THE MICROSTRUCTURE OF A PRESOLAR SPINEL GRAIN. T. J. Zega[1], C. M. O'D. Alexander[2], L. R. Nittler[2], and R. M. Stroud[1], [1]Code 6366, Materials Science and Technology Division, Naval Research Laboratory, 4555 Overlook Ave. SW, Washington, D.C. 20375. [2]Department of Terrestrial Magnetism, Carnegie Institution of Washington, 5241 Broad Branch Rd. NW, Washington, D.C., 20015. (tzega@nrl.navy.mil).

Introduction: Spinel ($MgAl_2O_4$) is the fourth most abundant presolar phase after nanodiamonds, silicates, and SiC [1]. Thermodynamic calculations predict that it will form from a gas of solar composition [2-3]. Spinel's occurrence in solar materials has been well documented (e.g., [4] and references therein), and it has been suggested, on the basis of IR spectra, to be present around evolved O-rich stars [5]. Microstructural and compositional information on presolar spinel can therefore provide insight into the circumstellar environment in which it formed and offer ground truth for observational astronomy. We previously reported on Cr-rich and Mg-Al presolar spinel grains [6-7]. Here we continue that effort and report data on a third presolar spinel.

Experimental: Grain UOC-S1 was identified in a mixed acid-resistant residue of unequilibrated ordinary chondrites (UOC) QUE 97008, WSG 95300, and MET 00452 [8]. Its anomalous O-isotopic composition, measured by automated mapping techniques with the Carnegie ims-6f secondary ion microprobe (SIMS), indicated a stellar origin. The Mg-isotopic composition of the grain was later determined with the Carnegie NanoSIMS 50L.

UOC-S1 was extracted and thinned in situ to electron transparency with an FEI Nova 600 focused ion beam scanning electron microscope (FIB-SEM) at the Naval Research Lab [9]. Grain microstructure and chemistry was investigated using a 200 keV JEOL 2200FS transmission electron microscope (TEM) equipped with an energy-dispersive X-ray spectrometer (EDS) and scanning-based TEM (STEM) bright- and high-angle annular dark-field (HAADF) detectors.

Results: UOC-S1 has $^{17}O/^{16}O = 5.35\pm0.36 \times 10^{-4}$ and $^{18}O/^{16}O = 1.29\pm0.08 \times 10^{-3}$. It plots within the Group-1 field for presolar oxide grains (Fig. 1), and comparison of its O-isotopic composition with that predicted by model calculations suggest that it formed in a low-mass ($\approx$1.4 $M_\odot$) AGB star with a metallicity of approximately 0.8 × solar [8,10]. Its Mg-isotopic composition ($\delta^{25}Mg = -4\pm11$, $\delta^{26}Mg = 241\pm14$) is consistent with this origin as well, with an inferred initial $^{26}Al/^{27}Al$ ratio of order 10^{-2}.

The FIB section of UOC-S1 contains a grain measuring approximately 165 nm × 350 nm (Fig. 1b). A selected-area electron-diffraction (SAED) pattern suggests that the grain is a single crystal (Fig. 2, inset). However, Au coats part of the grain's surface (from redeposition during the milling process) and currently precludes rigorous analysis of parts of the right- and left-hand sides. Additional milling should remove the Au and help verify that it is a single crystal. Measurements on the SAED pattern indicate interplanar spacings of 0.287 nm and 0.471 nm, consistent with the (220) and (111) *d*-spacings for spinel (S.G. Fd-3m, a_0=0.81nm). High-resolution TEM images reveal small domains where (111) lattice fringes are discontinuous (Fig 2, white arrowhead). EDS spectra show that the grain contains predominantly Mg, Al, and O with minor Fe, Ca, Cr, and Mn. Quantification of the spectra suggest that the grain is non-stoichiometric with an Al/Mg ratio of approximately 2.8. This is slightly higher than the Al/Mg ratio of 2.2 measured by SIMS,

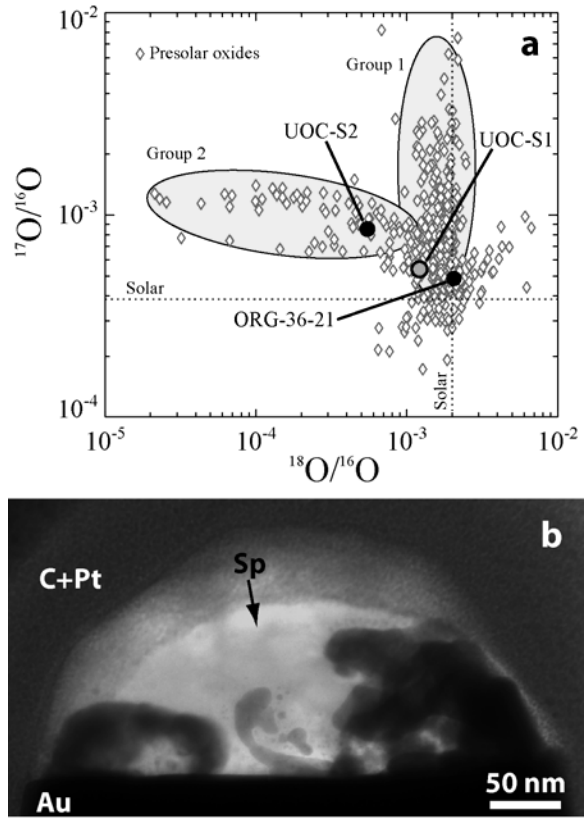

Fig. 1. (a) Three-O isotope plot showing the composition of grain UOC-S1 (filled gray circle with black outline) together with previously studied presolar spinels ORG-36-21 [6] and UOC-S2 [7] as well as other presolar oxides. **(b)** Bright-field STEM image of grain UOC-S1. Spinel (Sp) occurs sandwiched between the Au pedestal and the protective strap of C and Pt. The dark material on the left- and right-hand sides of the grain is Au re-deposited during FIB milling.

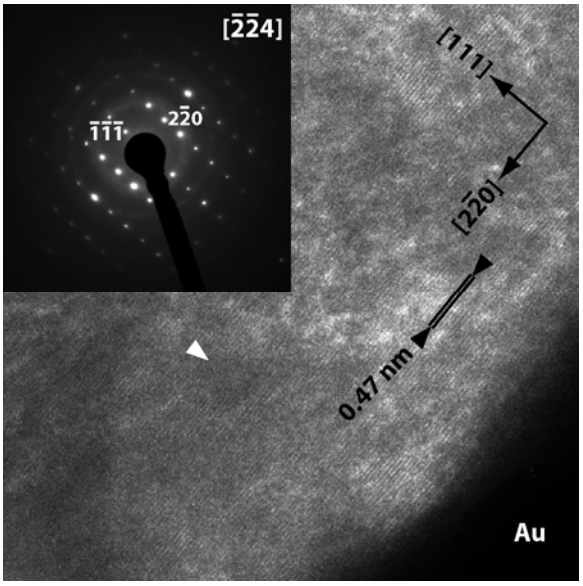

Fig. 2. HRTEM image of part of presolar spinel grain UOC-S1. Some (111) lattice fringes appear discontinuous in parts of the grain (e.g., the white arrowhead), suggesting localized disorder (note that grain is rotated relative to BF-STEM image in Fig. 1). The SAED pattern (inset) otherwise indexes to spinel (faint circles arise from Au and Pt particles re-deposited during FIB milling).

but within the relatively large uncertainty of the latter technique.

Discussion: Equilibrium thermodynamic calculations predict that spinel can condense from a gas of solar composition. At high temperature (e.g., 1501K, $P_t=10^{-3}$ atm), nearly pure $MgAl_2O_4$ is predicted to form by back reaction of hibonite ($CaAl_{12}O_{19}$) with gaseous Mg, whereas a spinel solid solution (relatively rich in Cr) will form at lower temperature (1221 K) via solid-state reaction of metal, plagioclase, and Mg-silicates [3]. The EDS data indicate that grain UOC-S1 is not a pure Mg-Al spinel, which, if equilibrium condensation was responsible for its formation, would argue for the lower condensation temperature. Indeed, this lower temperature was inferred as an upper limit for condensation of grain UOC-S2, a stoichiometric Fe- and Cr-bearing presolar spinel [7]. However, quantification of the EDS spectra from grain UOC-S1 reveals a departure from ideal stoichiometry, pointing to non-equilibrium condensation. The Cr- and Fe-rich composition of presolar spinel grain ORG-36-21 led to a similar conclusion [6].

Non-stoichiometric presolar spinels have been previously observed. Those with higher than stoichiometric Al/Mg ratios were hypothesized to have formed at high temperatures by replacement of corundum [11]. The presence of minor Ca, as measured by EDS, might argue against such a pathway as it could be a result of incomplete back reaction between hibonite and the circumstellar gas from which UOC-S1 condensed. Examination of additional non-stoichiometric spinel grains should reveal whether or not the presence of Ca is a general feature.

The 13-μm emission feature of IR spectra of O-rich AGB stars has been attributed to several phases including spinels [5, 12-14]. Although the data that we report here do not address the controversy over the identification of this emission feature, they do show that O-rich AGB stars can condense crystalline spinel grains.

References: [1] Nguyen, A. N., et al., 2007. *ApJ 656*, 1223-1240. [2] Ebel, D. S., 2006. In: *MESS II* (D. S. Lauretta and H. Y. McSween, Jr. Eds.). 253-277. Univ. of Arizona Press, Tuscon. [3] Yoneda, S. and Grossman, L., 1995. *GCA 59*, 3413-3444. [4] Brearley, A. J. and Jones, R. H., 1998. In: *Planetary Materials* (J. J. Papike, Ed.) 398p. Min. Soc. of America, Washington, D.C. [5] Posch, T., et al., 1999. *A&A 352*, 609-618. [6] Zega, T. J., et al., 2008. *LPS XXXIX*, Abstract #2424. [7] Zega, T. J., et al., 2009. *LPS XL*, Abstract #1342. [8] Nittler, L. R., et al., 2008. *ApJ 682*, 1450-1478. [9] Zega, T. J., et al., 2007. *MAPS 42*, 1373-1386. [10] Nollett, K. M., et al., 2003. *ApJ 582*, 1036-1058. [11] Zinner, E., et al., 2005. *GCA 69*, 4149-4165. [12] Kozasa, T. and Sogawa, H., 1997. *Astro. & Space Sci. 251*. [13] Onaka, T., et al., 1989. *A&A 218*, 169-179. [14] Speck, A. K., et al., 2000. *A&A Supp. Ser. 146*, 437-464.