

ROLE OF SYMMETRY IN MASS-INDEPENDENT OXYGEN ISOTOPIC COMPOSITION IN LABORATORY SYNTHESIZED SILICATES. S. Chakraborty*, Petia Yanchulova and M. H. Thiemens, University of California, San Diego, Department of Chemistry and Biochemistry, 9500 Gilman Drive, La Jolla, CA 92093-0356 (subrata@ucsd.edu).

Introduction: The oxygen isotopic composition of high temperature mineral phases, e.g., anorthite, melilite, perovskite, aluminous spinel, hibonite, calcic pyroxene, and forsterite-rich olivine, in the first condensates in the protoplanetary disk- calcium aluminum rich inclusions (CAIs), are distributed along a slope 1 line in a 3-isotope plot (in $^{18}\text{O}/^{16}\text{O}$ vs. $^{17}\text{O}/^{16}\text{O}$ space) with a significant enrichment in ^{16}O (~ 50 ‰ with respect to the terrestrial composition, with an equal amount of ^{17}O and ^{18}O) [1]. Most chondrules which formed shortly (< 1 My) after the CAIs [2] also display an oxygen isotopic distribution along the same slope 1 line, with less ^{16}O enrichment than CAIs [3, 4]. The O-isotopic distribution is striking because of the departure from the normal terrestrial mass dependent fractionation line observed for equilibrium and kinetic fractionation processes [5, 6]. As the most abundant in silicate bodies, defining the source of the anomalous isotopic distribution of oxygen is vital to understanding the formation and evolution of the solar system.

Symmetry and Mass-Independent Isotope Effect: After the failure to find the signatures of supernova debris in the meteorites, the initially proposed nuclear theory [1] was abandoned and chemical and photochemical based theories emerged. Since the first demonstration of a mass independent (MI) fractionation process in a chemical reaction during ozone formation (slope of 1, as in CAIs) through a gas-phase recombination reaction, such MI reactions have been proposed in the nebula for silicate formation [7-11].

The best example to represent the role of *Symmetry* in a chemical reaction for a MI isotope effect is *ozone*. A full physical chemical treatment of the apparently simple ozone formation reaction, $\text{O} + \text{O}_2 + \text{M} \rightarrow \text{O}_3 + \text{M}$, constitutes one of the greatest challenges in physical chemistry though it is recognized that quantum mechanics plays a crucial role in the isotopic selection process. The above reaction consists of two steps: (i) $\text{O} + \text{O}_2 \rightarrow \text{O}_3^*$ and, (ii) $\text{O}_3^* + \text{M} \rightarrow \text{O}_3 + \text{M}$. There may be two separate kinds of isotope effects involved in these two steps and the quantum delta zero-point energy (ΔZPE) effect may be operative in the first step (observed in experiments on formation of asymmetric isotopomers of ozone such as $^{16}\text{O}^{16}\text{O}^{18}\text{O}$) as reproduced by statistical, quantum-mechanical and, classical trajectory models, which is mass-dependent (MD) [12-14]. However, the slope-one line in ozone formation passes through zero (wrt initial O_2), which is only possible for a single stage fractionation requiring the second step to be responsible for the measured fractiona-

tion. The uncertainty and disagreements among different theoretical approaches lie with the defining the mechanism of the second step of stabilization of the vibrationally excited intermediate species (O_3^*). In symmetric molecules some state-to-state transitions are forbidden by symmetry, which could lead to reduced stabilization cross-sections and hence a lowered stabilization of symmetric molecules relative to asymmetric species within the specific lifetime (~ 100 ns) of O_3^* . Marcus and co-workers described this in terms of coupling of asymmetric and symmetric species to the exit channel (stable O_3 molecule) in an empirical fashion—“ η effect” (non-RRKM framework [8]). Using quasiclassical trajectory calculations, Schinke and co-workers [14] found that their treatment too required an ad hoc means of enhancement in the formation rate of asymmetric ozone relative to the symmetric species of the same order of magnitude (~15%) as that of Marcus et al. Recently using a mixed quantum-classical theory the origin of “ η effect” has been explained at the molecular level, where, it is demonstrated that the “ η effect” is not caused by the absence of some state-to-state transitions due to quantum symmetry selection rules, and does not occur during the stabilization step of the ozone forming process rather due to differences in the lifetimes of the metastable O_3^* states, i.e., in differences of tunneling rates in/out of the reaction channels for symmetric and asymmetric isotopomers due to distortion of vibrational wave functions by isotopic substitutions. A common feature though is that all have at the basis symmetry dependence for the effect.

It was experimentally demonstrated that the symmetry dependent MI isotopic fractionation is not unique to ozone chemistry but rather a general effect of particular relevance to oxygen. Chemical reactions such as $\text{CO} + \text{O} \rightarrow \text{CO}_2$, $\text{CO} + \text{OH} \rightarrow \text{COOH}^* \rightarrow \text{CO}_2 + \text{H}$, show a MI affect in O-isotopes where the symmetry determines the distribution of isotopes of oxygen in the product molecules [15, 16]. In this abstract, we report the result of our investigation to decipher the role of symmetry in SiO_2 formation in gas phase reactions.

Laboratory Experiments: Gas-phase oxidation was performed by vaporizing ultra high pure SiO nuggets (~ 2 mm in size) inside a vacuum chamber by an Excimer laser beam (248 nm, KrF, 120 mJ, 25 Hz) in two different ways: (set-I) in the presence of a known amount of ultra high purity O_2 of known isotopic composition and, (set-II) in the presence of a mixture of O_2 and H_2 in varied proportions of ~1 to 32 H_2/O_2 . For

both conditions, during vaporization white-colored solid oxides (SiO_x) are formed throughout the chamber, indicating gas-phase reaction in the SiO plume [17, 18] with the bath gas inside the chamber. In set-I, the residual O_2 was collected and measured for its isotopic composition in a Finnigan MAT 253 IRMS. For set-II, residual O_2 was collected after complete separation from H_2 and the isotopic composition determined. The solid SiO_2 products are also collected for both the sets of experiments and the oxygen isotopic composition determined after reaction of SiO_2 by CO_2 -laser fluorination.

Results and Discussion: The SEM analysis of product SiO_x formed in set-I and set-II experiments show a stoichiometry of SiO_2 . The O-isotopic compositions of the residual O_2 for set-I experiments lies on a line with slope of 0.516, with intercept close to zero (wrt initial O_2) with an effective fractionation factor of 48 ‰. However, for set-II experiments, the residual O_2 follows a MI nonlinear trend with non-zero intercept, and consequently requires a multi-step fractionation processes in the oxidation reaction chain [19].

The measured O-isotopic composition of product SiO_2 (Figure 1) for set-I and set-II experiments show MD and MI compositions for set-I and set-II experiments, respectively. In presence of H_2 (set-II), the maximum measured value of $\Delta^{17}\text{O}$ is 1.7 ‰. The main oxidation step for set-I is $\text{SiO} + \text{O}_2 \rightarrow \text{SiO}_2$ (group 1), whereas for set-II oxidation possibly happens through group 1 reaction (as above) plus through $\text{SiO} + \text{O}_x\text{H}_y \rightarrow \text{SiO}_2 + \text{O}_{x-1}\text{H}_y$ (group 2). A chemical kinetic model was developed using MATLAB incorporating all the possible reactions and tracked the time evolution of different species, which shows that the SiO_2 production via group-1 reaction is about 9 times more than that produced via group-2 reactions. Among all these

the importance of O_xH_y oxidation reactions as a source of MI composition and postulated that $\text{SiO} + \text{OH}$ is the MI channel in line with the known MI reaction $\text{CO} + \text{OH}$ [15]. Therefore, the measured $\Delta^{17}\text{O}$ values in set-II experiments are severely diluted. Using isotopic mass balance calculation, the compositions of SiO_2 formed via group 2 reactions are determined, which define a line of slope 1.09 (± 0.1) passing through the calculated SiO_2 composition ($\delta^{18}\text{O} = -18.4$ ‰, $\delta^{17}\text{O} = -9.5$ ‰) formed by the measured $\text{SiO} + \text{O}_2$ reaction [19].

Both the production channels of SiO_2 in the present experiment (i.e., $\text{SiO} + \text{O}_2$ and $\text{SiO} + \text{OH}$) follow through excited intermediates (i.e., SiO_2^* and SiOOH^*). Similar to $\text{O}_2 + \text{O}$ recombination, $\text{SiO} + \text{O}_2$ was expected to be MI contrary to the measurement (i.e., MD). This may be due to quick exchange between SiO_2 and O_2 reservoirs (at high plume temperature), which erased the MI signature in SiO_2 and a different experimental approach is required to decipher this channel (without exchange). However, the other symmetry governed OH oxidation channel does show MI signature (with slope 1) as demonstrated here and might be relevant for the solar nebula. SiO is a relevant solar nebular species and oxidized by OH in the hot (> 1000 K) inner nebula is plausible [20-22]. Regardless of whether self-shielding is operative or not, the final step leading to the solid formation is likely produces a MI fractionation. Further experiments are required to generate more complex silicate minerals with other cations.

References: [1] R. N. Clayton, et al. (1973) *Science*, 182, 485-488. [2] J. N. Connelly, et al. (2012) *Science*, 338, 651-655. [3] R. N. Clayton (2007) *Ann. Rev. Earth Planet. Sci.*, 35, 1-19. [4] M. H. Thiemens (2006) *Ann. Rev. Earth and Planet. Sci.*, 34, 217-262. [5] H. C. Urey (1947) *J. Chem. Soc.*, 18. [6] M. F. Miller (2002) *Geochim. Cosmochim. Acta*, 66, 1881-1889. [7] J. E. Heidenreich and M. H. Thiemens (1986) *J. Chem. Phys.*, 84, 2129-2136. [8] Y. Q. Gao and R. A. Marcus (2001) *Science*, 293, 259-263. [9] M. H. Thiemens and J. E. Heidenreich (1983) *Science*, 219, 1073-1075. [10] J. E. Heidenreich and M. H. Thiemens (1983) *J. Chem. Phys.*, 78, 892-895. [11] J. R. Lyons and E. D. Young (2005) *Nature*, 435, 317-320. [12] M. V. Ivanov and D. Babikov (2013) *Proc. Natl. Acad. Sci.*, 110, 17703-17707 [13] R. A. Marcus (2013) *Proc. Natl. Acad. Sci.*, 110, 17703-17707. [14] M. V. Ivanov and R. Schinke (2009) *Mol. Phys.*, 108, 259-268. [15] T. Röckmann, et al. (1998) *Science*, 281, 544-546. [16] A. K. Huff and M. H. Thiemens (1998) *Geophys. Res. Lett.*, 25, 3509-3512. [17] M. Jadrake, et al. (2009) *The J. of Phys. Chem. A*, 113, 10880-10885. [18] E. Fogarassy, et al. (1990) *App. Phys. Lett.*, 57, 664-666. [19] S. Chakraborty, et al. (2013) *Science*, 342, 463-466. [20] G. J. MacPherson and A. Boss (2011) *Proc. Natl. Acad. Sci.*, 108, 19152-19158. [21] F. J. Ciesla and J. N. Cuzzi (2006) *Icarus*, 181, 178-204. [22] W. Catherine, et al. (2010) *Astrophys. J.*, 722, 1607.

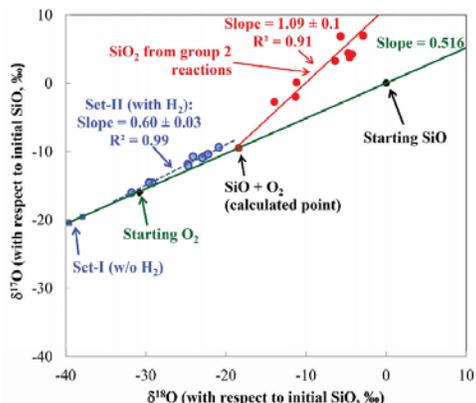


Figure 2. Measured oxygen isotopic composition of SiO_2 from set-I and set-II experiments. The calculated SiO_2 compositions from $\text{SiO} + \text{O}_x\text{H}_y$ reactions (group 2) follow a slope of 1.09.

O_xH_y channels, OH contributes the most. This indicate