

**OXIDATION STATE OF FE IN GIANT CLUSTER INTERPLANETARY DUST PARTICLES** A. J. Westphal<sup>1</sup>, R. Bastien<sup>2</sup>, A. L. Butterworth<sup>1</sup>, C. E. Jilly-Rehak<sup>1</sup>, R. C. Oglione<sup>3</sup>, M. Tomsick<sup>4</sup>, <sup>1</sup> Space Sciences Laboratory, U. C. Berkeley, Berkeley, CA, USA<sup>2</sup> NASA Johnson Space Center, Houston, TX, USA<sup>3</sup>, Washington University, St. Louis, MO, USA<sup>4</sup> Berkeley High School, Berkeley, CA, USA

**Introduction:** Quantitative Fe oxidation-state measurements by Urey and Craig almost 70 years ago were among the first effective tools for the classification of extraterrestrial materials[1], establishing the meteorite classification system still in use today. The oxidation state of comets was unknown, until the Stardust mission returned the first materials from a known primitive solar system body, the Jupiter-family comet Wild 2. Westphal *et al.*[2] used synchrotron x-ray absorption spectroscopy to measure the average Fe oxidation state of Wild 2. The oxidation state of Wild 2 was not consistent with that of any family of meteorites (Fig. 1). This was perhaps not surprising, but a comparison to that of chondritic-porous interplanetary dust particles (CP-IDPs)[3], which are thought to originate in comets, showed a surprising difference: Wild 2 was significantly more metal-rich than CP-IDPs. The measurements were carried out using identical methods, and on the same synchrotron x-ray microprobe at the Advanced Light Source (ALS) at Lawrence Berkeley National Laboratory, so the difference in oxidation state measurements appeared to be significant. The low abundance of magnetite in the CP-IDPs appeared to rule out oxidation during atmospheric entry as a source of the difference. Reduction of FeS to Fe metal through loss of S during aerogel capture was not consistent with observed oxidation state measurements of the respective samples[3].

Here we explore a possible origin for the difference in Fe oxidation state between Wild 2 and CP-IDPs. Small CP-IDPs dominated by Fe metal would be, on average, denser than the bulk material, and so would have a shorter residence time in the stratosphere, resulting in a collection bias in the stratospheric collections towards metal-poor particles. To test this hypothesis, we measured the oxidation state of Fe in particles sampled from giant cluster IDPs. The bulk density of giant cluster IDPs would be closer to the low density of the parent body, would have a residence time closer to that of small metal-poor CP-IDPs, and would thus avoid the collection bias exhibited by small CP-IDPs.

#### Methods:

**Collection:** The particles were collected in the stratosphere, on plates coated with silicone oil mounted on the leading edge of ER-2 aircraft. We extracted five particles from each of seven giant cluster IDPs in flags L2071, L2076, L2079 and L2083, in the Cosmic Dust Lab at NASA Johnson Space Center. We placed these particles on Nucleopore filters and rinsed them in hexane to remove the silicone oil.

We imaged the particles at high resolution on a Tescan Vega SEM, and determined their approximate compositions by SEM/EDX using an Oxford 80 mm<sup>2</sup> x-ray detector. We found that all particles from one of the clusters (L2071T) were non-chondritic (Al-rich) and were not included in this analysis, although an extraterrestrial origin for these particles has not yet been ruled out.

We analyzed 23 of these particles *in situ* on the nucleopore filters on x-ray microprobe beamline 10.3.2 at the ALS, using X-ray Absorption Near-Edge Spectroscopy (XANES). Here, a microfocused, monochromatic x-ray beam is used to measure the x-ray absorption spectrum of each particle by scanning in energy across the Fe edge at  $\sim 7110$  eV. The method is described in detail in Westphal *et al.*[2] and Oglione *et al.*[3]. In one dimension the beam was generally smaller than the particles, so we covered each particle in its entirety by making between one and seven XANES measurements. We used the “Quick XANES” technique to avoid problems arising from sample drift during the measurements. We did energy calibrations before each session using a standard procedure with Fe metal foil.

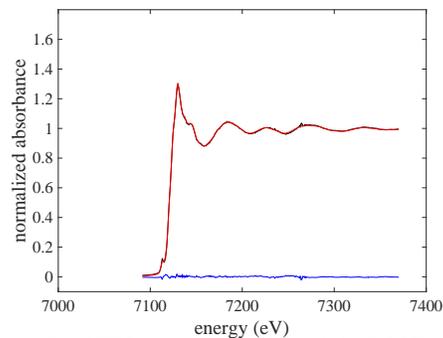


Fig. 1: XANES spectrum of particle L2071s1 (black). A non-negative linear least-squares fit to the spectrum from the standards library is shown in red and the residual of the fit in blue. This fit gives 10% metal, 8% sulfide and 82% Fe<sup>2+,3+</sup>.

#### Analysis:

For each spectrum, we did dead-time correction, background subtraction and slope-correction in the post-edge region due to a small energy-dependent position shift in the y-direction. An example of one of the processed spectra is shown in Fig. 1.

We found one particle, L2079n2, in which the Fe is almost entirely in metallic form throughout the particle. We found no similar particles in the earlier study of small CP-IDPs. The spectrum of this particle is shown in Fig. 2, and its image in Fig. 3.

Each spectrum can be compared with a library of standards to determine approximate mineralogy. Degeneracies in the spectra among various minerals with similar oxidation states prevent a unique reconstruction of mineralogy, but the oxidation state can be determined accurately because the position of the Fe absorption edge is related to the oxidation state. We carried non-negative least-squares fitting of each spectrum to a library of 56 standards, which included metals, sulfides, silicates, and oxides. Each spectrum thus yielded two measurements: the atomic fraction of Fe in metal, and the atomic fraction in sulfide, with the remainder as  $\text{Fe}^{2+,3+}$ .

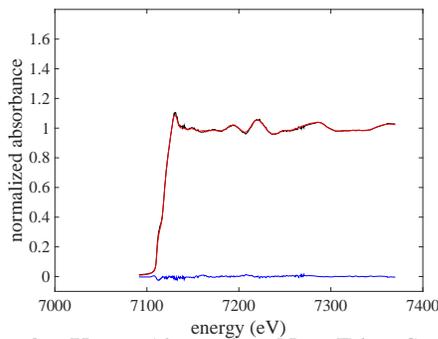


Fig. 2: X-ray Absorption Near-Edge Spectroscopy (XANES) spectrum of particle L2079n2 (black), fit (red) and residual (blue). This fit gives 80% metal, 12% sulfide and 8%  $\text{Fe}^{2+,3+}$ .

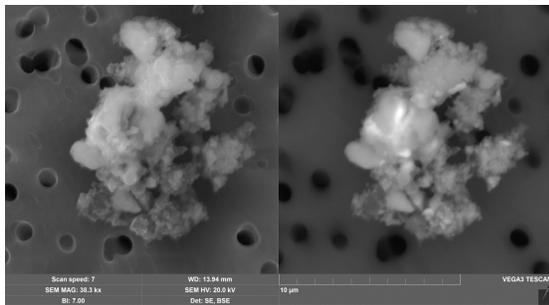


Fig. 3: Secondary Electron (left) and Back-Scatter (right) images of the metal-rich particle L2079n2.

To determine confidence limits on the average oxidation state of the particles, we first combined the results from each of the 23 particles into one average measurement. Each individual spectrum was weighted by the amplitude of the edge jump, corrected for the detector distance. We then used the bootstrap method, a Monte Carlo method in which oxidation states are determined from 10,000 random draws from the ensemble of individual spectra. A  $2\sigma$  confidence region is then drawn automatically around the individual points in the metal-sulfide-oxide parameter space. The resulting confidence limits are shown in Fig. 4.

## Discussion:

The  $2\sigma$  confidence region for giant cluster IDPs overlaps with that of Wild 2, but is not coincident with it. At low significance, giant cluster IDPs appear to be more oxidized than Wild 2. Of more significance is that the confidence region for giant cluster IDPs and that for small CP-IDPs is almost completely disjoint, with giant cluster IDPs being significantly more metal-rich, similar within confidence limits to Wild 2. Future measurements will constrain the cluster IDP oxidation state, to test consistency with Wild 2 and CP-IDPs.

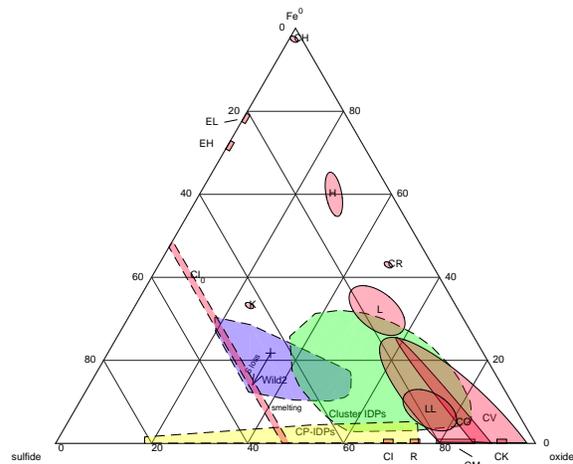


Fig. 4: Confidence limits on the mean oxidation state of cometary materials ("Wild 2", "CP-IDPs", and "Cluster IDPs"), compared with the range of oxidation states of various meteorite families.

A difference could be expected if the metal grains in IDPs are systematically larger than grains of other types, and are thus systematically depleted from the stratospheric collection of small particles. Although no systematic study has been done, there are hints that this may be the case in the Wild 2 collection. Two large Wild 2 particles, Simeio [4] and its twin Geminus, both captured in track 41 in the Stardust cometary collector, are unusually large monomineralic grains. If they followed a power-law size distribution with a typical index of  $\sim 3$ , smaller versions of Simeio and Geminus should be common in the Stardust cometary collection, but few have been reported. The origin of a different size distribution for metal grains as compared with grains of other phases is not clear.

**References:** [1] Urey H. C. and Craig H. (1953) GCA 4, 36 [2] Westphal A. J. et al. (2009) ApJ 694, 18 [3] Ogliore R. et al. (2010) EPSL 296, 278 [4] Humayun M. et al. (2015) LPSC LPSC XLVI, 2298.