

TENDER ENERGY X-RAY MICROSPECTROSCOPY REVEALS MICROSCALE HETEROGENEITY OF P AND S CHEMISTRY IN CM2 CHONDRITE. P. A. Northrup¹, S. Wirick² and G. J. Flynn³, ¹Stony Brook University (Stony Brook NY 11794, paul.northrup@stonybrook.edu), ²Focused Beam Enterprises (Westhampton, NY 11977), ³SUNY-Plattsburgh, 101 Broad St. Plattsburgh, NY 12901 flynn@plattsburgh.edu).

Introduction: There remains uncertainty about the chemical evolution of the condensing Solar Nebula, its chemical and physical heterogeneity, when in that process different materials accreted and therefore effectively captured speciation at the time, and how differentiation and processing in early bodies altered that speciation. Phosphorus is particularly enigmatic and not well understood. Tracking P chemistry through this process will improve our understanding of not only P but other details of nebular condensation and accretion. Phosphorus chemistry may provide information about oxygen fugacity, is intertwined with chemistry of S, Fe and Ca, and is also involved with organics. S is ubiquitous in those same processes; its wide range of compounds are critically involved in redox processes and in formation of organics. These questions pertain significantly to the sources and speciation of potentially bioavailable P as an essential nutrient for the initial development and long-term sustenance of life on early Earth, and potentially elsewhere in our Solar System. Bioavailability is highly dependent on speciation.

CM2 chondrites are composed of primitive material that has undergone some aqueous and mild thermal processing, but likely still retains some of its original character. A close examination of the microscale chemistry and texture should reveal details about its original state and the nature of the effects of processing. Comparisons to primitive chondritic porous IDPs (CP IDPs) we have previously measured [1] provide further constraints.

The Tender Energy Microspectroscopy beamline (TES) at the National Synchrotron Light Source is optimized for X-ray fluorescence (XRF) imaging, X-ray absorption spectroscopy (XAS), and speciation imaging applications, in the 2-5 keV energy range [2]. This includes the P and S K-edges at 2.15 and 2.47 keV, respectively. Using TES, we can *directly measure* the microscale chemical speciation of P and S, nondestructively and with minimal sample preparation.

Our current NASA LARS project is developing a submicron instrument to add to the TES beamline, for finer spatial resolution down to ~200 nm. Estimated completion is late 2021, with commissioning to follow.

Methods and Materials: A thin section of Northwest Africa 12748 was prepared under inert atmosphere to minimize chances of oxidation. This was measured under helium atmosphere at the TES

microprobe. XRF imaging at 2.7 and 4.1 keV showed relative distributions of Mg through Ca. An area near the center was selected for finer measurements. Selected pixels were probed by microbeam XANES (X-ray absorption near edge spectroscopy) by scanning incident beam energy across the absorption edge, to determine oxidation state and fingerprint particular chemical species. Speciation imaging was conducted for both P and S; this was accomplished by imaging with incident beam energy set at prominent spectral features distinctive of phosphides, phosphates, sulfides and sulfates.

Results: Speciation imaging (figs. 1, 2) shows the relative distributions of phosphates *vs* phosphides and sulfates *vs* sulfides, in two areas of NWA 12748. Microbeam S XANES of selected pixels found at least 3 different sulfide phases (fig.3) in addition to two sulfates so far. Microbeam P XANES found at least 2 different phosphate species (fig. 4), as well as two different phosphides (one is schreibersite) and some locations with mixed phosphide/phosphate (fig. 5). Identification of all of these species is under way.

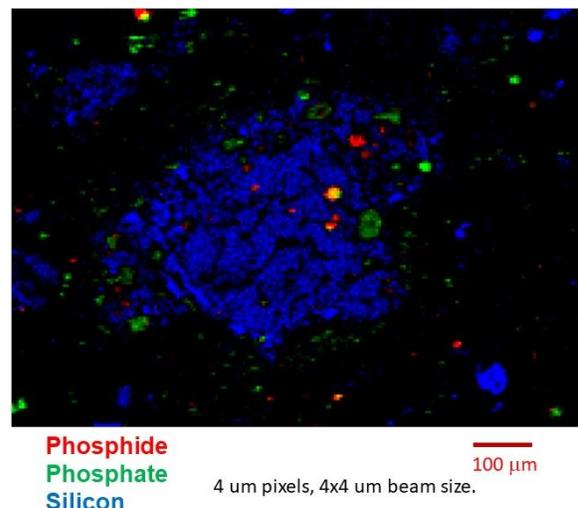


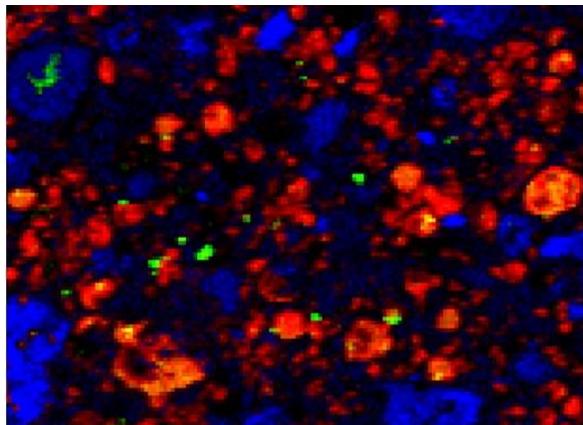
Figure 1. Map of phosphide (red), phosphate (green), with total Si (blue). Phosphide grains are small, mostly less than 10 μm , within matrix and associated with silicates. Phosphates are more abundant, as discrete grains as well as more dilute areas. Very fine grained P in the matrix is mostly phosphate. There are also some mixed phosphide/phosphate grains (appearing yellow).

Conclusions: The CM2 meteorite examined exhibits significant chemical and structural heterogeneity. This leads us to two main conclusions: 1) the initial material accreted to form the parent body was itself highly heterogeneous, and 2) the subsequent processing was incomplete, or acted heterogeneously itself, such that not all components reacted to the same extent.

This initial characterization is part of a larger study exploring details of the textural associations and reaction pathways in chondritic materials. We are using the combination of P and S speciation to explore local redox processes, and employing EXAFS (extended X-ray absorption fine structure) to identify local structure of these elements. We also seek to identify organic P and S components. This work has implications for interpretation and eventual measurement of return mission samples. The fine-scale heterogeneity also demands a higher spatial resolution probe, which will soon be available at TES.

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References: [1] Flynn, G. J. et al. (2020) *LPS LI*, Abstract #1226. [2] Northrup, P. A. (2019) *J. Synch. Rad.*, 26, 2064-2074.



Sulfide
Sulfate
Silicon

100 μm

Figure 2. Map of sulfide (red), sulfate (green), with total Si (blue). This shows numerous sulfide grains, apparent sulfide coatings of other grains, and a lot of fine-grained sulfides in the matrix, while there are fewer but discrete sulfate grains, including within the core of a chondrule. Beam size and pixel size were both 4 μm .

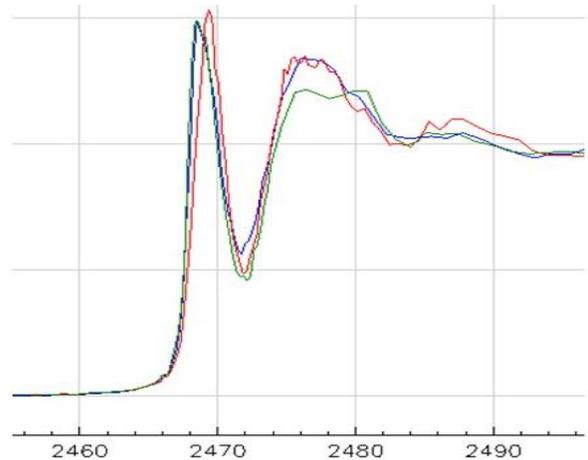


Figure 3. Microbeam S XANES (normalized absorbance vs incident energy in eV) of 3 different sulfide species found in the sample so far. One has been identified as troilite (blue spectrum). Beam size 10 μm .

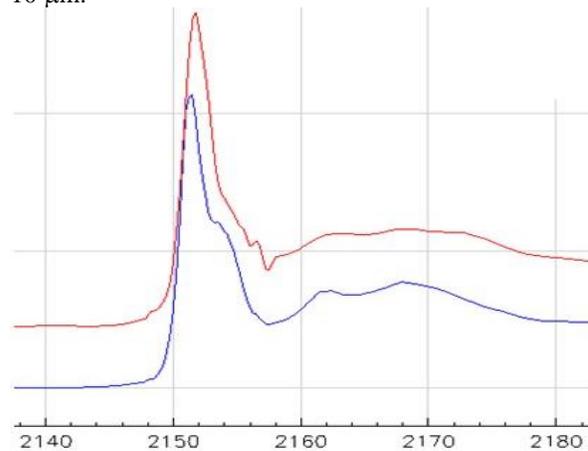


Figure 4. P XANES of two different phosphate species. The blue spectrum is fluorapatite, from a distinct 5 μm grain. The red one is as yet unidentified, but was intimately associated with a sulfide. Beam size 4 μm .

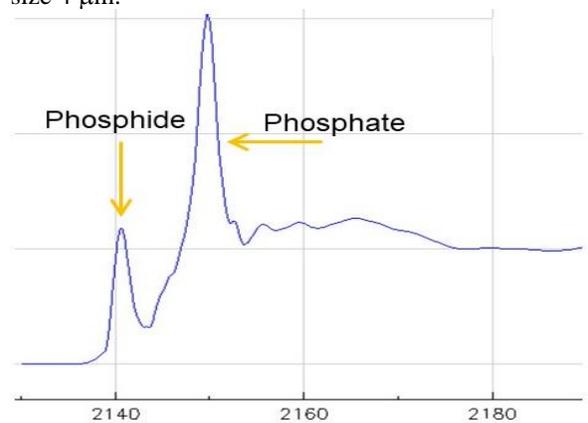


Figure 5. P XANES of a mixed phosphide and phosphate grain. Beam size 5 μm .