

LABORATORY OBSERVATION OF MASS-INDEPENDENT OXYGEN ISOTOPIC COMPOSITION IN SOLID SILICATES THROUGH GAS PHASE REACTION: COSMOCHEMICAL IMPLICATIONS. S. Chakraborty, Petia Yanchulova and M. H. Thieme*, University of California, San Diego, Department of Chemistry and Biochemistry, 9500 Gilman Drive, La Jolla, CA 92093-0356 (subrata@ucsd.edu).

Introduction: A wide range of oxygen isotopic compositions have been observed in meteorites, possibly reflecting heterogeneity in the solar nebula on length scales from sub-millimeter to planetary dimensions. A striking feature is the departure from the normal terrestrial mass fractionation line (represented by a slope $\frac{1}{2}$ line in a 3-isotope plot of oxygen). The oxygen isotopic composition of meteoritic material reveals that different groups lie on lines of differing slope values distinct from terrestrial. The CAI's (calcium-aluminum rich refractory inclusions), ordinary chondrites (H, L, LL), and C3 chondrites are distinctly grouped in 3-isotope space. Most carbonaceous chondrites are individually grouped following a trend with a slope lower than the CAI's, whereas the enstatite chondrites lie over the terrestrial fractionation line (TFL) [1-3].

Photo-chemical self-shielding of nebular CO (the most abundant oxygen carrying molecule in nebular environment) has been re-proposed as a process for generating water highly and equally enriched in ^{17}O and ^{18}O . The mixing of this water reservoir with an ^{16}O -rich solar reservoir is a proposed mechanism for producing the observed CAI line (slope one in oxygen 3-isotope plot) [4-7]. Experimentally measured oxygen isotopic fractionation data for CO photodissociation yields a wavelength dependent fractionation trend and is not totally supportive of self-shielding as a mechanism for generating a reservoir with equal ^{17}O and ^{18}O enrichment [8-9], consequently exploration of alternative mechanisms is warranted. One issue to be addressed irrespectively, is the mechanism by which the anomalous oxygen survives as water and becomes incorporated into meteoritic material and produces meteoritic bulk isotopic compositions. Apart from the CAI's oxygen isotopic distribution slope one line, the oxygen isotopic compositions of different chondritic groups is difficult to explain with a general two-component mixing model. A mass-independent effect in gas-phase [10] and condensed phase (over the grain surface [11]) chemical reactions is potentially important to explain the complex oxygen isotope map of early solar system materials. In any model, determining the isotopic fractionation factors associated with the gas to solid formation for oxygen is needed and presently unknown. A limitation is the lack of relevant measurements due to the difficulty in performing experiments. In this abstract, we describe experiments of the oxidation reaction of SiO to form SiO_x in the *gas-*

phase and present isotope results from the gas and solid phase products and reactants.

Experimental: Ultra high pure SiO nuggets ($\sim 2\text{-}4$ mm in size) were vaporized inside a vacuum chamber by an Excimer laser beam (248 nm) in two different ways for two different sets of experiments: (a) in the presence of a well-known amount of neat ultra high purity oxygen (of known isotopic composition) and (b) in the presence of a mixture of oxygen and hydrogen in varied proportions. During the vaporization process solid oxides (SiO_x) are formed throughout the chamber, indicating gas-phase reaction in the laser-induced hot (~ 2000 °C) plume as shown in Figure 1. In the first set of experiments the residual oxygen was collected and measured for its isotopic composition in a Finnigan MAT 253 IRMS. For the second set, residual oxygen was collected after complete separation from hydrogen and the isotopic composition determined. The solid SiO_x products are also collected for two of the second set of experiments and the oxygen isotopic composition determined after reaction of SiO_x by CO_2 -laser fluorination (using BrF_5). In one experiment, the amount of solid SiO_x was too small to process. To compensate for this, 7 to 10 experimental runs were performed with a carefully fixed H_2/O_2 ratio to produce sufficient solid for high precision isotopic analysis.



Figure 1. Microscopic image of SiO_x formed in the laser plume in gas phase: (a) the white SiO_x formed on the bottom plate of the reaction chamber; (b) SiO_x formed underneath the MgF_2 window of the reaction chamber.

Results and Discussion: The measured isotopic composition of residual oxygen for both experimental sets are shown in Figure 2. For oxidation by only oxygen, the left-over oxygen lies along a trend line of slope value close to 0.51, with an intercept close to zero (with respect to initial oxygen), e.g. strictly mass dependent. In the presence of H_2 , the residual oxygen follows a mass-independent (MI) nonlinear trend with non-zero intercepts. The non-zero intercepts require a multi-step fractionation process.

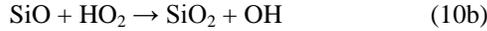
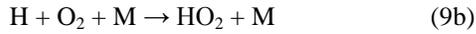
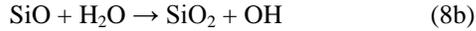
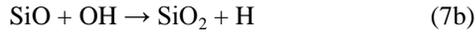
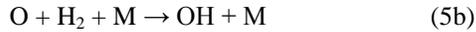
For set (a), the expected reactions for SiO are the following:

Neat O_2 (without H_2),



For set (b), the reactions are:

O_2 and H_2 (above 4 Rx as: 1b – 4b, and),



Comparing these sets of reactions (a and b), it is clear that the observed mass independent composition is not due to formation of ozone, otherwise, instead of a normal composition, a MI composition would have been observed for the case without H_2 (set (a)), as ozone formation is more favorable. However, the MI composition was seen in residual oxygen which was recycled through set (b) reactions, the reverse of that which should occur if ozone were a relevant reactant.

The isotopic composition of the product SiO_x also possess a MI composition (Figure 3). The extent of the MI component is about 0.6 ‰ for the experiments. Since the trend line for the silicate (red line in Figure 3) is not parallel to the mass dependent line (black line in Figure 3) the higher values of $\Delta^{17}\text{O}$ may be possible in the silicate phase in cases where the residual oxygen is less fractionated.

Since reaction (9b) is known to generate a MI effect [12], there is a possibility that residual oxygen acquires a MI character through these reaction channels (9b and 10b). To test this reaction channel, another set of experiments were performed where a mixture of O_2 and H_2 was photolyzed in a glass chamber (without presence of any metal) using the UV photons from the same Excimer laser. The residual oxygen from these experiments are also shown in Figure 2 and the measured oxygen isotopic compositions are mass dependently distributed (as that of set (a) experiments). The photolysis experiment of the O_2 and H_2 mixture indicate that the MI character measured in silicates from set (b) experiments are not originated from the HO_2 species, rather the MI composition in silicates is generated through reaction 7b, i.e., reaction of SiO with OH . A similar reaction (e.g., $\text{CO} + \text{OH}$) is known to produce MI effect [13].

Some indication of a MI fractionation in silicate production was previously obtained from the silicate formation reaction in the smoke chamber of GSFC [14] through OH oxidation. The present experiment clearly established the fact that MI composition in silicate is generated through OH oxidation. In the inner solar nebula, OH is a dominant species and oxidation through OH may be a route towards silicate formation and may give rise to the MI signatures in different

chondritic groups. Regardless of whether self shielding is operative or not, the final step leading to the solid sample is capable of producing a mass independent fractionation and we are in the process of evaluating the single stage fractionation factor to allow for development of relevant models.

References: [1] Clayton R. N. (1993) *Annual Review of Earth and Planetary Sciences*, 21, 115-149. [2] Clayton R. N. et al. (1973) *Science*, 182, 485-488. [3] Thiemens M. H. (2006) *Annual Review of Earth and Planetary Sciences*, 34, 217-262. [4] Clayton R. N. (2002) *Nature*, 415, 860-861. [5] Yurimoto H. and Kuramoto K. (2004) *Science*, 305, 1763-1766. [6] Greenwood J. P. et al. (2011) *Nature Geosci*, 4, 79-82. [7] Lyons J. R. and Young E. D. (2005) *Nature*, 435, 317-320. [8] Chakraborty S. et al. (2008) *Science*, 321, 1328-1331. [9] Chakraborty S. et al. (2009) *Science*, 324, 4. [10] Thiemens M. H. and Heidenreich J. E. (1983) *Science*, 219, 1073-1075. [11] Dominguez G. (2010) *Astrophysical Journal Letters*, 713, L59-L63. [12] Savarino J. and Thiemens M. H. (1999) *The Journal of Physical Chemistry A*, 103, 9221-9229. [13] Röckmann T. et al. (1998) *Science*, 281, 544-546. [14] Kimura Y. et al. (2007) *Meteoritics & Planetary Science*, 42, 1429-1439.

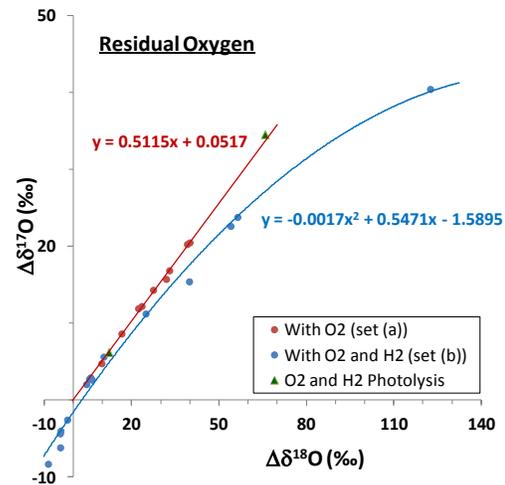


Figure 2. Oxygen isotopic compositions of left-over oxygen for set (a) and set (b) experiments. Also shows the compositions for photolysis of O_2 and H_2 mixture.

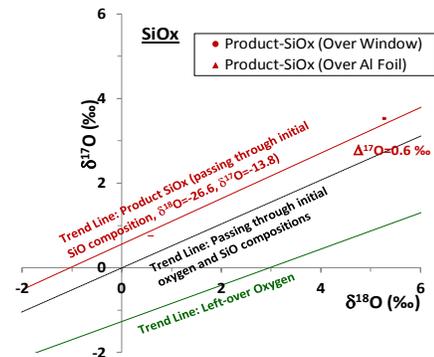


Figure 3. Oxygen isotopic compositions of product SiO_x . The red trend line shows the evolution of isotopic composition of silicate starting from the initial SiO .