INTERSTELLAR GRAINS IN METEORITES: DIAMOND AND SILICON CARBIDE

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ABSTRACT. Well-preserved interstellar grains occur in carbonaceous chondrites. Diamond (10–100Å) contains r- and p-process Xe (suggesting a supernovae connection), and appears to have formed by stellar condensation, not by interstellar shocks. \underline{SiC} (mainly 0.1–1 μ m) is labeled either with s-process Xe, Kr (red giant?) or with Ne^{22} , N^{15} (nova?), and shows large isotopic variations in N (100x), C (16x), and Si (1.3x). As Si is unaffected by H, He-burning, the Si variations reflect the isotopic heterogeneity of the ISM on the scale of individual stars; the Si compositions found thus far require at least 6 separate stars.

SiC accounts for only $\sim 4 \times 10^{-5}$ of the Si in meteorites, though it probably constitutes ~ 0.3 of the interstellar Si. Some of the difference may be due to destruction in the solar nebula, but most of it seems to represent an intrinsic deficiency of carbon star material in protosolar matter — perhaps due to high supernovae activity in the OB association from which the solar system probably formed. The presolar cosmic-ray exposure age of SiC is 41 (+20,-14) Myr, much shorter than the estimated 500 Myr lifetime of interstellar grains. The young age may be real — being supported by the log-normal size distribution and the fresh, uneroded crystal faces of SiC — but one cannot categorically rule out shortening of the age by late degassing of part of the SiC.

Interstellar carbon components in meteorites show the following distribution among chemical states, as a fraction of cosmic abundance: organic $\sim 4 \times 10^{-4}$, diamond 7×10^{-4} , graphitic/amorphous $\sim 2 \times 10^{-4}$, $SiC 4 \times 10^{-6}$. However, these values are not likely to be representative of the ISM, due to destruction and regeneration of carbon species in the solar nebula, and the intrinsic deficiency of carbon star material in protosolar matter.

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1. INTRODUCTION

Primitive meteorites often show isotopic anomalies that cannot be explained by known or plausible solar system processes, and are therefore attributed to the presence of interstellar grains. The coarse-grained parts of the meteorites, which were melted during formation of the solar system (chondrules, inclusions, metal grains), have largely assimilated and homogenized their interstellar grains and show only vestigial isotopic anomalies (<1 to 5%), for O and for refractories such as Mg, Ca, Ti, Cr, Sr, Ba, Sm, and Nd. These anomalies — including decay products of extinct radionuclides (Wasserburg, 1985) — have yielded important insights into stellar nucleosynthesis and processes in the early solar system. Having been covered in several reviews (Begemann, 1980; Clayton, 1982; Anders, 1987; Clayton, Hinton, and Davis, 1988), they will not be discussed here. Instead, we shall focus on the fine-grained matrix of the meteorites, whose constituents generally had a milder temperature history. This matrix contains well-preserved interstellar grains, of which 3 — diamond and 2 kinds of silicon carbide — were recently isolated after a 20 year search (Lewis et al., 1987; Tang, Lewis, and Anders, 1987; Tang and Anders, 1988a; Bernatowicz et al., 1987).

Nature has thoughtfully "labeled" each type of interstellar grain by an isotopically anomalous noble-gas component, which not only serves as a tracer during isolation, but also provides clues to the origin of the grains (Table 1). Type 1 SiC is present as separable grains, whereas Type 2 SiC is somehow associated with spinel $(MgAl_2O_4)$, and can be isolated only by destroying the spinel (Tang and Anders, 1988a). All three interstellar grain types show large isotopic anomalies in C, N, or both (Table 1).

2. DIAMOND

2.1. PROPERTIES

Interstellar diamond, first predicted by Saslaw and Gaustad (1969), was discovered by Lewis et al. (1987). This diamond, previously known by the noncommittal term $C\delta$, has isotopically normal C but decidedly anomalous N (Table 1). It consists of very small grains (median diameter 26 Å; Lewis, Bright, and Steel, 1987) and contains roughly equal amounts of crystalline and amorphous material. The latter differs from normal amorphous carbon by its white color and high chemical resistance, and apparently involves diamond-like sp³ rather than graphitic sp² bonding (Blake et al., 1988). It is not yet clear whether this amorphous material represents discrete domains (Lewis et al., 1987) or merely the outermost 1–2 atomic layers of the grains (Blake et al., 1988). The low density of $C\delta$ (2.22–2.33 g/cm³ vs. 3.51 g/cm³ for crystalline diamond) presumably reflects the presence of this amorphous material.

The IR spectrum of the $C\delta$ diamond (Lewis and Anders, in preparation) shows peaks at 2919 and 2849 cm⁻¹ (C-H stretch), 1774 cm⁻¹ (carboxyl, as confirmed by titration) and 1028–1403 cm⁻¹ (N in solid solution; $C\delta$ contains \sim 0.3% N; Lewis et al., 1983). Ion probe measurements show several atom percent of O and H, the latter enriched in D by 250–340% (Carey et al., 1987).

	Diamond	Type 1 SiC	Type 2 SiC
Name before identification	$C\delta$	$C\beta$	$C\epsilon$
Grain size, μ m	0.0025	0.1	0.1-2
Abundance, ppm	400	3	5
δC^{13} *	-38	~1300	~1500
δN^{15} *	-375	~-300	~-500
Noble-Gas Component	Xe-HL	Xe-S	Ne-E(H)
Fraction of Total Xe or Ne, %	5	0.01	0.2 ` ′
Enriched in	$Xe^{124,136}$	$Xe^{128,130,132}$	Ne^{22}
Nucleosynthetic Process	\mathbf{p} , \mathbf{r}	s	Explosive

TABLE 1
Interstellar Grains in Meteorites

2.2. ORIGIN

Two obvious origins of $C\delta$ — high static pressures or impacts in the solar system — are readily ruled out (Lewis et al., 1987). An attractive alternative is formation by collisions of graphitic¹ carbon grains in interstellar shocks, which may convert ~5% of the grains to diamond (Tielens et al., 1987). As this process is very fast (~ 10^{-12} s), both the diamond and the unconverted graphitic carbon would retain any Xe - HL initially present. However, meteoritic data contradict this model, failing to show the predicted large excess of unconverted graphitic C. The ratio graphitic C/diamond is not 20 but only <0.2 for C2 chondrites and ~5 for C3V chondrites. Moreover, this graphitic carbon lacks Xe - HL and matches $C\delta$ diamond neither in δC^{13} (-15 % vs. -38 %) nor in δN^{15} (-15 to -20 % vs. -375 %). Quite possibly interstellar shocks do make some diamond by the process of Tielens et al. (1987), but since meteoritic diamonds do not show its signature, another process must be sought.

A suitable candidate is chemical vapor decomposition, or CVD (Saslaw and Gaustad, 1969; Lewis et al., 1987). This process, now used commercially, makes diamond metastably by decomposition of CH_4 or other sp³-bonded carbon compounds in the presence of H_2 and atomic H (DeVries, 1987). In addition to crystalline diamond, it produces two partly amorphous, diamond-like materials -a-C and α -C:H— of lower density and hardness. The latter resembles $C\delta$ both in its low density $(1-3 \text{ g/cm}^3)$, usually $1.8-2.0 \text{ g/cm}^3$) and the presence of H.

Conditions in the atmospheres of late-type, carbon-rich stars are similar to those required for CVD synthesis of diamond (Saslaw and Gaustad, 1969; Wdowiak,

^{*} $\delta C^{13} = 1000 \, (R_{sample}/R_{standard} - 1)$ where $R = (C^{13}/C^{12})$

¹For the purposes of this paper, "graphitic" covers the entire continuum of sp^2 -bonded elemental carbon, from crystalline graphite through Buckminsterfullerenes to the most disordered amorphous carbon, all with their normal complement of surface-bound H and O atoms.

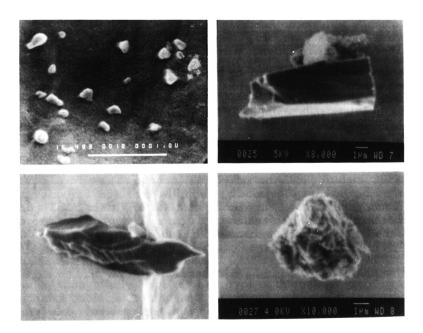


Fig. 1. SiC from C2 chondrites. (a) Type 1 SiC from Murray (Tang and Anders, 1988a). (b,c,d) Some of the larger bound SiC grains from Murchison. Note well-developed crystal faces in (b) and fracture surfaces in (c); all are fresh and uneroded. (Zinner et al., in preparation).

1987), and thus diamonds could probably condense in circumstellar shells. In the stellar radiation field, transparent grains are heated less than opaque grains (Draine, 1981), which would further favor diamond over graphitic C.

After the diamonds have formed in a circumstellar shell, they must somehow be impregnated with Xe-HL and associated noble gases. Xe-HL shows the signature of the r- and p-processes (Manuel et al., 1972; Heymann and Dziczkaniec, 1979), and hence presumably came from a supernova. The absence of a spike at mass 129 (formed originally as I^{129} , of 16 Myr half-life) shows that the trapping was chemically non-selective and presumably involved ion implantation (Lewis and Anders, 1981).

Two models have been proposed for implanting Xe-HL into diamonds. Clayton (1981) suggested that carbon grains condensed in the dust shell of a massive star during the red giant or planetary nebula stage, and were then overtaken by fast Xe-ions after the star had exploded as a Type II supernovae 10^2-10^5 years later. A problem with this model is that massive stars do not become carbon stars and thus do not reach the C/O ratio > 1 required for condensation of C under equilibrium conditions. However, if the reaction of C with H_2O is slow in the condensation zone, diamond could perhaps form and persist metastably even if C/O < 1.

Jørgensen (1988) solved the C/O problem by postulating two binary stars of 1-2 M_{\odot} . The less massive one becomes a carbon star that forms diamonds in its

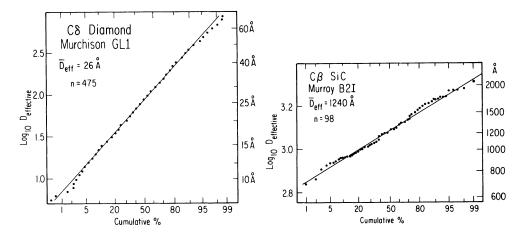


Fig. 2. Both diamond and Type 1 SiC show log-normal size distributions, suggestive of crystal growth from the vapor followed by conversion of small crystals to large ones. SiC distribution may be slightly truncated at high end, since the sample was isolated by centrifugation with cutoffs of 0.03 and 0.2 μ m. (Lewis, Bright, and Steel, 1987; Tang and Anders, 1988a.)

circumstellar shell while transferring matter through its Roche lobe to its companion that has become a white dwarf. When the latter reaches the Chandrasekhar limit and explodes as a Type I supernovae, Xe-HL ions ejected at $>10^3$ km/s implant themselves in the diamonds, as in the Clayton (1981) model. However, the diamond yield is very much lower, since the much longer time scale of evolution leaves only a minor fraction of the diamonds close enough to the supernovae to acquire Xe-HL. Both the high abundance of $C\delta$ diamonds — 10^{-3} of the cosmic complement of C in the meteorites — and the high $^{132}Xe-HL/C$ ratio (1.3 x 10^{-3} of cosmic) imply efficient production and trapping, i.e. close proximity.

3. SILICON CARBIDE

Both types of SiC are very much rarer than diamond (Table 1), but much coarser-grained. Type 1 SiC ($C\beta$) ranges from 0.06 to \sim 0.2 μ m (Fig. 1a), whereas Type 2 SiC ($C\epsilon$) runs mainly from \sim 0.1 to 1 μ m, with occasional grains up to 12 μ m (Fig. 1 b, c, d).

3.1. TYPE 1 SIC $(C\beta)$

The size distribution of $C\beta$ -SiC is sharply peaked and log-normal, like that of $C\delta$ diamond (Fig. 2). Such distributions usually form when a primary crystal-growth distribution is modified by conversion of small crystals to large ones ("Ostwald ripening"). Fragmentation would move the distribution in the opposite direction, producing small grains at the expense of large ones, and eventually yielding the power-law distribution that is generally assumed for interstellar grains (Mathis, Rumpl, and Nordsieck, 1977). By this criterion, the distributions in Fig. 2 are

young and unevolved. We note, however, that these distributions do not necessarily contradict a power-law distribution for the interstellar grain population as a whole. Such a distribution could arise from superposition of many log-normal distributions, especially if followed by some fragmentation of larger grains.

 $C\beta$ has several characteristics pointing to a red giant origin. It contains a Xe component (probably trapped by ion implantation) that strikingly resembles the predicted composition of s-process Xe, i. e. lacking the two lightest and two heaviest isotopes and showing a strong even-mass preference among the remaining 5 isotopes (Fig. 2 of Srinivasan and Anders, 1978; Fig. 5 of Tang and Anders, 1988b). The accompanying Kr also shows the signature of the s-process, but has variable isotopic ratios (Ott et al., 1988) implying variations in the s-process branches passing through radioactive nuclides (Se^{79} , Kr^{85}), caused by differences in neutron density and temperature. Interestingly, the neutron densities and temperatures inferred from meteoritic s-process Kr differ markedly from those for the solar system s-process (Ott et al., 1988).

 $C\beta$ also contains heavy carbon, of mean $C^{12}/C^{13} \simeq 40$ (Swart et al., 1983; Tang et al., 1988). Ion probe analyses show some variability in C^{12}/C^{13} , as well as isotopic anomalies in Si and N (Zinner, Tang, and Anders, 1987; Tang, Anders, and Zinner, 1988).

3.2. TYPE 2 SIC $(C\epsilon)$

The size distribution of $C\epsilon$ -SiC is not yet known, but most of the mass is in the 0.1-1 μ m interval. $C\epsilon$ contains "Ne-E", i.e. nearly monoisotopic Ne^{22} with at most minor amounts of other noble gases (Black and Pepin, 1969; Eberhardt et al., 1981; Tang and Anders, 1988a)². Very likely, the Ne^{22} comes from β^+ decay of 2.6 yr. Na^{22} , which was selectively trapped by the SiC. (Stellar nucleosynthesis can make Ne that is strongly enriched in Ne^{22} , but overproduces other noble gases. Thus a chemical enrichment by trapping of Na^{22} seems necessary; Arnould and Nørgaard, 1978). The short half-life of Na^{22} dictates a very short timescale for production, condensation of dust grains, and trapping, as provided by a nova (Clayton and Hoyle, 1976).

Like $C\beta$ -SiC, $C\epsilon$ -SiC contains Si of a distinctly non-solar isotopic composition, far beyond the range of previous meteorite analyses (Fig. 3; data from Zinner et al., in preparation). These isotopic compositions are not likely to have been altered in the solar system, as the instability of SiC in a solar gas precludes isotopic exchange or formation of "local" SiC that would dilute the presolar SiC. An important question is the number of discrete components and discrete stellar sources represented here. On such a 3-isotope plot with a common denominator, mixtures of 2 components lie on a straight line joining the 2 components, whereas mixtures of n components lie within an n-sided polygon whose vertices are the n components. A trivial solution is a triangle large enough to encompass all the points. But in the present case, a more meaningful answer comes from the 12 single grains analyzed

²Two types, Ne - E(L) and Ne - E(H), are distinguished, which are located in carrier phases of <u>low</u> and <u>high</u> density and release temperature, respectively. Only Ne - E(H) is being discussed here, as the carrier of Ne - E(L), $C\alpha$, has not yet been isolated. It appears to be some type of graphitic carbon (Eberhardt *et al.*, 1981).

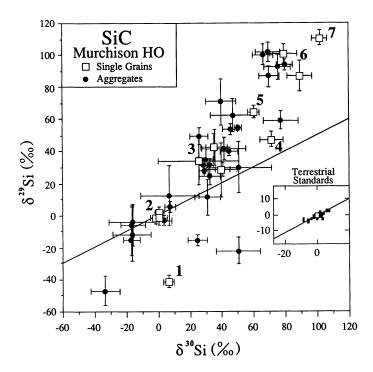


Fig. 3. Isotopic composition of Si in SiC from Murchison HO, relative to terrestrial Si (at 0,0). For definition of delta notation, see footnote to Table 1. Mass fractionation line is shown only for reference. Single grains are pure components, but with some surface debris, whereas aggregates are mixtures. Error bars $\pm 1\sigma$ indicate variations within each grain or aggregate, not analytical precision (which is shown in the inset). The 12 single grains represent about five pure components (1-5); at least 1 other is needed for an aggregate that lies off-scale. As Si is not affected by H, He-burning, these ≥ 6 components require ≥ 6 stars of distinctive isotopic composition. The dispersion of these 6 components indicates the isotopic heterogeneity of the ISM on the scale of single stars. (Zinner et al., in preparation.)

Ratio	Solar	Silicon Carbide		
	System	Absolute	$\odot = 1$	
C^{12}/C^{13}	89.9	10-160	0.12- 1.78	
$N^{14'}/N^{15}$	272.2	65- 6300	0.24- 23	
Si^{29}/Si^{28}	0.0506	0.043- 0.056	0.85- 1.11	
$C^{12}/C^{13} \ N^{14}/N^{15} \ Si^{29}/Si^{28} \ Si^{30}/Si^{28}$	0.0336	0.026- 0.037	0.78- 1.10	

TABLE 2
Isotopic Ratios in Meteoritic SiC^*

in this set. Pooling those whose error bars overlap within 2σ , we are left with 5 discrete components (plus at least one other represented by an aggregate that lies outside the polygon defined by these 5 components; Zinner *et al.*, 1987).

Since Si is unaffected by H- or He-burning under non-explosive conditions, these ≥ 6 Si components represent ≥ 6 discrete stars. The 30% dispersion of these 6 components in Fig. 3 ought to be a good measure of the isotopic heterogeneity of the interstellar medium, on the scale of at least individual stars. This is a new and important constraint for theories of the ISM.

The range of isotopic variation in SiC is shown in Table 2. The variations for C and especially N are much larger than those for Si, but they need not represent inter-star variations. Since C and N are affected by H- and He-burning, such variations are expected during evolution of a single AGB star.

4. DISCUSSION

4.1. ORIGIN OF SIC

SiC can condense from a cosmic gas only at C/O > 1 (well above the solar ratio of 0.42, Anders and Grevesse, 1988), and thus must have formed in carbon-rich stars. Of the various sources reviewed by Tielens (1988), carbon-rich giants and novae are the most important, with carbon stardust injection rates of 2 x 10^{-6} and 1 x 10^{-8} M_{\odot} yr⁻¹ kpc⁻³. Type II supernovae and WC 8-10 stars also are potential candidates (1 x 10^{-6} and 5 x 10^{-8}), although SiC has not yet been observed in their outflows.

Of the isotopic anomalies observed in SiC, Ne^{22} and N^{15} point strongly to a nova origin, while C^{12} , C^{13} , N^{14} , and s-process Kr, Xe are compatible with a wider range of stellar sources. The Si anomalies require explosive nucleosynthesis and hence ultimately a supernovae origin, but this could have happened one or several generations earlier. (However, W. D. Arnett (preprint, 1987) suggests a direct origin from the C-rich shell of a massive supernova.)

^{*} Data from Zinner, Tang and Anders (1987); Tang, Anders, and Zinner (1988); Zinner et al., (in preparation)

Carbon stars are thought to contribute about 1/3 of the total mass ejected from stars (Tielens, 1988), and since <u>all</u> of their Si is expected to condense as SiC (Larimer and Bartholomay, 1979), it is very surprising that primitive meteorites contain only 4×10^{-5} of their Si as SiC! Two factors may be invoked.

- 1. Some SiC was destroyed in the solar system by the enigmatic "chondrule-forming process" that flash-heated part of the dust to melting or even vaporization temperatures, producing chondrules and Ca-Al-rich inclusions (Anders, 1987). SiC would be irreversibly destroyed in the O-rich gas (C/O = 0.42), to an extent indicated by the fraction of such coarse-grained material. Some chondrite classes contain as much as 80% coarse-grained material, but the C2 chondrites on which our SiC data are based contain only 50%, so this process can deplete SiC by only a paltry factor of 2.
- 2. The solar system presumably formed in an OB association (Reeves, 1978; Schramm and Olive, 1982), where only massive, hence O-rich, stars had evolved to the mass-loss stage. They would produce no new SiC, and would actually destroy SiC after reaching the supernova stage. A possible indication of a supernova contribution to the early solar system is the presence of short-lived radionuclides, which imply late addition of $\sim 10^{-4}$ M_{\odot} of recently synthesized matter (Wasserburg, 1985; Schramm and Olive, 1982; but see Cameron, 1984). The $C\delta$ diamonds, representing $\sim 10^{-3}$ of the cosmic complement of C in primitive meteorites, also have a strong supernova signature in the form of Xe HL ($^{132}Xe HL/C \simeq 1.3 \times 10^{-3}$ of cosmic). It remains to be seen whether the required destruction of SiC is consistent with the observed addition of supernova material. Any remaining SiC deficiency must have been inherited from an earlier stage, by some combination of underproduction, overdestruction, and local heterogeneity.

4.2. AGE OF SILICON CARBIDE

In addition to its Ne^{22} "label," SiC from the Murray and Murchison meteorites contains a small amount of the rarest Ne isotope, Ne^{21} (Tang and Anders, 1988c). A nucleosynthetic origin of the Ne^{21} is unlikely, leaving cosmic-ray spallation of Si as the obvious source. But the recent cosmic-ray irradiation of the meteorites can account for at most 5% of the observed amount, and an early irradiation with solar energetic particles during the T-Tauri stage of the Sun (Caffee et al., 1987) can also be ruled out (Tang and Anders, 1988c).

The only remaining alternative seems to be a <u>presolar</u>, i.e. interstellar, cosmic-ray irradiation of the SiC. The length of this irradiation can be calculated (Tang and Anders, 1988c), using estimates of the interstellar galactic cosmic-ray spectrum (Reedy, 1987) and corrections for recoil losses of Ne^{21} from small SiC grains (Ray and Völk, 1983). The mean for 3SiC fractions from 2 meteorites is 41 ± 8 Myr (or, with allowance for systematic errors, $41 \ (+20,-14)$ Myr). As the SiC comes from ≥ 6 stars, this age should be fairly representative, yet it is an order of magnitude shorter than current estimates of the lifetimes of refractory interstellar grains, which have converged on 500 Myr (Seab, 1987; McKee, 1989). The discrepancy is real and would actually be even greater if part of the Ne^{21} came from another source (nucleosynthesis, early solar-system irradiation) making the age still shorter.

This discrepancy cannot be eliminated by plausible changes in cosmic-ray flux. The flux 4.5×10^9 yr. ago would have to be an order of magnitude lower than the present value, which is very unlikely. Shielding by an interstellar cloud could, in principle, reduce the effective flux, but for the required ~ 10 -fold reduction, the shielding density A would have to be as high as 400 g/cm^2 . At the center of a spherical cloud of M solar masses and N H_2 molecules/cm³:

$$A(g/cm^2) = 1.75 \times 10^{-5} N^{2/3} M^{1/3} \tag{1}$$

Thus for $N=10^4$ cm⁻³ and $M=10^5$ M_o, A is only 0.38 g/cm², and even with $N=10^6$ cm⁻³, A would be only 8.1 g/cm².

We are left with 3 alternatives.

- 1. The age is real, but the theoretical estimates of grain lifetimes are wrong.
- 2. The age is real, but grain lifetimes were shorter 4.5×10^9 yr. ago.
- 3. The age has been falsified by neon losses from the SiC.

We shall not examine 1), in the hope that someone else will. As for 2), grain lifetimes are determined mainly by supernovae shocks, and so a 10-fold decrease in lifetime would require a 10-fold increase in supernovae activity. So large an increase is unlikely on a galactic scale, but is at least conceivable on a local scale, e.g., the OB association from which the solar system apparently formed. We have already pointed out in Sec. 4.1 that the low abundance of SiC in meteorites may imply high supernovae activity in the protosolar OB association. Qualitatively, the short age of the SiC seems to call for exactly the same explanation, but it remains to be seen whether a self-consistent level of supernovae activity can account for both the abundance and age of the SiC.

Alternative 3) cannot be ruled out categorically, but requires very special, perhaps unrealistic, circumstances. The high temperatures and long timescales required for outgassing of SiC (~1 hr at 1500–1600 K; Tang and Anders, 1988a) are extremely rare in the interstellar medium. Moreover, the outgassing must not be total, else there would be no Ne^{22} left, and it must not be partial, else small grains would have less Ne than large grains, contrary to observation. A ~10:1 mixture of degassed and undegassed grains would work, and while such a mixture is not a priori unreasonable, it still requires a sustained heat source that outgassed the grains without melting. Such heat sources were available in the early solar system, but have affected only the coarse-grained fraction of meteorites, not the fine-grained fraction, which — according to current models — ought to contain most or all the SiC.

This question deserves further study, since models are not infallible, and we have little direct information on the location of SiC in the meteorite or its thermal history. In particular, single grains from known locations will have to be examined for Ne^{21} , Ne^{22} , other isotopes, radiation damage, and thermal history.

4.3. CHEMICAL STATE OF CARBON IN METEORITES

Nuth (1985) has suggested that the chemical state of carbon in primitive meteorites may reflect that in the Galaxy. Specifically, he noted that graphitic carbon is much

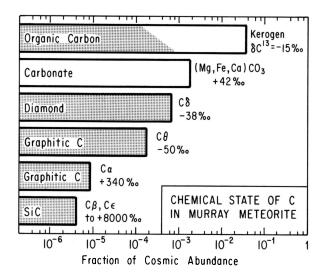


Fig. 4. Chemical state of C in primitive meteorites. Species classified as interstellar on the basis of isotopic anomalies are shaded. Diamond, not graphitic C, is the dominant form of elemental C. Total organic C is more abundant still, but only a minor, poorly known, fraction of this is interstellar. SiC accounts for only 4 x 10^{-6} of the total C rather than the \sim 0.03 expected if \sim 0.3 of the interstellar Si came from carbon stars. Apparently carbon star material was grossly underrepresented in the solar nebula. (Updated from Tang and Anders, 1988a.)

rarer than organic carbon, and in view of its higher heat resistance, it must have been at least as rare in the interstellar matter prior to solar-system reprocessing. Apparently graphitic carbon, though the thermodynamically stable form of C in carbon-star atmospheres, is quite rare in the Galaxy.

Following Tang and Anders (1988a), we shall reexamine this conclusion and its underlying assumptions, on the basis of the new data in Fig. 4.

Organic carbon still is the principal form, but judging from its modest deuterium enrichment (2-8-fold over terrestrial ocean water) and the rarity of Drich "hotspots" in interplanetary dust particles (Walker, 1988), only a minor part (\sim 1%?) seems to be well-preserved interstellar. Most of the organic carbon was altered in the solar system or formed de novo by grain catalysis from CO (Hayatsu and Anders, 1981; Lewis and Prinn, 1980). The CO may have been in part interstellar, in part the degradation product of reprocessed interstellar organic matter.

The new data Fig. 4 confirm that graphitic carbon is quite rare, actually being less abundant than diamond. The principal graphitic C component shown here $C\theta$ — probably should not even be counted, as it occurs as inclusions in $MgAl_2O_4$ (Tang et al., 1988), and thus must have formed as a minor product under unusual conditions (the cosmic Al/C ratio is only 8.4 x 10^{-3}). However, the upper limit for free graphitic C in C2 chondrites is comparable to the abundance of $C\theta$, and so the $C\theta$ value is a reasonable approximation of the total amount of graphitic C.

There are two reasons, however, why this distribution cannot be regarded as representative of the Galaxy.

- 1. Reprocessing. A substantial part of the original interstellar material was reprocessed in the solar nebula. Although the matrix of primitive chondrites (~50% for C2 chondrites) escaped heating to > 500 K, it did experience some reheating as well as alteration by liquid water in the meteorite parent bodies. This left the sturdier forms of carbon unaffected, but volatilized or altered the organic carbon. Counteracting these destructive processes, some organic and graphitic C was formed metastably from CO in the solar nebula (Hayatsu and Anders, 1981). Thus, one cannot readily relate meteoritic abundances of organic and graphitic carbon to interstellar abundances of these species.
- 2. Rarity of Carbon Star Material. We have argued in Sec. 4.1 that SiC is underabundant in meteorites by $\sim 10^{-4}$ relative to average interstellar matter, due to a deficiency of carbon star material in protosolar matter. But diamond and graphitic C also come from carbon-rich stars (not necessarily of the same class), and so they, too, may be underabundant. (Or, diamond may be overabundant if it came from a nearby supernova or red giant that contributed short-lived radionuclides.) Thus even the surviving interstellar component in meteorites may not be representative of average interstellar matter.

This does not mean that the solar system is somehow special. In the spirit of Sec. 4.1, and references cited therein, we suggest that a deficiency of carbon star material is to be generally expected in OB associations, after massive supernovae have destroyed most older stardust and filled the neighborhood with O-rich material, but before the less massive members of the association have evolved to carbon stars and replenished the carbon stardust. An OB association may be a bad place to look for average interstellar matter. There is another trend in the meteoritic data that provides a clue to carbon chemistry in stellar condensation. Each noble-gas component is associated with one or at most two specific chemical forms of carbon, e.g.:

- Xe HL with diamond, not SiC or graphitic C
 - Xe S with SiC, not diamond or graphitic C
 - Ne E with SiC and graphitic C, not diamond

The present data confirm this trend only down to the 1-10% level, and do not preclude minor "cross-contamination" below this level. Still, it appears that carbon condensation is selective in a given stellar type, favoring mainly one chemical form of C. The noble gas component characteristic of that stellar type thus associates mainly with one particular state of carbon.

Lastly, we must point out the high degree of observational selection in our data. The interstellar grain types isolated thus far — diamond and SiC — are exceptionally resistant in nature and in the laboratory. Less resistant types would have been destroyed by our isolation procedures, if they were not previously destroyed by thermal or aqueous alteration in the meteorite parent bodies. Future, more comprehensive work may give a broader representation of interstellar dust.

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REFERENCES

```
Anders, E. 1986, in Comet Nucleus Sample Return, (Paris: ESA SP-249), p. 31.
           -. 1987, Phil. Trans. R. Soc. Lon. [A], 323, 287.
Anders, E. and Grevesse, N. 1988, Geochim. Cosmochim. Acta., submitted.

Arnould, M. and Nørgaard, H. 1978, Astr. Ap., 64, 195.

Begemann, F. 1980, Rep. Prog. Phys., 43, 1309.

Bernatowicz, T., Fraundorf, G., Tang, M., Anders, E., Wopenka, B., Zinner, E., and Fraundorf, P.
Reidel), p. 317.
Eberhardt, P., Jungck, M. H. A., Meier, F. O., and Niederer, F. R. 1981, Geochim. Cosmochim.
Acta., 45, 1515.

Hayatsu, R. and Anders, E. 1981, Topics Curr. Chem., 99, 1.

Heymann, D. and Dziczkaniec, M. 1979, Proc. Lunar Planet Sci. Conf., 10, 1943.

Jørgensen, U. G. 1988, Nature, 332, 702.

Larimer, J. W. and Bartholomay, M. 1979, Geochim. Cosmochim. Acta., 43, 1455.

Lewis, J. S. and Prinn, R. G. 1980, Ap. J., 238, 357.

Lewis, R. S., and Anders, E. 1981, Ap. J., 247, 1122.

Lewis, R. S., Anders, E., Wright, I. P., Norris, S. J., and Pillinger, C. T. 1983, Nature, 305, 767.

Lewis, R. S., Bright, D., and Steel, E. 1987, Meteoritics, 22, 445.

Lewis, R. S., Tang, M., Wacker, J. F., Anders, E., and Steel, E. 1987, Nature, 326, 160.

Manuel, O. K., Hennecke, E. W., and Sabu, D. D. 1972, Nature, 240, 99.

Mathis, J. S., Rumpl, W., and Nordsieck, K. H. 1977, Ap. J., 217, 425.

McKee, C. 1989, in IAU Symposium 135, Interstellar Dust, eds. L. J. Allamandola and A. G. G.

M. Tielens, (Dordrecht: Kluwer), p. 431.

Nuth, J. A. 1985, Nature, 318, 166.

Ott, U., Begemann, F., Yang, J., and Epstein, S. 1988, Nature, 332, 700.

Ray, J. and Völk, H. J. 1983, Icarus, 54, 406.

Reedy, R. C. 1987, J. Geophys. Res., 92, E(?)697.
              Acta., 45, 1515.
 Reedy, R. C. 1987, J. Geophys. Res., 92, E(?)697.
 Reeves, H. 1978, in Protostars and Planets, eds. T. Gehrels (Tucson: Univ. Arizona Press), p.
              399.
 Saslaw, W. C. and Gaustad, J. E. 1969, Nature, 221, 160.
Schramm, D. N. and Olive, K. A. 1982, Annals N. Y. Acad. Sci., 395, 236.
  Seab, C. G. 1987, in Interstellar Processes, eds. D. J. Hollenbach and H. A. Thronson, Jr., (Dor-
 drecht: Reidel), p. 491.
Srinivasan, B. and Anders, E. 1978, Science, 201, 51.
Swart, P. K., Grady, M. M., Pillinger, C. T., Lewis, R. S., and Anders, E. 1983, Science, 220, 406.
Tang, M. and Anders, E. 1988a, Geochim. Cosmochim. Acta., 52, 1235.
           -. 1988b, Geochim. Cosmochim. Acta., 52, 1245.
 —. 1988c, Ap. J. (Letters), in press.
Tang, M., Anders, E., and Zinner, E. 1988, Lunar Planet. Sci., 19, 1177.
Tang, M., Lewis, R. S., and Anders, E. 1987, Meteoritics, 22, 462.
```

Tang, M., Lewis, R. S., Anders, E., Grady, M. M., Wright, I. P., and Pillinger, C. T. 1988, in Geochim. Cosmochim. Acta., 52, 1221.
Tielens, A. G. G. M. 1988, in Carbon in the Galaxy: Studies from Earth and Space, ed. J. Tarter, (NASA CP-), in press.
Tielens, A. G. G. M., Seab, C. G., Hollenbach, D. J., and McKee, C. F. 1987, Ap. J., 319, L109.
Walker, R. M. 1988, in Infrared Observations of Comets Halley and Wilson and Properties of the Grains, ed. M. S. Hanner, (NASA CP-3004), p.53.
Wasserburg, G. J. 1985, in Protostars and Planets II eds. D. C. Black and M. S. Matthews, (Tucson: Univ. Arizona Press), p. 703.
Wdowiak, T. J. 1987, Nature, 328, 385.
Zinner, E., Tang, M., and Anders, E. 1987, Nature, 330, 730.