

IN SITU IRRADIATION AND HEATING OF SYNTHETIC SiC AND IMPLICATIONS FOR THE ORIGINS OF C-RICH CIRCUMSTELLAR MATERIALS. T.J Zega^{1,2}, J.J. Bernal³, J.Y. Howe⁴, P. Haenecour¹, S. Amari⁵, and L.M. Ziurys^{3,6}, ¹Lunar and Planetary Laboratory and ²Department of Materials Science and Engineering, University of Arizona, Tucson, AZ; ³Department of Chemistry and Biochemistry, University of Arizona, Tucson, AZ; ⁴Dept. of Materials Science and Engineering and Department of Chemical Engineering and Applied Chemistry, University of Toronto, Ontario, Canada; ⁵Physics Dept. and McDonnell Center for the Space Sciences, Washington University, St. Louis, MO; ⁶Dept of Astronomy, University of Arizona, Tucson, AZ. (Email: tzega@lpl.arizona.edu).

Introduction: Primitive meteorites contain within them the preserved ashes of ancient stars. These ‘pre-solar’ grains condensed in gaseous circumstellar environments and made their way through the interstellar medium to our local part of the galaxy where the solar system was forming some 4.56 billion years ago. Since the initial discovery of this stardust in 1987 [1-3], several different types were identified over the ensuing three decades including oxides, silicates, metals, nitrides, and carbides [4]. The isotopic compositions, structures, and spatial relationships with other (solar-system) material in meteorites has provided a wealth of information on their origins. We have gleaned from such studies remarkable insight into stellar nucleosynthesis [5], thermodynamics of circumstellar envelopes [6], and how such grains could have survived chemical and physical processing in the early solar system [7].

Nanodiamond, SiC, and graphite were the first pre-solar grains identified in primitive meteorites [1-3, 8]. SiC and graphite are among the largest ($\leq 30 \mu\text{m}$) types of presolar materials and thus, also the most well studied [9]. They occur in different types of morphologies and structures and contain different isotopic compositions which reflect varied histories in RGB and AGB stars, novae, and supernovae [9]. SiC, in particular, was shown to predominantly occur in the 3C polytype, reflecting the thermodynamic conditions in which it formed [10]. Moreover, grains of SiC and other metal-carbides were observed inside of graphite [11], raising questions regarding the sequence in which these materials condensed. To better understand such materials, and moreover, how reduced C can form in what is known from astronomical observations [12] to be an otherwise H-rich environment (along with other abundant elements such as O, N, and S), we report here results on in situ experiments with synthetic SiC.

Samples and Methods: A 3C polytype of SiC (99% purity) was obtained from U.S. Research Nanomaterials. The powdered sample (45 to 65 nm particle size) was dropcasted onto SiN support films as part of the microelectromechanical systems (MEMS) chip used for in situ heating, which we have previously demonstrated on lunar soil grains [13,14]. Samples were dropcasted in methanol (‘wet’) and in air (‘dry’).

The MEMS chips were loaded into a Hitachi ‘Blaze’ heating holder and together loaded into the Hitachi H9000 transmission electron microscope (TEM) located at the intermediate voltage electron microscope tandem facility at Argonne National Laboratory (<https://www.nc.anl.gov/ivem/>). We heated the wetcast SiC grains at 5 °C/min to 1000 °C, and then held it isothermally and irradiated it with Xe at 150 keV to 15 displacements per atom (dpa) over approximately two hours. The second experiment was similar to the first except we used the drycast sample and irradiated it for 1 hour up to 3 dpa. Our general approach in conducting these in situ experiments is to identify a region on the grid containing a monodispersion of particles that can be monitored continuously. Bright-field TEM images, electron-diffraction patterns, and video were acquired throughout the experiment.

After heating and irradiation, the sample was analyzed at the University of Arizona using a Hitachi HF5000 aberration-corrected scanning TEM (S/TEM). The HF5000 is equipped with energy-dispersive X-ray and electron energy-loss spectrometers (EDS/EELS, respectively) for chemical analysis. The imaging analysis was carried out at 200 keV, whereas EELS analyses were performed at the C, K edge at 60 keV.

Results: Figure 1(a) shows one of the grid locations that was monitored in the experiment on the wet-cast sample. Particles are mostly monodispersed, but localized areas contain clumps of several particles. High-resolution TEM (HRTEM) imaging shows that the bulk of the interior of the large ($\geq 100 \text{ nm}$) particles contains the original 3C SiC structure. In comparison, smaller ($< 100 \text{ nm}$) particles show breakdown of the 3C structure on their edges. HRTEM reveals that sets of parallel lattice fringes containing interplanar d -spacings of 0.34 nm, which correspond to the (002) spacing for graphite, occur on the edges of most grains. In addition, localized parts of the edges contain complete breakdown of long-range order, whereas others contain small (1 nm) circular structures that are similar in size and shape to C_{60} .

We performed EELS spectrum imaging on several areas of one of the particles to confirm the HRTEM observations. The energy-loss near-edge structure is consistent with graphite on the edge of the particle with interior SiC. Filtered maps, constructed from the EELS spectrum images, show clearly the localized distribution of sp^2 -hybridized (planar trigonal) graphitic bonding on

the edge of the grain and sp^3 -hybridized (tetrahedral) SiC bonding in the core.

Discussion: Carbon-bearing material is thermodynamically predicted to form in circumstellar envelopes (CSEs) when the C/O ratio reaches or exceeds unity [15,16]. Driven by the triple-alpha reaction and dredge-up processes, C is supplied to the envelope where it can react with other elements to form graphite and metal-rich carbides such as SiC. In general, graphite is predicted to condense at temperatures that exceed those of SiC at pressures $\leq 10^{-4.5}$ bar [15,16].

Such calculations also make predictions on the kinds of microstructures that could form assuming such a gas is monotonically cooling from high temperature. At low pressures ($< 10^{-4.5}$ bar), such calculations predict graphite formation first, followed by SiC, in which case a microstructure of graphite encased inside of SiC is expected, assuming that these reactants are sufficiently abundant and have access to one another in the CSE. In comparison, at high pressures ($> 10^{-4.5}$ bar), SiC is expected to condense first, followed by graphite, which could generate a SiC core with surrounding C.

The former, to our knowledge, has not been observed, whereas the latter was reported by [11]. One of these SiC grains has a Si-isotopic composition indicating an origin in a massive star where high pressures are expected. The latter grain contains an isotopic composition that is consistent with origins in the lower pressure environment of an AGB star. Thus, alternative explanations for such a microstructure are required.

The experimental data we report here could provide new insight. The HRTEM data reveal a SiC remnant core surrounded by a graphite shell, consistent with the previous observations [11]. During the in situ heating and irradiation, Si atoms were knocked out of the SiC lattice. C was left behind where it reconstructed to form graphene, graphite, and structures that are similar in size and shape to C_{60} . We note that our in situ dynamic heating and irradiation experiments are consistent with previous static (heating only) experiments reported in the literature on SiC [e.g., 17]. In other words, our data suggest that thermodynamic conditions simply need to favor SiC condensation followed by heating and irradiation to form reduced C materials in circumstellar environments. The mechanism we propose here can account for both the grain structure and isotopic composition without the need of high pressures or supernovae environments to explain these materials.

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Acknowledgements: Research supported by NASA grant NNX15AJ22G (T.J.Z.), NSF grant AST-1515568 (L.M.Z.), and NASA Agreement No. NNX15AD94G. T.J.Z. acknowledges NASA (grants #NNX12AL47G and #NNX15AJ22G) and NSF (grant #1531243) for funding the instrumentation in the Kuiper Materials Imaging and Characterization Facility, UA.

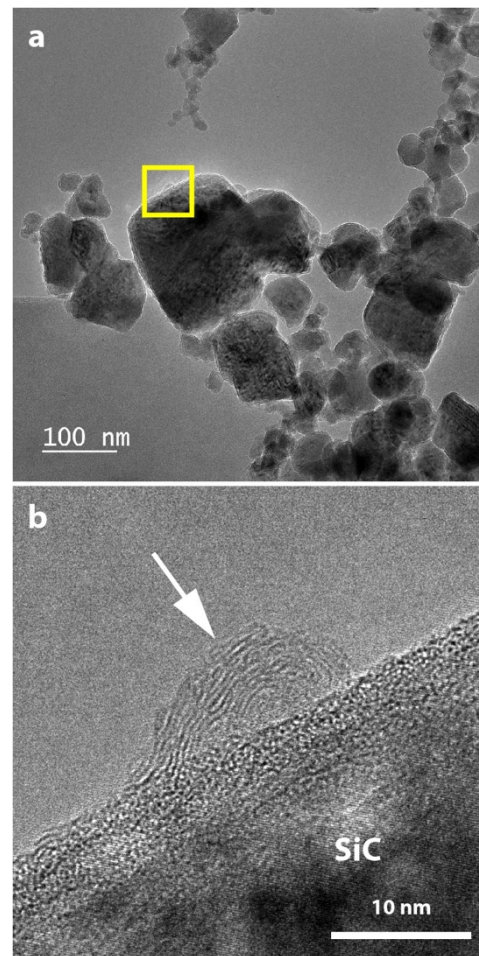


Fig. 1. TEM images of synthetic SiC and graphite. (a) SiC particles dispersed on MEMS support. (b) HRTEM image of graphite (white arrow) formed on edge of SiC.