

REDUCTION EXPERIMENTS OF AMORPHOUS SILICATES WITH THE MEAN COMPOSITION OF GEMS. J. Matsuno¹, A. Tsuchiyama¹, R. Noguchi¹, A. Miyake², N. Shimobayashi², S. Ichikawa³, N. Souma²,
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Introduction: GEMS (glass with embedded metal and sulfides) are spherical objects of <500 nm in diameter and characteristically included in anhydrous IDPs (Interplanetary Dust Particles), which are considered to be of cometary origin. Nanometer-sized (10-50 nm) Fe-Ni metals and Fe-Ni sulfides grains are embedded in SiO₂-rich silicate glass. Several origins of GEMS are proposed: they are preserved interstellar silicates [1] or formed by condensation from gas in the early solar system [2].

It is known by infrared astronomical observation that interstellar silicates are almost amorphous [3]. If they were brought to an inner region of the early solar system and heated, reduction of the silicates might occur. Reduction of FeO-bearing amorphous silicates of interstellar origin with carbonaceous materials was proposed as the origin of GEMS based on reduction experiments of thin amorphous olivine foils in a reducing atmosphere [4]. However, detailed process of the metal formation and textural relationship with glass were not discussed. In this experiment, in order to study possible GEMS origin by reduction of interstellar silicates, we synthesized amorphous silicates with the mean composition of GEMS and performed heating experiments under reductive atmosphere.

Experiment: We synthesized amorphous silicates for starting material of the reduction experiments. The chemical composition of the system MgO-FeO-SiO₂ was considered for simplicity. The mean composition of GEMS, where all Fe is considered as divalent, (MgO = 28 wt.%, FeO = 22 wt.%, and SiO₂ = 50 wt.%) was obtained from previous GEMS analyses [5-8]. Melt heated at 1873 K for 10 minutes at the oxygen fugacity of 0.5 log unit above the IW (Iron-wüstite) buffer ($fO_2 \sim 10^{-20}$ atm) using a H₂-CO₂ gas mixture was quenched. The quenched glass was cut and cubes of about 2 mm were made.

After that, we carried out heating experiment with the synthesized amorphous silicates. A cube of the starting material was put in a platinum envelope and heated at 1023 K for 1 – 48 hours under reducing condition at the oxygen fugacity of 1.5 log unit below the IQF (Iron-Quartz-Fayalite) buffer ($fO_2 \sim 10^{-23}$ atm) using a H₂-CO₂ gas mixture. The heating conditions were decided based on the previous experiment [4].

A heated sample was divided in two parts by a diamond saw. One is for powder X-ray diffraction analy-

sis (XRD; Geigerflex, Rigaku). The surface and polished cross-section of the other part were observed with a field emission-scanning electron microscope (FE-SEM; JSM-7001F, JEOL) and analyzed with energy-dispersive X-ray spectroscopy (EDS; Inca, Oxford). An ultra-thin section was made from a cross section by focused ion beam (FIB; Quanta 200 3DS, FEI) and observed with a transmission electron microscope with an EDS system (TEM; Tecnai 20 ST, FEI).

We also performed another heating experiment with a powder starting material of the amorphous silicate to examine the effect of the surface to volume ratio to the reduction.

Result and Discussion: The XRD analysis shows that clino-pyroxene was crystallized in the heated samples. Many cracks (typically ~10µm in length and ~1µm in width) were observed both on the surfaces and cross sections. Aggregates of polygonal or spherical objects with slightly FeO-rich margins were also observed on cross sections, and the cracks are present radially in the objects. On the surface and nearby the cracks, there are Fe metal grains of a few µm in size (Fig. 1a). Metal grains present in the cracks have euhedral shapes (Fig. 1b). Smaller Fe metal grains of about 500 nm were observed on the grain surfaces of the powder amorphous silicates (Fig. 1c).

In addition to the metal grains, smaller particles of 50-100 nm in size were also observed inside of the sample under FE-SEM and TEM (Fig. 2). The size of the particles increased with the heating duration. These particles were identified as magnetite or maghemite based on the chemical analysis by TEM-EDS, the lattice spacing of high-resolution TEM images, and TEM restricted diffraction patterns. Clino-pyroxene has stacking faults.

The texture of the run products described above strongly suggests crystallization processes as follows; (1) clino-pyroxene crystallized from the glass as spherulites followed by crystallization of magnetite or maghemite nano-particles between the pyroxene crystals, (2) cracks were formed by volume change by the pyroxene crystallization, and (3) metallic Fe grains were formed on the surface or along the cracks by reaction with the deductive gas. The crystallization of the metallic grains and the magnetite or maghemite nano-particles shows that reduction did not occur inside of the glass but only near the glass-gas interface.

The reduction should occur by H diffusion from the interface to the glass or O diffusion from the glass to the interface. Because O diffusion is slower than H diffusion, O diffusion should control the reduction. Diffusion coefficient of O atom, $D(O)$, was estimated to be $\sim 4 \times 10^{-17}$ m²/s at 1023 K by extrapolation of Arrhenius relation of data for basalt glass [9,10]. Thus, the diffusion distance, $X(O) \sim [D(O)t]^{1/2}$, is ~ 1 μ m for $t = 3$ hrs. This value is consistent with the reduction was limited only near the glass-gas interface. Another possible controlling process for the reduction is diffusion of Fe²⁺ from the glass to the interface, where reduction reaction occurs to form metals. In this case, the diffusion distance, $X(Fe)$, is ~ 3 μ m at 1023 K for 3 hrs. when the diffusion data [11] are extrapolated.

The size of Fe metal grains in the previous reduction experiments [4] is similar to those in GEMS, while those in the present experiments are larger. This may be due to the difference of the sample size and shape. In the previous experiments [4], thin films of amorphous silicate with olivine composition (typically 50 to 100 nm in thickness) were used, and Fe-Ni metal grains of 2 – 50 nm in size were formed. In contrast, Fe metal grains of ~ 500 nm were formed on the grain surfaces of the glass powder (\sim a few to several tens μ m in size), and a few μ m grains on bulky glass samples. The smaller (or thinner) the glass sample size, the diffusion area, which can supply Fe from the glass, becomes narrower, and the metallic iron grains become smaller.

If metallic iron grains were formed by reduction of FeO-bearing amorphous silicates for GEMS, metallic nano-grains can be formed as discussed above. That is, the grains should be formed only around the interface. In contrast, TEM observation for natural GEMS shows that metal grains are uniformly embedded in amorphous silicates. So, the present study suggests that metal grains in GEMS are not reduction products and probably formed together with amorphous silicates at the same time of GEMS formation.

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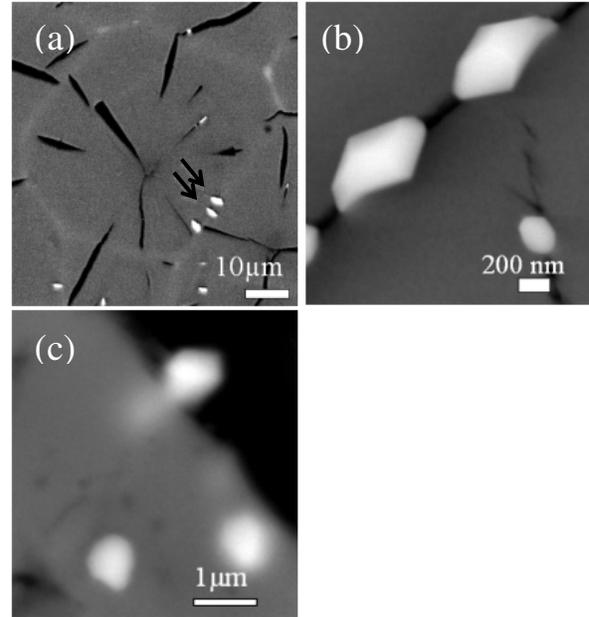


Figure 1: FE-SEM back scattered electron images of heated samples at 1023 K. (a) A polished cross section of a cube sample, heated for 14 hours. (b) A surface of a cube sample, heated for 3 hrs. (c) The surface of a powder grain heated for 48 hours. White particles in these images are Fe metals. Black lines in both (a) and (b) are cracks. Arrows in (a) shows minor cracks.

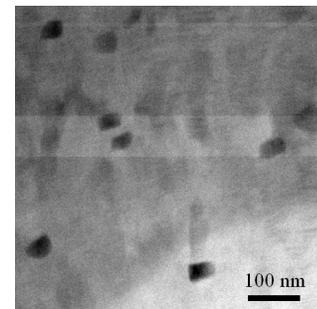


Figure 2: A TEM micrograph of heated sample at 1023 K for 48 hours. Black particles are magnetite or maghemite.