TRANSMISSION ELECTRON MICROSCOPY AND SECONDARY ION MASS SPECTROMETRY OF AN UNUSUAL Mg-RICH PRESOLAR Al$_2$O$_3$ GRAIN.

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Introduction: Presolar oxide and silicate grains have been subdivided into four groups based on oxygen isotope characterisitcs that derive from different circumstellar origins. Transmission electron microscopy (TEM) data has been reported previously for only two Al$_2$O$_3$ grains from Group 1 and none from the other groups [1]. The two Group 1 grains, which most likely originated in asymptotic giant branch (AGB) or Red Giant stars, exhibited different structures and compositions. One was corundum and contained trace amounts of Ti. The other was amorphous in structure and stochiometric Al$_2$O$_3$ in composition. These data indicate that circumstellar condensation conditions can vary dramatically even for stars of similar mass and composition, and that the conditions are not restricted to thermodynamic equilibrium. An important outstanding question is whether there is any correlation between circumstellar origin, as determined by oxygen isotope measurements, and the grain structure and composition. Previous TEM investigations of four (two Group 1 and two Group 2) presolar hibonite (CaAl$_{12}$O$_{19}$) grains [2], showed equilibrium microstructures in all cases. We report here on the first TEM study of a Group 2 presolar Al$_2$O$_3$ grain.

Methods: The Al$_2$O$_3$ grain (114-12) was identified by automated oxygen isotope mapping of a acid-resistent residue of the Orgueil meteorite (CI) [3] using the Cameca ims 6f at the Carnegie Institution of Washington, and additional isotope measurements were performed at Washington University in St Louis, using the Cameca NanoSIMS 50.

An electron-transparent section of the grain was prepared at the Naval Research Laboratory using the in situ focused ion beam (FIB) lift-out technique with a FEI Nova 600 FIB-SEM and an Ascend lift-out tool [4]. TEM studies were carried out with a JEOL 2200FS field-emission scanning transmission electron microscope, equipped with a Noran System Six energy-dispersive spectroscopy system, and a Gatan Ultrascan 1000 CCD camera.

The diffraction data were analyzed using the commercial software packages CRISP, ELD and PhiDO. Quantitative diffraction peak positions, intensities, d-spacings and angles were determined with the ELD software using polycrystalline Al as an ex situ calibration standard. Possible phase and zone identifcations were determined using PhiDO by fit of the experimental data to simulations using crystallographic parameters from all (Al,Mg)-oxide phases in the PDF database.

Results and Discussion: Figure 1 compares O and Al isotopic data for grain 114-12 with those of other presolar oxides. For comparison, the unusual spinel grain OC2 [5] and the two Group 2 hibonite grains previously analyzed by TEM are also indicated. Grain 114-12 has an extreme ^{18}O depletion, moderate ^{17}O enrichment and the highest inferred ^{26}Al/^{27}Al raito of any presolar oxide. Moreover, it is also moderately enriched in ^{25}Mg, ^{49}Ti and ^{50}Ti (by 18%, 9% and 10% respectively), relative to terrestrial isotopic composition. The other Ti ratios are normal within 3% errors. Interestingly, although SEM-EDS and the TEM results indicate high bulk Mg contents, the NanoSIMS measurement indicated a surface Al/Mg ratio of ~1500.
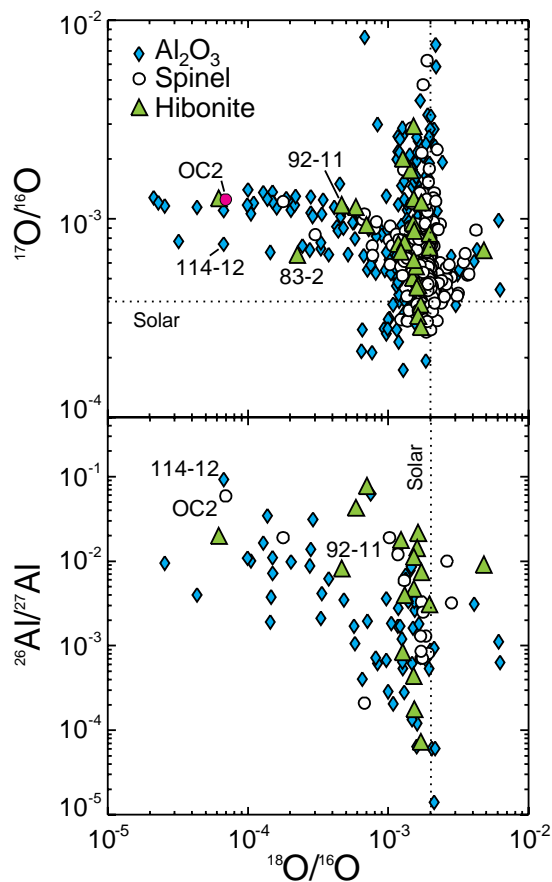
Figure 1. Oxygen and inferred Al isotope data from presolar oxide grains.
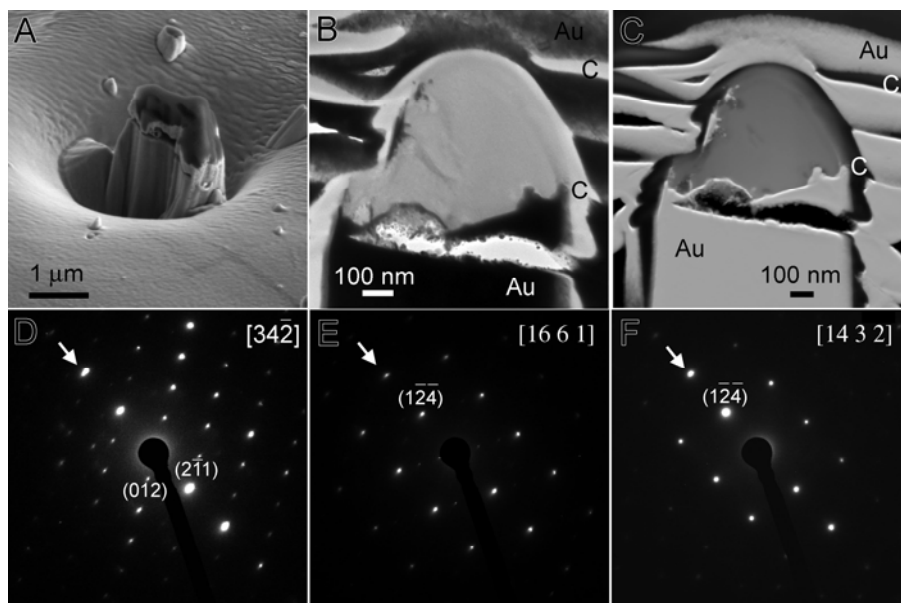
Figure 2. A. SEM image of grain 114-12. B. Bright-field TEM image of the FIB lift-out section of grain 114-12. The grain is sitting on a Au substrate, and surrounded by FIB-deposited C and re-deposited Au. C. Z-contrast dark-field STEM image. D. –F. Selected area diffraction patterns. The arrow indicates the axis about which the sample was tilted.

Low-mass (LM) AGB stars undergoing cool bottom processing are favored as the sources of Group 2 grains [nollett], though an intermediate-mass (IM) AGB origin is more likely for grain OC2 [6]. The high ^{26}Al contents and ^{25}Mg excess of 114-12 are reminiscent of OC2, but the $^{17}O/^{16}O$ ratio is lower than can be explained by models of IM-AGB stars. More likely, the grain formed in an LM-AGB star, though there are difficulties quantitiatively reproducing all of the isotopic data.

Electron microscopy imaging (Figure 2) shows that the grain is v-shaped, with two legs each ~ 1 micrometer long and 0.5 micrometers in diameter. In bright-field TEM imaging there is faint contrast that could be attributed to diffraction effects, however in high-resolution mode, the lattice appeared coherent across the entire grain. In Z-contrast dark-field image mode (Fig. 2C), the grain appears to uniform in composition. The dark "wish-bone" shaped feature near the center of the grain indicates the prescence of a void, rather than a subgrain. The composition was measured using energy dispersive spectroscopy in both TEM mode and STEM mode, to look for compositional variations, in particular gradients in Mg content and none were found. The EDS-determined composition was: 95 wt.% Al_2O_3, 3.6 wt.%, MgO 1.3 wt.% TiO_2.

Selected-area diffraction patterns were obtained at several different sample tilts. The patterns could not be indexed to corundum, spinel ($MgAl_2O_4$) or any of the more common polymorphs of Al_2O_3. A self-consistent indexing was identified in which the pattern in Fig 2D is attributed to a crystallite with tetragonal form (a=0.796 nm, c= 1.1745 nm) of $MgAl_{26}O_{40}$,

(PDF-20-0660), and the patterns in Fig 2E and F are attributed to a second crystallite with a hexagonal form (a=0. 7849 nm, c=1.6183 nm) of Al_2O_3 (PDF 021-0010). There is registry of the lattices, as indicated by the arrow on the patterns. The atom positions for these phases have not been determined, although the lattice parameters suggest that they are stacking variations of the face-centered packing of Al-O tetrahedral-found in the spinel structure (a=0.790 nm for pure Al_2O_3). Further work is planned to confirm these phase identifications and identify the crystallite grain boundaries.

No thermodynamic or kinetic data is available for the specific polytypes identified in this grain. However, the structural data suggest non-equilibrium condensations conditions. For equilibirum condensation, corundum with minor Al_2O_4 spinel inclusions would be expected. Liquid Al_2O_3 can be quenched to form spinel, at cooling rates greater than 100 K/s. The identification of the grain as consisting of tetrahedrally coordinated phases, suggests rapid, non-equilibrium condensation.

References: [1] Stroud R.M., Nittler, L.R. & Alexander C.M. O'D. (2004) *Science* 305, 1445-1447. [2] Zega T.J. et. al (2006) *MAPS* 41 Suppl., 5375. [3] Zinner E. et al. (2005) *GCA* 69, 4149-4165. [4] Zega T.J. et al. (submitted) *MAPS*. [5] Lugaro M. et al. (2007) *Astron. & Astrophys.* 461, 657-664. [6] Nollett K.M., Busso M. & Wasserburg G.J. (2003) *ApJ* 582, 1036-1058.