

SULFUR SPECIATION IN GRAVES NUNATAKS GRA 95229 AND MURCHISON: SIMILARITIES AND DIFFERENCES.

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Introduction: The broad objective of this work is to constrain the environments in which organosulfur compounds form and provide insight into how such compounds may have been altered from their primordial state. Recent work on the extracted insoluble organic matter in Murchison show that it exhibits a very diverse suite of sulfur compounds including elemental sulfur and sulfur-containing exocyclic compounds such as alkyl and aryl disulfides, heterocyclic compounds, as well as aromatic rings of alkylated thiophenes, benzothiophenes, and dibenzothiophenes [1]. A very prominent sulfate peak possibly representing sodium sulfate or magnesium sulfate is also present [1]. We speculated that sulfates in some chondrites not heated above ~200°C could have preaccretionary origins and Murchison maybe one such chondrite. In order to identify sulfates in another primitive chondrite and locate sulfur-bearing domains in situ, we used the X-Ray Absorption Near Edge Spectroscopy (XANES) and X-ray Fluorescence (XRF) techniques available at the Stanford Synchrotron Radiation Lightsource (SSRL). In this abstract, we present the data for Murchison and our initial results for the chondrite Graves Nunataks GRA 95229.

Samples & Analytical Methods: We acquired XRF and sulfur XANES data on CR2 GRA 95229 and CR2 Murchison. Both carbonaceous chondrites show signatures of moderate amount of aqueous processing [e.g., 2, 3] and are rich in amino acids [e.g., 4, 5]. Five areas in Murchison and four areas in GRA 95229, each $\leq 1 \times 1 \text{ mm}^2$ in size were studied. The areas probed were predominantly interchondrule matrix regions and fine-grained rims around calcium-aluminum inclusions and chondrules. Some domains within the high temperature, refractory phases were also probed by μ -XANES.

Several multiple energy "maps" across the sulfur absorption edge at 2471.1 eV, 2472.6 eV, 2473.5 eV, 2476.4 eV, 2480.1 eV, 2482.3 eV, 2482.8 eV, 2500.0 eV were collected. Each energy was chosen to exploit a specific sulfur oxidation state or species. Each sulfur species will have a specific response at each energy mapped, which can be traced back to the sulfur XANES. Putting the normalized fluorescence response into a matrix of energy gives a (nearly) pixel by pixel map, which is sufficient for distinction of sulfur species. To validate the maps, μ -XANES spectra collected on specific points (ca. 50 in each; $\sim 3 \mu\text{m}^2$ in size) in each map. The methods used also allows detection of other elements, e.g., phosphorus (2014 eV), silicon (1740 eV), aluminum (1487 eV) and magnesium (1254 eV; phases with high concentration), when set up for multiple energy imaging of sulfur. The collected energies for elemental mapping of these elements spanned a range ± 35 eV, centered at the peak energies.

Results: For the first time, cysteine ($\text{C}_3\text{H}_7\text{NO}_2\text{S}$) at 2473.5 eV, a sulfur-bearing amino acid is identified in the fine-grained material in Murchison. Cysteine is more abundant in the matrix regions, away from the refractory phases, and are always present with mackinawite (2469.5 eV) or troilite (2470.9 eV) and sulfate (2482.5 eV). In one specific matrix area, the cysteine co-exist with gypsum (~ 2486 eV). Murchison shows the presence of a separate peak at 2482.5 eV due to other sulfate minerals (magnesium sulfate, aluminum-bearing sulfate, iron-sulfate?), which are more abundant than gypsum. The Fe, Ni sulfides form a boundary layer around CAIs with smaller domains of pure FeS present. The XRF maps clearly show co-localization of multiple phases in some of the regions.

The CR chondrite GRA 95229 show some interesting differences in sulfur speciation, but no clear organic sulfur signature in the one matrix-rich area for which the data has been processed. This region contains mono- and disulfides, elemental sulfur, and sulfate. Elemental sulfur is always co-located with sulfate and generally exist in areas with relatively lower silicon contents. A large $120 \times 150 \mu\text{m}^2$ phosphorus-rich region was identified in the matrix, which contains some troilite but exhibits a weak sulfate peak. Smaller regions ($40\text{-}60 \mu\text{m}^2$) rich in phosphorus are abundant in this region of the matrix. Phosphorous has been noted in iron rich meteorites and considered important biochemical precursor phases [e.g., 6].

Remaining processed data from GRA 95229, differences and similarities in the sulfur speciation observed in CM and CR chondrites, and the implications of these observations will be presented at the meeting.

References: [1] Bose M. et al. (2017) *Meteoritics & Planetary Science* 52:546–559. [2] Brearley A. J. 2006. The action of water. In: *Meteorites and the Early Solar System II*. (Eds.) Lauretta D, McSween H. Y. Jr. and Leshin L. Arizona University Press, Tucson, pp. 587–624. [3] Busemann H. et al. (2007) *Meteoritics & Planetary Science* 42:1387–1416. [4] Cronin J. R. and Pizzarello S. (1983) *Advances in Space Research* 3:5–18. [5] Martins X. et al. (2007) *Meteoritics & Planetary Science* 42:2125–2136. [6] Pasek M. A. (2008) *Proceedings of the national Academy of the United States of America* 105:853–858.

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