquire an O-isotope anomaly from ozone during photochemical transformation of surface adsorbed water in the ozone rich environment (Shaheen et al., 2010). With these experiments in mind we have begun to investigate how silicate minerals can acquire O-isotope anomaly in similar environment. Since Mars has an ozone-O<sub>2</sub> and some water environment, especially in the past, a record of this interaction might be stored in surface minerals, particularly in the absence of tectonics, surface minerals may exist as such for extended time periods

We have conducted a series of laboratory experiments using the JSC-Mars-Simulant to mimic interactions between the atmosphere-hydrosphere-geosphere and photochemical transformations on Mars. The goal of these experiments is to understand how oxygen carrying mineral in JSC-Mars Simulant will change its O-isotopic composition on exposure to UV light in the presence of ozone and plus or minus water and understand the role of the hydrosphere during photochemical transformations. Four sets of experiments include: 1) JSC-Mars simulant-H<sub>2</sub>O- O<sub>3</sub>-UV light; 2) Fe<sub>2</sub>O<sub>3</sub>- H<sub>2</sub>O-O<sub>3</sub>-UV light; 3) CuO- O<sub>3</sub>-H<sub>2</sub>O-UV light; 4) TiO<sub>2</sub>-H<sub>2</sub>O-O<sub>3</sub>-UV; and two controls a) JSC-Mars simulant-UV; b) JSC-Mars simulant-H<sub>2</sub>O were also conducted. The rationale behind using ozone in these experiments is that O<sub>3</sub> molecule it is the driver of oxidative processes and possesses the highest isotopic enrichment ( $\delta^{17}\text{O} = 65$ - $117$  ‰ and  $\delta^{18}\text{O} = 73$ - $135$  ‰ with  $^{17}\Delta$  values of 25- 40 ‰). Ozone can transfer its O-isotope anomaly to other oxygen carrying molecules and especially solids ( Shaheen et al., 2007; Thiemens and Shaheen 2014). The reaction products (O<sub>2</sub>, H<sub>2</sub>O<sub>2</sub> and H<sub>2</sub>O) were collected after 18hr of exposure to UV light and their oxygen triple isotopic composition was measured using a Finnigan 253 Isotope Ratio Mass spectrometer. The premise to use individual minerals in set 2,3,4 was to identify the specificity of individual minerals present in the JSC-Mars simulant. The oxygen sample produced from ozone decomposition with the UV light showed large depletion compared to the initial ozone ( $\delta^{17}\text{O} = 67$  ‰ and  $\delta^{18}\text{O} = 68$  ‰,  $^{17}\Delta = 32$  ‰) used in these experiments with an array  $\delta^{17}\text{O} = 0.7064 * \delta^{18}\text{O} + 0.775$ ). The JSC-Mars simulant and other O-carrying mineral after exposure to ozone and UV light will be analysed for the O-triple isotopic composition.

These experiments will help us to estimate various oxidants and free radicals that can interact with organic matter and to decide the future sites for Mars sample return where organic materials may have been preserved.

Agee et al., Doi: 10.1126/Science.1228858, 780 (2013).

Thiemens and Shaheen (2014) Treatise on Geochemistry, 2<sup>nd</sup> edition.

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