IDENTIFICATION OF ORGANIC AND ELEMENTAL SULFUR IN THE FINE-GRAINED MATRIX OF GRAVES NUNATAKS GRA 95229. M. Bose[1*] and R. Root[2], [1]Center for Isotope Analysis, School of Earth and Space Exploration, Arizona State University, Tempe, AZ 85281-6004. [2]Department of Soil, Water & Environmental Science, University of Arizona. Tucson, AZ 85721-0038. (*Maitrayee.Bose@asu.edu)

Introduction: The sulfur speciation and isotopic signatures of organosulfur compounds (i.e., containing H, C, N, O and S) carry information about their formation mechanism, and can provide insight into how such materials may have been altered to their present state. We aim to look for sulfur isotopic anomalies in organosulfur compounds to look for mass independent isotopic signatures, which can be produced by photochemical reactions in the early solar nebula [e.g., 1]. In order to locate organosulfur materials for detailed isotopic characterization, they need to be identified first in the meteorite thin sections. We used the X-ray absorption near edge spectroscopy (XANES) and multiple energy micro X-ray Fluorescence (ME μ-XRF), techniques available at the Stanford Synchrotron Radiation Lightsource (SSRL), to study thin sections of CR2 carbonaceous chondrite GRA 95229 and CM2 chondrite Murchison.

Recent work on the extracted insoluble organic matter in Murchison shows 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 [2]. A very prominent sulfate peak possibly representing sodium sulfate or magnesium sulfate is also present [2]. We will also discuss key differences and similarities between the two meteorite samples that belong to different classes.

Significant sulfur isotope heterogeneity has been observed in Murchison by [3]. With our approach, the heterogeneity within meteorite sections can be sampled at the micron-scale. It is plausible that the sulfur-bearing organic materials are fragile and so may not withstand the harsh separation processes, and our *in situ* approach would enable their discovery.

Samples & Analytical Methods: Both carbonaceous chondrites CR2 GRA 95229 and CM2 Murchison show signatures of moderate amount of aqueous processing [e.g., 4, 5] and are rich in amino acids [e.g., 6, 7]. Five areas in Murchison and four areas in GRA 95229 thin sections, each ≤1×1mm^2 in size were studied using XRF. The areas probed were interchondrule matrix and fine-grained rims around calcium aluminum inclusions and chondrules.

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; ~3 μm^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).

Results: We observe co-localization of multiple phases in both meteorites. GRA 95229 exhibits peaks of mono- and di-sulfides, sulfate, and a broad peak around 2472.5 eV corresponding to elemental sulfur and thiol (Figure 1). This peak at 2472.5 eV (called ES&T henceforth) has been previously reported in Murchison [2] but is much more prominent & abundant (~90 % of the spectra show it) in GRA 95229. ES&T always co-exists with sulfate within the 3 μm^2 region in the low resolution maps, and generally exist in areas with relatively lower silicon contents. We also identified a large ~120×260 μm^2 silicate grain rich in aluminum in the matrix of GRA 95229, which contains some troilite and sulfate peak. Smaller domains (<15 μm in size) rich in phosphorus and calcium are distributed throughout this large grain.

The abundance of troilite is higher in Murchison

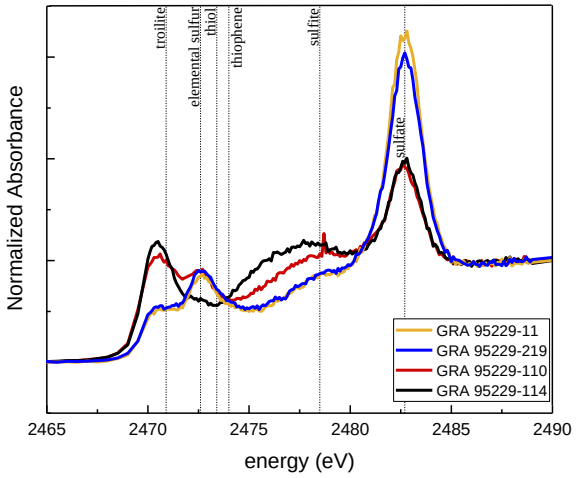

Figure 1: Typical μ-XANES spectra in GRA 95229 showing the numerous peaks with different sulfur speciation. Each datapoint often shows multiple peaks.

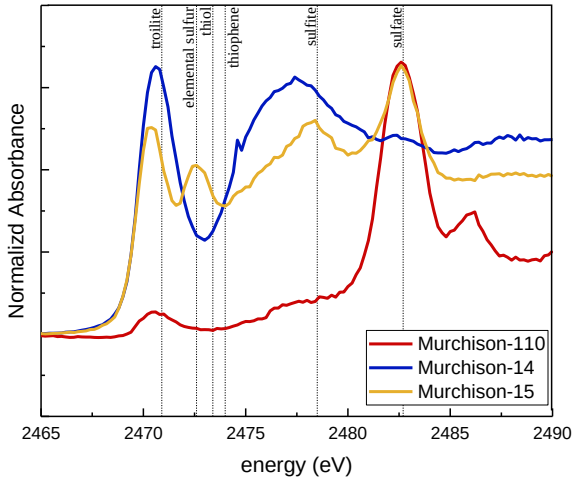

Figure 2: Typical µ-XANES spectra in Murchison spots showing different sulfur speciation.

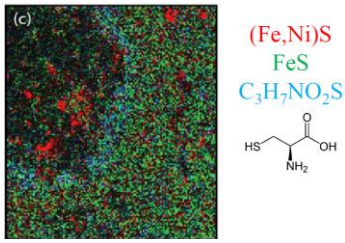

Figure 3: Low resolution RGB map on Murchison showing a portion of an igneous inclusion and the fine-grained rim and matrix. The distribution of thiol, specifically cysteine $C_3H_7NO_2S$ is shown in blue.

than in GRA 95229 (Figure 2). In Murchison, the ES&T peak is always present with mackinawite or troilite and sulfate. 37% of spectra in the Murchison matrix and 20% in the fine-grained rims around igneous inclusions show presence the ES&T peak. In fact, the thiol distribution was clearly observed in a fine-grained rim in Murchison (Figure 3). The Fe, Ni sulfides are primarily within the inclusion while the pure FeS present dominates the fine-grained rim and matrix. Finally, P-bearing assemblages were not identified in the regions probed in Murchison.

Discussion: The interchondrule matrix is the prime location for the presence of elemental sulfur and thiol molecule, possibly cysteine. Qualitatively cysteine appears to be more abundant in GRA 95229 than Murchison because of the presence of a broader peak at the relevant energies. Aqueous alteration of GRA 95229 is limited to its matrix [8]. Therefore, the formation of thiols during the secondary alteration process is a possibility. Thiol is always present with sulfate, and if the sulfate is asteroidal in origin, then by proxy, the thiol molecules could be produced by the same process. However, evidence of such reaction pathways in currently unknown. Cysteine readily produces disulfides under certain conditions, and this might explain the data for Murchison, which shows simultaneous presence of sulfides and ES&T in some regions of the matrix.

Phosphides and calcium sulfates could be possible phases for the large assemblages found in GRA 95229. These assemblages reported in several CV and CO chondrites [e.g., 9] may have formed by reactions in the solar nebula between P-bearing metal and matrix [e.g., 10]. Alternatively, transformation due to secondary alteration events in the parent body could have formed them [11].

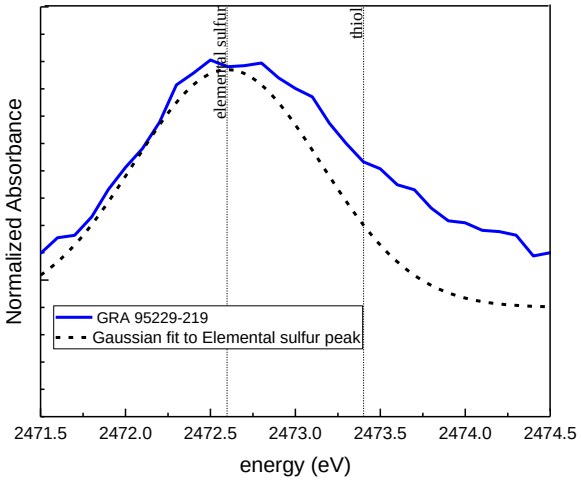

Figure 4: Gaussian fit to the elemental sulfur peak to calculate the residual due to the presence of thiol.

We are attempting to do a better fit to the peak between 2471.5 eV and 2475.5 eV, in order to quantify the abundance of the elemental and thiol peaks accurately (e.g., Figure 4). In addition, high resolution maps of both these meteorites to locate larger domains rich in elemental and organic sulfur are scheduled in Feb. These new results and their implications will be presented at the meeting.

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