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Phosphorous Condensation from the Solar Protoplanetary Disk: Evidence from the Primitive Interplanetary Dust

George Flynn (1), Sue Wirick (2) and Paul Northrup (3)
(1) Dept. of Physics, SUNY-Plattsburgh, Plattsburgh, NY, USA (george.flynn@plattsburgh.edu), (2) Focused Beam Enterprises, Westhampton, NY 11977 USA, (3) Stony Brook University, Stony Brook NY 11794, USA.

Abstract

Equilibrium condensation from a gas of Solar composition leads to Fe-metal interacting with P at 1248 K to form schreibersite and, as the gas cools further, S interacting with Fe-metal to form troilite at 704 K. Primitive interplanetary dust particles (IDPs), believed to preserve the condensates from the Solar Protoplanetary Disk contain abundant Fe-sulfide. We mapped P in primitive IDPs and determined the P-speciation, finding P predominantly in oxidized rather than reduced form, in conflict with the models.

1. Introduction

Equilibrium condensation models starting with a gas of Solar composition predict that P condenses in reduced form as schreibersite [1]. The anhydrous chondritic porous (CP) IDPs are believed to be the best preserved samples of the original condensates from the Solar Protoplanetary Disk currently available for laboratory analysis [2]. Thus, the mineralogy of CP IDPs tests the predictions of condensation models. However, there have been no comprehensive studies of P speciation in CP IDPs.

The recently commissioned Tender Energy Spectroscopy (TES) instrument (Beamline 8BM, National Synchrotron Light Source II, Brookhaven National Laboratory) can map elements by x-ray fluorescence (XRF), and provide speciation by K-edge X-ray Absorption Near-Edge Structure (XANES) spectroscopy of the elements from P to Ca. It provides us with the opportunity to locate P hot-spots and use P-XANES to determine P speciation.

2. Samples and Techniques

The ~10 µm chondritic porous interplanetary dust particles (CP IDPs) are dust from asteroids and comets collected by NASA from the Earth's stratosphere. These CP IDPs are anhydrous, unequilibrated aggregates of more than 10^4 individual grains. They have compositions similar to the CI carbonaceous chondrite meteorites, and contain some mineral grains and organics that preserve pre-solar isotopic compositions. All these factors indicate CP IDPs are minimally processed samples of the original dust grains from the Solar Protoplanetary Disk.

NASA's stratospheric dust collections include many non-chondritic, mono-mineralic grains – mostly olivine, pyroxene and sulfide -- 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, fine-grained CP IDPs. Thus, the composition of the primitive CP IDP parent body can only be determined by adding to the fine-grained, CP IDPs the *correct amount* of this non-chondritic material.

The introduction 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 break up on impact, producing a cluster of fragments of various sizes over several hundred microns on the collector. The fragments are generally anhydrous, consisting of many large mineral grains embedded in a matrix very similar to that of 10 µm CP IDPs [3]. This provides the opportunity to determine the elemental and mineralogical composition of the CP IDP parent body at a significantly larger size scale, since a single large cluster IDP contains more than 100 times the mass of one ~10 µm CP IDP.

We mapped the spatial distribution of elements from Mg to Ca in 9 large, cluster IDPs, most of which were of the anhydrous CP-type, and determined the P speciation by P-XANES spectroscopy of the P hot-spots. These IDPs were analyzed while still in the silicone oil in which they were collected to minimize interaction with the atmosphere.

3. Results

We obtained P-XANES spectra of 17 P 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 general consistency in the peak position of these 17 spectra, e.g. in L2009 R1 (Figure 1). Comparison with apatite and schriebersite, demonstrates that oxidized P is the dominant form of P is these IDPs.

However, not all spots in these cluster IDPs exhibit the same P-XANES spectrum. Most spectra show no shoulder on the high energy side of the major absorption peak, However, Spot 6 in L2009 R1 (Figure 1) and a few other spots exhibit a distinct broadening. Ingall et al. [4] performed P K-edge XANES spectroscopy of 12 apatite-group minerals and found that each exhibited "a distinct shoulder or widening on the main absorption peak" consistent with the broadening seen in Spot 6 of L2009 R1 and a few other P hot-spots. The absence of a shoulder in spots with sufficient signal to noise to detect it (e.g., Spot 1 in L2009 R1) indicates there are at least two different P-bearing minerals in these cluster IDPs, one exhibiting a shoulder consistent with apatite and a second, more common, phase without a shoulder.

4. Summary and Conclusions

The majority of the mass of P in these IDPs is in the larger hot-spots, so our P-XANES results show the P in large, cluster IDPs is found predominately in oxidized form (e.g., phosphate) rather than reduced forms (phosphides). The absence of schreibersite indicates either P did not condense from the disk as schreibersite or that schreibersite was subsequently altered to oxidized P in these primitive dust samples. Alternatively, P condensation may have occurred under different conditions than assumed in most of the equilibrium nebular condensation models. For example, equilibrium condensation from cosmic gas made by total vaporization of highly dust-enriched systems produces whitlockite at 1350 K from a gas of 10^{-3} bar with an enrichment of 1000x the dust of CI composition relative to a system of Solar composition [5]. This model also predicts formation of pyrrhotite, the common Fe-sulfide in CP IDPs, at 1380 K. A P-XANES spectrum of whitlockite reported by Kar et al. [6] has a shoulder on the high energy side of the absorption peak, but one reported in Ingall et al. [4] does not have a pronounced shoulder. Measurements are in progress to compare the shape and peak energy of our IDP spectra with a whitlockite standard under our analysis conditions. The presence of oxidized P in primitive IDPs may indicate that P minerals in primitive CP IDPs formed under atypical conditions compared to those assumed for equilibrium condensation under Solar conditions.

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Figure 1: P-XANES spectra of 6 spots on L2009 R1 show consistency in peak position. The shoulder on the high energy side in Spot 6 is consistent with apatite. Noise level reflects the P mass in each spot.