TRANSMISSION ELECTRON MICROSCOPY ANALYSIS OF A PRESOLAR SPINEL GRAIN.

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Introduction: Stars shed their ashes in stellar winds or explosive events such as supernovae. Some stardust, having survived interstellar transport and processing in the solar nebula, is preserved in primitive meteorites and interplanetary dust particles. Analysis of the chemistry and structure of such presolar grains can therefore provide insight into ancient circumstellar proceses and serve as ground-truth measurements for observational astronomy.

SiC, graphite, and diamond were among the first presolar phases recognized [1-3]. Since then, many other phases have been identified, e.g., silicates, metal, and nitrides [4-7]. Oxides have also been identified, and we have used coordinated methods to investigate the structure and chemistry of several types including Al_2O_3 [8], hibonite [9-10], and Cr-rich spinel [11].

Mg-Al spinel ($MgAl_2O_4$) is the fourth-most abundant presolar-grain type after nanodiamonds, silicates, and SiC [5]. However, its detailed structure and composition have not been previously investigated partly due to its smaller size (typically ≤ 0.5 μm) relative to other types of presolar grains. Here we continue our coordinated efforts and report the first microstructural data on a Mg-Al spinel grain, UOC-S2.

Experimental: UOC-S2 was located by [12] in a mixed acid-resistant residue of the primitive unequilibrated ordinary Antartic chondrites (UOC) QUE 97008, WSG 95300, and MET00452. It was identified as an isotopically anomalous presolar grain by automated measurement of O isotopes with the Carnegie ims-6f ion probe and its Al-Mg isotopic composition was subsequently determined with the Carnegie NanoSIMS 50L.

Following the SIMS analysis, UOC-S2 was extracted in situ and thinned to electron transparency using an FEI Nova 600 focused ion beam scanning electron microscope (FIB-SEM). We used extraction and milling techniques similar to those described by [13], except that this grain was Pt-welded to a Cu halfgrid rather than removed with a microtweezer. We analyzed the FIB section using a 200 keV JEOL 2200FS transmission electron microscope (TEM) equipped with energy-dispersive and electron energyloss spectrometers as well as scanning-TEM (STEM)-based bright-field and high-angle annular-dark-field (HAADF) detectors.

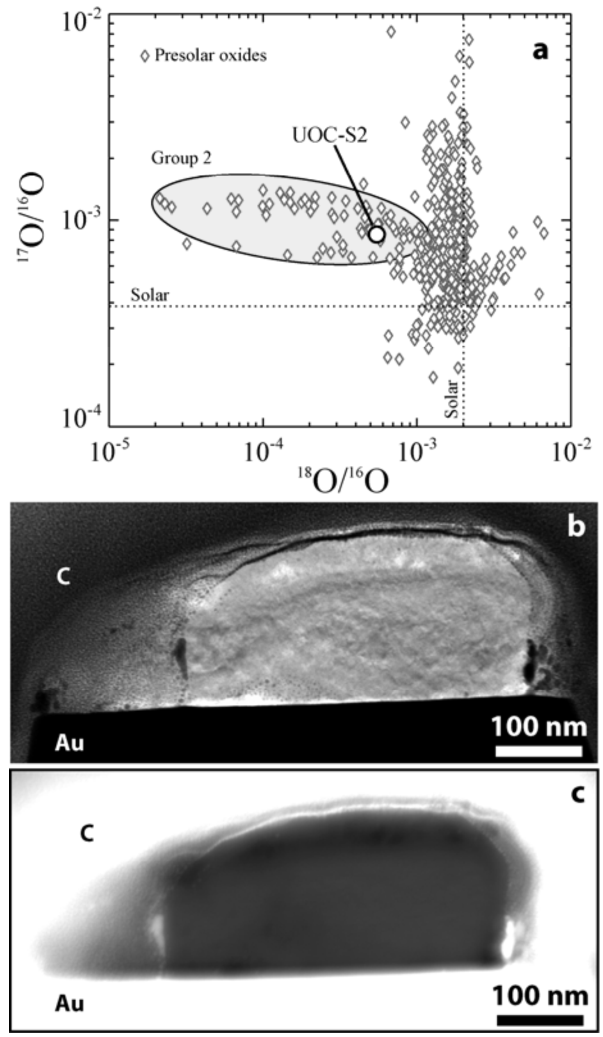

Fig. 1 (a) Oxygen isotopic composition of presolar spinel grain UOC-S2 (large circle) shown relative to other presolar oxides (diamonds). **(b)** STEM bright-field image showing grain coated with C and sitting on Au pedestal. **(c)** STEM-HAADF image.

Results: UOC-S2 has $^{17}O/^{16}O = 8.52 \times 10^{-4}$, $^{18}O/^{16}O = 5.49 \times 10^{-4}$, $\delta^{25}Mg/^{24}Mg = 256 \pm 10‰$, and $\delta^{26}Mg/^{24}Mg = 1020 \pm 17‰$. Its oxygen isotopic composition plots within the Group-2 field for presolar oxide grains (Fig. 1a). The large ^{18}O depletions of Group-2 oxide grains are believed to signify coolbottom processing [14] by which low-mass asymptotic-giant-branch (AGB) stars cycle envelope material through hotter regions near their H shells. Comparison of the oxygen isotopic composition of UOC-S2 with that predicted by model calculations suggest that it formed in a low-mass (≈1.4 $M_{\odot}$) star [12,15].

The FIB section of UOC-S2 contains a grain measuring approximately 500 nm × 150 nm (Fig. 1b,c). Selected-area electron-diffraction (SAED) patterns show that the grain is a single crystal. Measurements of SAED patterns from multiple orientations are consistent with a cubic structure based on a Mg-Al spinel lattice constant (space group Fd-3m, a_0 = 0.8103 nm). The grain contains some stacking disorder as revealed by SAED and high-resolution imaging.

HAADF imaging shows uniform contrast across the grain (Fig. 1c), indicating that it has a homogeneous composition. Energy-dispersive X-ray analysis shows that the grain contains Mg, Al, Cr, Fe, and O. Quantification of EDS spectra from two different areas of the grain confirm a uniform composition and give an average formula of $Mg_{0.98}Fe_{0.01}Al_{1.94}Cr_{0.06}O_4$.

Discussion: Although the O isotopic composition of grain UOC-S2 indicates an origin in an ABG star of relatively low mass, the grain's unusual ^{25}Mg enrichment is inconsistent with models of such stars. [12] suggested that this grain originated in a star that was part of a binary system which experienced mass transfer from a more massive stellar companion.

The SAED patterns show that grain UOC-S2 is a single-crystal spinel that contains some minor stacking disorder. Such disorder presumably resulted from structural perturbations during growth. Equilibrium-thermodynamic calculations indicate that spinel ($MgAl_2O_4$) should condense from a gas of solar composition, but the purity of the spinel should vary with condensation temperature [16]. At higher temperature, nearly pure $MgAl_2O_4$ is predicted to condense, but additional impurities are expected with decreasing condensation temperature. For example, nearly pure $MgAl_2O_4$ will condense at 1500 K ($P_t = 10^{-3}$ atm), but a spinel solid solution, which is much richer in Cr, is predicted to condense at 1221 K at the expense of Cr-bearing metal, plagioclase, and Mg-silicates [16]. Our EDS measurements indicate that UOC-S2 contains significant Cr and some Fe, suggesting the possibility that this spinel condensed at a relatively lower temperature than its high-temperature counterpart. The total pressure of the calculations is higher than might be expected for a stellar outflow. Generally, lower total pressures (< 10^{-3} atm) lead to lower condensation temperatures. Thus, 1221 K might be considered an upper limit for the stability of Cr-bearing spinel. However, we note the possibility that slower diffusion at lower temperature could be problematic for grain growth via solid-state reactions involving multiple phases. Alternatively, condensation of spinel could have been suppressed until the conditions in the stellar envelope reached the stability field for higher Cr-containing spinel.

[17] reported that Al/Mg ratios in some presolar spinel grains deviate from ideal stoichiometry. They suggested that those grains with higher-than-stoichiometric Al/Mg ratios could have formed at high temperature through replacement of corundum in the stellar envelope. In comparison, the EDS measurements on grain UOC-S2 are consistent with stoichiometric spinel. Analysis of additional FIB sections will help to clarify whether this trend holds for other presolar spinels.

The identification of spinel in O-rich stars is not without controversy. Several groups have examined the 13-µm-emission feature in the infrared spectra of O-rich AGB stars and have assigned it to a number of different phases including aluminum-oxide [18], corundum with a silicate mantle [19], SiO_2 and other polymerized silicates [20], and spinel [21]. The TEM data that we report show that O-rich AGB stars can condense single-crystal spinel grains.

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