

## Coordinated Analyses of an Altered Presolar Silicate Grain in the Miller Range 07687 Carbonaceous Chondrite

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Presolar grains are particles of dust that condensed in the gaseous envelopes that surrounded ancient stars and the ejecta of stellar explosions such as novae and supernovae (SNe). Such presolar grains are identifiable based on their anomalous isotopic compositions and are found preserved in primitive materials including meteorites, micrometeorites, interplanetary dust particles, and comet samples returned by the NASA Stardust mission [e.g., 1]. The structure and chemistry of presolar grains hold information on their thermodynamic origins and subsequent alteration histories. Here we discuss the coordinated analysis of a presolar silicate grain in the Miller Range (MIL) 07687 CO3 chondrite.

Isotopically anomalous grains were identified via nanoscale secondary ion mass spectrometry (NanoSIMS) raster-ion-imaging in a petrographic thin section of the MIL 07687 chondrite at Washington University [2]. One grain, ‘MIL 10b2-5 ol’ was selected from an altered region of MIL 07687 [2] for extraction using focused-ion beam scanning-electron microscope (FIB-SEM) techniques [3] and subsequent analysis using transmission electron microscopy (TEM). An electron transparent cross-section of MIL 10b2-5 ol was prepared using the Thermo-Fisher G3 FIB-SEM located at the University of Arizona’s Lunar and Planetary Laboratory (LPL). A Pt fiducial marker was deposited on top of the grain to protect it from the ion beam and to mark the location of the grain in cross-section. Two additional Pt fiducial markers measuring 100 nm in thickness were deposited on either side of the grain fiducial to assist in the thinning process. A C capping layer was then deposited on top of the Pt fiducial markers to protect the grain of interest from Ga<sup>+</sup> implantation and amorphization. The FIB section was then thinned to electron transparency (<100 nm) and analysed using the 200 keV Hitachi HF5000 scanning TEM (S/TEM) at LPL. The HF5000 is equipped with a cold FEG, 3<sup>rd</sup>-order spherical aberration corrector for STEM mode, STEM-based secondary electron (SE), bright-field (BF), and dark-field (DF) imaging detectors, as well as an Oxford Instruments X-Max<sup>N</sup> 100 TLE energy dispersive x-ray spectroscopy (EDS) system with dual 100 mm<sup>2</sup> windowless silicon-drift detectors (solid angle of 2 sr).

NanoSIMS analysis reveals MIL 10b2-5 ol contains enrichments in <sup>17</sup>O relative to solar system values with <sup>17</sup>O/<sup>16</sup>O ( $\times 10^{-4}$ ) =  $5.65 \pm 0.10$  and <sup>18</sup>O/<sup>16</sup>O ( $\times 10^{-3}$ ) =  $1.81 \pm 0.02$ , placing it in the Group-1 field of presolar grains, consistent with origins in the circumstellar envelope of an asymptotic giant branch/red giant branch (AGB/RGB) star [2, 4]. However, recent work suggests that some Group-1 grains thought to originate in AGB/RGB stars could instead have condensed in the ejecta of SNe [5-7]. Without Mg-isotopic data, such origins cannot be ruled out, though only a small fraction (~3-12%) of Group-1 silicates are thought to have SN origins [5-7]. S/TEM imaging below the Pt fiducial marker reveals an elongated, fine-grained (~10 to 20 nm) domain with orthogonal dimensions of approximately 400 × 85 nm (Fig. 1a-b, dashed line). EDS mapping of the region reveals spatial correlations among O, Si, Mg, and Al (Fig. 1c-e). Additionally, an Fe-rich composition is present as a rim that surrounds the MIL

10b2-5 ol domain and varies in thickness (~10 to 30 nm), precluding selected-area electron-diffraction (SAED, Fig. 1f). SAED patterns were obtained across the domain and reveal that MIL 10b2-5 ol is polycrystalline, with d-spacings consistent with orthopyroxene. The matrix contained within the FIB section is dominated by fine-grained (<100 nm), compact material that contains a mixture of amorphous and crystalline phases. EDS mapping of the entire FIB section reveals that the bulk of the matrix exhibits spatial correlations between O, Si, Mg, Al and S, with localized regions where only Fe and O correlate. A SAED pattern was obtained from one of the FeO regions and indexing is consistent with ferrihydrite.

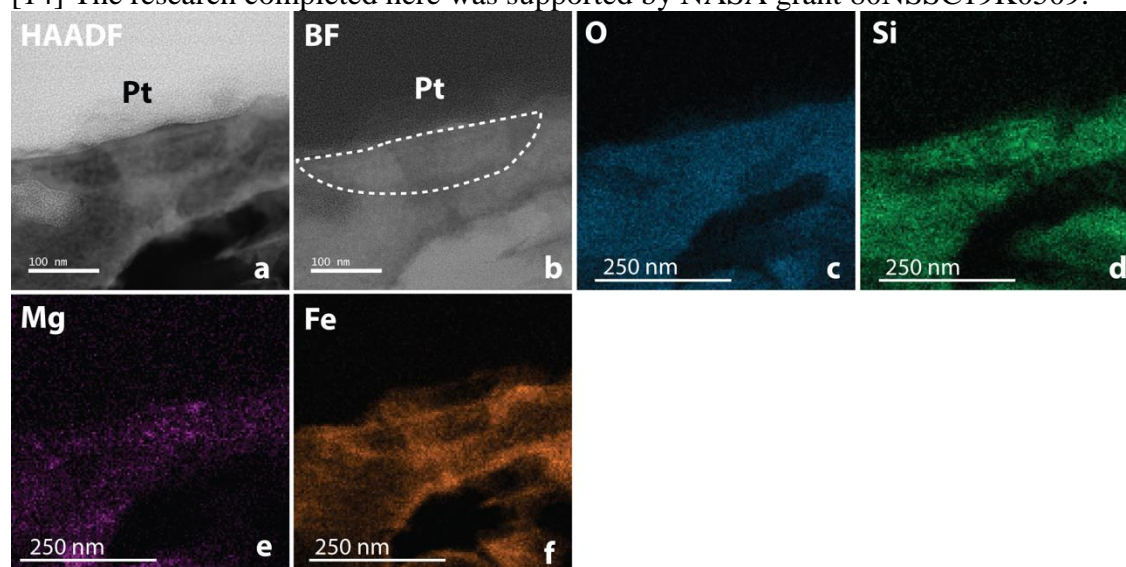
The MIL 07687 chondrite matrix contains mixed regions of Fe-rich (relatively altered) and Fe-poor (relatively unaltered) material. Previous work indicates that the Fe-rich regions are dominated by fibrous ferrihydrite crystals [2]. The FIB section containing MIL 10b2-5 ol was extracted from an Fe-rich, relatively altered region. While we observe isolated grains of ferrihydrite in the matrix contained within the FIB section, it is not a dominant phase, which is contradictory to previous work [2, 8]. Nevertheless, the presence of ferrihydrite is consistent with previous descriptions of aqueous alteration of fine-grained matrix under highly oxidizing conditions, or terrestrial weathering [2]. The Fe-rich rim that surrounds MIL 10b2-5 ol is also consistent with secondary alteration and we hypothesize is the result of Fe-diffusion into the grain from the surrounding matrix.

Comparison of the O-isotopic composition of MIL 10b2-5 ol with nucleosynthetic models suggest that it formed in a close-to-solar metallicity, approximately 1.35 solar mass AGB/RGB star [9-10]. Comparison of the structure and chemistry of presolar grains with equilibrium thermodynamic model predictions can provide first-order constraints on the thermodynamic origins of such grains. The orthopyroxene solid solution is predicted to condense from a gas of solar composition at 1366 K and 1190 K assuming total pressure of  $10^{-3}$  and  $10^{-6}$  respectively [11]. We hypothesize that nanocrystalline pyroxene grains condensed in a stepwise manner through equilibrium processes as temperatures cooled in the host circumstellar envelope and mechanically accreted to form the MIL 10b2-5 ol assemblage. Such origins are consistent with previous work that suggests polycrystalline presolar grains could be the result of multistep condensation processes [e.g., 12-13]. Following parent body accretion, MIL 10b2-5 ol was subsequently altered, along with the surrounding matrix, but preserved its isotopically anomalous composition.

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[14] The research completed here was supported by NASA grant 80NSSC19K0509.



**Figure 1.** S/TEM data on MIL 10b2-5 ol. a-b) HAADF and BF STEM images with MIL 10b2-5 ol indicated by dashed white line in BF image. c-f) False color EDS maps of MIL 10b2-5 ol for O, Si, Mg, and Fe.