ISOTOPIC AND TEM INVESTIGATIONS OF VARIATIONS IN PRESOLAR GRAPHITE MORPHOLOGY. 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: As discovered during previous studies of Murchison "onion" and "cauliflower" presolar graphites [1, 2], the degree of graphitization among presolar graphites is quite variable. Along with these morphological variations (as described below), corresponding isotopic/elemental trends have also been seen (e.g. higher trace element content in more turbostratic cauliflowers) [1]. These morphological variations probably reveal differences in formation conditions, rather than being ascribed to later processing or heating [3]. For example, changes in the rapidity of formation or in the circumstellar chemical environment (e.g. C/O ratio in the gas) could alter their degree of graphitization. From correlated transmission electron microscopy (TEM) and NanoSIMS isotopic investigations of the graphite morphologies and their internal constituents, we hope to learn more about the circumstellar environments in which they formed. In this abstract, we look more narrowly at the chemical and isotopic properties of turbostratic round graphites (both "platy" and "scaly" morphologies as defined in [4]).

Experimental: Graphites from the Murchison KFC1 density and size separate (2.15-2.20 g cm^{-3}, >1 μm) [5] were deposited from suspension onto a glass slide, embedded in resin, and 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). Selected TEM grids were then mounted into a clamping holder and imaged in the NanoSIMS in ^{12}C, ^{13}C, ^{16}O, ^{17}O, ^{18}O, and secondary electrons.

Results: Figure 1 shows TEM cross-sections of various morphological types of KFC1 graphites (SEM-based classifications of unsliced round graphites from LFC and KFC1 are available elsewhere [1, 2]). By comparing their relative abundances, one can attempt to reconcile the TEM morphological types seen (highly graphitic, platy, scaly, etc.) with the onions and cauliflowers from SEM-based studies. In SEM-based studies of 581 KFC1 round graphites, 87% were classified as onions, 10% as cauliflowers, and 3% as other round types, whereas TEM studies of 1077 sliced KFC1 graphites found 86% well-graphitized grains (clearly onions), 10% with platy morphology, and 4% with a scaly morphology (likely cauliflowers). The other TEM category (comprised of aggregates, polycrystalline, non-spherical graphite, etc.) is not included, as it contains some non-round graphites. Despite reasonable

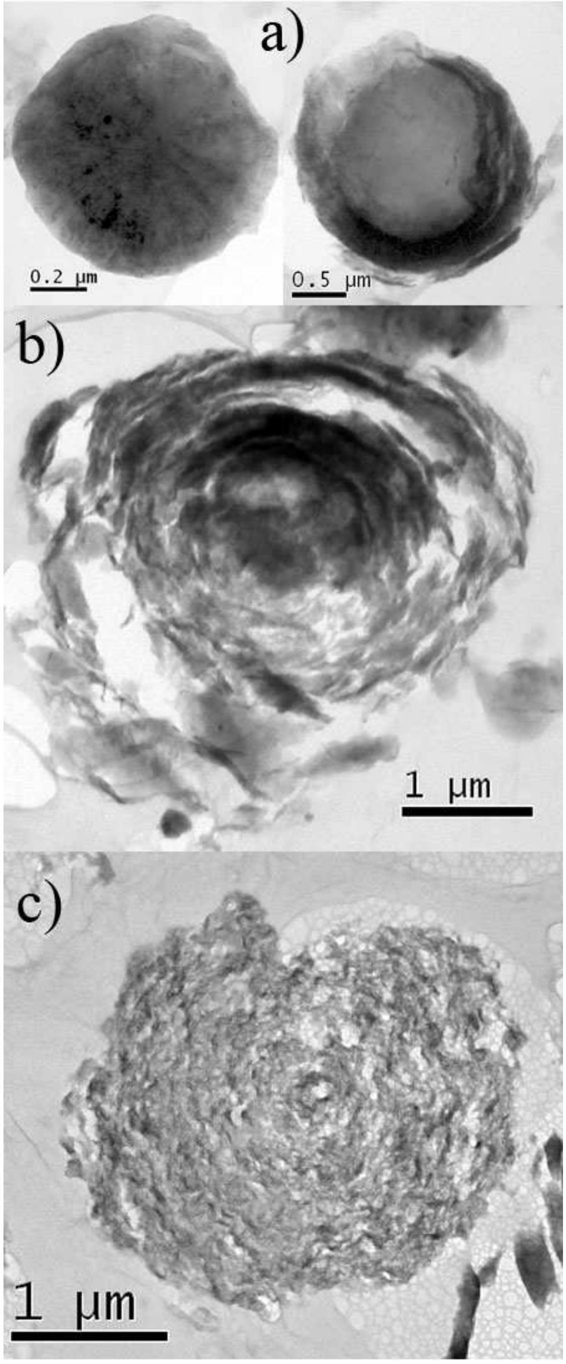

Fig 1a) highly graphitic graphites (with or without a nanocrystalline core) having regularly-stacked graphene sheets which form a dense concentric shell structure with a smooth surface b) platy graphites with continuous concentric layers and a relatively smooth surface and c) scaly graphite with short, curved and discontinuous (turbostratic) concentric layers and cauliflower-like surface.

agreement between SEM and TEM-based groups, there are some difficulties with morphological groups not based on quantitative measures of the degree of graphitization. For example, most KE3 graphites were considered onions in SEM studies, but TEM cross-sections of their interiors look quite turbostratic [6]. This suggests that many platy KFC1 graphites may have been called onions in SEM-based studies, whereas later TEM-based publications considered them as cauliflowers and focused more narrowly on highly graphitic onions (with or without a nanocrystalline core) [3, 7].

KFC1 platy graphites commonly contain refractory carbides, and most of the carbide-containing graphites (~90%) show significant enrichments in s-process elements. The median (and average) s-process enrichment is ~220x solar among carbides within platy graphites, as measured by the Mo/Ti ratio. In terms of their s-process enrichment or in the abundance of carbides found within them, platy graphites are not distinct from the highly graphitic onions [3,7].

S-process element enrichment has not yet been seen in carbides within scaly cauliflower graphites (Fig. 1c), although the data are limited with only 44 graphite slices (~3% of 1355) classified as scaly cauliflowers. Although this is a relatively small sample, the scaly cauliflowers appear less likely to have internal carbides (<5%) in comparison to highly graphitic onions or platy graphites, of which 15-20% contain internal carbides. Only one contains an internal TiC, and no Zr or Mo was detected (Zr/Ti < 0.006 or <1.3x solar and Mo/Ti < 0.007 or <6.4x solar). Another scaly graphite slice contains Si-rich grains, which could be either SiC or a Si-rich oxide (as yet unidentified). Numerous graphite slices have adjacent or peripheral Cr-rich grains, suspected to be chromites which are commonly found in KFC1 residues. Also various suspected oxides (TiO, AlMgO) have been found with EDXS. However it is unlikely that the oxides are presolar, and most are probably not internal to the graphites.

Subsequent NanoSIMS isotopic analysis has been done on many highly graphitic onions (N=70) and numerous platy graphites (N=19), but no data is yet available from the rare scaly cauliflowers. A wide range of carbon isotopic ratios are seen in both platy ($9<{}^{12}C/{}^{13}C<340$) and highly graphitic grains ($5<{}^{12}C/{}^{13}C<900$), although the onions appear more well represented towards the ^{12}C-rich end. Platy graphites have an average (and median) $^{12}C/^{13}C$ of ~175, whereas highly graphitic onions average $^{12}C/^{13}C$~270 (median ~200). Both groups of grains are isotopically normal in O within errors.

Although not quantitative, the oxygen signal from EDXS (O/C count ratio) can be used to compare the O content between the various morphological groups. Using this measure, the O content does increase as the graphites become more turbostratic. O/C count ratios of 0.10 (±0.05), 0.06 (±0.03), and 0.03 (±0.02) were found for the scaly cauliflower (N=11), platy (N=17), and highly graphitic onion (N=57) groups (avg. and st. dev.). The EDXS background (resin and holey carbon film) generally gave low O values, so the increased O in turbostratic graphites cannot be explained by a larger contribution from the sample background.

Discussion: Unlike the turbostratic KE3 supernova (SN) graphites [6], many carbides within platy graphites did contain significant s-process enrichment, suggesting an AGB origin. Thus, the turbostratic morphology does not appear unique to one particular type of stellar source. However, the KFC1 platy graphites are in general less turbostratic than those from KE3; some appear turbostratic only towards the surface, with nanocrystalline interior regions lacking evidence of regular stacking of graphene sheets (similar to rim-core nanocrystalline phase from [3]). As noted above, no instances of s-process enriched carbides have yet been found within scaly graphites. The single carbide-containing scaly cauliflower (with a pure TiC) is consistent in composition to those found within KE3 graphites of SN origin. TEM studies of slightly less dense fractions (KFA or KFB) with their higher abundances of scaly cauliflowers are desirable to better characterize these graphites and determine their likely stellar source. The difficulties in classifying graphite morphologies suggest that more quantitative measures should be used, such as domain sizes in (002) dark field images or the (002) lattice spacing from diffraction patterns. Unfortunately, such methods were not used for graphites measured in the NanoSIMS thus far.

The apparent increase in O content as graphites become more turbostratic might not be coincidental, since studies of synthetic graphite have shown that addition of small amounts of O can make graphites more turbostratic [8]. The more turbostratic structure of cauliflowers could result from a higher O/C ratio in the gas from which they condense. The turbostratic morphology (with O cross-linked between graphite layers in the structure [8]) also might aid in the retention of O anomalies.

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