COORDINATED ISOTOPIC AND TEM STUDIES OF PRESOLAR GRAPHITES FROM MURCHISON.

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Introduction: Previous microstructural (SEM) and isotopic studies of the Murchison KFC1 separate (2.15-2.20 g/ml) found many presolar graphites with an average size of 1.5 microns [1,2]. Carbon isotopic ratios ranged over 3 orders of magnitude (from 0.02 to 80 times the solar value of 89). Two morphological types of presolar graphites were found, with dense "onion" graphites and less dense "cauliflower" graphites, although these types are not isotopically distinct in carbon. Further transmission electron microscope (TEM) studies of the "onion" graphites revealed numerous internal refractory carbides ((Ti,Zr,Mo,Ru)C) and also some graphites with a nanocrystalline core surrounded by a well-graphitized rim [3]. Due to their small size, TEM analyses of graphites that had been isotopically characterized were not possible. In the present work, more graphites were examined in TEM, including the larger "cauliflower" graphites omitted from the earlier study, and isotopic analysis was performed on the same samples examined in the TEM.

Experimental: Graphites were obtained from the KFC1 density and size separate (2.15-2.20 g cm^{-3}, >1 μm) of the Murchison meteorite [4]. These graphites were deposited from suspension onto a glass slide, embedded in resin, and then sliced into □100 nm sections with an ultramicrotome. The 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). 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 [5].

Results: The graphite morphologies were split into two morphological types, in accordance with previous classification [2]. Figure 1 shows typical TEM images of a) a normal onion graphite, b) an onion graphite with a nanocrystalline core and graphitic outer rim, and c) a cauliflower graphite. Many graphites could not be easily classified in this scheme though, especially when damaged during slicing. Selected-area diffraction (SAD) patterns of onion graphites show strong {100}, {110}, and {002} diffraction peaks, indicative of fully crystalline graphites with regular stacking. Similar patterns are obtained from the 50-500 nm thick rim layers of rim-core onion graphites. However, the central core region of these graphites (Fig. 1b) only show {100} and {110} peaks, indicating a nanocrystalline structure consisting of clusters of polycyclic aromatic hydrocarbons (PAHs) [3]. The cauliflower graphites (Fig. 1c) show the {100} and {110} peaks, along with {002} peaks with varying intensity, indicating that the stacking of graphene sheets in the c-direction in cauliflower graphites is irregular and lacking in long-range continuity. The microstructure of cauliflower graphites appeared quite similar to that of many of the KE3 supemova graphites [6]. However, considerable differences were found in the chemical composition of their internal carbides and in the oxygen isotopic ratios.

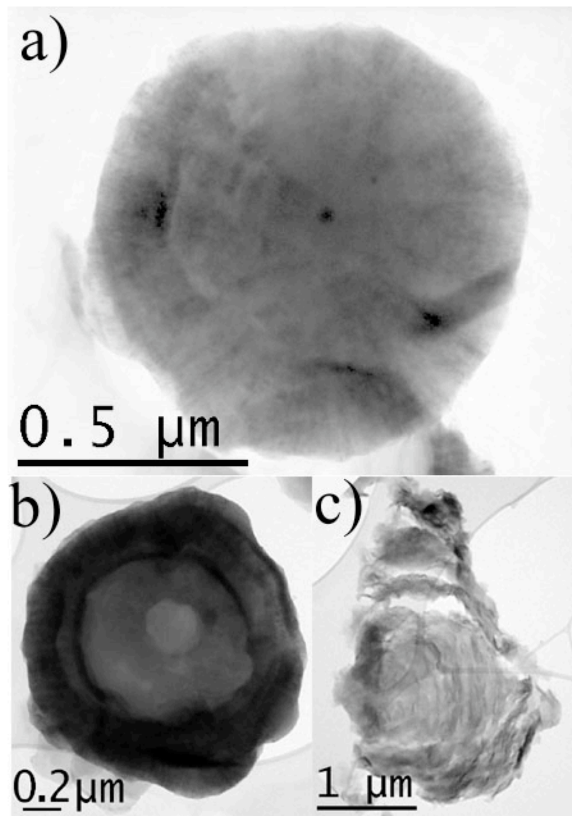

Figure 1. TEM images of a) onion graphite with central carbide grain, b) rim-core onion graphite with 280-350 nm thick rim and nanocrystalline core, and c) cauliflower graphite with irregular graphitic stacking.

Since the chemistry and structure of internal grains (in conjunction with isotopic information) can yield detailed information about the gas from which an individual graphite condensed, graphites were searched for internal grains in the TEM. Table 1 summarizes the properties of internal carbides found within graphites of various types. Many refractory carbides were found within the onion graphites. Fig. 1a shows an onion graphite with a 30-nm-diameter central refractory carbide, which is likely the nucleation site for the graphite. Though nucleation of graphite on higher-temperature condensates clearly occurred, it does not appear to be the dominant formation mechanism for graphites. Cauliflower graphites also commonly contain refractory carbides with chemical compositions similar to those in the onion graphites. Quantitative elemental analysis with EDXS showed that most of the carbides within all types of graphites have appreciable 4d-TM (transition metal) content (Zr, Mo, and Ru). TiC and the other refractory carbides have similar crystal structures (FCC; a = 4.4 - 4.5 Å), allowing formation of solid-solution phases with Ti, Zr, Mo and Ru. The Zr, Mo and Ru contents of carbides within all graphites averaged to 14, 13, and 4 at. %, respectively (metals basis only for a more accurate calculation), although these concentrations are quite variable among the carbides (as indicated by the large standard deviations). Maximum concentrations of Zr, Mo, and Ru are 100, 77, and 44 at. %, respectively (two zirconium carbides were found with no measurable Ti). Most carbides (90% of 100 internal grains studied) have clearly measurable 4d-TM content (>1 at. %). When multiple refractory carbides were found within the same graphite, the carbides had similar overall 4d-TM content. Other trace elements (Ca, V, Cr, Fe, and Ni) were also seen in varying amounts within the carbides. Some differences were seen among the graphite types, such as apparently lower Zr in carbides found in the core region of rim-core graphites.

Table 1. Carbides in KFC1 Graphites.

Type	# graph-ites	% w/ carbide[1]	Zr at. %[2]	Mo at. %[2]	Ru at. %[2]
Onion	55	22%	25 ± 25	12 ± 9	5 ± 10
Onion w/ rim-core	80	14%	1 ± 4	9 ± 10	4 ± 7
Cauli-flower	119	13%	7 ± 12	13 ± 8	3 ± 7
Other	59	12%	20 ± 23	18 ± 21	6 ± 9
Totals	313	15%	14 ± 21	13 ± 11	4 ± 8

1. 100 refractory carbides were found within 46 different graphites 2. Atomic % calculated using metals basis.

Along with the refractory carbides and several kamacites found within the KFC graphites, ruthenium-iron metal grains were also found. Eight ruthenium-iron grains (Ru_xFe_{1-x} with 0.66<x<0.77) were found within one 4 μm diameter cauliflower graphite. Three major zone axis patterns showed one of these Ru-Fe grains to be hexagonal (a = 2.8Å, c = 4.4Å), 6-8% larger than the Ru-Fe metal reported in the literature. Patterns from the other Ru-Fe grains were consistent with this structure. Seven refractory carbide grains with significant 4d-TM content were also found within this graphite. Another Ru-Fe grain was found within a different cauliflower graphite, again along with numerous 4d-TM-rich carbides, although its crystal structure was not determined. NanoSIMS measurements of this second cauliflower graphite were made, showing a presolar $^{12}C/^{13}C$ ratio (15 ± 6).

Figure 2 shows NanoSIMS measurements of C and O isotopic ratios on graphites that contain internal carbides, most of which have significant 4d-TM content. These graphites cover the wide range of carbon isotopic ratios previously observed [2]. Based on their high $^{12}C/^{13}C$ ratios, the group of graphites at right ($100<^{12}C/^{13}C$ ratio <500) could be considered as SN candidates. However, the carbides found in Murchison KE3 graphites of supernova origin [6] have no measureable 4d-TM content (upper limit of 0.3 at. % in over 500 carbides from 12 different SN graphites). Thus, the high 4d-TM content in the carbides of many KFC graphites precludes supernovae as their stellar source. Recent modeling results [7] suggest that low metallicity AGB stars can produce higher than solar $^{12}C/^{13}C$ ratios as well as the observed high s-process enrichments (seen in Zr, Mo, and Ru). Noble gas anomalies found in KFC graphites also suggest an AGB origin [8]. Therefore we consider low metallicity AGB stars as a possible source of KFC1 graphites with isotopically light carbon.

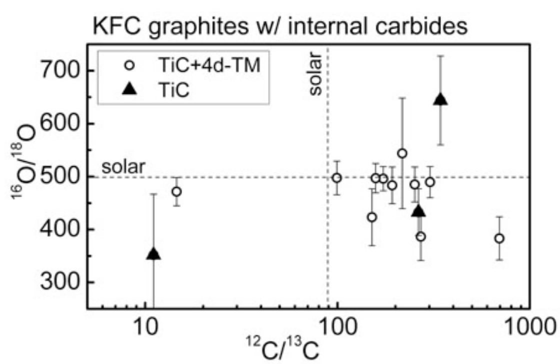

Figure 2. C and O isotopic ratios of graphites which contain either 1) (Ti,Zr,Mo,Ru)C solid-solution carbides or 2) pure TiCs (no Zr, Mo, or Ru).

References : [1] Amari S. *et al.* (1993) *Nature, 365,* 806. [2] Hoppe P. *et al.* (1995) *GCA., 59,* 4029. [3] Bernatowicz T. J. *et al.* (1996) *ApJ., 472,* 760. [4] Amari S. *et al.* (1994) *GCA, 58,* 459. [5] Stadermann F. J. *et al.* (2002) *LPS XXXIII,* Abstract #1796. [6] Croat T. K. *et al.* (2003) *GCA, 67,* 4705. [7] Amari S. *et al.* (2001) *ApJ.*, *546*, 248. [8] Amari S. *et al.* (1995) *GCA*, *59*, 1411.