**Comparison of Nickel XANES Spectra and Elemental Maps from a Ureilite, a LL3.8 Ordinary Chondrite, Two Carbonaceous Chondrites and Two Large Cluster IDPs.** S. Wirick<sup>1</sup>, G. J. Flynn<sup>2</sup>, S. Sutton<sup>1,3</sup>, M. E. Zolensky<sup>4</sup>, Center for Advanced Radiation Sources, Univ. of Chicago, Chicago, IL 60637, USA,(<u>swirick@bnl.gov</u>), <sup>2</sup>Dept. of Physics, Plattsburgh University NY 12901, USA, <sup>3</sup> Dept of Geophysical Sciences, Univ. of Chicago, Chicago IL 60637, USA, <sup>4</sup>NASA Johnson Space Center, Houston, TX, 77058, USA

**Introduction:** Nickel in the extraterrestrial world is commonly found in both Fe-Ni sulfide and Fe-Ni metal forms [1] and in the pure metal state in the interior of iron meteorites where it is not easily oxidized. Ni is also found in olivine, pyroxene and glasses and in some melts the partitioning of Ni between the olivines and glass is controlled by the amount of S in the melt [2]. Its most common valence state is  $Ni^{2+}$  but Ni also occurs as Ni<sup>0</sup>, Ni<sup>+</sup>, and Ni<sup>3+</sup> and rarely as Ni<sup>2-,</sup> Ni<sup>1-</sup> and  $Ni^{4+}$  [3]. It's valence state in olivines is  $Ni^{2+}$  in octahedral coordination on the M1 site and rarely on the M2 site.[4]. The chemical sensitivity of X-ray absorption near-edge structure (XANES) spectroscopy is well established and can be used to determine not only valence states but also coordination sites [5]. We report here Ni XANES spectroscopy and elemental maps collected from 2 carbonaceous chondrites, 2 large cluster IDPs, 1 ureilite and 1 LL3 orginary chondrite.Using XANES it may be possible to find a common trait in the large cluster IDPs that will also be found in meteorite samples.

Sample and Analysis: Both cluster IDPs remain in the silicon oil in which they were collected, protecting them from interaction with the atmosphere since collection. They are both identified as chondritic porous (CP) IDPs from their element abundance patterns and the lack of identification of any hydrated minerals. L2009R2 cluster #13 is spread over an area approximately 250  $\mu$ m in size and contains ~50 aggregates between 10 and 25 microns in size and many more <10 micron sized fragments. L2009R1 cluster #14 is spread over an area ~200 microns in size and contains more than 80 aggregates between 10 and 35 microns and many more particles smaller than 10 microns. To collect Ni XANES spectroscopy one needs a sufficient signal to the detector. Only 10 areas in L2009R2 cluster #13 produced a high enough Ni signal to obtain spectra. L2009R1 cluster #14 had a higher overall Ni content and 18 areas contained enough Ni to obtain spectra.Nickel XANES spectra were also collected from 2 carbonacous chondrites; Allende and Sutter Mills # 12.The Allende sample is a thin section, ~30 microns thick and rich in Ni. Five areas from 2 chondrules were analyzed. Sutter Mills #12 is a crushed, size fractionated sample with particle sizes <200 microns. Nickel XANES spectra were collected from 14 different particles. An LL3.8 stony meteorite,

ALH84086-5, and a ureilite, META78008, were also analyzed. Chosen from the Ni map, Ni XANES spectra were collected from 8 areas in and around 1 chondrule in ALH84086-5. For META78008, Ni XANES spectra were collected from 24 areas in an olivine rich region. Both samples are polished thin sections ~ 30 microns thick. The data was collected at the Center for Advanced Radiation Sources, University of Chicago X26A beamline located at the NSLS, BNL, Upton, NY. Maps were collected at 9 keV for Allende, Sutter Mills #12 and ALH84086-5. Maps for META78008 were collected at 11 keV, for L2009R1 cluster #14 at 13 keV and for L2009R2 cluster #13, at 19 keV. Micro XRD data was collected on only the 2 IDPs. The Ni XANES spectra were collected using a silicon 111 channel cut monochromator. The focused beam size is ~ 10 microns.

**Results:** *Maps*: Due to the 10 micron beam size Ni maps from the CP IDPs and the Sutter Mills #12 samples are useful for indicating where Ni hot spots occur but provide little morphological information. It is interesting to note that CP IDP L2009R1 cluster #14 contained many more Ni rich areas than L2009R2 cluster #13. Overall Ni counts were higher in L2009R1 cluster #14. Also interesting to note is for the Sutter Mills #12 sample nearly all of the particles contained Fe and Ni and there were many particles that contained more Ni than Fe and this is especially true for the very small particles. Figure 1 is a composite of Ni maps from META78008, ALH84086-5 and Allende.



Figure 1. A. Ni map from ureilite sample META78008. B. Ni map from stony chondrite ALH84006-5 and C. Ni map from Allende.Red circles indicate areas where spectra were collected.

Fig.1A shows that much of the Ni found in META78008 occurs between the olivine grains and in dark areas presumed to be high in carbon. We have Ni maps from several other ureilite samples and they all follow this trend. In the ALH84086 Ni map (fig.1B) a Ni rich area can be found in the upper left corner and what the rest of the map shows a Ni containing compound that is intruding into the chondrule. The Ni map for Allende (fig.1C) shows large areas of Ni rich compounds. And the Ni does not spatially occur with either Cr or Ca.

*XANES:* The most common feature in the Ni XANES spectra is an absorption around 8350 eV (white line) suggesting a Ni<sup>2+</sup> in an octahedral coordination site.



Figure 2. Ni XANES spectra from A. ALH84086-5, B. L2009R2 cluster #13, C. META78008, D.L2009R1 cluster #14, E. Allende, and F.Sutter Mills #12. The Y scale is arbitray units.

There are exceptions. Spectra in L2009R1 cluster #14, Allende and ALH84086 contain a shoulder at 8342 eV suggesting there are other coordination sites for the Ni besides octahedral. Another common spectrum found in Sutter Mills #12, and Allende samples has similar spectral features as a nickel sulfide standard (Aldrich 343226) thought the fit is not perfect. ALH84086-5 is unique in this data set in having a strong absorbing region between 8332-8338 eV and plots near to a Ni foil spectrum with the exception of a sharp absorption peak at 8342 eV. L2009R2 cluster #13, META78008, and Allende spectra contain broad absorption in the 8332-8338 eV region but this absorption is weak compared to ALH84086. Sutter Mills #12 and L2009R1 cluster #14 spectra contain a small absorption at 8334 eV. L2009R2's Ni spectra deviate from the other samples with spectra containing a strong, well defined absorption at 8342 eV. There is also a sharp, well defined peak at 8352 ev. Sutter Mills #12 also has a spectrum with a well defined peak at 8348 eV.

**Discussion:** One goal in this study was to infer a source for CP IDPs. There are 2 commonly cited sources for CP IDPs; comets and carbonaceous asteroids both with C concentrations similar to CP IDPs. Comets emit dust in the inner Solar System and colli-

sions in the asteroid belt also produce dust. L2009R1 cluster #14 has Ni spectra similar to the meteorite samples we analyzed. The asteroid belt is a likely source for this sample based solely on the Ni XANES data. The Ni XANES spectra of L2009R2 cluster #13,Allende and ALH84086-5 have similar spectrum to each other, but distinct from the other samples we analyzed. Micro XRD data from L2009R2 cluster #13 indicates it contains about 50% amorphous material. The spectra common to L2009R2 cluster #13 and ALH84086-5 could represent Ni in a glass. Both L2009R1 cluster # 14 and META78008 display a reduction of the Ni white line. Work done by Y. H. Chin et al., looking at a Au-Ni gold system found the Ni white line was reduced with the introduction of more Au. The spectra in L2009R1 cluster #14 and META78008 may display a similar effect due to increased concentrations of Fe or another metal [6]. For the sharp absorption feature at 8352 in the Sutter Mill's sample, D. J. Haynes, et al. obtained a similar spectrum for a Ni (3wt%) substituted Ba-hexaaluminate sample and believed this was the result of either a 4 or 5 plus coordination for an  $Ni^{2+}[7]$ .

Conclusions: Using Ni XANES spectroscopy and elemental mapping we have analyzed different types of meteorites in an attempt to determine the parent source of 2 large cluster CP IDPs. One of the CP IDPs, L2009R1 cluster #14 trends toward the 2 carbonaceous chondrites and the ureilite though we did not find any Ni spectra in L2009R1 cluster #14 similar to spectra found in the Sutter Mill's and Allende from the Fe-Ni-S mineral. The other IDP, L2009R2 cluster #13 did not contain any Ni XANES spectra similar to the other materials and only contained one sharp pre-edge absorption feature similar to one observed in ALH84086-5. In addition the high abundance of non-diffracting, amorphous, material in L2009R2 cluster #13 is consistent with spectroscopic observations of comets but inconsistent with meteorites.

Acknowledgements: We thank Cyrena Goodrich for providing the ureilite sample and Steve Simon for providing the stony chondrite. This work was supported by NASA Cosmochemistry grant NNX10AJ17. The X26A microprobe is funded by DoE Geosciences (DE-FG02-92ER14244). NSLS is funded by DoE.

**References:** [1] Zolensky, M.& Thomas,K. Geochim.Cosmochim.,59(22),4707-4712,1995[2]Li, C. et al.,Chem. Geo. 201, 295-306, 2003[3]Greenwood, N.N. Chemistry Elements ( $2^{nd}$  Ed.)Butterworth-Heinemann pub.1997[4]De Hoog et al., Chem. Geo. 270,196-215,2010[5]Calas, G. et al., Nucl. Instr. Methods Phys. Res. B97, 155-161,1995[6]Chin, Y-H., et al., J. Catalysis, 244, 153-162,2006[7]Haynes,D.J., et al., Catalysis Today,154,210-216,2010