Pergamon

Geochimica et Cosmochimica Acta, Vol. 67, No. 24, pp. 4679–4691, 2003

0016-7037/03 $30.00 + .00

doi:10.1016/S0016-7037(03)00461-7

Pristine presolar silicon carbide

THOMAS J. BERNATOWICZ,* SCOTT MESSENGER, OLGA PRAVDIVTSEVA, PATRICK SWAN, and ROBERT M. WALKER
Laboratory for Space Sciences and Department of Physics, Washington University, St. Louis, MO 63130-4899, USA

(*Received April* 30, 2003; *accepted in revised form July* 3, 2003)

Abstract—We report the results of a study of 81 micrometer-sized presolar SiC grains in the size range 0.5–2.6 μm from the Murchison (CM2) carbonaceous chondrite. We describe a simple, nondestructive physical disaggregation technique used to isolate the grains while preserving them in their pristine state, as well as the scanning electron microscopy energy-dispersive X-ray mapping procedure used to locate them.

Nine-tenths of the pristine SiCs are bounded by one or more planar surfaces consistent with cubic (3C polytype) crystal faces based on manifest symmetry elements. In addition, multiple polygonal depressions (generally <100 nm deep) are observed in more than half of these crystal faces, and these possess symmetries consistent with the structure of the 3C polytype of SiC. By comparison of these features with the surface features present on heavily etched presolar SiC grains from Murchison separate KJG, we show that the polygonal depressions on pristine grains are likely primary growth features. The etched SiCs have high densities of surface pits, in addition to polygonal depressions. If these pits are etched linear defects in the SiC, then defect densities are quite high (as much as 10^8 –10^9/cm^2), about 10^3–10^4 times higher than in typical synthetic SiCs. The polygonal depressions on crystal faces of pristine grains, as well as the high defect densities, indicate rapid formation of presolar SiC.

No other primary minerals are observed to be intergrown with or overgrown on the pristine SiCs, so the presence of overgrowths of other minerals cannot be invoked to account for the survival of presolar SiC in the solar nebula. We take the absence of other primary condensates to indicate that further growth or back-reaction with the gas became kinetically inhibited as the gas-phase densities in the expanding asymptotic giant branch (AGB) stellar atmospheres (in which most of the grains condensed) became too low. However, we did observe an oxygen peak in the X-ray spectra of most pristine grains, implying silica coatings of as much as several tens of nm thickness, perhaps due to oxidation of the SiC in the solar nebula.

We see little or no evidence on the pristine grains of the surface sputtering or cratering that are predicted theoretically to occur in the interstellar medium (ISM) due to supernova shocks. A possible implication is that the grains may have been protected during their residence in the ISM by surface coatings, including simple ices. Residues of such coatings may indeed be present on some pristine SiCs, because many (60%) are coated with an apparently amorphous, possibly organic phase. However, at present we do not have sufficient data on the coatings to draw secure inferences as to their nature or origin.

A few irregular pristine SiCs, either fragments produced by regolith gardening on the Murchison parent body or by grain–grain collisions in the ISM, were also observed. *Copyright © 2003 Elsevier Ltd*

1. INTRODUCTION

The study of presolar grains found in primitive meteorites has yielded new, often otherwise inaccessible information about stellar nucleosynthesis, stellar evolution, and the formation of solids in stellar ejecta. The principal focus of most presolar grain studies has been the determination of isotopic structures of both major and minor elements. The interpretations of these detailed structures in terms of stellar nuclear physics and dynamics have contributed significantly to our understanding of element synthesis (Bernatowicz and Zinner, 1997; Bernatowicz and Walker, 1997; Zinner 1998). Progress has also been made in understanding the composition and structure of presolar grains in terms of grain condensation and the physico-chemical conditions in stellar environments (Lodders and Fegley, 1995, 1997; Sharp and Wasserburg, 1995; Bernatowicz et al., 1996; Daulton et al., 2002, 2003; Chigai et al., 2002; Croat et al., 2003). However, the potential use of presolar grains as monitors of the environments to which they have been exposed has been virtually unexplored, except for some notable work on their progressive destruction with increasing severity of metamorphism on meteorite parent bodies (e.g., Huss and Lewis, 1995; Huss 1997), and on their destruction by oxidation reactions in the solar nebula (Mendybaev et al., 2002). It is important to consider that because the grains formed in various kinds of circumstellar winds and supernova ejecta, they necessarily had to migrate from these environments via the interstellar medium (ISM) into the protosolar nebula, and finally become incorporated into cometary and asteroidal parent bodies, samples of which come to us in the form of interplanetary dust particles and meteorites. Any of these environments could have left its mark on the surviving presolar grains, particularly on their surfaces, which therefore might serve as monitors of various processes.

Hitherto it has not been possible to study the surfaces of presolar grains as they occur in their parent meteorites—in the parlance used in this paper, in their "pristine" state—because of the typical means by which they are isolated for study. The very effective dissolution methods developed to prepare presolar grain concentrates for isotopic studies (Amari et al., 1994) can alter grain surface morphologies (as we will demonstrate here

* Author to whom correspondence should be addressed (tom@wuphys.wustl.edu).

for the case of presolar SiC), as well as entirely destroy petrographic context. A notable exception is the case of internal crystals sequestered within larger presolar grains, such as the various carbides and other minerals found within presolar graphite (Bernatowicz et al., 1991, 1996; Croat et al., 2003). In this case, the graphite serves as a protective envelope that preserves the original characteristics of the internal crystals as well as their petrographic context, but it also prevents them from recording some effects of external processing environments.

In this paper we describe a simple physical disaggregation technique coupled with an X-ray mapping procedure used to locate micrometer-sized presolar SiC grains from the Murchison (CM2) carbonaceous chondrite, that preserves them in their pristine state. We then describe pristine SiC surface characteristics and overall morphologies determined by high-resolution field emission scanning electron microscopy (FESEM), and compare these features to those of presolar SiC grains that have been prepared using chemical dissolution techniques. We show that the pristine SiC grains exhibit a wide range of morphologies, ranging from euhedral crystals with primary growth features preserved in exquisite detail, to anhedral (probably) fragmented grains. Still others have a rounded appearance or possess surface coatings. Overall, the pristine grains appear to have experienced a variety of postformation histories.

2. MATERIAL AND METHODS

In the present work we studied SiC grains from the Murchison (CM2) carbonaceous chondrite, which have been shown by secondary ion mass spectrometry (SIMS) analysis of individual grains to be >99% presolar (Hoppe et al., 1994, 1996, 1998; Zinner et al., 2001). However, because isotopic characterization before scanning electron microscopy (SEM) study cannot be used in the present work, special care had to be taken to avoid contamination by terrestrial SiC dust. To minimize possible transfer of contaminant terrestrial SiC from the meteorite surface, a ~2-g piece of the meteorite was first coated with epoxy to fix surface contamination, then split in half within a clean laminar flow hood. About 30 mg of matrix was excavated with a dental tool from the interior, and ultrasonicated for several hours in a mixture of isopropanol (80%) and deionized water (20%). The sample was separated by centrifugation into five size fractions based on Stokes' Law settling for spheres having the density of SiC: >10 μm, 3–10 μm, 1–3 μm, 0.1–1 μm, and <0.1 μm. Each size fraction was processed in 10 cycles, starting with the largest. The cycle began with 1 h of ultrasonication followed by centrifugation. Liquids with suspended matrix grains smaller than the desired size range were decanted into another tube, and the settled grains were resuspended by ultrasonication for 30 min in a fresh mixture of isopropanol and water. This was repeated 9 times per size range, after which the decanted liquids were centrifuged to settle the smallest grains, and the supernatant was decanted.

The 1–3 μm size fraction was studied in the present work. Aliquots of suspended material were deposited on polished graphite planchets (20 mm in diameter) that previously had been ultrasonicated in soapy water, rinsed, and dried with pressurized nitrogen. Each mount was checked in the SEM for contamination by terrestrial SiC before sample deposition. Murchison grains were deposited in 24 steps, allowing the sample to dry completely between steps. Each deposit consisted of 7 μL of very dilute aliquot. This procedure provided full coverage of the mount surface, while ensuring uniform distribution of the material. Twenty-two such graphite mounts were prepared.

Individual grains of SiC were located in the SEM using a variant of the X-ray mapping technique previously developed to locate SiC grains in situ in polished sections of primitive meteorites (Alexander et al., 1990). The method is based on the fact that the yield of characteristic X-rays from Si bombarded by high-energy electrons is higher from a grain of SiC (where half the atoms are Si) than from a silicate mineral where the atomic concentration of Si is much lower. By setting an appropriate counting threshold for individual pixels, it is possible to locate small, rare SiC grains in the sea of silicate minerals that constitute primitive meteorites.

Although the detailed parameters vary depending on the particular X-ray system used as well as on the morphology of the grains being detected, the general principles are clear. The first requirement is to have an X-ray system that will display pixels in a binary image only if the counting parameters satisfy certain conditions, e.g., Si counts greater than, and Mg counts less than, certain preset threshold values. For X-ray mapping we used a JEOL JSM-840A SEM equipped with a NORAN VANTAGE digital X-ray analysis system. The Si-Li thin window X-ray detector was capable of transmitting carbon X-rays and had an energy resolution of 130 eV.

The threshold parameters are determined by measuring the respective count rates from a calibration SiC standard and from the general background due principally to silicate minerals. If the Si threshold is too low, there will be many false displays of "candidate" pixels. If the threshold is too high, smaller SiC grains will be missed. A first estimate of an acceptable threshold value is to require that the probability of a false display—i.e., one due simply to a statistical fluctuation of the normal background counting rate—be very small. If the mean Si background count per pixel is N_b and the Si threshold is N_t, the probability that a given pixel equals or exceeds N_t is given by the error function of $(N_t - N_b)/N_b^{1/2}$. For an X-ray image array of 256 × 256 pixels, to limit the background contribution to one false pixel per image requires a count rate for that pixel of at least 4.3 times $N_b^{1/2}$ in excess of N_b, i.e., a ratio $N_t/N_b \geq 1 + 4.3/N_b^{1/2}$. This shows that, in principle, the threshold does not have to be raised very high above the signal from the background to get a good rejection of spurious counts. In practice, for a thick deposit of background silicate grains with $N_b = 20$ counts/pixel, a threshold of 43 counts/pixel was satisfactory to limit their average contribution to a single false pixel/256^2 image, in agreement with this expectation. The addition of the criteria that the O and Mg counts be < 10 per pixel further suppresses the number of false displays due to statistical fluctuations of the silicate background. However, considerable caution must be used in imposing such additional counting criteria, as they can lead to missing small (or thin) SiC grains.

Once a candidate pixel has been located, the region around this point is mapped in Si X-rays at higher magnification to distinguish real events (i.e., actual SiC grains) from those due to statistical fluctuations. The presence of a C signal in an appropriate proportion to the Si signal clinches the identification of a candidate as a SiC grain. The crystal is then imaged in secondary electrons at different magnifications, and these photos are used to relocate the grains for subsequent study.

Because the number density of SiC grains is very small (matrix-normalized SiC abundance in Murchison ~15 ppm; Huss, 1997), the Si photon counting rate is maximized to increase the grain location rate. Thus, the X-ray detector should be placed as close to the sample as possible, and the bombarding electron current should be maximized. Clearly, care must be taken to ensure that the electronic detection system does not saturate at high counting rates, as this would obviate the detection scheme. The choice of bombarding electron energy is chosen to optimize the yield of Si photons per incident electron (roughly 1.5–3 times the characteristic X-ray energy; Goldstein et al., 1992). However, to locate very small grains, the energy needs to be reduced as much as is practical to ensure that the excitation is confined to the smallest volume possible.

The efficiency of detection of SiC grains varies with their size. Provided that the grains are large enough to encompass several pixels, and also provided that they are sufficiently thick to produce the maximum count rate, then the detection efficiency is unity. However, when the grain itself becomes small with respect to the pixel size, the efficiency drops. The efficiency of detection of grains of a given area also depends on the grain thickness. Platelet grains that lie in the plane perpendicular to the electron beam will not be detected at all if they are too thin. In Figure 1 we show the results of efficiency measurements as a function of grain size for presolar SiC grains in a section of the Murchison meteorite polished with Al oxide. The data were obtained by first mapping an area under standard conditions to locate grains whose sizes were determined by measurements at higher magnification, then the specimen stage was set to a new random starting location and

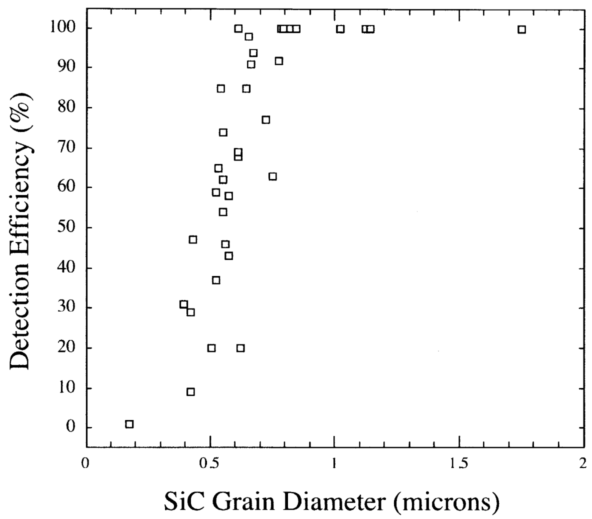

Fig 1. Detection efficiency for automated SEM energy dispersive X-ray identification of pristine presolar SiC grains in an A1 oxide-polished section of the Murchison meteorite, as a function of grain diameter. See text for discussion of experimental conditions.

the region containing the grain was remapped under the standard conditions. This process was repeated 100 times, and the efficiency was defined as the fraction of the runs in which a given grain was detected. As expected, because of the (unknown) variation in the thickness of the grains, some points fall well below the average efficiency curve. The maximum detection efficiencies determined for a given diameter are therefore best regarded as representative values for fairly equant grains.

It should be clear that the choice of specific mapping parameters is somewhat arbitrary and that these are best determined for a specific problem by a trial-and-error process. In the work described here, using the energy dispersive X-ray spectrometry (EDS) system previously noted, we found that the following mapping parameters were satisfactory: electron beam current = 5 nA; magnification = 400×; array size = 256^2 pixels; pixel width = 0.9 μm; electron acceleration voltage = 10 kV; Si counts for 1–3 μm SiC = 44–110; Si background counts = 20; Mg, O counts < 10; detection threshold Si counts > 43. With these parameters, a "thick" sample deposit (see below) resulted in ~1 candidate/256^2 pixel image, of which ~1 in 10 was SiC, and the rest due to statistical fluctuations in the silicate background. An example of a SiC grain detected using this mapping scheme is shown in Figure 2.

Although the rate at which SiC grains can be located is greatest with a "thick" deposit in which the meteoritic material is deposited in a contiguous layer whose thickness exceeds the range of Si photons, this is not optimal for either characterizing or picking grains once they are found. Instead we used "thin" deposits in which the grains were spread thinly on a low Z substrate of graphite. This increased the number of maps required to locate SiC grains but resulted in cleaner observation and picking conditions.

The pristine SiC grains that were located by the above procedures were imaged at high spatial resolution using a Hitachi S-4500 field emission scanning electron microscope (FESEM) operated at low (1–3 kV) voltages. Three of the (noncoated, euhedral—see "Results") pristine grains were analyzed for their C and Si isotopic compositions by NanoSIMS ion microprobe to confirm their presolar origin. The Cameca NanoSIMS is a new generation instrument, which enables isotopic measurements at 100-nm scales while providing substantially improved sensitivity in comparison to earlier generation ion probes (Stadermann et al., 1999). Its primary value for this study was the ability to measure the pristine SiC grains in situ, despite their being located within piles of insulating matrix material. The isotopic measurements were performed by isotopic imaging of the grains and surrounding material. The images were acquired by rastering a 1-pA 16-keV Cs^+ primary ion beam over areas of 10–20 μm on a side, simultaneously collecting the secondary $^{12,13}C^-$ and $^{28,29,30}Si^-$ ions with five electron multipliers. Sample charging was effectively controlled by the use of an electron flood gun. The surrounding matrix material served as an isotopic standard for the correction of instrumental mass fractionation and relative detector sensitivities.

To investigate the possible presence of silica coatings on the surfaces of the pristine SiC grains, we obtained from E. F. Fullam, Inc. several pyrolitic graphite discs on which had been deposited SiO films of various thickness (10 nm, 30 nm, 100 nm, 200 nm), which were used to calibrate the O K-α peak in EDS spectra. The O-signal was determined by gaussian fitting of the peak with background subtraction, using NORAN Vantage software. The standards were measured multiple times in different spots with the focused (0.3 nA) electron beam oriented normal to the standard surface, and at several acceleration potentials (2 kV, 3 kV, 4 kV, and 5 kV). We then compared O signals from (effectively) infinitely thick SiO and high-purity SiO_2 standards at the various voltages to obtain conversion factors between SiO and silica oxygen signals. For the pristine SiCs, we used the same measurement conditions as for the standards, and chose grains with flat regions on the surfaces that could be oriented perpendicular to the electron beam with stereo imaging. For our nonoxidized terrestrial SiC standard, we used micrometer-sized synthetic SiC grains manufactured by the Superior Graphite Co. that were analyzed using the same EDS procedures.

3. RESULTS

3.1. Size and Shape Characteristics of Pristine SiC Grains

As noted in "Material and Methods," we investigated the separate of size range nominally 1–3 μm (on the basis of Stokes' Law settling). We chose this size range because the grains are sufficiently large to be detected using the X-ray mapping protocol outlined above, and within this constraint, are as representative as possible of the bulk Murchison SiC population. Amari et al. (1994) have previously determined the size distribution of Murchison presolar SiC, and found that the peak of the number distribution occurs at grain diameters of ~0.4 μm, with ~70% of the grains falling within the range 0.3–0.7 μm, whereas grains ≥3 μm represent <0.01% of the SiC. We therefore did not search the largest SiC fractions (>10 μm and 3–10 μm), because such grains would not only be very rare but also atypical of the Murchison SiC grain population.

Figure 3 is a size histogram of the 81 pristine presolar SiC grains characterized in our 1–3 μm size separate. The histogram results are in general agreement with the size expectations based on Stokes' Law settling, taking into account that these expectations are based on spherical grains, such that a fraction of grossly nonspherical grains less than 1 μm in diameter is expected to be present. However, the following points should be noted. First, the smallest observed diameter of 0.5 μm corresponds closely to the expected experimental cutoff size, below which SiC grains simply cannot be found with our detection protocol (see Fig. 1). Second, for grains ~0.4 –~0.8 μm in diameter the detection efficiency is still less than unity, and this plus the fact that ≲1-μm grains fall below or near to the size limit imposed by settling criteria means that these grains are certainly underrepresented in the Figure 3 distribution. Third, while the distribution for grains 1–3 μm does show the expected increase in frequency with decreasing grain size down to ~1 μm, it cannot be taken as representative of the SiC in Murchison within this size range because of the detection restrictions on shape noted above. Specifically, platy grains may not give sufficient signal for detection. Thus, while the size frequency distribution of SiC grains of 1–3 μm shown in

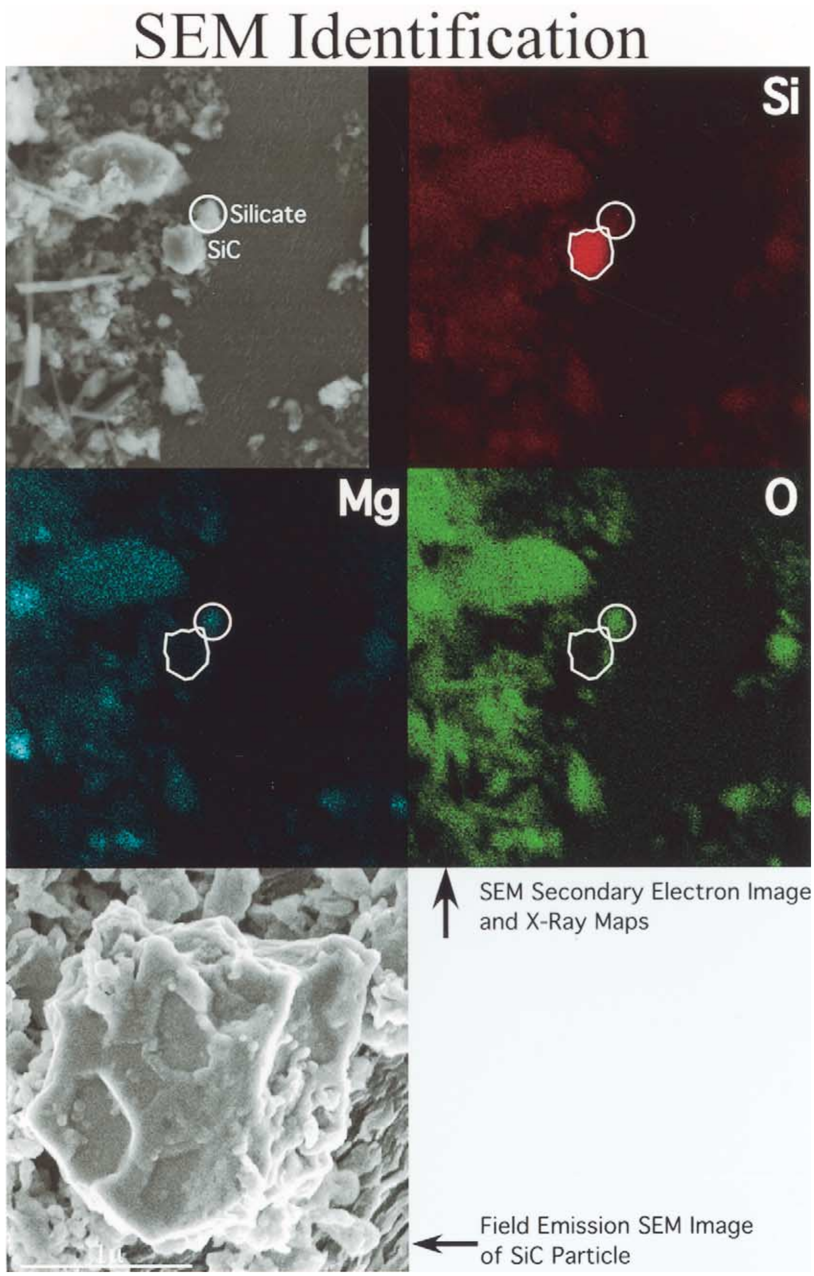

Fig 2. SEM secondary electron image (upper left) and energy dispersive 256 × 256 pixel X-ray maps (elements Si, Mg and O) of a field of Murchison matrix grains. A SiC grain is detected because of its high Si X-ray signal, as well as its low Mg and O X-ray signals, compared to nearby silicate grains (one of which is shown circled). The detected SiC grain is shown at high spatial resolution in the FESEM image at lower left.

Figure 3 is roughly compatible with the distribution of Amari et al. (1994) for diameters in excess of ~1 μm, it should certainly not be construed as representing the actual distribution for Murchison in the size range displayed. The geometric mean diameter (i.e., the square root of the product of orthogonal maximum and minimum projected grain diameters), and dispersion about the mean of the distribution shown in Figure 3, are 1.36 ± 0.48 μm, with a range from 0.5 to 2.6 μm. This range corresponds to ~30% by number of the Murchison SiC population.

From FESEM images we calculated aspect ratios (b/a) based on projected image maximum (a) and minimum (b) diameters. Figure 4 is the frequency distribution of these aspect ratios. The row of rectangles above the plot gives a visual impression of the numerical values for the aspect ratios. The mean and dispersion about the mean of the distribution are b/a = 0.78 ± 0.15, and 72% of the grains have aspect ratios ≥0.7, meaning that most pristine SiC grains are roughly equant. This is not unexpected, because detailed crystallographic studies (Daulton et al., 2002, 2003) have shown that 80% of presolar SiCs from Murchison are the 3C (cubic) polytype, for which the principal growth directions are the four isotropically distributed <111>

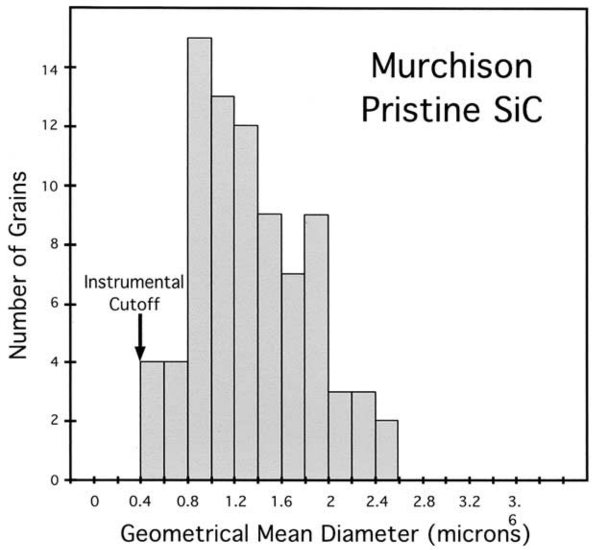

Fig 3. Grain size distribution of the 81 pristine presolar SiC grains from Murchison studied. This distribution does *not* represent the actual size distribution of SiC in Murchison, as discussed in the text.

zones. The crystals are often twinned, however the most common type of twin is polysynthetic across {111} planes (Daulton et al., 2003), so that these principal growth directions are unchanged. For the remaining 28% of the grains having aspect ratios ≲0.6, roughly half appear to be irregular fragments while the other half have an elongated crystal shape. It is possible that at least some of the latter type are the 2H variety (3% of presolar SiCs) and/or 3C-2H intergrowths (17% of presolar SiCs), some examples of which exhibit needle-like morphologies (Daulton et al., 2002, 2003).

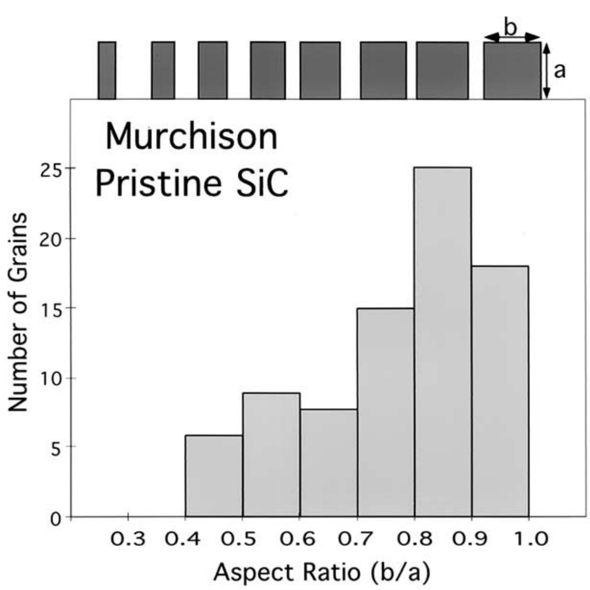

Fig 4. Histogram of aspect ratios *b/a* for the 81 pristine SiCs studied. The quantities *a* and *b* are the maximum and minimum projected diameters of grains, respectively, obtained from FESEM images. The shapes shown at the top of the figure give a visual impression of the aspect ratios in the range shown.

Table 1. Morphologies of pristine presolar SiC grains.

Grain morphology	% of total*
Grains with crystal faces	89
Euhedral crystals	20
Grains with polygonal decorations on crystal faces	54
Irregular grains	11
Coated grains	60
Other	
Rounded	4
"Etched"	7

[a] Based on field emission SEM imaging of 81 SiC grains from Murchison.

3.2. Grain Surface Morphologies

Images of presolar SiC published in research and review articles have tended to foster the impression that this material is often in the form of near-perfect euhedral crystals. However, such crystals, in fact, do not typify the majority of SiC grains from acid-dissolution residues, nor are they generally representative of pristine presolar SiCs, as we discuss below. On the basis of FESEM images of the 81 pristine grains from Murchison, we characterized the grains in terms of several surface morphology classes: 1) those having at least one visible crystal face, including both euhedral and subhedral forms; 2) those exhibiting regular geometric features on crystal faces; 3) those that are irregular and/or possibly fragments (i.e., the converse of class 1); 4) those that have apparent surface coatings in FESEM images; 5) those that are rounded or have surface features similar to chemically etched SiC grains. It should be noted that, with the exception of (1) and (3), these classes are not mutually exclusive, so that the sum of all five classes does not total 100%. The abundances of these classes, based on FESEM images, are summarized in Table 1. In the following subsections, we describe these classes in turn and draw only such inferences as follow directly from the observations; in the "Discussion" section we take up broader implications and issues.

3.2.1. Crystal Faces

A large fraction (89%) of pristine SiC grains are bounded in part by one or more planar surfaces (Table 1). Of these, 22% (i.e., 20% of all SiCs studied) are bounded by a sufficient number of planar surfaces that the terms "euhedral crystal" (Fig. 5a–d) or "subhedral crystal" (Fig. 5e,f) are appropriate for them. In using these terms, we do not imply that the planar surfaces are necessarily smooth, but only that requisite symmetry elements of the SiC are sufficiently apparent that these planar surfaces can be construed to be real crystal faces that manifest the molecular structure of the SiC. Specifically, we require that the angles between planar surfaces correspond to interfacial angles appropriate for (typically cubic) SiC. In determining the interfacial angles from SEM images, however, one must ensure that the viewing direction is roughly parallel to the direction of the zone containing the faces to prevent large systematic errors. Whether this condition is satisfied can be

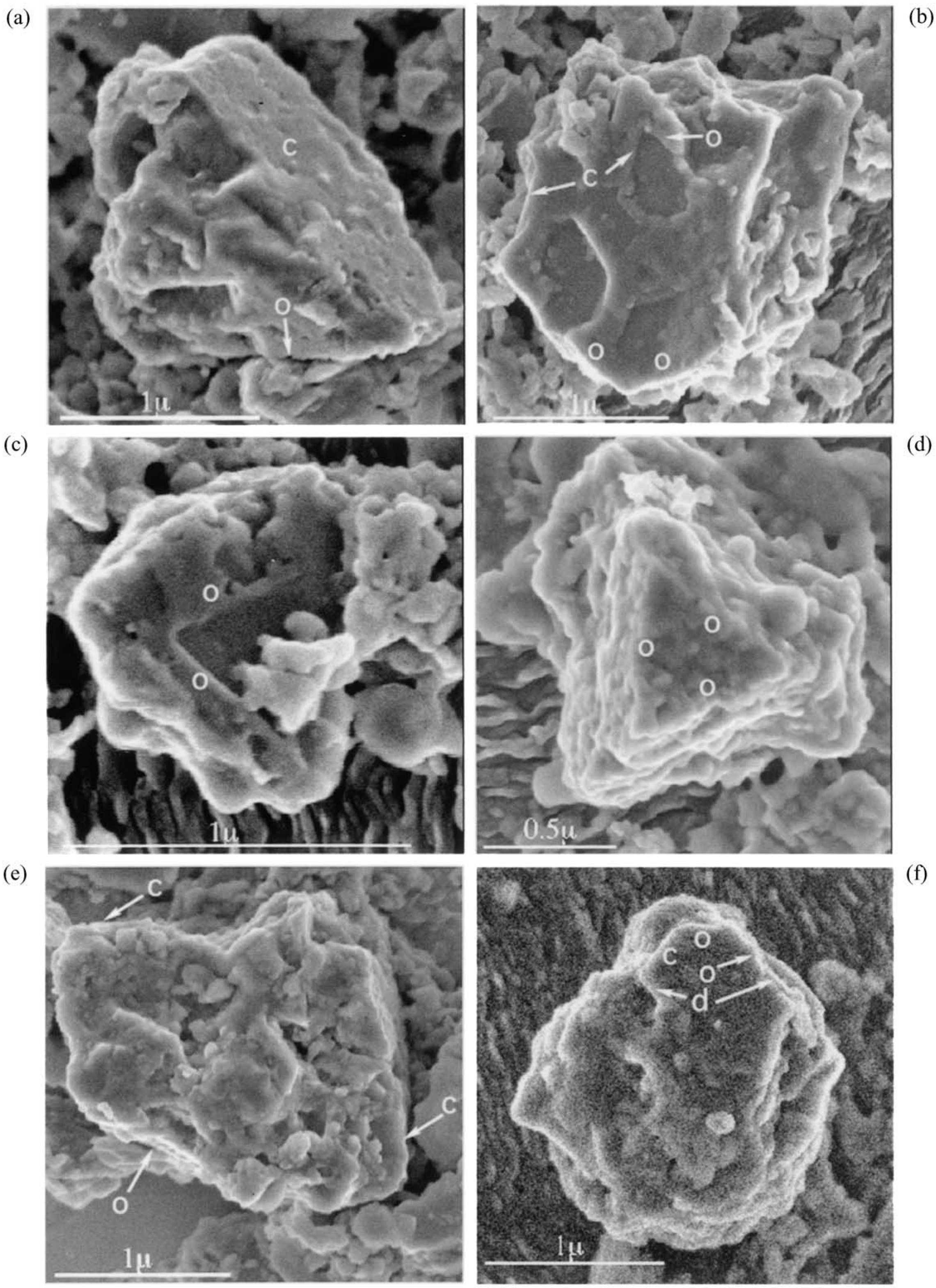

Fig 5. FESEM images of sample pristine presolar SiC grains from Murchison exhibiting primary growth crystal faces (a-f) and polygonal depressions (a-c). Scale bars are 1 μm, except for (d) where the scale bar is 0.5 μm. Letters within panels indicate forms for cubic SiC crystals: c = cube, o = octahedron; and d = dodecahedron. Panels (a) - (d) show "euhedral" crystals with several well-developed faces. The grain in panel (d) has surface pits and stratification similar to features in some artificially etched presolar SiC grains (cf. Fig. 6d). Panels (e) and (f) show subhedral crystals with few and/or imperfectly developed faces. See text for discussion.

evaluated if multiple crystal forms are evident on the same grain. For example, the crystal in Figure 5f is viewed along a cubic <110> zone direction. The forms cube (c = {100}), octahedron (o = {111}), and dodecahedron (d = {110}) can be identified self-consistently as symmetry elements of a cubic crystal on the basis of the measured angles between these forms (c ˆ o ∼ 55°; d ˆ o ∼ 35°; o ˆ o ∼ 70°). In some cases, multiple instances of a single form can reveal the essential symmetry elements. The crystal in Figure 5d, although somewhat corroded in appearance, has side faces whose top edges meet at angles ∼ 60°, consistent with the interpretation that this is a cubic crystal consisting only of octahedral {111} forms that is viewed along a <111> zone direction. Examples such as these illustrate that crystal faces are indeed present on pristine presolar SiC grains, so it is reasonable to assume that even for cases where only one planar surface is evident on a SiC grain, the surface is probably a crystal face. It follows that most of the pristine presolar SiC grains from Murchison studied here (89%) entered the solar nebula substantially intact, and that their external morphologies, developed during growth in circumstellar outflows, were partly or nearly completely preserved despite having been subject to a wide variety of potentially destructive environments (ISM, solar nebula, meteorite parent body) since their formation.

3.2.2. Polygonal Decorations on Crystal Faces

The preservation of original surface features is even more complete than indicated by the mere presence of crystal faces. In about half of all pristine grains (54%; Table 1), the crystal faces are also decorated with shallow (generally <100 nm deep), polygonal depressions (e.g., Fig. 5a–c). Crystallographic control of the development of these features is manifest, because the boundaries of the depressions often parallel crystal faces that are present and/or have angular relationships that correspond to interfacial angles in 3C SiC crystals (Fig. 5b,c). Two possibilities for the origin of these features are that: 1) they represent primary growth features, developed during the formation of the crystal faces themselves, or 2) they are the result of subsequent chemical dissolution (etching) of crystal faces (e.g., in the meteorite parent body or solar nebula). In general, it is difficult to differentiate these processes from the surface morphology alone, because the results of both are influenced by the underlying crystal structure and the presence of lattice defects. Nonetheless, in the present case we can observe the consequences of chemical etching of presolar SiC for comparison with surface features of pristine SiC grains, because very pure separates of presolar SiC have been prepared by subjecting Murchison and other meteorites to a variety of harsh chemical reagents (HF, HCl, $HClO_4$, H_2SO_4, NaOH; Amari et al., 1994).

To investigate the second possibility (above), we imaged SiC grains from the Murchison KJG separate (nominal size 1.5–3 μm; Amari et al., 1994) in the FESEM under the same conditions as those used for the pristine grains. Examples of etched KJG grains are shown in Figure 6. Our interpretation of these images hinges on the following suppositions: if the surface polygonal features on the pristine grains are the result of etching rather than crystal growth, we would expect the chemical treatment to result simply in more of the same kinds of features. On the other hand, if these are primary growth features, then the chemical treatment could result in alteration of such features on the KJG grains and/or the creation of new kinds of surface features. Inspection of Figure 6 shows that the effects of etching vary from grain to grain. Some grains appear to be severely corroded (Fig. 6d–f), whereas others show little evidence of chemical attack (Fig. 6c), which we take to indicate the importance of defect densities (through preferential chemical attack of lattice defects) in the development of etch features (see below). Many grains (e.g., Fig. 6b) fall between these two extremes, and show new features that are apparently the result of etching, along with the same kinds of polygonal depressions observed on the pristine grains (e.g., Fig. 6a). In particular, while the overall crystal shape of etched grains is preserved, often the etched grain surfaces have numerous small pits (<100 nm; Fig. 6b), some irregular and some exhibiting crystallographic control, that are not generally observed on pristine grains. Stratification along <111> directions reflecting development of relief parallel to {111} planes is also evident in some etched grains (Fig. 6b,d). Although surfaces on a small fraction (7%) of the pristine grains (e.g., Fig. 5d) resemble those of the etched grains, most do not. The principal result of etching presolar SiC appears to be surface corrosion and/or the production of small pits and/or stratification. Overall, while etched grains share some of the same morphologic features of the pristine grains, the characteristics of ensembles of each kind of grain are reasonably distinct.

It is likely that selective chemical attack of lattice defects is responsible for the development of the additional surface features observed on the etched KJG SiC grains. High-resolution transmission electron microscopy and electron diffraction studies of presolar SiC (Daulton et al., 2003) have shown that high densities of stacking faults (planar defects) are often present, so preferential etching of these faults is a plausible source of the stratification observed in some of the etched SiCs. No data are available for linear dislocations in presolar SiC; however, studies of synthetic SiC (e.g., Berezina et al., 1970; Gorin et al., 1970) show that linear defects (edge and screw dislocations) are preferentially etched and produce surface pits. We thus infer that these are a plausible source of the pits and corrosion features observed in the KJG grains. In this regard, we note that screw dislocations are, in fact, the growth mechanism of SiC, as has been firmly established through countless studies (see Verma, 1953; Frantsevich, 1970), so that the presence of this type of linear defect in presolar SiC is practically assured. It seems reasonable to infer, therefore, that the variation in the extent of chemical attack of the KJG SiC grains is related to variation in the number density of structural defects from grain to grain. If we interpret the pits observed in the surfaces of many etched KJG grains as indicating the location of linear defects (e.g., Fig. 6b,d), then the defect number density in these pitted grains is apparently quite high, $\sim 10^8$–10^9/cm^2, ∼3 to 4 orders of magnitude greater than in typical synthetic SiCs. This high defect density likely indicates conditions of rapid grain growth. For the small fraction of KJG grains showing few pits (e.g., Fig. 6c), the size of the grains places only an upper limit, in the range $\sim 10^7$–10^8/cm^2, on the defect number density.

We note in passing that it is unlikely that the inferred high linear defect densities (specifically the densities in excess of those observed in synthetic SiC) are in part due to “latent

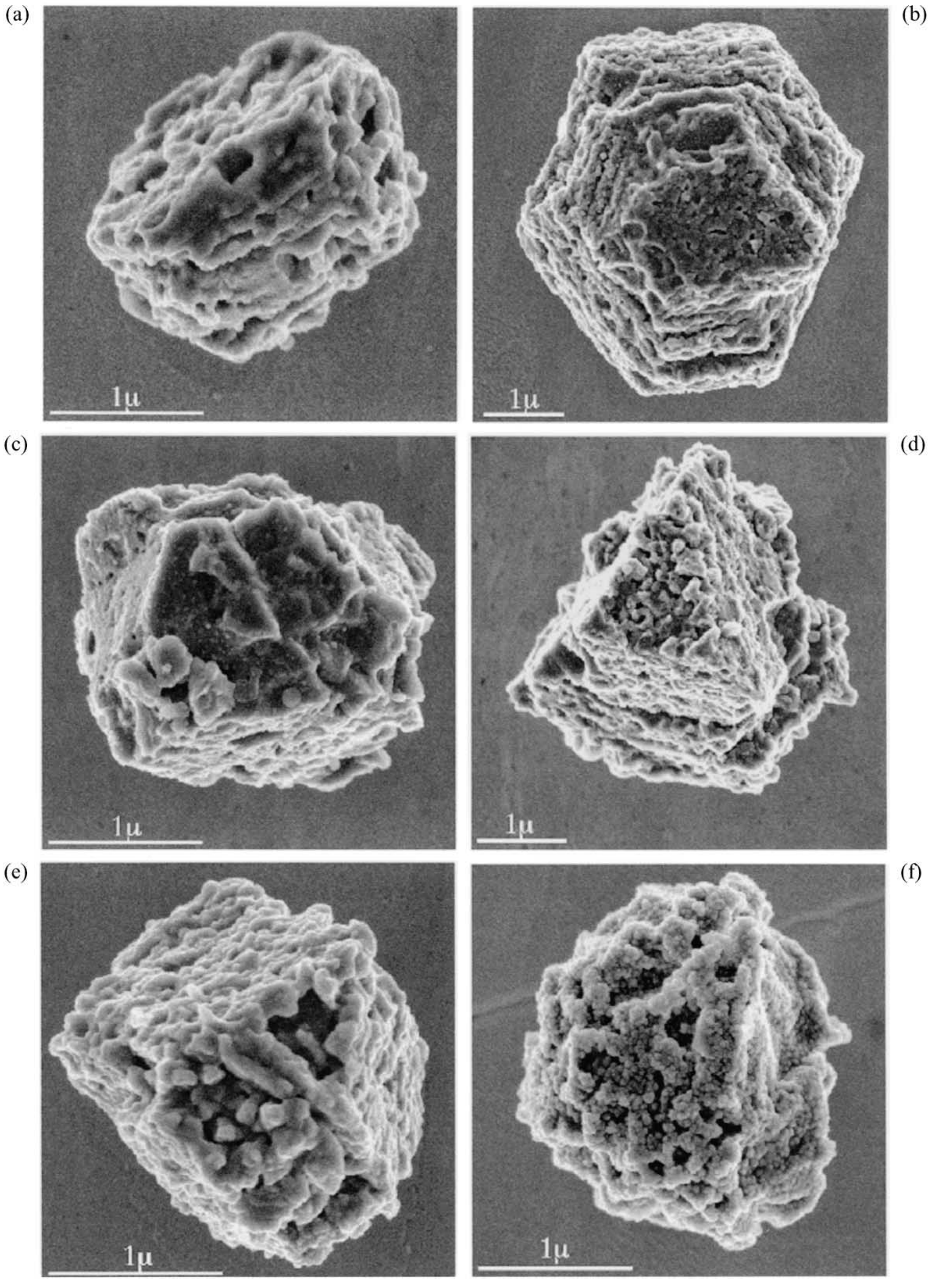

Fig 6. FESEM images of chemically etched presolar SiC grains from Murchison SiC separate KJG (Amari *et al.,* 1994). See text for discussion.

tracks" produced by exposure of SiC to low-energy galactic cosmic rays (GCR) or to solar flares in the solar system. The principal reason is that because SiC is a semiconductor, it is not expected to be able to register charged particle tracks at all. This can be tested experimentally, but to our knowledge it has not been done. Also, the flux of GCR at the low energies needed to produce tracks in SiC in the ISM is unknown. These uncertainties preclude any reliable analysis, and we will not further consider this possible source of defects.

The above considerations lead us to conclude that the polygonal depressions observed in more than half of the pristine SiC grains (e.g., Fig. 5a–c; Table 1) are primary growth features, resulting from incomplete filling of near-surface lattice sites during the formation of the crystals in their circumstellar environments. The depressions most likely represent areas of incomplete convergence of growth fronts from multiple screw dislocations. Overall, the high inferred defect densities, coupled with the presence of polygonal surface depressions, suggest that the SiC crystal growth was initially rapid but was later effectively quenched when the gas phase became too rarefied for continued growth.

Isotopic studies of presolar SiC grains indicate that the majority (>95%) originate around low mass carbon asymptotic giant branch (AGB) stars (Zinner, 1998; Daulton et al., 2002; 2003), meaning that the surface features observed in most pristine SiC grains must originate in the mass outflows (envelopes) of such stars. As concluded by Lodders and Fegley (1997) on the basis of trace element abundance patterns (Amari et al., 1995), circumstellar SiC probably formed in the inner regions of carbon star envelopes where temperatures are sufficiently high for thermochemical equilibrium to be maintained. In the outer regions of the envelopes, however, the temperatures and pressures rapidly drop with increasing distance from the stellar photosphere because of adiabatic gas expansion (Daulton et al., 2002, 2003), so that continued growth progressively becomes kinetically inhibited and eventually ceases. The complete absence of overgrowths of less refractory phases on SiC surfaces points to the arresting of heterogeneous nucleation in the stellar outflow, as well as effective cessation of back-reactions of SiC with the gas that would have resulted in the formation of primary phases such as forsterite on SiC at lower temperatures (Lodders and Fegley, 1995). We note in passing that the experimental protocol used here would not have precluded the detection of SiC grains overgrown by such primary silicate material had they been present in our samples, as evidenced by the fact that more than half of the pristine SiC grains detected were indeed coated with a fine-grained or amorphous material (see section 3.2.4).

3.2.3. *Irregular Grains*

About one-tenth of the 81 pristine SiC grains studied show no evidence of crystal faces and thus represent cases for which formation conditions were unfavorable for their development or in which the grains were fragmented (Table 1). In general it is difficult to decide, but at least a few grains are sufficiently nonequant that they are plausibly fragments (e.g., Fig. 7f). Moreover, even some of the grains that have well-defined sets of crystal faces appear to have surfaces that may have resulted from fracturing (e.g., the upper end of the crystal in Fig. 5b). Because the SiC grains were once part of an asteroidal regolith, it is possible that some instances of fragmentation occurred in this environment. However, we have seen no other evidence of regolith processing, such as collisional "zap" pits (as occur in lunar regolith grains) in any of the pristine SiCs studied. It is thus worthwhile to consider other environments where fragmentation may also have occurred. For example, theoretical studies suggest that that fragmentation may occur as the result of grain–grain collisions induced by supernova shocks in the ISM (Jones et al., 1997). We will consider this possibility later (see "Discussion").

3.2.4. *Coated Grains*

An interesting observation is that 60% of the pristine SiC grains appear to be coated with a thin (<100 nm) layer of an apparently very fine-grained or amorphous material. Examples of coated grains are displayed in Figure 7a–d. At present we do not know very much about the nature of these coatings, but we do have some observations that constrain possible explanations and suggest future experiments. The major peaks in EDS spectra of coated SiC grains are from Si and C. In some cases a very small Al peak is observed. A much larger O peak (representing up to several atom % O) is often present. The Si and C are certainly due in part to fluorescence of the underlying SiC. This is also likely the case for Al, which is detected in half of the KJG grains. Very minor Mg is sometimes seen in the EDS spectra of both coated and uncoated SiCs, but is often attributable to adjacent or adhering silicate grains.

One obvious possibility is that the coatings are simply experimental artifacts, namely very fine-grained material that adhered to the surface of the grains during sample deposition and evaporation of the suspension liquid. Although this may account for coatings in some cases, in other cases it does not. For instance, in Figure 7b–d, the graphite substrate in the vicinity of the grains appears to be free of any coating, and in some cases the coatings are evident only on part of the grain surfaces (Fig. 7d).

Another possibility is that the coatings are silica (SiO_2), caused by oxidation of the presolar SiC in the solar nebula, as discussed in the context of careful recent experiments on SiC oxidation by Mendybaev et al. (2002). These authors have shown that under oxidizing conditions ($\log fO_2 >$ IW-3), silica forms a thin layer on SiC and mediates the loss of C as CO to the ambient gas, whereas under more reducing conditions ($\log fO_2 <$ IW-6), there is active oxidation of essentially bare SiC surfaces (which lose both Si and C to SiO and CO vapor, respectively). Because the oxygen fugacities in the solar nebula may have ranged within 3 to 4 log units of IW-6 (Rubin et al., 1988), both mechanisms may have played a role in the weathering of presolar SiC. Comparison of EDS spectra of noncoated pristine SiC with vapor-deposited films of SiO_2 (having thicknesses ranging from 10 nm to 200 nm) implies silica surface layers in the range of 8 nm to 15 nm on the pristine presolar SiC, compared to ≤2.5 nm coatings on a terrestrial SiC standard (Macke et al., 1999). Interestingly, EDS measurements of Murchison KJG presolar SiC show O concentrations similar to those seen in the pristine SiC grains. In the production of the KJG separate (Amari et al., 1994), the SiC grains were subjected to strongly oxidizing agents (e.g., $Na_2Cr_2O_7$, $HClO_4$ and

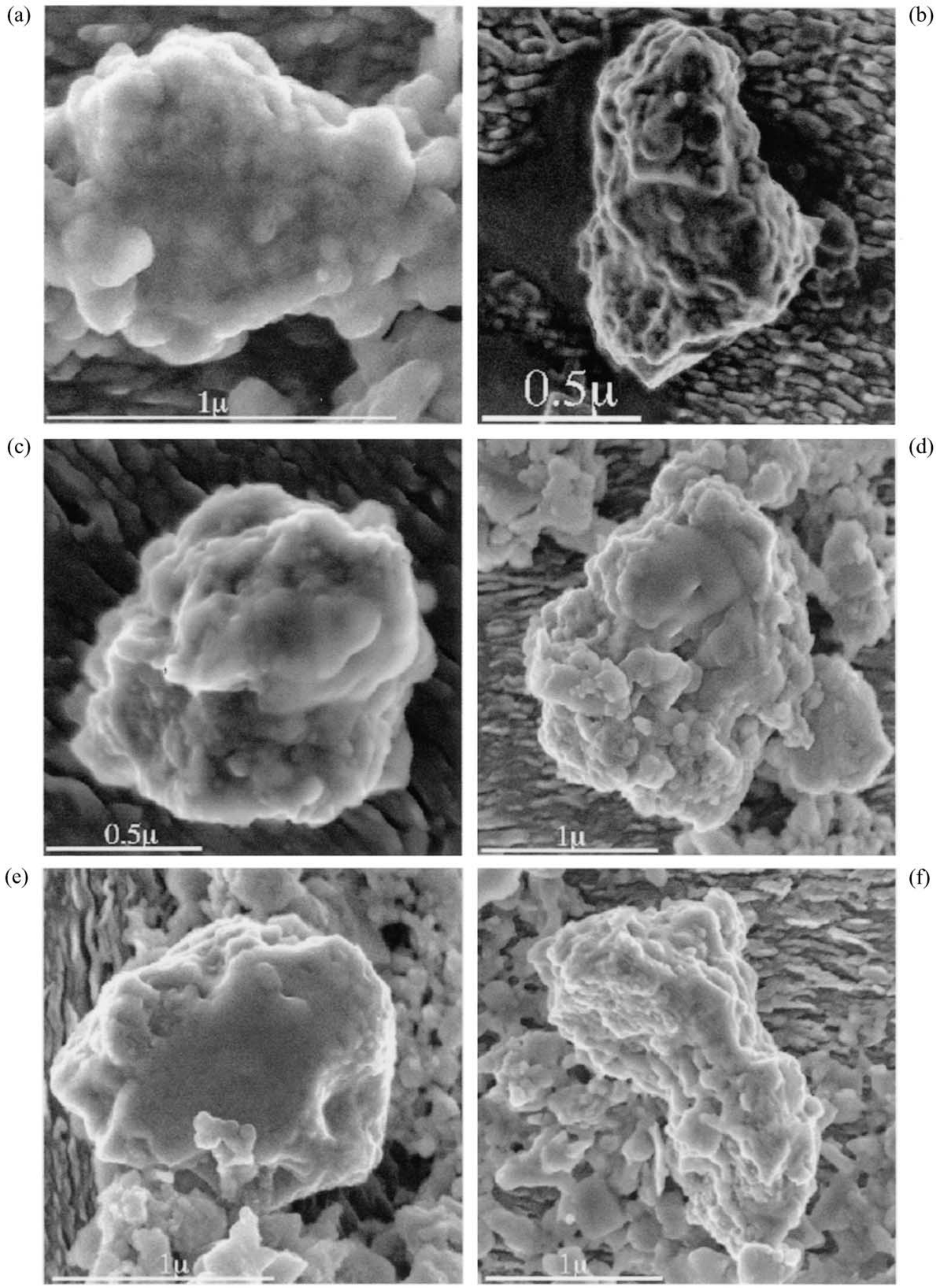

Fig 7. FESEM images of coated (a - d), rounded (e), and irregular (f) pristine presolar SiC grains from Murchison. In panels (b - f) the graphite planchet substrate is visible in the background. Scale bars are indicated in the panels. See text for discussion.

H_2SO_4), so the similarity of the O concentrations of the pristine SiC grains to those of the KJG separate again suggests that the pristine grains have been oxidized in nature at some time in their history.

Obviously, it is desirable to be able to view the pristine SiC grains in cross section, and to study in detail the structural and compositional transition from grain interior to surface. We have made an initial attempt at this, by producing an ultrathin section of a noncoated pristine grain using the focused ion beam (FIB) technique (Stroud et al., 2002). The sectioned grain was one of the 81 grains reported here, and transmission electron microscopy investigation of the section revealed the presence of a nanocrystalline or amorphous silicate rim ranging in thickness from 15 to 50 nm (Stroud et al., 2003). This result is broadly consistent with the silica rim thicknesses inferred by EDS analyses of other presolar SiCs, but unfortunately the sample support film failed before it could be determined whether the rim silicate was silica or not. We intend to investigate other pristine SiCs in the future using the FIB technique. For the present, we note, however, that we have observed no pervasive increase in the concentration of O in the grains that are obviously coated, as opposed to apparently noncoated pristine SiC grains, so the identification of the coatings as simply thick silica surface layers is not strongly indicated.

The above considerations leave us with the possibility that the coatings are material deposited passively on the surfaces of the pristine SiC grains, either in the solar system or in the ISM. It is possible that they are some form of organic carbon, since we seldom observe Mg in the EDS spectra of the coated grains (indicative of a prominent silicate component), and also because the coatings, unlike most silicates, sometimes appear to be electron beam-sensitive when they are spot-analyzed in the SEM. An intriguing possibility is that some of the coatings on pristine SiCs represent the remnants of organic mantles that resulted from processing of ices condensed on the grain surfaces (e.g., by ultraviolet photolysis and sublimation; Greenberg, 1976; Sandford et al., 1997) while the grains were still part of the ISM. Alternatively, the coatings might be amorphous SiC produced by ion irradiation in interstellar shock waves, as suggested by A. Jones (private communication, 2003). The coating thickness is appropriate for shock velocities of the order of 100 s of km/s. Given that the sputtering yield per incident ion is generally less than unity, this implies that most incident species implant. Thus, in this case the coating composition would reflect the interstellar gas abundances of the most abundant elements that are incident on the grains from the gas phase, having been shock-accelerated (H, He, C, O, N, and perhaps Mg, Si, and Fe). In any event, grain processing in the ISM may have left a signature in the isotopic composition of the organic elements H, C, O, and N (Tielens, 1997), which in principle may be revealed by future NanoSIMS analyses of the coatings.

3.2.5. Rounded and Etched Grains

A few of the pristine SiC grains have etch-like or rounding features (Table 1). None of these grains has any obvious coating. An example of a grain that has etch-like features is shown in Figure 5d. This grain has surface pits and stratification reminiscent of the KJG etched grains (Fig. 6d). A rounded grain is shown in Figure 7e. Both features are suggestive of chemical corrosion, and plausible means by which this may have occurred are oxidation reactions in the solar nebula and/or hydrothermal processes on the Murchison parent body that were arrested before complete destruction of the grains. If this is true, then the rounded and etched grains simply represent more extreme examples of the oxidation of the pristine SiC grains that we have already noted above. We will consider the implications of oxidative grain destruction in the "Discussion" that follows.

4. DISCUSSION

As noted in the "Introduction," the presolar SiC grains studied here necessarily have been exposed to many different environments before their laboratory recovery from the Murchison meteorite: the stellar atmospheres in which the vast majority of them formed, the ISM, the solar nebula, and the Murchison parent body regolith. At least some of these environments have imprinted their signatures on the grains. The development of crystal faces certainly occurred in the stellar atmosphere. The presence of polygonal depressions on the faces of pristine SiCs, and the high defect densities apparent in etched SiCs, both indicate conditions of rapid crystal growth. Comparison of chemically etched presolar SiCs with their pristine counterparts further indicates that the chemical processing used to isolate SiC grains for isotopic study only superficially affects the surfaces of SiCs in the $\sim$1 μm size range, enlarging defects but not destroying primary growth features such as crystal faces or polygonal depressions. On the other hand, the lack of less refractory primary phases (e.g., silicates that are predicted to form subsequent to SiC) on the SiC point to an effectively rapid arresting of SiC condensation and/or kinetic inhibition of subsequent reactions of the SiC with the parent gas phase in the stellar atmosphere.

A long-standing question in the study of the presolar SiC isolated by chemical means for isotopic studies (Amari et al., 1994) has been whether it was intergrown with or overgrown by other phases that may have been destroyed in the chemical processing. Prior work on locating presolar SiC in situ in the CM meteorites Murchison and Cold Bokkeveld (Alexander et al., 1990) indicated that the answer to this question is "no." The present study affirms this conclusion. In particular, it shows that primary oxide or silicate minerals sheathing the SiC do not exist and therefore cannot have been responsible for its survival in the solar nebula or in the ISM. The general question of the survival of presolar SiC in the solar nebula has been considered recently in detail in the context of SiC volatilization experiments by Mendybaev et al. (2002). They conclude that the lifetimes of presolar SiC grains exposed to a hot ($T \geq 900°C$) nebula are quite short (less than several thousand years) compared to nebular cooling timescales, so that the SiCs that did survive likely accreted late or in outer parts of the nebula. As discussed earlier, there is some evidence that even the surviving presolar SiCs were surficially oxidized, and the study of the nature and extent of surface oxidization remains as a challenging and important task for the future.

Theoretical studies of the survival of presolar grains in stellar atmospheres and in the ISM have evaluated the efficacy of mechanisms of grain alteration and destruction. Here we summarize the conclusions of Jones et al. (1997) with regard to these processes. It is unlikely that any significant destruction of SiC grains will occur as the result of drift velocity between the grains and gas in stellar mass outflows, since these are small ($\sim$1 km/s) compared to threshold velocities for sputtering ($\sim$35 km/s). Similarly, because these outflows impinge on the ISM with velocities ($\sim$5–20 km/s) less than the sputtering threshold, no significant sputtering is expected to occur in these shock fronts. However, energetic supernova shocks (as much as several hundred km/s) traversing interstellar clouds at intervals of a few $\times$ 10^7 y are thought to induce grain–grain collisions that lead to comminution of SiC grains of the size studied here, as well as surface sputtering from collisions of grains with gas and cratering by smaller particles. The present study of pristine SiC grains reveals no definitive evidence of such processing. Since $\sim$90% of the grains studied here have diameters $\geq$0.8 μm (representing between 5–10% of the Murchison SiC population; Amari et al., 1994), it is possible that by virtue of their large size they have escaped catastrophic collision events; however, they should not have escaped the effects of inertial sputtering, because this process is relatively insensitive to grain size (Jones et al., 1997).

As we have shown, crystal faces are present on practically all (89%) of the grains, and nanometer-scale surface features developed during their formation have been preserved on more than half of them. It can thus no longer be argued that the acid dissolution processing used to isolate presolar SiC may have removed the original surfaces of the grains and with them the evidence of grain weathering (Jones et al., 1997). Although some of the irregular grains studied here may represent the products of grain–grain collisions in the ISM, they may simply represent grains that have been shattered in the Murchison parent body regolith.

A facile solution to this difference between theory and observation consists in assuming that only a subset of those grains that were unprocessed in the ISM survived incorporation into the solar system, while those that were processed were either comminuted to sizes smaller than studied here, or else were entirely destroyed (Jones et al., 1997). It is difficult to evaluate this argument from the study of the pristine grains themselves; however, there are other data that can be used to evaluate the plausibility of this “all or nothing” hypothesis. Numerous studies have revealed a dependence of isotopic composition on grain size for Murchison SiC, for example $^{14}N/^{15}N$ (Hoppe et al., 1996), $^{20}Ne/^{22}Ne$, $^{4}He/^{22}Ne$ (Lewis et al., 1990), $^{80}Kr/^{82}Kr$, $^{86}Kr/^{82}Kr$ (Lewis et al., 1994), $^{50}Ti/^{46}Ti$, $^{50}Ti/^{49}Ti$ (Amari et al., 1996), $^{88}Sr/^{86}Sr$ (Podosek et al., 2003), and $^{138}Ba/^{136}Ba$ (Prombo et al., 1993). These trends presumably reflect a dependence of isotopic composition and the densities of stellar envelopes (hence the sizes of grains condensed) on stellar characteristics such as metallicity and mass. For example, the Z subclass of presolar SiC (with large excesses in ^{30}Si and deficiencies in ^{29}Si), which consist mostly of small ($<$2 μm) grains, are consistent with stellar models of low mass ($<$2.3 M_{Sun}), low metallicity AGB stars (Hoppe et al., 1997). If SiC grains in the ISM were extensively processed by shocks such that pervasive comminution of grains occurred, then it is difficult to understand how the observed isotopic covariance with grain size could have been preserved. Leaving aside the possibility that ISM grain processing theory is fundamentally flawed in either its assumptions or implementation, we can think of two hypotheses to account for the observed state of preservation of the pristine SiC grains: that the SiC grains sampled by the solar nebula represent relatively unprocessed (“new”) grains produced by stars in a short time interval before the formation of the solar system, or else that they were somehow protected against sputtering and communition in the ISM. In the current absence of any reliable means for assessing the exposure ages of presolar SiC in the ISM (Ott and Begemann, 2000), it is not possible at present to evaluate rigorously the first hypothesis. We only point out that the mean time interval between the production of the grains and their incorporation into the solar nebula would have to be much less than the mean lifetime against grain destruction in the ISM, estimated theoretically to be $\sim$5 $\times$ 10^8 y for silicates and graphite, and up to three times longer for SiC (Jones et al., 1997). With regard to the second hypothesis, we return to our speculation that some of the coatings observed on many pristine SiCs may be carbonaceous residues of processed ices that mantled the grains in the ISM. Icy mantles present on the SiC grains during their residence in the ISM, whether chemically processed or not, would certainly have served to protect them against inertial sputtering, and possibly may have mitigated the effects of grain–grain collisions. However, we note that most dust destruction is thought to occur in the warm ISM, where any icy mantles would be removed, leaving only more refractory residues on the grain surfaces. It is therefore important to investigate the chemical and isotopic compositions of the coatings on pristine SiCs to see whether they had their ultimate source in the ISM, and therefore can provide further information on the processing of grains in this environment.

Acknowledgments—We thank Ernst Zinner and Sachiko Amari for helpful discussions. We also thank Bob Macke for his efforts in the early phases of this study. This work was supported by NASA grant NAG5-10426.

Associate editor: U. Ott

REFERENCES

Alexander C. M. O’D., Swan P. and Walker R. M. (1990) In situ measurement of interstellar silicon carbide in two CM chondrite meteorites. *Nature* **348,** 715–717.

Amari S., Lewis R. S., and Anders E. (1994) Interstellar grains in meteorites: I. Isolation of SiC, graphite, and diamond; size distributions of SiC and graphite. *Geochim. Cosmochim. Acta* **58,** 459–470.

Amari S., Zinner E. and Lewis R. S.(1996) Ca and Ti isotopic compositions of size-separated SiC fractions from the Murchison meteorite. *Lunar Planet. Sci. XXVII*, 23–24 (abstr).

Amari S., Hoppe P., Zinner E., and Lewis R. S. (1995) Trace-element concentrations in single circumstellar silicon carbide grains from the Murchison meteorite. *Meteoritics* **30,** 679–693.

Berezina I. N., Shestakova N. A., Gurevich M. A., and Reifman M. B. (1970) Structural defects in silicon carbide single crystals. In *Silicon Carbide* (ed. I. N. Frantsevich), pp. 22–30. Consultants Bureau, New York.

Bernatowicz T. J. and Walker R. M. (1997) Ancient stardust in the laboratory. *Physics Today* **50 (*12*),** 26–32.

Bernatowicz T. J, Zinner E (1997), eds., *Astrophysical Implications of the Laboratory Study of Presolar Materials. AIP Conference Proceedings.* **402,** New York.

Bernatowicz T. J., Amari S., Zinner E. K., and Lewis R. S. (1991) Interstellar grains within interstellar grains. *Astrophys. J.* **373,** L73–L76.

Bernatowicz T. J., Cowsik R., Gibbons P. C., Lodders K., Fegley B., Jr., Amari S., and Lewis R. S. (1996) Constraints on stellar grain formation from presolar graphite in the Murchison meteorite. *Astrophys. J.* **472,** 760–782.

Chigai T., Yamamoto T., and Kozasa T. (2002) Heterogeneous condensation of presolar titanium carbide core-graphite mantle spherules. *Meteorit. Planet. Sci.* **37,** 1937–1951.

Croat T. K., Bernatowicz T., Amari S., Messenger S. and Stadermann F. J.(2003) Structural, chemical and isotopic microanalytical investigations of graphite from supernovae. *Geochim. Cosmochim. Acta*. **67**(24)**,** 4705–4725.

Daulton T. L., Bernatowicz T. J., Lewis R. S., Messenger S., Stadermann F. J., and Amari S. (2002) Polytype distribution in circumstellar silicon carbide. *Science* **296,** 1852–1855.

Daulton T. L., Bernatowicz T. J., Lewis R. S., Messenger S., Stadermann F. J. and Amari S.(2003) Polytype distribution of circumstellar silicon carbide. Microstructural characterization by transmission electron microscopy. *Geochim. Cosmochim. Acta*. **67**(24)**,** 4743–4767.

Frantsevich I. N. (1970) Theoretical and practical aspects of silicon carbide. In *Silicon Carbide* (ed. I. N. Frantsevich), pp. 1–6. Consultants Bureau, New York.

Goldstein J., Romig A., Newbury D., Lyman C., Echlin P., Fiori C., Joy D., and Lifshin E. (1992) Scanning Electron Microscopy and X-Ray Microanalysis. Plenum Press, New York.

Gorin S. N., Korsakova M. D., Palaguta Z. I., and Pletyushkin A. A. (1970) The etching of cubic silicon carbide crystals. In *Silicon Carbide* (ed. I. N. Frantsevich), pp. 192–203. Consultants Bureau, New York.

Greenberg J. M. (1976) Radical formation, chemical processing, and explosion of interstellar grains. *Astrophys. Space Sci.* **39,** 9–18.

Hoppe P., Amari S., Zinner E., Ireland T., and Lewis R. S. (1994) Carbon, nitrogen, magnesium, silicon, and titanium isotopic compositions of single interstellar silicon carbide grains from the Murchison carbonaceous chondrite. *Astrophys. J.* **430,** 870–890.

Hoppe P., Strebel R., Eberhardt P., Amari S., and Lewis R. S. (1996) Small SiC grains and a nitride grain of circumstellar origin from the Murchison meteorite: Implications for stellar evolution and nucleosynthesis. *Geochim. Cosmochim. Acta* **60,** 883–907.

Hoppe P., Annen P., Strebel R., Eberhardt P., Gallino R., Lugaro M., Amari S., and Lewis R. S. (1997) Meteoritic silicon carbide grains with unusual Si-isotopic compositions: Evidence for an origin in low-mass, low-metallicity asymptotic giant branch stars. *Astrophys. J.* **487,** L101–L104.

Hoppe P., Kocher T., Eberhardt P., Amari S., and Lewis R. S. (1998) Carbon- and nitrogen-isotopic compositions of individual, submicrometer-sized presolar silicon carbide grains. *Meteorit. Planet. Sci.* **33,** A71 (abstr)..

Huss G. R. (1997) The survival of presolar grains in solar system bodies. In *Astrophysical Implications of the Laboratory Study of Presolar Materials* (eds. T. J. Bernatowicz and E. Zinner), pp. 721–748. AIP, New York.

Huss G. R. and Lewis R. S. (1995) Presolar diamond, SiC, and graphite in primitive chondrites: Abundances as a function of meteorite class and petrologic type. *Geochim. Cosmochim. Acta* **59,** 115–160.

Jones A. P., Tielens A. G. G. M., Hollenbach D. J., and McKee C. F. (1997) The propagation and survival of interstellar grains. In *Astrophysical Implications of the Laboratory Study of Presolar Materials* (eds. T. J. Bernatowicz and E. Zinner), pp. 595–613. AIP, New York.

Lewis R. S., Amari S., and Anders E. (1990) Meteoritic silicon carbide: Pristine material from carbon stars. *Nature* **348,** 293–298.

Lewis R. S., Amari S., and Anders E. (1994) Interstellar grains in meteorites: II. SiC and its noble gases. *Geochim. Cosmochim. Acta* **58,** 471–494.

Lodders K. and Fegley B., Jr.. (1995) The origin of circumstellar silicon carbide grains found in meteorites. *Meteoritics* **30,** 661–678.

Lodders K. and Fegley B., Jr.. (1997) Complementary trace element abundances in meteoritic SiC grains and carbon star atmospheres. *Astrophys. J.* **484,** L71–L74.

Macke R. J., Bernatowicz T., Swan P., Walker R. M. and Zinner E.(1999) Non-chemical isolation of silica and presolar SiC from Murchison. *Lunar Planet Sci.* **XXX,** Abstract #1435, Lunar and Planetary Institute, Houston (CD-ROM).

Mendybaev R. A., Beckett J. R., Grossman L., Stolper E., Cooper R. F., and Bradley J. P. (2002) Volatilization kinetics of silicon carbide in reducing gases: An experimental study with applications to the survival of presolar grains in the solar nebula. *Geochim. Cosmochim. Acta* **66,** 661–682.

Ott U. and Begemann F. (2000) Spallation recoil and age of presolar grains in meteorites. *Meteorit. Planet. Sci.* **35,** 53–63.

Podosek F. A., Prombo C. A., Amari S. and Lewis R. S.(2003) s-Process isotopic compositions in presolar SiC from the Murchison meteorite. *Astrophys. J.* (in press).

Prombo C. A., Podosek F. A., Amari S., and Lewis R. S. (1993) s-Process Ba isotopic compositions in presolar SiC from the Murchison meteorite. *Astrophys. J.* **410,** 393–399.

RubinA. E., FegleyB., BrettR.(1988). Oxidation state in chondrites. In *Meteorites and the Early Solar System* (eds. J. F. Kerridge and M. S.Matthews). pp. 488–511. University of Arizona Press.

Sandford S., Allamandola A. and Bernstain M.(1997) The composition and ultraviolet and thermal processing of interstellar ices. In *From Stardust to Planetesimals* (eds. Y. J. Pendleton and A. G. G. M. Tielens), A.S.P. Conf. Series **122,** pp. 201–213.

Sharp C. M. and Wasserburg G. J. (1995) Molecular equilibria and condensation temperatures in carbon-rich gases. *Geochim. Cosmochim. Acta* **59,** 1633–1652.

Stadermann F. J., Walker R. M. and Zinner E.(1999) Sub-micron isotopic measurements with the CAMECA NanoSIMS. *Lunar Planet Sci.* **XXX,** Abstract #1407, Lunar and Planetary Institute, Houston (CD-ROM).

Stroud R. M., O'Grady M., Nittler L. R. and Alexander C. M. O'D.(2002). Transmission electron microscopy of an in situ presolar silicon carbide grain. *Lunar Planet Sci.* **XXXIII,** Abstract #1785, Lunar and Planetary Institute, Houston (CD-ROM).

Stroud R. M., Nittler L. R., Alexander C. M. O'D. Bernatowicz T. J. and Messenger S. R.(2003). Transmission electron microscopy of non-etched presolar silicon carbide. *Lunar Planet Sci.* **XXXIV,** Abstract #1755, Lunar and Planetary Institute, Houston (CD-ROM).

Tielens A. G. G. M. (1997) Deuterium and interstellar chemical processes. In *Astrophysical Implications of the Laboratory Study of Presolar Materials* (eds. T. J. Bernatowicz and E. K. Zinner), pp. 523–544. AIP, New York.

Verma A. R. (1953) *Crystal Growth and Dislocations*. Academic Press Inc., London. 182 pp.

Zinner E. (1998) Stellar nucleosynthesis and the isotopic composition of presolar grains from primitive meteorites. *Annu. Rev. Earth Planet. Sci.* **26,** 147–188.

Zinner E., Amari S., Messenger S., Nguyen A., Stadermann F. J., Walker R. M., and Lewis R. S. (2001) Isotopic analysis of small presolar SiC grains with the NanoSIMS ion microprobe. *Meteorit. Planet. Sci.* **36,** A231 (abstr)..