
**Introduction:** Surface deposits on lunar pyroclastic green (Apollo 15) and orange (Apollo 17) glass spherules have been attributed to condensation from the gas clouds that accompanied fire-fountain eruptions [1-4]. The fire fountains cast molten lava high above the lunar surface and the silicate melt droplets quenched before landing producing the glass beads. Early investigations showed that these deposits are rich in sulfur and zinc [5-7]. The deposits (Fig. 1A) are extremely fine-grained and thin, so that it was never possible to determine their chemical compositions cleanly by SEM/EDX or electron probe x-ray analysis because most of the excited volume was in the underlying silicate glass. We are investigating the surface deposits by TEM, using focused ion beam (FIB) microscopy to extract and thin the surface deposits. Here we report on chemical mapping of a FIB section of surface deposits of an Apollo green glass bead 15401 using the ultra-high resolution JEOL 2500 STEM located at NASA Johnson Space Center.

The surface deposits shown in Fig. 1A were imaged by field emission SEM and selected for FIB extraction because of the variety of morphologies seen. Elongate, rod-shaped crystals and bowl-shaped morphologies are typical of the surface deposits, and the region chosen includes these morphologies. We anticipated that with one FIB extraction in this area we could sample the variety of shapes and perhaps compositions that are present.

**FIB extraction:** A FEI dual beam instrument was used to perform Ga⁺ ion beam milling in order to extract the region of interest. Prior to FIB extraction, the sample had been coated with ~ 10 nm of carbon for SEM imaging and EDX analyses. An electron-beam assisted carbon strap was deposited over the target region, and then a Pt layer was deposited over the C in order to protect the region during ion-milling. A lower energy Ga⁺ beam was used to thin the sample to minimize ion-beam induced damage to the specimen.

**TEM Mapping Results:** Surface deposits on an Apollo green glass spherule are shown in Figure 1A with the location of the extracted FIB section given by the yellow line. The entire FIB section was coated by a thin deposition layer ranging from ~ 50 to 100 nm in thickness. High resolution SEM images of the two regions that have been mapped are shown in Figs. 1B and 1C. TEM bright field images of the FIB section containing features in 1B and 1C are shown in Fig. 2A and 2B, respectively. Multi-element overlays of x-ray maps of features in 1B and 1C are shown in Figs. 2C and 2D, respectively. In Fig. 2C, we have overlain Zn in red, Fe in green, S in blue and Si in gray-level. The underlying white region is the top of the silicate glass sphere. The prominent large red feature is composed of Zn and O. We are uncertain if the O is the result of oxidation while the material has been on earth. The green sphere and triangular region in the uppermost portion of silicate glass are composed of Fe-Ni metal. The violet color overlying the Fe-Ni metal spheroid is FeS, and a small region of S (blue) partially overlies the FeS and ZnS. A thin layer of Fe metal is draped over the FeS and S. Finally, draped over the amorphous Zn,O layer is a very thin layer of Si. We suggest that the Fe-Ni metal embedded in the top surface of the glass bead is not a part of the surface deposit, but is the result of auto-reduction of iron in the silicate melt, possibly by the mechanism described in [8], oxidation of graphite to CO, with oxygen liberated by the reduction of Fe. This whisker-like surface deposit is dominated by amorphous Zn.

In Fig. 2D, the x-ray map of a cross-section of a part of the bowl-shaped feature (see Fig. 1C, 2B) is shown. This feature displays a lacy texture, being primarily amorphous with tiny (< 20 nm) crystallites distributed throughout the matrix. This area displays a very complex chemical stratigraphy of mostly amorphous deposits. In the map, Mg is red, sulfur is green, Zn is blue and Si is shown in gray-level. The glass bead is overlain by a Zn-S rich region to the right. This material is overlain by a band rich in Mg, Zn and S. Overlying that is a S dominated region (the black area inside the S-rich region is a hole produced by ion-thinning in the FIB). Overlying the S-rich region is a thin layer of S and Si. Finally, draped over the whole deposit is a very thin Si layer, similar to that seen in the area shown in Fig. 2C. For the first time Mg has been documented as one of the constituents of the lunar spherule surface deposits. The use of FIB and HRTEM imaging/mapping has revealed chemical and textural complexities of surface deposits on lunar volcanic beads not previously known.

Figure 1A. FE-SEM overview of surface deposits on lunar green glass spherule 15401. Yellow line represents the FIB extracted ROI. 1B. Close-up SEM view of the feature shown in Fig 1A (black box). FIB cross section of this feature is shown in Figs. 2A and 2C. 1C. Close-up SEM view of the feature shown in Fig. 1A (blue box). FIB cross section of this feature is shown in Figs. 2B and 2D.

Figure 2. A-B. TEM bright field images of FIB cross sections of features in Figs. 1B and 1C, respectively. Red boxes represent regions mapped by TEM. C-D. Element maps of regions in Figs. 2A-B, respectively (explanation in text).