SILICON CARBIDE WITHIN PRESOLAR GRAPHITE.

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Introduction: Most presolar silicon carbides (SiCs) are believed to form in the circumstellar environment of asymptotic giant branch stars (AGB) stars, since the distribution of carbon isotopic ratios in mainstream SiCs matches well with the ratios derived from observations of AGB stars. Recent work on high-density Murchison KFC graphites [1] suggests many of these also have an AGB origin as significant s-process enrichments, which are only expected in AGB stars, are found in their internal carbides [2]. However, unlike the SiCs and AGB stars themselves, most of these graphites are ^{12}C-rich ($100 < ^{12}C/^{13}C < 400$), suggesting low metallicity sources. Composite grains (e.g. SiCs found within graphite or graphite found within SiC) are of particular interest, as they are a clear case in which both phases form in nearby environments. Two such composite grains have been previously reported, a graphite with an internal SiC [3] and a SiC with possible graphite sub-grains [4]. Extensive studies of KFC graphites [2, 3] have shown that SiCs within graphite are rare (found in ~1 of every 1000 graphite slices). Here we report results of transmission electron microscopy (TEM) and NanoSIMS investigations of a single onion-type graphite spherule that contained many internal SiCs.

Experimental: Graphites were obtained from the KFC1 density and size separate (2.15-2.20 g cm^{-3}, >1 μm) of the Murchison meteorite [1]. 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). The TEM grid was then mounted into a clamping holder and imaged in the NanoSIMS for ^{12}C, ^{13}C, ^{16}O, ^{18}O, ^{28}Si, and secondary electrons. EDXS quantitative analysis of Fe and Ni was done using ilmenite and nickel titanate standards.

Results: TEM investigations of this graphite spherule showed numerous internal Si-rich crystals (N=21) and two internal iron-nickel grains. Figure 1 shows this graphite's nanocrystalline core at an orientation where some of the internal grains are visible. Convergent beam electron diffraction (CBED) patterns were obtained from 8 of 21 SiC candidates. Five of these were conclusively shown to be 3C-SiC using <011> zones (cubic, a=4.3 Å, space group #216, F -4 3 m). Figure 2a shows an image and diffraction pattern both taken at an [011] orientation. To ensure correct polytype identification of 3C-SiC, five low-index crystallographic zones were inspected for one of the SiCs,

and intra-zone angles were consistent with those of 3C-SiC. Single diffraction patterns from two of the others were ambiguous, and could be indexed to either 3C-SiC or a hexagonal polytype (e.g. 2H-SiC). The remaining SiC (Fig. 2b) had streaks instead of discrete spots along one direction in the [011] diffraction pattern, resulting from a high density of stacking faults along the (111) growth direction (also visible in the TEM image). It has a sufficiently high density of stacking faults to be considered a 1D disordered grain [5], and as such cannot be attributed to a particular polytype. Stacking faults are commonly found along {111} growth directions in 3C–SiC, although the variability in defect density among SiCs within this graphite (Figs 2a and 2b) is surprising.

Energy dispersive x-ray spectra were obtained from all internal grains (21 SiCs and two FeNi grains). These data were used for grain identification in cases where the crystal structure was not determined, and help distinguish SiC from other refractory carbides (e.g. TiC, ZrC) with nearly identical crystal structures. SiC spectra showed Si and C, along with other elements sometimes seen in background spectra (O, Cu and occasionally trace amounts of Ca, Fe, and Cr). Quantitative analysis of the Si/C ratio was not attempted due to the strong C signal from the holey carbon grid and from the graphite. However, the average Si/C count ratio in the internal SiCs was 7x higher than values measured in the graphite background. In contrast, the Si/C count ratios measured in other refractory carbides (e.g. TiC or ZrC) are roughly identical to the value in graphite. Al and Ti (normally the most abundant trace elements in Murchison SiCs [6]) were not detected, with upper limits of 1.0 and 0.2 at. %,
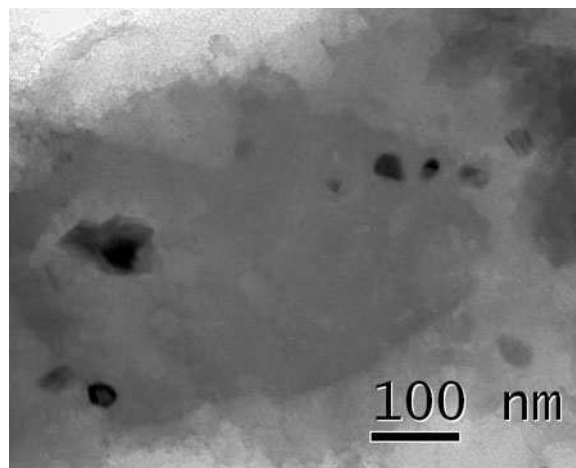

Figure 1. Bright-field (BF) TEM image of numerous internal SiCs (up to ~100nm in size) within a KFC onion graphite.
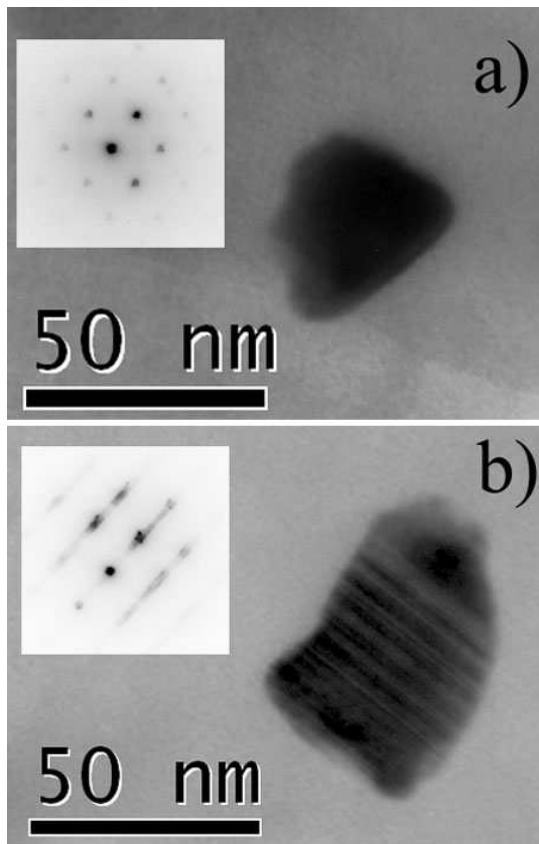
Figure 2. Bright-field images and CBED patterns of different SiCs within graphite: a) 3C-SiC grain and b) 1D disordered grain. In 2b, streaking in the CBED pattern is perpendicular to stacking faults seen along a (111) growth direction in the BF image.

respectively (using 2σ of background).

Two iron-nickel grains were also found within this graphite, with approximate diameters of 61 and 17 nm and compositions of $Fe_{92}Ni_8$ and $Fe_{77}Ni_{23}$. The two differ significantly in Ni content, with Ni/Fe ratios of 0.082 ± 0.008 [9.5%] and 0.30 ± 0.03 [10.9%]. Due to progressive damage to the support grid, crystal structure information was not obtained for these grains. However, the compositions are consistent with kamacites previously found within other graphites [2]. Such metallic iron grains (mostly kamacite with variable Ni content) are commonly found in KE3 graphites of supernova (SN) origin. Although rare, iron grains have also been found within certain KFC graphites (N=14, in ~1% of graphite population). Most of these are nearly pure iron, and a few have been identified as kamacites. A single iron carbide was also identified, but unlike these grains it had high chromium content.

NanoSIMS analysis. Isotopic analyses of ^{12}C, ^{13}C, ^{16}O, ^{18}O, and ^{28}Si were performed on the SiC-containing graphite. An anomalous C isotopic composition with $^{12}C/^{13}C = 110 \pm 2$ (solar ratio: 89) was observed, whereas the $^{18}O/^{16}O$ ratio was normal within

errors. Discrete Si-rich regions within the graphite were seen, which appear to be from the internal SiCs. Spatially correlated with the Si signal were higher O counts. We believe this is due to O secondary ion yield enhancement in the SiC phase or at the phase boundary, since the absolute O content of the SiC should be lower than that of graphite. Oxygen yield enhancements of this type have been previously seen from titanium carbides inside graphite [7]. The C isotopic ratio of the internal SiCs is indistinguishable from that of the entire graphite, but due to the small size of the SiCs and the overwhelming amount of C in the surrounding graphite, it is not clear whether this represents the true C isotopic composition of the SiC. The sample was not completely consumed during these measurements, leaving the possibility of later Si isotopic measurements. The data indicate that a cumulative total of 3000 ^{28}Si counts can be detected from a single internal SiC before it is consumed. Assuming similar counting rates, roughly a $\pm 10\%$ precision on Si isotopic ratios could be achieved, which should be sufficient to distinguish mainstream SiC from a SiC-X grain of SN origin.

Discussion: From considerations of thermochemical equilibrium condensation models, there are considerable difficulties with condensing either SiC or iron before graphite in AGB outflows [8]. Rather high pressures are required (>10 dyne/cm^2) for SiC formation prior to graphite in a gas of solar composition, which may explain the rarity of such composite grains. Pressures needed to form iron before graphite are even more extreme (>100 dyne/cm^2), and may indicate iron abundances greater than the solar ratios. Despite the lack of a measurable ^{18}O enrichment generally seen in SN graphites, this graphite is more likely of SN than AGB origin. The presence of iron-nickel grains also points toward a SN origin, as such grains are commonly found within other known SN graphites. Isotopic measurement of Si from within the SiCs may shed further light on the stellar source of this graphite. TEM observations done after the preliminary NanoSIMS measurements show that numerous SiCs remain for future SIMS studies.

References: [1] Amari, S. et al (1994) *GCA 58*,459. [2] Croat, T.K. et al. (2005) *ApJ 631*, 976. [3] Bernatowicz, T.J. et al. (1996) *ApJ. 472*,760. [4] Stroud, R.M et al. (2002) *Lunar Planet Sci.* **XXXIII**, abstract #1785. [5] Daulton, T.L. et al. (2003) *GCA 67*, 4743. [6] Amari, S. et al. (1995) *Meteoritics 30*, 679 [7] Stadermann, F.J. et al (2005) *GCA 69*,177. [8] Lodders, K. and Fegley, B. Jr. (1995) *Meteoritics 30*, 661.