

## INTERNAL GRAINS WITHIN KFC GRAPHITES: IMPLICATIONS FOR THEIR STELLAR SOURCE.

T. K. Croat, F.J. Stadermann, and T. J. Bernatowicz, Laboratory for Space Sciences and Department of Physics, Washington University, St. Louis, MO 63130, USA, tkc@wustl.edu.

**Introduction:** Despite the assumed contribution of AGB carbon stars to the presolar grains population, few Murchison KFC graphites ( $\approx 4\%$ ) appear in the  $40 \leq {}^{12}\text{C}/{}^{13}\text{C} \leq 70$  range typically observed in the photospheres of AGB stars and in isotopic measurements of presolar silicon carbides. Instead, most have lighter carbon (75% with  ${}^{12}\text{C}/{}^{13}\text{C} > 90$ ) and a significant group has very heavy carbon (15% between  $0 \leq {}^{12}\text{C}/{}^{13}\text{C} \leq 20$ ) [1]. On the basis of bulk isotopic composition alone, a supernova (SN) origin was thought possible for many of the isotopically light carbon graphites, as they fall into the same carbon isotopic range as most SiC-X grains. Recent coordinated TEM and nanoSIMS studies of the same graphite population have shown that many in this light carbon group also contain refractory carbides with s-process enrichments (high Zr, Mo and Ru), indicative of an AGB origin. There is a much smaller subset which likely do have a SN origin, namely those containing pure TiCs without s-process elements or other rare phases (such as iron, iron carbide, and metallic osmium) unlikely to form before graphite around AGB stars.

**Experimental:** Graphites were obtained from the KFC1 density and size separate ( $2.15\text{-}2.20 \text{ g cm}^{-3}$ ,  $>1 \mu\text{m}$ ) of the Murchison meteorite [2]. These graphites were deposited from suspension onto a glass slide, embedded in resin, and then sliced into  $\leq 100 \text{ nm}$  sections with an ultramicrotome. The slices were examined in a JEOL 2000FX analytical TEM equipped with a NORAN Energy Dispersive X-ray Spectrometer (EDXS). The accuracy of quantitative analysis was improved by direct fitting of the background spectrum and by experimental k-factor determinations from lead titanate, lead molybdate, and lead zirconate standards. Selected TEM grids were then affixed to a gold mount with carbon paint and analyzed in the NanoSIMS.

**Results:** Many graphites ( $N=959$ ) from the KFC1 residue have been examined; most are spherules but they often differ in their microtexture. The onion graphites ( $N=340$ ) consist of well-graphitized layers that are coarsely aligned over hundreds of nanometers and gradually curve to form the concentric structure. Turbostratic cauliflower graphites ( $N=241$ ) also show a roughly concentric structure formed by contorted layers, but the ordered domains are of limited thickness ( $<50\text{nm}$ ) and many gaps are visible in cross-section. Along with onion and cauliflowers, crystalline and polycrystalline graphites, aggregates of multiple spherules and other graphites often lacking a clear concentric structure are present within the residue. Represent-

tatives from all of these types (except for crystalline/polycrystalline ones) have been shown to be presolar in the NanoSIMS.

*Internal carbides within graphites.* Both onions and cauliflowers commonly contain internal refractory carbides, with  $\approx 15\%$  of slices showing these small ( $\approx 20 \text{ nm}$ ) internal grains. From observations of single ultramicrotomed slices, we only observe  $\approx 5\text{-}10\%$  of the volume of the entire spherule. Therefore the true fraction of carbide-containing graphites is clearly larger than 15%. Textural evidence from the carbides as well as models of condensation around carbon stars show that carbides form first and are then incorporated into the graphite, rather than forming later by ex-solution [3, 4]. EDXS measurements of the refractory carbides showed (Ti,Zr,Mo,Ru)C forming over a wide compositional range, with 1-95 at.% Ti, 0-80 at.% Zr, 0-38 at.% Mo, and 0-30 at.% Ru (metals basis). The Zr, Mo, and Ru concentrations relative to Ti far exceed the solar ratios. For carbides of the typical size, Mo and Ru (and sometimes Zr) will be below the detection limit if present only at solar values, and yet Zr, Mo, and Ru are measured in 75%, 80%, and 30% of carbides, respectively. Few carbides ( $\approx 12\%$ ) showed no significant enrichment above solar values in any of the s-process elements. Other trace elements (V, Cr, Fe, and Ni) are also commonly found.

Large s-process enrichments (Zr, Mo and Ru relative to Ti) within carbides are diagnostic in that they are unique to AGB stars. However, chemical fractionation during condensation must be considered as it can alter these elemental ratios, depending on the condensation temperatures of the various competing stable phases. Knowledge of the condensation temperatures of ZrC, MoC and TiC is helpful in assessing possible chemical fractionation in carbides. These have been computed for a range of pressures and C/O ratios, both at solar-like compositions and at s-process enriched compositions [5]. ZrC condenses at the highest temperature in all cases, whereas MoC and TiC are generally comparable, especially after s-process enrichment (10x-100x solar) slightly raises the MoC condensation temperature. ZrC condenses at the highest temperature in all cases, whereas MoC and TiC both condense before graphite at nearby temperatures. S-process enrichments (10x-100x) increase both the ZrC and MoC condensation temperature, moving MoC from slightly below TiC to slightly above it. The effects of other elements within the solid solution on the condensation temperatures (eg. Zr in TiC) though are not well

known. The Zr/Mo ratio is a good indicator of the degree of chemical fractionation, as Zr and Mo abundances and the condensation temperatures of their carbides track each other for all values of the overall s-process enrichment. Most grains (N=126) show Zr/Mo ratios less than solar (relatively Mo-rich with avg.  $Zr/Mo = 0.58$  or 13% of solar ratio), indicating that chemical fractionation has likely occurred, due to Zr depletion from the gas by higher-temperature condensation. Four Zr-rich ( $Zr/Mo \gg 4.7$ ) grains are also seen, and are presumably high-temperature condensates that fell out of equilibrium with the gas as they cooled. These assertions are based on the roughly correct assumption that the solar Zr/Mo ratio approximates that found in most AGB stars. The Mo/Ti ratio should be minimally affected by fractionation, as both of these carbide phases condense at a similar temperature. Figure 1 shows the calculated s-process enrichments derived from the measured Mo/Ti ratios and then normalized to the solar value. Large s-process enrichments are seen, with a median enrichment of  $\approx 200x$  above solar ratio. EDXS spectra from carbides of SN origin also give us confidence that the effect of chemical fractionation on Mo/Ti and Zr/Ti ratios is limited. In hundreds of SN carbides, no s-process elements were ever found above the measurement threshold. Photospheric abundance estimates from N-type carbon stars show lower enrichments in s-process elements (typically 10-100x) [5]. However, the carbides may have condensed from an inhomogeneous gas, such that their chemical composition was not representative of the star's bulk composition. Taken together, these observations imply that an AGB origin rather than a SN origin is likely for carbide-containing graphites (which as argued comprise a large fraction of all graphites).

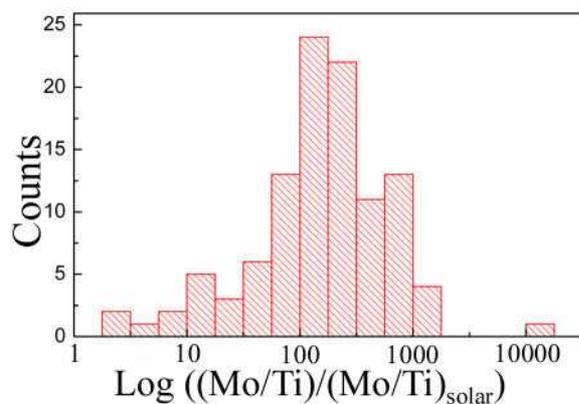


Figure 1. Calculated s-process enrichment in carbides from Mo/Ti ratios normalized to solar values.

NanoSIMS isotopic measurements of C and O of carbide-containing onion graphites are shown in figure 2, grouped according to degree of s-process enrich-

ment. The graphites with s-process enriched carbides fall in the light carbon range ( $100 < ^{12}C/^{13}C < 400$ ). The C ratios and the s-process enrichments in the moderate and heavy enriched groups both exceed those typically measured in AGB stars. However, local regions in the He intershell, where thermal pulses occur, are expected to create both  $^{12}C$  and s-process elements. Condensation of carbides and graphites could occur before such regions are well mixed. However, there is no exact correlation between  $^{12}C$ -richness and s-process elements.

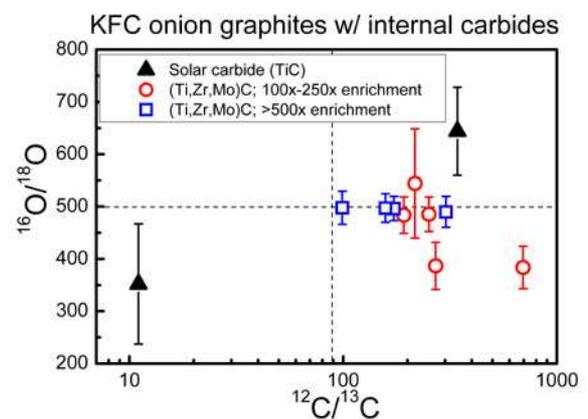


Figure 2. NanoSIMS C and O isotopic ratios of carbide-containing graphites grouped according to degree of s-process enrichment in internal grains.

Despite the clear indications that most of the light carbon graphites are of AGB origin, a smaller subset of the KFC graphites have a likely SN origin based on their internal grains. The pure TiCs (triangles) in figure 2 are consistent in composition with the previously measured carbides in SN graphites. Also, rare phases have been found (including iron and iron carbide, and metallic osmium) that likely would not condense before graphite in AGB ejecta, instead requiring the iron overabundances found around SN. A 50nm metallic osmium grain (hexagonal;  $a=2.77\text{\AA}$  and  $c=4.45\text{\AA}$ ) was also found within an onion graphite with a chemical composition of  $Os_{79}Mo_{10}Ru_9Fe_2$ . Although metallic Os (like other ultra-refractory phases) is an expected high temperature condensate, its very low solar abundance ( $[Os/H]=1.4$ ) generally kinetically inhibits its formation. Since Os is predominantly an r-process element, such a large grain suggests condensation in SN ejecta.

**References:** [1] Hoppe, P. et al. (1995) *GCA* 59, 4029. [2] Amari, S. et al. (1994) *GCA* 58, 459. [3] Bernatowicz, T.J. et al. (1996) *ApJ*. 472,760. [4] Croat, T.K. et al. (2003) *GCA* 67, 4705. [5] Lodders, K. and Fegley, B. Jr. (1995) *Meteoritics* 30, 661.