TEM STRUCTURAL AND COMPOSITIONAL STUDIES OF PRESOLAR SIC GRAINS AND THEIR RELATION TO RAMAN SPECTRA. S. A. Singerling[1], N. Liu[2], L. R. Nittler[3], C. M. O'D. Alexander[3], R. M. Stroud[4], [1]Nova Research, Inc., Alexandria, VA 22308, USA, sheryl.singerling.ctr@nrl.navy.mil, [2]Department of Physics, Washington University in St. Louis, St. Louis, MO 63130, USA, [3]Carnegie Institution of Washington, Washington, DC 20015, USA, [4]U.S. Naval Research Laboratory, Code 6366, Washington, DC 20375, USA.

Introduction: Presolar grains are the oldest solids in the solar system, predating its formation and having largely formed in circumstellar environments (e.g., asymptotic giant branch (AGB) stars, novae, core-collapse supernovae). As such, presolar grains provide the only available laboratory samples of these environments against which observational and theoretical predictions can be tested. The most well-studied presolar grains are silicon carbide (SiC), which are divided into several groups (mainstream (MS), X, Y, Z, A+B, C, PNG) based on isotopic compositional differences [e.g., 1] .

Synthetic SiC can form in numerous crystalline polytypes, a result of specific growth conditions, e.g., temperature, pressure, gas composition. A prior transmission electron microscope (TEM) study of 508 presolar SiC grains of unknown isotope composition revealed that presolar SiC grains are predominantly cubic 3C (~80%), hexagonal 2H (~3%), or intergrowths of the two polytypes (~17%) [2]. Given that ~90% of SiC grains belong to the MS group, this polytype distribution determination applies largely to the MS grains in the analyzed size range (0.32–0.70 μm). Subsequent TEM studies expanded on this work by determining the polytypes of grains belonging to the groups of X, Y, Z, A+B, and C [3–8]. Altogether these studies determined the polytypes for 28 non-MS grains, of which 21 were X, 1 Y, 2 Z, 3 A+B, and 1 C.

Previous work by [8] demonstrated the utility of micro-Raman spectroscopy as a screening tool for locating grains from rare isotope groups and with unusual crystal structures. Our current study seeks to: 1) determine which polytypes are present in the rarer presolar SiC grain groups (X, Y, Z, A+B); 2) look in more detail at MS grains with Raman spectral features that indicate non-3C polytypes and/or crystal disorder; and 3) determine minor element and sub-grain compositions of SiC grains.

Methods: We used TEM to analyze 6 grains with previously reported SIMS and Raman data [8]—3 MS (M2-A1-G312, M2-A1-G648, M2-A1-619), 2 X (M2-A1-G674, M2-A2-G1036), and 1 Y (M2-A1-G670). The MX-AX portion of the grain names is suppressed hereafter. The FIB section preparation and TEM analyses were performed at the U.S. Naval Research Laboratory. Focused ion beam (FIB) sections were extracted from the SiC grains and supporting Au foil with an FEI Helios FIB-SEM. Bright field (BF) images and selected area electron diffraction (SAED) patterns were collected on a JEOL 2200FS TEM, and high angle annular dark field (HAADF) STEM images and energy dispersive spectroscopy (EDS) X-ray maps/spectra were collected with a Nion UltraSTEM-200X, equipped with a Bruker Xflash SSD system, all at 200 kV.

Results: The grains (Fig. 1) range in size from 640 nm to 1530 nm in their longest dimension, and in shape from circular to highly elliptical. MS grain G312 has multiple domains that all index to 3C with varying levels of stacking disorder, and appears to have fractured when pressed into the Au foil. MS grain G648 and Y grain G670 are single domain 3C, and MS G619 appears to be a single domain of 4H. X grains G674 and G1036 have multiple domains, with diffraction patterns that indicate intergrowths of 3C and 2H (3C-2H). Stacking faults were observed in all of the grains except G619 and G648.

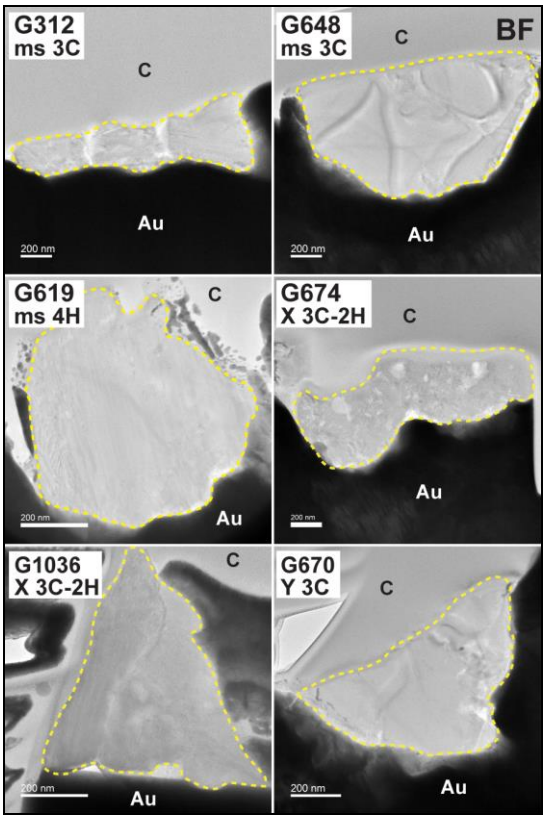

Figure 1. TEM bright field images of 6 presolar SiC grains. Scale bars are all 200 nm. The SiC grains are outlined in dashed yellow lines, and the labels Au and C refer to the Au foil and protective C layers, respectively.

EDS X-ray maps (Fig. 2) were collected from 3 presolar SiC grains—G670, G674, and G1036. G670 (3C Y grain) contains a few TiN inclusions that are ≤100 nm in their longest dimension. G674 (3C-2H X grain) contains several Fe, Ti, Ni, and/or V-bearing inclusions that are ≤30 nm in their longest dimension, and the SiC has moderate abundances of Al (0.75 at.%), Mg (0.46 at.%), and N (1.8 at.%). G1036 (3C-2H X grain) does not appear to contain inclusions, but the SiC has high abundances of Al (2.0 at.%), Mg (1.7 at.%), and N (4.4 at.%). Additionally, the grain contains cracks that show O, Ca, and F retention from acid dissolution.

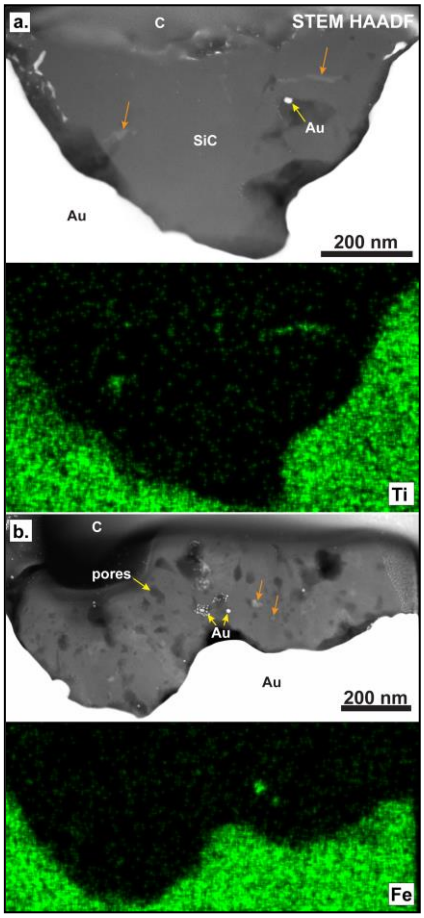

Figure 2. STEM HAADF images and EDS X-ray maps of (a) 3C Y grain G670 and (b) 3C-2H X grain G674. The inclusions in each grain are indicated by the orange arrows in the HAADF aimges. Bright white material within the grain is Au from redeposition during sample preparation. Abundant porosity is visible in (b).

Discussion: Comparing our TEM observations with the Raman spectroscopic observations (Fig. 3), we confirm prior results from [8] which showed that deviation of the transverse optical (TO) peak position (Si-C bond stretching) from the reference 3C position (799 cm^{-} from [9]) is generally a good indication of a non-3C polytype. Exceptions in the present data are MS grain G648, which is a well-ordered 3C crystal but has a downshifted peak position in its Raman spectrum (that is, falls below the 3C reference line in Fig. 3), and MS grain G619, which is a single domain 4H crystal but has a distinctly double-peaked Raman spectrum with one peak falling well below the 4H reference line. One possible explanation for these discrepancies is that the original grains contained multiple domains, but that these other domains were not sampled in the FIB sections.

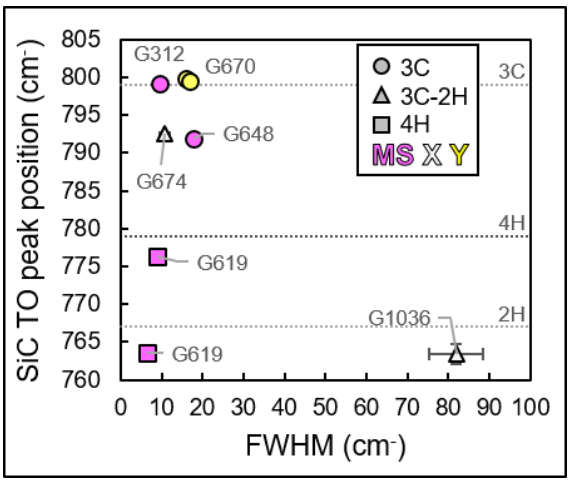

Figure 3. SiC grain Raman TO peak position versus peak width (FWHM); data are from [8] and reference lines from [9]. The symbol shape indicates the TEM-determined polytype, and the color indicates the isotope group.

This study represents only the second TEM analysis of a Y grain; the other being [3] in which the grain was identified as 3C-2H. In both crystal structure and the occurrence of Ti-rich inclusions [8, 10], this grain is very similar to prior MS grain results, which indicates similar condensation conditions in the dusty envelopes of low- and high-metallicity AGB stars.

Our results confirm that Raman spectroscopy is a useful method for searching for unusual presolar SiC grains with crystal structures, microstructures, and subgrains that provide evidence of the broader range of SiC condensation conditions and subsequent processing histories. Further work is required to obtain a more statistically significant sample size for constraining the polytype distributions and common subgrains of rare isotope groups of presolar SiC.

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