Polytype Distribution in Presolar SiC: Microstructural Characterization by Transmission Electron Microscopy.

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Introduction: Presolar dust grains predate the formation of the solar system, originating in circumstellar outflows and supernova ejecta. Their isotopic compositions are characteristic of the different nucleosynthetic processes that occurred in their stellar sources at various stages of stellar evolution. The two most abundant forms of presolar grains, isolated from primitive meteorites, are nm-sized diamond [1] and µm- to subµm-sized SiC [2]. Both are ubiquitous in primitive chondritic meteorites at 300 - 1800 ppm (diamond) and 1 - 28 ppm (SiC) [3]. SiC is particularly interesting because, in the laboratory, it is known to form hundreds of different polytype structures and the formation of a particular polytype is sensitive to growth conditions.

The first astronomical evidence of SiC in dusty envelopes of carbon stars came from a relatively broad 11.3 µm infrared (IR) feature attributed to emission by SiC particles between the transverse and longitudinal optical phonon frequencies [4, 5]. Later attempts to identify the crystallographic structure of circumstellar SiC from IR spectra [6-8] have generated considerable controversy over the techniques and interpretation of the data [9-13]. The outstanding question of polytypes in presolar SiC has bearing on the physical conditions, such as temperatures and pressures, at which SiC condense from circumstellar outflows and supernova ejecta.

Discussion:

Unfortunately, there are few microstructural studies of presolar SiC. Analysis of individual 1.5 - 26 µm SiC grains from the Murchison L-series separate by Raman spectroscopy and ion probe mass spectroscopy have shown all grains exhibiting anomalous isotopic compositions were of the cubic β-SiC structure [14]. However, grains of this size are atypical, comprising less than 0.2% of the total population by number [15]. Therefore, we studied presolar SiC in the fine-grain size fraction, KJB, of the Murchison separate by transmission electron microscopy (TEM). Of the nine Murchison K-series size separates, KJB is reported to contain the highest SiC abundance (1.91 ppm of the bulk meteorite corresponding to over 1/3 the mass of SiC in Murchison) and highest purity (97% SiC) [15]. Furthermore, KJB is a representative sampling of the total SiC population since 70% of the Murchison SiC population lies within 0.3 - 0.7 µm, characteristic of 90% of the grains in KJB (Figure 1). Importantly, secondary ion mass spectrometry (SIMS) analysis of individual SiC grains in KJH, KJG, KJF [16], KJE [17, 18], KJC [19], and KJB [20] indicate > 99% are presolar grains. In all of these studies, no significant amounts of isotopically normal SiC were reported, indicating these separates contain few SiC grains that are solar nebula products or terrestrial contamination.

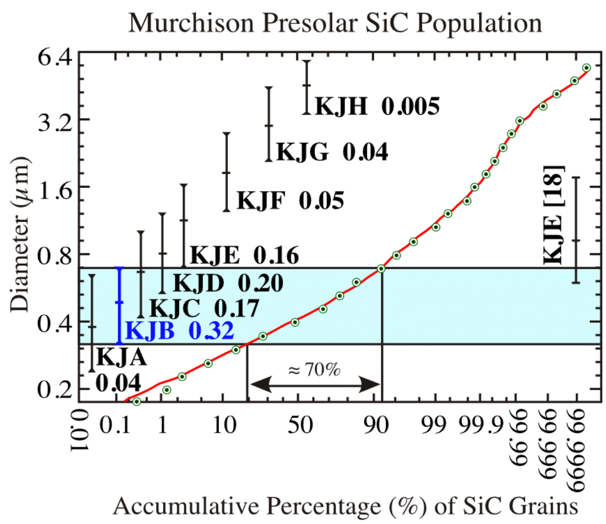

Figure 1. Murchison SiC size distribution measured by scanning electron microscopy (SEM). The dominant size range (omitting 5% tails in either end of distribution) is shown by vertical bars. Mean size is shown by the horizontal bar. The relative mass within each size fraction is also indicated.

High-resolution (HR)- TEM lattice images and selected area electron diffraction (SAED) demonstrate only two SiC polytypes are present in KJB; cubic 3C (β-SiC) and hexagonal 2H (α-SiC) (Figure 2). Intergrowths of these two polytypes are frequently observed. The 3C grains are often multiply twinned with double diffraction present in the SAED patterns, complicating polytype identification. Both 3C and 2H grains exhibit stacking faults but are generally well ordered. Less common than other grain types, heavily disordered SiC grains are also observed. The density of stacking faults in these grains is so high that their structure is one of randomly stacked tetrahedral closed packed planes.

There are inherent difficulties in determining relative abundances of grain types using SAED and HR-TEM images. Difficulties arise because of the finite tilt range of the TEM goniometer and from the fact only two dimensional crystallographic information is contained in any one combination of SAED pattern and HR-TEM image. The simplest method to identify

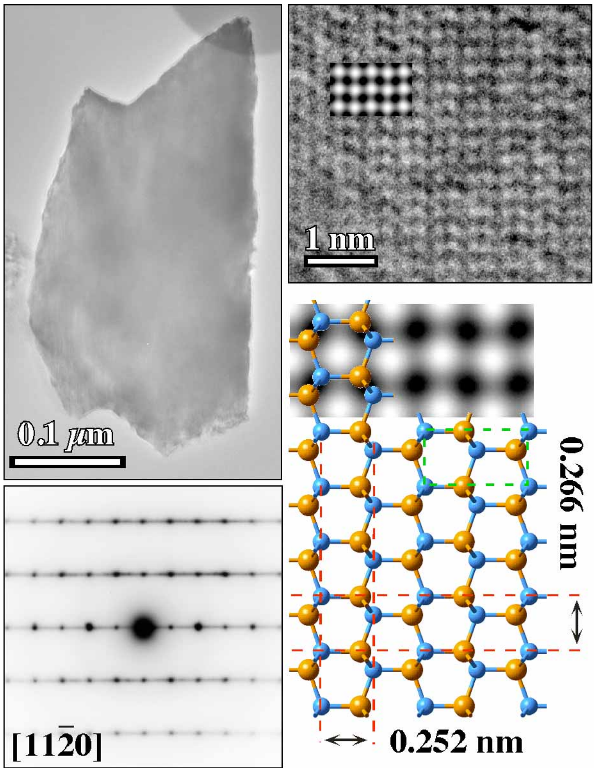

Figure 2. Bright-field image, HR-TEM lattice image, and SAED pattern for 2H α-SiC in Murchison KJB. An atomic model for the [11-20] zone axis is also shown superimposed on a simulated HR-TEM image using a defocus value matching the HR-TEM imaging condition. The green box is the 2H unit cell.

a polytype is to orient a grain along a high symmetry zone axis perpendicular to the tetrahedral stacking direction. Because of the finite goniometer tilt limits, a fraction of randomly oriented grains will have no suitable high symmetry zone axes accessible. This fraction varies with SiC polytype, skewing measured distributions. Nonetheless, the actual distribution (Table 1) can be estimated by applying appropriate normalization corrections. This was accomplished by calculating, ε_i, the intrinsic fraction of randomly oriented crystals having at least one suitable zone axis for identification (i.e., hexagonal <11-20> or cubic <111>) within the TEM goniometer tilt limits. In addition to crystal symmetry, ε_i is also dependent on twin- and polytype intergrowth- microstructure. The errors in Table 1 reflect only the uncertainties in determining the twin- and polytype intergrowth microstructure, since not all of the possible twin or intergrowth domains are visible along any one <011>/<11-20> direction. Sampling errors are ~ 1%.

The KJB separate contains a significant number of SiC grains containing 2H structure (16.09 ± 2.64 %) as both intergrowths and single crystals. Bulk and individual isotopic data [16-20], together with the abundance of these 2H grains, suggest their presolar origin. Furthermore, isotopic analysis of a TEM characterized 2H α-SiC from Murchison KJE by nm-scale SIMS (NanoSIMS) directly establish the grain as presolar (mean $^{12}C/^{13}C = 65$, $^{14}N/^{15}N = 575$). Hence, we unambiguously show presolar SiC occurs as the 2H α-SiC polytype in addition to the 3C form.

Table 1:
Murchison KJB SiC Polytype Distribution
(Based on TEM analysis of 107 Grains)

Grain Type	Population (%)
3C	82.42 ± 1.95
2H/3C	11.57 ± 2.64
2H	4.52 ± 0.08
Disordered	1.50 ± 0.03
All other polytypes	< 1

The occurrence of only the 3C and 2H polytypes (and their intergrowths) in presolar SiC can be understood in terms of thermochemical equilibrium calculations, which predict SiC condenses at $T \leq 1633$ K for any $C/O \geq 1.05$ at the relatively low pressures (< 100 dyne-cm^{-2}) believed to exist in grain forming, carbon star outflows [21]. Temperatures at which 2H (~ 1473 - 1723 K) and 3C (~ 1570 - 2000 K) are known to form and remain stable fall within this range. However, all higher order SiC polytypes are known to form only at T > 2100 K. This explains why only two (2H and 3C) out of a possible several hundred different polytypes are observed in presolar SiC.

References: **[1]** Lewis RS, Ming T, Wacker JF, Anders E, Steel E, 1987 *Nature* 326, 160. **[2]** Bernatowicz T, Fraundorf G, Tang M, Anders E, Wopenka B, Zinner E, Fraundorf P, 1987 *Nature* 330, 728. **[3]** Huss GR, Lewis RS, 1995 *GCA* 59, 115. **[4]** Treffers R, Cohen M, 1974 *Astrophys. J.* 188, 545. **[5]** Forrest WJ, Gillett FC, Stein WA, 1975 *Astrophys. J.* 195, 423. **[6]** Blanco A, Borghesi A, Fonti S, Orofino V, 1994 *Astr. Astrophys*. 283, 561; 1998 *Astr. Astrophys*. 330, 505. **[7]** Groenewegen MAT, 1995 *Astr. Astrophys.* 293, 463. **[8]** Speck AK, Barlow MJ, Skinner CJ, 1997 *MNRAS* 288, 431. **[9]** Papoular R, Cauchetier M, Begin S, LeCaer G, 1998 *Astr. Astrophys*. 329, 1035. **[10]** Speck AK, Hofmeister AM, Barlow MJ, 1999 *Astrophys. J.* 513, L87. **[11]** Andersen AC, Jäger C, Mutschke H, Braatz A, Clément D, Henning T, Jørgensen UG, Ott U, 1999 *Astr. Astrophys*. 343, 933. **[12]** Mutschke H, Andersen AC, Clément D, Henning T, Peiter G, 1999 *Astr. Astrophys.* 345, 187. **[13]** Henning T, Mutschke H, 2001 *Spectrochim. Acta* A 57, 815. **[14]** Virag A, Wopenka B, Amari S, Zinner E, Anders E, Lewis RS, 1992 *GCA* 56, 1715. **[15]** Amari S, Lewis RS, Anders E, 1994 *GCA* 58, 459. **[16]** Hoppe P, Amari S, Zinner E, Ireland T, Lewis RS, 1994 *Astrophys. J.* 430, 870. **[17]** Hoppe P, Strebel R, Eberhardt P, Amari S, Lewis R, 1993 *Meteorit.* 28, 363. **[18]** Hoppe P, Strebel R, Eberhardt P, Amari S, Lewis RS, 1996 *GCA* 60, 883. **[19]** Hoppe P, Kocher, T, Eberhardt P, Amari S, Lewis RS, 1998, *Met. Planet. Sci.* 33, A71. **[20]** Zinner E, Amari S, Messenger S, Nguyen N, Stadermann F, Walker R, Lewis R, 2001 *Met. Planet. Sci.*, 36, A231. **[21]** Lodders K, Fegley B, 1995 *Meteorit.*, 30, 661.