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Polymorphism in Presolar Al_2O_3 Grains from Asymptotic Giant Branch Stars

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We report microstructural and isotopic analyses of two presolar Al_2O_3 grains. Aluminum oxide is important cosmically, because its presence has been detected in the infrared spectra of the circumstellar envelopes of O-rich asymptotic giant branch stars and because it is predicted to be the first solid to condense in these stellar environments. The two grain structures, one corundum and the other amorphous, confirm that asymptotic giant branch stars produce both phases. The variation in structure and Ti content demonstrates that Al_2O_3 can condense in the absence of TiO_2 seed clusters but that Ti may be important in determining the crystal structure.

The molecular cloud from which the solar system formed contained the dusty ejecta of ancient stars, including red giant branch (RGB) stars, asymptotic giant branch (AGB) stars, and supernovae. The majority of this presolar circumstellar dust was extensively processed and destroyed during solar system formation. However, some presolar dust grains escaped processing, retain the isotopic signatures of extrasolar stellar origins, and are found in primitive meteorites and interplanetary dust particles (*1–3*).

In addition to providing information about nucleosynthesis in the progenitor stars, presolar grains provide physical data that can be used to constrain circumstellar dust condensation models (*4*) and aid in the interpretation of infrared (IR) spectra of remote stars. Circumstellar dust condensation models (*5–7*) have predicted that Al_2O_3 is the first solid phase to condense as the gaseous outflows from O-rich giant stars cool from high temperatures. The simplest models are equilibrium thermodynamic calculations that assume homogeneous nucleation. In principle, these models can be improved upon by allowing for heterogeneous nucleation and kinetically driven reactions (*8–11*), but eventually the accuracy of the models must be weighed against physical data from actual stellar dust. The best source of this data has historically been IR spectra obtained from the circumstellar envelopes of RGB and AGB stars, both of which have features that indicate a mixture of amorphous and crystalline dust phases. However, the level of detail that these spectra provide does not rigorously constrain the dust formation models; for instance, it has not allowed researchers to determine whether Al_2O_3 condenses directly or by adsorption onto TiO_2 seeds (*9*, *10*). Laboratory analyses of presolar Al_2O_3 grains bridge this information gap by providing complete chemical, isotopic, and structural profiles of individual dust grains.

Although several C-rich presolar grain types—including nanodiamonds, SiC, and graphite—have been well studied by transmission electron microscopy (TEM) (*4*, *12–14*), there have been no previous structural studies of presolar oxide grains, despite more than a decade of isotopic analyses (*15*). This is because of the rarity of the grains (~1% of micrometer-sized refractory oxides in meteorites) and the difficulty of extracting ultrathin TEM sections of particular grains of submicrometer-to-micrometer size among thousands of others. The former problem is alleviated by the use of automated search techniques, which have led to the identification and isotopic analysis of ~200 presolar Al_2O_3 grains (*16*, *17*). The latter problem was solved by the adaptation of focused ion beam (FIB) lift-out techniques (*18–20*). We report correlated structural and isotopic data for two presolar Al_2O_3 grains found in an acid-resistant residue of the Tieschitz ordinary chondrite (*21*).

The grains, named T96 and T103, were identified by automated O isotope measurements by means of a Cameca ims-6F ion microprobe (*18*, *21*, *22*). After the O analyses, the grains were manually analyzed for Al-Mg isotope systematics (Table 1). The oxygen isotopic ratios place the grains within the majority Group 1 defined for presolar oxide grains (*16*) (Fig. 1), consistent with an origin in the outflows of O-rich RGB or AGB stars. An AGB origin is indicated by large enrichments of ^{26}Mg, resulting from the decay of the now extinct ^{26}Al. The inferred $^{26}Al/^{27}Al$ ratios for the two grains are within the range expected for O-rich AGB stars. Comparison with nucleosynthesis models (*23*) indicates that the parent stars of the grains had masses about two times the mass of the Sun and near solar metallicity.

After isotopic analysis, sections of these grains were prepared for TEM studies with the use of an FIB lift-out (*18*, *21*). Despite the similar isotopic signatures, the structures of the grains are radically different. Grain T103 is a single crystal of corundum (α-Al_2O_3), which exhibits sharp Bragg diffraction (Fig. 2) and strong diffraction contrast. The other grain, T96, is amorphous, or very finely nanocrystalline, and exhibits only diffuse diffraction with no diffraction contrast when tilted. The grains also have different chemical compositions, as determined by energy-dispersive x-ray spectroscopy: T103 shows trace amounts [~0.1 weight percent (wt %)] of Ti, whereas T96 shows only Al_2O_3, to a detection limit of ~0.05 wt % for Ti. The Ti appears to be distributed in T103 as a solid solution. No subgrains were observed in either Al_2O_3 grain (*24*).

The structures of presolar grains reflect both the circumstellar dust condensation conditions and subsequent processing histories. It is important to consider how processing in the interstellar medium (ISM), solar system, or laboratory may have affected the structures. The grains retain their stellar isotopic

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signatures, which indicates that they experienced little chemical or isotopic processing after their formation. The effects of laboratory processing are limited to the removal of grain surfaces during the acid dissolution of the parent meteorite, and surface amorphization (depth of <20 nm) by the Cs^+ and O^- ion sources of the ion probe and the Ga^+ source of the FIB.

In principle, processing in the ISM by supernova shock waves or cosmic rays could alter the microstructure of Al_2O_3 grains without changing the isotopic composition. Supernova shocks can vaporize, sputter, or fragment dust grains (*25*, *26*); the survival of the presolar Al_2O_3 grains studied indicates that they did not experience many such shocks. A heating event would be required to recrystallize T103 to corundum from a previous amorphous or metastable crystalline structure. In terrestrial studies, the transformation of the metastable phases of Al_2O_3 to corundum begins at 700 K (*27*), well above typical interstellar grain temperatures of ~15 K (*28*). It is possible to heat interstellar dust by absorption of starlight (*28*) and/or by gas-grain collisions in supernova shocks (*29*), but it is not efficient for large grains such as those studied here. Heating by grain-to-grain collisions in shocks would be more likely to vaporize or fragment the grains than to anneal them (*26*). Moreover, interstellar silicates are exclusively amorphous (*30*), showing no evidence of thermal annealing.

Intense radiation damage of a previously crystalline grain is a possible explanation for the amorphous structure of T96. The radiation dose required for amorphization depends on radiation parameters (ion energy, ion mass, and incident angle), grain size, materials-specific atomic displacement energies, crystallinity, and ambient temperature. For single-crystal silicates with a grain size of 10 to 100 nm, experimental studies show that amorphization doses are within the realm achievable in the ISM, and this has been suggested as an explanation for the lack of detected crystalline silicates (*30*). However, T96 is one to two orders of magnitude larger than those silicates, and even for grains of comparable size, corundum has a higher amorphization dose than silicates (*31*). Moreover, Daulton *et al.* conducted a TEM analysis of several hundred presolar SiC grains (*12*) that were comparable in size to our Al_2O_3 grains but more susceptible to radiation-induced disorder (*32*), and their analysis revealed that most of them were crystalline. This result indicates that micrometer-sized presolar dust grains from AGB stars, at least those grains that survive in meteorites, were not significantly processed by radiation in the ISM. Thus, although some processing in the ISM cannot be ruled out, it is most likely that the observed structures of T96 and T103 are essentially the original structures into which the grains condensed around their parent AGB stars.

The differences in the structure and composition of the two grains have important consequences for dust condensation models and interpretation of IR spectra from circumstellar dust envelopes of O-rich AGB stars. Although it is agreed that Al_2O_3 will condense in these stars, there is long-standing disagreement, in both the condensation modeling and the IR spectroscopy communities, as to what form(s) the condensates take.

Equilibrium thermodynamic calculations predict that Al_2O_3 will be the first dust phase to condense in the circumstellar environment of O-rich AGB stars (*5*, *33*). However, there is a kinetic barrier to the homogeneous nucleation of Al_2O_3; that is, the concentration of molecular species with an Al_2O_3 stoichiometry in the stellar gas is very low (*9*). For this reason, some models assume heterogeneous nucleation of Al_2O_3 on TiO_2 seed clusters (*9*, *10*). The lack of any observed subgrains in T103 and T96 indicates that Al_2O_3 is indeed the first solid species to condense and argues against the TiO_2 seed models. To constitute 0.1 wt % of the ~1-μm T103 grain, a single TiO_2 seed would form a 60-nm TiO_2 subgrain that would have been observed by TEM. If, instead, the Ti were present as multiple seeds that were too small to produce significant imaging contrast, a polycrystalline grain structure would be expected rather than the observed single-crystal microstructure. The Ti appears to have been incorporated into T103 as a solid solution during the growth of the corundum grain rather than as the initial nucleation source. However, Ti may still be important for determining the crystal structure of the condensate. Terrestrial studies of synthetic Al_2O_3 show that trace amounts of Ti in solid solution can stabilize corundum relative to other structures (*27*). T96, which has no detectable Ti, is amorphous. Given the similar masses and metallicities of the progenitor stars indicated by the isotope data, the differences in the grains' Ti content and structure likely reflect a local difference in the condensation environments, such as pressure, temperature, cooling rate, or inhomogeneous Ti distributions.

That we find direct evidence for both crystalline and amorphous Al_2O_3 dust originating from O-rich AGB stars is directly relevant to an ongoing controversy among observational astronomers over the interpretation of features in the IR spectra of this class of stars. A narrow feature at 13 μm and a broad feature peaking close to 12 μm appear in spectra from some of these stars (*34*) and have been attributed to crystalline and amorphous Al_2O_3, respectively. The 13-μm feature was first reported in 1986 (*35*) and has been variously attributed to corundum or other crystalline Al_2O_3 (*36*, *37*), polymerized silicates (*34*), and spinel (*38*). As yet, none of these assignments has been definitively ruled out because of the complexity of the spectra and the uncertainty in obtaining reference spectra from appropriate laboratory dust analogs. It is plausible that two or more of these phases contribute to the feature to varying degrees. An objection to the assignment of this fea-

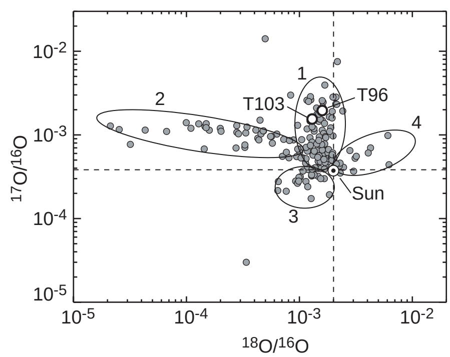

Fig. 1. Oxygen isotope plot of presolar Al_2O_3 grains. Grains from Groups 1 (including T96 and T103), 2, and 3 are all believed to have originated in O-rich RGB and AGB stars (*16*). The origin of the Group 4 grains is enigmatic.

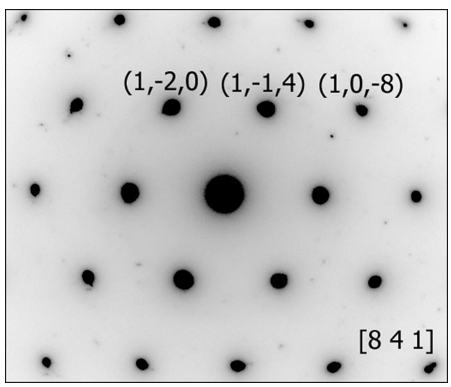

Fig. 2. Electron diffraction pattern from T103 indexed to the corundum structure.

Table 1. Isotopic and physical data for presolar Al_2O_3 grains. For comparison, solar isotopic ratios are $^{17}O/^{16}O = 3.83 \times 10^{-4}$ and $^{18}O/^{16}O = 2.005 \times 10^{-3}$.

Grain	Size (μm)	Structure	$^{17}O/^{16}O^a \pm 1\sigma$	$^{18}O/^{16}O \pm 1\sigma$	$^{26}Al/^{27}Al \pm 1\sigma$
T96	0.7×1.2	Amorphous	1.96×10^{-3} $\pm 0.04 \times 10^{-3}$	1.59×10^{-3} $\pm 0.05 \times 10^{-3}$	6.4×10^{-5} $\pm 0.7 \times 10^{-5}$
T103	0.5×1.0	Corundum	1.55×10^{-3} $\pm 0.07 \times 10^{-3}$	1.30×10^{-3} $\pm 0.11 \times 10^{-3}$	28.2×10^{-5} $\pm 0.6 \times 10^{-5}$

ture to corundum has been that a corresponding feature expected at 22 μm is not observed. However, the amplitude of the 22-μm feature is known to vary with grain shape (*37*) and is much lower in intensity than the 13-μm feature, and thus it may be too weak to resolve. Based on the structure and oblong shape of T103, crystalline corundum appears to be a likely contributor to the 13-μm feature. The assignment of the broad asymmetric feature peaking near 12 μm to amorphous Al_2O_3 is less debated, and this assignment gains further support from the amorphous nature of T96.

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Reverse Methanogenesis: Testing the Hypothesis with Environmental Genomics

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Microbial methane consumption in anoxic sediments significantly impacts the global environment by reducing the flux of greenhouse gases from ocean to atmosphere. Despite its significance, the biological mechanisms controlling anaerobic methane oxidation are not well characterized. One current model suggests that relatives of methane-producing *Archaea* developed the capacity to reverse methanogenesis and thereby to consume methane to produce cellular carbon and energy. We report here a test of the "reverse-methanogenesis" hypothesis by genomic analyses of methane-oxidizing *Archaea* from deep-sea sediments. Our results show that nearly all genes typically associated with methane production are present in one specific group of archaeal methanotrophs. These genome-based observations support previous hypotheses and provide an informed foundation for metabolic modeling of anaerobic methane oxidation.

Anaerobic oxidation of methane (AOM) in marine sediments has been estimated to consume more than 70 billion kilograms of methane annually (*1*). Analyses of pore waters from methane-oxidizing sediments along continental margins have mapped extensive zones of sulfate and methane depletion, which define the geographic and geochemical boundary conditions for AOM (*2–4*). Combined geochemical and biological evidence indicate that microbial consortia, largely composed of archaea and sulfate-reducing bacteria (SRB), can couple methane oxidation to sulfate reduction (*5*, *6*). Current models suggest that methane is converted by methanotrophic archaea to carbon dioxide and reduced by-products (possibly including molecular hydrogen), which are subsequently consumed by sulfate-reducing bacteria (*6*). In anoxic deep-sea sediments, AOM catalyzes the formation of authigenic carbonates with highly depleted ^{13}C content, thereby providing an enduring geochemical signature for past and present methane oxidation (*7–9*). Microbial mediation of AOM significantly influences both local and global biological and biogeochemical processes. The process reduces methane flux to the water column, stimulates subsurface microbial metabolism, and also supports vigorous deep-sea chemolithotrophic communities that derive energy from one of its by-products, hydrogen sulfide.

Although no archaeal methanotrophs have yet been isolated in pure culture, phylogenetic, isotopic, and biochemical analyses indicate that several different methanogen-related archaeal groups are involved in AOM (*10–13*). Two groups of putative anaerobic methane-oxidizing *Archaea* (ANME-1 and

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