TEM STUDY OF INTERNAL CRYSTALS IN SUPERNOVA GRAPHITES. T. K. Croat, T. Bernatowicz, F.J. Stadermann, S. Messenger, and S. Amari, Laboratory for Space Sciences and Department of Physics, Washington University, St. Louis, MO 63130-4899, USA, tkc@wuphys.wustl.edu.

Introduction: Our coordinated TEM and isotopic study of ten different supernova (SN) graphite spherules from the KE3 size separate of the Murchison meteorite has revealed the presence of many internal crystals, mostly titanium carbides (TiCs), which were accreted during the graphite growth [1]. The morphology and chemical composition of the internal grains indicate that these formed first, underwent variable amounts of weathering, and were finally incorporated into the graphite during its growth. The micrometer-sized graphites were apparently effective at capturing previously formed grains (some graphites contained hundreds of grains). These graphites thus acted as a "time capsules" that preserved the morphology and isotopic and chemical compositions of encapsulated grains formed at earlier times and higher temperatures.

The types of internal grains trapped within the graphites allow the phase condensation sequence to be inferred, which in turn places constraints on the pressure and composition of the gas from which the SN graphites condensed. Some graphites contain a sufficient number of grains to allow various morphological and compositional trends to be discerned as a function of the distance from the graphite center, which is a rough measure of the time at which an individual grain was incorporated. These trends give further clues as to the physical processes that were operating during condensation in the expanding SN ejecta.

Table 1. Isotopic Compositions of KE3 SN graphites.

	$^{12}C/^{13}C$	$^{16}O/^{18}O$	$\delta^{29}Si$ ($^o/_{oo}$)	$\delta^{30}Si$ ($^o/_{oo}$)
Solar	89	499	0	0
d7	107.1 ± 0.4	49 ± 1	-325 ± 53	-539 ± 42
e3	282 ± 3	298 ± 11	-52 ± 28	-43 ± 29
e6	231 ± 2	290 ± 12	-1 ± 32	-11 ± 32
e7	92.2 ± 0.6	100 ± 3	-227 ± 47	-290 ± 45
e10	125.2 ± 0.7	174 ± 7	-85 ± 31	-123 ± 30
e11	81.5 ± 0.4	320 ± 10	-66 ± 29	-79 ± 29
e15	59.7 ± 0.3	236 ± 9	11 ± 63	-93 ± 59
f131	110.0 ± 0.3	84 ± 18	-279 ± 48	-317 ± 29
f331	190 ± 1	202 ± 3	412 ± 62	369 ± 59
f542	1583 ± 18	351 ± 16	-139 ± 26	-92 ± 38

Experimental: The KE3 graphite spherules were mounted on gold foil, characterized in the SEM, and then analyzed for C, O, and Si with a Cameca IMS3f ion probe. After isotopic characterization, graphites with O and/or Si compositions indicative of a SN ori-gin [2] were picked from the mount, embedded in resin, and sliced with an ultramicrotome. The 70 nm thick slices were retrieved on holey carbon-coated copper TEM grids and examined in a JEOL 2000FX analytical TEM equipped with a NORAN Energy Dispersive X-ray Spectrometer (EDXS).

Results: Isotopic results for the SN graphites are summarized in Table 1 (along with 1σ errors and the solar values). Ten KE3 graphites were selected for TEM study on the basis of large excesses in ^{18}O combined with significant deviations in their Si isotopic ratios from the solar values (typically ^{28}Si excesses), indicative of a SN origin. Aside from the ubiquitous presence of TiCs, the SN graphites showed considerable variations in other properties. Table 2 summarizes the number and types of internal grains within the SN graphites, along with the average V/Ti ratio and geometrical mean diameter of the internal TiCs. The TiC abundances ranged over two orders of magnitude (25-2300 ppm) and the average geometrical mean grain size ranged from 30 to 230 nm among the SN graphites. No obvious scaling relationship was found between the graphite size and the average size of the internal TiCs. Although most were euhedral, the crystals showed varying degrees of surface corrosion; also, some crystals were anhedral and had extensive internal disorder. About 25-40% of the TiCs were surrounded by amorphous or partly amorphous rims (of thickness 2-15 nm). These diverse morphological features (along with the variations in chemical composition) suggest that the TiCs formed first, underwent weathering in the gas, and finally were incorporated in the graphites. NanoSIMS analysis of both the carbon [3] and oxygen isotopes [4] in individual TiCs confirmed that these internal grains were also of presolar origin.

In four of the SN graphites, some TiCs have iron-rich subgrains (metallic iron, kamacite, and taenite) that are epitaxially attached to their crystal faces. Many structure-specific orientation relationships were found between the two phases (e.g., [001] kamacite // [001] TiC), which shows that one phase heterogeneously nucleated on the other. Of the ~40 composite TiC/Fe grains found, several had multiple iron-rich subgrains nucleated on the same TiC, establishing that these iron-rich subgrains formed *after* the TiCs. A few kamacites were also found as isolated grains within their host graphites, independent of any TiCs.

Internal Crystals in Supernova Graphites: T. K. Croat et al.

Table 2. Internal grains within KE3 SN graphites.

	Internal grains	TiC (ppm)	Avg. TiC diam. (nm)	Avg. V/Ti ratio
d7	21 TiC	2200	232 ± 130	0.072 ± 0.006
e7	3 TiC	140	122 ± 8	0.14 ± 0.01
e10	55 TiC 1 kamacite	1040	187 ± 95	0.109 ± 0.02
e15	86 TiC	2300	76 ± 32	0.099 ± 0.03
f331	15 TiC	290	126 ± 48	0.086 ± 0.01
f542	1 TiC	25	84	0.200 ± 0.004
e3	57 TiC, 1 TiC/Fe 1 kamacite	1330	33 ± 19	0.07 ± 0.02
e6	29 TiC, 8 TiC/Fe	992	136 ± 55	0.10 ± 0.02
e11	167 TiC, 31 TiC/Fe	958	31 ± 8	0.10 ± 0.03
f131	5 TiC 1 TiC/Fe	114	92 ± 17	0.13 ± 0.03

EDXS analyses reveal that V is typically in solid solution within the TiC, often along with trace concentrations of Fe and Ca. Most graphites had V/Ti ratios, averaged over all internal TiCs, that were below the solar ratio of 0.122, although there were exceptions (e.g., e7, f131, and f542) with V/Ti in excess of the solar value. Within a single graphite, the V/Ti ratios from different TiCs typically varied over a range much larger than the typical analytical uncertainty of ~2 %. This real variation in the V/Ti ratios may reflect differences in the temperatures at which the individual TiCs condensed. Vanadium carbide is less refractory than TiC, so TiCs condensing at a higher temperatures likely will have lower V/Ti ratios than those condensing later at lower temperatures.

Trends vs. Radial Distance: Various trends in the chemical composition and size of TiCs were seen as a function of the radial distance of a TiC from the center of the host graphite spherule, which is related to the time at which the TiC was captured. Radial distance was determined from the distance of the TiC from the center of the slice, combined with the distance of that slice from the spherule's center, as inferred from the section diameter. In most SN graphites, no trend was seen in the TiC size vs. distance from the graphite center, implying that TiC growth was largely complete when graphite growth began, and/or that graphite growth was far more rapid than TiC growth. The notable exception was e3, which showed a clear increase in the TiC size vs. distance, indicating that TiC growth was occurring during graphite condensation. Other SN graphites showed weak negative trends, suggesting that at the time of graphite formation, TiCs in the gas were being corroded.

Trends were commonly seen in the V/Ti ratio of TiCs, both as a function of radial distance and TiC grain size. That chemical trends are seen at all (along with the wide distribution of V/Ti ratios) suggests that TiCs did not maintain chemical equilibrium with the surrounding gas subsequent to incorporation into their host graphite, but rather reflect the stoichiometry acquired at the time they formed. Four SN graphites (e3, e6, e10 and f131) showed clear increases in the V/Ti ratio of TiCs towards the exterior of the graphite. This implies that as growing TiCs were exposed to the cooling gas they progressively evolved towards higher V/Ti ratios, with TiCs accreted near the end of graphite growth having time to acquire the most V. Only one SN graphite (e11) showed the opposite trend, a strongly negative correlation between the V/Ti ratio and radial distance. However, in this case, there were clearly two different grain populations, with higher V/Ti grains near the graphite center and lower V/Ti grains towards the exterior, as well as a pronounced deficit of TiC crystals between the two regions. This gap plausibly represents a temporal cessation of TiC accretion by the growing graphite spherule as it traversed pockets of ambient gas with variable number densities of previously formed TiCs. Thus, the negative trend in e11 may simply be the result of the sampling of two distinct TiC populations with different V/Ti. Graphite d7 also showed a weak negative trend, but here the range of measured V/Ti ratios was quite small (0.06 to 0.08).

Several of the SN graphites (e3 and e15 as well as e11) showed markedly higher V/Ti ratios in the larger TiCs. In e3, such an increase is consistent with the positive trends in both size and the V/Ti ratio vs. distance. The TiC grains in this graphite apparently continued growing during graphite formation, adding material that was more V-rich. The increases in V/Ti with size in e15 cannot be explained by this means, since there is no correlation of V/Ti with radial position in the graphite. Such TiC size dependence might occur if only some of the grains continued growing at lower temperatures, simultaneously becoming more V-rich, while other grains had their growth arrested, keeping their lower V/Ti ratios. However, in such a case, the preferential growth of some grains (such as size-dependent growth favoring larger grains) is required.

References: [1] Croat T. K. et al., (2002) *Lunar Planet Sci.* XXXIII*, Abstract # 1315*. [2] Amari S., Zinner E., and Lewis R., (1995) *Ap.J.,* **30***, L147. [3] Stadermann et al., (2002) *Lunar Planet Sci.* XXXIII*, Abstract # 1796*. [4] Stadermann et al., (2003) this volume.