

CHLORINE, PHOSPHOROUS, AND SULFUR IN PRIMITIVE INTERPLANETARY DUST PARTICLES: IMPLICATIONS FOR CONDENSATION FROM THE SOLAR NEBULA. G. J. Flynn,¹ S. Wirick,² and P. Northrup³, ¹SUNY-Plattsburgh, 101 Broad St., Plattsburgh, NY, 12901 (flynnj@plattsburgh.edu), ²Focused Beam Enterprises, Westhampton, NY 11977, ³Stony Brook University, Stony Brook NY 11794.

Introduction The abundances and speciations of Cl, P, and S can constrain the condensation conditions in the Solar Protoplanetary Disk, and P and S play particularly important roles 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.

The moderately volatile elements are also important to constrain condensation from the Solar Nebula. Using the Solar composition and the thermodynamic properties of the gas and various minerals the condensation temperature and mineral host of each element has been modeled. While many elements remain in their first solid host, in some cases this initial host interacts with the remaining gas at a lower temperature to form another mineral. For example, Fe condenses as metal at 1334K, but as the Nebula continues to cool the Fe-metal interacts with the remaining gas to form Fe-sulfide (Troilite) at 664K. Phosphorous has a more complicated condensation behavior making it particularly valuable as a cosmo thermometer. Modeling by Fegley and Schaefer [2] indicates that P condenses from a cooling gas of Solar composition at 1285K as a phosphide, schreibersite (Fe₃P). This schreibersite reacts with the gas at lower temperatures forming fluorapatite, Ca₅(PO₄)₃F, at 712K and whitlockite, Ca₃(PO₄)₂, at 680K. The whitlockite then reacts with gaseous HCl to form chlorapatite, Ca₅(PO₄)₃Cl, at 470K. So the mineralogy of the P-bearing grains in primitive material should indicate the temperature range when these grains were isolated from further interaction with Nebular gases, constraining the lowest temperature reached in the grain forming region.

The record of condensation in most extraterrestrial materials is overprinted by aqueous or thermal alteration on parent bodies. But one class of extraterrestrial material, the anhydrous, chondritic porous interplanetary dust particles (CP IDPs), collected by NASA from the stratosphere after gentle deceleration in the upper atmosphere, never experienced significant aqueous or thermal processing making them the best

preserved samples of the original condensates from the Solar Nebula currently available for laboratory study [3]. These ~10 μm CP IDPs, dust from asteroids and comets collected by NASA from the Earth’s stratosphere, are anhydrous aggregates of more than 10⁴ individual, mostly sub-micrometer grains.

However, NASA’s stratospheric collections include many non-chondritic, monomineralic grains -- volatile-poor olivine and pyroxene as well as calcophile-rich sulfides -- collected along with the fine-grained CP IDPs. Some of these larger mineral grains (many >10 μm in size), have fine-grained, chondritic material (i.e., small bits of typical CP IDPs) adhering to their surfaces, indicating they are larger fragments of the same parent as the ~10 μm CP IDPs [4]. Cluster IDPs, larger IDPs that fragment on impact with the collector, include both fine-grained CP IDP material and larger mineral grains [4, 5]. Characterizing anhydrous cluster IDPs allows determination of the elemental and mineralogical compositions of the CP IDP parent body at a significantly larger size scale [4, 5], since a single large cluster IDP contains >100 times the mass of a ~10 μm CP IDP [5], making it possible to expeditiously search for rare, minor phases including those hosting P and Cl.

Samples and Measurements: The Tender Energy Spectrometer (TES) instrument, on beamline 8BM of the National Synchrotron Light Source II (NSLS-II) at Brookhaven National Laboratory, has a user-tunable spot size, varying from 10x25μm, with a flux of up to 10¹¹ photons/s, down to 1x2 μm, with a flux of up to 10⁹ photons/s. A helium sample environment permits x-ray fluorescence (XRF) element mapping down to 1 eV, for abundance mapping of elements as light as Na. The tunable monochromator (2 to 5 keV) is optimized for K-edge X-ray Absorption Near-Edge Structure (XANES) spectroscopy of P to Ca. We previously reported P and S mapping and XANES measurements on nine large, cluster IDPs [6], but the mapping energy, just above the S K-edge, precluded Cl analysis. We recently performed XRF mapping and Cl-XANES analyses on six of these cluster IDPs: L2005 AS9, L2005 AS10, L2005 AS11, L2008 Z2, L2009 R1, and L2036 AL14. Each particle exhibited several Cl hot-spots, which we analyzed by Cl-XANES. These IDPs had been transferred to a Kapton film by the NASA Johnson Space Center Curatorial Facility in the silicone oil in which they were collected. The oil is expected to inhibit interaction of the small grains with the atmosphere. We identified three spatial associations between Cl and either P or S:

- 1) high-Cl phosphate,

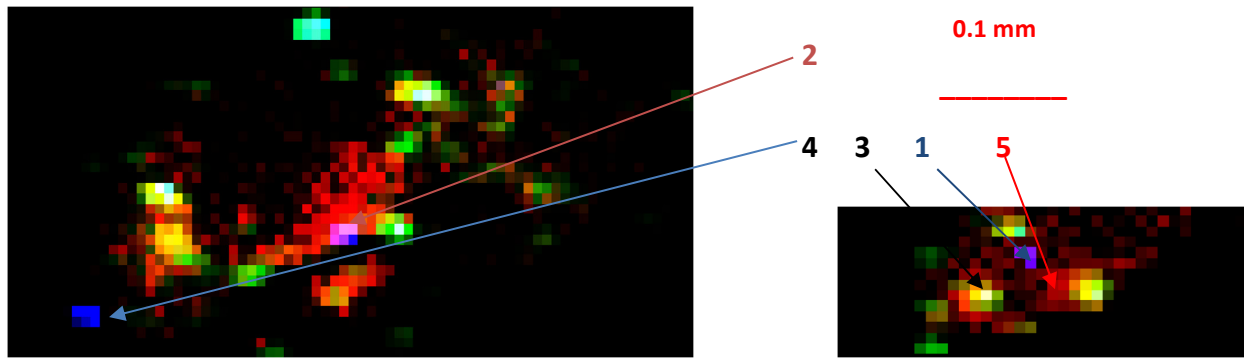


Figure 1: Three color map showing Cl (red), S (green), and P (blue) in the two areas of the L2036 AL14 cluster IDP. (An 0.1 mm scale bar is shown in red.)

- 2) much lower Cl phosphate. and,
- 3) sulfide with significant Cl and P.

In addition, we observed Cl hot-spots not associated with P. All four types occur in L2036 AL14 (Figure 1). The same Cl associations were observed in several of the other cluster particles. We also measured a chlorapatite to determine its Cl-XANES spectrum.

Discussion: L2036 AL14 was distributed on Kapton in two distinct regions mapped separately (Figure 1).

P grains. All of the P hot-spots, which were identified in our prior work, had P-XANES spectra demonstrating they were phosphates not phosphides [6]. However, most of the spectra were inconsistent with either fluorapatite or whitlockite, lacking the shoulder on the high energy side of the pre-edge peak characteristic of these minerals [6], so the bioavailability of these phosphates is not known.

Some of these phosphates, e.g. Spots 1 and 4, blue pixels in the RGB map (Figure 1), had Cl below our detection limit, with the Cl:S:P background corrected count ratio in the Spot 1 pixel of 0:15:17 and in the Spot 4 pixels of 0:14:25. The low Cl in these spots indicates that some phosphate grains in these primitive IDPs did not interact with HCl gas, suggesting they were isolated from the Solar Nebular gas before it cooled below ~420K in the region where they formed.

Other phosphates, e.g. Spot 2 (magenta), had much higher Cl spatially associated with the P. Spot 2 has a background corrected Cl:S:P count rate ratio of 37:310:40. This grain is located in a high S region of the particle, so the S in this pixel may not be in the phosphate grain. Higher spatial resolution is required to determine if these are Cl-rich phosphates. The Cl-XANES spectra of this spot is inconsistent with chlorapatite (Figure 2).

S grains. We previously identified several high-P sulfide/sulfate grains in these cluster IDPs [6], possibly similar to the grains identified in CM meteorites by Nazarov et al. [7], who suggested the P-bearing sulfides in CM chondrites formed under reducing conditions in

the Solar Nebula. Finding such grains in primitive IDPs would support that idea. Cl was spatially associated with these high-P sulfide/sulfate grains, e.g., Spot 3 (white) with a Cl:S:P count ratio of 25:480:7. The small shift in the Cl-XANES peak position compared to Cl associated with the phosphate grains (Spot 2) suggests a different bonding environment (Figure 2). Some other sulfides (green in Figure 1) had no detectable Cl.

Other Cl hot-spots. We also observed Cl hot-spots, e.g. Spot 5 (red) not associated with P or Si. The Cl:S:P count rate in this pixel was 20:370:1, suggesting a possible association of Cl with S in this area. The Cl-XANES spectrum of Spot 5 is similar to the Cl spatially associated with P in Spot 2 (Figure 2)

To confirm these spatial associations will require either improved spatial resolution, which will soon be possible with a new end station on Beamline 8BM, or by extraction of the grains for TEM characterization.

References: [1] Pasek, M.A. (2006), PhD Thesis, Univ. of Arizona. [2] Fegley and Schaefer (2010) Cosmochemistry, in Principles and Perspectives in Cosmochemistry, Springer-Verlag. [3] Ishii et al. (2008) Science, 319, 447-450. [4] Flynn et al. (2006) 37th LPSC, Abst. #1216. [5] Thomas, K.L. et al. (1995) Geochim. Cosmochim. Acta, 59, 2797-2815. [6] Flynn, G.J. et al. (2019), 50th LPSC, Abst. #1403. [7] Nazarov et al. (2008) Petrology, 17, 101-123.

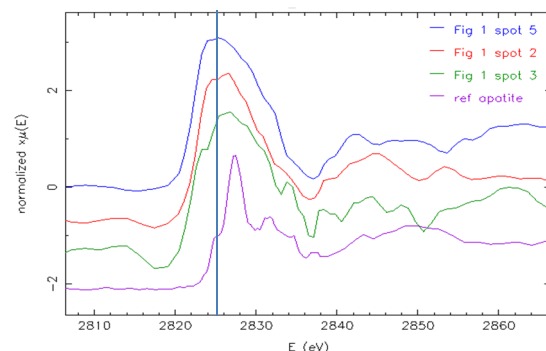


Figure 2: Cl-XANES spectra of three spots on the L2036 AL14 cluster IDP and chlorapatite.).