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# SILICON NITRIDE FROM SUPERNOVAE

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## ABSTRACT

Seven presolar silicon nitride ($Si_3N_4$) dust grains have been identified (five unambiguously and two probably) in separates of the Tieschitz (H3.6) and Murchison (CM2) meteorites, confirming previous tentative identifications of this mineral as a presolar component. These rare ($\gtrsim$2 ppb in Murchison) grains have isotopic compositions similar to those of the uncommon class of meteoritic SiC known as grains X (~60 ppb in Murchison), namely $^{28}$Si and $^{15}$N excesses relative to solar, both $^{13}$C excesses and deficits, and extremely high inferred $^{26}Al/^{27}Al$ ratios. These isotopic compositions coupled with Ca and Ti isotopic anomalies seen in some SiC grains X point to an origin in Type II supernova ejecta for SiC grains X, and by analogy for the $Si_3N_4$ grains as well. However, substantial discrepancies exist between the isotopic characteristics of the grains and the compositions predicted by supernova models.

*Subject headings:* dust, extinction — nuclear reactions, nucleosynthesis, abundances — supernovae: general

## 1. INTRODUCTION

Some presolar dust grains formed in stellar atmospheres or in expanding supernova ejecta survived the formation of the solar system with little processing and became incorporated into primitive meteorites. These grains retain the isotopic and chemical signatures of their stellar sources and thus provide information about stellar nucleosynthesis and about the physical and chemical conditions in stellar atmospheres. The most extensively studied presolar grains—SiC, graphite, and diamond—are all carbon-rich (e.g., Anders & Zinner 1993; Ott 1993), although a relatively small number of presolar oxide grains have also been found (Huss et al. 1994; Nittler et al. 1994).

In addition to C-rich and O-rich grains, prior work gave some evidence for presolar silicon nitride in meteorites. The first hint that such grains are present in meteorites came from stepped combustion experiments of acid residues of the ordinary chondrites Inman and Tieschitz that revealed the presence of a N-rich phase with isotopically heavy N (Alexander et al. 1990). Electron diffraction studies of the same residues identified the mineral silicon nitride ($Si_3N_4$), and no other nitrides, suggesting that $Si_3N_4$ is the $^{15}$N-enriched carrier (Lee et al. 1992). In an ion-probe study of single grains in a Tieschitz residue, Alexander (1993) found a Si-rich, C-poor grain (TZ-2) with isotopically extremely light Si. Ion-probe measurements of single grains in the Murchison (CM2) separate KJE (average size 1.14 $\mu$m) revealed a Si- and N-rich grain, named KJE853 (Hoppe et al. 1994c). In addition to its unusual Si-isotopic composition, KJE853 also had isotopically anomalous C and N. Comparison of negative secondary ion ratios of C, CN, and Si from KJE853 with those measured in synthetic silicon nitride ($Si_3N_4$) and silicon oxynitride ($Si_2N_2O$) strongly suggested that this grain was one of these two minerals.

We report here the identification of seven additional presolar silicon nitride grains. The grains were located by ion-imaging in the ion microprobe: two in the Tieschitz separate T8 (size 0.5–5 $\mu$m), three in the Murchison separate KJG (average size 3.02 $\mu$m), one in Murchison KJD (average size 0.81 $\mu$m), and one in Murchison KJE.

## 2. RESULTS

In this study we used ion-imaging to map the $^{28}Si^-/^{30}Si^-$, $CN^-/C^-$, and $Si^-/C^-$ ratios in grains dispersed on Au foil to quickly locate grains with unusual isotopic and elemental ratios. For example, grains from the uncommon (~1%) subclass of meteoritic SiC known as grains X have $^{28}Si/^{30}Si$ ratios much higher than the solar value (Amari et al. 1992; Nittler et al. 1993; Hoppe et al. 1994b). The technique of ion-imaging has been previously described by Nittler et al. (1994) and Hoppe et al. (1994b). Imaging searches of Tieschitz separate T8 and Murchison separates KJD, KJE, and KJG (details of sample preparation may be found in Nittler et al. 1994 and Amari, Lewis, & Anders 1994) identified 127 candidate grains with high $^{28}Si/^{30}Si$ ratios. Thin window energy-dispersive X-ray spectroscopy (EDS) in a scanning electron microscope and the $Si^-/C^-$ ion signal ratio measured in the ion microprobe identified most of these as SiC (Table 1 and Fig. 1). However, two Tieschitz grains, three Murchison KJG grains, one KJD grain, and one KJE grain had $Si^-/C^-$ ion ratios much higher than SiC. Furthermore, EDS analysis of these Tieschitz and KJG grains showed silicon and nitrogen X-ray peaks, but no oxygen (Fig. 1). By comparison with EDS spectra obtained on synthetic $Si_3N_4$, we identified the grains as $Si_3N_4$. However, without further information (from electron diffraction or laser Raman spectroscopy, for example), we cannot distinguish between the two known structures of the mineral: $\alpha$-$Si_3N_4$ and $\beta$-$Si_3N_4$. EDS data do not exist for the isotopically similar Si-rich, C-poor KJD and KJE grains and the previously reported grains TZ-2 and KJE853. However, they are probably

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TABLE 1

Isotopic and Elemental Data for Presolar $Si_3N_4$ and SiC Grains X

| Grain | $\delta^{29}Si$ (‰)[a] | $\delta^{30}Si$ (‰) | $^{12}C/^{13}C$ | $^{14}N/^{15}N$ | $^{26}Al/^{27}Al$ | $CN^-/C^-$ | $Si^-/C^-$ |
|---|---|---|---|---|---|---|---|
| SiC Grains X[b] ..... | −750 to +125 | −770 to −45 | 18–6800 | 13–250 | 0.006–0.060 | 0.02–3.5 | 0.82–1.37 |
| TZ-2[c] .............. | −470 ± 61 | −285 ± 40 | 53 ± 3 | n.m.[d] | n.m. | n.m. | >10 |
| KJE853[e] ........... | −43 ± 56 | −271 ± 50 | 157 ± 33 | 18 ± 1 | n.m. | 15.7 | 188 |
| T8SIN-1[f] ........... | n.m. | −372 ± 60 | n.m. | n.m. | n.m. | n.m. | n.m. |
| T8SIN-2[f] ........... | n.m. | −262 ± 90 | n.m. | n.m. | n.m. | n.m. | n.m. |
| KJD-155-8[f] ......... | n.m. | −530 ± 70 | n.m. | n.m. | n.m. | 2.0 | 10.1 |
| KJE-159-8[f] ......... | n.m. | −190 ± 60 | n.m. | n.m. | n.m. | 7.0 | 32.8 |
| KJGM2-9-6 ........ | <−44 | −160 ± 60[f] | 33 ± 1 | 101 ± 6 | 0.067 ± 0.004 | 2.0 | >3.7 |
| KJGM2-155-5...... | −190 ± 11 | −326 ± 13 | 168 ± 12 | 77 ± 2 | 0.216 ± 0.005 | 12.2 | 8.5 |
| KJGM4-49-7....... | −229 ± 9 | −359 ± 10 | 83 ± 7 | 39 ± 3 | >0.0012 | 3.9 | 18.3 |

Note.—All errors are 1 $\sigma$.

[a] $\delta^{i}Si \equiv [(^{i}Si/^{28}Si)_{Sample}/(^{i}Si/^{28}Si)_{Terr} - 1] \times 1000$.

[b] Ranges observed by Amari et al. 1992, Nittler et al. 1993, Hoppe et al. 1994b, and in this Letter.

[c] Alexander 1993.

[d] "n.m." means not measured.

[e] Hoppe et al. 1994c.

[f] Measured by ion-imaging.

$Si_3N_4$ as well. We found no $Si_3N_4$ grains with isotopically normal or heavy Si.

Morphologically, the $Si_3N_4$ grains have a blocky appearance, similar to most presolar SiC (Hoppe et al. 1994a), and do not have the needle-like shape previously reported for Tieschitz $Si_3N_4$ (Lee et al. 1992). Presolar $Si_3N_4$ is less abundant than SiC by about a factor of 3000 in our Murchison residues. Because $Si_3N_4$ may be preferentially dissolved during the chemical treatments used in our sample preparation, we obtain a lower limit of about 2 ppb for the abundance of presolar $Si_3N_4$ in the Murchison meteorite.

Subsequent to ion-imaging and SEM examination, $^{28}Si$-rich candidate grains were analyzed in the ion microprobe under

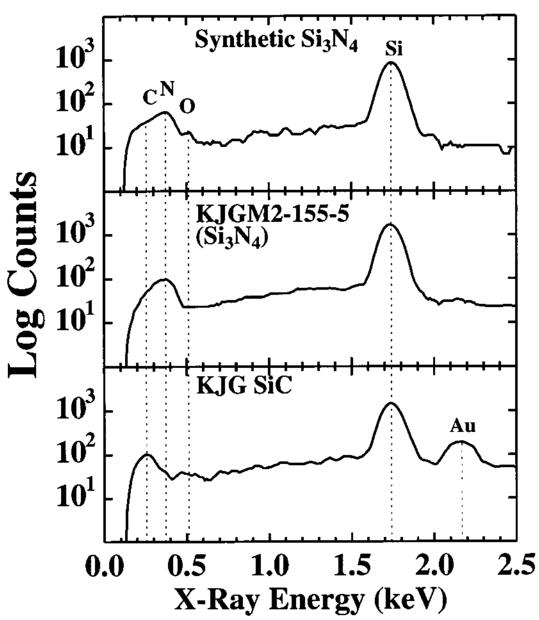


Fig. 1.—EDS spectra produced by 5 keV electrons for a synthetic $Si_3N_4$ grain and two Murchison grains with anomalous isotopic compositions. Synthetic $Si_3N_4$ may contain minor amounts of oxygen (Lee et al. 1995), accounting for the O peak in the standard spectrum. The low-energy tail in this spectrum is due to a C coating. Grain KJGM2-155-5 shows Si and N peaks similar to those of the $Si_3N_4$ standard, and we thus identify this grain and others with similar spectra as $Si_3N_4$. The Au peak in the SiC spectrum is produced by the mounting substrate.

high–mass-resolution conditions for their isotopic compositions of C, N, Si, Mg–Al, Ca, and Ti, following previously described techniques (Zinner, Tang, & Anders 1989). Not all of these elements were measured in all of the grains, both because of variable concentrations of trace elements and small grain sizes. The two $Si_3N_4$ grains from Tieschitz and the two grains from KJD and KJE unfortunately were sputtered away by the $Cs^+$ ion beam before their isotopic compositions could be measured at high mass resolution. The Murchison $Si_3N_4$ grains have isotopic compositions very similar to those of SiC grains X, and the two types of grains will be discussed here together. Isotopic and elemental data for the $Si_3N_4$ grains and SiC grains X are presented in Table 1 and Figures 1–4.

Unlike typical ("mainstream") circumstellar SiC grains, which are enriched in the heavy isotopes of Si relative to solar, the presolar $Si_3N_4$ grains and SiC grains X are enriched in $^{28}Si$. On a $\delta^{29}Si$ versus $\delta^{30}Si$ three-isotope plot (Fig. 2), a few of the grains lie on or near a mixing line of slope 1 between solar system Si ($\delta^{i}Si \equiv 0$) and pure $^{28}Si$ ($\delta^{i}Si = -1000$‰). Most of the grains, however, have larger $^{30}Si$ than $^{29}Si$ depletions and cluster around the line $\delta^{29}Si = 0.67 \times \delta^{30}Si + 9.3$. A few grains lie significantly above and below these two lines.

Mainstream SiC grains have $^{13}C$ and $^{14}N$ excesses, characteristic of partial H-burning by the CNO cycle (Hoppe et al. 1994a). In contrast, the $Si_3N_4$ grains and SiC grains X have large $^{15}N$ excesses, with $^{15}N/^{14}N$ ratios up to a factor of 21 higher than solar, and $^{12}C/^{13}C$ ratios ranging from 18 to 6800 (Fig. 3). SiC grains X also have, on average, higher N contents than mainstream SiC, as indicated by higher $CN^-/C^-$ secondary ion ratios.

The $Si_3N_4$ grains and SiC grains X also are characterized by large $^{26}Mg$ excesses, almost certainly from the decay of $^{26}Al$, with inferred initial $^{26}Al/^{27}Al$ ratios between 0.006 and 0.60 (Table 1 and Fig. 4). The $^{26}Al/^{27}Al$ ratio of one $Si_3N_4$ grain is given as a lower limit because of $^{27}Al$ interference from a neighboring Al-rich grain on the sample mount. None of the $Si_3N_4$ grains have sufficient Ca or Ti for isotopic analyses of these elements. However, several grains X have excesses in $^{44}Ca$, evidently from the decay of short-lived $^{44}Ti$ ($\tau_{1/2}$ = 52 yr), with inferred initial $^{44}Ti/^{48}Ti$ ratios between 0.003 and 0.37, as well as excesses in $^{49}Ti$ and/or $^{50}Ti$ (Amari et al. 1992; Nittler et al. 1995; Strebel et al. 1995).

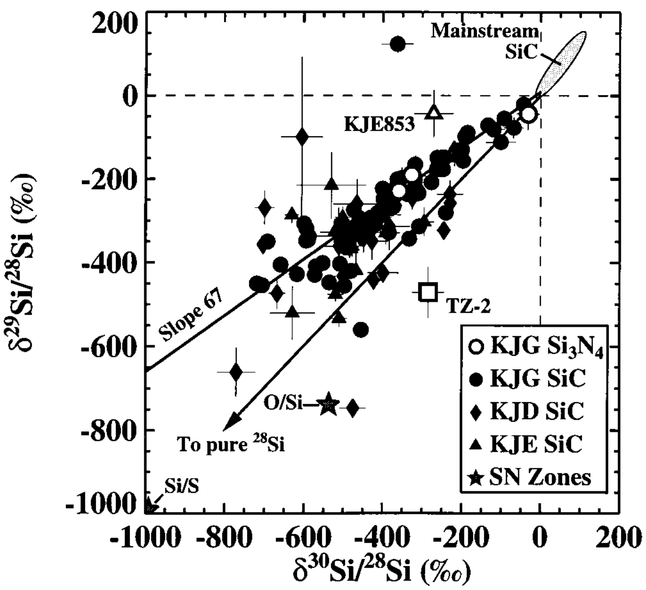


FIG. 2.—Si isotopic ratios in presolar $Si_3N_4$ grains and SiC grains X from Murchison separates KJG, KJD, and KJE, plotted as $\delta$ values, deviations from the solar isotopic ratios in permil (‰). Also shown are previously analyzed $Si_3N_4$ candidates KJE853 (Hoppe et al. 1994c) and TZ-2 (Alexander 1993), the range of Si-isotopic ratios of typical ("mainstream") presolar SiC, and the ratios predicted in the O/Si and Si/S zones of a 25 $M_\odot$ star (Meyer et al. 1995). Presolar $Si_3N_4$ and SiC grains X have excesses in $^{28}$Si, relative to the heavier Si isotopes, probably due to mixing of $^{28}$Si from the O/Si and Si/S zones. Most of the grains fall near a line of slope 0.67, with larger depletions in $^{30}$Si than $^{29}$Si. Dashed lines indicate solar ratios in this and subsequent figures.

## 3. DISCUSSION

Type II supernovae have been proposed as the most likely stellar sources for SiC grains X (Amari et al. 1992), and such an origin is qualitatively consistent with most of the isotopic signatures found in these grains and thus those in the isotopically similar $Si_3N_4$ grains as well. The ejected matter from a Type II supernova is usually assumed to be comprised of material from concentric zones that have different isotopic compositions due to their different nuclear burning histories

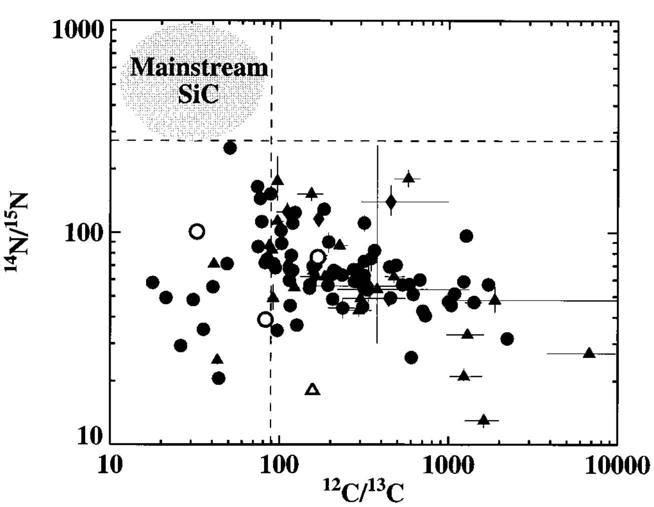


FIG. 3.—Carbon and nitrogen isotopic ratios of Murchison presolar $Si_3N_4$ and SiC grains X; symbols are the same as in Fig. 2. Mainstream SiC falls in the upper left quadrant. $Si_3N_4$ grains and grains X have $^{15}$N excesses, relative to solar, and carbon that ranges from isotopically very heavy to very light.

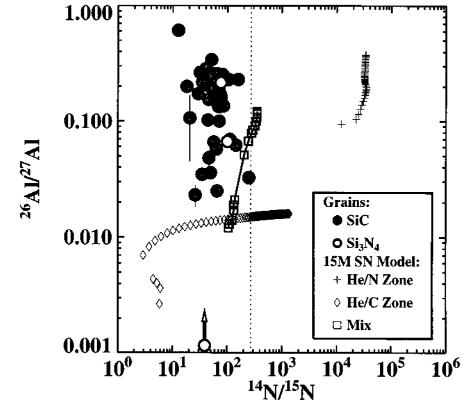


FIG. 4.—Al- and N-isotopic ratios in KJG $Si_3N_4$ and SiC grains X are compared to theoretical predictions for a 15 $M_\odot$ supernova (Woosley & Weaver 1995; Zinner et al. 1995). Shown are the ratios predicted for different points in the He/N and He/C zones and for a model of mixing of zones in the SN ejecta. The extremely high $^{26}Al/^{27}Al$ ratios coupled with low $^{14}N/^{15}N$ ratios observed in the grains cannot be explained by current supernova models.

during the star's presupernova evolution and during the explosion itself. Selective mixing of these zones is required to explain the main features of our data, but such mixing is indicated both by astronomical observations (e.g., Shigeyama & Nomoto 1990) and by hydrodynamic models (e.g., Müller, Fryxell, & Arnett 1991). In addition, simple supernova mixing models have successfully reproduced the isotopic compositions of a class of graphite grains from the Murchison meteorite (Zinner et al. 1995). SiC grains X and presolar $Si_3N_4$ have both high and low $^{12}C/^{13}C$ ratios. High $^{12}C/^{13}C$ ratios point to a contribution from the He/C zone of the presupernova star, and $^{15}$N excesses are also predicted for this zone from explosive nucleosynthesis, although the total N abundance in this zone is low (Woosley & Weaver 1995). High $^{26}Al/^{27}Al$ ratios and low $^{12}C/^{13}C$ ratios point to a significant contribution from the overlaying He/N shell, where H-burning has occurred. To reproduce the Si, Ca, and Ti isotopic compositions observed in these grains, material from inner zones where O is burned to $^{28}$Si and where $^{44}$Ti and $^{49}$V are produced must be mixed with material from the He/C and He/N zones.

Although the isotopic signatures of presolar silicon nitride and SiC grains X can thus be *qualitatively* understood within the framework of Type II supernovae, major problems arise in attempting to *quantitatively* match the compositions of the grains with current supernova models (Meyer, Weaver, & Woosley 1995; Woosley & Weaver 1995). Perhaps the most serious difficulty comes from the extremely high $^{26}Al/^{27}Al$ ratios combined with $^{15}$N excesses. These $^{26}Al/^{27}Al$ ratios extend to higher values (up to 0.6) than are predicted anywhere in the supernova models of Woosley & Weaver (1995) (e.g., the maximum is 0.4 in a 15 $M_\odot$ star). Furthermore, the highest ratios are predicted for the He/N zone. Since this zone contains much more nitrogen than the He/C zone (≈300:1 in the 25 $M_\odot$ star of Meyer et al. 1995), and this nitrogen is essentially pure $^{14}$N from CNO-cycle burning, mixtures of the two regions that have high $^{26}Al/^{27}Al$ ratios should also have high $^{14}N/^{15}N$ ratios, not the low $^{14}N/^{15}N$ ratios observed in the grains. This difficulty is illustrated in Figure 4, where the isotopic ratios predicted for different points along the He/C and He/N zones in a 15 $M_\odot$ SN, and for a mixing model in the same star (Zinner et al. 1995), are compared with the grain data. Explosive H-burning in novae may produce large amounts of both $^{26}Al$ and $^{15}N$, but this process would also produce large excesses of $^{13}C$, i.e., low $^{12}C/^{13}C$ ratios (Wiescher et al. 1986; Politano et al. 1995). Moreover, novae are not expected to produce the $^{44}Ti$ or $^{49}Ti$ observed in several SiC grains X. Explosive H-burning is not predicted to occur in Type II supernovae.

Another puzzle is posed by the silicon isotopic ratios. Since H-burning does not affect Si isotopes, the Si isotopic ratios in the He/N zone should be unchanged from their initial values, usually assumed solar. However, *n*-capture in the He/C shell produces excesses in $^{29}Si$ and $^{30}Si$, and O-burning produces copious amounts of pure $^{28}Si$ deep in the star. Mixing of these zones can result in $^{28}Si$ enrichments, but supernova models do not predict the higher depletion of $^{30}Si$ relative to $^{29}Si$ observed in most of the $Si_3N_4$ grains and SiC grains X, at least not in zones with appreciable amounts of silicon. For example, a simple two-component mixture between pure $^{28}Si$ and the *s*-processed silicon in the He/C zone would result in compositions falling below the slope 1 line in Figure 2, in contrast to most of the grain data.

Formation of $Si_3N_4$ requires a reducing environment ($C/O > 1$), as well as sufficiently high concentration of N. Equilibrium condensation calculations indicate that for physical and chemical conditions typical of carbon star envelopes, $Si_3N_4$ is not stable, relative to SiC and other nitrides such as TiN and AlN (Lodders & Fegley 1995). This may, in fact, help explain why no silicon nitride grains have been found that isotopically resemble the mainstream population of SiC, which probably did form around carbon stars (Hoppe et al. 1994a). On the other hand, the supernova region with $^{15}N$ enrichments and $C/O > 1$, namely the He/C zone, has a very low nitrogen abundance, much lower relative to carbon than carbon star envelopes and the $^{14}N$-rich He/N shell. The presence in meteorites of $^{15}N$-enriched $Si_3N_4$ grains, rather than $^{14}N$-enriched ones from the He/N zone, is thus rather puzzling. Perhaps the nitrogen abundance in the He/C zone is much higher than the models predict. Alternatively, Russell et al. (1995) suggest that shock effects during the supernova explosion may lead to regions with high enough nitrogen pressure for the formation of $Si_3N_4$. Finally, the high N contents of the SiC grains X may be due to $Si_3N_4$ present either as subgrains or in solid solution with SiC.

## 4. SUMMARY

Ion microprobe measurements in meteoritic acid residues, coupled with SEM-EDS analysis, have resulted in the unambiguous identification of five members of a new type of presolar grain in meteorites, $Si_3N_4$. Two additional isotopically anomalous grains were found which are probably $Si_3N_4$. This work confirms previous tentative identifications of presolar $Si_3N_4$ (Lee et al. 1992; Alexander 1993; Hoppe et al. 1994c). These rare dust grains are isotopically similar to SiC grains of type X and thus probably formed in the same stellar environments. Ca, Ti, and Si isotopic ratios in the grains X point to Type II supernova as sources, and they and C, N, and Al isotopic signatures indicate extensive mixing of the supernova ejecta. However, major discrepancies between model predictions for these stars and the observed isotopic compositions of the grains present a challenge for future stellar modeling.

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