

P SPECIATION IN LARGE, CLUSTER INTERPLANETARY DUST PARTICLES. G. J. Flynn¹, S. Wirick² and P. Northrup³, ¹SUNY-Plattsburgh, 101 Broad St., Plattsburgh, NY, 12901 (flynn@plattsburgh.edu), ²Focused Beam Enterprises, Westhampton, NY 11977, ³ Stony Brook University, Stony Brook NY 11794.

Introduction: The abundance and speciations of P play a particularly important role in biology and the origin of life. The most common elements in cells are H, C, N, O, P, and S. Of these, P is least abundant, but P is a critical structural element in DNA and RNA. This gives rise to the “Phosphorous Problem” in the origin of life. Pasek [1] noted the availability of dissolved P in water on the Earth is low. Phosphate minerals such as apatite, whitlockite and monetite are the major carriers of P on Earth, but they are poorly soluble in water and inert [1]. This prompted the idea that exogenous delivery of reactive P by interplanetary dust particles (IDPs) or meteorites was important to life’s origin. Pasek and Lauretta [2] modeled delivery of C, N, and P to Earth and found carbonaceous chondrites, which have high concentrations of these elements, were not an adequate source of organic compounds, and that iron meteorites provided critical reactive P as schreibersite, a phosphide mineral, to Earth’s early surface.

In the current era, iron meteorites deliver an insignificant amount of P to the Earth compared to that from the accretion of interplanetary dust (Figure 1), and equilibrium condensation modeling predicts that P is hosted in schreibersite in primitive dust [3]. We have begun measuring the distributions and speciations of moderately volatile elements, including P, in the IDPs. P x-ray absorption near-edge structure (XANES) spectroscopy cleanly distinguishes phosphates (peak at ~2153 eV) from phosphides (~2144 eV).

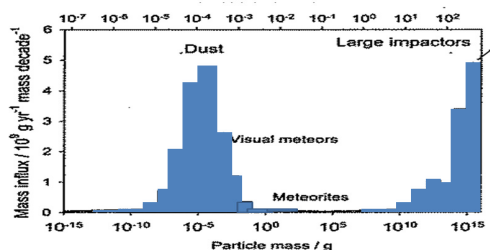
We reported a measurement of P speciation using the prototype Tender Energy Spectroscopy (TES) instrument at the National Synchrotron Light Source, using the 1 mm beamspot to characterize P over one entire large cluster IDP [4]. The newly commissioned TES instrument, on beamline 8BM of the National Synchrotron Light Source II (NSLS-II) at Brookhaven National Laboratory has significantly improved capabilities over the prototype. TES was designed to fill the gap between low energy (C, N, O) spectroscopy and hard x-ray (typically elements from Ca to Pd) micro-spectroscopy. TES has a user-tunable spot size varying from 10x25 μm , with a flux of up to 10^{11} photons/s, down to 1x2 μm , with a flux of up to 10^9 photons/s. A helium sample environment permits x-ray fluorescence (XRF) element mapping down to 1 eV, for quantitative abundance mapping of elements as light as Na. The tunable monochromator (2 to 5 keV) is optimized for K-edge XANES of P to Ca.

The use of large area collectors in the NASA Johnson Space Center Cosmic Dust collection program facilitated the collection of larger size extraterrestrial particles, many with diameters >25 μm . Although a few remain intact, many fragment on impact, producing a cluster of fragments of various sizes over several hundred microns on the collector [5]. The fragments are generally anhydrous, consisting of many large mineral grains embedded in a matrix very similar to the ~10 μm chondritic porous (CP) IDPs. Analysis of these large cluster IDPs provides an opportunity to characterize the CP IDP parent body at a larger size scale [6] and should provide insight into the compositions and mineralogies of larger dust that vaporizes in the atmosphere producing radio meteors that have a significant impact on the properties of the Earth’s upper atmosphere [7].

We mapped the elements from Mg to Ni in 9 large, cluster IDPs (Figure 2), and performed P-XANES analysis of all P hot-spots intense enough to produce useful spectra. This produced spectra of 17 P hot-spots: 0 in L2005 AS9, 1 in L2005 AS10, 3 in L2005 AS11, 0 in L2008 Z1, 1 in L2008 Z2, 6 in L2009 R1, 1 in L2009 R2, 0 in L2021 S1, and 5 in L2036 AL14. We found a general consistency of these 17 P-XANES spectra, e.g. the 6 P hot-spots in L2009 R1 (Figure 2). Comparison with apatite and schreibersite (Figure 3), demonstrates that phosphate is the dominant form of P in these IDPs.

However, not all spots in these cluster IDPs exhibit the same P-XANES spectra. Most of the P-XANES spectra of these cluster IDPs show no shoulder on the high energy side of the major absorption peak. However, Spot 4 in L2009 R1 (Figure 2), Spot 2 in L2005 AS11 (Figure 3) and a few other spots exhibit a distinct shoulder on the high energy side of the major absorption peak. Ingall et al. [8] performed P K-edge XANES spectroscopy of 12 apatite-group minerals and found that each exhibited “a distinct shoulder or widening on

Figure 1: Mass per mass decade accreting onto Earth from various sources. (From Plane et al. [7]).



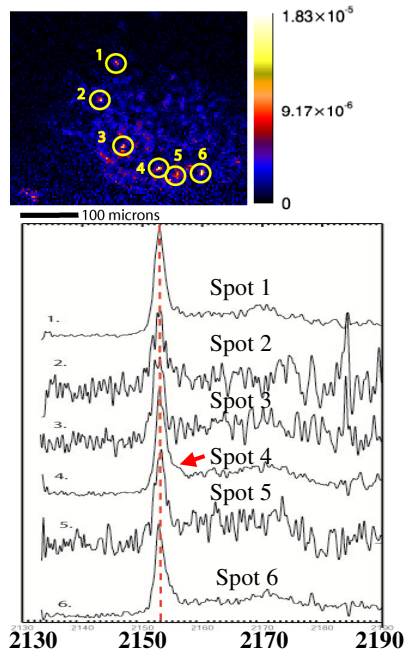
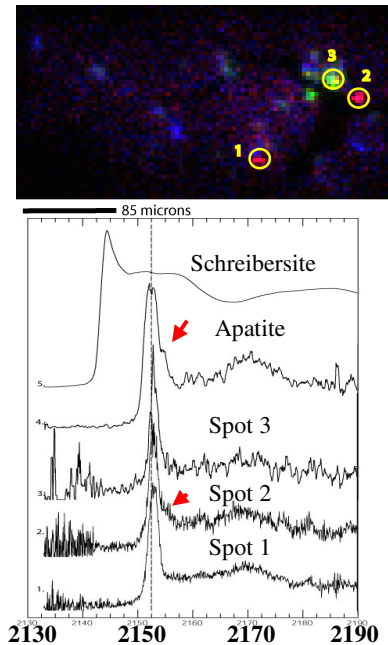


Figure 2 (left) P map (blue pixels are likely scatter from silicone oil, marking the boundary of the oil spot) and P-XANES spectra of 6 spots on L2009 R1 show general consistency in the peak shape and position. The shoulder on the high energy side of the peak in Spot 4 is consistent with apatite. The noise level reflects the P mass in each spot.

Figure 3: (right) Map (P = red, S = green, Mg = blue) of L2005 AS11 shows overlap of S and P in Spot 3 (yellow). P-XANES spectra of L2005 AS11 show slight shifts in peak position. Comparison with apatite and schreibersite shows no evidence of phosphide in L2005 AS11.



the main absorption peak, centered at approximately 2155.6 eV,” consistent with the shoulder seen in Spot 4 of L2009 R1, Spot 2 of L2005 AS11 and a few other IDPs. The absence of this shoulder in several spots with good enough signal to noise to detect it indicates that there are at least two distinctly different P-bearing minerals in large cluster IDPs, one phase exhibiting a shoulder consistent with apatite and a second, more common, phase without this shoulder.

In most cases the P was spatially separated from the S. However, we identified several spots (e.g., Spot 3 in Figure 3) where, at the resolution of the TES instrument, the element maps show P spatially associated with S. The S-XANES spectrum clearly identifies the spot as a sulfide. However the P-XANES spectrum is consistent with phosphate. This overlap of P with S is interesting since it could identify a P-bearing sulfide like the ones reported by Nazarov and coworkers in several CM chondrites [9]. Although Nazarov et al. [9] found these P-bearing sulfides in aqueously processed CM meteorites, they suggested the phase was a primary nebula product. Thus it would be particularly significant if one were identified in a primitive, anhydrous CP IDP. We have no P-XANES spectra of P-bearing sulfides from CM meteorites for comparison, so higher spatial resolution analysis or extraction of these grains is required to characterize the P-bearing mineral.

The majority of the mass of P that we mapped is in the larger grains, so our P-XANES results demonstrate the P in large, cluster IDPs is found predominately in oxidized form (e.g., phosphate) rather than more reduced forms like phosphides. We were not able to determine the P concentration since parts of these cluster

IDPs are thick compared to the P fluorescence escape depth. However, smaller IDPs have $\sim 2\times$ CI P [10]. IDPs deliver organic matter and make a significant contribution of P, far exceeding that from meteorites, to the surface of the early Earth. The bioavailability of P from phosphates may be underestimated by Pasek [1] since Atlas and Pytkowicz [11] indicate complex coatings on apatites enhance their solubility in seawater, an effect important for the small phosphates in IDPs

If, as indicated by Pasek [1], phosphates are not bioavailable it is important to consider that much of the dust incident on the top of the Earth’s atmosphere is vaporized, producing meteors. This vaporized material is expected to recondense into meteoric smoke particles [7], which then accrete onto the Earth. The specific form of P contributed to the Earth’s surface by meteoric smoke particles, now and under the atmospheric conditions of the early Earth, needs to be assessed since it may be important to the origin of life.

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