GRAPHITE WHISKERS DISCOVERED IN CV3 METEORITES. Marc Fries[1] and Andrew Steele[2], [1]NASA Jet Propulsion Laboratory, Pasadena CA, Marc.D.Fries@jpl.nasa.gov, [2]Geophysical Laboratory, Carnegie Institution of Washington, Washington DC, a.steele@gl.ciw.edu.

Introduction: We report the serendipitous discovery of a small number of graphite whiskers (GWs), a rare polymorph of carbon, in a range of settings within several CV3 meteorites [1]. Currently accepted growth conditions for GWs indicate that this unusual phase requires that the parent mineralogy experienced high temperature processing in contact with a carbon-containing gas.

Description of Graphite Whiskers:

Morphology. GWs are essentially rolled spindles of graphite, somewhat tapered towards one end and typically microns in length (Figure 1). They are distinct from carbon nanotubes, which are seamless tubes of graphite, and from carbon fibers, which typically consist of soild, mixed turbostratic and graphitic carbon.

GW Synthesis. The formation conditions of GW are not adequately characterized, but the laboratory synthesis methods available in literature involve temperatures ranging up to 2273 K in flowing gas [2] and ~3900 K in an arc discharge [3]. One study shows that, on the basis of thermodynamics calculations, growth of graphite whiskers is preferred over planar graphite at high temperatures [4]. GWs have been described in only three terrestrial settings, all of which contained graphite deposited or altered at high temperatures [5-7]. One study of GW synthesized from charcoal found a range of morphologies including shorter, conical GW, spindle-shaped whiskers, and other variations [8]. These shapes are arguably the result of heteroatom contaminants arising from a natural carbon sample as opposed to the high-purity gases used to produce GW in other laboratory experiments. It is reasonable to expect that such a range of shapes can be expected in meteoritic and other natural settings. While further work is required to properly refine GW formation conditions, the bulk of available information implies that the presence of GW implies that the parent mineralogy experienced high temperature exposure to a carbon-containing vapor. Alternatively, GW may pre-date their parent mineral assemblages. It is worth noting that both the high temperature necessary for GW synthesis and their rarity in natural settings make them an unlikely laboratory contaminant.

Raman Spectra. Investigation by Tan et al showed that GWs feature unique Raman spectral features that simplify their identification, namely a second-order carbon D (disorder) band (or D*) around 2680 cm^{-1} [9,10] that exceeds the first-order D band intensity. This feature is unknown in other carbon polymorphs or in any other mineral phase. GW were identified in this study using Raman imaging, with follow-up SEM imaging in an attempt to directly image GW where they are exposed in fresh fracture surfaces.

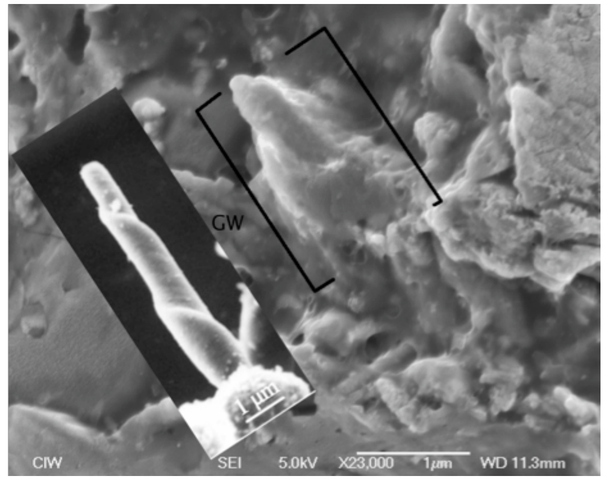

Figure 1: GW tip emerging from fresh fracture surface in an Allende CAI, in an SEM image co-located with a Raman measurement. Inset: Image of synthetic GW showing spindle shape. Scale is different from background image, but note similarities in morphology and size with Allende GW example. Inset adapted from [9].

Provenance in CV3 Meteorites: Following their initial discovery within an inclusion in an olivine grain within a chondrule in the QUE 94366 carbonaceous chondrite, GW were subsequently found as a minor phase in the rim of a dark inclusion in the NWA 3118 CV3 and within CAIs in the Allende CV3. This study constitutes a general survey of possible GW localities in multiple examples of CV meteorites, and there is ample room for follow-on exploration in other meteorite features and different meteorite types.

QUE 94266 Chondrule Inclusion. A cluster of GW were found within a ~10 μm opaque inclusion within a type IA chondrule olivine grain, as examined in thin section. This is a spherical assembly including chromite, a sulfide, and GW without additional carbon phases. The chondrule bears signs of high temperature synthesis and/or processing in the form of refractory eskolaite (Cr_2O_3) inclusions proximal to the GW-bearing inclusion. The inclusion is completely enclosed within the grain and was examined *in situ.*

NWA 3118 Dark Inclusion Rim. A small segment of dark inclusion rim in the NWA 3118 was found to contain GW as seen in Raman spectra. The mineralogy of the rim is predominantly andradite ($Ca_3Fe_2(SiO_4)_3$) and hedenbergite ($CaFeSi_2O_6$). D* peak intensity in this example is relatively low, possibly due to very small GWs, or morphology somewhat more like conical GWs.

Allende CAIs. Nine CAIs, examined in a mixture of thin section and fresh fracture surfaces, yielded the Raman signatures of nine GWs. All nine were found in five of the CAIs, scattered through a total of 37 Raman images to cover the preponderance of CAI surface available to analysis. A single GW example was found at the CAI/CV matrix boundary, and the remaining eight were found in the CAI interiors.

Discussion: The discovery of GWs in these settings carries with it a set of implications, as follows.

Mineralogy. Given our current understanding of GW as a high-temperature phase produced from a carbon-containing gas, the simplest explanation is that each of these settings was at one time exposed to such a gas. For the chondrule inclusion, this means that a small amount of hot gas was trapped within. The gas may have been a primary volatile present in the chondrule melt, or a later product of evaporation of an earlier carbonaceous phase during a chondrule re-heating event. The parent chondrule shows evidence of high temperature processing in the form of eskolaite inclusions and its nearly single-crystal olivine composition, so either hypothesis is reasonable at this point.

GW in dark inclusion rims are likewise reasonable given the presence of abundant carbonaceous precursor material and high temperature processing history of dark inclusions [e.g. 11]. Further examination in additional samples may help constrain dark inclusion origins.

The presence of GW in CAIs is especially interesting and surprising. CAIs were actually investigated with the expectation that they would serve as examples of features with high-temperature processing history without carbonaceous material, to serve as a comparison against the other GW examples. Several options exist as GW formation hypotheses for this example. GW may have existed as a free-floating species that predated CAI condensation, and were trapped during CAI formation. GWs may have nucleated and grown in/on CAIs during/after CAI formation, or they may have grown during CAI remelting events. Each of these requires only the presence of a high temperature, carbon-containing gas and at present insufficient data exists to discern between the hypotheses. The possibility exists that all three formation methods are valid, and this question will be addressed in further study. Nearby, young stellar systems can also be examined through astronomical observations for signs of GWs once standard absorption spectra are available.

Astronomy: The presence of GWs in CAIs in particular suggests that whiskers were present during the earliest condensation of our solar system. This may place GWs very near the young Sun during a period of active outflow, and so the possibility exists that they were expelled from around our young Sun and similar stars to populate interstellar space. Previous literature has speculated that carbonaceous, needle-like phases may be a reasonable explanation for observed discrepancies in distant supernovae brightness and attenuation of cosmic background radiation (CMB) [12-16]. Graphite whiskers have been specifically identified as a candidate phase, even though reports of natural examples of GW were lacking at the time [17]. The discovery of GW in meteoritic settings allows direct measurement of relevant GW properties to test this hypothesis.

A Comment. Given the extensive research done on CAIs, it is initially curious that GWs have not been reported. We believe this is simply a matter of instrument sensitivity to GWs. The vast bulk of previous CAI research features electron beam methods, which are somewhat insensitive to carbon relative to typical CAI mineralogy. Raman spectroscopy is not only sensitive to carbonaceous phases, but acts as a direct probe of crystalline structure as opposed to elemental identity. Electron beam techniques would "see" little beyond the polished cross-section of a GW exposed at a thin section surface, whereas Raman uses a visible-light excitation beam that can penetrate into the sample surface sufficient to resolve a whisker's shape in many cases. It is likely – to the point of near-certainty – that GWs have been examined in the past using an electron probe. The reasonable interpretation of the resulting sub-micron, carbon-containing bleb would be to write it off as contamination rather than identify it as a rare carbon polymorph.

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