Polytype distribution of circumstellar silicon carbide: Microstructural characterization by
transmission electron microscopy

T. L. DAULTON,‡1,2, T. J. BERNAVOWICZ,3 R. S. LEWIS,4 S. MESSINGER,3 F. J. STADERMANN,3 and S. AMARI3
1Materials Science Division, Argonne National Laboratory, Argonne IL, 60439-4838, USA
2Marine Geosciences Division, Naval Research Laboratory, Stennis Space Center, MS 39529-5004, USA
3Laboratory for Space Sciences and Department of Physics, Washington University, St. Louis, MO 63130-4899, USA
4Enrico Fermi Institute, University of Chicago, Chicago, IL 60637-1433, USA

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Abstract—Silicon carbide (SiC) is a particularly interesting species of presolar grain because it is known to
form on the order of a hundred different polytypes in the laboratory, and the formation of a particular polytype
is sensitive to growth conditions. Astronomical evidence for the formation of SiC in expanding circumstellar
atmospheres of asymptotic giant branch (AGB) carbon stars is provided by infrared (IR) studies. However,
identification of the crystallographic structure of SiC from IR spectra is controversial. Since >95% of the
presolar SiC isolated from meteorites formed around carbon stars, a determination of the structure of presolar
SiC is, to first order, a direct determination of the structure of circumstellar SiC. We therefore determined the
polytype distribution of presolar SiC from the Murchison CM2 carbonaceous meteorite using analytical and
high-resolution transmission electron microscopy (TEM). High-resolution lattice images and electron diffraction
of 508 individual SiC grains demonstrate that only two polytypes are present, the cubic 3C (β-SiC) polytype (79.4% of population by number) and the hexagonal 2H (α-SiC) polytype (2.7%). Intergrowths of these two polytypes are relatively abundant (17.1%). No other polytypes were found. A small population of one-dimensionally disordered SiC grains (0.9%), whose high density of stacking faults precluded classification as any polytype, was also observed. The presolar origin of 2H α-SiC is unambiguously established by tens-of-nanometers-resolution secondary ion mass spectroscopy (NanoSIMS). Isotopic maps of a TEM-characterized 2H α-SiC grain exhibit non-solar isotopic compositions of $^{12}$C/$^{13}$C = 64 ± 4 and $^{14}$N/$^{15}$N = 575 ± 24. These measurements are consistent with mainstream presolar SiC thought to originate in the expanding atmospheres of AGB carbon stars. Equilibrium condensation calculations together with inferred mineral condensation sequences predict relatively low SiC condensation temperatures in carbon stars. The laboratory observed condensation temperatures of 2H and 3C SiC are generally the lowest of all SiC polytypes and fall within the predictions of the equilibrium calculations. These points account for the occurrence of only 2H and 3C polytypes of SiC in circumstellar outflows. The 2H and 3C SiC polytypes presumably condense at different radii (i.e., temperatures) in the expanding stellar atmospheres of AGB carbon stars. Copyright © 2003 Elsevier Ltd

1. INTRODUCTION

Presolar dust grains predate the formation of the solar system, originating in circumstellar outflows and supernovae ejecta. Their widely ranging isotopic compositions reflect nucleosynthetic processes that occurred in the different star types at various stages of stellar evolution. Such dust grains mix into the interstellar medium (ISM) from which subsequent generations of star systems form. As our own protosolar nebula evolved, most of its presolar material was extensively mixed and reprocessed, leading to pervasive isotopic homogeneity that obscured the detailed information concerning the histories and origins of this presolar material. However, some refractory presolar grains survived accretion into primitive bodies and experienced only minimal alteration. Among these grains, those that have isotopic compositions distinct from the average compositions of the solar system in a manner that cannot be produced by mass fractionation, cosmic-ray-induced spallation reactions, or by radioactive decay in situ subsequent to the formation of the solar system can be identified as presolar.

The two most abundant forms of presolar grains isolated from primitive meteorites, diamond (Lewis et al., 1987) and SiC (Bernatowicz et al., 1987; Tang† and Anders, 1988), were discovered by tracking the carriers of anomalous noble gas components in density and size separated acid dissolution residues. Presolar SiC is characterized by isotopic anomalies in Si and C (Zinner et al., 1987, 1989; Tang† et al., 1989), as well as in minor and trace elements: N (Zinner et al., 1987, 1989), Ne, Xe (Tang† and Anders, 1988; Zinner et al., 1989; Lewis et al., 1994), Ar, Kr (Lewis et al., 1994), 26Al (Zinner et al., 1991a), Ca (Amari et al., 2000), Ti (Ireland et al., 1991; Amari et al., 2000), Sr (Podosek et al., 2002), Zr (Nicolussi et al., 1997), Mo (Nicolussi et al., 1998), Ba (Ott and Begemann, 1990; Zinner et al., 1991b; Prombo et al., 1993), Nd, Sm (Zinner et al., 1991b), and Dy (Hoppe and Ott, 1997). The highly anomalous noble gas components, Ne-E(H) and Xe-s, led to the discovery of presolar SiC. Xe-s isotopes show an enrichment of even-numbered isotopes ($^{129}$Xe, $^{130}$Xe, and $^{132}$Xe) and depletion of odd ($^{127}$Xe, $^{131}$Xe), reflecting differences in neutron capture cross sections. They are thought to be produced by β-process (slow neutron capture) nucleosynthesis

* Author to whom correspondence should be addressed (tdaulton@nrlscc.navy.mil).
‡ Present address: Marine Geosciences Division, Naval Research Laboratory, Stennis Space Center, MS 39529-5004, USA.

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isotopically anomalous SiC grains have the tendency, albeit incomplete, meteoritic evidence suggesting that all SiC grains exhibiting anomalous isotopic compositions were of the cubic SiC structure. However, grains of this size are atypical, comprising less than 0.2% in number and 5% in mass of the total population (Amari et al., 1994). Therefore, there are numerous reports of grain size dependence of isotopic compositions for Murchison SiC, e.g., 

\[ ^{14}N/^{15}N \] (Hoppe et al., 1996a), 
\[ ^{26}Ne/^{22}Ne, ^{3}He/^{22}Ne \] (Lewis et al., 1990), 
\[ ^{86}Kr/^{82}Kr, ^{88}Kr/^{82}Kr \] (Lewis et al., 1994), 
\[ ^{50}Ti/^{46}Ti, ^{50}Ti/^{49}Ti \] (Amari et al., 1996), 
\[ ^{88}Sr/^{86}Sr \] (Podosek et al., 2002), and 
\[ ^{138}Ba/^{136}Ba \] (Prombo et al., 1993), further emphasizing that the structural characterization by Virag et al. (1992) of the atypical large diameter L-series fraction grains may not be representative of the total presolar SiC population.

Transmission electron microscopy (TEM) is used here to unambiguously determine the distribution of polytypes in presolar SiC grains isolated by acid dissolution from the Murchison CM2 carbonaceous meteorite. In particular, the fine-grained KJB size fraction was examined, because of all KJ series separates it most closely represents the Murchison SiC population. Inasmuch as the population of presolar SiC in primitive meteorites can be regarded as a representative sample of the SiC produced in stellar outflows, the results obtained provide definitive data on the polytype distribution from these outflows to which astronomical measurements and condensation models can be compared. Daulton et al. (2002) presented preliminary results of this work based on analysis of almost half as many presolar SiC grains as described here, but without detailed treatment. Here we present complete results for 508 grains, including a thorough discussion of our experimental techniques and analysis of the SiC crystal structures, as well as a review of previous work on SiC polytype synthesis and the thermodynamics of SiC condensation. In light of these considerations, we then propose a simple hypothesis for circumstellar SiC formation that places the formation of the grains in their proper astrophysical context.
2. EXPERIMENTAL

2.1. Samples and Instrumentation

2.1.1. Sample preparation

Presolar SiC was isolated from fusion-crust-free fragments of the Murchison (CM2) carbonaceous chondrite by acid dissolution. At one stage of the dissolution process, nanodiamonds were extracted from the residue as a colloid. The resultant greenish-white SiC residue, KJ, was suspended in a 4:1 mixture of isopropanol with H$_2$O (acidified with HCl), and separated into nine size fractions by centrifugation: KJA (0.24–0.65 μm, mean 0.38μm), KJB (0.32–0.70 μm, mean 0.49μm), KJC (0.42–1.02 μm, mean 0.67μm), KJD (0.54–1.23 μm, mean 0.81 μm), KJE (0.70–1.65 μm, mean 1.14 μm), KJE’ (1.25–2.79 μm, mean 1.86 μm), KJG (2.11–4.46 μm, mean 3.02 μm), KJI (3.38–5.87 μm, mean 4.57 μm), and KJJ (>5 μm). The size ranges quoted are based on scanning electron microscopy (SEM) analysis of grain diameters which omit the 5% tails in either end of the size distributions, while the mean is mass-weighted. The KJB-KJE fractions dominate the mass distribution of the KJ residue. Complete details of the acid dissolution and density separation procedures can be found in Amari et al. (1994).

The KJB separate was chosen for measurement of the distribution of presolar SiC polytypes. Of the nine Murchison size separates, KJB is reported to contain the highest SiC abundance (1.91 ppm of the bulk Murchison SiC) and highest purity (97% SiC) (Amari et al., 1994). Furthermore, KJB is a representative meteorite corresponding to over 1/3 the mass of SiC) and highest purity reported to contain the highest SiC abundance (1.91 ppm of the bulk Murchison SiC). The size ranges quoted are based on scanning electron microscopy (SEM) analysis of grain diameters which omit the 5% tails in either end of the size distributions, while the mean is mass-weighted. The KJB-KJE fractions dominate the mass distribution of the KJ residue. Complete details of the acid dissolution and density separation procedures can be found in Amari et al. (1994).

2.1.2. Transmission electron microscopy

A JEOL JEM-3010 analytical transmission electron microscope, operating at 300 KeV with a LaB$_6$ filament, an EM-30022 HT pole piece, and a measured point-to-point resolution of 2.1 Å was used for structural microcharacterization. This instrument is equipped with a side-entry motorized 5 axes goniometer, a Noran energy dispersive X-ray spectroscopy (EDXS) system, a Gatan 764 multiscan camera (MSC), and a Gatan imaging filter (GIF200) capable of electron energy loss spectroscopy (EELS). A double-tilt specimen holder allowed tilts of ±45° by ±30° along orthogonal axes. All high-resolution (HR)-TEM images were recorded near Scherzer defocus using no objective aperture and the electron optical magnifications were typically 600K–1000K. Lattice image simulations were performed by multislice calculations using the HR-TEM package of the Cerius II lattice modeling software running on a Silicon Graphics Indigo II workstation, and crystallographic analysis was performed using an advanced version of the software package Sphere (Daulton, 1992).

2.1.3. Nanometer-scale secondary ion mass spectrometry

A Cameca NanoSIMS, operating at 16 kV with a Cs$^+$ ion beam (~1 pA) focused to a probe diameter of 100 nm was used for isotopic compositional imaging. The NanoSIMS has a coaxial, normal-incident probe (primary) and extraction (secondary) ion-optical system
and was designed for multicollected mass spectra. The measured spatial resolution of this NanoSIMS is 30 nm for the Cs+ probe (200 nA for O+). Five mass-separated secondary ion signals (13C, 12C, 15N, 12C15N, and 30Si) were acquired in parallel using movable electron multipliers located in a large magnetic sector mass analyzer. High mass resolution was used to completely separate possible interfer-
ences. Images were recorded at 256 × 256 pixel resolution with acquisition times of several hours (~ 200 ms/pixel). An optical micro-
scope and secondary electron images were used to position the spec-
imen.

2.2. SiC Polytype Structures

Silicon carbide exhibits an extensive range of well ordered structures. Baumhauer (1912) discovered the first three SiC structures, referring to them as “types,” and subsequently coined the term polytype (Baumhauer, 1915). Polytypes of SiC arise from different periodic stacking sequences of bilayers. There are six different bilayers each consisting of two close packed planes (Fig. 2). Bilayers stack to form vertex-sharing tetrahedral cages of SiC (or SiC4) with a C (or Si) atom at the center of each cage. The stacking sequence does not significantly alter bond lengths or affect bulk density (3.2 g·cm−3) (see Tairov and Tsvetkov, 1982). With a Si-C bond distance δ = 1.89 Å, bilayers are spaced 4/3 δ ≈ 2.52 Å apart. If the number of bilayers in the unit cell is even, the symmetry must be hexagonal, otherwise it is cubic or rhombohedral. Rather arbitrarily, the rhombohedral and hexagonal classes of SiC polytypes are collectively called α-SiC and the cubic class (consisting of one member) is called β-SiC (Thibault, 1944).

A number of notation schemes are used to describe SiC polytypes. In the Ramsdell (1947) notation, a polytype is denoted by the number of bilayers in the unit cell followed by C, H, or R, denoting the crystal symmetry (i.e., cubic, hexagonal, or rhombohedral). The fundamental bilayers are denoted a, b, a, b, c, b, a, c, and b, c, a. In the earlier Zhdanov (1969) notation, sheet tetrahedra are assigned a positive or negative sense defined by a relative rotation of π radians about the stacking direction (Fig. 2). The successive number of tetrahedral layers, having tetrahedra with a common positive or negative sense, is counted in each subspecies present. For example, the polytype denoted 6H (i.e., [..AaBbCcAaCcBb..]) in the subseries notation (Fig. 2) has two subspecies each consisting of three tetrahedral layers of the same sense, {. . . + + + − − − . . .}, and in the Zhdanov notation is denoted (33). The polytype denoted 3C (i.e., {. . .AaBbCc..}) in the Ramsdell notation has an infinite number of tetrahedral layers of the same sense in one subspecies, {−−− . . .}, and is denoted (≈) (Fig. 2). Often SiC polytypes have stacking sequences such as 15R (i.e., {. . .AaBbCcBbAaCcAaBbCcAaCcBbAaCcBb..}) that repeat [..+−+−+−−−+−−−+−−−+−−−..] (denoted (232323), and abbreviated (23)), Subscripts denoting repeat sequences are nested as in the long periodicity polytype [[33,6),(33),4], denoted 174R in the Zhdanov notation. The Zhdanov notation is useful in describing high-resolution lattice images of SiC under defocus conditions that correctly reproduce the projected lattice (Fig. 2). In comparison, the Ramsdell notation is not unique since subscripts are used to distinguish different polytypes with the same notation such as 51R and 51R, which are uniquely specified in the Zhdanov notation as [(33),32], and [(22),23]. Other polytype notation schemes (Wells, 1950; Jagodziński, 1954; Wyckoff, 1963) will not be discussed here. On the order of a hundred different SiC polytypes have been reported in the literature (see Verma and Krishna, 1966; Shaffer, 1969), the two most relevant to this work are discussed in detail below.

2.2.1. Hexagonal 2H(11) α-SiC polytype

The smallest unit cell (lowest order) SiC polytype is hexagonal (space group P6mc, unit cell lengths a = 3.08 Å, c = 5.03 Å). This structure is formed by the stacking sequence {. . .AaBb..}, and is denoted 2H in the Ramsdell notation and (11) in the Zhdanov notation. Hexagonal 2H α-SiC is isostrophic to hexagonal 2H diamond (lonsdaleite). It is the only polytype with a 1 in its Zhdanov symbol; in other words, no other polytype contains subsequences of 2H order. Tetrahedral planes in 2H α-SiC are parallel in unit cell thickness, but in other polytypes this is not the case. The first high-resolution lattice images and corresponding structure models were obtained in parallel using experimental and theoretical HR-TEM lattice image simulations (e.g., see Cowley and Moodie, 1957) of 2H SiC along <1120> show that a range of image contrast, often differing from the lattice symmetry, is produced depending on defocus (Fig. 3). Under defocus conditions that reflect only the arrangement of the geometric centers of the unresolved Si-C atom pairs, a rectangular array of bright and dark dot contrast is produced. Under defocus conditions that reflect the arrangement of the open channels in the 2H <1120> projected structure, a zigzag bright and dark dot contrast pattern is produced. The zigzag pattern differs in line width and rotation. The orientation of the rhombic arrays alternate along the [001] direction, reflecting the Zhdanov symbol for the structure, (11).

2.2.2. Cubic 3C(11) β-SiC polytype

The second smallest unit cell SiC polytype is cubic (space group F-33m, unit cell length a = 4.36 Å). This structure is formed by the stacking sequence {...AaBbCc...} of three bilayers, and is denoted 3C in the Ramsdell notation and (∞) in the Zhdanov notation. Cubic 3C β-SiC is isostrophic to cubic 3C diamond and consists of two inter-
penetrating face-centered cubic (fcc) sublattices, one lattice entirely Si and one entirely C, which are separated by the displacement vector a/4 [111]. Tetrahedra lie in [111] planes and the 3C stacking sequence of tetrahedral planes is best viewed in HR-TEM images along the <011> zone axes.

Unlike 2H SiC and other α-SiC polytypes, HR-TEM lattice images of 3C SiC along <011> exhibit a simple and direct relationship between atomic structure and image contrast. Multi-slice image simulations predict that either the columns of unresolved (400)-spaced C-Si atom pairs or the open channels in the structure are imaged as bright ovals/dots depending on the defocus (Fig. 4). Since the geometric arrangement of these is similar, the predominant change observed in <011> oriented 3C SiC upon varying defocus near the Scherzer condition is a contrast reversal. The 3C polytype does not produce a lattice image under any defocus condition or orientation that is similar to those produced by 2H SiC along <1120> (see Figs. 3 and 4).

2.2.3. Higher order α-SiC polytypes (unit cells larger than 3C)

Lattice images of α-SiC along zone axes perpendicular to the tetra-
heiral stacking direction and analogous to 3C <011> will display a characteristic zigzag contrast pattern reflecting their Zhdanov symbol, under defocus conditions where the symmetry of the open channels in the structure is reproduced. Under such imaging conditions, SiC polytypes are easy to identify from HR-TEM images (Fig. 2). Furthermore, the different polytypes can be readily identified by their electron diffraction patterns (Fig. 2).

2.2.4. Relative abundance of terrestrial SiC polytypes

Natural SiC (moissanite) is a rare terrestrial mineral. It was synthe-
sized before being discovered in nature (Acheson, 1893). The first natural specimens were found in acid residues of the Canyon Diablo meteorite (Moissan, 1905), and these were questioned to be contami-
nants from synthesized SiC abrasives (Mason, 1967). Numerous early works, particularly in the Russian literature, report the terrestrial oc-
currence of natural SiC in kimberlites, granitoids as well as in igneous, metamorphic, and sedimentary rocks (for a review see Kaminskiy et al., 1990; Lyakhovich 1980). However, their significance is dif-
cult to evaluate because the question of contamination (see Milton and Vi-
taliano, 1985) was often not rigorously addressed. Recent studies, however, confirmed the natural occurrence of SiC in mineral concentrates of diamond-bearing kimberlites and lamproites from Fuxian, China (Leung et al., 1990a, 1990b) and Yakutia, Russia (Mathe et al., 1995) as well as in diamond as inclusions (Moore et al., 1986; Moore and Gunney, 1989; Otter and Gunney, 1989; Jaques et al., 1989; Leung 1990).

By far, the most abundant naturally occurring terrestrial SiC reported in the literature is 6H(33) α-SiC which is followed in abundance by large projected charge density and is highly dependent on instrumental parameters such as defocus, as well as specimen thickness and orien-
tion. In general, the relationship between the image contrast and the atomic structure is not straightforward. Multi-slice HR-TEM lattice image simulations (e.g., see Cowley and Moodie, 1957) of 2H SiC along <1120> show that a range of image contrast, often differing from the lattice symmetry, is produced depending on defocus (Fig. 3). Under defocus conditions that reflect only the arrangement of the geometric centers of the unresolved Si-C atom pairs, a rectangular array of bright and dark dot contrast is produced. Under defocus conditions that reflect the arrangement of the open channels in the 2H <1120> projected structure, a zigzag bright and dark dot contrast pattern is produced. The zigzag pattern differs in line width and rotation. The orientation of the rhombic arrays alternate along the [001] direction, reflecting the Zhdanov symbol for the structure, (11).
Fig. 2. Silicon carbide polytype structures. Polytypes of SiC are formed by those periodic stacking sequences of bilayers that produce tetrahedral sheets. Atomic models of the six unique (fundamental) bilayers (bA, cA, aB, cB, aC, and bC) of SiC (top left) based on three principle close packed planes (A, B, and C) (lower left) are shown. Blue atoms represent C and orange atoms represent Si. The two basic stacking arrangements, A-B and A-C, that form planes of vertex-sharing parallel and antiparallel tetrahedra, respectively, are shown (lower left). Atomic models of the four simplest, 3C/∞, 2H/11, 4H/22, and 6H/33, polytypes are shown superimposed on calculated HR-TEM lattice images produced using defocus conditions that reproduce the symmetry of the projected lattice (center column). Schematic illustrations of diffraction patterns (including forbidden reflections in some cases) are also shown (right column).
15R/(23), (often intergrown with 6H) which is followed in abundance by 33R/(3332). Cubic 3C has only been observed as a trace component in the form of inclusions within (Marshintsev et al., 1982) as well as overgrowths on 6H SiC found in 15R SiC while Leung et al. (1990a, 1990b) and Leung (1990) reported epitaxial overgrowths of 3C SiC on 6H SiC clusters. The only other report of 3C-SiC (in the salt zone of the Wyoming Green River Formation) is an abstract lacking details (Regis and Sand, 1958). Natural 3C SiC is terrestrially extremely rare and natural 2H SiC has never been reported forming terrestrially.

Large-scale commercial SiC (Carborundum) is produced by heating carbon and silica together with sawdust and salt (to assist in escape of evolved CO gases and convert impurities into volatile chlorides, respectively) in an electric furnace up to 3000 K (method of Acheson, 1893). The most abundant SiC polytype produced by the Acheson process is 6H followed by 15R and 4H/(22) (Verma and Krishna, 1966). Both 3C and 2H SiC are generally not recovered in significant amounts from this process since both are reported to transform irreversibly at high temperature to the 6H polytype via 2H -> 3C -> 6H (Krishna et al., 1971; Krishna and Marshall, 1971a; Bootsma et al., 1971) and 2H -> 6H (Krishna and Marshall, 1971b).

Many processes have been developed to synthesize SiC with higher elemental and polytype purity: crystallization from solution, C implantation into Si substrates, and forms of vapor condensation known in the literature as sublimation (Lely method; Lely, 1955), seeded sublimation (modified Lely method; Taivov and Tsvetkov, 1978), gaseous cracking, chemical vapor deposition (CVD), as well as molecular beam epitaxy (MBE). All together, these processes synthesize on the order of a hundred different SiC polytypes that, however, are not exploited commercially at a significant scale yet. Therefore, only 6H, 15R, and 4H SiC have significant potential as terrestrial contaminants in meteorite specimens, and the following section shows their abundance is constrained to be <0.2% by number in Marchion KJB.

3. RESULTS

3.1. Microstructural Characterization of Presolar SiC

The distribution of SiC polytypes present in the circumstellar outflows was determined from TEM measurements of over 508 randomly selected grains in the Murchison KJB separate. Sample deposition on a-C TEM support films deposits the grains in random orientations, often in clusters. Only isolated, individual SiC grains were examined. The diameters of the analyzed grains (defined as the square root of their projected area) ranged from 0.18 to 0.39 µm (omitting the 5% tails in either end of the size distribution) with a mean of 0.27 µm. It should be noted that the TEM and SEM (Amari et al., 1994) size measurements cannot be directly compared because of a number of factors such as resolution, differences in sample deposition, and attrition losses of the original separate over the years.

The structure of a crystal, or in this case polytype, can be determined by analysis of selected area electron diffraction (SAED) patterns, convergent beam electron diffraction...
(CBED) patterns, and HR-TEM lattice images from a set of crystallographic directions. Together with a crystallographic analysis of the relative orientations of the different high symmetry zone axes, the structure of a crystal can be well determined. However, such analyses are time prohibitive for the large number of grains examined in this study. Therefore, identification of polytype was performed by the most straightforward methods, namely from SAED patterns and HR-TEM lattice images recorded along a low-index zone axis perpendicular to the tetrahedral stacking direction of a grain.

Kikuchi bands, imaged by CBED, were used to guide tilting of the grains to suitable zone axes. The average crystal structure was determined by SAED from the entire grain while local structure within a grain was determined by SAED from small regions of the grain. High-resolution lattice images recorded from thin areas were used to further characterize the grain microstructure. The position of each grain examined and the tilt angles used were recorded to insure that no grain was analyzed twice.

Lattice images and SAED patterns demonstrate that only two SiC polytypes are present in KJB: cubic 3C β-SiC and hexagonal 2H α-SiC. Grains exhibiting epitaxial intergrowth of these two polytypes were also present. A small number of one-dimensionally disordered SiC grains that could not be classified as any polytype were also observed. No other SiC polytypes were observed out of the over 508 individual grains examined.

3.1.1. Microstructure of presolar 3C β-SiC

All 3C β-SiC grains showed varying concentrations of stacking faults along the <111> directions. A fraction of the 3C SiC grains possessed “rotational” disorder about the <011> axis evident in their diffraction patterns by the presence of slightly arced [111] Bragg reflections and diffuse Kikuchi bands. The origin of this disorder is discussed later. Single crystals of 3C SiC were the most commonly observed grains. However, many 3C SiC grains were multiply twinned (Fig. 5) with double diffraction present in the SAED patterns, complicating polytype identification.

One of the lowest energy interfaces in SiC corresponds to twinning across close-packed tetrahedral planes. This twin structure results when the stacking sequence is abruptly reversed, e.g., \{AaBbCcBbAa\}, by the introduction of a stacking fault. In coincident site lattice (CSL) notation, this twin struc-
tions arise from twinning across (111) or (111) planes produce extra Bragg reflections along a zone axis. For example, in [011] SAED patterns, \( \Sigma = 3 \) twinning across (111) and (111) edge-on planes produce extra Bragg reflections, whereas no extra reflections arise from twinning across (111) or (111) inclined planes (see Fig. 6). Each inclined-twin domain will have a <114> zone coincident with the [011] zone axis of the twin-related primary domain; [\( \overline{4}11 \)] for (111) inclined domains and [\( 4\overline{1}1 \)] for (111) inclined domains. Since <011> zones contain all the diffracted beams present in <114> zones, no extra reflections are created by the inclined-twin domains. Furthermore, no lattice fringes are visible from inclined \( \Sigma = 3 \) twin domains because the projected lattice plane spacings along <114> are 1.31 Å-spaced [\( \overline{1}13 \)] and 1.54 Å-spaced [022] that are beyond the resolution of the TEM instrument used in this study. Nonetheless, the presence of inclined twin domains can be inferred by comparing dark field images formed by <114> zone axis reflections, such as [\( \overline{1}13 \)], to dark field images using a reflection unique to <011> zones, such as [111]. However, considering the large number of grains analyzed, such an analysis would be time-prohibitive. Therefore, \( \Sigma = 3 \) twin domains associated with inclined {111} planes were not detected in this work. This point has relevance for the determination of the polytype distribution as discussed in Section 3.2.

It is common to observe <011> SAED patterns from 3C \( \beta \)-SiC grains that exhibit extra reflections at positions 1/3{111} along one or both edge-on {111} plane normals. These reflections do not reflect a modification of the 3C unit cell as shown by Bender et al. (1986) for fcc Si; rather they arise from plural scattering produced by the presence of \( \Sigma = 3 \) twin domains (Fig. 6).
6). A diffracted electron beam emerging from one twin domain can act as the principal beam for a second twin domain that diffracts the beam again. The 1/3{111} reflections occur along one direction if the twinning is predominantly across one set of edge-on planes and along both directions if major twinning is across both sets of edge-on planes (Fig. 6). The strength of the 1/3{111} reflections depends on the electron path length through the twin domains as well as the arrangement of the...
domains. The 1/3{111} reflections are accompanied by an intensity modulation of every third {111} lattice fringe along the associated direction in corresponding HR-TEM lattice images (Bender et al., 1986).

Complex twin microstructures are present in presolar 3C β-SiC (Fig. 7). An example of multiple Σ=3 twinning in a SiC grain is shown in Figure 7a. The diffraction pattern from the whole grain contains two sets of double diffraction spots that reveal this grain has two large domains, each with its own Σ=3 twin structure, and sharing a common Σ=3 boundary. This is confirmed by SAED of each separate domain. Examples of mixed Σ-twin microstructures in SiC grains are shown in Figure 7b and Figure 7c, where SAED reveals that the grains have two domains containing Σ=3 twin microstructure that are...
related by a high order $\Sigma = 9$ ($38.94^\circ$) twin boundary. This is also confirmed by SAED of each domain. Additional high order twin boundaries observed in presolar SiC grains are $\Sigma = 19$ ($\theta = 26.53^\circ$), $\Sigma = 73$ ($\theta = 13.44^\circ$), and $\Sigma = 649$ ($\theta = 4.50^\circ$) (Fig. 8).

Grain boundaries having $\Sigma = 9$, 19, and 33 ($\theta = 20.05^\circ$) are usually observed in epitaxial CVD films where separate $<011>$ oriented fcc grains growing on the substrate impinge (e.g., see Narayan et al., 1990; Doriganc et al., 1997). High
energies and their formation is much less energetically favor-
order grain boundaries (see Table 1) have large interfacial
boundaries with interface angles
one zone axis, i.e., 3C
studied (although detailed examination was restricted to only
fraction of 3C-SiC single crystals present. The fractions of all
[011] zone axis, therefore this is only an upper limit for the
approximately 10.7% of these single crystals exhibited
(0.91%), [62.439 {3}].
51b 16.099 [1 5] [10 1]
51a 16.599 [1 5] [10 1]
41 55.877 [3 4] [8 3]
43 80.631 [6 5] [5 3]
33a 20.505 [1 4] [8 1]
33b 58.992 [4 5] [5 2]
45 45.980 [3 2] [3 2]
25 26.525 [1 3] [6 1]
27 31.586 [2 5] [5 1]
19 26.525 [1 3] [6 1]
17 86.268 [4 3] [3 2]
11 50.479 [2 3] [3 1]
9 38.942 [1 2] [4 1]
3 70.529 [1 1] [2 1]

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<th>Second Diffraction Twin Planes</th>
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<td>{3 7 7}</td>
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3.1.2. Microstructure of presolar 2H/3C intergrowth SiC

Figure 9 shows an example of a Murchison KJB SiC grain
whose electron diffraction pattern has a set of extra reflections
that are inconsistent with 3C SiC twin reflections or double
diffraction. The extra reflections are most evident along the
horizontal row of Bragg reflections that intersect the primary
beam, (000). If the reflections arose from 3C Σ=3 double
diffraction, there should be two equally spaced 1/3[111]
reflections between (000) and the primary (111) peak, as op-
posed to the one diffraction spot actually present. This set of
extra Bragg peaks is consistent with reflections along the
<1120> zone of a domain of 2H α-SiC. In fact, diffraction
patterns from separate 2H and 3C SiC domains could be
isolated using the smallest SAED aperture (Fig. 9), further
demonstrating this grain is an intergrowth of two SiC pol-
types. The streaking in the 2H diffraction pattern indicates the
presence of stacking faults along the [0001] direction. As
expected, the bright-field (BF) images of the intergrowth grain
show stacking faults in the 2H domain along the [0001] tetra-
hedral stacking direction. However, HR-TEM shows that long-
range 2H order is also present (Fig. 9). The diffraction pattern
of the 3C domain contains diffuse streaking of lesser intensity
along several (111) directions, indicating a lower density of
stacking faults, consistent with the BF image. Two thirds of this
intergrowth grain is in the form of 2H SiC.

The proportion of 2H to 3C order in different SiC inter-
growth grains varied from predominantly 2H to predominantly
3C. The 3C domains of the intergrowth grains displayed a
range of Σ=3 twin microstructures and stacking fault densities.
Stacking faults are observed in 2H domains, but no twinning is
observed. Although each 3C domain in an intergrowth grain
has four sets of cubic <111> directions that can serve as an
homoepitaxial growth interface to a 2H domain, in almost all
intergrowth grains there was a single dominant 2H-domain
orientation. In those cases, either a single 2H domain or par-
allel, alternating 2H and 3C lamellae were observed. In compar-
ison, only one intergrowth grain was observed to have two
different prevailing 2H-domain orientations.

It is important to note that only those 2H domains associated
with edge-on 3C {111} planes will produce phase contrast
lattice fringes and clearly recognizable SAED reflections. The
2H domains associated with inclined 3C {111} planes will not
have any hexagonal high symmetry zone axis in coincidence
with the imaged 3C {111} axis; the closest hexagonal low index
zone, <1011>, is separated by ~11.5° from the imaged 3C
{111}. Consequently, inclined 2H domains are hard to detect
because they do not produce phase contrast lattice fringes and
produce only weak diffraction patterns. This point has rele-
vance for the determination of polytype distributions as dis-
cussed in Section 3.2.

3.1.3. Microstructure of presolar 2H α-SiC

An example of a single crystal 2H α-SiC grain is shown in
Figure 10. Diffuse striations in the [1120] SAED pattern along
the [0001] direction indicate the presence of a moderate num-ner of stacking faults. High-resolution lattice images show that
long-range 2H order is present in the grain (Fig. 10). There is
no analog in 2H SiC of a 3C Σ=3 twin boundary, (e.g.,

order grain boundaries (see Table 1) have large interfacial
energies and their formation is much less energetically favor-
able than Σ=3 boundaries. Evidence that high order grain
boundaries with interface angles < 20° are unstable is evident
by the previously discussed rotational disorder about the
<011> axis in the SAED patterns (Fig. 8) of ~ 16.5% of the
3C-SiC Murchison population (defined as single polypeptide
3C-
SiC grains). This rotational disorder can be attributed to Σ
disorder at a grain boundary in the form of a range of high order
Σ boundaries (with small interface angles) that arise from the
growth instabilities of the high energy boundaries.

Single crystals of 3C SiC, defined as grains with very faint to
no visible twin reflections present in their diffraction patterns
represented 66.4% of the 3C-SiC Murchison population, and
approximately 10.7% of these single crystals exhibited Σ-disor-
order. Not all possible twin planes are visible along any one
[011] zone axis, therefore this is only an upper limit for the
fraction of 3C-SiC single crystals present. The fractions of all
3C-SiC Murchison grains exhibiting visible, well defined
Σ-twin boundaries are approximately Σ=3 (32.6%), Σ=9
(0.91%), Σ=19 (0.23%), Σ=73 (0.23%), and Σ=649 (0.23%).
A recent study of a pristine (i.e., not isolated by acid disso-
lution) 3C-SiC grain from the Cold Bokkeveld (CM2) carbon-
aceous chondrite reported evidence for randomly oriented
graphite included in the grain (Stroud et al., 2002). In that
work, the SAED pattern of the Σ=3 twinned SiC exhibited
superimposed diffraction rings that indexed to graphite: 0.342
nm (002) and 0.212 nm (100). No similar diffraction rings were
observed in the over 508 individual KJB SiC grains examined
here. In addition, no sets of non-SiC reflections (e.g., from
internal subgrains) were identified in any of the KJB SiC grains
studied (although detailed examination was restricted to only
one zone axis, i.e., 3C <011> and 2H <1120>).
Fig. 9. Intergrowth SiC grain containing predominantly 2H with one 3C growth domain from Murchison KJB. The SAED pattern from the entire grain is a composite of diffraction patterns from the 2H [11\overline{2}0] and 3C [011] oriented SiC domains. A bright field image of the grain is shown along with progressively magnified high-resolution lattice images showing cross-lattice planes. Inset in the high-resolution image is a simulated lattice image calculated under defocus/thickness conditions which match the lattice fringes in the micrograph. Long-range 2H order is evident in the lattice images of the 2H SiC domain.
twinning across tetrahedral \{0001\} planes) because such a 2H twin domain would be identical to the original lattice. For twinning to occur in 2H SiC, a high-energy twin interface must form instead. Since lower energy structures, such as stacking faults, can more readily form to relieve strain, the formation of a 2H-twin interface is energetically unfavorable in comparison with stacking fault formation. It is thus not surprising that electron diffraction and HR-TEM show no evidence of twinning in 2H SiC grains and that, within the same 2H/3C intergrowth grain (see Fig. 9), higher densities of stacking faults are observed in the 2H domains than in the 3C domains.

One 2H $\alpha$-SiC grain in Murchison contained two $\alpha$-SiC domains sharing common [1120] zone axes that were misoriented by 2.4°. The smaller of two domains contained a high density of stacking faults and was disordered. Another 2H $\alpha$-SiC grain in Murchison appeared in bright field imaging to be three discrete grains in a cluster, however these were in fact slightly misoriented domains of a single 2H $\alpha$-SiC grain. The three domains shared common [1120] zone axes misoriented by 3.0°, 2.4°, and 2.2° from one another, also the domains were rotated by several degrees about their [1120] axes. Some 3C $\beta$-SiC grains exhibited a similar microstructure consisting of several 3C domains sharing common [011] axes that were misaligned by small angles.

3.1.4. Microstructure of presolar one-dimensionally disordered SiC

An example of a SiC grain in which the tetrahedral stacking is heavily disordered is shown in Figure 11. The SAED diffraction pattern shows heavy streaking along one crystallographic direction, corresponding to a high density of stacking faults. The BF image of the grain shows numerous parallel striations. Both SAED and HR-TEM lattice images show no clear evidence of any dominant polytype order. Only short-range order (over several unit cells) of different polytypes was observed by HR-TEM. The density of stacking faults in these grains is so high that their structure is best described as randomly stacked, tetrahedral close-packed sheets, and therefore they cannot be classified as any polytype structure.

3.1.5. Higher order polytypes of presolar SiC

Several percent of the SiC grains examined in Murchison KJB did exhibit a few very weak diffraction spots in their SAED patterns suggesting either 4H or 6H order. However these SAED patterns also contained diffuse striations (e.g., stacking faults), and double diffraction spots. Furthermore, HR-TEM lattice images did not show evidence of 4H or 6H order that repeated more than several unit cells in any of SiC grains examined. Therefore, no conclusive evidence for small domains of 4H or 6H order was found, other than what could be expected from random stacking faults.

3.2. Abundance Distribution of Presolar SiC Polytypes

There are difficulties inherent in determining relative abundances of grain types using SAED patterns and HR-TEM images from a limited set of crystallographic directions (as in this work where one direction was examined). Difficulties arise because of finite tilt range of the TEM goniometer and the fact only two-dimensional crystallographic information is contained in SAED and HR-TEM data. Because of the finite tilt limits of the goniometer, a fraction of the randomly oriented grains will have no suitable high symmetry zone axes accessible for polytype identification. This fraction varies among SiC polytypes with distinctly different crystallographic symmetries (i.e., cubic, hexagonal, and rhombohedral). For example, there are six coplanar \(<1120>\) hexagonal directions lying in the (0001) plane compared to twelve \(<011>\) cubic directions isometrically distributed in three dimensions. Consequently, the fraction of grains that can be identified varies with crystal system,
biasing TEM measured polytype distributions. Nonetheless, the true distribution can be estimated from TEM measurements with appropriate corrections applied.

The relationship between the actual number of grains, \( N \), of a particular polytype, and the number \( N_T \) identified by TEM can be described as

\[
N = N_T \left( e_i (e_o)^{-1} \right)
\]

where \( e_i \) is the intrinsic fraction of randomly oriented crystals that have at least one zone axis perpendicular to the tetrahedral stacking direction (e.g., cubic <011> and hexagonal <1120>) within the TEM goniometer tilt limits. The parameter \( e_o \) represents an observer bias arising from the relative difficulty in tilting a polytype perpendicular to the tetrahedral stacking direction and is difficult to quantify. When possible, grains were tilted until identified, in order that \( e_o \) approached unity. In practice, \( e_o^{2H} \ll e_o^{3C} \), meaning \( e \)-corrected abundances with \( e_o \) assumed 1 (as here) are underestimations of the actual 2H SiC population. Over 90% of the grains examined in the TEM were successfully identified. Most of the unidentified grains were revealed upon tilting to be part of a random cluster of grains, and consequently were not examined further.

The parameter \( e_i \) was calculated for goniometer tilt limits of \( \pm 45^\circ \) and \( \pm 30^\circ \) (solid angle \( 4\pi \times 0.1179 \)) using an advanced version of the software package Sphere (Daulton, 1992). Relevant crystallographic zone axes of a polytype(s)/twin-structure configuration were mapped onto the surface of a unit sphere. The relevant zones were <011> for 3C SiC, <1120> for 2H SiC, and 3C <011> zones coincident with 2H <1120> for 2H/3C SiC intergrowths. Random grain orientations were modeled by rotating the mapped sphere using a spherically symmetric probability distribution. The fraction of random grain orientations that had at least one relevant zone axis within the goniometer tilt range defined in a fixed coordinate system were determined. The results of the calculations are given in Table 2 and the errors represent the standard statistical error of ten replicate calculations of \( 10^7 \) random grains.

In addition to crystal symmetry, \( e_i \) is highly dependent on twin and polytype-intergrowth microstructure. This is because the presence of \( \Sigma \)-twin boundaries in a 3C SiC grain increases the number of unique <011> orientations. Furthermore, each 3C-twin domain has four sets of cubic <111> directions and each can serve as a growth interface to differently oriented 2H domains. The greater the number of uniquely oriented 2H domains, the greater the number of unique <1120> orientations. Unfortunately, there is uncertainty in determining the actual grain microstructure because not all 3C \( \Sigma = 3 \) twin planes are visible, e.g., the inclined twin planes. In addition, in 2H/3C intergrowth grains, only those 2H domains associated with edge-on 3C {111} planes will be visible. The correction factors in Table 2 assume that the only domains present are the visible ones. If invisible 3C-twin domains or 2H domains were

Fig. 11. One-dimensionally disordered SiC grain from Murchison KJB. The SAED pattern has intense streaking along the tetrahedral sheet stacking direction indicating a high density of stacking faults, as confirmed by the bright-field and HR-TEM lattice images.
among the very large Murchison L-series SiC grains (1.5 µm) as both intergrowths and single crystals, in addition to the presolar (see Sect. 2.1.1). This observation, coupled with the large abundance of 2H SiC grains in KJB, as described above, leads us to conclude that 2H must also be a presolar SiC polytype. Indeed, from the analysis of 508 grains, 2H appears to be the only non-cubic polytype of presolar SiC. Moreover, no 4H, 6H, 15R, or higher SiC polytypes were observed, essentially ruling out the possibility of terrestrial SiC contaminants in KJB (see Sect. 2.2.3).

3.3. Isotopic composition of a 2H α-SiC Murchison Grain

To definitively establish the presolar origin of 2H α-SiC grains isolated from Murchison, we performed an isotopic analysis of a TEM-characterized 2H SiC grain (Fig. 12) from the KJE separate using NanoSIMS. The grain is 5.1 µm long with a serrated perimeter and a needle-like morphology. The long dimension of the needle is rotated in the (1120) plane by ≈ 43° from the [0001] crystallographic direction. Although the needle-like morphology is not uncommon, most presolar SiC grains are roughly equant in aspect ratio. Isotopic-composition maps of 12C/13C and 14N/15N for the grain are shown in Figure 13. The grain is clearly isotopically anomalous as shown by the differences in isotopic composition between the terrestrial a-C support film and the grain. The mean C isotopic composition of the grain is 12C/13C = 64 ± 4 (terrestrial = 89), and the mean N isotopic composition is 14N/15N = 575 ± 24 (terrestrial = 272), both within the range of mainstream presolar SiC. These isotopic results reaffirm our conclusion that 2H is also a presolar SiC polytype.

4. DISCUSSION

4.1. Presolar SiC Polytypes: Condensates or Thermal Transformation Products?

We propose that the SiC polytype distribution in Murchison KJB reflects original growth abundances as opposed to post-growth thermal transformation in the solar nebula. Appreciable transformation of 2H SiC → 3C SiC and 3C SiC → 6H SiC require at least 1673–1773 K and 1973 K, respectively (Krishna.

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**Table 2. Correction factors for Polytype Distribution Measurement Corresponding to TEM Goniometer Tilt Range of ± 45 and ± 30.**

<table>
<thead>
<tr>
<th>Polytype</th>
<th>Microstructure †‡</th>
<th>UniqueDirections</th>
<th>εi</th>
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<td>2H</td>
<td>0 × Σ = 3</td>
<td>6 &lt;1120&gt;</td>
<td>0.60243 ± 0.00019</td>
</tr>
<tr>
<td>3C</td>
<td>1 × Σ = 3</td>
<td>12 &lt;011&gt;</td>
<td>0.98590 ± 0.00139</td>
</tr>
<tr>
<td>3C</td>
<td>2 × Σ = 3</td>
<td>18 &lt;011&gt;</td>
<td>0.99808 ± 0.00037</td>
</tr>
<tr>
<td>3C</td>
<td>3 × Σ = 3</td>
<td>24 &lt;011&gt;</td>
<td>0.99988 ± 0.00003</td>
</tr>
<tr>
<td>3C</td>
<td>1 × Σ = 9</td>
<td>22 &lt;011&gt;</td>
<td>0.99992 ± 0.00017</td>
</tr>
<tr>
<td>3C</td>
<td>1 × Σ = 19</td>
<td>22 &lt;011&gt;</td>
<td>0.99948 ± 0.00004</td>
</tr>
<tr>
<td>3C</td>
<td>1 × Σ = 73</td>
<td>22 &lt;011&gt;</td>
<td>0.99988 ± 0.00003</td>
</tr>
<tr>
<td>3C</td>
<td>1 × Σ = 649</td>
<td>22 &lt;011&gt;</td>
<td>0.99731 ± 0.00004</td>
</tr>
<tr>
<td>3C/2H</td>
<td>0 × Σ = 3</td>
<td>6 &lt;011&gt; &lt;1120&gt;</td>
<td>0.60243 ± 0.00019</td>
</tr>
<tr>
<td>1 × 2H</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>3C/2H</td>
<td>0 × Σ = 3</td>
<td>10 &lt;011&gt; &lt;1120&gt;</td>
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<tr>
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<td>0 × Σ = 3</td>
<td>12 &lt;011&gt; &lt;1120&gt;</td>
<td>0.98590 ± 0.00139</td>
</tr>
</tbody>
</table>

† n × Σ = b indicates the number, n, of unique 3C twin boundaries of order b.
‡ n × 2H indicates the number, n, of unique 2H domains.

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**Table 3. Murchison KJB SiC Polytype Distribution.**

<table>
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<tr>
<th>Grain Type</th>
<th>Populationb (% by number)</th>
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</thead>
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<tr>
<td>3C</td>
<td>79.35 ± 6.66</td>
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<td>− 0.20</td>
</tr>
<tr>
<td>2H/3C Intergrowths</td>
<td>17.08 ± 0.32</td>
</tr>
<tr>
<td></td>
<td>− 5.70</td>
</tr>
<tr>
<td>2H</td>
<td>2.70 ± 0.22</td>
</tr>
<tr>
<td></td>
<td>− 0.91</td>
</tr>
<tr>
<td>Disordered</td>
<td>0.89 ± 0.20</td>
</tr>
<tr>
<td></td>
<td>− 0.20</td>
</tr>
<tr>
<td>All other polytypes</td>
<td>&lt; 0.20</td>
</tr>
</tbody>
</table>

b εi corrected, assuming ε0 = 1.
et al., 1971; Krishna and Marshall, 1971a; Bootsma et al., 1971). In comparison, experimental studies of volatization kinetics predict that SiC grains (diameter ≤ 1 μm) would be destroyed by reducing nebular gases ≥ 1173 K in less than several thousand years (Mendybaev et al., 2002). Furthermore, the P3 presolar noble gas abundances in CV3 meteorites imply that the constituents of the meteorite, before and following accretion, experienced peak temperatures < 870 K (Huss, 1997). Murchison has a lower metamorphic grade (CM2), so its constituents experienced still lower temperatures. Although 6H SiC can also form directly by condensation, the fact that we identified no intergrowths or single crystals of the 6H polytype in presolar SiC supports the proposition that the population does not contain thermal transformation products. If 6H SiC (or higher order polytypes) were present, sampling statistics constrain their abundance to be < 0.2% (Table 3). Therefore, only a very small fraction of the population, at most, could be thermal transformation products.

4.2. Stellar Sources of Presolar SiC

Isotopic studies of individual SiC grains isolated from meteorites show that they fall within several distinct presolar populations. The majority of presolar SiC grains (~ 94%), designated “mainstream” (Hoppe et al., 1994b), have individual grain isotope compositions characterized by AGB star s-process isotopic signatures in one or several of the following elements: Kr, Sr, Zr, Mo, Xe, Ba, Nd, Sm, and Dy (see Zinner et al., 1991b; Prombo et al., 1993; Lewis et al., 1994; Hoppe and Ott, 1997; Nicolussi et al., 1997, 1998; Podosek et al., 2002). Furthermore, the distribution of $^{12}$C/$^{13}$C ratios (between 10–100) in mainstream grains is similar to that of carbon star envelopes (Anders and Zinner, 1993; Alexander, 1993). Silicon and Ti isotopic compositions in mainstream SiC grains are a result of the combined contributions from both the initial compositions of the parent AGB stars and nucleosynthesis in the He-shell of these stars. The variations in the initial composi-

Fig. 12. Circumstellar 2H α-SiC crystal from Murchison KJE. Its presolar origin is confirmed by NanoSIMS isotopic analysis (cf. Fig. 13). This SiC crystal has a needle-like morphology with a serrated perimeter. Although this grain morphology is not uncommon, most SiC in Murchison have a roughly unit (equant) aspect ratio.
tions of AGB stars can be explained by galactic chemical evolution (Timmes and Clayton, 1996; Clayton, 1997) and/or heterogeneities in the ISM (Lugaro et al., 1999).

Although their definitions vary slightly in the literature, four minor SiC subpopulations have also been classified: X, Y, Z, and A+B. Type X (~1% of total population) have relatively large inferred 26Al/27Al ratios, and are defined as having excesses in 28Si (deficits in 29Si and/or 30Si) (Amari et al., 1992). Some X grains contain 44Ca daughters of the short-lived 44Ti (Amari et al., 1992; Hoppe et al., 1996b) that are only produced by explosive nucleosynthesis in supernovae (see Woosley and Weaver, 1995). Type Y (~1%) are defined by 12C/13C >100 and 14N/15N >272 (solar) (Amari et al., 2001a; Hoppe et al., 1994b). Type Z (~1%) are defined by 12C/13C <120 and large excesses of 30Si relative to 29Si (Alexander, 1993; Hoppe et al., 1997). Type Y and Z grains are believed to form around AGB stars with lower-than-solar metallicities (Zinner et al., 2001b). Type A+B grains (~3–4%) are characterized by their low 12C/13C ratios (<10), a wide range of 14N/15N ratios (40–10000), and a Si isotopic distribution that is very similar to that of mainstream grains (Hoppe et al., 1994b; Amari et al., 2001b). Both J-type carbon stars and CH stars have been proposed as their sources (Lodders and Fegley, 1998).

We assume that the SiC in Murchison is a representative sample of SiC from all kinds of astronomical sources. Given that 95–96% of the SiC grains in Murchison come from carbon AGB stars (99% if possible small contributions from J-stars and/or CH stars is included), then to first order the distribution of polytypes of presolar SiC from Murchison can be taken as the mean distribution in all circumstellar environments.

The contribution of supernovae (~1%) to the SiC population is too small to account for the observed abundance of 2H SiC grains, and we thus conclude that both 3C and 2H SiC polytypes must form in the circumstellar outflows from AGB stars. In principle, supernovae contributions could account entirely for the small subpopulation of one-dimensionally disordered grains (~<0.9%; Table 3), but without isotopic information on these grains it is currently impossible to evaluate this possibility. Nonetheless, future TEM microstructural studies of a sufficiently large number (several tens) of isolated X-grains, identified as such by SIMS ion imaging, could provide a definitive answer to the question of the crystal structure of SiC formed in supernova outflows.

4.3. SiC Polytpe Growth and Circumstellar Condensation

As argued above, the majority (>95%) of presolar SiC is of AGB star origin. Since the range of isotopic compositions found in these grains suggest that many AGB sources with a range of metallicities contributed dust to the solar nebula (Gal- lino et al., 1994; Alexander, 1993; Lugaro et al., 1999), at best only general inferences on formation conditions can be extracted from the grain microstructures. Nevertheless, although physical parameters such as temperature gradients, pressure gradients, gas species, elemental abundances, irradiation fluxes, etc. vary among AGB stars, the physical environments of SiC grain condensation should be restricted to a limited range of conditions. For this reason, it is justified to use microstructures of circumstellar SiC to deduce general information about grain forming regions.

There is not yet a detailed understanding of the parameters that affect SiC polytype formation, although many theories have been proposed (see Tahirov and Tsvetkov, 1982; Matsumi, 1993; Fissel, 2000). No conclusive theory has emerged, and it remains enigmatic why under certain growth conditions only one particular polytype forms. Although many factors
such as source gas (Si/C ratio, molecular species, and pressure) and nature of growth surface can influence polytype growth, it is clear that temperature and kinetics play an important role. Since atmospheres of carbon stars are heterogeneous with many factors not well constrained, we decided to focus on temperature for a first order model of grain condensation.

A range of formation temperatures is reported in the literature for the most common SiC polytypes. However, it is not straightforward to deduce something akin to a phase diagram of SiC polytype formation from these studies because different processes are used to synthesize SiC and, for a particular process, many experimental parameters vary among investigations. Therefore, the temperature dependent diagram of SiC polytype formation reported by Knippenberg (1963), although alluring, is of limited use. The most pertinent data are found in studies that examine the relative temperature dependence of several polytypes synthesized by a given process in which only a few experimental parameters are varied. From such studies, general trends in the temperature dependence of SiC polytype formation are inferred and used here to interpret circumstellar SiC microstructures.

The 2H polytype of SiC is considered to be the lowest temperature polytype and was first synthesized by condensation on 1773 K graphite surfaces exposed to pyrolytically decomposed methyltrichlorosilane (CH$_3$SiCl$_3$) gas (Merz and Adamsky, 1959). Others using this technique reported that 2H SiC formed between 1573–1723 K and was surrounded by regions of 3C SiC (Patrick et al., 1966; Powell, 1969; Berman and Ryan, 1971; Addamiano, 1982; Vetter et al., 2001). Furthermore, Patrick et al. (1966) reported almost entirely 3C SiC formed above 1700 K, consistent with the reported 2H -> 3C SiC transformation temperature of 1773 K (Krisha et al., 1971; Bootsma et al., 1971). Although 3C can form above 2000 K, having a wide range of condensation temperatures, 3C is the only SiC polytype reported to grow near 2H SiC growth regions at low condensation temperatures. The 2H SiC polytype has also been synthesized by low pressure (1.3 x 10$^{-3}$ dynes/cm$^2$) vapor condensation on slightly off-axis [0001] 6H-SiC substrates at 1473 K from pulsed laser ablated 3C SiC (Stan et al., 1994).

For any given vapor condensation process in which temperature is the major parameter varied, all polytypes other than 2H and 3C have formation temperatures greater than that of 3C SiC, however, under certain conditions their condensation temperature can be suppressed. For example, MB deposition of 3C SiC occurs between 1273–1573 K while 6H SiC deposition occurs > 1623 K on slightly off-axis [0001] 6H-SiC substrates from the decomposition of SiH$_4$, C$_2$H$_6$ and H$_2$ mixed gases (Kern et al., 1998). However, only 3C SiC grew on off-axis oriented substrates regardless of growth conditions (Kern et al., 1998). Polytype growth by vapor deposition is highly dependent on the material, orientation, preparation, and polarity (C-faced or Si-faced surface) of the substrate (see Matsunami, 1993; Taitrov and Tsvetkov, 1982). In fact, surface steps produced by 6H deposition substrates are used to suppress 3C SiC nucleation on terraces at low temperatures to promote 6H SiC growth; this technique is called step-flow or step-controlled epitaxy (Matsunami, 1993).

In CVD studies of growth on slightly off-axis [0001] 6H-SiC substrates at 10$^5$ dynes/cm$^2$ using SiH$_4$, C$_2$H$_6$ and H$_2$ gases, 3C SiC grew at 1373 K and 6H SiC grew between 1373–1773 K (Kimoto et al., 1993). In CVD studies using single-source organosilane precursor silacylobutane (c-C$_4$H$_4$SiH$_2$) at 6.7 x 10$^{10}$ dynes/cm$^2$, exclusively 3C SiC formed on [0001] oriented 6H-SiC substrates between 1073–1273 K and a mixture of 3C, 4H and 6H SiC formed at 1373 K (Yuan et al., 1995). Using sublimation-condensation (modified Lely process) on [0001] oriented 3C-SiC substrates at 10$^5$ dynes/cm$^2$, 3C SiC is reported to form up to 2423 K while 6H (and some 15R) SiC formed above 2373 K (Yoo and Matsunami, 1991). In comparison, the transformation of the 3C-SiC substrate to 6H SiC was observed at 2523 K (Yoo and Matsunami, 1991). In another sublimation growth study, the deposition of predominantly 4H SiC was reported at 2473 K at 1.3 x 10$^6$ dynes/cm$^2$ while deposition of predominantly 6H occurred at 2623 K at 5.3 x 10$^4$ dynes/cm$^2$, on [0001] oriented 6H-SiC substrates (Kanaya et al., 1991).

These studies demonstrate that the range of growth temperatures (e.g., lowest growth temperature) for a SiC polytype depends on both the synthesis process and physical parameters. However, certain conditions, such as the ratio of available Si/C in the gas (Fissel, 2000) or the preparation of the substrate (Matsunami, 1993), are reported to favor, for example, 6H over 3C SiC growth. Although temperatures in the above cited experiments cannot be directly compared because of differences in the experimental setups, distinct trends are present. Hexagonal 2H is the lowest temperature SiC polytype in stability and growth temperature. As temperature is increased, the next SiC polytype to form is 3C. If temperature is increased further, 2H SiC formation will cease. Cubic 3C SiC has a wide range of growth temperatures and as temperature is increased further, the general trend in the collective studies is that higher order SiC polytypes begin to grow along with 3C SiC, until temperatures exceed the 3C formation range. In this respect, 2H and 3C can be considered the lowest temperature SiC polytypes.

Equilibrium thermochemical calculations have been performed that thoroughly map the parameter space of P, T, and C/O (Sharp and Wasserburg, 1995; Lodders and Fegley, 1995), and can be used to predict condensation sequences and initial condensation temperatures for various presolar grain species in carbon star envelopes. These calculations necessarily assume that chemical equilibrium is reached in the grain formation environment. It has been argued that gas-grain equilibrium is approached near the AGB stellar photosphere where high temperature condensates form, based on the good agreement between observed and predicted mineral species (Bernatowicz et al., 1996) as well as on trace element abundance patterns in circumstellar SiC (Amari et al., 1995b; Lodders and Fegley, 1997).

The mineral species that condense from stellar envelopes depend critically on the gas C/O ratio. The CO molecule readily forms in circumstellar shells and is the most strongly bonded diatomic molecule which is not easily disassociated. Therefore, only when C/O > 1 will carbon be available for graphite and carbides to condense. Some further constraints on condensation pressures, temperatures, and C/O ratios in carbon star atmospheres can be obtained from the inferred condensation sequence of various carbon-bearing presolar minerals. Bernatowicz et al. (1996) found that the refractory carbide TiC as well as
condensation temperature. Carbide condensation temperatures are dis-

persive communication). The minerals plotted are stable below their

considered, and the data reported by them were results from calcula-

tions that used the thermodynamic parameters for 3C SiC (K. Lodders,

private communication). The minerals plotted are stable below their

condensation temperature. Carbide condensation temperatures are dis-

played as envelopes, with the lower boundary of the envelope for C/O

= 1.05 and the upper boundary for C/O ≥ 1.2. For graphite, the

condensation temperature is rather insensitive to pressure but strongly

dependent on C/O, but for TiC and SiC the opposite is true. Curves

labeled a, b, c and d are model P-T profiles for atmospheres of low mass

AGB carbon stars of 1.5 and 3 times M_☉, having solar metallicity

(except for enhanced C) and an effective (i.e., photospheric) tempera-
ture of 2800 K (from the spherical geometry simulations of Jørgensen

et al., 1992). Curves a and b are for carbon stars with C/O = 1.02 at

two different values of the surface gravity g, whose values are shown

in the legend as the logarithm of the acceleration in g units. Curves

a (Log g = +0.5) correspond to photospheric radius R = 160–115 R_☉,

for 3–1.5 M_☉, respectively, and curves b (Log g = −0.5) correspond

to photospheric radius R = 510–360 R_☉. Curves c are for the same

physical parameters as curves b, except for elevated C/O = 1.35,

showing that increasing C/O shifts the temperature profile to lower

pressures for any given temperature.

solid solutions of TiC, MoC and the very refractory carbide

ZrC often occur within presolar graphite spherules. They in-
ferred that formation of Ti, Mo, and Zr carbide solid solutions
preceded graphite formation, because frequently these refrac-
	ry carbides are located in the center of graphite spherules and

clearly served as nucleation sites for graphite condensation. In

comparison, despite the many sectioned graphite grains exam-

ined to date (e.g., see Croat et al., 2002), SiC was only once

observed to occur within graphite (Bernatowicz et al., 1996).

The implied typical formation sequence is therefore TiC con-
densation (and TiC, MoC, ZrC solid solutions), followed by

graphite condensation, and finally by SiC condensation.

As shown in Figure 14, the condensation temperatures of

TiC and SiC are insensitive to the C/O ratio, but are strongly

dependent on total gas pressure. On the other hand, the con-
densation temperature of graphite is rather insensitive to the

total gas pressure, but is strongly dependent on the C/O ratio.

This fortunate circumstance permits constraints to be placed on

these various parameters by reference to the inferred condensa-
tion sequence. For example, if the C/O ratio is ∼1.5, con-
densation of TiC before graphite can only occur at pressures

>1000 dynes/cm². Pressures of this magnitude are characteristic of

photospheres of carbon stars, however most photospheric tem-

peratures (mean 2650 K, σ = 250 K) are far too high for

any grains to condense (cf. Lodders and Fegley, 1995 and

references therein). Lower C/O ratios and lower pressures are

therefore required to produce the observed condensation se-
quence of TiC -> graphite, with plausible values in the range

1.2 ≥ C/O > 1.0 and p < ∼100 dynes/cm² (Bernatowicz et al.,

1996). In comparison, the distribution of C/O ratios of carbon

stars inferred from astronomical observations is relatively

sharply peaked with a median of C/O = 1.1 and σ = 0.16

(Lambert et al., 1986 cf. Lodders and Fegley, 1995). Although

a few carbon stars were reported to have C/O > 1.4, the ma-

jority of the carbon star population is consistent with the C/O

range suggested by the inferred grain condensation sequence. It

is likewise consistent with the observational requirement that

SiC condensation must follow the condensation of graphite (for

p < 100 dynes/cm², ∼1.1 > C/O > 1, as inferred by Sharp and

Wasserburg, 1995). Grain formation must therefore be re-

stricted to the stellar atmosphere, at distances greater than the

photospheric radius, where temperatures tend to fall off rather

rapidly. Figure 14 shows some model temperature profiles for

atmospheres of low (1.5–3 × solar) mass carbon AGB stars

(Jørgensen et al., 1992). It is seen that several model tempera-

ture profiles indeed produce the observed sequence TiC ->

graphite -> SiC, provided that the C/O ratio does not much

exceed unity.

The temperature range for SiC condensation in the major-

ity of carbon stars can be estimated from Figure 14 (i.e., Sharp and

Wasserburg, 1995; Lodders and Fegley, 1995) by using C/O =

1.1 (the median ratio inferred from astronomical observation) and

by assuming that the inferred mineral condensation se-

quence (TiC -> graphite -> SiC) discussed previously is

characteristic of the majority population of carbon stars. These

assumptions predict that grain condensation occurs between

total gas pressures of 3–300 dynes/cm². In this pressure range,

the predicted temperatures for equilibrium SiC condensation

are ∼1500–1670 K. A slightly lower C/O = 1.05 predicts grain

condensation at pressures of 0.3–30 dynes/cm² and SiC con-
densation between ∼1422–1590 K. Even for C/O = 1.20,

predicted SiC condensation temperatures are constrained to be

no greater than 1770 K. Condensation temperatures predicted

by the chemical equilibrium calculations represent the tempera-

ture at which vapor and condensates coexist in equilibrium; how-

ever, because of the effect of undercooling the actual

condensation temperatures can be somewhat lower.

It is important to emphasize that these relatively low con-
densation temperatures are a direct consequence of the low

pressures in AGB atmospheres predicted from the inferred

condensation sequence of minerals (TiC -> graphite -> SiC),

and that these low temperatures undoubtedly play an important

role in the kinds of polytype structures that are ultimately

produced. Temperatures at which 2H SiC are known to grow

and remain stable, ∼1473–1723 K, (Patrick et al., 1966;

Krishna et al., 1971; Stan et al., 1994) largely fall within the

range predicted for SiC formation in most circumstellar atmos-

pheres by equilibrium thermodynamics (Sharp and Wasser-

burg, 1995; Lodders and Fegley, 1995). Additionally, in the

very same experiments that synthesized 2H SiC the formation of

predominantly 3C SiC was observed at temperatures >1700 K

(Patrick et al., 1966). Formation of 3C SiC in those experi-

ments occurs slightly above the temperature range predicted

for SiC condensation in AGB stars, but the agreement is per-
haps as good as can be expected from laboratory experiments that may only approximate the formation conditions and gas compositions appropriate for AGB atmospheres. Nonetheless, as previously discussed, all of the higher order SiC polytypes are only known to form at temperatures higher than that of 3C SiC under similar conditions for a given vapor condensation process. This plausibly explains why only two polytypes (2H and 3C) out of a possible order of a hundred different kinds are observed in presolar SiC.

Mass outflows in AGB atmospheres are often characterized in terms of spherically symmetric, smoothly varying spatial functions of T, P, and composition (e.g., see, Cherchneff et al., 1992; Cadwell et al., 1994; Chigai et al., 1999). However, there is considerable evidence that the mass outflows are considerably more complicated than depicted in such models, and in fact are often clumpy and frequently depart from spherical symmetry (e.g., Olofsson, 1996; Weigelt et al., 1998). Fortunately, to construct a tentative framework in which to interpret the observational results presented here, we need not be concerned with the global aspects of stellar atmosphere mass outflows. We need only to consider the progressive physical and chemical changes in a representative parcel of gas within the mass outflow. We therefore make the simplifying assumption that the parcel behaves as a closed system as it moves outward from a location close to the stellar photosphere to locations at larger radii. Neglecting any consideration of the specific rate at which this transport occurs (and thus about the kinetics of grain growth), or how transport rates may vary among parcels, we simply assume that as a parcel moves outward it expands adiabatically. Consequently, its temperature decreases monotonically with time, and the number density of gas contributing to grain growth in the parcel also decreases (at a rate faster than the temperature). These changes induce the parcel to evolve chemically. Although we can hardly expect this general picture to depict the grain formation process in detail, we do expect that the inferred polytype formation sequence and required physical conditions will be broadly correct.

In regard to the majority population of carbon stars (1 < C/O < 1.2), the typical sequence of mineral condensation (TiC -> graphite -> SiC) inferred from the laboratory study of presolar grains and interpreted with the aid of equilibrium thermodynamics, leads to the conclusion that relatively low pressures prevail in the regions of circumstellar atmospheres where the grains condense. This conclusion is essentially independent of any stellar atmosphere model. The equilibrium condensation behavior of SiC (Fig. 14) shows that at these low pressures, the formation of SiC can only occur at relatively low temperatures that are considerably less than the experimental formation temperatures of most SiC polytypes. Indeed, comparison of these equilibrium thermodynamic temperatures with experimental data on the formation of SiC polytypes leads to the conclusion that only 2H and 3C polytypes are likely to grow in circumstellar atmospheres. This prediction is verified by the laboratory observations carried out in the present work. With these points in mind, we propose that close to the carbon star photosphere, photon and particle irradiation fluxes, as well as temperature, are sufficiently high to prevent nascent nucleating clusters from reaching critical size for sustained condensate growth. Therefore, there will be a “no growth region” for dust close to the star. At radii in the stellar atmosphere where the irradiation fluxes and temperatures are sufficiently low, the highest temperature condensates such as TiC and graphite can form (Sharp and Wasserburg, 1995; Lodders and Fegley, 1995). At farther radii, the highest temperature SiC polytype observed in Murchison, 3C, will be first to condense and grow. It has been argued that the 3C polytype is the most stable structure for SiC nuclei (Tairov and Tsvetkov, 1982), suggesting that 3C SiC nuclei have a higher probability of reaching critical size over nuclei of other polytypes. Higher order SiC polytypes may indeed nucleate at higher temperatures (corresponding to smaller radii) than 3C growth regions or even along side 3C SiC at the highest 3C growth temperatures, but for their growth to occur would require that these less stable SiC nuclei reach critical size, in some cases, under conditions of larger irradiation fluence. This could contribute to the lack of polytypes of order higher than 3C in circumstellar SiC. At still larger atmospheric radii, in expanded cooler gas regions with smaller irradiation fluences, the lowest temperature polytype, 2H SiC, would grow. At intermediate radii in the SiC growth region, intergrowth grains might form directly or by 2H SiC heteroepitaxial growth on preexisting 3C SiC grains which were transported to cooler regions in AGB mass outflows by stellar radiation pressure.

The observed relative frequency of occurrence of 3C and 2H SiC crystals is also consistent with the scenario outlined above. Since the rate of grain nucleation from the gas varies as the square of the number density of any gas species contributing to grain growth (McDonald, 1963), we predict that the polytypes nucleating at higher temperatures and higher gas number densities will be more abundant than polytypes nucleating later at lower temperatures and lower number densities in the expanding gas parcel. Not only will the nucleation rate of lower temperature forms of SiC be reduced because of the decreasing number density of Si in the expanding gas, but also because of the prior removal of Si into the SiC already formed at higher temperatures (cf. Lodders and Fegley, 1995). In qualitative accord with these expectations, single crystals of 3C SiC, which formed at higher temperatures than 2H SiC and therefore at higher gas phase Si number densities, are far more numerous than single crystals of 2H SiC (see Table 3).

5. SUMMARY AND CONCLUSIONS

Silicon carbide is an important species of stardust, and isotopic studies of many different elements reveal that nearly all presolar SiC was produced in low mass AGB carbon stars. Under the simple and reasonable assumption that presolar SiC in primitive meteorites is a representative sample of the sum of SiC produced by the many different types of stellar sources, a determination of the structure of presolar SiC thus translates, to first order, into a direct determination of the structure of SiC produced by AGB stars. Although IR astronomical studies detect SiC in the mass outflows from carbon stars, these studies can only distinguish between cubic SiC (β-SiC) and non-cubic SiC (all hexagonal and rhombohedral polytypes, collectively termed α-SiC), and even this crude differentiation has been controversial. Thus, the direct TEM determination of SiC crystal structure provides a reference standard that can aid in the understanding of which subset of physical properties (e.g., size,
shape, crystallographic structure) is relevant for interpreting IR spectra of SiC from carbon stars. Further, on the order of a hundred different polytypes of SiC have been synthesized in the laboratory. The particular polytypes produced in any process depend on specific physical and chemical conditions such as temperature, pressure, the composition of precursors, and (in cases of deposition) the microstructure of substrates. Therefore, the distribution of polytypes in presolar SiC is used here to evaluate models of grain formation in circumstellar atmospheres.

Our principal experimental result is that presolar SiC occurs in only the two simplest polytypic forms: cubic 3C (~80%) and hexagonal 2H (~3%), and intergrowths of these two forms (~17%), in addition to a small number of one-dimensionally disordered SiC grains (~0.9%). The presolar origin of at least one 2H grain is demonstrated based on the anomalous $^{12}$C/$^{13}$C = 64 ± 4 (terrestrial = 89), and $^{14}$N/$^{15}$N = 575 ± 24 (terrestrial = 272) isotopic composition of the grain. In fact, this is the first report of 2H SiC forming in nature. We further conclude that the measured polytype distribution reflects original growth abundances and is not altered by post-formation thermal transformation. Therefore, we interpret the observed structural simplicity as the result of the specific physical conditions in AGB circumstellar atmospheres. In particular, total gas pressures in the extended stellar atmospheres exterior to carbon star photospheres are quite low (<100 dyne/cm$^2$), so SiC condensation in these atmospheres is restricted to relatively low temperatures (at least several hundred degrees below 2000 K). In general, laboratory studies have shown that at these low temperatures, 2H and 3C are the most stable SiC polytypes to form in vapor condensation processes, and that for any given set of physical conditions, all SiC polytypes of higher order than 2H and 3C form at greater temperatures than those at which these two polytypes form. A simple hypothesis that accounts for the observations is that 3C SiC first condensed at small radii (high temperatures) and 2H SiC condensed at larger radii (lower temperatures) in AGB atmospheres. At intermediate radii in the SiC growth region, intergrowth grains might form directly or by 2H SiC heteroepitaxial growth on pre-existing 3C SiC grains which were transported to cooler regions in AGB mass outflows by stellar radiation pressure.

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† M. Tang appears as T. Ming in the author list of the cited journals and in publication databases.