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Type II Supernova Matter in a Silicon Carbide Grain from the Murchison Meteorite

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The circumstellar silicon carbide (SiC) grain X57 from the Murchison meteorite contains large amounts of radiogenic calcium-44 (20 times its solar system abundance) and has an anomalous silicon isotopic composition, different from other circumstellar SiC grains. Its inferred initial ^{44}Ti/Si and ^{44}Ti/^{48}Ti ratios are 1.6×10^{-4} and 0.37. In addition, it contains radiogenic magnesium-26; the inferred initial ^{26}Al/^{27}Al ratio is 0.11. The isotopic and elemental data of X57 can be explained by selective mixing of matter from different zones of a typical type II supernova of 25 solar masses during its explosion. The high ^{44}Ti/Si ratio requires contributions from the innermost nickel zone of the supernova to the SiC condensation site, as similarly suggested by astronomical observations.

Meteorites contain refractory dust grains that are believed to be of circumstellar origin (*1*). These grains provide information about stellar nucleosynthesis, stellar evolution and mixing of material in the interior of stars, physical and chemical conditions in stellar atmospheres during grain formation, and the inventory of stars that contributed dust to the protosolar nebula. After formation in the atmospheres of stars and passage through the interstellar medium, these dust grains went into the ancestral molecular cloud from which our solar system formed. Refractory dust grains survived the formation of the solar system inside small planetary bodies and comets, and they are carried to Earth by meteorites.

Identified circumstellar grains include SiC, diamond, graphite, corundum (Al_2O_3), spinel ($MgAl_2O_4$), silicon nitride (Si_3N_4), and carbides of Ti, Zr, and Mo (*1*). One class of SiC grains, the X grains, constitute approximately 1% of all SiC grains separated from meteorites (*2*, *3*). The X grains are characterized by strong isotopic enrichments relative to their solar system abundances of ^{28}Si (up to threefold), ^{15}N (up to 20-fold), and in many grains, ^{12}C (up to 80-fold). They also show large excesses of ^{26}Mg and, in some cases, also of ^{44}Ca and ^{49}Ti. These excesses are believed to be a result of the in situ decay after grain formation of the radionuclides ^{26}Al (half-life $T_{1/2}$ = 716,000 years), ^{44}Ti ($T_{1/2}$ = 47 years), and ^{49}V ($T_{1/2}$ = 330 days). Corresponding initial ^{26}Al/^{27}Al and ^{44}Ti/^{48}Ti ratios range up to 0.61 and 0.16, respectively.

On the basis of their enrichments in ^{28}Si and the presence of ^{44}Ti at the time of grain formation, type II supernovae have been suggested as the most likely stellar sources of the X grains (*2*). These supernova stars are believed to consist of a Ni core surrounded by concentric layers that experienced different stages of nuclear burning (*4*–*6*) (Fig. 1). The isotopic signatures of the X grains suggest deep and inhomogeneous mixing of matter in the supernova ejecta. When the X grain data are quantitatively compared with model predictions for the ejecta of typical type II supernovae (*5*, *6*), some discrepancies do exist. In particular, the large ^{15}N excesses, high initial ^{26}Al/^{27}Al ratios, and enrichments of ^{29}Si relative to ^{30}Si cannot be satisfactorily explained. These differences point to deficiencies in the understanding of current type II supernova models or to an alternate origin [for example, type I supernovae (*2*)] of the X grains.

To provide constraints for supernova models from X grain data, we analyzed more than 6000 individual SiC grains separated from the Murchison meteorite by ion imaging with the University of Bern ion microprobe. Grains from fractions KJD and KJE having sizes around 1 μm (*7*) were dispersed on gold foils. Digitized isotopic images of $^{12}C^-$, $^{28}Si^-$, and $^{30}Si^-$ ions emitted from the SiC grains under bombardment with Cs^+ ions were acquired with a CCD (charge-coupled device) camera, and X grains were found by searching for grains with low ^{30}Si/^{28}Si ratios (Fig. 2). The 43 X grains we identified were subsequently analyzed with high mass resolution for the isotopic compositions of C, N, Mg-Al, Si, and Ca-Ti. Because the grains are small, only a limited number of these elements could be analyzed on each grain.

The isotopic data of most X grains agree with those obtained previously, and the same general problems are encountered when the grain data are compared with predictions from current type II supernova models. An exception is X57, which has a distinct Si isotopic signature and a comparatively low ^{26}Al/^{27}Al ratio. Besides the generally observed ^{28}Si enrichment, it has an excess of ^{30}Si over ^{29}Si, falling well below the array formed by the majority of the X grains in a three-isotope representation (Fig. 3). Magnesium in X57 is monoisotopic ^{26}Mg, and the inferred initial ^{26}Al/^{27}Al ratio is 0.11 (Table 1). In addition, X57 has a

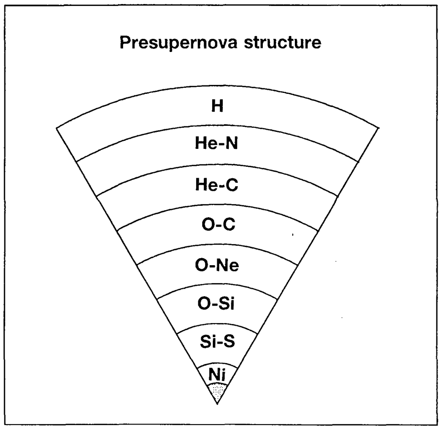

Fig. 1. Schematic section through a $25M_\odot$ type II supernova. Zones are designated according to their most abundant elements. The spatial extent of the zones is not accurately indicated. The shaded area represents the supernova remnant. [Adapted from (*5*)]

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^{44}Ca enrichment of 20 times the solar system abundance. Attributing this excess to the decay of ^{44}Ti, we obtain initial ^{44}Ti/Si and ^{44}Ti/^{48}Ti ratios of 1.6×10^{-4} and 0.37 (Table 1), representing the largest ^{44}Ti concentration discovered in circumstellar grains to date.

Anomalies in ^{44}Ca abundance from the decay of ^{44}Ti have been predicted to occur in meteoritic samples (*8*), and it was pointed out that ^{44}Ti can be produced in a supernova (*9*). For a detailed comparison of the isotopic compositions measured in X57 with predictions from supernova models, we used the yields for a large number of nuclides in the eight distinct zones (Fig. 1) presented by Meyer *et al.* (*5*) based on the calculations of Weaver and Woosley (*4*) for a 25 solar mass ($M_{\odot}$) type II supernova. The ^{44}Ti is most abundant in the innermost Ni zone, which experienced a freezeout from nuclear statistical equilibrium [compare with (*5*)]. Smaller amounts of ^{44}Ti can be expected in the overlying Si-S and O-Si zones (Fig. 1), which experienced, respectively, complete and partial O burning. The ^{44}Ti/^{48}Ti ratios are 0.50 for the Ni zone, 0.06 for the Si-S zone, and 1.80 for the O-Si zone. Hence, the presence of extinct ^{44}Ti with $^{44}\text{Ti}/^{48}\text{Ti} = 0.37 \pm 0.11$ in X57 implies that the Ni or O-Si zone, or both, contributed matter to the condensation site of X57. Furthermore, because the condensation of SiC requires $C/O \geq 1$ (*10*), a significant contribution from the He-C zone, which is rich in C and poor in O because of partial He burning, is necessary. The ^{44}Ca can be also produced in the O-rich zones; however, the condition $C/O \geq 1$ precludes a direct production of the excess ^{44}Ca in the supernova, justifying the assumption that the ^{44}Ca excess of X57 originates from the in situ decay of ^{44}Ti.

Mixing all matter from the He-C zone to the O-Si zone gives $C/O = 0.16$. Consequently, to preserve the condition $C/O \geq 1$, the mixing must be selective. In particular, contributions from the O-rich zones (O-C, O-Ne) must be limited. Hydrodynamic models of supernova explosions predict fingers and mushroomlike structures rising from the interior to the outer portions of the ejecta as a result of Rayleigh-Taylor instabilities (*11*). These structures allow mixing of matter from nonneighboring regions with little contamination of matter from the intermediate zones. Taking up this possibility, the simplest X57 formation scenario would be a mixture of matter from the He-C and O-Si zones. Such mixing can reproduce the ^{44}Ti/^{48}Ti ratio and Si isotopic composition of X57. However, the ^{44}Ti/Si ratio of such mixtures is $\leq 1.4 \times 10^{-5}$, an order of magnitude lower than the ratio measured in X57. From trace-element data of SiC grains (*12*), it is justified to assume that the original Ti/Si ratio is roughly preserved (within a factor of 2) during condensation of SiC; thus, even when uncertainties in the nucleosynthetic yield of ^{44}Ti are considered, the observed high ^{44}Ti/Si ratio requires the addition of matter from the innermost Ni zone. Mixing only Ni and He-C zone material in any proportion cannot reproduce the measured Si isotopic composition. Mixing matter from the He-C, O-Si, Si-S, and Ni zones can reproduce the ^{44}Ti/^{48}Ti and ^{44}Ti/Si ratios and the Si isotopic composition of X57 but gives too low a value of ^{26}Al/^{27}Al (≤ 0.007). The highest ^{26}Al/^{27}Al ratio (0.20) is found in the He-N zone, which lies above the He-C zone and experienced H burning. Because the absolute abundance of ^{26}Al in the He-N zone is low, large amounts of matter from this zone have to be added in order to reproduce the ^{26}Al/^{27}Al ratio of X57. We have tested more than 40,000 different mixtures from the seven inner zones and find that a mixture of material from the He-N, He-C, O-Si, Si-S, and Ni zones in a ratio of 1:0.05:0.025:0.005:0.005 (mass fractions of the total zone that must be mixed) gives the best match with the isotopic data of X57 (Table 1).

Our mixing model is characterized by two necessary constraints, independent of the mixing details: (i) the need to mix material from the Ni zone with the outer portions of the ejecta, independently confirming similar conclusions derived from photometric, x-ray, and gamma-ray observations of supernova light curves [for example, (*13*)], and (ii) the need to limit the contribution of matter from O-rich zones in the supernova ejecta. Although we have considered only the specific case of a $25M_{\odot}$ type II supernova model of metallicity identical to that of the sun (metallicity is the mass fraction of elements heavier than He), these two constraints appear to hold in a much more general sense. Calculations of nucleosynthetic yields for supernovae in the mass range $11M_{\odot}$ to $40M_{\odot}$ and metallicities from 0 to 1 times the solar value (*6*) imply that ^{44}Ti will only be ejected in considerable amounts by those type II supernovae that eject large quantities of matter from their Ni zones. Furthermore, nuclear burning makes all zones between the C-rich (He-N, He-C) and Si-rich (O-Si, Si-S) zones rich in O, leading to the necessity of limiting the contributions from these intermediate zones to

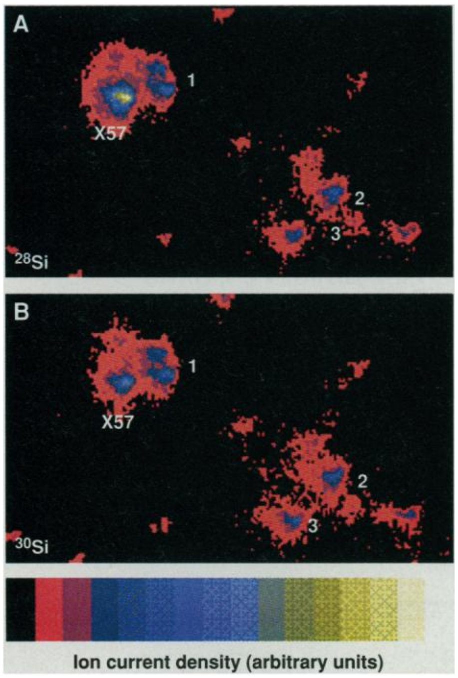

Fig. 2. Images of (**A**) $^{28}Si^-$ and (**B**) $^{30}Si^-$ ions emitted from circumstellar SiC grains (≈1 μm) separated from the Murchison meteorite. One grain, X57, shows a strong excess in ^{28}Si relative to ^{30}Si as compared to typical SiC grains, which are labeled 1 to 3.

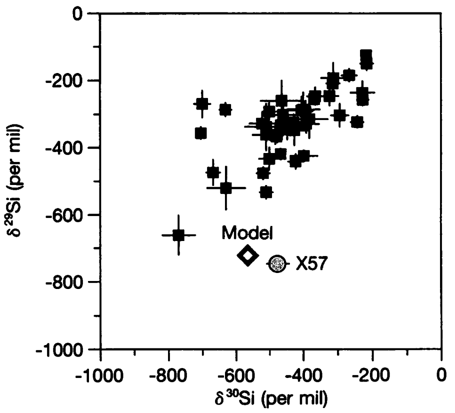

Fig. 3. Silicon isotopic compositions of SiC X grains from Murchison separates KJD and KJE. The data of X57 can be reproduced by a mixing model for a $25M_{\odot}$ type II supernova explosion. Compositions in per mil deviation from the terrestrial values are given by $\delta^{i}\text{Si} = 1000 \times [(^{i}\text{Si}/^{28}\text{Si})_{\text{sample}}/(^{i}\text{Si}/^{28}\text{Si})_{\text{terrestrial}} - 1]$, where $i = 29$ and 30.

Table 1. Isotopic and elemental ratios of grain X57 compared to those from the $25M_{\odot}$ type II supernova model. Errors are 1σ.

Source	^{44}Ti/^{48}Ti	^{44}Ti/Si	^{26}Al/^{27}Al	δ^{29}Si (per mil)	δ^{30}Si (per mil)
Grain X57	0.37 ± 0.11	$(1.6 \pm 0.4) \times 10^{-4}$	0.11 ± 0.03	-747 ± 16	-475 ± 33
Model	0.31	1.2×10^{-4}	0.085	−722	−564

the SiC condensation site.

The necessity for large contributions from the He-N zone (70% of the mass making up X57) may indicate that present type II supernova models underestimate the production of ^{26}Al in the H-burning (He-N) zone and also in zones that experienced advanced burning stages. Although the isotopic and elemental abundance pattern of X57 is fully compatible with an origin in a typical type II supernova, those of the majority of the X grains are not. This incompatibility implies either that most X grains injected into the protosolar nebula came from atypical type II supernovae or even from other stellar sources (for example, type I supernovae) or that the production of N, Al, and Si and the layering in presupernova stars is not fully understood by current type II supernova models.

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Corundum, Rutile, Periclase, and CaO in Ca,Al-Rich Inclusions from Carbonaceous Chondrites

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Four calcium,aluminum–rich inclusions from four carbonaceous chondrites—Allende, Acfer 082, Acfer 086, and Acfer 094—were studied by transmission electron microscopy. All inclusions contained at least two of the oxides periclase (MgO), rutile (TiO_2), calcium oxide (CaO), and corundum (Al_2O_3). The oxides (50 to 200 nanometers in size) were found inside and at grain boundaries of the constituent minerals of the inclusions. Determining how these oxides formed may provide insight about condensation processes in the early solar nebula and the origin of refractory inclusions in chondrites. Formation of these oxides by exsolution is considered unlikely. An origin by kinetically controlled condensation appears more probable.

Calcium,aluminum–rich inclusions (CAIs) found in carbonaceous chondrites contain refractory minerals such as spinel, melilite, fassaite, hibonite, grossite, and perovskite (*1*), mineral phases that may be early condensates from a cooling solar nebular gas (*2*). The CAIs contain isotopically anomalous oxygen (*3*), show evidence for the existence of short-lived nuclides such as ^{26}Al (*4*), and represent the oldest material formed in the solar system (*5*). Therefore, CAIs contain valuable information about the very first processes in the solar nebula.

According to thermodynamic calculations (*2*), corundum was the first solid oxide to condense from the cooling solar nebula. Thus, its mineralogical and textural characteristics are of particular interest for the understanding of the formation of solids in the solar nebula. However, corundum has been identified in very few inclusions [for example, Lancé (*6*), Murchison (*7*), and Allende (*8*)].

Because CAIs are usually studied by scanning electron microscope, electron microprobe, and ion microprobe, corundum and other simple oxides may not be found, as a result of their small grain size. Therefore, we performed a transmission electron microscopy (TEM) study of four CAIs from different carbonaceous chondrites (*9*).

Three type A inclusions (*10*) from Acfer 082, Acfer 086, and Allende (*8*) and one spinel-perovskite spherule from Acfer 094 were investigated (*11*, *12*). The CAIs were characterized by scanning electron microscopy and electron microprobe and then thinned for TEM studies by conventional ion-beam techniques (*13*). All phase identifications were made on the basis of compositional analyses and structural characterizations based on selected-area electron diffraction (SAED) patterns.

The CAIs in Acfer 082, Acfer 086, and Allende contain ~70% (by volume) blocky melilite [Åkermonite content, 4 to 13 mol % (Åk$_{4-13}$)] crystals that enclose euhedral spinels (15 to 20 volume %, 10 to 80 μm), typically pure $MgAl_2O_4$ in composition. Fassaite (5 to 10 volume %, 200 to 300 μm) and perovskite (~10 volume %, 50 to 80 μm) occur as irregularly shaped, anhedral grains enclosed within the melilite (*14*). Some Fe,Ni metals were found in Acfer 082 and Allende CAIs, enclosed within melilite and, more rarely, the spinels. In the Allende CAI, some hibonite laths (20 to 50 μm) and several Os-, W-, and Re-rich particles (up to 60 μm) are present (*8*). The CAI in Acfer 094 is a 100-μm spinel-perovskite spherule (*11*). Apart from spinel (~65 volume %) and perovskite (~5 volume %), which are found in the core of the inclusion, the CAI consists of melilite (~10 volume %, Åk$_{7-10}$) and fassaite (~20 volume %), which basically occur as constituents of the outer layer. All inclusions studied are unweathered, and their interiors do not contain secondary alteration products.

In addition to these mineral phases, we found in all four CAIs oxides that have not been described before and are not predicted to be stable under equilibrium condensation conditions (Table 1). Inclusions of rutile (TiO_2) were identified in CAIs from all four chondrites (Fig. 1A). Energy dispersive spectroscopy (EDS) analyses and SAED confirm that the grains are single crystals and almost pure TiO_2 in composition. As a result of contributions from the surrounding matrix, 50-nm grains contain up to 1 weight % FeO or MgO, or both. The rutile grains range from 50 to 100 nm in size and typically occur as rounded grains located at grain boundaries between spinels and between spinel and perovskite (Fig. 1A). Rarely, the tiny inclusions are embedded within the interiors of the spinels or

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