CRYS TAL STRUCTURE, MORPHOLOGY, AND ISOTOPIC COMPOSITIONS OF PRESOLAR $\text{Al}_2\text{O}_3$ GRAINS IN UNEQUILIBRATED ORDINARY CHONDrites. A. Takigawa$^{1,2,3}$, R. M. Stroud$^4$, L. R. Nittler$^1$, E.P. Vicenzi$^{2,4}$, A. Herzinger$^2$, C. M. O’D. Alexander$^1$, and G. R. Huss$^1$, 1Department of Terrestrial Magnetism, Carnegie Institution of Washington, 5241 Broad Branch Road NW, Washington, DC 20015, USA, 2atakigawa@ciw.edu, 3Kyoto University, Kyoto, Japan, 4Naval Research Laboratory, Washington DC, USA, 5Smithsonian Institution, Suitland, MD, USA, 6National Institute of Standards and Technology, Gaithersburg, MD, USA, 7University of Hawai’i at Mānoa, Honolulu HI, USA

Introduction: Corundum, the thermodynamically stable phase of $\text{Al}_2\text{O}_3$, is predicted to be the most abun-
dant refractory dust species condensed in envelopes around oxygen-rich asymptotic giant branch (AGB) stars [e.g., 1]. Infrared spectroscopic observations have revealed that more than 90% of semi-irregular variables and 20% of Mira variables show single peaks at 13 $\mu$m [e.g., 2, 3] and corundum is the most plausible dust species capable of emitting the 13-$\mu$m feature [4].

Most presolar $\text{Al}_2\text{O}_3$ grains have been identified from acid-residues of chondrites [e.g., 5]. The grain morphology and crystal structure of presolar grains may reflect condensation conditions in circumstellar envelopes of AGB stars (e.g., a cooling rate and chemical composition of a surrounding gas) and processing in the interstellar medium (ISM) and protosolar disk (e.g., irradiation with accelerated ions by supernova (SN) shocks, grain-grain collisions, and alteration in meteorite parent bodies). Morphologies and crystal structures of a large number of presolar SiC and graphite grains have been investigated by transmission electron microscopy (TEM) [6-8]. TEM studies of presolar oxide grains (hibonite, spinel, and $\text{Al}_2\text{O}_3$) have been much more limited, however, due to their small sizes and low abundance relative to oxide grains with solar isotopic compositions [8-11]. There are also few studies on the morphology of presolar $\text{Al}_2\text{O}_3$ grains [12, 13] because isotopic measurements used to identify presolar grains alter the grain surfaces. Presolar amorphous $\text{Al}_2\text{O}_3$, corundum, and crystalline $\text{Al}_2\text{O}_3$ with a hexagonal form have been identified [10, 11] but the relationship between interior crystal structure and morphology of presolar $\text{Al}_2\text{O}_3$ grains has not been studied.

Using scanning electron microscopy (SEM) we obtained detailed secondary electron images, energy dispersive X-ray spectroscopy (EDS), electron backscattered diffraction (EBSD) patterns, and cathodoluminescence (CL) spectra of each grain prior to isotopic measurements. Focused ion beam (FIB) lift-out sections were made from the identified presolar grains and the interior structures were observed.

Experiments: The $\text{Al}_2\text{O}_3$ grains were identified from acid residues of QUE97008 (LL3.05) by EDS and observed in detail by field emission (FE) SEM at the Carnegie Institution of Washington (CIW). Previously identified alumina grains from Semarkona (LL3.0), Roosevelt County 075 (H3.1), and Bishunpur (LL3.15) were also used in this study [13]. CL spectra were obtained with a FE-SEM equipped with a Gatan Mono CL4 system at National Institute of Standard and Technology. EBSD analysis was performed with an FEI Nova 600 FIB-SEM equipped with an HKL EBSD system at the Naval Research Laboratory (NRL).

Isotope measurements were performed with the Cameca NanoSIMS 50L ion-microprobe at CIW. Oxygen isotopes of 163 grains were measured using ~100 nm Cs+ beam rastered over each of the grains. Secondary ions of $^{16}\text{O}$, $^{17}\text{O}$, $^{18}\text{O}$, $^{27}$Al$^{16}\text{O}$, and $^{24}$Mg$^{46}\text{O}$ were simultaneously detected. An O+ beam was used to measure the Mg-Al isotopic compositions of the presolar and some solar $\text{Al}_2\text{O}_3$ grains. Secondary ions of $^{24}\text{Mg}$, $^{25}\text{Mg}$, $^{26}\text{Mg}$, $^{27}\text{Al}$, and $^{48}\text{Ti}$ were simultaneously measured. Micron-sized Burma spinal grains were used as a standard to correct the instrumental mass fractionation and to determine the relative sensitivity factor of secondary Mg and Al ions.

Ultra-thin sections of presolar grains QUE053, 060, and 067 were prepared with the NRL FIB-SEM. TEM studies were carried out at NRL with a JEOL 2200FS field-emission scanning transmission electron microscope (STEM). We obtained electron energy loss spectra (EELS) of grains QUE060 and 053 with a monochromated, probe-corrected FEI Titan STEM at NIST.

Results: Figure 1 shows the oxygen isotopic compositions of presolar grains. Eight presolar grains from QUE97008 and one from RC 075 were newly found. Grain QUE060 is classified into Group 2 [3] and has a subhedral shape with clear flat facets. The surface is smooth except for a face with a cavity indicated by C in Fig. 2c. EBSD patterns taken on multiple locations of face B taken prior to SIMS measurements index to that of corundum, which indicates that the surface of the grain (<30 nm in depth) is corundum. TEM diffraction patterns of the FIB section indicated that the grain consists of multiple corundum crystallites.

Dark-field TEM image (Fig. 2d) showed large (>100 nm) and small (<30 nm) scale orientation variation. The large-scale misorientation observed on the right side of the grain (Fig. 2d) seems to relate to the cavity shown in Fig. 2c. Voids (10-20 nm) were also observed on the right domain of the grain in the bright-field TEM imaging (Fig. 2c). The EEL spectra from the voids and adjacent areas were indistinguishable, other than in total intensity. Small-scale distortions occur
uniformly within the grain. The CL spectrum of QUE060 displayed at least five peaks that were not observed on the synthetic corundum grains. These may reflect the internal defect structure of the grain. EDS spectra showed that the Mg/Al ratio of QUE060 is ~0.01, and the NanoSIMS measurement revealed this high Mg content to be essentially pure radiogenic \(^{26}\text{Mg}\), with inferred initial \(^{26}\text{Al/}^{27}\text{Al}\)~0.01, similar to other Group 2 grains [5].

QUE053 is a small Group 1 grain (<500 nm) with a large \(^{17}\text{O}\) excess and small \(^{18}\text{O}\) deficit (Fig. 1). This grain was not faceted, but showed an EBSD pattern of corundum. No excess of \(^{26}\text{Mg}\) was detected. The diffraction pattern was indexed to corundum but also showed satellite spots indicating stacking disorder or a second phase.

QUE067 is a thin Group 4 grain with very irregular morphology. Its \(^{27}\text{Al/}^{26}\text{Mg}\) ratio was three times lower than in QUE060, but its inferred \(^{26}\text{Al/}^{27}\text{Al}\) ratio was similar. The CL spectrum of this grain was very similar to that of QUE060, although the larger dataset of presolar grains displayed a wide variation of CL spectral features that do not correlate with chemical and isotopic compositions or EBSD patterns. No EBSD patterns of crystals were obtained from the grain surface but TEM observation on the FIB section showed that the interior of QUE067 was corundum, not amorphous.

**Discussion:** The subhedral shape and smooth surface of QUE060 suggest that this grain was likely single crystalline corundum when it condensed in a circumstellar envelope of a low-mass AGB star, and that the polycrystalline nature, voids and distorted crystal structure inside the grain are secondary features.

The abundance of \(^{26}\text{Mg}\) formed by decay of \(^{26}\text{Al}\) is much higher than the solubility of MgO in corundum, which is less than 200 ppm at \(<1880^\circ\text{C}\) [14]. However, no evidence for precipitates or other segregation of Mg was observed. Thus it appears that the excess Mg is accommodated by the local lattice distortions indicated in the dark-field TEM data (Fig. 2d).

A possible process to form large-scale misorientation and the cavity is grain-grain collisions in a SN shock in the ISM [15]. A high velocity collision creates a shockwave propagating inside the grain, finally forming a crater [15]. Small-scaled distortions may have also formed by collisions with small particles (~50 Å) in the ISM. Such collisions are less destructive than with larger grains, but their probability is high [15]. Irradiation of corundum with 50keV \(\text{He}^+\) ions causes partial amorphization within 300 nm in depth and slightly shifts the stacking of closed-packed oxygen layers [16]. Ion bombardment in the ISM may also contribute to the small-scale distortions.


**Figure 1.** Oxygen isotopic compositions of presolar Al\(_2\)O\(_3\) grains.

![Figure 1](image1.png)

**Figure 2.** a) SEM image (65° tilt) of grain QUE060. b) Selected area diffraction pattern and c) bright-field STEM image of the QUE060 FIB lift-out section. White arrows indicate voids or bubbles. d) Dark-field TEM image using a diffraction spot shown by arrow in Fig. b.)