Coordinated Isotopic and TEM Studies of a Supernova Graphite

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This work is a continuation of our study of presolar graphite spherules from supernovae [1, 2]. We report the results of a combined isotopic and transmission electron microscope (TEM) study of an unusually large (12 μm diameter) presolar graphite spherule from the Murchison (CM2) density separate KE3 (1.65-1.72 g cm^{-3} [3]) that has previously shown to be rich in super-nova grains. The spherule, KE3e#10, was mounted on gold foil, characterized in the SEM, and then analyzed using a CAMECA IMS3f ion probe. The $^{12}C/^{13}C$ of 125 ± 1 verifies the presolar origin of the spherule (solar = 89). In addition, minor element compositions point to a supernova (SN) origin for KE3e#10 -- there are large excesses of ^{18}O ($^{16}O/^{18}O$ = 174 ± 7) and ^{26}Mg (inferred $^{26}Al/^{27}Al$ = (9.5 ± 0.4) x 10^{-3}), as well as an enrichment of ^{28}Si (δ^{29} = -85 ± 31 per mil; δ^{30} = -123 ± 30 per mil). The Ti-isotopic pattern of the grain (large excess of ^{49}Ti) bears the signature of neutron capture in the He/C zone of a SN, and can be explained if the Ti in the He/C zone is mixed with that of close-to-solar composition [4].

After isotopic characterization, the grain was embedded in resin and sliced into 70 nm sections with a diamond ultramicrotome. We studied 37 sections in the TEM, and detected many (55) internal TiC crystals, which correspond to 770 ppm of the graphite by volume. The TiC crystals are large, with geometric mean diameters ranging from 0.03 μm up to 0.5 μm (average = 0.2 μm). The high abundance and large size of the TiC crystals imply high gas pressures in the SN outflow at the time of grain formation. The mean TiC size requires a minimum of 10^6 Ti atoms/cm^3 for a formation time of 1 year. For scale, this is 3 dyne/cm^2 (3 microbar) in a gas of solar composition. Textural evidence and compositional variation among grains (below) indicate that the TiCs formed prior to (and were accidentally included in) the graphite. We infer that TiC was *not* in chemical equilibrium with the gas from which the graphite formed, however. Unlike the euhedral TiCs in SN graphite KE3d#7 [1], these TiCs all show evidence of chemical weathering before inclusion in the graphite. All TiC crystals have rounded corners, some are very corroded, and ~1/4 of them have 3–15 nm amorphous rims (Fig.1). NanoSIMS studies of several unrimmed TiCs [5] show that they are enriched in O relative to the surrounding graphite, but have similar $^{16}O/^{18}O$. Whether this O enrichment is related to the corrosion is still unclear.

The chemical composition of each TiC was measured using energy-dispersive X-ray spectrometry (EDXS) in the TEM. V is in solid solution in the TiC, (mean concentration ~10 at. %). Figure 2 shows the distribution of V/Ti in the 55 TiC grains, with a mean (0.112) equal to the solar value (0.122) within error

(excluding four grains with abnormally low V/Ti). The large dispersion of V/Ti values about the mean (σ/μ = 17%) reflects a real variation in the degree of solid solution of V in TiC (analytical uncertainty is ~2%). Trace elements (Fe, P, Ca) were also detectable in (about half of) the *rimmed* TiC grains, together comprising ~1 at. % on average. Fe is detectable in most rimmed and unrimmed TiCs at about 0.2 at. %. In a few rimmed grains Fe is as much as 1.5 at.%. In these, P is also high (2 − 4 at. %) as well as Ca (0.5 −1.5 at. %). Si was detected at ~1 at. % in the graphite.
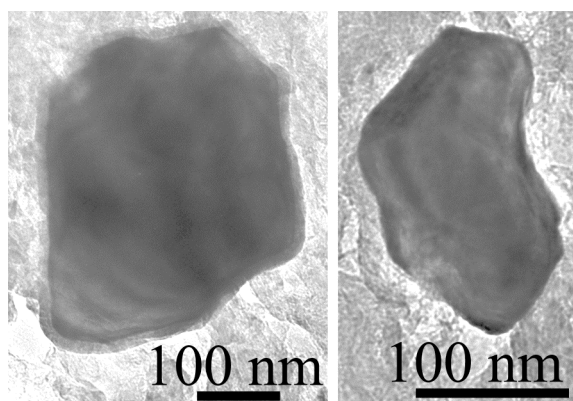

Figure 1. TiC crystals in Murchison SN graphite spherule KE3e#10. The left TiC has rounded corners and a 15 nm amorphous rim enriched in Fe, P and Ca. The right TiC is unrimmed, but is severely corroded.
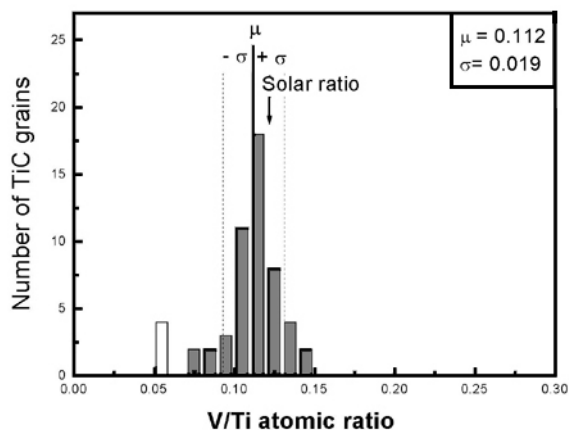

Figure 2. V/Ti distribution for 55 internal TiC crystals in Murchison graphite spherule KE3e#10. The mean value (excluding the 4 unshaded data) is equal to the solar value of 0.122 within error.

The large number of sections of KE3e#10 permits a search for possible TiC chemical and morphological trends as a function of radial distance (and thus of graphite growth history) from the spherule center. Radial distance was determined from the distance of the TiC crystal from the geometrical center of the

graphite section in which it is found, combined with the distance of that section from the spherule's center as inferred from the section diameter. If the TiCs are accreted by contact with the surface of the growing graphite spherule, there should be a constant number per volume of graphite if the TiC grain number density in the gas did not change relative to the number density of gaseous carbon species contributing to spherule growth. Dividing the spherule into 10 equal volume shells, we find that the innermost 2 shells have 24 TiCs, whereas the outermost 2 shells have only 3 TiCs. The intermediate six shells have 4 ± 1 TiC/shell. Thus, there seems to have been a *decrease* in the number density of TiC grains in the gas as the spherule grew. There is no evident increase of TiC size with distance from the spherule center, as expected, since TiC growth was clearly over by the time the TiC was captured by the growing graphite (as shown by TiC *corrosion*). There is also no correlation of degree of corrosion, or the presence of rims, with distance from the spherule center.   The rims and corrosion thus cannot be an artifact of the chemical procedures used to prepare the KE3 separate, since the grains closest to the spherule surface would more likely be subject to chemical attack.

Although there is considerable scatter in V/Ti (much larger than measurement uncertainty) among grains at roughly the same radius, there appears to be a correlation (Fig. 3) of V/Ti in TiC with radial distance.
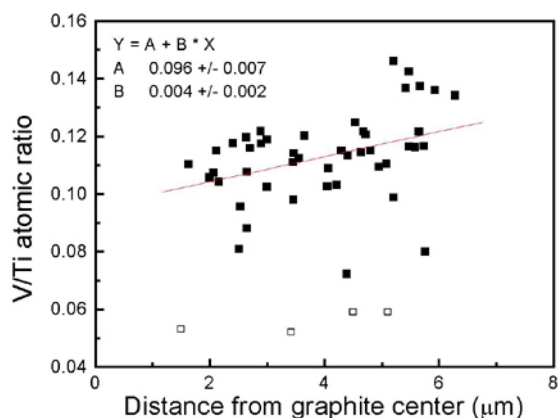

Figure 3. Variation in V/Ti with distance of TiC crystals from the center of KE3e#10 graphite spherule. The line is a least-squares fitting to the data. The 4 crystals (open symbols) at the lower extreme of the distribution in Fig. 1 were not included in the fitting.

This variation implies a progression towards complete solid solution of the more volatile vanadium carbide in TiC [6] during the time that the graphite spherule was growing. We note that some TiCs have V/Ti ratios *greater than* solar (Fig. 2). If V/Ti in the gas phase was initially solar, these grains may reflect relative enrichment of V in the cooling gas as the result of the prevention of TiC from further equilibration with V in the gas after it is incorporated into graphite. The four crystals with very low V/Ti (shown as open symbols in

Figs. 2 and 3) appear to be unrelated to the general trend defined by the other TiCs, and probably had a different history prior to incorporation into the graphite. Perhaps this indicates turbulent mixing of distinct gas parcels in the SN outflow.

In addition to TiC, we found a 75 nm Fe-Ni rich crystal in KE3e#10 at a radius of 2 μm, similar to the rimmed kamacite crystals found in SN graphite KE3d#8 [2]. Its composition is $Fe_{80}Ni_{17}Cr_3$ and the structure is that of kamacite (BCC with a lattice parameter of 0.288 nm). It has a subhedral morphology with rounded edges, again suggesting corrosion, and an Fe-enriched, 4 nm amorphous rim of composition $Fe_{92}Ni_4Cr_4$. As in KE3d#8, we thus have both TiC and kamacite crystals that are rimmed. The origin of these amorphous rims is unclear. Chemical back-reaction with an evolving gas phase is one possibility, although it does not directly account for the similar rim thicknesses on such compositionally dissimilar minerals. Another possibility is surface damage caused by grain impact (of order 100 km/sec) with slower moving gas [2]. Regardless of whether either of these is correct, it is clear that the rimmed grains in KE3e#10 must have had a different history prior to incorporation into the graphite than the unrimmed TiC grains, which implies again turbulent mixing in the SN outflow.

Finally, we found two unusual crystals (0.1 μm and 0.2 μm) in KE3e#10 that were identified by EDXS and electron diffraction patterns as chromite. This oxide is not, however, predicted to condense at any temperature in a gas of solar composition, regardless of C/O ratio. The oxygen isotopic composition of the 0.2 μm crystal was determined by NanoSIMS to be solar within error, so the chromite, *per se*, is not presolar. We note that both crystals were located close to the exterior of the spherule, so that it is possible that the chromite was precipitated between surficial graphite layers in the Murchison parent body. Alternatively, it is possible that the chromite represents a reaction product of a presolar Fe-rich mineral (Fe or Fe_3C) with the K-dichromate solution used to remove kerogen in the preparation of KE3 [3]. It cannot have been produced by reaction of kamacite, since no Ni (which would generally accompany Fe) was detected.

References: [1] Bernatowicz T. *et al.* (1998) *Lunar Planet Sci*. **XXIX**, Abstract #1393; **[2]** Bernatowicz T. *et al.* (1999) *Lunar Planet Sci*. **XXX**, Abstract #1392; **[3]** Amari S., Zinner E. & Lewis R. (1995) *Ap.J.* **447**, L147; **[4]** Meyer B. *et al.* (1995) *Meteoritics* **30**, 325; Woosley S. and Weaver T. (1995) *Ap. J. Suppl. Ser.* **101**, 181; **[5]** Stadermann F. *et al.*, this conference; **[6]** Lodders K. & Fegley B. (1995) *Meteoritics* **30**, 661.