MICROSTRUCTURE OF SILICON CARBIDES FOUND WITHIN PRESOLAR GRAPHITE. K. M. Hynes, T.K. Croat, and T. J. Bernatowicz, Laboratory for Space Sciences and Department of Physics, Washington University, St. Louis, MO 63130, USA, khynes@hbar.wustl.edu.

Introduction: Many presolar SiC and graphite grains show evidence of an origin in AGB outflows, and yet differ considerably in their carbon isotopic ratios [1]. These differences presumably result from changing chemical and isotopic conditions as the stars become more carbon-rich (and thus more ^{12}C-rich). Laboratory measurements of presolar grains can aid our understanding of this evolution. Of particular interest are the rare graphites with internal SiCs, whose constituents clearly condense around the same star, and might form during the transition between the SiC and graphite-forming periods. The study of these phase assemblages may give unique insight into the conditions required for their formation, and such studies have been used to guide and validate models of condensation in circumstellar outflows [2]. Here we report results of transmission electron microscopy (TEM) investigations of several SiC-containing graphites, one of which contains both SiC and TiC internal grains.

Experimental: Graphites were obtained from the KFC1 density and size separate (2.15-2.20 g cm-3, >1 μm) of the Murchison meteorite [3]. These graphites were deposited from suspension onto a glass slide, embedded in resin, and then sliced into ~100 nm sections with an ultramicrotome. The slices were examined in a JEOL 2000FX analytical TEM equipped with a NORAN Energy Dispersive X-ray Spectrometer (EDXS). EDXS quantitative analysis was done using basaltic glass and lead oxide compound standards.

Results: Table 1 summarizes the microstructural data from internal SiCs found within KFC1 graphites during TEM investigations thus far. This work produced new results for graphites 2-4, whereas results from graphite 1 were presented in [4]. All of the SiC-containing graphites are of the “onion” type, with well-crystallized graphitic layers forming concentric shells. All but graphite #2 also had nanocrystalline cores.

The presence of SiC in graphite #2 was mentioned in [2], although this identification was based on EDXS and lacked a crystal structure determination and other details. Further TEM investigations of graphite #2 uncovered five different SiC grains within the graphite slice (Figure 1a). The SiCs were euhedral, with geometrical mean sizes ranging from 15 to 60 nm. All SiCs were found towards the exterior of the graphite slice, and thus did not act as nucleation centers for the graphite, as is seen for many TiCs. The estimated SiC abundance with respect to graphite (as calculated from the areal fraction) is relatively high (~1%), similar to that calculated for graphite #1. These SiC abundances

Table 1. Properties of SiC found within graphites.

Graphite #	# SiCs	SiC size (nm) [1]	Polytype	Ref
1	23	35 (13-83)	3C-SiC, 1D disordered	4
2	5	39 (15-61)	3C-SiC, intergrowth	2, this work
3	1	26	3C-SiC with twinning	this work
4	1	35	3C-SiC	this work

1. Geometrical mean size (average and range presented when multiple grains are present.

are about an order of magnitude higher than the highest TiC abundances calculated (both in KFC1 and KE3 carbide-containing graphites). Three separate internal SiCs had patterns consistent with 3C-SiC (from [001], [111], and [112] FCC zones). A fourth SiC contained a low-index zone axis pattern showing spots from both the 2H-SiC [0001] hexagonal zone and the 3C-SiC [111] zone, indicating an intergrowth of the two phases. Dark-field images of the 2H and 3C spots indicated that either the interface plane happened to be perpendicular to the TEM beam, or that a fine-scale mixture of the two phases was present. A similar situation occurred in one of the KJG SiC-X grains [5].

Graphite #3 was a rim-core onion contained a single ~25nm subhedral SiC, again found toward the outside of the slice (Figure 1b). Several low-index zone axis patterns were found, all of which had spacings matching those expected from FCC 3C-SiC (e.g. [111]). However, extra spots and unexpected intraplanar angles in certain zone axis patterns show that twinning is present, introducing uncertainty in the polytype determination.

Graphite #4 is unique in that along with the SiC there is a twinned TiC within the slice, which is the first instance of such a phase assemblage. Both internal grains are located within the nanocrystalline core, although neither is central (Figure 1c). The SiC is a ~35nm euhedral grain, showing faceting along {111} planes. A single zone axis pattern of the SiC was indexed to the [011] zone of a ~4.5Å FCC phase, likely the 3C-SiC polytype. Also there is no evidence of extra spots from twinning, intergrowths, or higher order polytypes. The TiC within graphite #4 contained three separate crystal domains, all of which indexed to a ~4.5Å FCC structure (consistent with the known carbide phase). However, the orientation relationship

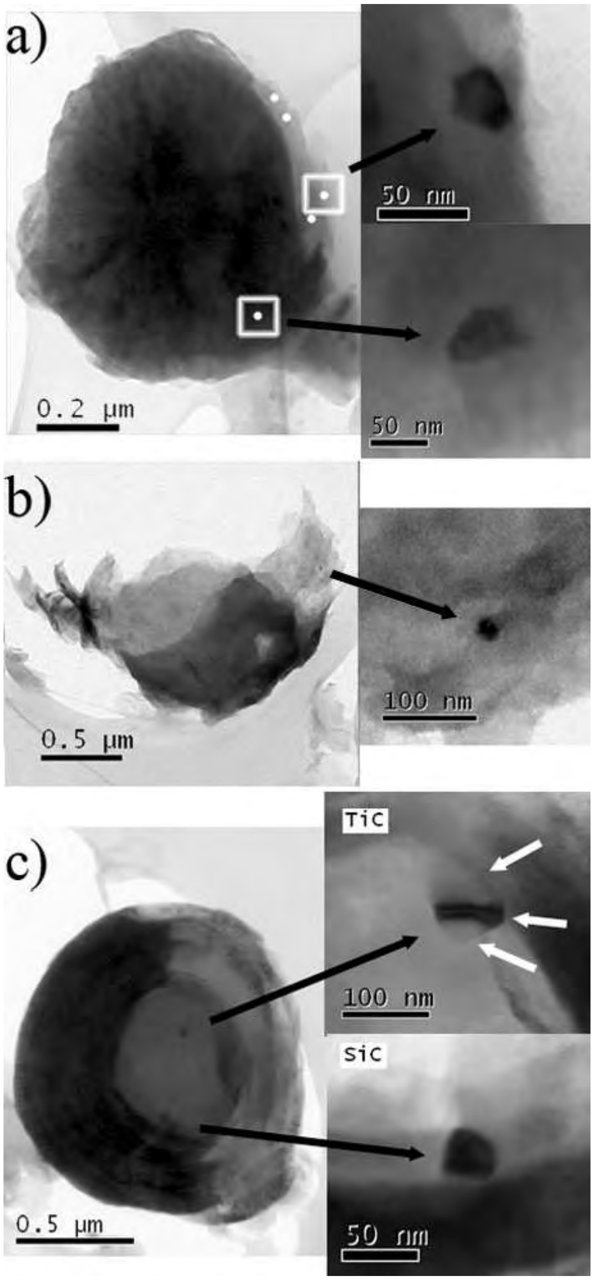

Figure 1. a) graphite #2 with SiC positions indicated (white dots) and inset of faceted SiCs; b) graphite #3 with small internal SiC; and c) graphite #4 showing twinned TiC and SiC (white arrows indicate separate twin domains).

between the presumably-twinned subdomains has not yet been determined. Multiply-twinned carbides have not been seen before within presolar graphites, but are generally taken as indicative of relatively rapid growth. EDXS shows all subdomains to be chemically similar, with a weighted-average composition of $(Ti_{88}V_{12})C$, similar in composition to that of most carbides found within KE3 supernova (SN) graphites [6], but distinct from those found within other KFC1 graphites (85% of which show s-process element enrichment [1]).

Elemental analysis using EDXS was done on all SiCs, typically showing only Si and C (along with slight O present in the background). The Si/C count ratios in these SiCs are > 0.1 (avg Si/C~0.25), so they show at least an order of magnitude more Si counts than are expected from the intrinsic Si peak of the detector. Trace amounts of Fe (<1 at.%) were occasionally present. For these SiC spectra, 2σ upper limits can be placed on Ti (<0.2 at.%), Zr (<0.3 at.%), and Mo (<0.3 at.%), so they are clearly not the isostructural refractory phases commonly found within presolar graphite. Al and Mg (which are commonly measurable in SiC-X grains [5]) are also not seen, with upper limits of 0.8 at.% and 1.0 at. %, respectively.

Discussion: Despite these new discoveries, SiC remains a rare constituent of graphites and is found only within 0.3% of KFC1 graphites (in 4 of ~1500 slices searched). Therefore the general conclusions from [2] hold, wherein ubiquitous refractory carbides condense before graphite at higher temperatures and are found within graphite, and SiCs generally condense after graphite at lower temperatures and are thus rarely found within graphite.

Graphites with the onion morphology from KFC1 residues are almost always presolar, and most that contain internal grains appear to have an AGB origin [1]. However, since we currently lack isotopic data, we can only speculate on their stellar source of the SiC-containing graphites based on chemical and morphological comparisons to previously-studied grains. SiC has not been found in the ~12 known KE3 graphites of supernova origin analyzed thus far [6]. Also, the SiCs did not show evidence of ^{26}Mg of radiogenic origin, as was seen in 3 of 4 SiC-X grains studied [5]. It is thus unlikely that these are SN grains, although we cannot definitively rule out this origin. NanoSIMS isotopic studies will aid in determining their likely stellar sources. In particular, graphite #2 may yield sufficient Si counts so as to clearly distinguish between supernova and AGB sources on the basis of the Si isotopic composition.

Acknowledgements: We thank R. Lewis (Univ. of Chicago) and S. Amari (Washington Univ.) for preparing the Murchison KFC1 samples.

References: [1] Croat, T.K. et al. (2005) *Ap.J.*, *631*, 976. [2] Bernatowicz, T.J. et al. (1996) *Ap.J.*, *472*, 760. [3] Amari, S. et al. (1994) *GCA*, *58*, 459. [4] Croat, T.K. and Stadermann, F.J. (2006) *LPS XXXVII*, Abstract #2048. [5] Hynes, K.M. et al. (2006) *LPS XXXVII*, Abstract #2202. [6] Croat, T.K. et al. (2003) *GCA*, *67*, 4705.