TEM STUDIES OF HIGH DENSITY PRESOLAR GRAPHITES FROM THE ORGUEIL METEORITE. T. K. Croat[1], T.J. Bernatowicz[1], and M. Jadhav[2] [1]Laboratory for Space Sciences and Department of Physics, Washington University, St. Louis, MO 63130, USA, tkc@wustl.edu [2]University of Hawai'i at Mānoa, Hawai'i Institute of Geophysics and Planetology, Honolulu, USA.

Introduction: High-density (HD) presolar graphites exhibit diverse isotopic signatures, which has led to different members of this group being ascribed to a variety of stellar sources (low-metallicity AGB, Type II SNe, and post-AGB stars experiencing a late thermal pulse) [1]. The Orgueil (ORG) HD graphite separate [2] has provided many new large (5-20µm) graphites that are ideal for correlated TEM and NanoSIMS studies. Here, we present TEM results from 3 ORG HD graphites with the aim of clarifying the morphological differences between the various graphite density separates from ORG and Murchison. We also search for internal grains that can yield further clues as to the stellar source of the graphites.

Samples and Experimental Methods: Three graphites (OR1f3m11, OR1f3m26 and OR1f3m34) from the Orgueil meteorite OR1f density and size separate (2.02-2.04 g cm^{-3}, >1 µm) were picked from grain mounts after a series of NanoSIMS and Resonant Ionization Mass Spectrometry (RIMS) measurements [1], embedded in resin, and then sliced into ~100 nm ultramicrotome sections. The graphite cross-sections and any internal grains were examined with analytical TEM (including diffraction, bright-field (BF) and dark-field (DF) imaging, and EDXS).

Results and Discussion: Figure 1 shows the C and O isotopic ratios from the 3 graphites studied here along with those from other ORG graphites [1]. The high density (HD) graphites (including OR1f, OR1g and OR1i with progressively higher densities) lack the large ^{18}O and Si anomalies common in low-density (LD) graphites (e.g. OR1d) and have higher ^{12}C enrichments on average. The graphites from this study (3m11, 3m34, and 3m26) have $^{12}C/^{13}C$ ratios of 16.4 ± 0.1, 97.1 ± 0.7 and 560 ± 4, respectively; minor element isotopic ratios from these 3 are currently unreliable due to mount contamination but will be remeasured by NanoSIMS on ultramicrotome sections.

Graphite morphology: The OR1f graphites have densities between those of the well-studied Murchison KE3 (1.6-2.05 g cm-3, >1 µm [3]) and KFC1 (2.15-2.2 g cm-3, >1 µm [4]) graphite separates. BF and DF {002} images from 3m26 (Fig 2a and 2b) show morphological features of both HD and LD graphites, with multiple onion-like regions (having a nanocrystalline core surrounded by a well-graphitized layer) all embedded within turbostratic graphite layers. The rim-core onions could have formed by independent nucleation and growth before being cemented into a larger

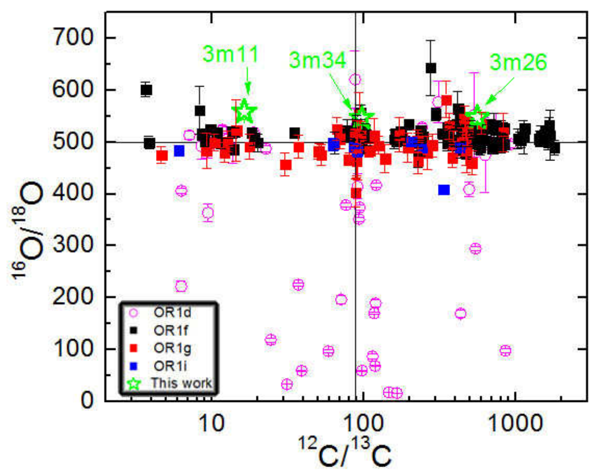

Fig.1. C and O isotopes from both low-density (OR1d) and HD (OR1f, g, i) Orgueil graphites along with the 3 OR1f graphites from this TEM study.

graphite; aggregates of this type have been seen within the KFC1 separate [5]. Graphites 3m11 and 3m34 do not show such onion graphite subcomponents; however, the morphology of 3m11 (Fig 2c) is otherwise similar to the turbostratic layered regions of 3m26. These layered regions in HD graphites (such as 3m11 in Fig 2c) show longer DF {002} domains than do those of LD graphites, but with similar widths. Since the bonding in the plane of the graphene sheets is much stronger than that between stacks of adjacent graphene sheets, graphitization commonly proceeds in this manner, with faster growth along in-plane direction and slower growth in the c-axis stacking direction. DF images of 3m34 (Fig 2d) reveal slightly thicker bright domains (30-80µm), indicating a somewhat higher degree of graphitization. Overall, OR1f graphites show a degree of graphitization intermediate between those of KFC1 HD "onions" [4] and of the OR1d or KE3 turbostratic LD graphites [3], as expected based on their densities.

Internal grains: Like many SN graphites, OR1f3m34 had a high number density of internal TiCs (Fig 3a), with a TiC abundance of ~1250 ppm and an average grain diameter of ~30nm. Electron diffraction from 12 Ti-rich grains were all consistent with the known TiC crystal structure (fcc; a=4.4Å). Unlike the SN graphites [3], its internal carbides were s-process enriched with an average composition of $Ti_{81}Mo_9V_5Fe_4Ru_1$, corresponding to (Mo/Ti) ratios of ~100x the solar ratio. Several metallic RuFe grains of average composition $Ru_{66}Fe_{34}$ (e.g. Fig 3d) were found

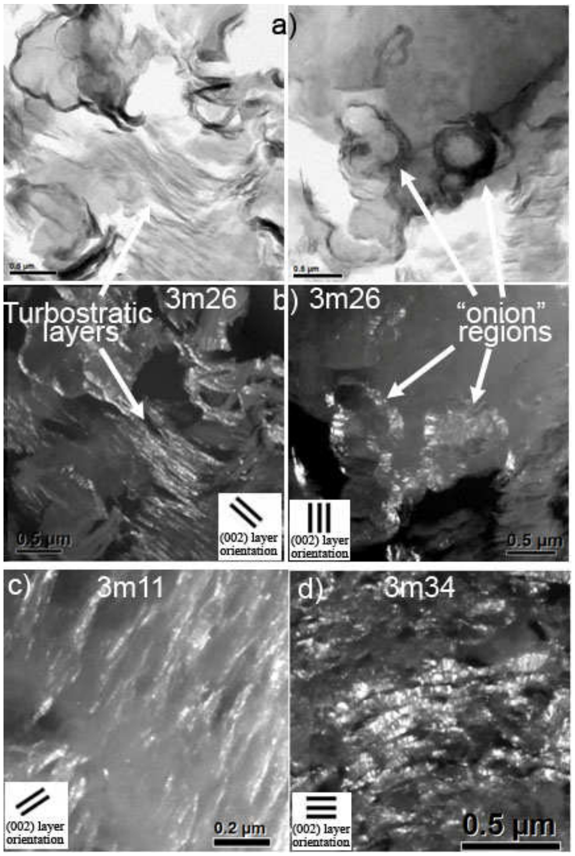

Fig. 2. a) BF (top row) and b) DF {002} (middle row) images of two OR1f3m26 graphite cross-sections and DF {002} images from c) OR1f3m11 and d) OR1f3m34. Bright regions in DF {002} images indicate regularly stacked graphene sheets oriented in the direction indicated by the inset schematic.

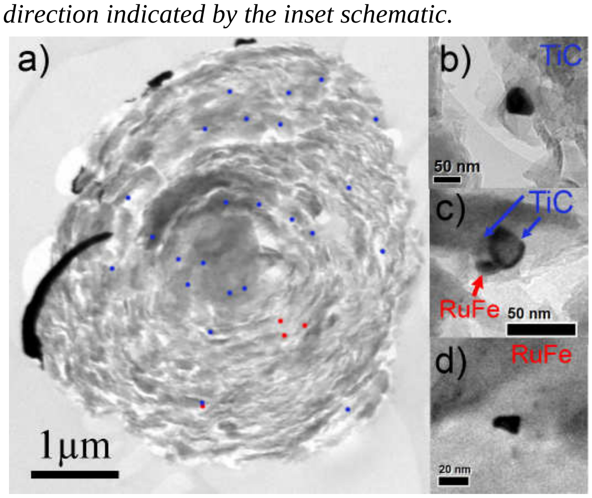

Fig. 3. a) Graphite cross-section from 3m34 with positions of internal TiC and RuFe grains b) TiC grain at [011] orientation c) composite TiC/RuFe metal grain and d) RuFe metal grain at [1-21-3] orientation.

and one was indexed to the known close-packed hexagonal (a=2.7Å, c= 4.5Å) phase (also seen in KFC1 graphites; [5]). This graphite also contained a unique TiC/RuFe composite grain (Fig 3c) which consisted of two twinned TiC domains sharing a common {220} plane, one of which had an attached ~20 nm RuFe subgrain. The RuFe subgrain of approximate composition $Ru_{62}Fe_{34}Mo_4$ (Ti excluded) was identified as a 3.05Å CsCl simple cubic phase based on [101], [102] and [301] zones. This RuFe crystal had a well-defined orientation relationship with the TiC, with the TiC (200) plane parallel to the RuFe (010), and the [101] CsCl and [001] TiC zones being coincident. No TiC grains were found in either 3m11 or 3m26, with upper limits of ~30 and ~10 ppm, respectively. However a single 80 nm diameter internal SiC grain with composition $(Si_{96}Al_4)C$ (no Mg detected) was found in one 3m26 cross-section (Fig 4), which yields a SiC abundance of ~40 ppm. The domain that comprised most of the grain indexed to the 3C-SiC polytype (based on [112] and [011] zone patterns), but a separate SiC domain (15 x 70 nm and apparent at right in Fig. 4b) had a d-spacing consistent with 2H but not 3C. Such 2H/3C intergrowth polytypes are seen in ≈20% of presolar SiCs [6].

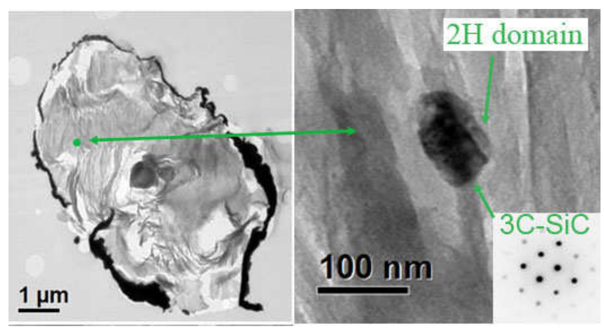

Fig. 4 a) OR1f3m26 graphite cross-section with internal SiC position indicated and b) internal SiC grain at 3C-SiC [011] orientation with separate 2H domain along upper right edge attached to 3C-SiC {111} plane.

The highly s-process enriched carbides from 3m34 suggest an AGB origin, whereas presence of SiCs in HD graphites (such as that found within 3m11) often indicates a massive star origin [7]. Thus, preliminary TEM results agree with HD graphites having a diverse set of stellar sources [1]. NanoSIMS measurement of the graphite cross-sections and their internal grains are planned to verify these preliminary attributions.

References: [1] Jadhav M. et al. (2013) *GCA 113*, 193. [2] Jadhav M. et al. (2006) *New Astron. Rev. 50*, 591. [3] Croat et al. (2003) *GCA 67*, 4705. [4] Croat et al. (2005) *Ap. J. 631*, 976. [5] Croat et al. (2008) *Met. Planet. Sci. 43*, 1497. [6] Daulton et al. (2003) *GCA 67*, 4743. [7] Croat et al. (2010) *Astron. J. 139*, 2159.