

Element Mapping in Interplanetary Dust Particles: A Test for Contamination and an Effort to Determine Conditions in the Solar Nebula

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Introduction

As the solar nebula cooled and collapsed, the first material to condense from the gas formed small dust grains. These original dust grains were incorporated into larger bodies, including asteroids, comets, moons, and planets. A characterization of the most primitive dust grains from our solar system would provide constraints on the chemical composition, temperature, pressure, and oxygen fugacity of the solar nebula at the time our solar system began to form, about 4.6 billion years ago.

Planetary differentiation and subsequent rock formation events on the Earth were so severe that no useful record of early solar system processes is preserved in the terrestrial rocks. The most primitive of the meteorites, which are generally accepted to be fragments of the asteroids orbiting in the belt between Mars and Jupiter, offer a better hope of preserving early solar system material. The CI carbonaceous chondrite meteorites have a chemical composition very similar to that of the Sun's photosphere (except for the elements H and He and the noble gases, which were gases in the region where the CI meteorites condensed) [1]. Thus the CI meteorites are believed to have preserved the chemical composition of the primitive solar nebula. However, the CI carbonaceous chondrites have not preserved the mineralogy of the original solar system condensates, and it is the mineralogy of the primitive dust that is critical for determining the properties of the solar nebula. The CI meteorites have been highly altered by aqueous processing on their parent body. This processing turned their original silicate minerals into clay and produced other secondary minerals as well. Some meteorites (e.g., the anhydrous carbonaceous chondrites like Allende) have not experienced significant aqueous processing. But all known anhydrous meteorites are depleted in the moderately volatile elements (including Mn, Zn, Cu, Ga, Ge, and Se), as compared with the CI meteorites. This depletion is attributed to the formation of the anhydrous meteorites at a high temperature or, to explain the observed depletion of Mn, to their subsequent thermal processing at a high temperature [2] (above ~1200°C).

Interplanetary dust particles (or IDPs), which are

believed to be fragments from comets and asteroids, have been collected from the Earth's stratosphere by NASA since the mid-1970s. The IDPs range from about 5 to about 50 μm in size. One subgroup, called the porous, chondritic IDPs, have never experienced significant aqueous or thermal processing. These anhydrous IDPs are the samples that may allow us to look back in time and examine dust that appears not to have been significantly altered since the formation of our solar system. The characterization of the minerals in these primitive, anhydrous IDPs will allow a direct test of the mineral condensation sequences that have been proposed on the basis of models of the cooling of the gas in the solar nebula. But these porous, chondritic IDPs come to us as individual, 10- μm particles, and those particles are generally aggregates of many thousands of distinct individual micron- or submicron-sized grains, so they must be analyzed at the submicron scale.

This project has three major objectives. The first one is to determine the host phase(s) of the elements in the primitive, anhydrous IDPs in order to track the incorporation of these elements into the solid phase during nebula condensation. The second is to determine the host phase(s) of the elements in the hydrated IDPs in order to understand the redistribution of these elements during aqueous alteration, which may provide clues about the composition, temperature, and pH of the fluid on the asteroids. The third is to determine the abundances of the minor elements, particularly the biologically important elements such as P and S, in the organic matter previously identified in the IDPs by using the scanning transmission x-ray microscope (STXM) at the National Synchrotron Light Source (NSLS).

In addition, we will use these element maps to assess the degree of contamination of the IDPs during stratospheric residence. We have used the x-ray microprobe (XRM) on beamline X26A of the NSLS, as well as transmission electron microscopy (TEM), energy-dispersive x-ray (EDX), and electron microprobe measurements for the lighter elements, to determine that the average bulk chemical composition of the IDPs is enriched relative to the CI meteorite composition by a factor of 2 to 4 for the moderately

volatile elements Na, K, P, Mn, Cu, Zn, Ga, Ge, and Se, and it is enriched ~30 times CI for Br [3]. However, Arndt et al. [4], who have reported similar bulk enrichments by using proton-induced x-ray emission (PIXE), attribute the enrichments to contamination by stratospheric aerosols during the weeks to months when these IDPs reside in the Earth's atmosphere before they are collected. Rost et al. [5] provide support for the contamination hypothesis by reporting on enrichments of some of these elements on the edges of the IDPs by using time-of-flight secondary-ion mass spectrometry (TOF-SIMS), but TOF-SIMS is notorious for producing false edge-effects, particularly on irregularly shaped samples like the IDPs. Thus, one major objective of this work is to map the spatial distributions of the moderately-volatile elements by x-ray fluorescence (XRF), which does not suffer from edge effects.

Methods and Materials

Untramicrotome thin-sections, ~70 to 120-nm thick, were prepared from three IDPs, two of which were anhydrous (named L2009F3 and L2011*B2) and one that was hydrated (L2008U13). L2011*B2 is a fragment of a "cluster IDP," a large particle so weak that it broke into tens or hundreds of fragments upon collection. This fragment is coated with a layer of organic matter, previously analyzed by C and O x-ray absorption near-edge structure (XANES) spectroscopy using the STXM at the NSLS.

We mapped the spatial distribution of most of the elements from Mg to Zn, with <200-nm spatial resolution, in one section of each of these three IDPs by using the XRM on beamline 2-ID-D of the Advanced

Photon Source (APS). Element maps were obtained by plotting the signal intensity at each pixel for each element's region of interest in the XRF spectrum, as shown in Fig. 1 for L2008U13. A bulk chemical analysis of each section was obtained by integrating over the spectra of all pixels on the particle. In addition, we obtained spectra of the hot-spots for each element by integrating the spectra over the pixels corresponding to the element hot-spot. Each section will be analyzed by analytical TEM (ATEM) to determine the major element mineralogy, morphology, and mineralogy by electron diffraction of each of the trace element hosts identified by using XRM.

Results

The anhydrous IDP L2009F3 showed grains enriched in Fe, Ni, and S. The Fe/Ni count rate at each of these spots is ~8, suggesting they are high-Ni Fe-sulfides. No S-rich spots having a lower Ni content were found in L2009F3.

All of the Ni-rich spots in the hydrated IDP L2008U13 are also rich in Fe and S, suggesting they are high-Ni Fe-sulfides. These grains have a Ni/Fe count ratio of ~25. However, L2008U13 also contains several Fe- and S-rich spots that have a much lower Ni/Fe ratio (~2.5). Thus, the two groups of Fe-sulfides in the hydrated IDP are quite different in composition from those in the anhydrous IDP. The study of additional IDPs of both types may allow us to compare the compositions of primary Fe-sulfide with that produced during aqueous alteration, although no trend is obvious in these initial results.

A single high-K spot in L2008U13 is also enriched

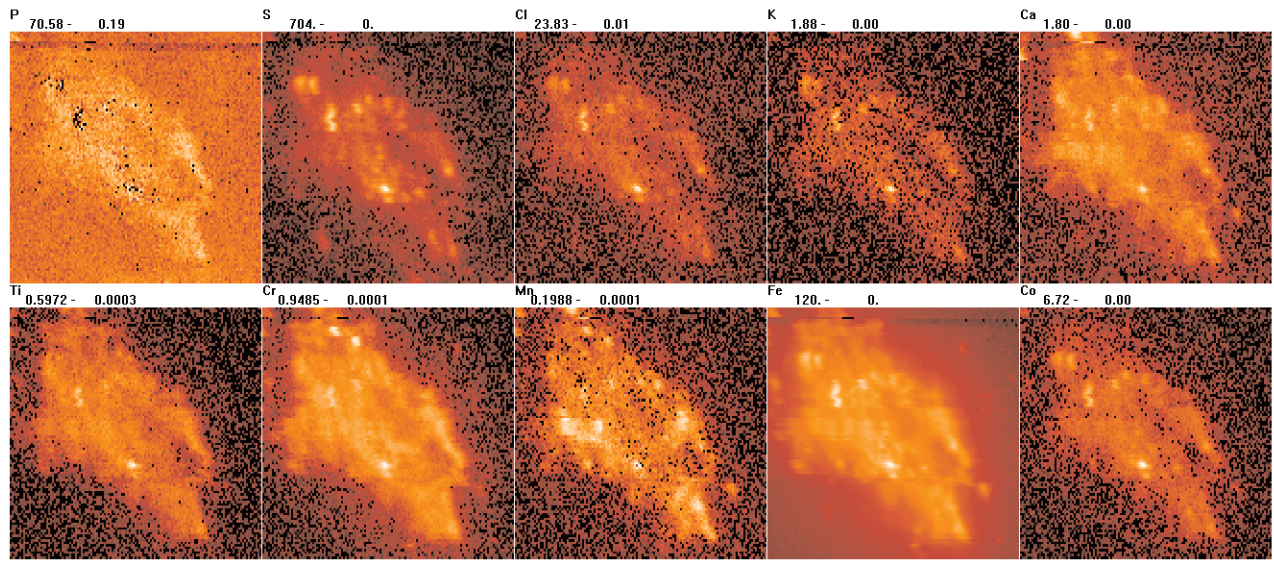


FIG. 1. Element distribution maps in L2008U13 prepared by plotting the intensity of x-rays in an energy window corresponding to the energy range of the fluorescence x-rays from the K-alpha emission of each element. These maps show no evidence of element concentrations along the edge of the particle, suggesting that contamination by stratospheric aerosols does not contribute significantly to any of the elements mapped.

in S relative to the particle average. One high-Mn spot was also detected in L2008U13. This spot is also enriched in Mg, but it is much lower in S and Ni than the particle average, possibly being a carbonate.

Although we can speculate on the mineral hosts of several of the trace elements we detected, the second stage of this project, ATEM analysis of the same ultramicrotome sections mapped by synchrotron XRF, will provide compelling mineral identifications by quantitative major element analysis and electron diffraction analysis of each of these host grains.

L2011*B2 was selected for these analyses because it includes an organic-rich spot that was pushed away from the particle during microtome preparation. S is clearly enriched in this region, but P is below the detection limit in this region and in the particle as a whole. Of the important biogenic elements, P is the least abundant in the solar nebula and may be the most critical with regard to the origin of life. Thus it is important to map the IDPs with sufficient dwell time to identify the P host and to determine how readily available P is in these particles for participation in organic reactions. The section of L2011*B2 also has three high-Cr spots, also enriched in Ca and Ti.

Any contamination of the IDPs by stratospheric aerosols would be expected to be concentrated on or near the surface. Mackinnon and Mogk [6] detected a S-rich surface layer on several IDPs by using scanning Auger spectroscopy. They attributed the S-enrichment to the accretion of stratospheric aerosols. In order to enrich the moderately volatile elements by a factor of 2 to 4 over CI, the edge of each IDP would have to contain a comparable amount of each of these elements so that, in the whole interior of the section, an enrichment could easily be seen in the element maps.

By using 3-D fluorescence computed microtomography with ~2- μ m spatial resolution at Sector 13 of the APS, Sutton et al. [7] showed that the moderately volatile elements Br and Zn were not located on the surfaces of the four IDPs examined in that study. The new analyses at beamline station 2-ID-D confirm the Zn measurements by Sutton et al. [7] and significantly extend them, since the maps show no evidence for surface enrichments of the moderately volatile elements K, Mn, and Cu. To the contrary, each of the moderately volatile elements detected in these three IDPs is concentrated in one or a few isolated grains in the interior of each IDP. The surface enrichment of S detected by Mogk et al. [6] is not seen, but we did not expect to detect this S layer because it was very thin in Mackinnon and Mogk's analysis [6], and it was below our detection limit when spread over the ~100- to 200-nm analysis spot of these measurements.

Discussion

The results confirm the earlier measurement by Sutton et al. [7] that shows that Zn is not surface-

correlated and extend them to the moderately volatile elements K, S, Mn, and Cu. They indicate that the bulk enrichments in the moderately volatile elements reported in IDPs by Flynn et al. [3] are not contamination (as suggested by Arndt et al. [4]) and are likely to be indigenous.

Each of the elements we mapped is concentrated in only a few hot-spots. The identification of the host minerals by ATEM should provide constraints on the conditions of the solar nebula at the time of grain formation, and on the composition, temperature, pH, etc. of the fluid that produced the aqueous alteration.

The organic material in L2011*B2 also hosts S, but a longer dwell time will be required to determine the content of the important biogenic element P.

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