DEVELOPMENT OF A MOLECULAR BEAM TECHNIQUE TO STUDY EARLY SOLAR SYSTEM SILICON REACTIONS; *Q. W. Dong* and *M. H. Thiemens*, Department of Chemistry, 0356, University of California, San Diego, La Jolla, CA 92093

Silicon monoxide is one of the major gas phase silicon bearing components observed in astronomical environments.[1,2,3] Silicon oxide serves as the major rock forming material for terrestrial and meteoritic bodies.[4] It is known that several gas phase reactions produce mass independent isotopic fractionations[5] which possess the same $\delta^{17}O/\delta^{18}O$ ratio observed in Allende inclusions.[6] The general symmetry dependence of the chemically produced mass independent isotopic fractionation process suggests that there are several plausible reactions which could occur in the early solar system which may lead to production of the observed meteoritic oxygen isotopic anomalies. An important component in exploring the role of such processes is the need to experimentally determine the isotopic fractionations for specific reactions of relevance to the early solar system. It has already been demonstrated that atomic oxygen reaction with CO,[7] a major nebular oxygen bearing species, produces a large (~90 ‰), mass independent isotopic fractionation. The next hurdle regarding assessing the involvement of symmetry dependent isotopic fractionation processes in the pre-solar nebular is to determine isotopic fractionation factors associated with gas phase reactions of metallic oxides. In particular, a reaction such as $O + SiO \longrightarrow SiO_2$ is a plausible nebular reaction which could produce a $\delta^{17}O \approx \delta^{18}O$ fractionation based upon molecular symmetry considerations. While the isotopic fractionations during silicate evaporation and condensation have been determined,[8] there are no isotopic studies of controlled, gas phase nucleation processes. In order to carefully control the reaction kinetics, a molecular beam apparatus has been constructed. This system produces a supersonic, collimated beam of SiO molecules which is reacted with a second beam of oxygen atoms. An important feature of molecular beams is that they operate at sufficiently low pressures and high temperature in the jet that avalanche nucleation and clustering processes may be avoided.

The oxidation reaction of silicon monoxide (SiO) is conducted in a vacuum chamber equipped with a silicon monoxide molecular beam and a radio frequency (rf, 13.56 MHz) glow discharge flow system which produces atomic oxygen from O_2. Commercial silicon monoxide powder is used as the volatile SiO precursor. The SiO beam is provided by high temperature jet expansion through a ~0.1mm aperture into a high vacuum chamber. The beam gun is designed for heats to 1900 °C and is made of an alumina tube using tungsten as the heating element. The temperature of silicon monoxide is monitored by a thermocouple inside the alumina tube and close to the nozzle exit. A second jet of oxygen atoms, produced in the rf discharge, is admixed with the SiO jet and the reaction product (SiO_x) is condensed on a silver plated copper substrate. The actual temperature on the surface of substrate is not known, but may be assumed to be below room temperature for a nozzle temperature of 1700 °C. The substrate is maintained at low temperature via vacuum feedthroughs to a cryogenic reservoir. The total pressure of the reaction is about 18μm. The inert gas used for the backing pressure of the SiO molecular beam is ~6 Torr. The presumed O atom flux under the output power (40 W) of generator for an oxygen pressure 200~400 militorr is estimated at 10^{17}~10^{18} (molec. cm^{-2} s^{-1}),[9] which insures an excess of oxygen atoms. The silicon monoxide vapor pressure is then the kinetic rate limiting factor for the reaction.

The SiO_x condensation product has been examined by a scanning electron microscope equipped with an energy dispersive spectrometer (SEM/EDXS). The deposition rate of the vapor on the substrate is estimated at over 1000Å per minute. The semi-transparent thin film of 50μm thickness on the surface of the substrate has been examined for surface morphological characteristics and elemental analysis with X-ray spectroscopy. Using fused quartz and starting

SiO material as the references for the unknown thin film, a stoichiometry for the condensate collected on the substrate of $SiO_{1.8}$ is obtained. At least two reaction possibilities to account for this stoichiometry may be considered. If, during warm-up and cool down periods for the gun body, a small amount of SiO vapor may have exited the nozzle and condensed on the collection surface prior to oxygen plasma ignition, a stoichiometric number between one and two for oxygen with each silicon would be observed. Alternatively, and more likely, the reaction:

$$SiO_{(g)} + O_{(g)} + M \longleftrightarrow [SiO_{2(g)}]^* + M \longleftrightarrow SiO_{2(s)} + M$$

is collisionally limited, e.g., there are insufficient molecular collisions for stabilization of the vibrationally excited SiO_2^* species and re-dissociation occurs. Therefore, a mixture of SiO_2 and unreacted SiO is achieved. The collisional dependence of this process will be investigated by third body pressure and compositional variations. Based upon the present observations and analytical examinations, it is apparent that the beam system has successfully produced gas phase nucleation. The morphological characterizations are of interest for comparison with, e.g. interstellar grains recovered from meteoritic material. Ultimately, the physico-chemical characterization of the relevant parameters, such as molecular number density, composition, temperature and time (viz. kinetics) will be of importance in evaluation of interstellar grains and their histories. The molecular beam apparatus and collection features are such that studies involving other astrophysically interesting molecules, e.g. AlO, FeO_x and MgO may be studied, thus providing an enhanced kinetic-mechanistic understanding of the initial nucleation processes in the pre-solar nebular. Isotopic analyses will be of even greater interest since they are of direct importance in the interpretation of meteoritic isotopic measurements.

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