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Silicon, carbon, and nitrogen isotopic studies of silicon carbide in carbonaceous and enstatite chondrites

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Abstract—Both carbonaceous and enstatite chondrites contain complex populations of silicon carbide (SiC) grains. SiC in carbonaceous chondrites contains highly anomalous Si, C, and N. Individual SiC grains and aggregates of sub-micron SiC analysed in this study show variations in δ^{29}Si and δ^{30}Si exceeding 120 per mil, δ^{13}C values ranging from −300 to +24,500, and δ^{15}N values between −390 and −960. This range of isotopic compositions suggests that the total SiC population consists of families of grains formed in a variety of stellar sites (ZINNER *et al.*, 1989; TANG *et al.*, 1989). One such family, common to Orgueil and Murchison, and distinguished by a platy surface morphology, contains consistently anomalous Si defining a binary mixing array in the Si three-isotope diagram. On formation, these grains incorporated varying proportions of two exotic Si components, one enriched in ^{28}Si, the other in ^{29}Si and ^{30}Si relative to normal Si. Grains belonging to this family are consistently enriched in ^{13}C and ^{14}N relative to the solar isotopic compositions of these elements. The most plausible source for these grains is the circumstellar envelope of a low-mass red giant star on the Asymptotic Giant Branch (AGB) (GALLINO *et al.*, 1990). In this case, the ^{28}Si-rich component represents the seed composition preserved in the stellar envelope, to which was added ^{29}Si and ^{30}Si produced by neutron capture during He-burning. Enrichments in ^{13}C and ^{14}N are attributable to proton capture following convective dredge-down of H into the top of the He layer. The poor correlation of C and N with Si isotopes in the platy SiC grains suggests condensation over a number of convective mixing episodes, which enriched the stellar envelope in ^{13}C and ^{14}N to differing degrees.

Silicon carbide grains in Indarch differ in size and surface texture from those found in the carbonaceous chondrites. None of the Indarch grains analysed in this study contains isotopically anomalous Si or C, an observation difficult to reconcile with high concentration of the ^{22}Ne-rich component, Ne-E(H), found in Indarch acid residues (HUSS, 1990). The grains analysed in this study either belong to a SiC family distinct from that presumed to host Ne-E(H), or formed in a region characterised by isotopically normal Si and C but anomalous Ne. In the former case, a solar-system origin for the grains analysed in this work cannot be ruled out.

INTRODUCTION

EARLY CARBON ISOTOPIC studies revealed that the C2 chondrite Murchison contained an oxidation-resistant phase highly enriched in ^{13}C (SWART *et al.*, 1982; YANG and EPSTEIN, 1984). This phase was found to persist in acid-dissolution residues of the meteorite, allowing it to be concentrated relative to isotopically normal material for more detailed study. Its acid resistance and breakdown temperature in stepwise-heating experiments led SWART *et al.* (1982) to suggest that this phase might also be the carrier of the anomalous noble gas components Ne-E(H) (rich in ^{22}Ne) and Xe-S (dominated by isotopes made in s-process nucleosynthesis) found previously in Murchison residues (SRINIVASAN and ANDERS, 1978). Ion microprobe studies confirmed that ^{13}C enrichments in Murchison were concentrated in micron-sized grains, some with δ^{13}C values as high as +7000 (NIEDERER *et al.*, 1985; ZINNER and EPSTEIN, 1987). Ion microscopy carried out by ZINNER and EPSTEIN (1987) showed Si$^+$ ion emission spatially associated with the ^{13}C-rich carbon, suggesting silicon carbide as a possible carrier phase. The search culminated with identification of SiC by transmission electron microscopy (TEM) in several Ne-E- and Xe-S-rich residues of the Murray (C2) meteorite (BERNATOWICZ *et al.*, 1987), and ion probe measurements which showed that this phase contained not only anomalous C, but Si and N with unusual isotopic compositions as well (ZINNER *et al.*, 1987).

Silicon carbide grains in the C2 meteorites show features characteristic of material formed outside, and presumably prior to, the solar system. They are required to have condensed from a gas with C/O > 1 (LARIMER and BARTHOLOMAY, 1978), in contrast to the refractory oxide and silicate phases in their host meteorites. The isotopic compositions of their constituent atoms, Si and C, differ strongly from solar values (ZINNER *et al.*, 1987, 1989; TANG

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et al., 1989; STONE *et al.*, 1990, 1991). The same is true of trace N, Ne, Kr, Xe, Ca, Ti, Sr, Ba, and Nd incorporated in the grains (TANG and ANDERS, 1988; OTT *et al.*, 1988; ZINNER *et al.*, 1989, 1991a; OTT and BEGEMANN, 1990; LEWIS *et al.*, 1990; IRELAND *et al.*, 1991). At least some fraction of the SiC contains excess spallation ^{21}Ne relative to bulk Murchison, suggesting a period of pre-solar irradiation (ZINNER *et al.*, 1989; LEWIS *et al.*, 1990).

Now that the existence of these exotic grains has been established, particular goals in further isotopic studies are to identify the environments in which they formed and to investigate the nucleosynthetic processes acting in those environments. Silicon, carbon, and nitrogen isotopic compositions, and the abundances of Ne-E and Xe-S, vary widely among SiC grain size fractions (*e.g.*, TANG *et al.*, 1988; TANG and ANDERS, 1988; ZINNER *et al.*, 1989). Large variations are also observed in Si, C, and N isotopic compositions amongst the coarsest SiC grains analysed individually in the ion microprobe (TANG *et al.*, 1989; ZINNER *et al.*, 1989; ALEXANDER *et al.*, 1990). It was believed until recently that the isotopic variability of Si must have originated through explosive nucleosynthesis in novae or supernovae; however, the combined presence of H-burning, He-burning, and s-process nucleosynthesic signatures in the C, N, and noble gas isotopic compositions of SiC pointed to an origin in red giant stars. The incompatibility between isotopic variations in Si and those in C, N, and the noble gases led to the interpretation that populations of grains with distinct Si isotopic compositions must have originated in (as many as six) separate red giant stars (TANG *et al.*, 1989; ZINNER *et al.*, 1989; ALEXANDER *et al.*, 1990). Clearly, a starting point for understanding the astrophysical phenomena through which these grains formed and evolved must be separation of the complex SiC population into its constituent families of related grains.

We undertook this work in an attempt to look for and understand the isotopic covariation of Si, C, and N in meteoritic SiC. In producing and characterising our acid residues, it became apparent that the goal of separating SiC into genetically related families of grains could best be achieved, at least for coarse grain sizes, by (1) using textural criteria observable by scanning electron microscopy (SEM) and (2) by confining our attention to grains large enough to be analysed individually. We attempted to enhance the efficiency of our search for families of related grains by producing residues from meteorites of different classes, since it seemed conceivable that the processes responsible for the distinctive features (*e.g.*, oxidation state, abundance of refractory material) of these classes might also have selected amongst various types of pre-solar material (HUSS, 1990).

EXPERIMENTAL METHODS

Acid residues

Four meteorites were chosen for examination: Orgueil (CI), Murchison (CM2), Leoville (C3V), and Indarch (E4). These differ principally in their bulk compositions, contents of refractory phases, overall "matrix" abundance, oxidation state, and degree of hydrothermal alteration, all dictated by P, T and fO_2 conditions which might have governed the preservation of SiC (HUSS, 1990). It was hoped that the comparative SiC contents of these meteorites would indicate the solar system processes crucial to SiC survival or destruction, potentially pointing to other samples rich in this and other exotic phases. Previous attempts to isolate SiC used the isotopically anomalous noble gas tracers Ne-E and Xe-S to indicate the abundance of SiC (TANG *et al.*, 1988; TANG and ANDERS, 1988; ANDERS, 1988). Early noble gas studies of the Leoville (MATSUDA *et al.*, 1980) and Indarch (CRABB and ANDERS, 1982) meteorites showed little evidence of Ne-E or Xe-S (though optimal methods for revealing these components, involving stepwise extraction of Ne and Xe from strongly oxidised acid residues, were not employed in either study). Accordingly, we included these meteorites in our set of samples to search for SiC components *not* associated with anomalous noble gases. Since commencing this work, HUSS (1990) has reported moderately high Ne-E concentrations in both Qingzhen (EH3) and Indarch, and SiC has been observed in Qingzhen (ALEXANDER *et al.*, 1991). The SiC abundance determined for Indarch in the course of this work, and that inferred by HUSS (1990) from Ne-E measurements, is discussed below.

Acid residues were prepared from whole meteorite samples (*i.e.*, without preliminary separation of chondrules and refractory inclusions from matrix material). As detailed below, comparison between SiC abundances found in these residues and those produced from matrix separates (TANG *et al.*, 1988; TANG and ANDERS, 1988; SWAN *et al.*, 1989; ZINNER *et al.*, 1989) provides information about the siting of the SiC. The dissolution procedures adopted follow those developed by the Chicago group for isolation of SiC (ALAERTS *et al.*, 1980; TANG *et al.*, 1988; TANG and ANDERS, 1988); the processing scheme is summarised in Fig. 1. Centimetre-sized pieces of each sample (some including fusion crust) were rinsed with distilled H_2O, methanol and benzene, then dissolved in 9 M HF/1 M HCl at approximately 50°C. For Indarch, rich in Fe-Ni metal, the HF treatment was preceeded by treatment with 3 M HCl. Fresh reagents were added as required to sustain reaction, typically at 6–12 hourly intervals, and sample tubes were sonicated for 30–60 minutes after each change. Each HF/HCl step was followed by treatment first with 6 M HCl and then with 1 M $AlCl_3$, successfully preventing formation of insoluble fluorides. After 4–6 of these cycles, the samples were again treated with organic solvents, followed by two further HF/HCl steps, leaving "CF" residues.

At this stage, the standard procedure was modified to allow recovery of coarse refractory material (such as hibonite and spinel) for Mg and Ti isotopic studies. The residues were suspended in methanol, to which CS_2 was added, forming a denser, immiscible phase. After vigorous

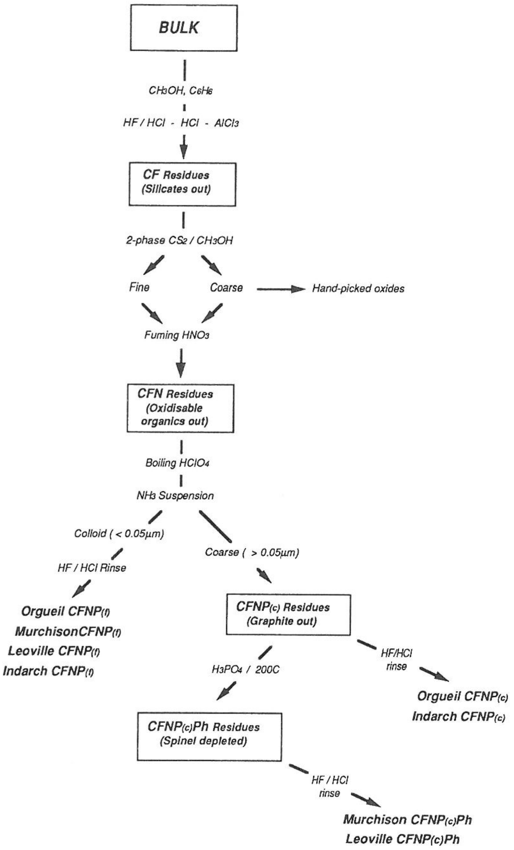

FIG. 1. Flowchart indicating methods used to concentrate SiC, as discussed in text. Procedures (reaction times, number of cycles per step) varied somewhat between samples according to amounts of metal/silicates/organics, etc. to be removed.

shaking, fine-grained material, especially black carbonaceous matter, separated into the methanol phase, whereas coarse, dense grains sank freely into the CS_2. After decanting the fine-grained suspension, centrifuging and drying, coarse grains could be hand-picked from the Orgueil and Murchison CS_2 fractions. (No attempt was made to recover equivalent material from Leoville; treatment of the Indarch residue in the above manner failed to yield any coarse material in the CS_2 phase.)

After recombining the coarse and fine fractions, the CF residues were oxidised, first in fuming HNO_3 (two changes, each 6–8 hours at 50–80°C) and then in boiling $HClO_4$ (two changes, each 1–2 hours). Reaction with $HClO_4$ was terminated on (sudden) bleaching of the formerly black suspensions, leaving small quantities of pale grey material. This was reacted briefly with HF/HCl, to dissolve any silica formed in the previous steps (*cf.* ZINNER *et al.*, 1987) and to remove a gelatinous orange precipitate formed on cooling of the $HClO_4$.

The oxidised "CFNP" residues were taken up in 5 ml of NH_3 solution, sonicated to suspend fine material (principally Cδ diamond, which was found to form a colourless colloid in basic solution by TANG and ANDERS, 1988 then separated into supernatant "$CFNP_{(f)}$" and residual "$CFNP_{(c)}$" fractions. This procedure was repeated 5–6 times, transferring the bulk of each residue into the fine-grained (<.05 μm) fraction. These fine-grained samples were given a final wash in HF/HCl to ensure removal of silica, rinsed, and stored under distilled methanol. The procedure was terminated at this stage for the Indarch and Orgueil residues, whose microgram-sized coarse fractions had become invisible in the base of their sample tubes.

The comparatively abundant coarse material remaining in the Murchison and Leoville residues was heated in 5 ml of 100% H_3PO_4 to ~200°C for three hours. The samples were observed to decrease in volume and darken (*cf.* TANG *et al.*, 1988); however, the treatment appears to have been terminated prematurely, as the final residues of both samples retain substantial quantities of spinel. In preference to risking contamination in weighing of the microgram residues, weights were estimated from optical microscope and SEM grain counts of aliquotted material. These values (presented in Table 1) are estimated to be accurate to within a factor of about two, adequate for comparative purposes.

Grain identifications

Aliquots of the residues were mounted on Au foils for SEM, electron probe, and ion probe analyses, using techniques similar to those described by MCKEEGAN *et al.* (1985). The 0.13 mm 99.99% Au foils were anchored by cold pressing (using a clean, stainless steel tool guided to form a flat Au surface) onto slotted upper surfaces of brass ion probe stubs. After briefly re-annealing the Au (hardened by pressing), the foils were washed in methanol and sputter-cleaned in an ion mill with 10 kV Ar^+ ions.

Acid residue grains were dispersed over the foils from a drop of distilled methanol and embedded by gentle pressing, using a second, work-hardened Au foil mount. The press was changed for each sample, to prevent carry-over of the few grains which inevitably lodged in its surface. Embedding with a second clean foil was found preferrable to pressing with a quartz disc (MCKEEGAN *et al.*, 1985); the latter method failed to embed grains uniformly over the slightly undulating surfaces of the mounts and appeared also to result in Si contamination of the foil surfaces. Grains up to 10 μm, pressed deeply into the Au foils, showed little tendency to charge under ion probe primary beam currents of up to 2 nA, though some charging occurred under electron beams of ~10 nA.

After mounting, grains were examined in the SEM. SiC could be tentatively distinguished from other possible Si-bearing phases (such as silica precipitated during the chemical processing), by its high yield of Si X-rays (SWAN *et al.*, 1989). Identifications made with the SEM were confirmed by semi-quantitative wavelength-dispersive X-ray analyses for C, N, and O in the electron probe. In addition to those SiC grains located and characterised in the SEM, a number of SiC grains were found as C^- "hot spots" in ion images. The sizes and surface textures of these grains are unknown. Judging from the intensity of their Si^- and C^- emission (and the fact that several sputtered away during analysis) most are (or were) on the order of ~1 μm.

Ion probe isotopic analyses

(1) Silicon. The isotopic compositions of Si, C, and N in selected grains and aggregates were determined using the Panurge IMS-3f ion microprobe (HUTCHEON *et al.*,

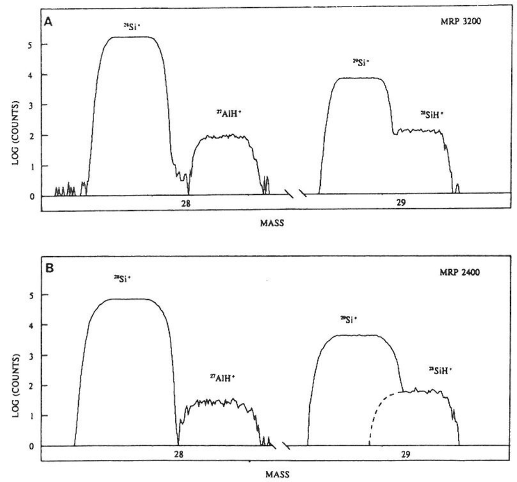

FIG. 2. Mass spectra showing resolution of isobars $^{28}Si^+$-$(^{27}AlH)^+$ and $^{29}Si^+$-$(^{28}SiH)^+$ at high mass resolving power (a), and partial overlap between $(^{28}SiH)^+$ and $^{29}Si^+$ at MRP = 2400 (b). The extent to which Si^+ ion yields can be maximised by degrading mass resolving power is dictated by overlap of intense $(^{27}AlH)^+$ beams (arising from Al-oxide grains in the residues) on $^{28}Si^+$ at resolving powers <2400.

1987). For the majority of the analyses, silicon was analysed as positive secondary ions, produced by a 0.2–0.5 nA $^{16}O^-$ primary beam rastered over a 20 μm square region surrounding each grain. The low sputter rate, <0.5 $\mu m\ hr^{-1}$, ensured preservation of material for C and N isotope studies. An 8 μm field aperture in the sample image plane transmitted only those ions originating at the centre of the rastered field, suppressing background Si^+ emission (from adjacent grains and impurities in and on the Au foil). In those cases in which the field aperture did not fully mask the sample grain, ion images were checked for other sources of Si^+ emission. Hibonite grains (containing a few percent SiO_2) were found to be the predominant source of spurious Si signals in the residues; these could be identified in ion images by their strong Al^+ and Ca^+ emission and, if necessary, avoided.

A mass resolving power (MRP) of greater than 3000 is required to separate fully hydride interferences $(^{28}SiH)^+$ and $(^{29}SiH)^+$ from isobaric Si^+ peaks, as shown in Fig. 2a. The high $(^{28}SiH)^+/^{29}Si^+$ ratios encountered when sputtering fine-grained material from the $CFNP_{(f)}$ series of residues required isotopic data to be taken at full resolving power. However, in order to maximise secondary ion transmission when analysing individual SiC grains, which yielded lower $(^{28}SiH)^+/^{29}Si^+$ ratios, resolving power was reduced to ~2400. This choice ensured separation of $^{28}Si^+$ from $(^{27}AlH)^+$ (arising from adjacent Al-bearing oxide grains), whilst limiting hydride tail contributions due to $(^{28}SiH)^+$ to <2 per mil of $^{29}Si^+$ signals (Fig. 2b), and yielding an ~2-fold gain in sensitivity. The overlap between $(^{28}SiH)^+$ and $^{29}Si^+$ was estimated at less than 2 per mil of the $^{29}Si^+$ signal both by peak stripping (Fig. 2b), and comparison of $^{29}Si/^{28}Si$ ratios measured at high and low MRP in synthetic SiC. The data reported here have not been corrected for this interference, as it proves negligible in comparison to isotopic effects intrinsic to the samples, and smaller than the typical statistical uncertainties due to ion counting in the $^{29}Si^+$ measurements.

Additional Si isotopic measurements were made in conjunction with subsequent C isotopic analyses. In these runs, Si was analysed as Si^- ions, sputtered by a ~0.1 nA Cs^+ primary ion beam defocussed over a 20 μm diameter area around the sample grain. The higher MRP of ~3500 required for concurrent C isotopic measurements (see below) ensured that the Si^- peaks were free of isobaric interferences. As for positive ion analyses, a field aperture was employed to minimise Si^- background contributions.

Nine of the negative ion analyses of Si isotopes were made on grains previously analysed using positive secondary ions, in order to check that sample grains could be relocated for C and N analyses, and to confirm the positive ion results. The comparison between measurements made with positive and negative secondary ions is shown in Fig. 3. The precision of the negative ion analyses is somewhat lower than that of the original data, due to the reduced transmission of the spectrometer at higher MRP. Nonetheless, the two sets of measurements are in full agreement, validating the positive ion results and confirming that the micron-sized SiC grains could be reliably relocated.

Sample Si isotopic compositions are expressed as $\delta^{29}Si$ and $\delta^{30}Si$, per mil deviations of $^{29}Si/^{28}Si$ and $^{30}Si/^{28}Si$ ratios, respectively, from values measured in synthetic SiC grains (5–10 μm grinding abrasive), mounted in an identical fashion to sample material. Sample to standard comparisons were made separately for the positive and negative secondary ion data, and in the former case relate data taken at the same mass resolving power. As an indication of the reproducibility of the data, the total scatter of Si isotope measurements on the synthetic SiC grains is shown in Fig. 4. For positive ion data this amounted to < ±2 per mil over the course of the study and was better than ±1.5 per mil on any given day, whilst the negative ion results scattered over a larger range of ±4 per mil, with a daily variability of ~ ±3 per mil. Instrumental mass fractionation for positive ion analysis of SiC, calculated by comparison of standard runs (made at high MRP) to the ref-

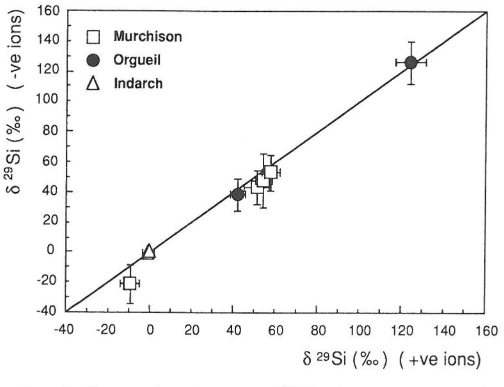

FIG. 3. Comparison between $\delta^{29}Si$ values measured with positive and negative secondary ions on the same sample grains. The data intersect a line of slope 1, indicating (1) good agreement between the Si^+ and Si^- measurements, (2) homogeneity of the grains over the depth sputtered in successive analyses, and (3) reliable relocation of grains on the sample mounts.

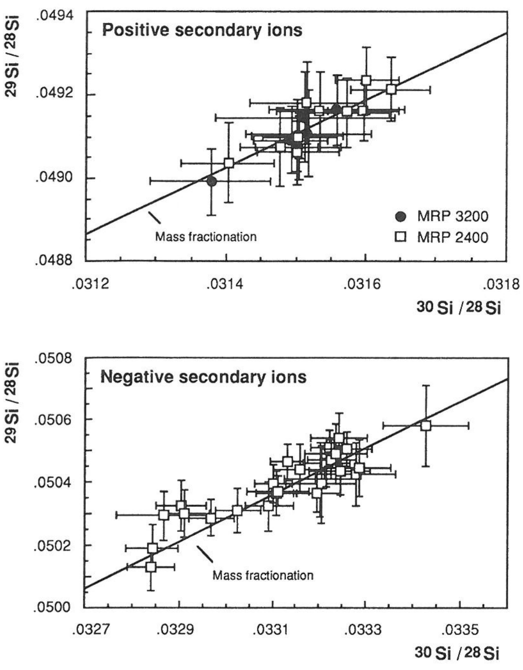

FIG. 4. SiC standard grain analyses made in the course of this work. Analyses of Si^+ secondary ions are shown in the top panel, analyses of Si^- secondary ions in the lower panel. Note that mass fractionation is much less for Si^- than Si^+ analyses. A power law mass-fractionation line drawn through the mean of the high MRP Si^+ data (dark symbols, top panel) intersects the normal $^{29}Si/^{28}Si$ value of 0.0506331 (BARNES *et al.*, 1975) at $^{30}Si/^{28}Si = 0.033464 \pm 0.000040$, in agreement with the value of 0.033450 ± 0.000066 calculated from the Si^- data. Note that standard data taken at low MRP (open symbols, top panel) are not substantially displaced from the fractionation line, indicating <2% interference of $(^{28}SiH)^+$ at $^{29}Si^+$. Indicated uncertainties are $\pm 2\sigma$.

erence $^{29}Si/^{28}Si$ value of 0.0506331 (BARNES *et al.*, 1975) is −30.3 per mil per amu, and that for negative ion analysis is −5.2 per mil per amu. This enrichment of the lighter Si isotopes is characteristic of ion probe Si isotope measurements. It is noteworthy that the $^{30}Si/^{28}Si$ ratios of the same SiC runs, corrected individually for fractionation using a power law fractionation function, indicate reference $^{30}Si/^{28}Si$ ratios of 0.033464 ± 0.000040 (positive secondary ions) and 0.033450 ± 0.000066 (negative secondary ions), in agreement with the value 0.033474 suggested by ZINNER *et al.* (1989), but differing significantly from the accepted value of 0.0336214 (BARNES *et al.*, 1975).

(2) Carbon. Carbon isotopic compositions were measured in a second series of runs, after heating the sample mounts to ~450°C in air for periods of 8–12 hours to remove carbonaceous material which might have survived the SiC separation procedure, and contaminants residing on the sample surfaces. Isotopic measurements were made on C^- secondary ions sputtered by a ~0.1 nA Cs^+ primary beam, as described above for Si^- analyses. A MRP of ~3500 was used to resolve the $^{13}C^-$ signal from interference by $(^{12}CH)^-$ ions. In order to check for spurious C contributions, the Si^-/C^- ion yield was measured for each sample grain and compared to the mean value measured for synthetic SiC standard grains. In all but two cases the Si^-/C^- ratios of sample grains agreed with that of the standard (1.28 ± .15). The low Si^-/C^- ratios shown by two grains (Orgueil G3 and Murchison G7; see Table 2) indicate extraneous carbon contributions and suggest that the $\delta^{13}C$ values measured on these grains may underestimate their true values. No corrections have been applied to these data, however, as the $\delta^{13}C$ value of the contaminant is unknown. Neither of these grains was analysed subsequently for N isotopes.

Carbon isotopic data are expressed as $\delta^{13}C$ values (analogous to $\delta^{29}Si$ and $\delta^{30}Si$ values) relative to the conventional PDB standard, for which $^{13}C/^{12}C = 0.011235$ (CRAIG, 1957). Delta values were first calculated relative to the mean $^{13}C/^{12}C$ ratio measured on synthetic SiC standard grains and these results adjusted to the PDB scale using a $\delta^{13}C_{PDB}$ value of −30.0‰ for the standard SiC (analysed in bulk by conventional mass spectrometry). The mean $^{13}C/^{12}C$ ratio for synthetic SiC grains measured by ion probe was 0.010488 ± 0.000034 (2σ, $n = 25$ analyses) representing an instrumental fractionation of −37.6 per mil. Deviation of individual standard analyses from this mean value amounted to < ±6.5 per mil over the course of the study, and < ±3 per mil on any given day.

(3) Nitrogen. In their initial work on meteoritic SiC, ZINNER *et al.* (1987) showed that isotopic measurements could be made on trace amounts of N contained in SiC. Sputtering does not produce monatomic N secondary ions, but generates intense CN^- emission from C-rich samples. This allowed N isotopes to be measured on a subset of the grains analysed for Si and C, in a third series of runs, using procedures similar to those described by ZINNER *et al.* (1989). A defocussed ~0.2 nA Cs^+ primary beam was used and the secondary beam masked by an 8 μm field aperture. The analyses were made at a MRP of ~6500. Under these conditions overlap between $(^{13}C_2)^-$ and $(^{12}C^{14}N)^-$ was eliminated, and well-resolved $(^{12}C^{15}N)^-$ and $(^{13}C^{14}N)^-$ signals could be collected at the mass 27 position, allowing C and N isotopic ratios to be determined simultaneously. The C isotopic data measured in this way (Fig. 5) showed satisfactory agreement with the results of $^{13}C^-/^{12}C^-$ analyses and confirmed that previously analysed grains had been relocated. A single exception (Orgueil G4; Table 2) gave $\delta^{13}C$ values of +907 and +609 in two successive analyses, compared to its original value of +1240, and these runs gave distinct Cn^-/C^- ratios of 0.05 and 0.46, respectively. This may represent a case of mistaken identity, or the original grain may have been a composite.

Cn^-/C^- ratios were measured during each analysis but cannot be used to calculate absolute N concentrations due to lack of a suitable N-bearing SiC standard. Nitrogen data are presented as $\delta^{15}N$ values, relative to the conventional air N standard ($^{15}N/^{14}N = 0.003676$; JUNK and SVEC, 1958). In order that data produced in this study be directly comparable to those of the Washington University group (ZINNER *et al.*, 1987, 1989, 1991b), we chose the same compound used previously, 1-hydroxybenzotriazole hydrate ($C_6H_5N_3O \cdot H_2O$) with $\delta^{15}N_{AIR} = -12$, as a working standard. The fact that N isotopic fractionation accompanying CN^- emission from this compound (−11 per mil) may differ from that accompanying emission from SiC adds some uncertainty to $\delta^{15}N$ measurements made in this way, though as discussed by ZINNER *et al.* (1989), this

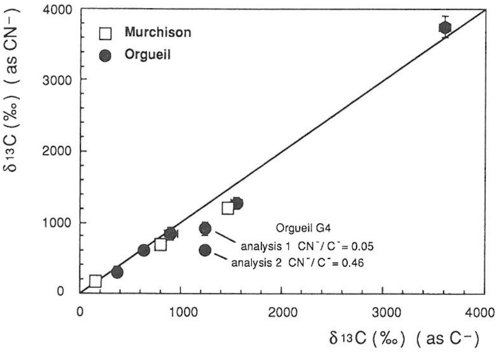

FIG. 5. Comparison between $\delta^{13}C$ values measured on the same sample grains using C^- and $(CN)^-$ secondary ions. The data show reasonable agreement with the 1:1 line. The tendency of the $(CN)^-$ analyses to yield values lower than those originally measured using C^- secondary ions may reflect build-up of carbonaceous contaminants (with normal $\delta^{13}C$ values) during and after the C^- analyses. Orgueil G4 (indicated) is either heterogeneous, or was mislocated in repeat analyses (though these analyses gave similar $\delta^{15}N$ values of -706 ± 106 and -748 ± 43).

source of systematic error is likely to be small and will not affect the conclusions drawn below.

RESULTS

Acid residues

Details of the coarse-grained acid residues examined in this study are summarised in Table 1 (the weights and mineral contents of the fine-grained samples have not been determined). In all of the residues, silicon carbide is a minor phase relative to oxides, ranging in fractional abundance from ~1% in Leoville $CFNP_{(c)}Ph$ to ~20% in Indarch $CFNP_{(c)}$. The Orgueil and Indarch residues, not processed through H_3PO_4, are dominated by spinel. In addition, a few grains of chromite and hibonite occur in the Orgueil sample. Both Orgueil and Indarch contain small grains (<2 μm) showing only a Ti X-ray line, possibly TiO_2 as suggested by ALEXANDER *et al.* (1989), a Ti-fluoride, or in the case of Indarch, perhaps osbornite, TiN. Titanium carbide, as observed by BERNATOWICZ *et al.* (1991), is a further possibility, though it is unlikely that coarse grains of this phase would have survived the acid dissolution procedures. Several grains showing only a Sn X-ray line (possibly cassiterite, SnO_2) occur in the Indarch residue. The final H_3PO_4 treatment applied to the Murchison and Leoville residues substantially reduced their spinel contents. However, spinel persists as coarse (mostly >1 μm) rounded grains at the 10–20% level in both these residues, in which hibonite and corundum are the major phases. Both residues also contain grains showing only a Ti X-ray line. The high corundum and hibonite contents of Murchison $CFNP_{(c)}Ph$ and Leoville $CFNP_{(c)}Ph$ most likely reflect the abundance of refractory aggregates and inclusions in the parental samples of these residues. Murchison residues described by ZINNER *et al.* (1989) contain SiC amounting to ~6 ppm of initial *matrix* material (*i.e.*, ~3 ppm of total meteorite, assuming ~50% matrix in Murchison), accompanied by only ~1 ppm of oxide grains. In comparison, the Murchison residue prepared in this study is equivalent to 3.4 ppm SiC accompanied by ~70 ppm insoluble oxides, indicating a much lower ratio of SiC to oxides in the refractory component of Murchison than in its matrix.

These observations highlight an interesting feature of the variability in SiC/refractory oxide ratios of the three carbonaceous chondrites examined—differences in this ratio are governed by differences in oxide abundance, with SiC concentrations remaining comparatively uniform. This conclusion is similar to that reached by HUSS (1990), who inferred the abundance of SiC in a large number of chondrites from their Ne-E(H) concentrations.

Table 1. Coarse-grained acid residues (>0.1 μm fractions)

Sample	Initial weight	Acid treatment(1)	Residue fraction (ppm)(2)	SiC fraction (ppm)(2)		Other phases(3)
				<1 μm	>1 μm	
Orgueil	2.10 g	CF, N, P	30	3	0.6	Sp, Chr, (Co), (Hib)
Murchison	9.89 g	CF, N, P, Ph	95	3	0.4	Sp, Chr, Cr-Sp, Hib, Co
Leoville	2.76 g	CF, N, P, Ph	400	4	<0.2	Sp, Chr, Cr-Sp, Hib, Co
Indarch	10.85 g	C, CF, N, P	2	0.3	0.1	Sp, Chr, (Co)

(1) C: 3M HCl, CF: 1M HCl/10M HF, N: fuming HNO_3, P: boiling $HClO_4$, Ph: H_3PO_4/200°C.

(2) Expressed as fractions of bulk meteorite. Residue weights estimated from SEM grain counts, considered accurate to a factor of ~2.

(3) Sp: spinel, Chr: chromite, Cr-Sp: Cr-spinel, Hib: hibonite, Co: corundum. Phases noted in brackets present at <2%.

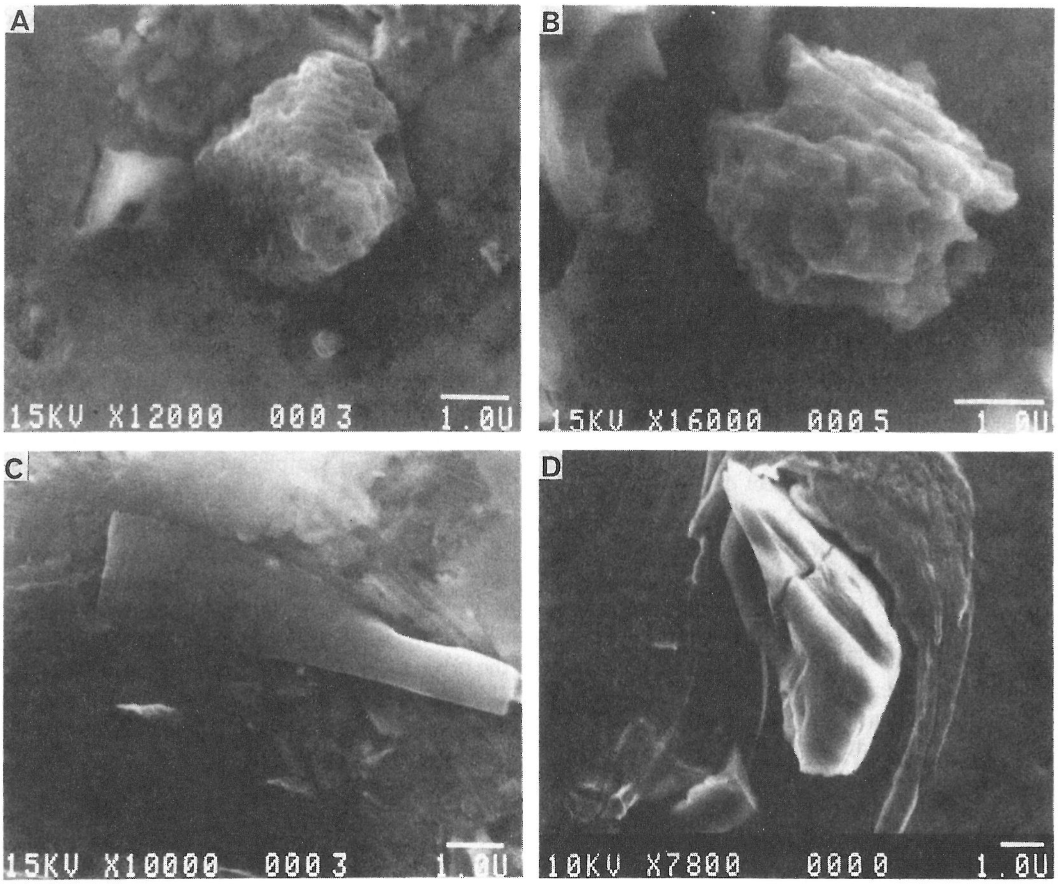

FIG. 6. SEM micrographs showing SiC grains from acid residues. Note the "platy" surface texture of SiC from Orgueil (a) and Murchison (b), in contrast to the conchoidally fractured and smooth surfaces of SiC grains in Indarch (c and d). The scale bar is 1 μm in all images.

There are discrepancies between the absolute SiC concentrations estimated by HUSS (1990) and those determined in this work, however, especially in the case of Leoville. It is difficult to compare the two sets of abundance estimates, since both may have been affected by losses during chemical processing and the abundances reported in this work do not include SiC in the CFNP$_{(f)}$ series of residues. Perhaps the tendency for the abundance of coarse-grained (>1 μm) SiC relative to fine SiC (<1 μm) to diminish from Orgueil to Murchison to Leoville reflects the same metamorphic process responsible for the variation in Ne-E(H) concentrations observed by HUSS (1990).

Silicon carbide in the Indarch CFNP$_{(c)}$ residue appears to occur at an abundance approximately one-tenth that in the carbonaceous chondrites (Table 1). This relative abundance is roughly in agreement with the Ne-E(H) data reported by HUSS (1990), though as in the case of the carbonaceous chondrites, the absolute SiC abundance inferred from the Ne data is 2–3 times higher than that estimated in this work.

The contrasting abundances and grain sizes of SiC between carbonaceous and enstatite chondrites are also reflected in the physical characteristics of the grains. The coarse SiC grains encountered in the carbonaceous chondrite residues occur in (at least) two forms (Fig. 6, *cf.* TANG *et al.*, 1989). Of the 22 coarse grains (from 2×2 μm to 9×10 μm) found in Orgueil (8), Murchison (11) and Leoville (3), 18 are approximately equant and characterised by a "platy" surface texture. Where grain shapes were evident, the "plates" appeared stacked normal to a 6-fold symmetry axis. This morphology suggests a $\langle 0001 \rangle$ cleavage or parting in hexagonal SiC (Fig. 6a), though some grains of this type may in fact possess cubic symmetry (WOPENKA *et al.*, 1989). The remaining grains from Murchison and Leoville are rounded and smooth-surfaced. TANG *et al.*

(1989), ZINNER *et al.* (1989), and WOPENKA *et al.* (1989) report a somewhat higher relative abundance of what are described as "smooth-surfaced" grains (as opposed to "fluffy," "fuzzy," or "weathered" types) in their Murchison residues, and in addition they distinguish two types of smooth-surfaced grains—those with crystal faces and those with conchoidally fractured surfaces. However, it is uncertain whether differences between the coarse SiC population described by WOPENKA *et al.* (1989) and that reported here reflect heterogeneity in Murchison or differences in the starting materials (*i.e.*, presence or absence of coarse material) from which the two residues were prepared. The low abundance of smooth grains in our Murchison residue, and the apparent absence of these grains in our Orgueil sample, are unlikely to reflect differences between our extraction procedures and those employed by the Chicago group. The platy surface textures of some grains may have been enhanced by acid etching but are not artifacts of the procedure. Processing as far as the $HClO_4$ step failed to produce any platy grains in the Indarch residue. Nor can the platy textures have been etched by treatment with H_3PO_4, because platy grains are the sole type encountered in the Orgueil residue (which was never exposed to H_3PO_4). The H_3PO_4 treatment applied to Murchison and Leoville in this work was apparently milder than that employed by TANG *et al.* (1988), as it failed to dissolve spinel completely. In comparing our observations of acid residues with the observations of other workers, it should also be borne in mind that our method of locating SiC, by SEM searches, may have introduced a bias towards finding the distinctive "platy" variety of SiC.

In the Indarch residue, SiC occurs exclusively as smooth-surfaced grains, and the proportion of coarse grains is higher than in the carbonaceous chondrite residues. The largest grain observed in the Indarch $CFNP_{(c)}$ residue, 20 × 23 μm, is much larger than any of the grains found in Orgueil, Murchison, or Leoville. Both equant and bladed forms are present, the latter showing conchoidal fracture surfaces in several cases (Fig. 6c and d). Bladed SiC grains in the Indarch residue resemble the smooth-surfaced Murchison grains described and illustrated by TANG *et al.* (1989; Fig. 1, upper photos) and ZINNER *et al.* (1989; Fig. 4, upper right and lower left photos). In addition to SiC, the coarse Indarch residue contains grains (up to 10 μm) of an unidentified Si- and N-bearing phase. The most likely candidate for this phase is Si_3N_4, rather than sinoite (Si_2N_2O), as electron probe analyses show no indication of O (note that sinoite is also reported to be soluble in HF/HCl; CRABB and ANDERS, 1982). Si_3N_4 is a plausible companion to the reduced phases found in E-chondrites, and has been observed both *in situ* in, and in acid residues prepared from, the EH3 chondrite Qingzhen (ALEXANDER *et al.,* 1991).

Isotopic results

The Si, C, and N isotopic compositions of SiC aggregates and individual coarse grains from the various acid residues are presented in Tables 2–4 and illustrated in Figs. 7–12. The dimensions and surface textures of those individually analysed grains characterised with the SEM are also tabulated. Note that the mineralogy and SiC contents of the finer-grained $CFNP_{(f)}$ samples are unknown. Isotopic analyses of these samples were made by rastering the primary beam over clumps of uncharacterised material, and it is presumed, but not certain, that the bulk of Si and C ion emission originated from fine-grained SiC. For clarity, the following discussion of the isotopic data deals separately with (1) the platy SiC grains in the coarse Orgueil and Murchison residues, (2) aggregates and uncharacterised SiC grains from Orgueil and Murchison, and (3) SiC from Indarch.

(1) Coarse SiC in Orgueil and Murchison—$CFNP_{(c)}$ residues. Silicon isotopic measurements were made on grains belonging to the class of coarse, platy SiC grains described above. Results are listed in Table 2 and illustrated in Fig. 7. All of the platy grains found in Orgueil (8 out of 8 SiC grains >2 μm) and Murchison (9 of 11) were analysed. Unfortunately, the sole coarse (~1.5 μm) platy SiC grain observed in Leoville could not be relocated in the ion probe for isotopic analyses. Though the Si data have been discussed previously (STONE *et al.,* 1990, 1991) several points may be stressed again here.

Silicon in grains belonging to this group is consistently isotopically anomalous. In contrast to the fine-grained SiC in Orgueil, Murray and Murchison (see below, and ZINNER *et al.,* 1987, 1989), these grains show a simple, linear distribution of Si isotopic compositions in the Si three-isotope plot of Fig. 7. The slope of this array, $\delta^{29}Si/\delta^{30}Si$ ~1.4, precludes mass-dependent fractionation or addition of any one isotope as possible causes of isotopic variability. The array does not intersect the normal Si isotopic value ("N" in these and subsequent figures), suggesting that the grains are formed from mixtures of two exotic Si components, neither related to solar Si. The $^{29}Si/^{30}Si$ ratio of the component enriched in ^{29}Si and ^{30}Si is given by the slope of the

Table 2. Platy SiC from Orgueil and Murchison

δ^{29}Si (per mil) $\pm 2\sigma$(1)	δ^{30}Si (per mil) $\pm 2\sigma$(1)	δ^{13}C (per mil) $\pm 2\sigma$(2)	(Si^-/C^-)(4)	δ^{15}N (per mil) $\pm 2\sigma$	CN^-/C^-	Notes
Orgueil CFNP$_{(c)}$. Coarse grains (>2 μm)						
42.2 ± 3.8	46.9 ± 4.4	1548 ± 57	1.16	−394 ± 76	1.6	10 × 11 μm
67.5 ± 9.4	75.4 ± 9.6	518 ± 17	1.08	—	—	3 × 3 μm
15.7 ± 7.7	35.9 ± 8.0	741 ± 55(3)	0.86(3)	—	—	(Photo Fig. 6a) 3 × 3 μm
43.0 ± 6.5	51.5 ± 9.9	1240 ± 17	1.10	−706 ± 106(5)	0.05(5)	8 × 7 μm
75.4 ± 7.0	70.7 ± 7.7	620 ± 11	1.19	−817 ± 38	0.11	6 × 4 μm
23.8 ± 6.4	41.2 ± 4.7	366 ± 26	1.13	−864 ± 53	0.11	4 × 5 μm
69.6 ± 6.4	68.6 ± 9.8	3603 ± 53	1.25	−962 ± 26	1.0	3 × 2 μm
124.2 ± 7.0	110.7 ± 7.2	903 ± 65	1.16	−902 ± 50	0.09	4 × 5 μm
Murchison CFNP $_{(c)}$Ph. Coarse grains (>2 μm)						
26.1 ± 8.0	40.8 ± 8.3	—	—	—	—	3 × 3 μm
51.2 ± 6.0	55.7 ± 6.0	1468 ± 43	1.19	−461 ± 48	0.17	4 × 5 μm
33.5 ± 26.3	42.7 ± 29.9	—	—	—	—	2 × 2 μm
−9.6 ± 4.5	24.6 ± 6.3	794 ± 30	1.19	−890 ± 41	0.06	4 × 4 μm
45.0 ± 10.5	66.9 ± 12.4	432 ± 50	1.08	—	—	(Photo Fig. 6b) 2 × 2 μm
58.1 ± 4.2	68.2 ± 4.3	155 ± 27	1.35	−855 ± 40	0.15	6 × 4 μm
49.5 ± 11.3	54.6 ± 9.6	353 ± 41(3)	0.76(3)	—	—	2 × 3 μm
75.3 ± 9.3	71.9 ± 12.6	5188 ± 64	1.35	—	—	2 × 3 μm
54.6 ± 4.1	54.2 ± 4.7	515 ± 42	1.24	—	—	4 × 4 μm

(1) Data tabulated are Si^+ secondary ion data. (2)Data tabulated are C^- secondary ion data. (3)(Si^-/C^-) indicates extraneous carbon. (4)Individual data ± ~0.05. SiC standard gives 1.28 ± 0.15. (5)Possibly extraneous N. Repeat analysis gave $CN^-/C^- = 0.46$.

array in co-ordinates of $^{29}Si/^{28}Si$ *vs.* $^{30}Si/^{28}Si$, and equals ~2.1. In the same co-ordinates, the array intersects the ($^{30}Si/^{28}Si$) axis at 0.013, indicating a minimum ~1.3% abundance of ^{30}Si (at $^{29}Si = 0$) in the ^{28}Si-rich component.

The data shown in Fig. 7 are in good agreement

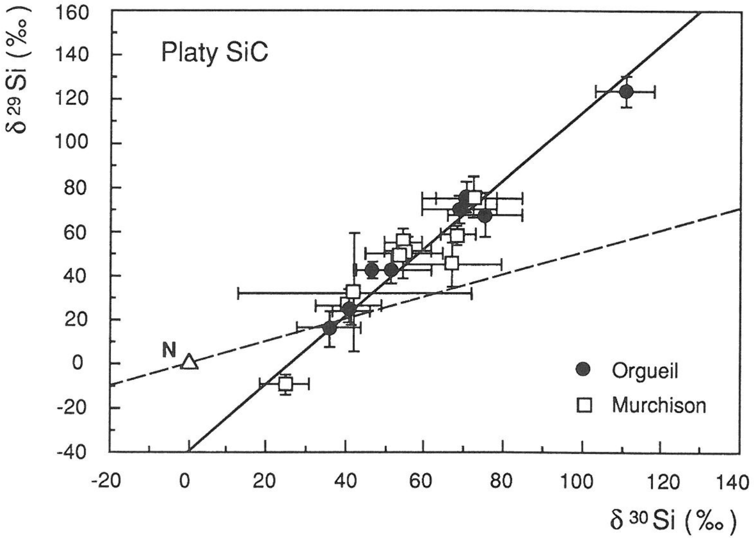

FIG. 7. Si isotope analyses of coarse platy SiC from Orgueil (dark circles) and Murchison (open squares) CFNP$_{(c)}$ residues. Note that the weighted, least-squares fit to the data (solid line) bypasses the point (N) corresponding to normal Si. Its slope of ~1.4 is distinct from that produced by mass fractionation, shown as a dashed line of slope 0.5. Uncertainties indicated are ±2σ.

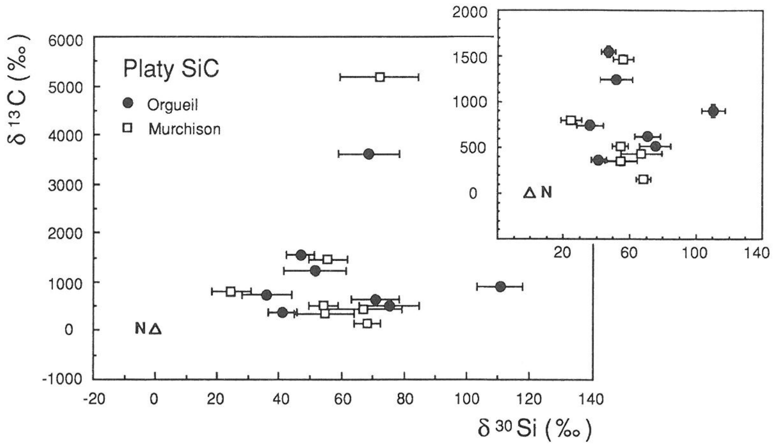

FIG. 8. Carbon isotopic compositions (shown as $\delta^{13}C$ values) plotted against silicon isotopic compositions for platy SiC from Orgueil (dark circles) and Murchison (open squares). Detail in the range $0 < \delta^{13}C < 1600$ is shown in the inset. Note that C isotopic measurements could only be made on 15 of the 17 grains originally analysed for Si isotopes. The point "N" represents the solar Si and C isotopic compositions. Indicated uncertainties are $\pm 2\sigma$.

with other analyses of coarse Murchison SiC (TANG *et al.*, 1988; ZINNER *et al.*, 1989; AMARI *et al.*, 1991). Nine grains (those described as equidimensional) from the Murchison acid residue HO (TANG *et al.*, 1989; ZINNER *et al.*, 1989) conform to the array in Fig. 7, and appear to belong to the same SiC population as the platy grains. A further ~70 grains (in the size range from 1.6–6 μm) from another Murchison residue KJG (AMARI *et al.*, 1991) have Si isotopic compositions distributed about the same correlation line as in Fig. 7. However, the spread of these data is greater than observed in the 17 analyses reported here; $\delta^{30}Si$ values for a number of the KJG grains extend out to the ^{30}Si-poor side of the array by as much as ~40 per mil. Mixing of two isotopically invariant components cannot account for the outliers amongst the KJG grains. If these outliers belong to the family of "platy" grains described above, then a mixing process in which one or both end-members varied somewhat in their Si isotopic compositions must be invoked.

There are several physical scenarios which might account for the binary mixing trend shown by the Si isotopic measurements. One is that the coarse grains are composites—formed by aggregation of fine-grained precursors belonging to two isotopically distinct populations. However, the grains appear in SEM images (*e.g.*, Fig. 6a and b) to be single crystals, and Si isotopic inhomogeneities were not detected while sputtering through grains during analysis. Alternatively, mixing may have involved gas-phase heterogeneity in the region in which the grains formed or gas-grain isotopic exchange post-dating their formation. In the former case, the platy grains may have formed in an environment characterised by isotopic heterogeneity over the length-scales sampled during condensation of grains or by temporal variations during the period in which the grains formed. In the latter, differing degrees of Si isotope exchange between a family of grains and an isotopically distinct gas phase could account for the Fig. 7 array.

Further constraints on the mixing process are provided by the C and N isotopic compositions of the platy SiC grains. As shown in Fig. 8, the grains are consistently enriched in ^{13}C, with $\delta^{13}C$ values ranging from +155 to ~5190. Importantly, there is no evidence of a correlation between Si and C isotopic compositions; those grains representing extreme degrees of ^{13}C enrichment, with $\delta^{13}C$ values of +155 and ~5190, have very similar $\delta^{30}Si$ values, of +68 and +75, respectively. Nitrogen in the platy grains is consistently enriched in ^{14}N. Delta N-15 values range from −394 to −962 (Fig. 9), the latter representing a ~25-fold enhancement in ^{14}N over the solar N isotopic composition. The Orgueil grain, G14, in which this extreme value occurs is also characterised by a high $\delta^{13}C$ value of ~3600, and it is noteworthy that the $^{13}C/^{12}C$ and $^{14}N/^{15}N$ ratios of this grain are ~0.2× and ~0.3× the ratios produced by equilibrium proton capture in CNO-cycle nucleosynthesis. Unfortunately, only seven of the grains originally analysed for Si isotopes survived in sufficient quantities for N analysis; in particular it was not possible to measure N in Murchison grain G8, with an even more extreme ^{13}C enrichment.

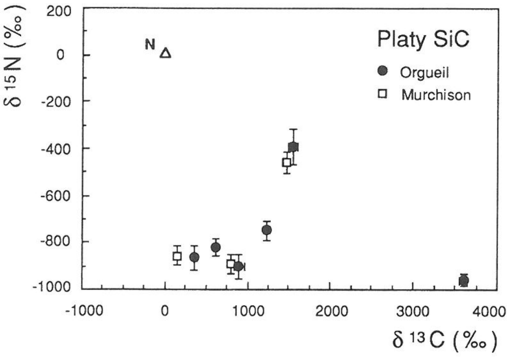

FIG. 9. Variation of nitrogen isotopic compositions (plotted as $\delta^{15}N$ values) with carbon isotopic compositions (as $\delta^{13}C$) in the platy SiC grains from Orgueil (dark circles) and Murchison (open squares). The absence of a correlation between these isotopic ratios applies also to variation between N and Si isotopes. Only nine of the platy SiC grains survived, or produced sufficiently intense $(CN)^-$ beams, for N analyses. The point "N" denotes the solar N and C isotopic compositions. Indicated uncertainties are $\pm 2\sigma$.

Other than in the case of Orgueil G14 noted above, there is little evidence of a correlation between excess ^{13}C and ^{14}N in the platy grains, nor between their N and Si isotopic compositions.

The C and N data rule out simple binary mixing models for the platy SiC grains. In order to account for the spread of C and N isotopic compositions, more than two components must have participated in the formation of the grains, or the components involved must have varied in their C/Si and C/N ratios during condensation of SiC. The well-correlated isotopic variation of Si presumably arises through the involvement of several "components" sharing a common Si isotopic composition, disguising the multi-component nature of the array in Fig. 7. For example, products of nucleosynthetic processes such as H-burning, which do not affect the Si isotopes, could be highly enriched in ^{13}C and ^{14}N and varied in their C/N ratios, whilst retaining the Si isotopic composition of their seed material.

(2) Fine-grained SiC in Orgueil and Murchison. Silicon and carbon analyses were made on several otherwise uncharacterised grains from the Murchison and Orgueil $CFNP_{(c)}$ mounts. A number of analyses were also made of aggregates of sub-micron SiC from the Orgueil $CFNP_{(c)}$ and $CFNP_{(f)}$ samples. The results of these analyses are grouped in Table 3 and illustrated in Figs. 10 and 11. This fine-grained material contains anomalous Si ranging in isotopic composition over a much broader area of the Si three-isotope diagram than does Si in the coarse, platy SiC grains (Fig. 10). The isotopic compositions of the fine-grained SiC scatter to both sides of the correlation line (Fig. 7) defined by the platy grains. In addition to grains with isotopic compositions like those of coarse Orgueil and Murchison SiC, this material must therefore contain (at least) two additional grain populations, with compositions in the ($\delta^{29}Si > 0$, $\delta^{30}Si < 0$) and ($\delta^{29}Si < 0$, $\delta^{30}Si > 0$) quadrants of Fig. 10. Similar conclusions apply to the fine-grained SiC in Murchison and Murray analysed by ZINNER *et al.* (1987, 1989) and to SiC in a number of the ordinary chondrites studied by ALEXANDER *et al.* (1990).

The C isotopic compositions of aggregates and uncharacterised grains in Orgueil and Murchison range even more widely than those of the platy SiC grains. For clarity in Fig. 11, the extreme range of isotopic compositions is plotted logarithmically, showing $^{12}C/^{13}C$ ratios rather than delta values. Delta C-13 values for these grains vary from −303

Table 3. Fine-grained SiC from Orgueil and Murchison.

$\delta^{29}Si$ (per mil) $\pm 2\sigma$	$\delta^{30}Si$ (per mil) $\pm 2\sigma$	$\delta^{13}C$ (per mil) $\pm 2\sigma$
Orgueil $CFNP_{(c)}$. Uncharacterised individual grains (~1 μm)		
54 ± 65	46 ± 35	2750 ± 80
31.9 ± 8.9	29.1 ± 10.4	4260 ± 990
47.0 ± 10.4	46.9 ± 10.9	1100 ± 50
Murchison $CFNP_{(c)}Ph$. Uncharacterised individual grains (~1 μm)		
25 ± 18	−19 ± 20	17,710 ± 580
8 ± 17	51 ± 20	−304 ± 24
Orgueil $CFNP_{(c)}$. Aggregates of fine grains (<1 μm)		
49.1 ± 11.5	62.2 ± 11.2	—
30.8 ± 10.1	40.0 ± 10.4	—
Orgueil $CFNP_{(f)}$. Aggregates of fine grains (<0.1 μm)		
−5 ± 21	59 ± 34	—
40 ± 17	51 ± 25	—
40 ± 17	42 ± 20	—
24.2 ± 8.0	22.1 ± 8.8	—
42 ± 16	−23 ± 21	—
−1.3 ± 4.7	17.9 ± 5.9	—
15 ± 18	19 ± 20	24,500 ± 850
27 ± 15	10 ± 15	9250 ± 1200
29 ± 10	45 ± 12	2070 ± 150
45 ± 12	−5 ± 15	1770 ± 180
−20 ± 8	22 ± 11	1322 ± 200
31 ± 10	27 ± 11	920 ± 180

Note: Analyses listing C isotopic data made using negative secondary ions. All others analysed as Si^+.

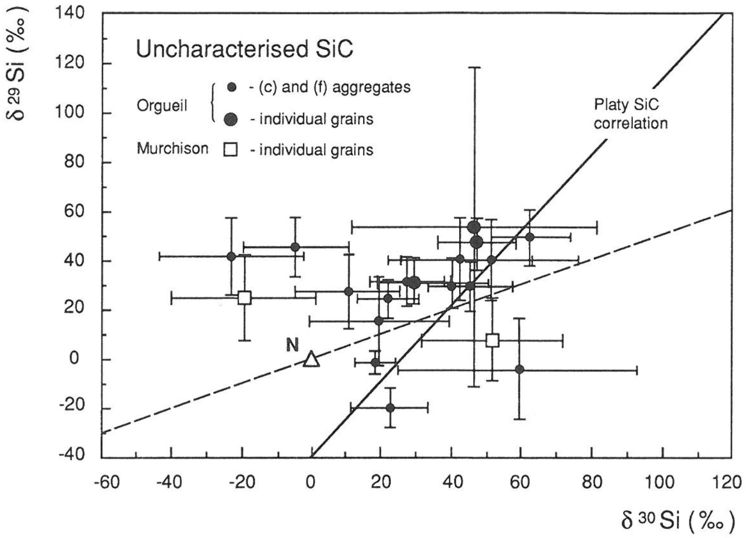

FIG. 10. Silicon isotope analyses of fine-grained SiC measured as individual ~1 μm grains (Orgueil, large dark circles; Murchison, open squares) and as aggregates of grains ~0.1 μm or smaller from Orgueil (small dark circles). Silicon isotope compositions of these grains scatter widely about the trend shown by coarse platy SiC in Orgueil and Murchison, denoting the presence of further exotic Si components in the fine-grained material. The point labelled "N" denotes normal Si, and the dashed line indicates compositions related to normal Si by mass fractionation. Uncertainties are ±2σ.

to 24,500, thus covering a range of $^{12}C/^{13}C$ ratios from greater than the solar value (89) through to values predicted for proton capture in the CNO cycle (~4). The negative $\delta^{13}C$ value found in one of the Murchison grains is particularly significant, as it implies the involvement of a ^{12}C-rich component (in addition to any material with a near-solar $^{12}C/^{13}C$ ratio) in formation of the grains.

(3) Indarch residues. Silicon analyses of the Indarch $CFNP_{(c)}$ and $CFNP_{(f)}$ residues are presented in Table 4 and illustrated in Figs. 12a (individual grains) and 12b (aggregates). The isotopic compositions of coarse grains from Indarch $CFNP_{(c)}$ cluster around the point corresponding to normal Si, and define a trend roughly parallel to a mass-dependent fractionation trajectory of slope 0.5. It should be noted that the heaviest isotopic composition measured in an individual grain ($\delta^{30}Si = +12$) occurs in one of the N-rich grains, not in SiC. It is possible that the instrumental fractionation for the Si,N phase is different to that for SiC, in which case normalisation of this analysis to SiC standard measurements may have resulted in an incorrect estimate of the fractionation intrinsic to the grain. Two data points suggest small deficits in ^{29}Si, but additional analyses are required to confirm this effect, as both fall within ~3σ of the mass-fractionation line. Note that these measurements and the standard analyses to which they are normalised were made at high MRP. The effects are not due to normalisation of the sample data to standard runs at low resolving power, which could result in apparent ^{29}Si deficits due to hydride interferences in the standard measurements.

Silicon in fine-grained material from the Indarch $CFNP_{(c)}$ and $CFNP_{(f)}$ residues also clusters around the normal isotopic composition. Several analyses show enrichment in heavy Si isotopes. One of these falls slightly off the mass-fractionation line, suggesting enrichment in ^{29}Si, or depletion in ^{28}Si or ^{30}Si in some fraction of the aggregated grains sputtered during this analysis. This is potentially an important observation; because most of the SiC grains in the Indarch residues appear to contain normal Si (as indicated by the coarse grain data shown in Fig. 12a) the net anomaly recorded in this run may signify the presence of a highly anomalous Si component contained in a small fraction of the $CFNP_{(f)}$ grains. A further separation of the Indarch $CFNP_{(f)}$ residue in the hope of enriching this component, and future measurements at higher precision will be required to clarify the possible presence of anomalous Si in Indarch SiC.

In keeping with these results, ALEXANDER *et al.* (1991) found isotopically normal Si in a number of Si,N-bearing grains (presumed to be Si_3N_4) from the EH3 chondrite Qingzhen. In contrast to the

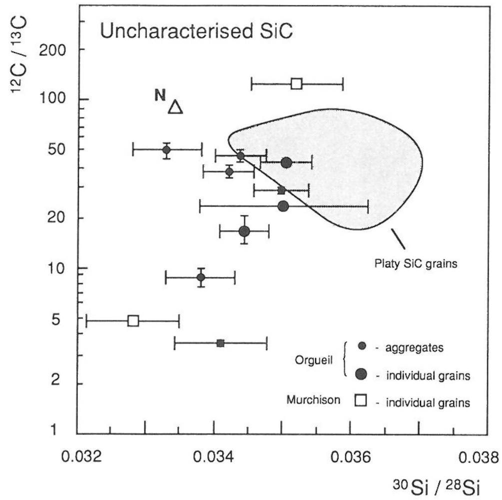

FIG. 11. Carbon and silicon isotopic variations in fine-grained SiC from Orgueil and Murchison. For clarity, the data are shown as isotopic ratios ($^{12}C/^{13}C$ and $^{30}Si/^{28}Si$) rather than delta values, and the C data have been plotted logarithmically to illustrate their extreme variability. For comparative purposes, note that $^{12}C/^{13}C$ ratios found in the platy SiC grains range from ~14 to ~77. The point labelled "N" indicates the solar C and Si isotopic ratios. Uncertainties are $\pm 2\sigma$.

scant evidence of isotopically anomalous SiC in Indarch, however, the sole SiC grain encountered by ALEXANDER *et al.* (1991) was found to have $\delta^{29}Si$ and $\delta^{30}Si$ values of +50 and +58, respectively.

Negative $\delta^{13}C$ values were measured in three Indarch SiC grains. The range of values, $-37 < \delta^{13}C < -4$, is comparable to that of trace carbon released at high temperatures in stepwise combustion of Indarch (GRADY *et al.*, 1986) and is typical of solar-system reservoirs.

ISOTOPIC VARIABILITY OF METEORITIC SILICON CARBIDE

The search for SiC in CM meteorites was originally motivated by the suggestion of a common carrier for excess ^{13}C and the exotic noble gas components Ne-E and Xe-S (SWART *et al.*, 1982). It was not anticipated that, once isolated, SiC would be found to exhibit an extensive *range* of Si, C, and N isotopic compositions, complicating models for the origin of these grains. Major questions posed by the data relate to (1) the nuclear processes and stellar sites responsible for isotopic variation in the total SiC population, (2) distinctions between fine-grained SiC and the family of platy grains common to Orgueil and Murchison, (3) the origin of well-correlated Si isotopic variations in the platy SiC and why these variations are decoupled from those in C and N isotopes, and (4) the source of isotopically normal SiC in Indarch.

It should be stressed at the outset that the isotopic variability observed in SiC from the carbonaceous chondrites cannot arise from physical or nuclear processing (after formation) of an initially uniform population of grains. The wide range of Si three-isotope data (Figs. 7 and 10) relative to any mass-dependent fractionation line (of slope 0.5) rules out kinetic processes such as evaporation, sputtering, or diffusive isotopic separation in accounting for gross Si isotopic differences amongst the grains. Because the fraction of "anomalous" atoms in the grains is so large (>10% in SiC with $\delta^{13}C \sim 25{,}000$), nuclear processes such as spallation or neutron capture *in situ* can also be discounted. Isotopic variation in these grains must be ascribed to stellar nucleosynthesis.

Nucleosynthetic components and stellar origins for SiC in carbonaceous chondrites

Clues to the stellar origins of SiC in the carbonaceous chondrites may be found by comparing the isotopic compositions of this material with nucleosynthetic model calculations. In general, production of ^{28}Si is dominated by oxygen-burning in supernovae and their precursor stars, whereas production of the neutron-rich Si isotopes is divided between contributions from He-, C-, and Ne-burning (WOOSLEY, 1986; CLAYTON, 1988). The latter two processes are associated with supernovae, while He-burning occurs in a variety of stellar environments including red giants, supernovae, and Wolf-Rayet stars. Silicon produced by O-burning ranges from pure ^{28}Si to compositions containing small amounts of ^{30}Si (THIELEMANN and ARNETT, 1985; WOOSLEY, 1986). Relative yields of ^{29}Si and ^{30}Si in He-, C-, and Ne-burning vary with the nucleosynthetic conditions (WOOSLEY, 1986), such that mixtures of these components with O-burning products encompass the Si isotopic variations observed in SiC. Condensation of SiC from undiluted C-, Ne-, or O-burning components (*e.g.*, in supernova outflows) is unlikely due to the low C/O ratios resulting from these processes. The isotopic signatures of these processes could be inherited by SiC grains formed in late-generation stars, however. Also, small amounts of C-, Ne-, or O-burning products with high $^{29,30}Si/O$ ratios, added to C-rich regions of supernovae, could impart their Si isotopic signatures without lowering C/O ratios below the threshold for SiC condensation. Carbon-13 and nitrogen-14 enrichments found in the majority of SiC grains

Table 4. Indarch SiC.

δ^{29}Si (per mil) ± 2σ	δ^{30}Si (per mil) ± 2σ	δ^{13}C (per mil) ± 2σ	Notes
Indarch CFNP$_{(c)}$ Coarse grains (>2 μm)			
−1.1 ± 2.8	−3.7 ± 4.7	−36.8 ± 5.5	—
−3.0 ± 3.5	−3.0 ± 4.5	−3.8 ± 9.8	—
1.4 ± 2.3	5.3 ± 3.5	−23.4 ± 7.7	—
−0.6 ± 2.9	2.3 ± 2.9	—	20 × 23 μm
−6.5 ± 7.3	−3.0 ± 8.0	—	—
−1.1 ± 5.2	−5.2 ± 5.6	—	4 × 4 μm
−10.5 ± 5.9	−6.5 ± 8.0	—	(Photo Fig. 6d) 8 × 2 μm
2.8 ± 1.9	11.9 ± 2.3	—	Si$_3$N$_4$ (?) 10 × 10 μm
−19.8 ± 17.4	−0.5 ± 18.1	—	2 × 3 μm
−2.4 ± 5.3	−4.4 ± 7.1	—	3 × 3 μm
1.6 ± 2.5	6.7 ± 3.0	—	10 × 1 μm
Indarch CFNP$_{(c)}$. Aggregates of fine grains (<1 μm)			
4.0 ± 11.0	4.6 ± 12.5	—	—
−0.6 ± 7.3	−5.6 ± 9.6	—	—
1.6 ± 3.0	3.3 ± 4.2	—	—
0.7 ± 2.7	5.0 ± 3.3	—	—
Indarch CFNP$_{(f)}$. Aggregates of fine grains (<0.1 μm)			
12.7 ± 6.4	18.1 ± 9.0	—	—
10.0 ± 12.7	−2.3 ± 6.2	—	—
5.6 ± 10.4	6.5 ± 8.9	—	—
15.7 ± 7.5	12.3 ± 7.5	—	—

Note: Analyses listing C isotopic data made using negative secondary ions. All others analysed as Si$^+$.

point to H-burning contributions, while excess ^{12}C (found in one grain in the course of this work, and in several others by AMARI *et al.*, 1991) requires a He-burning source.

The isotopically varied SiC population could be derived from a large number of separate stars, marked by distinct isotopic compositions (TANG *et al.*, 1989; ZINNER *et al.*, 1989; ALEXANDER *et al.*, 1990). A smaller number of stars could account for the population if these stars contained active Si-, C-, and N-producing regions. Possible sources combining sites for Si, C, and N isotope production with regions in which C/O > 1 (allowing SiC to condense; LARIMER and BARTHOLOMAY, 1978) include He-burning layers of progenitors to Type II supernovae, red giant stars on the Asymptotic Giant Branch (AGB), and C-rich Wolf-Rayet (WC) stars. Theoretical studies indicate that all are capable of producing ^{29}Si and ^{30}Si in appropriate abundances, as well as s-process isotopes and excess ^{22}Ne characteristic of meteoritic SiC (ARNETT, 1987; HASHIMOTO *et al.*, 1989; PRANTZOS *et al.*, 1988; GALLINO *et al.*, 1990; CASSÉ and PAUL, 1982; CASSÉ, 1983). He-burning in Type II supernovae and WC stars is a more likely source of ^{12}C-rich SiC, while AGB stars can produce abundant ^{13}C through episodic H-burning (see below). Observational evidence that red giant stars are the major source of C-rich interstellar dust (BODE, 1988; GEHRZ, 1988), combined with the similarity between ^{12}C/^{13}C ratios in SiC and carbon-rich red giant stars (TANG *et al.*, 1989), favours red giants as the major SiC sources.

Clearly, a large number of possible stellar sources may be represented amongst the total SiC population of carbonaceous and ordinary chondrites. Discrimination between these sources is difficult in the case of fine-grained SiC analysed as aggregates, and where isolated, unrelated grains have been studied. More specific conclusions can be drawn regarding families of related grains, such as those separated by grain size (LEWIS *et al.*, 1990; AMARI *et al.*, 1991), which show coherent Ne, Kr, and Xe isotopic systematics, and the family of platy SiC identified in this work.

Platy SiC in Orgueil and Murchison

The distinctive morphology and well-correlated Si isotopic compositions (Fig. 7) of the platy SiC found in Orgueil and Murchison set these grains apart from other types of SiC (Fig. 10) in their host meteorites. It should be noted that these grains were

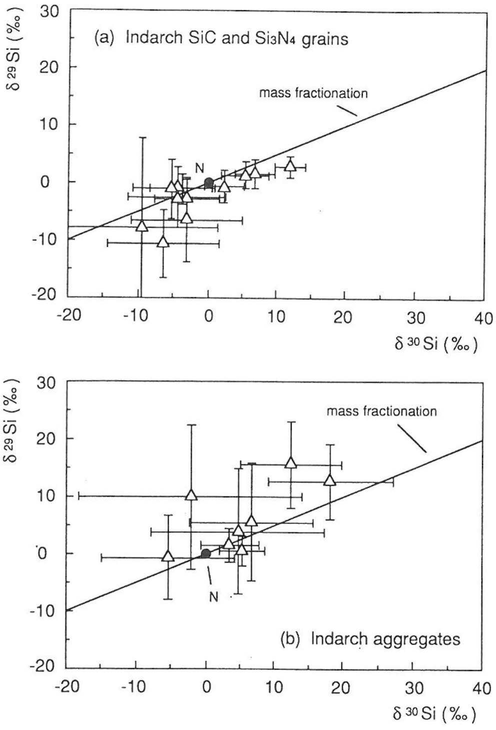

FIG. 12. (a) Si isotope analyses of coarse-grained SiC and Si_3N_4 (?) from the Indarch $CFNP_{(c)}$ residue. Analyses tend to cluster about the normal point (N) and the mass-fractionation trajectory passing through normal Si (solid line). Note the reduced scale compared to Figs. 7 and 10. Uncertainties are $\pm 2\sigma$.

(b) Analyses of aggregates of fine-grained SiC in the Indarch $CFNP_{(c)}$ and $CFNP_{(f)}$ residues. Again note the reduced scale relative to Figs. 7 and 10. Uncertainties are $\pm 2\sigma$.

first selected for analysis on the basis of their similar surface textures, and that the coherent Si isotopic systematics revealed by ion probe analyses reinforced the impression that they constitute a single family with a common origin. The issue of whether these grains formed around a single, isotopically heterogeneous star containing ^{28}Si-rich and ^{29,30}Si-rich components, or a number of related stars, remains unresolved. The poor correlations among Si, C, and N isotopes are more easily reconciled with a number of parental stars, which differed in their H- and He-burning yields. If the grains originated in separate stars, however, these must have shared the same, non-solar, ^{28}Si-rich seed composition, and produced ^{29}Si and ^{30}Si under similar conditions in order to yield the isotopic array shown in Fig. 7. Red giant stars of similar age, formed in close association with one another, might satisfy these criteria.

Constraints available from analyses of SiC have provided an impetus for nucleosynthetic modelling, and attention has focussed on low-mass AGB stars as a source for SiC. Helium-burning and neutron capture proceeding from the reaction $^{13}C(\alpha, n)^{16}O$ in intershell regions of AGB stars may account for characteristics of SiC such as excess ^{22}Ne and s-process effects in both light and heavy elements (IBEN and RENZINI, 1982; GALLINO *et al.*, 1990; CLAYTON *et al.*, 1991). An important feature which makes these stars likely sources of SiC is the evolution of cool, carbon-rich envelopes enriched in He-burning products by convective exchange with the stellar interior. Silicon carbide has been observed in the envelopes of several red giants, and C isotopic compositions measured in these stars compare well with the range found in the platy SiC grains (LEAHY *et al.*, 1987; MARTIN and ROGERS, 1987; LAMBERT, 1989).

Theoretical models predict that, in thermally pulsing AGB stars, dredge-down of H from the stellar envelope into the He layer produces an intershell region enriched in ^{13}C (and ^{14}N). Subsequent He-burning (producing ^{12}C and ^{22}Ne) engulfs the intershell region and supplies neutrons for s-process synthesis *via* the reaction $^{13}C(\alpha, n)^{16}O$. Convection initiated by the He-burning pulse then mixes ^{12}C, ^{13}C, ^{14}N, ^{22}Ne, and s-process isotopes up to the stellar envelope (IBEN and RENZINI, 1982; GALLINO *et al.*, 1990; CLAYTON *et al.*, 1991). Within this framework, the Si isotopic trend of Fig. 7 could be interpreted as the product of mixing between a ^{28}Si-enriched precursor component preserved in the stellar envelope and freshly synthesized Si from the He layer of such a star. The following discussion examines the models in the light of isotopic effects preserved in the platy SiC grains.

First, the poor correlations between Si, C, and N isotopes suggest that the grains sampled the products of several dredge-up cycles marked by different isotopic compositions and relative abundances of C, N, and Si. Alternatively, prompt condensation of SiC after a single dredge-up event, on a timescale shorter than that required to mix the stellar envelope, could account for the isotopic variability. If the grains formed over a number of thermal pulses, then changes in parameters, such as initial H fraction, temperature, and neutron exposure, responsible for C and N isotopic shifts from pulse to pulse, had little effect on the $^{29}Si/^{30}Si$ production ratio, preserving the Si isotope correlation. Though the production ratio appears insensitive to burning conditions in successive pulses, the value of ~2.1 estimated from the slope of Fig. 7 is at variance with theoretical predictions of ~0.94 (GALLINO *et* *al.*, 1990) and ~0.6–1.1 (CLAYTON *et al.*, 1991). Agreement between AGB model predictions and measured s-process effects in heavy elements such as Kr and Xe (LEWIS *et al.*, 1990) and Ba (ZINNER *et al.*, 1991) is somewhat better than for Si (this work) and Ti (IRELAND *et al.*, 1991). This suggests that current models are limited by uncertainties in cross-section data for competing (n, γ), (n, α) and α-particle reactions amongst the light elements. A further point of comparison between AGB models and the platy-grain data concerns the prevalence of anomalies in the proton-capture isotopes ^{13}C and ^{14}N in the SiC grains. Evolutionary models imply that dredge-up of ^{12}C from the He shell drives the C/O ratio of the stellar envelope past the threshold value of ~1 required for SiC condensation. The isotopic data suggest, however, that H-burning also contributes C to the envelope and that the threshold for SiC formation is reached well before the $^{12}C/^{13}C$ ratio exceeds the solar value.

Local and exotic SiC

The presence of large isotopic anomalies in SiC from the carbonaceous chondrites identifies these grains as extra-solar in origin. It appears that this exotic SiC resides in the matrix, not in refractory material (HUSS, 1990), because residues produced from the matrix of carbonaceous chondrites (*e.g.*, ZINNER *et al.*, 1989) contain similar quantities of SiC to those produced from meteorites in bulk (this study). The same conclusion has been reached *via* SiC abundance measurements made by X-ray mapping (SWAN *et al.*, 1989; ALEXANDER *et al.*, 1989). Like other material of pre-solar origin present in the matrix of carbonaceous chondrites (such as D-rich organic compounds, YANG and EPSTEIN, 1984; EPSTEIN *et al.*, 1987), SiC must have experienced a low-temperature history in the solar nebula. Exposure to the hot, oxidising conditions responsible for formation of chondrules and refractory inclusions should have resulted in SiC breakdown (LARIMER and BARTHOLOMAY, 1978).

In contrast to SiC in the carbonaceous chondrites, the isotopic data for Indarch SiC (and Si_3N_4) suggest formation in isotopic equilibrium with a gas of solar Si and C isotopic composition. It is therefore important to establish whether Indarch SiC grains of the type analysed in this work host the Ne-E(H) found in Indarch residues (HUSS, 1990). If not, Indarch might be inferred to contain other pre-solar phases, or pre-solar SiC grains so rare (and therefore also ^{22}Ne-rich) that none were encountered in this study.

The low abundance of SiC preserved in Indarch (~0.4–1.3 ppm; this study and HUSS, 1990) contrasts with the large fraction of Si expected to condense as SiC during cooling of a C-rich gas of solar composition. For example, in a cooling solar gas with a C/O ratio of ~1.1, 50% of the Si destined to form silicates condenses as SiC before undergoing reactions with $Mg_{(g)}$ and CO to produce Mg silicates (LARIMER and BARTHOLOMAY, 1978). The fact that less than ~10^{-5} of the bulk Si in Indarch survives in SiC indicates that retrograde equilibration between gas and solid phases continued down to temperatures below the stability limit of SiC. If this process destroyed exotic SiC with the same efficiency as it destroyed SiC predicted to have formed in the solar system, then exotic SiC should not be found in the E-chondrites. Either the Ne-E(H) in these meteorites is hosted by another phase, or like the SiC of carbonaceous chondrites, the exotic SiC of E-chondrites is part of a "matrix" component which never experienced high temperatures in the solar nebula (HUSS, 1990). If the latter is true, it follows that the oxidation state of the high-temperature component of meteorites is a poor guide to likely SiC concentrations.

CONCLUSIONS

Carbonaceous and enstatite chondrites contain distinct types of SiC. Silicon carbide grains in carbonaceous chondrites contain large Si, C, and N isotopic anomalies, indicating an extra-solar origin. The SiC analysed (thus far) from the enstatite chondrite Indarch contain Si and C of near-normal isotopic composition, and the possibility that these formed in the solar system cannot be ruled out on the basis of the available data.

The total SiC population of carbonaceous chondrites is a complex mixture of families of grains marked by distinct morphologies and Si isotopic characteristics. Isotopic differences amongst the total population of SiC may reflect a variety of nucleosynthetic processes, operating in a number of separate stars (TANG *et al.*, 1989; ZINNER *et al.*, 1989).

One family of texturally distinctive, platy SiC grains, common to Orgueil and Murchison, appears to have formed by mixing of two exotic Si components. Four criteria may be inferred for the source of this family of grains: (1) C/O > 1; (2) a density high enough to permit condensation; (3) the presence of two Si components, enriched in ^{28}Si and $^{29,30}Si$, respectively; and (4) variable degrees of enrichment in ^{13}C and ^{14}N, decoupled from Si isotope effects. In combination with measurements of s-process isotope effects (*e.g.*, ZINNER *et al.*, 1991a) and astronomical evidence for dust production by red giant stars (Bode, 1988; Gehrz, 1988), these constraints suggest an origin in the circumstellar envelope of an AGB star. There is good qualitative agreement between isotopic measurements of platy SiC and model predictions for grains formed episodically in an AGB envelope. Further insight into the stellar source may follow more detailed modelling aimed at reproducing the $^{29}Si/^{30}Si$ production ratio and the C isotopic compositions recorded by the platy SiC grains.

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