

EXPERIMENTAL AQUEOUS ALTERATION OF AMORPHOUS SILICATE SMOKES. L. J. Chizmadia¹, J. A. Nuth III² and F. J. M. Rietmeijer³, ¹NASA Astrobiology Institute, Institute for Astronomy, University of Hawai'i, Honolulu, HI 96822 lchiz@ifa.hawaii.edu, ²Astrochemistry Laboratory, NASA Goddard Space Flight Center, Greenbelt, MD 20771, Joseph.A.Nuth@nasa.gov, ³Department of Earth & Planetary Science, University of New Mexico, Albuquerque, NM 87131 fransjmr@unm.edu.

Introduction: Nuth and his colleagues have created amorphous non-stoichiometric silicate smokes of various compositions by combustion from gas-phase precursors [1]. These smokes have metastable eutectic compositions and have similar infrared spectra as the materials observed in circumstellar and cometary dust [1]. These smokes were characterized with TEM techniques and were found to be composed of chains of rounded amorphous particles 10-50 nm in size [2,3].

Subsequent annealing experiments showed that the Mg silicate smokes anneal into 200-250nm sized particles of forsterite, tridymite and periclase at 1000-1100 K in up to 30 hours [1,2]. The Fe silicate smoke required higher temperatures (~1300 K) to anneal in the same time scale as the Mg smoke [1].

Amorphous silicate materials have been reported in the matrices of several primitive carbonaceous chondrites (e.g. CM2 Murchison, CO3 ALHA77307, the ungrouped chondrite Acfer094, CM2 Y-791198 and the anomalous chondrite Tagish Lake) [4-8]. Those in the fine-grained rims of Y-791198 are similar to aggregate IDPs in terms of textures and mineralogy [7]. Could amorphous non-stoichiometric silicate material, similar to that found around nascent stars and in cometary dust, have been incorporated into the matrices of carbonaceous chondrites and then have altered into some of the observed secondary phases?

Methods: Mg-Si-O smokes created at 800K in October 2003 and Fe-Si-O smokes created at 500K in September 2003 were acquired from Joe Nuth's laboratory in the summer of 2005. Two batches of experiments were done at two experimental temperatures (~25°C and ~5°C), one of each composition. Approximately 1.5 mg of amorphous silicate smoke was sealed in a 1.5 mL centrifuge tube and left at the experimental temperature. A 250 mL bottle of distilled H₂O was also left at temperature. 72 hours later, 1.5 µL of distilled H₂O at temperature was added to each tube. At the appropriate time step, the tubes were filled with 100% ethanol at temperature in order to stop any hydration reactions. Preliminary experiments with the Mg silicate smoke showed that the ethanol successfully prevented any further reaction for at least 1 month. In preparation for TEM characterization, each tube was placed in an

ultrasonic bath to disperse the altered smoke into suspension in the ethanol. A 0.5 µL drop of this suspension was applied to 200 mesh Cu TEM grids with lacey formvar and characterized with the EFTEM at the Biological Electron Microscopy Facility at the University of Hawai'i, using an acceleration voltage of 100 kV and an emission currents of 8 and 16 µA.

Results: Initially, both the Fe and Mg smokes are powdery and have static electricity. The Fe smoke is black and shows rust-colored particles in suspension. The Mg smoke is dark gray and forms an opaque suspension.

When characterized with TEM, both compositions are composed of chains of rounded amorphous particles in two size populations (Fe: 5-10 and 20-30 nm; Mg: 5-10 and 20-100 nm), similar to the results of [2,3]. Based on the interaction of the Fe-smokes with the e⁻ beam, they are magnetic. Controls were prepared without H₂O and exposed to the same environments as the hydration samples. After 21 days, the controls were still dark in color, powdery and had static electricity. When characterized, both compositions were composed of rounded amorphous particles with bimodal size distributions, identical to the smoke samples initially characterized. These observations are consistent with the control smokes not having reacted with atmospheric H₂O vapor.

After exposure to distilled H₂O for 21 days, the Fe silicate smokes show no signs of hydration; they remain black and at the bottom of the tubes. Rust-colored particles can be seen when the smoke is suspended into ethanol. No textural changes were observed with TEM; samples from both temperatures are composed of rounded amorphous particles with the same bimodal size distribution (Figure 1) and exhibit a magnetic interaction with the e⁻ beam.

The Mg silicate smokes, however, show an immediate reaction to the addition of H₂O. A viscous gel forms within a minute of exposure to liquid H₂O. With continued exposure, the ~25°C smoke lightens in color: chocolate-colored at 1 day, yellow and white at 2 days, cream-colored at 3 days, off-white at 5 days, white at 7 days. The smoke refrigerated at ~5°C, shows the same trend at a slower rate, achieving caramel-colored at 7 days and cream-

colored at 21 days. Mg-smokes at both temperatures show evidence for the formation of gas during the reaction. At as early as 3 days, mm-sized bubbles are observed at $\sim 25^{\circ}\text{C}$ and the $\sim 5^{\circ}\text{C}$ samples form a ring ~ 5 mm above the bottom of the tube.

TEM observations show the development of hydration features in the Mg smoke. After 24 hours' exposure to H_2O , the Mg smoke is an amorphous gel, showing no signs of its initial particulate nature. This gel is very sensitive to the e- beam and within a few seconds, bubbles begin to appear and grow with continued exposure to the e- beam. After 3 days in contact with water, the $\sim 25^{\circ}\text{C}$ experiments show $\sim 50\text{nm}$ crystallites. They appear poorly crystalline with wavy lattice fringes. This is most likely due to interaction with the e- beam. The subsequent time steps show the crystallites grow somewhat more resistant to the e- beam. At 10 days, the crystallites are stable enough to image the lattice spacing, although, even at $8\ \mu\text{A}$ the crystallites still damage within 10 seconds. They are ~ 0.7 nm apart (Figure 2), consistent with serpentine. The $\sim 5^{\circ}\text{C}$ experiments contain crystallites at 5 days. These are ~ 20 nm in width. This suggests that the $\sim 25^{\circ}\text{C}$ experiments produced thinner crystallites before 3 days but they are easily destroyed by the e- beam and therefore were not observed. Though crystals grow within the Mg-smokes, the amorphous gel material is still the most abundant phase from both temperature batches.

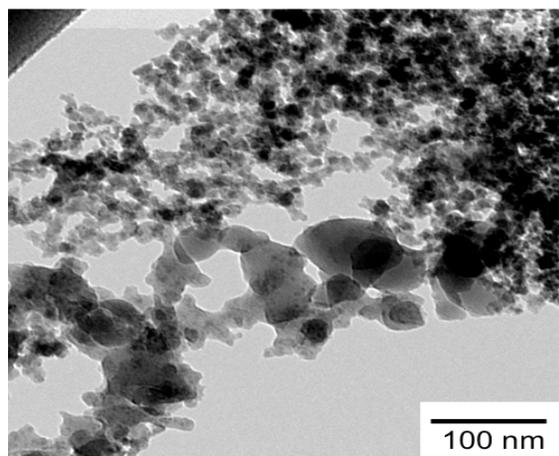


Figure 1: Transmission electron microscope image of amorphous Fe silicate smoke particles after exposure to distilled H_2O at $\sim 25^{\circ}\text{C}$ for 14 days.

Discussion: The immediate reaction of the Mg silicate smoke with H_2O implies that there may be no pristine unhydrated amorphous material remaining in the fine-grained materials of the carbonaceous chondrites. The dominance of the amorphous gel throughout the hydration experiments demonstrates

the robust nature of this material and starts to explain how it can survive the earliest stages of aqueous alteration in the matrices of carbonaceous chondrites. However, the production of serpentine suggests that if amorphous silicate material were incorporated into the fine-grained materials of carbonaceous chondrites, it would alter into the secondary phases observed on a very short time scale. Therefore, in the lightly altered chondrites which contain amorphous material, perhaps it is primary amorphous material which is responsible for the incipient crystallization of nano-crystalline serpentine, as reported by [7].

The resistance of the Fe silicate smoke to hydration is intriguing. [1] observed no changes at the temperatures and timescales that the Mg silicate anneals to crystallize olivine; the Fe silicate smoke required either higher temperatures or longer heating times. We will continue our experiments to see if, with longer times or higher temperatures, the Fe silicate will succumb to the hydration. If it does not, this may indicate that the presence of Fe in the initial amorphous material may retard hydration and explain the survival of amorphous material in the matrices of carbonaceous chondrites.

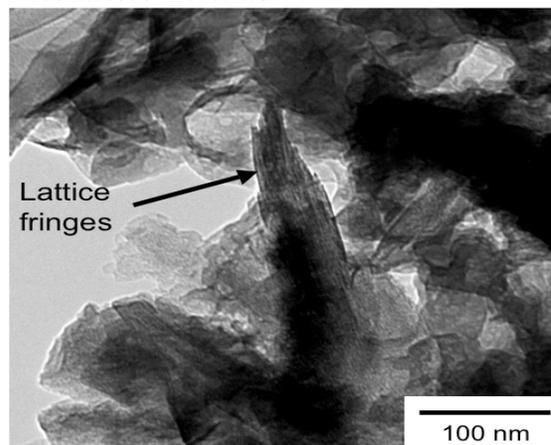


Figure 2: Transmission electron microscope image of a serpentine crystal grown in amorphous Mg silicate smoke exposed to distilled H_2O at $\sim 25^{\circ}\text{C}$ for 21 days.

References: [1] Nuth J. A. et al. (2002) *Meteoritics & Planet. Sci.*, 37, 1579-1590. [2] Rietmeijer F. J. M. et al. (1986) *Icarus* 66, 211-222. [3] Fabian D. et al. (2000) *Astron. Astrophys.*, 364, 282-292. [4] Barber D. J. (1981) *GCA*, 45, 945-970. [5] Brearley A. J. (1993) *GCA*, 57 1521-1550. [6] Greshake A. (1998) *GCA*, 61, 437-452. [7] Chizmadia L. J. and Brearley A. J. (2003) *LPSC XXXIV*, Abstract#1419. [8] Greshake A. et al. (2005) *Meteoritics & Planet. Sci.*, 40, 1413-1431.