TRANSMISSION ELECTRON MICROSCOPY ANALYSIS OF A PRESOLAR Cr-RICH SPINEL GRAIN.
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Introduction: In the pure form, chromite ($FeCr_2O_4$), is not predicted by thermodynamic equilibrium calculations to condense from a gas of solar composition because Fe is expected to condense into metal grains [e.g., 1 and references therein). That presolar chromite grains were recently reported [2] is therefore interesting because detailed structural and compositional analysis of them could provide insight into the thermodynamics of the circumstellar environments in which they formed. Here we report the results of a coordinated isotopic and microstructural analysis of a presolar Cr-rich spinel grain from a residue of the Orgueil CI chondrite.

Methods: A fragment of the Orgueil CI chondrite was treated with CsF and HF acids to obtain an acid-resistant residue rich in organic matter and refractory oxides [2-4]. Following plasma etching to remove organics, an aliquot of the residue was dispersed onto clean Au foils for SIMS analysis. Automated O-isotopic analysis of ~2,700 grains identified six that are anomalous: one Al_2O_3 [5] and five Fe- and Cr-rich oxide grains, tentatively identified as chromite [2]. Subsequent NanoSIMS measurements at Washington University confirmed the O isotopic anomalies and small Mg anomalies in two grains [2].

We used an FEI Nova 600 focused ion beam scanning electron microscope (FIB-SEM) at the Naval Research Laboratory to make electron-transparent sections of one of the chromite grains (ORG-36-21) in order to investigate its structure and composition. We used FIB methods similar to those described by [6] except that the grain was welded, in situ, to a Mo grid rather than extracted with a microtweezer. The FIB section was examined with a 200 keV JEOL 2200FS transmission electron microscope (TEM) equipped with an energy-dispersive spectrometer (EDS), in-column energy (Omega) filter, and bright- and dark-field scanning TEM (STEM) detectors.

Results: ORG-36-21 has an $^{18}O/^{16}O$ ratio close to solar and is moderately enriched (by ~30%) in ^{17}O. Although not extreme by presolar-grain standards, its O isotopic composition lies outside the range of known solar-system materials and lies within the Group-1 field [7] for presolar oxide grains (Fig. 1a). Its Mg isotopic composition is solar within ~1% error. Comparison with models [8] suggests it probably formed in a low-mass (~1.18 $M_{\odot}$) red giant branch (RGB) or asymptotic giant branch (AGB) star of approximately solar metallicity.

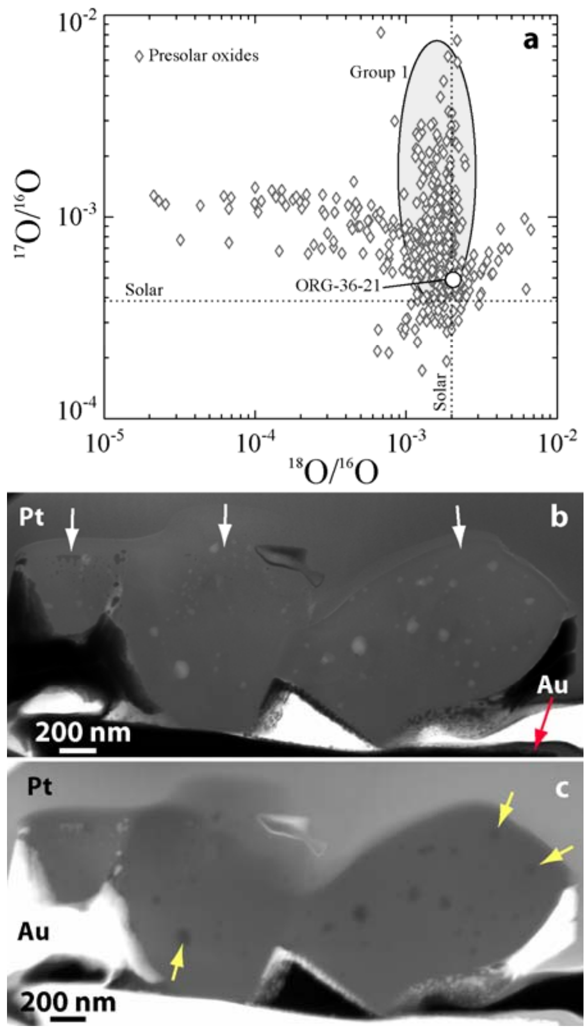

Fig. 1. (a) O isotopic ratios of grain ORG-36-21 compared to those of several hundred presolar oxide grains [10]. **(b)** Bright-field STEM image (white arrows point to the three grains). **(c)** Z-contrast HAADF image (yellow arrows point to precipitates).

The FIB section of ORG-36-21 contains three distinct grains (Fig. 1b,c) with sizes of approximately 428 nm x 411 nm, 963 nm x 865 nm, and 1.3 μm x 876 nm (height and width). Selected-area electron-diffraction (SAED) patterns acquired from each of the grains fit, to within two percent relative error, a cubic structure

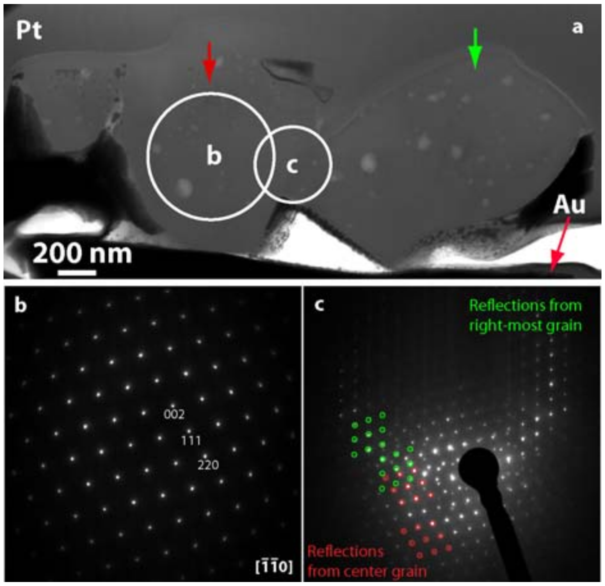

Fig. 2. (a) Bright-field STEM image. Circles indicate areas from which SAED patterns **(b,c)** were acquired. **(b)** SAED from center grain (red arrow in **a**) down the [-1-10] zone axis. **(c)** SAED from the right-most grain (green arrow in **a**); same orientation as **(b)**. Reflections from both the center and right-most grains (red and green circles, respectively) occur. The diffuse intensity ring of reflections**,** partly higlighted by the top set of green circles, indicates that the right-most grain is closely oriented to the center grain. Similar observations were made for the left-most grain (but are not shown here).

based on chromite spinel lattice constants (space group Fd-3m, a_0 = 0.827 nm). The SAED patterns acquired from the bulk crystals and the interfaces between them reveal that the three grains are oriented to within a few degrees of one another (Fig. 2).

Bright-field images of the three grains have non-uniform contrast, each containing small regions of relatively bright areas (Fig. 1b) that occur heterogeneously throughout the crystals. Z-contrast imaging with a high-angle annular-dark-field (HAADF) detector shows that these regions have, on average, lower atomic number than the bulk crystals (cf., Figs. 1b&c). The low-Z regions range in size from approximately 6- to 94-nm wide with an average width of approximately 27 nm. Bright-field imaging indicates that the low-Z regions are euhedral and have a rhombic morphology in at least one orientation.

Energy-dispersive X-ray spectra show that the bulk grains and the low-Z regions contain Fe, Cr, Ti, Ni, Mg, Al, and O. Quantification of the x-ray spectra shows that the bulk grains have similar compositions to one another with an average composition of $(Fe_{0.63}Mg_{0.35}Ni_{0.03})_{\Sigma=1}(Cr_{1.44}Al_{0.27}Mg_{0.17}Ti_{0.12})_{\Sigma=2}O_4$. In comparison, the low-Z regions contain on average $[(Fe_{0.65}Mg_{0.31}Ni_{0.04})_{\Sigma=1}(Cr_{1.22}Al_{0.36}Mg_{0.16}Ti_{0.27})_{\Sigma=2}O_4]$ about two times more Ti than the bulk crystals. SAED patterns acquired from areas consisting mostly of the Ti-rich material show no signfication variation in either geometry or intensity from those of the bulk crystal. High-resolution TEM (HRTEM) images from one of the Ti-rich areas reveal lattice fringes from (111) planes that are continuous across the interface with the bulk crystals, suggesting structural coherency in at least one orientation. We therefore infer that these Ti-rich regions are precipitates rather than inclusions.

Discussion: The bright-field TEM images and SAED patterns acquired from ORG-36-21 reveal that it is polycrystalline. The isotopic homogeneity of the three grains and the observation that they occur in close orientation indicates that they are not random grains that came together during sample preparation, but more likely grew together during circumstellar condensation. The precipitates within the bulk crystals presumably formed during cooling because their relatively higher Ti content made them chemically incompatable with their host crystal. The rhombic morphology of the precipitates suggests that they had sufficient time to solidify euhedral grains, but their varied grain size could suggest differences in their rates of crystallization.

The O and Mg isotopic composition of ORG-36-21 indicates that it formed in a low-mass AGB or RGB star of solar composition. Most recent thermodynamic equilibrium calculations which aim to model the condensation of a cooling gas of solar composition predict that $MgAl_2O_4$, rather than chromite ($FeCr_2O_4$), will condense as the stable spinel phase [e.g., Fig. 1 in 1]. Calculations by [9] showed that chromite could condense from a solar gas prior to metal under highly oxidizing conditions, but there is no reason to expect such conditions in the kind of low-mass stellar outflow from which ORG-36-21 originated. More recent calculations by [1 – see plate 7] predict that Cr-rich spinel could condense from a gas of solar composition. However, the Fe contents of this theoretical spinel are probably much lower than observed for ORG-36-2, possibly pointing to non-equilibrium condensation. High Fe contents in some presolar silicate grains have led to similar conclusions [11].

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