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# Atomic Scale Analysis of Terrestrial and Extra-Terrestrial Geomaterials Using Atom Probe Tomography

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From the electron microprobe to the secondary ion microprobe to laser-ablation ICP-MS, steady improvements in the spatial resolution and chemical detection limits of geochemical micro-analysis have been central to generating new discoveries. Continual improvements in instrumentation and experimental technique have now allowed Atom Probe Tomography (APT), and particularly laser assisted field evaporation, to open new areas of nanoscale analysis in inorganic geomaterials. Specifically, APT provides sub-nm scale spatial resolution in three dimensions with ppm level detection limits and typically less than one Da mass resolution [1].

Despite these improvements in APT, silicates and other metal-oxide materials prevalent in geomaterials still present some analytical challenges due to their electrical resistance, low thermal conductivity, and strong metal-oxygen bonds. As seen previously, oxide materials tend to field evaporate as cluster ions containing cations bonded to oxygen [2,3]. In previous investigations, we have successfully analyzed a range of olivine compositions from Fo0 to Fo90, however, the nature of oxide field evaporation does not typically allow for atomic scale resolution reconstructions as was observed in platinum group alloys [4].

In this work, we show the first APT analysis of an extra-terrestrial silicate glass bead acquired during the Apollo 15 space mission. Astronauts Dave Scott and Jim Irwin acquired the low-Ti green glass sphere on the Apennine Front. SIMS analyses of these glass beads has recently provided the first evidence for high volatile contents in the lunar interior [5]. APT analysis was conducted on a the surface of a single bead after FIB specimen preparation (Figure 1, [6]) using a laser pulse energy of 10 pJ and a 500 kHz repetition rate. A representative mass spectrum is shown in Figure 2. Peaks are resolved with a mass resolution better than 0.25 Da. Similar to other silicate chemistries analyzed, the glass bead tends to field evaporate as a mixture of Si, Mg, Fe, Ca, Al and O, as well as their associated monoxide clusters. Substantial mass interferences occur at m/q of 28 ($Si^{+}$, $Fe^{++}$, $CaO^{++}$), 56 ($2Si^{+}$, $Fe^{+}$, $Ca^{+}$), 40 ($Ca^{+}$, $MgO^{+}$) and 20 ($Ca^{++}$, $MgO^{++}$). At this point, these interferences cannot be resolved. Al has little intereferences and simple counting of Al in the analyses (7.45 at% Al) agrees well with published microprobe analyses (8.39 at%). The elements appear to be distributed randomly in x-y-z space (Figure 3). Nearest neighbor analysis from all of the species illustrates some Mg segregation at less than 0.5 nm scales, at the expense of Si species (Figure 4). All of these results suggest that the glass was well homogenized prior to ejection but the solidification rate was intermediate, allowing some Mg segregation, which is again not unexpected based on the high Mg concentration in the melt [7].

References:

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[6] The APT instrumentation used in this research was enabled via NSF grant DMR-1040456

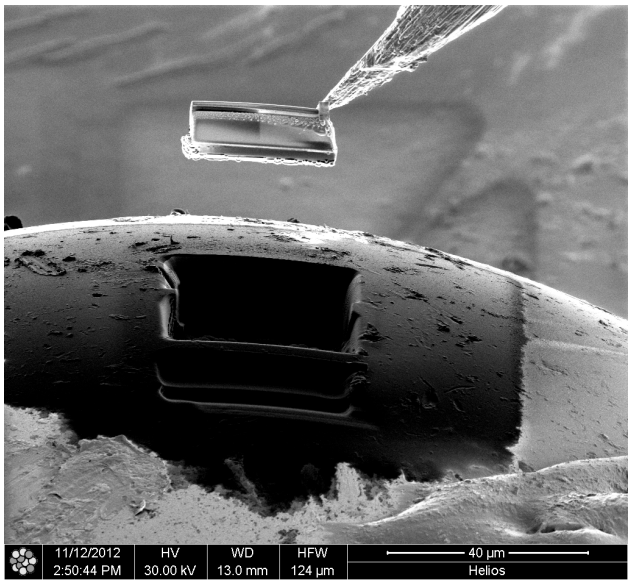


**Figure 1.** FIB induced secondary electron image of the APT specimen preparation, showing a section lifted out from the lunar glass bead.

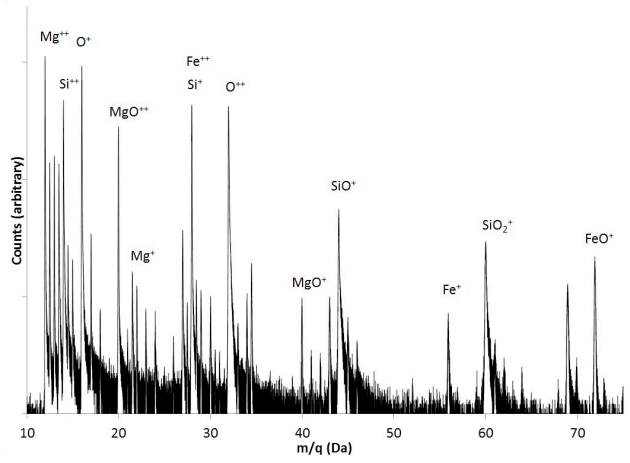


**Figure 2.** Mass spectrum of a lunar glass bead specimen acquired using laser assisted APT. Mass resolution better than 0.25 Da is illustrated.

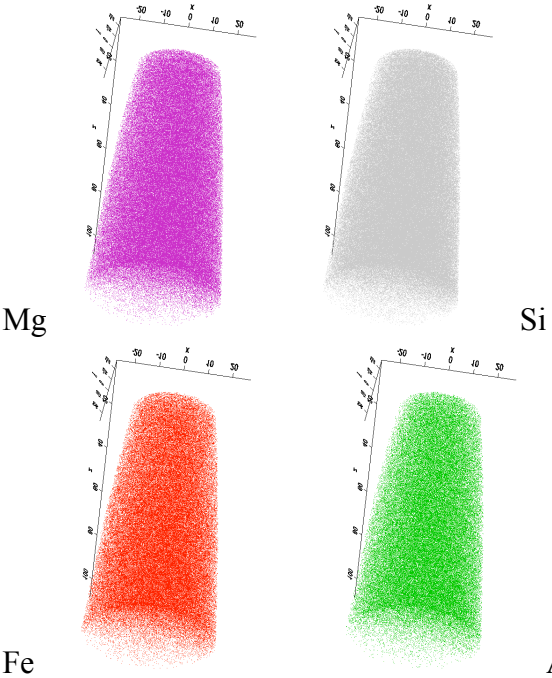


**Figure 3.** Atom probe tomography reconstruction (same volume) illustrating the distribution of Mg, Si, Fe, and Al species. Visual inspection implies a homogeneous distribution.

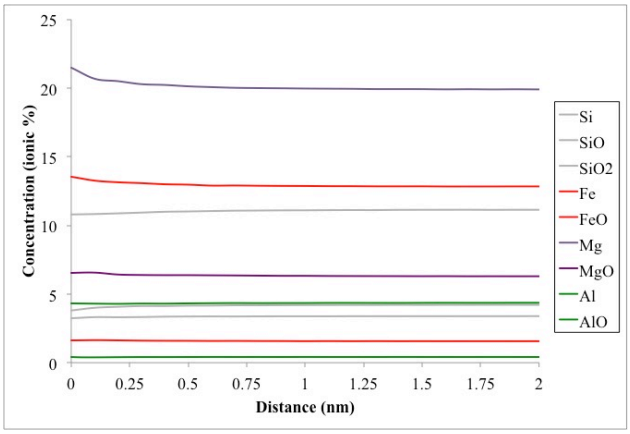


**Figure 4.** Nearest neighbor analysis of the different ionic species. Mg appears to be slightly segregated within 0.5 nm, which is compensated by a decrease in Si species.