ULTRA-REFRACTORY ATTOGRAM INCLUSIONS IN COMET DUST- FIRST CONDENSATES?

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Introduction: The Stardust mission returned preserved materials that were located at the edge of the solar nebula disk at the time that Jupiter family comets accreted from silicates, other relatively high temperature phases and low temperature materials that included ices formed at ~30K [1]. We have found that one of the collected comet particles called Inti [2,3], the particle that produced track #25, contains sub-femtogram inclusions that have properties consistent with those predicted to be "first condensates", the highest temperature condensates that form in cooling gas of solar composition. Although the actual timing of their formation is of course unknown, if they are condensates, they would have formed, at least locally, before condensation of the lower temperature phases that dominate primitive meteorites. The Inti inclusions are found inside a ~25 µm cometary Ca, Al rich Inclusion (CAI). There is no present evidence that similar inclusions are common in cometary materials but they do exist and are likely to be high temperature components that formed in the inner solar nebula and were transported beyond the orbit of Neptune [1].

Inclusions: The ultra-refractory inclusions in Inti include both nitrides and high temperature metal alloy. The nitrides are the most common and ~20 have been studied by various TEM techniques. Only a few metal inclusions have been seen but in at least two cases they appear to be directly associated with nitrides.

Nitrides: The nitrides are predominately TiN and they have been called Osbornite [2] but only a few have well characterized composition or crystallography due to their small size and usual location as ~30nm inclusions embedded in ~100nm thick microtome slices. They cannot strictly be Osbornite because they normally contain vanadium in concentrations ranging from ~5% to V/Ti >1. In the majority of cases the Ti/V ratio is roughly consistent with the solar value of ~8. The nitride grains that we worked on range from rounded to subhedral and from 10nm to 100nm. They have been found as inclusions inside several phases including anorthite, spinel and aluminous diopside. Nitride inclusions >20nm size are found in concentrations >10 μm^{-3} indicating a bulk abundance on the order of 10 ppm. They appear to be ubiquitous in Inti and we have not determined that they are absent from any major phase.

Metal: The metal alloy inclusions are much rarer than nitrides in Inti and are trace components in this comet particle that is otherwise devoid of other Fe bearing phases. The best characterized metal occurrence is a 80 nm grain found projecting beyond the edge of a larger anorthite grain. Fortunately the geometry, assumed to result from fracturing during microtomy, allows analysis without background interference from other phases. As seen if Figure 1, the grain rests on a larger anorthite host although it may have not been attached to this host before microtomy. However, the metal grain does have small amounts of anorthite host material bonded (upper left) to it and it is clear that it was originally embedded in anorthite. The bulk of the grain is FeNi with ~1000X enrichment of PGEs above solar. Analysis of the center of the grain yields 2.9 wt % Ni, 2.1% Pt, 1.4% Os, 1% Ir and 0.9% Ru. The relative PGE abundances are consistent with solar ratios. The metal grain itself has a 15nm inclusion of a Mo,W phase seen on the upper right. EDX analyses of this inclusion indicates that is 27% Mo and 8.7% W but these are lower limits due to analytical overlap from elements in the PGE host grain above or below the subgrain. The MoW grain dramatically shows up as a distinct crystalline inclusion in the dark field image (figure 1). FeNi metal appears to be attached to least two of the TiN inclusions although because of substrate effects it has not yet been practical to look for PGE enrichments.

Origins: Although there are other possible origins, the presence of these ultra-refractory sub-femtogram inclusions in multiple CAI minerals suggests that they formed before the formation of major CAI phases such as spinel, anorthite and aluminous diopside. TiN is a very rare mineral in meteorites but it has been found in CH/CB [4] and enstatite chondrites [5]. Meibom recently described a >20µm osbornite grain in a CAI from a the CH/CB-like meteorite Isheyevo [6]. This grain was associated with PGEs but it differs from the Inti nitrides in both size and V content. Its vanadium content was less than the detection limit of 300ppm, two orders of magnitude less that commonly seen in Inti nitrides.

Condensation calculations [7(plate 9) ,8] indicate that while osbornite cannot condense from solar composition gas with C/O= 0.5, it is the first solid to condense from an otherwise solar gas with just under twice the solar C/O. Calculations by Ebel [7] indicate that this occurs only in the limited range of C/O between 0.965 and 0.975 although this tiny range might be expanded by the presence of V in solid solution. This result also depends upon the relative high-temperature thermodynamic stabilities (equations of state) for Ti_2O_3, TiO, TiN and TiC.

If the numerous attogram Inti nitride grains are condensates from gas with just the right C/O ratio, they provide intriguing insight into nebular processes. They are tiny and they have not been reported in lower temperature phases such as forsterite. They apparently did not have time to grow to significant size and they were sequestered in common CAI phases before later phases formed. That they could form at all is remarkable because the needed conditions are enhanced C (or depleted 0) and some mechanism to buffer the C/O ratio with a percent accuracy. Perhaps the nitride grains formed under oscillating conditions with condensation occurring every time the C/O ratio was just right. Because (Ti,V)N is an exceedingly robust physical material its seems plausible that it this exotic phase would not be easily be destroyed once it formed, even for such small particles. For the same reason it is plausible that these grains are, in fact, extra-solar condensates formed in the atmospheres of C-rich AGB stars.

The metal grains, particularly the Mo,W grain are also an interesting clue. The Inti nitrides and metal grains were found within a micron of each other and we assume that they formed in related environments. Fe metal can condense at all C/O ratios [9,10]. However the refractory metal in meteoritic CAIs is often depleted in Mo and W and this has been an argument for formation in highly oxidizing conditions [11]. The presence in Inti of a MoW rich inclusion in a metal grain enriched in PGEs suggests reduced conditions, consistent perhaps with TiN formation.

A possible explanation for the TiN and Mo,W bearing PGN-rich metal is that Inti formed in a region of the solar nebula that had been enriched in carbonaceous material. Fukui and Kuramoto [12] have suggested that high C/O ratios can be obtained in the central regions of the solar nebula due to differential inwards transport rate of gas from organic materials that evaporate near 0.3 AU and of ice that evaporates near 3AU. We have not seen other phases such as TiC or SiC that are predicted to from at C/O >1. We have seen evidence of possible Si in a few nitride inclusions hinting at the possible presence of SiN or sinoite Si_2N_2O.

Comparison with Meteorites: A key issue is how these attogram nitride and metal inclusions in a cometary CAI compare with meteoritic CAIs. We have not found evidence for the them in the meteoritic literature but perhaps they have not been looked for in with appropriate TEM techniques. We urge researchers to look for attogram nitride and PGE inclusions in CAIs and other meteoritic materials.

References: [1] Brownlee et al. (2006) *Science 314*, 1711-1716. [2] Zolensky et al. (2006) *Science 314*, 1635-1639. [3] Simon et al. (2008) submitted to MAPS [4] Grokhovsky, V.I. (2006) MAPS [5] Casanova, I. (1992) MAPS [6] Meibom, A. et al. (2007) ApJ 656, L33-L36 [7] Ebel, D.S. (2006) Meteorites and the Early Solar System p 253 Univ of Arizona press. [8]Sharp, C.M. and Wasserburg, G. J. (1995) GCA 59, 1633-1652. [9] Lodders, K and Fegley, B. (1997) Workshop of Parent-Body and Nebular Modification of Chondritic Materials. P37. [10] Lodders, K. and Fegley, B. In Astrophys. Implications of the Lab Study of Presolar Materials (eds. T.J. Bernatowicz and E. Zinner). AIP Conference Proceedings 402. p. 391-424 [11] Fegley, B. and Palme, H. (1985) EPSL 72, 311-326. [12] Fukui, T.; Kuramoto, K. (2005) Workshop on Oxygen in the Earliest Solar System, LPI Cont. 1278., p.18.

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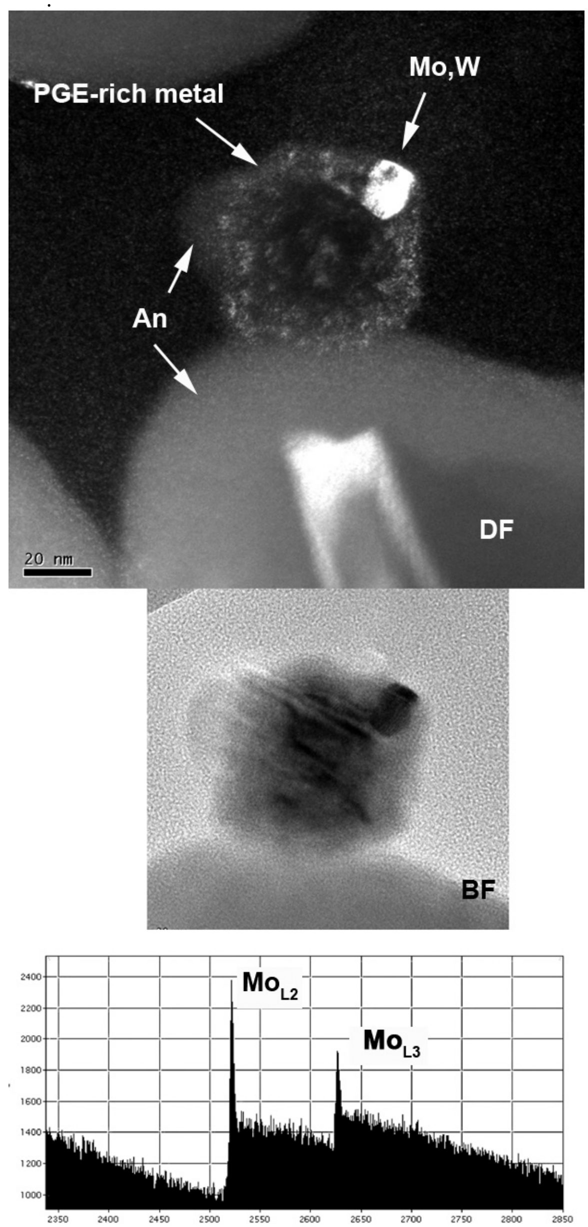

Figure 1 Dark field (DF) and bright field images of a Inti PGE-rich grain that has small Mo,W inclusion on the upper right. The substrate and adhering material are anorthite (An). The EELS spectrum shows Mo in the Mo,W inclusion.