

**MINERAL FORMATION AND GROWTH WITH ANOMALOUS OXYGEN ISOTOPIC COMPOSITION ON SILICEOUS DUST SURFACES.** S. Chakraborty\* 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 formation of metal oxide dust is a complex process and theoretical chemistry of these reactions on dust particles is poorly known. Dust is ubiquitous in the universe and constitutes about 10 % in planetary nebulae [1, 2]. Dust particles are predominantly of two types— carbonaceous and siliceous. Dust particles are significantly processed during their lifetime within the stellar region through diffuse, dense or molecular clouds to new stars or its planetary system. Simple condensation at the cooler region of the stellar outflow does not produce complex minerals (i.e., Forsterite-  $\text{Mg}_2\text{SiO}_4$ , Fayalite- $\text{Fe}_2\text{SiO}_4$ , etc.).

One intriguing observation associated with refractory silicate minerals found in primitive meteorites is their unique oxygen isotopic compositions. The O-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  $^{16}\text{O}$  (~ 50 ‰ with respect to the terrestrial composition, with equal changes of  $^{17}\text{O}$  and  $^{18}\text{O}$ ) [3-7].

For the solar nebula, the measured distribution of O-isotopic compositions is commonly explained using different reservoirs of distinct compositions within the nebula. Photochemistry (i.e., CO photodissociation) was also invoked to create an isotopically distinct water reservoir [8]. However, so far the explanations are not satisfactory due to several complicating unknowns [9]. It has been recently shown that through gas phase oxidation reaction ( $\text{SiO} + \text{OH}$ ) simple silicate ( $\text{SiO}_2$ ) could be formed with O-isotopic compositions similar to the slope values as that of the meteorites [10], which means that the isotope effect in this formation reaction erases the initial signature of the initial species (i.e., SiO and OH). These types of reactions are possible under nebular conditions and will generate isotopically distinct reservoirs within the nebula during chemical reactions, and the photochemical signature stored in OH (via photochemistry of CO) will be lost.

The chemistry of transformation of siliceous dust (SiO) to a complex silicate mineral is mechanistically poorly understood at best. The chemistry of the growth of silicate dust and the O-isotopic composition of meteorite silicate may be directly linked to this formation process, in which case previous isotopic signatures from shielding are lost. We have designed experiments to study the silicate formation of dust analogs and re-

ported the preliminary findings [11]. Here we report results from the more complex mineral formation through surface assisted oxidative reactions on dust analogs of complex compositions.

**Experimental:** Grain surfaces were prepared by a chemical vapor deposition (CVD) technique. SiO powder and SiO powder mixed with powders of  $\text{Al}_2\text{O}_3$ , TiO, FeO, MgO in varying proportions are loaded in a tantalum boat filament inside a vacuum chamber ( $< 10^{-7}$  mbar) and heated at  $\sim 1600$  °C (Fig. 1). A collector plate covered with pre-cleaned Al-foil was placed 1.5 cm above the boat-heater and kept at LN<sub>2</sub> temperature by flowing LN<sub>2</sub> (home-made LN<sub>2</sub> cryostat). During vaporization of the powders, several monolayers were deposited on the face-down surface (covered with Al-foil) of the collector plate. A separate arrangement was made to boil H<sub>2</sub>O at 90°C and the vapor was sprayed directly over the SiO layers via a spray nozzle on the top of the monolayers (after the filament was turned off). The LN<sub>2</sub> flow was continued during the entire time of the reaction (mimicking low-temperature grain-surface reactions). After the desired reaction time, LN<sub>2</sub> flow was terminated and the system brought to room temperature (~ 30 min). The cryostat was subsequently opened, and the products were collected from the col-

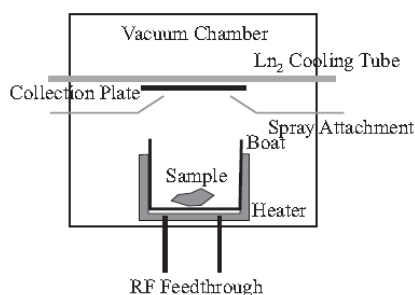


Fig. 1. Schematic of experimental apparatus.

lector plate by removing the Al-foil (the foil was treated as a sample). Each sample was examined with an optical microscope and photographed and stored in a vacuum desiccator. When sufficient samples were collected the samples were analyzed with an environmental (e)-SEM (FEI Scios DualBeam FIB/SEM at Calit2, UCSD) for morphology by placing a small piece of Al-foil sample in the SEM sample holder using double-sided tape. Following SEM analysis, EDX analysis was performed on the formed grains identified in SEM analysis for elemental composition. EDX compositional analysis of the background deposit was also performed for comparison. The O-isotopic compositions of the product silicate minerals were performed for few samples by scraping off the samples from the Al-foil

and loaded in the CO<sub>2</sub>-laser fluorination boat. Following CO<sub>2</sub>-laser fluorination treatment, evolved oxygen was purified and measured in MAT 253 isotope ratio mass spectrometer for triple-oxygen isotopic composition.

**Results:** Figure 2 shows the degree of oxidation (by color, light yellow to dark brown). The morphology of the samples (by high-resolution SEM) vary with the initial composition of the mixture (powder) and the amount of water sprayed. Fig. 2 shows the morphology difference in oxidation process with 1 and 3 aliquots of water vapor (when only SiO powder was used). When powders of (SiO + FeO + MgO + TiO<sub>2</sub> + Al<sub>2</sub>O<sub>3</sub>) of equal proportion were used, cauliflower-type growths were observed that changed to pebble-like structures when the H<sub>2</sub>O vapor amount was reduced from 3 aliquots to 1. The stoichiometry shows a wide variety of compositions. With pure SiO, the O and Si atom-% are in a 2:1 ratio, whereas, when mixed elements are present, the relative compositions of the element in the growth varied significantly. As an example, for experiments with 1:1 mixtures of SiO and Al<sub>2</sub>O<sub>3</sub>, the stoichiometry of the background deposit was (Si: Al:O = 1:3:2), whereas the cauliflower type growth has a stoichiometry of 1:0.8: 2, indicating incorporation of Al was limited. Similar elemental fractionations among different particle growths were measured and will be discussed. The elemental analysis shows a stoichiometry of SiO<sub>2</sub>. The measured O-isotopic compositions of the products are striking as shown in Fig 4. SiO<sub>2</sub> produced on the collector plate are off the mass-fractionation line (slope = 0.52) passed through the initial H<sub>2</sub>O and SiO compositions, following a trend line of slope 1.2.

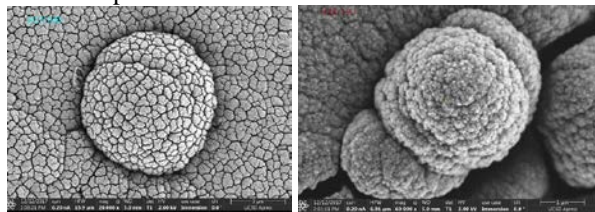


Fig 2. SEM images of SiO<sub>x</sub> (4-5 μm) showing the morphology difference resulted by the change in oxidation condition.

The oxygen isotopic compositions were measured in 4 Al-silicate (bulk) samples and in 3-isotope oxygen plot, the trend line (time evolution) follow a slope of 0.7 (Fig 3). Previously, O-isotopes were measured in pure silicate products and a slope of ~1 was obtained. The lower slope value for Al-silicate may be due to the higher fraction of O from Al<sub>2</sub>O<sub>3</sub> contributed to the final product.

**Discussion:** The preliminary results of the present experiments are very encouraging showing a special kind of oxidation pathway involving an existing sur-

face. SiO oxidation by OH in gas phase produced slope 1 trend line [10], the similar oxidation by OH on the surface might have the potential to proceed in an anomalous way. Experiments show that metal oxide surfaces are reconstructed by hydroxylation when water absorb on the surface [12, 13]. This mechanism is not totally understood and will be discussed in the conference.

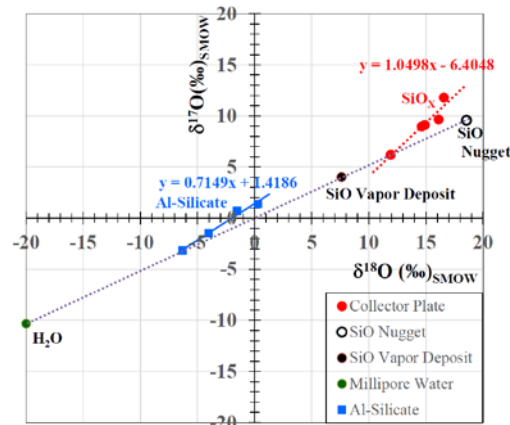


Fig 3. Oxygen three-isotope plot showing the compositions of SiO<sub>2</sub> formed on the collector plate following a trend line of slope 1.2. The SiO vapor deposit layer is depleted compared to the initial SiO Nugget by ~ 11‰ and lie over the mass-fractionation line as shown in the figure.

The OH oxidation scheme on grain surfaces is experimentally observed the process and are relevant process likely operational in the solar nebula. The observation of a mass independent process is consistent with theory and it also is significant as the actual grain formation overwrites the effect of shielding.

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**References:** [1] T. P. M. Goumans and S. T. Bromley (2012) *Monthly Notices of the Royal Astronomical Society*, 420, 3344-3349. [2] G. Stasińska and R. Szczerba (1999) *Astronomy and Astrophysics*, 352, 297-307. [3] R. N. Clayton, et al. (1973) *Science*, 182, 485-488. [4] M. H. Thiemens (2006) *Annual Review of Earth and Planetary Sciences*, 34, 217-262. [5] R. N. Clayton (2007) *Annual Review of Earth and Planetary Sciences*, 35, 1-19. [6] H. C. Urey (1947) *J. Chem. Soc.*, 18. [7] M. F. Miller (2002) *Geochimica Et Cosmochimica Acta*, 66, 1881-1889. [8] J. R. Lyons and E. D. Young (2005) *Nature*, 435, 317-320. [9] S. Chakraborty, et al. (2008) *Science*, 321, 1328-1331. [10] S. Chakraborty, et al. (2013) *Science*, 342, 463-466. [11] S. Chakraborty, et al. (2016) *LPSC XLVII*, 2242. [12] J. Ahdjoudj and C. Minot (1998) *Surface Science*, 402-404, 104-109. [13] H. Tamura, et al. (2001) *Journal of Colloid and Interface Science*, 243, 202-207. [14] C. Minot (2004) *Surface Science*, 562, 237-246.