TRANSMISSION ELECTRON MICROSCOPY ANALYSIS OF A PRESOLAR Cr-RICH SPINEL GRAIN.
T. J. Zega¹, L.R. Nittler², C.M.O’D. Alexander², and R.M. Stroud¹. ¹Materials Science and Technology Division, Naval Research Laboratory, Code 6366, 4555 Overlook Ave. SW., Washington DC, 20375 (tzega@nrl.navy.mil). ²Department of Terrestrial Magnetism, Carnegie Institution of Washington, 5241 Broad Branch Rd., NW, Washington, DC 20015-1305.

Introduction: In the pure form, chromite (FeCr₂O₄), 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 Al₂O₃ [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 microweever. 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 ¹⁸O/¹⁶O ratio close to solar and is moderately enriched (by ~30%) in ¹⁷O. 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-I 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☉) red giant branch (RGB) or asymptotic giant branch (AGB) star of approximately solar metallicity.

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.
The diffuse intensity ring of reflections 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 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).

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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 $(\text{Fe}_{0.63}\text{Mg}_{0.35}\text{Ni}_{0.04})\Sigma_{1}(\text{Cr}_{1.22}\text{Al}_{0.36}\text{Mg}_{0.16}\text{Ti}_{0.27})\Sigma_{2}\text{O}_{4}$. In comparison, the low-Z regions contain on average $(\text{Fe}_{0.65}\text{Mg}_{0.31}\text{Ni}_{0.04})\Sigma_{1}(\text{Cr}_{0.44}\text{Al}_{0.32}\text{Mg}_{0.17}\text{Ti}_{0.12})\Sigma_{2}\text{O}_{4}$. In 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 MgAl2O4, rather than chromite (FeCr2O4), 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].

**References:**