Fe- AND Cr-XANES ANALYSES OF LARGE CLUSTER INTERPLANETARY DUST PARTICLES. G. J. Flynn[1], S. R. Sutton[2,3], S. Wirick[2], A. Lanzirotti[2], and W. Rao[4], [1]Dept. of Physics, SUNY-Plattsburgh, Plattsburgh, NY 12901 (george.flynn@plattsburgh.edu), [2]CARS, Univ. of Chicago, Chicago IL 60637, [3]Dept of Geophysical Sciences, Univ. of Chicago, Chicago IL 60637, [4] College of Agriculture, Univ. of Kentucky, Lexington, KY, 40506.

Introduction Chondritic porous interplanetary dust particles (CP IDPs) are, most likely, not a complete or representative sample of their parent body. A typical ~10 μm size CP IDP is an aggregate of >10^4 submicron grains having diverse mineralogies. The stratospheric collections include many non-chondritic, mono-mineralic grains, collected along with the fine-grained CP IDPs. Some of these mono-mineralic grains, which include volatile-poor olivine and pyroxene as well as chalcophile-rich sulfides, have fine-grained, chondritic material (i.e., small bits of CP IDPs) adhering to their surfaces. This indicates that at least some of the non-chondritic grains found on the stratospheric collectors are fragments from the same parent as the CP IDPs. Thus, the bulk elemental and mineralogical composition of the CP IDP parent body can only be reconstructed by adding to the fine-grained, chondritic IDPs the correct amount of this non-chondritic material [1]. Cluster IDPs, which are typically ~100 times the mass of 10 μm CP IDPs contain large mono-mineralic grains, sampling the parent body at a much larger size scale than 10 μm CP IDPs.

We have previously reported synchrotron x-ray fluorescence (XRF) elemental and x-ray diffraction (XRD) mineralogical characterization of several large cluster IDPs [1]. Five of the eight cluster IDPs we examined were anhydrous, as demonstrated by the absence of the small d-spacings characteristic of clays in the XRD patterns, and showed minimal evidence of alteration during atmospheric deceleration, i.e., only a very minor amount of magnetite in XRD and Zn/Fe >0.3xCI, criteria previously identified as correlating with a low degree of thermal alteration [1].

Although the 5 to 15 μm CP IDPs are enriched relative to CI in many moderately volatile elements, with a mean enrichment of ~4xCI for Cu, Zn, Ga, Ge, and Se [2], the average composition of the five anhydrous cluster IDPs that show no evidence for element loss during atmospheric deceleration is generally consistent with a CI composition.

Of the elements enriched over CI in the ~10 μm CP IDPs, Zn is present in the highest amount and is most accurately determined in our XRF analysis. While Zn in the ~10 μm CP IDPs is ~4xCI, the mean Zn content of the five cluster IDPs is only 1.2xCI [1]. If these cluster IDPs consist of a mixture of fine-grained CP IDP material and large olivine, pyroxene, and sulfide, then more than 70% of the mass of the cluster particles

must be in these larger mineral grains [3], although the volume fraction of the large mineral grains would be smaller because of the density difference between the crystalline and the porous fine-grained material. The CP IDPs appear to sample the matrix of a parent body that is dominated by larger crystalline grains. This is consistent with the XRD results, which show these cluster IDPs are a mixture of pyrrhotite, fosterite and enstatite. This result suggests that the CP IDPs are not a representative sample of their parent body.

Fe-XANES: Fe is a major element (~18.5%) in chondritic meteorites, and the Fe-oxidation state correlates with the mineralogy of meteorites. Urey and Craig [4] showed that meteorite groups can be distinguished from one another by their Fe-oxidation states. We have begun a project to systematically determine the Fe oxidation states of these cluster IDPs by Fe X-ray Absorption Near-Edge Structure (XANES) spectroscopy.

Olgiore et al. [5] have compared the oxidation state of Fe in 194 fragments, totaling ~300 ng, of the Comet 81P/Wild 2 particles collected by the Stardust spacecraft with that of 15 CP IDPs and concluded that the Wild 2 particles contain much more Fe-metal than the CP IDPs, indicating they did not originate from similar parent bodies. But the Wild 2 particles include large mineral grains, some >10 μm in size, not included in the CP IDPs [3]. Thus, our Fe-XANES measurement of anhydrous cluster IDPs that incorporate larger grains from the CP IDP parent body, comparable in size to some of the larger Wild 2 particles collected by Stardust, provides a further test of Ogliore et al's [5] result.

Thus far, we have performed Fe-XANES on four large anhydrous cluster IDPs – three CI-like L2009R2, L2008Z2, L2005AS10, and one Zn-depleted – L2009R1.

Fe-metal can easily be distinguished from Fe 2+ or Fe-3+ by its Fe-XANES spectrum (see Figure 1). None of the four klarge anhydrous cluster IDPs has an Fe-XANES spectrum similar to Fe-metal, indicating that Fe-metal is not the dominant Fe-bearing phase in any of these particles. The three large anhydrous IDPs with CI-like compositions have Fe-XANES spectra consistent with Fe 2+ being the dominant Fe oxidation state, but none are consistent with fayalite (see Figure 1). Differences between the individual spectra indicate that these three clusters must be mixtures of at least two different Fe 2+ bearing phases. The low-Zn cluster IDP has a distinctly different Fe-XANES spectrum,

Figure 1: Fe-XANES spectra of Fe-metal, fayalite, and hematite compared to the average over the CI-like IDP L2009R2.
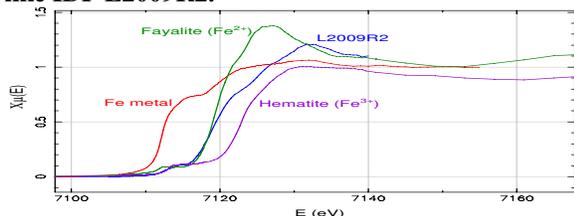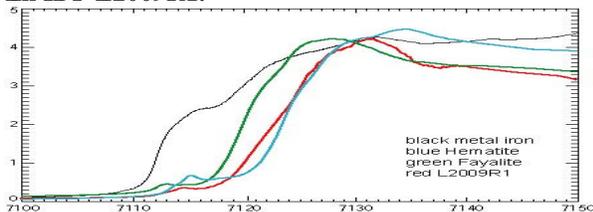

Figure 2: Fe-XANES spectra of Fe-metal, fayalite, and hematite compared to the average over the low-Zn IDP L2009R1.

Figure 3: Cr-XANES spectra at seven individual spots on L2008Z2.
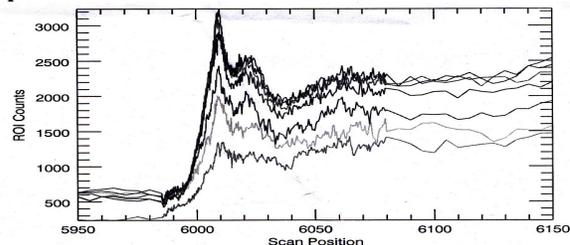

Figure 4: Averaged Cr-XANES spectrum of L2008Z2 (blue) compared to the average of three analyses of different spots on a chromite powder (red) and 5 spots on a diopside powder (green).

consistent with the presence of significantly more Fe 3+ than the other three cluster IDPs (see Figure 2), possibly due to magnetite $[(Fe^{+3})_2(Fe^{+2})O_4]$ formation due to entry heating.

Cr-XANES: The Cr oxidation state is also a useful indicator of the oxygen fugacity [6], with the common oxidation states being *+2, +3, and +6.* We have, thus far, performed full Cr-XANES mapping of one anhydrous large cluster IDP – L2008Z2. Because Cr is significantly less abundant than Fe and we employed the same analysis time (~3-days for the entire particle), the individual Cr-XANES spectra were noiser than the individual Fe-XANES spectra (see Figure 3). However, even these individual spectra are of sufficient quality to exclude the presence of significant amounts of Cr 6+ by the absence of the large Cr 6+ pre-edge feature, and to demonstrate that most of the Cr in L2008Z2 is present as Cr 3+.

The incident x-ray beam is polarized, which can result in variation in the XANES spectrum with crystal orientation. Because of the large number of individual crystals in the cluster IDP, this is not a problem with the IDP analysis, but can complicate the analysis of standards. Two potential Cr 3+ hosts are chromite and Cr-bearing silicates. We measured powdered standards of chromite and Cr-bearing diopside. Although the main features of both spectra are similar, they are distinguishable. The average Cr-XANES spectrum of L2008Z2 is best fit by a mixture containing about equal quantities of chromite and Cr-bearing diopside.

Conclusions: Fe-XANES analysis indicates that L2009R2, L2008Z2 and L2005AS10 consist of a mixture of at least two Fe-bearing phases, each dominated by Fe with a valance near Fe^{2+}. The absence of large
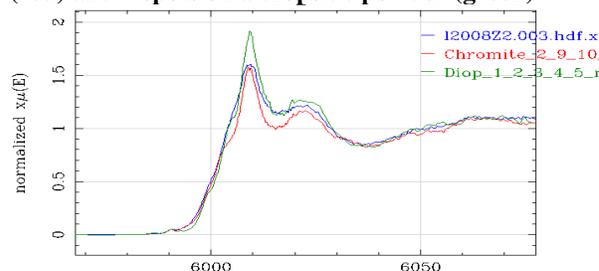
amounts of Fe-metal in these three cluster IDPs suggests that even at the size scale of the cluster IDPs the anhydrous IDP parent body is different from the Wild 2 particles analyzed by Ogliore et al. [5]. L2009R1, an anhydrous low-Zn cluster IDP, has a mean Fe oxidation state closer top Fe^{3+}, possibly reflecting the production of a significant amount of magnetite by atmospheric heating. The Cr in L2008Z2 is present predominantly as Cr 3+. If we model the L2008Z2 average Cr-XANES spectrum as a mixture of the Cr-bearing diopside and chromite, the L2008Z2 spectrum is consistent with about equal amounts of chromite and the Cr-bearing silicate.

References: [1] Flynn, G. J. et al. *Lunar & Planet. Sci XXXIX*, Abs. #1391 (2008). [2] Flynn, G. J. et al., Meteoritics, 28, 349 (1993). [3] Flynn, G. et al. *Lunar & Planet. Sci. XL*, Abs. #1166 (2009). [4] Urey, H. C. and Craig, H., Geochim. Cosmochim. Acta, 4, 36-82 (1953). [5] Ogliore, R. et al. *EPSL*, 296, 278-286 (2010). [6] Sutton, S. R. et al. LPSC XXVII, 1291-1292 (1996)