TEM STUDIES OF PRESOLAR SIC GRAINS: INSIGHTS INTO CIRCUMSTELLAR CONDITIONS AND IMPLICATIONS FOR IR SPECTROSCOPY. S. A. Singerling[1*], N. Liu[2], L. R. Nittler[3], C. M. O'D. Alexander[3], R. M. Stroud[1], *NRC-NRL Postdoc, sheryl.singerling.ctr@nrl.navy.mil, [1]U.S. Naval Research Laboratory, Code 6366, Washington, DC 20375, USA, [2]Department of Physics, Washington University in St. Louis, St. Louis, MO 63130, USA, [3]Carnegie Institution of Washington, Washington, DC 20015, USA.

Introduction: Presolar circumstellar grains are the oldest solids available for study in the solar system, predating its formation by up to a few billion years [1]. The grains' circumstellar origins are inferred from their anomalous isotopic compositions. Transmission electron microscopy (TEM) is uniquely suited for chemical and structural studies of these grains and, together with isotopic compositional information, can yield insights into circumstellar conditions as well as guide models for interpretations of astronomical IR spectral observations of dust in stellar environments.

Silicon carbide (SiC) grains are the most well-studied type of presolar grain and are divided into several groups based on isotopic compositional differences. Stellar environments for the SiC grains in this study include C-rich asymptotic giant branch (AGB) stars with ≥solar metallicities for the mainstream (MS) grains, C-rich AGB stars with <solar metallicities and/or >solar masses for the Y grains, and core-collapse supernovae (CCSNe) for the X grains [e.g., 2].

Crystal structures and minor element and subgrain compositions of presolar SiC grains can provide useful constraints on their formation conditions. The stacking order of the Si-C pairs in SiC varies as a function of temperature, pressure, gas phase composition, substrates, and so forth. Prior TEM analyses of presolar SiC grains as well as IR astronomical spectral studies of circumstellar SiC dust have found that the cubic 3C polytype is the most common structure, followed by the hexagonal 2H polytype and intergrowths of the two [e.g., 3–10]. Thermodynamic equilibrium calculations predict the formation of different gas phase condensates as a function of temperature, pressure, and C/O ratios in circumstellar environments [e.g., 11–14].

Data from [8] indicate that at least 10% of presolar SiC grains exhibit Raman features that are suggestive of non-3C polytype structures. Given that both Raman and IR spectra derive from atomic vibrations along Si-C bonds, grains with unique Raman spectra could also give rise to IR spectra that deviate from the predominant 3C spectral distribution. Our current study seeks to: 1) gain insights into dust formation under a wide range of conditions in the different circumstellar environments, and (2) provide guidance for better constraining the interpretation of astronomical IR spectra.

Methods: Eight presolar SiC grains with previously reported isotopic compositional (NanoSIMS) and µ-Raman data [8] were selected for FIB-TEM analyses—4 MS (G312, G619, G620, G648), 1 Y (G670), and 3 X (G506, G674, G1036) grains. The FIB sections were prepared with a FEI Helios Dualbeam FIB-SEM. The TEM work was performed at 200 kV on a JEOL 2200FS [bright field (BF) images, "dirty" dark field (DDF) images, selected area electron diffraction (SAED) patterns] and a Nion UltraSTEM-200X [high angle annular dark field (HAADF) STEM images and energy dispersive spectroscopy (EDS) X-ray spectra].

Results: The grains range in size from 640 to 1230 nm, and in shape from circular to highly elliptical. All but one grain (MS G648) contain multiple crystal domains, determined with SAED and DDF imaging. MS G312, G648, and G620 and Y G670 contain only 3C crystal domains. MS G619 (2H-4H) and X G506 (3C-8H), G674 (3C-2H-10H-14H), and G1036 (3C-2H) are intergrowth grains containing crystal domains with non-3C polytypes.

For the seven grains for which we collected EDS data (excludes G648, which was lost after one TEM session), five contain regions enriched in the minor elements Al, N, and/or Mg, and all but one contain subgrains. Regions of high-density stacking faults in MS G312 are enriched in Al and N and contain a higher abundance of subgrains (TiC and AlN) (Fig. 1a). The Al,N-rich regions of SiC in MS G620 are limited to the grain boundary, and a single, large (~100 nm), equant TiN subgrain is present at the interface between the Al,N-poor and -rich SiC (Fig. 1b–c). In MS G619, Al,N-rich SiC alternates with Al,N-poor SiC several times moving concentrically outward from the center of the grain (Fig. 1d–e). Abundant TiC subgrains (elongate and equant) and voids are associated with the Al,N-rich SiC, and one Fe-metal and one CaS subgrain are also present. Y G670's Al and N contents are below detection limit, but four elongate TiC subgrains were observed. X G506 does not contain regions enriched in the minor elements; however, it contains numerous, small (~1–10 nm), equant ZrC subgrains. X G674 contains irregular patches enriched in Al, Mg, and N as well as several Fe-bearing, mostly equant subgrains and numerous voids (Fig. 1f). X G1036 contains the highest overall abundance of Al, Mg, and N of the seven grains studied; however, no subgrains were observed in the grain.

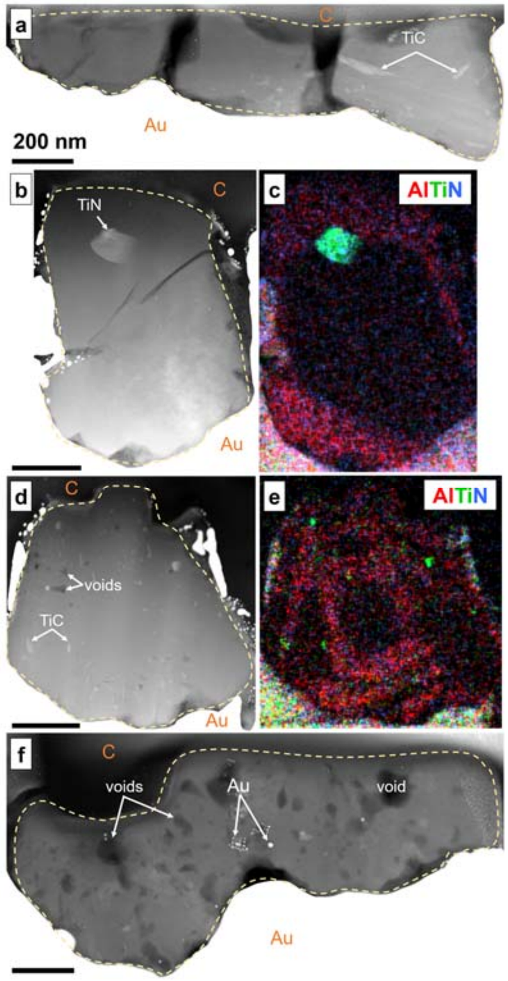

Figure 1. STEM HAADF images and EDS X-ray maps of presolar SiC grains: (a) MS G312, (b–c) MS G620, (d–e) MS G619, and (f) X G674. The SiC grains are outlined.

Discussion: The structural and elemental compositional observations of the grains studied in this work allow us to gain insights into circumstellar conditions as well as the potential effects of such features on IR spectra.

Circumstellar conditions. Using theoretical condensation temperatures in addition to observations of the presolar grains themselves (subgrain morphologies as well as comparing the orientation distributions and the extent of compositional heterogeneity between subgrains present in the same SiC host), we were able to determine which subgrains formed as a result of condensation from a gas at higher temperature and which formed from exsolution from SiC at lower temperature.

For the grains of this study which originated in AGB stars, the subgrains mostly formed by exsolution (MS G312, G619, Y G670). MS G620's TiN subgrain and MS G619's Fe-metal subgrain are exceptions, likely having condensed and been subsequently incorporated into SiC. We also determined that the MS grains reflect formation under a range of C/O ratios, from 0.98 (G620) to 0.99 (G619) to ≥1.03 (G312), based on the phases present and the temperature versus C/O ratio plots in [14]. In G619, the Al,N-zoning implies that temperature cycling and/or changes in pressure occurred as the grain grew. This hypothesis is further supported by the polytypes observed for this grain (2H-4H), where 4H is consistent with formation at higher temperature and 2H with formation at lower temperature [5].

For the grains of this study which originated in CCSNe, the subgrains formed by condensation (X G506, G674). For G674, the formation of Fe-bearing subgrains prior to the SiC requires Fe enrichment in the gas relative to solar, if thermodynamic equilibrium was maintained, which itself requires mixing of the He/C and Fe/Ni zones in CCSNe [15]. In all three X grains, we found evidence for rapid crystallization, including multiple crystal domains, higher order polytypes, abundant stacking faults in the 3C domains, and abundant voids.

IR Spectroscopy. The influence of structural and compositional features in presolar SiC grains on their Raman spectra implies that these same features may also influence the IR spectra. Specifically, higher order (non-3C,2H) polytypes, intergrowths of multiple polytypes, crystal defects, voids, impurities (e.g., Al and N), and subgrains could, in principle, all affect IR spectra to the extent that grains with these features are missed entirely or misinterpreted in astronomical observational work. Future work determining the effect of each of these factors on IR spectra would be useful in better matching observations from TEM studies of presolar SiC grains to the dust from their stellar sources.

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