ISOTOPIC AND MICROSTRUCTURAL STUDIES OF LOW DENSITY GRAPHITES WITH EXTREME C ANOMALIES.

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Introduction: Most low-density (LD) graphites (~60%) exhibit clear supernova (SN) isotopic signatures (such as large ^{28}Si and ^{18}O enrichments; [1]), but the stellar origins of others, even those with extreme ^{12}C or ^{13}C enrichments, are less clear. Chemical and phase information from inclusions within graphite and the condensation sequences inferred from these assemblages can be used, in conjunction with thermodynamical models, to better constrain the conditions under which they formed [2, 3]. Here we present new TEM-NanoSIMS results from four LD graphites with the most extreme C isotopic anomalies to identify their stellar sources and to look for trends in condensation behaviors that correlate with isotopic anomalies.

Experimental: Graphites from the KE3 density and size separate (1.75-1.92 g cm^{-3}, >1 μm) of the Murchison (MUR) meteorite [1] were selected based on extreme C anomalies from NanoSIMS bulk measurements (Fig 1). These graphites were picked from the mounts, embedded in resin, and then sliced into ~70 nm ultramicrotome sections. The slices were retrieved on holey carbon-coated copper TEM grids and examined in TEM (imaging, EDXS, crystal structure) followed by NanoSIMS imaging mode measurements on graphite cross-sections (see Table 1).

Results: *^{13}C-rich graphites.* As is common among the ^{13}C-rich graphite subgroup [4], the ^{13}C-rich graphite KE3i021 had a low TiC abundance of 25 ppm. However, one section (of 18 studied) taken from nearer the graphite center did contain a cluster of five carbides (Fig. 2). These were (Ti,V)C grains without s-process enrichments that ranged from 30-130nm in size. The carbides were significantly more ^{18}O rich than the surrounding graphite, whereas both had similar C isotopic ratios (see Fig 1 and Table 1). The combination of similar ^{12}C/^{13}C ratios and different ^{16}O/^{18}O ratios may result from carbide and graphite formation in isotopically similar environments (SN environment as indicated by the large ^{18}O enrichment), followed by differential dilution of minor element anomalies, which are better retained in the carbide than its host graphite. The KE3i021 graphite cross-section result is consistent with the prior bulk measurement (Fig. 1), suggesting that significant carbide inclusions were not encountered during the earlier bulk measurement. The reverse of this scenario can conceivably explain results from the ^{13}C-rich graphite KE3i461. Here, the disparity between the earlier more ^{18}O-enriched bulk measurement and the later measurement of TiC-free graphite cross-sections might be due to significant ^{18}O counts in the earlier measurement from sputtering of a more isotopically extreme TiC inclusion.

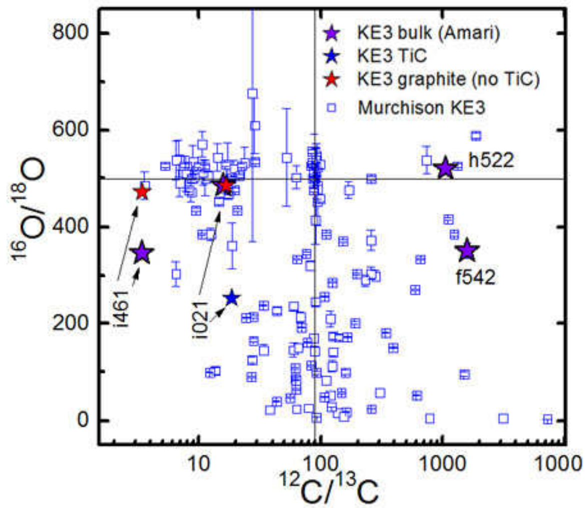

Fig. 1. C and O isotopic anomalies from Murchison KE3 graphites from this study (star symbols) along with MUR KE3 population. Purple symbol indicates graphite bulk measurement, blue is for TiC only and red is for TiC-free graphite ultramicrotome slices (NanoSIMS imaging mode measurement).

Extremely ^{12}C-rich graphites. As was true for the ^{13}C-rich subgroup [4], both of the extremely ^{12}C rich graphites examined (KE3f542 and KE3h522) had very low TiC abundances; KE3f542 had 1 TiC in 17 graphite ultramicrotome sections (25ppm) and KE3h522 had none in 4 sections (<92 ppm). The single TiC in f542 had high Ca content and slightly elevated V content (Ca/Ti and V/Ti atomic ratios of 0.06 and 0.19 whereas 0.008 and 0.1 are typical values for TiCs in LD graphite). However, it had no s-process enrichments of the type commonly found in HD graphites of AGB origin, and was instead more similar to SN TiCs. Due to failure of the TEM substrate, confirmation of the TiC structure via electron diffraction and further isotopic studies were not possible. While KE3h522 did not contain TiC, it did contain other internal grains including a SiC grain as well as several tungsten (W)-rich grains (Fig. 3). The ~40nm SiC was found near the graphite's surface and was identified as the 3C-SiC polytypes based on diffraction patterns from the [011] and [112] FCC zones. Six separate W-rich grains (of sizes 30 - 50 nm) were found in two different graphite slices, with EDXS compositions in the range of

Table 1. LD graphite (MUR KE3) isotopic ratios

Graphite	^{12}C/^{13}C	^{16}O/^{18}O	δ^{29}Si	δ^{30}Si
i021 bulk	15.76 ±0.06	486 ±5	-5±40	-54±47
i021 TiCs	18.5 ±0.4	253 ±47	n/a	n/a
i021 graphite[1]	16.7 ±0.3	486 ±21	n/a	n/a
i461 bulk	3.40 ±0.01	346 ±4	-252±83	97±125
i461 graphite[1]	n/a	472 ±11	-123±97	-128±29
f542 bulk	1586 ±17	351 ±16	-139±25	-92±38
h522 bulk	1053 ±8	521±4	-32±18	-23±22

1. NanoSIMS imaging mode measurement of TiC-free graphite (in contrast to bulk graphite measurements which may have had TiC inclusions).

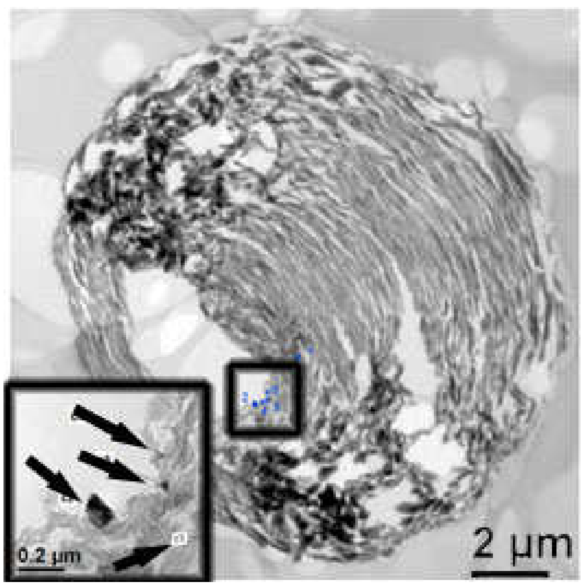

Fig.2. Bright-field (BF) TEM images of KE3i021 ^{13}C-rich graphite with inset showing cluster of TiCs.

$W_{100-x}Fe_x$ ($4<x<22$). Tilting studies were done in an attempt to determine the crystal structure, but no strongly diffracting zones were found, suggesting that the grains may be amorphous and only visible due to Z contrast. W was not detected in the nearby graphite regions, and the dense (thicker) regions that contained W grains (Fig. 3a) had diffraction profiles similar to thinner central regions.

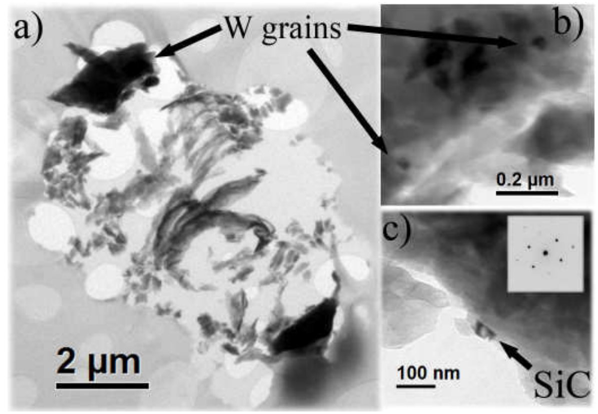

Fig.3. Bright-field (BF) TEM images of a) KE3h522 ^{12}C-rich graphite that contains W-rich grains b) closeup of W-rich grains and c) SiC found at the edge of a different h522 graphite section (not pictured) with inset SAD pattern of [011] FCC zone.

Discussion: The results from KE3i021 suggest that more members of the ^{13}C-rich subgroup are of massive star origin despite lacking bulk O anomalies, but that the ^{18}O enrichments are more difficult to detect due to poor minor element anomaly retention in graphite and lower abundances of anomaly-retaining TiCs. Here, the scientific value of higher spatial resolution NanoSIMS imaging mode measurements are clear (e.g. large difference in i021 ^{16}O/^{18}O ratios from Fig. 1), and lead to attribution to a SN rather other stellar sources, such as born-again AGB stars, that have been proposed for other ^{13}C-rich graphites [5]. The properties of the TiC inclusion in ^{12}C-rich graphite KE3f542 are more similar to SN carbides than AGB ones, which along with its ^{18}O enrichment, suggest a SN origin. Further studies of extreme ^{12}C-rich graphites, in particular NanoSIMS isotopic measurements of internal TiCs which may carry more extreme (undiluted?) anomalies, are warranted. The ^{12}C-rich KE3h522 contains the first W-rich inclusions yet found, and apparently constitute a new presolar grain subtype; both W metal and WC are predicted high T condensates [6] for C>O environments.

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References: [1] Amari S. et al. (1995) *ApJ, 447*, L147. [2] Fedkin et al. (2010) *GCA, 74*, 3642. [3] Croat T.K. et al. (2003) *GCA, 67*, 4705. [4] Croat T.K. et al. (2012) *MAPS, 75, 5242.* [5] Jadhav M. et al. (2008) ApJ, 682, 1479. [6] Lodders K. and Fegley Jr, B. (1995) *Meteoritics, 30, 661.*