

## COMPARISON OF FE OXIDATION STATES IN INTERPLANETARY DUST PARTICLES AND MATRIX FRAGMENTS OF PRIMITIVE CHONDRITES:

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The valence state of Fe has been determined in four chondritic IDPs, L2005 J24, L2011 P12, L2011 N1 and W7027 C5, and on 50  $\mu\text{m}$  fragments of three primitive chondrites, Murchison, Orgueil and Semarkona, using a micro-XANES technique. We have clearly identified 2 distinct types of IDPs, based on differences in their Fe oxidation states. One type, represented by L2005 J24 and L2011 P12, has about 90% of the Fe in the trivalent state and is very similar to Orgueil, while the second type, represented by L2011 N1 and W7027 C5, has 33-43% Fe in trivalent state. All four particles showed similar patterns for major and trace element composition.

**Introduction:** Interplanetary dust particles (IDPs) are considered to come mainly from comets or the asteroid belt region. Such small bodies might still preserve some information on early solar system processes. The oxidation states of transition metals in primitive solar system materials are of interest in constraining the oxygen fugacity of early condensation environments [1]. We are exploring the suitability of the micro X-ray Absorption Near Edge Structure technique for this purpose.

**Techniques:** Measurements were done at the synchrotron x-ray fluorescence (XRF) microprobe beam line X26A at the National Synchrotron Light Source, Brookhaven National Laboratory, Upton, NY. Using a small, 50  $\mu\text{m}$ , monochromatic beam we measured x-ray absorption spectra in fluorescence mode, whereby the incident monochromatic photon energy was changed by small increments and Fe  $K_{\alpha}$  fluorescence x-rays coming from the sample were detected with a Si(Li) detector. More details about the setup can be found in Bajt et al. [2]. The region within few tens of eV around the main absorption edge is known as the XANES region. The synchrotron is an extremely bright x-ray source which enables one to get good statistical XANES data on very small samples, like IDPs. Good energy resolution of the whole setup ( $\sim 1.5$  eV) allows one to detect and resolve small pre-edge resonances which are only few eV below the main absorption edge. These pre-edge peaks are due to electronic transitions from 1s to unoccupied 3d states and are good indicators about local atomic environment. The energy of the pre-edge peak was defined to be the centroid of a Gaussian fit to the peak after background subtraction. All XANES spectra were determined relative to the position of the magnetite pre-edge peak (our standard). Measurements performed on well-characterized samples with known Fe oxidation state showed a linear relationship between a relative energy position of the pre-edge peak and  $\text{Fe}^{3+}/(\text{Fe}^{2+}+\text{Fe}^{3+})$  ratio [2]. Iron in these samples was present only in the +2 or +3 valence state. In addition to pre-edge peak positions we also used first derivatives to see changes in overall shape of Fe XANES spectra.

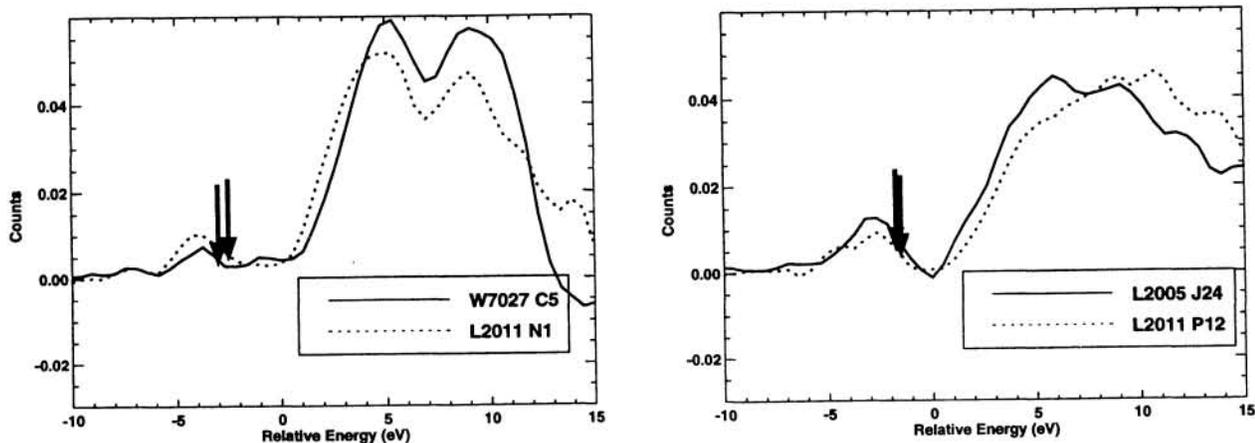
**Results and Discussion:** Four IDPs from the NASA collection (L2005 J24, L2011 P12, L2011 N1 and W7027 C5) were chosen for this exploratory study. All four particles have been characterized as C or C? in the NASA JSC catalogue. Large IDPs between 30 and 40  $\mu\text{m}$ , were selected to maximize the signal. Thus far only one particle, L2011 P12, was analyzed by TEM. This particle consists mainly of Fe-rich serpentine (cronstedtite) and Mg-rich serpentine. We also measured trace element composition using synchrotron XRF microprobe. Trace element data normalized to Fe and to CI are chondritic except for Br which is enriched by a factor of 5 to 30. The Zn content is between 0.6 and 1.2 times CI indicating a relatively low atmospheric entry heating temperature for all four particles. Based on major and trace element composition we can not see any big difference among these particles.

Fe K XANES results of IDPs were quite different. Using the pre-edge peak technique we can place four IDPs in two groups. Two IDPs, L2011 N1 and W7027 C5, have about 35-45 % Fe in trivalent state. IDPs L2005 J24 and L2011 P12 are much more oxidized, both showing

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about 90% of Fe in trivalent state. Since the Zn content in all four IDPs is much the same (about 0.6 to 1.2 CI) we suspect that the differences are not due to entry heating effects. We did not observe any correlation between Zn content and the iron oxidation state in IDPs. None of the four IDPs shows the distinct XANES signature of magnetite, which is also an indicator of high atmospheric entry heating temperature. The above results are based on the assumption that the total Fe is a sum of the  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  valence states only. We can not exclude the presence of  $\text{Fe}^0$  in any of the four measured IDPs. Fe metal would show up as a shift of the main absorption edge to lower energy. This assumption is supported by a series of measurements done on mixtures of known proportions of fayalite and Fe metal, and magnetite and Fe metal which show the effect of small amounts of Fe metal on the pre-edge peak position in Fe XANES spectra. Unfortunately such a shift can be easily misinterpreted as an artificially high  $\text{Fe}^{3+}/(\text{Fe}^{2+}+\text{Fe}^{3+})$  ratio [3]. Assuming that  $\text{Fe}^0$  is present in 1 wt.% we estimate that the maximum error in the oxidation state determination is less than 10%. Fe metal is rare in IDPs, having been identified in only three of the 30 IDPs tabulated in the review article by Mackinnon and Rietmeijer [4].

We also measured Fe XANES data on isolated 50  $\mu\text{m}$  matrix fragments of three primitive chondrites: Orgueil, Murchison, and Semarkona, and compared them to the IDP data. The pre-edge peak position and the overall shape of the Fe XANES data of Orgueil matrix matched well with those of L2005 J24 and L2011 P12 suggesting that the Orgueil matrix contained mainly oxidized Fe. Measurement on the Murchison matrix showed some similarities to L20011 N1 and W7027 C5 for the XANES region above the main absorption edge but in general Murchison is not as similar to the second group as Orgueil is to the first group. The spectrum from Semarkona matrix fragment was almost identical to Fe XANES spectra of the magnetite standard, having  $\text{Fe}^{3+}/(\text{Fe}^{2+}+\text{Fe}^{3+})$  ratio of 0.67. Previous measurement on a piece of a different Semarkona fragment [5] showed a presence of  $\text{Fe}^0$ ,  $\text{Fe}^{2+}$ , and  $\text{Fe}^{3+}$ . These results confirm large inhomogeneities in Fe oxidation states proportions within the Semarkona matrix.



**Figures 1a and 1b** show first derivatives of Fe K-XANES spectra of four IDPs. First group, W7027 C5 and L2011 N1 have a distinct double peak feature on the main absorption edge and the derivative of the pre-edge peak position is shifted to the left as compared to the second group of IDPs, L2005 J24 and L2011 P12. The arrows point to the pre-edge peak positions in the non-derivative spectra.

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