REFRACTORY CARBIDES IN INTERSTELLAR GRAPHITE; Thomas J. Bernatowicz¹, Sachiko Amari¹ and Roy S. Lewis², ¹McDonnell Center for the Space Sciences & Physics Department, Washington University, St. Louis MO 63130-4899, USA; ²Enrico Fermi Institute, University of Chicago, Chicago IL 60637-1433, USA.

Previous transmission electron microscope (TEM) investigations of interstellar graphite (C-α) grains [1] have shown that they sometimes contain small (tens of nm) crystals of TiC. The laboratory study of these polyminerallic assemblages, coupled with thermodynamic modelling, opens the possibility of exploring grain formation conditions (composition, temperature and pressure) in stellar atmospheres in unprecedented detail. Here we report preliminary results of TEM studies on suites of interstellar graphitic spherules in the KFCl density separate (2.15-2.20 g/cc) from the carbonaceous chondrite Murchison, aimed at expanding the database on the composition and abundance of 'interstellar grains within grains.' The approach used here results in greatly increased mineralogical data on interstellar graphite and is complementary to previous work on individual spherules in which isotopic data were also obtained [1]. Details of the extraction procedure for KFCl have been described previously [2]. KFCl consists largely of well-graphitized spherules (mean diameter = 1-2 μm). The 12C/13C ratios (from 0.02-80 times the solar value of 89) measured in several hundred individual spherules clearly establish their presolar origin [3].

In preparation for TEM study of the graphite, an 8μm diameter gelatin cylinder was affixed to a pre-cleaned glass slide with RTV silicone cement. The graphite particles were then deposited from suspension in an area <1mm² on the glass within the cylinder; the deposit was imbedded in resin (which was detached from the slide after curing) and sliced into sections 50nm thick with an ultramicrotome equipped with a diamond knife. Each slice thus produced contained ultra-thin sections of many (>30) graphite grains. The slices were retrieved on Cu TEM grids covered with holey C films, and were examined for the composition and structure of their included graphite sections in many different orientations using a JEOL-2000FX TEM equipped with a Noran (EDS) X-ray detector sensitive to elements with Z ≥ 5.

Internal study of the KFCl spherules (e.g., by direct imaging and convergent beam diffraction) reveals that they typically have a composite structure, with an amorphous C core surrounded by a well-graphitized shell. Whether this structural transition represents a change in kinetics during spherule growth or some post-formational surface transformation (e.g., caused by subsequent irradiation by energetic photons) is unknown, but the frequency of such spherules suggests that mechanisms involved in their formation must be rather pervasive. A noteworthy exception to this rule occurs in the case of spherules having refractory carbide inclusions at their centers that evidently served as heterogeneous nucleation sites for carbon; in these cases the spherules are well-graphitized throughout. However, randomly distributed refractory carbide crystals (5-70 nm) occur in many, perhaps most, of the KFCl spherules. They have been observed in one-third of the 34 spherules studied to date, but this is certainly a lower limit due to the difficulty of detecting these small crystals (because of poor contrast) when they are in non-diffracting orientations.

X-ray spectra of the included crystals show that they are typically refractory carbides of Ti, Zr and Mo in variable proportions, suggestive of solid solution among these elements. Compositions range from pure Ti carbides to Mo and Zr carbides with only a few percent Ti. In Figure 1 we show data from three KFCl graphite spherules (designated A, G and Q) from a single slice, each having more than one carbide crystal. The elemental data are displayed as atomic ratios relative to Ti that have been normalized to the corresponding ratios in the solar system. It is evident that all of these crystals have Zr/Ti and Mo/Ti much greater than solar values, up to factors of several thousand. While the s-process can produce significant enhancements in these ratios (e.g., between 1 and 2 orders of magnitude above the solar values in the He-shells of AGB stars [4]), it is difficult to produce enhancements as great as those observed. Because the relative proportions of Ti, Zr and Mo vary appreciably from crystal to
crystal within the same graphite spherule, it appears likely that the Mo and Zr enrichments relative to Ti are in part due to chemical fractionation accompanying formation of the crystals. In particular, such chemical variation arises as a natural consequence of differences in condensation temperatures amongst the Zr, Mo and Ti carbides. There is, however, no tendency for crystals near the center of a given graphite spherule to be more refractory (i.e., to have higher Zr/Ti and Mo/Ti) than crystals near the rim (Fig. 1). The simplest explanation for these observations is that the crystals formed prior to carbon condensation, and subsequently (in the case of crystals that did not serve as heterogeneous nucleation sites for carbon) were randomly incorporated into growing carbon spherules.

Equilibrium condensation models [5-7] show that the relative condensation temperatures of Zr, Mo and Ti carbides and graphite depend in a complicated manner on the C/O gas ratio, pressure and degree of metal enrichment above solar obtaining in the stellar atmosphere. Despite restriction to equilibrium conditions, the models enjoy some success. For example, with C/O near unity under moderately low pressure, the formation of pure Zr, Mo and Ti carbides may occur prior to graphite condensation, consistent with the above observations. In the case of Zr and Mo, this is particularly favorable when the s-process has enriched these elements one to two orders of magnitude relative to solar proportions [8]. There is thus reason to believe that in the future, refined thermodynamic models (taking, e.g., solid solution into account) coupled with elemental data on refractory interstellar grains should be able to place realistic constraints on physical conditions and compositions of stellar atmospheres.


Figure 1: Mo/Ti and Zr/Ti atomic ratios in carbides from three KFC1 graphite spherules compared to solar [8] ratios (Solar Zr/Ti=0.0048, Mo/Ti=0.0011). Fractional errors in solar-normalized elemental ratios are <30% for all values less than 1000, and ~50% for greater values. Shading of symbols indicates approximate location of carbide crystals in a given spherule; none of the crystals are located in the exact centers of their host spherule.