

TIC AND RUTILE WITHIN A SUPERNOVA GRAPHITE.

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Introduction: The origin of rutile grains (TiO₂) found within presolar graphites (e.g. primary condensate or from secondary alteration) is unclear, given that the host graphites form in C-rich environments and rutile likely in O-rich ones [1]. The Orgueil graphite OR1dm3-6 has ¹²C, ¹⁵N and ¹⁸O excesses indicative of a supernova (SN) origin [2, 3], and also contains hundreds of Ti-rich internal grains, both TiC and rutile [4]. Detailed studies of the chemistry, phase, O isotopic composition and spatial distribution of Ti-rich grains within g6 SN graphite strongly suggest that the rutile grains do not form secondarily (e.g. via oxidation of existing TiCs), but rather are also a primary SN condensate and are indicative of compositional changes (mixing) in SN ejecta.

Experimental Methods: After isotopic studies [2, 3], OR1d3m-6 was ultramicrotomed and studied in TEM [4]. Subsequent NanoSIMS measurements of ¹⁶O, ¹⁸O, ²⁸Si, ²⁹Si, and ³⁰Si were made on TiC and rutile-containing graphite sections.

Results and Discussion: Chemical compositions (EDXS) and images were collected from 118 separate Ti-rich internal grains within 7 g6 graphite cross-sections. Due to their unusually high O content, SN TiCs cannot be distinguished from rutile grains on that basis, so 76 Ti-rich grains were identified by their distinctive electron diffraction patterns (TiC, FCC, a= 4.4Å and TiO₂ tetragonal, a= 4.9Å, c=3.1Å). Fifty two rutile grains and 13 TiCs were found, along with 4 Ti-rich grain patterns that may indicate a different Ti-oxide polymorph. Three SiC and two kamacite grains were also found. The TiCs fall into two groups based on size and composition, with the larger ones (80-130 nm) showing significantly higher V and lower Al content (avg. V/Ti and Al/Ti at. ratios of 0.30 and 0.01 as opposed to 0.15 and 0.40 respectively from smaller (<30 nm) TiCs. The clear increase in V/Ti ratio vs. grain size is consistent with large TiCs experiencing extended growth times at lower T and thus incorporating more V (since VC is less refractory than TiC). The high Al content in some small carbides (not seen previously among SN TiCs) may indicate formation of the structurally-similar Ti₃AlC phase (4.2Å cubic). Other than having somewhat higher O content, the rutile grains are similar in size and composition to the small TiCs. Analysis of several central cross-sections show TiCs predominantly clustered towards the outside of the graphite's surface, whereas rutile grains are spread throughout its volume. Thus, oxidation of existing TiCs to form rutile after encapsulation in graphite is unlikely to occur, which gives credence to primary condensation of rutile in SN ejecta. NanoSIMS O isotopic images of a g6 cross-section containing two large TiC show ¹⁶O/¹⁸O of 156±33 in the carbides and 315±23 in the graphite (2 σ errors). The ¹⁸O counts from small TiCs and rutiles were insufficient to allow a separate determination of their isotopic composition. Along with more extreme O anomalies in TiC than in graphite, O isotopic dilution towards normal nearer the graphite's surface is also present, effects similar to those seen in [5].

References: [1] Croat T. K. 2007. *Met. & Planet. Sci.* 42: A34. [2] Croat T. K. et al. 2009. *LPSC XL*, A2175. [3] Jadhav, M. et al. 2006. *New Astron. Rev.* 50:591-595. [4] Jadhav, M. et al. 2008. *LPSC XXXIX*, A1047. [5] Stadermann F.J. et al. 2005 *Geochim. Cosmochim. Acta* 69, 177-188.

Table 1. TiC and rutile grain properties within g6 graphite

Phase	#	Diam. (nm)	O/Ti cnt ratio	Al/Ti at. ra- tio	V/Ti at. ratio
Rutile	52	25 +/-7	1.33+/- 0.60	0.46+/- 0.37	0.15+/- 0.02
Small TiC	10	19 +/-6	0.96+/- 0.57	0.40+/- 0.21	0.15+/- 0.01
Large TiC	3	98 +/- 26	0.23+/- 0.04	0.01 +/- 0.01	0.30+/- 0.08