MICROSCALE HETEROGENEITY OF SULFUR CHEMISTRY IN CARBONACEOUS CHONDRITES: MICROBEAM XANES. J. Jung[1], P. Northrup[2], T. D. Glotch[2], G. Flynn[3], and L. Flores[2], [1]Department of Physics and Astronomy, Stony Brook University, (Stony Brook NY 11794, jessica.jung@stonybrook.edu), [2]Department of Geosciences, Stony Brook University (Stony Brook NY 11794), [3]SUNY-Plattsburgh, 101 Broad St. Plattsburgh, NY 12901.

Introduction: The early history of the condensing Solar Nebula is still largely unknown in its chemical and physical composition and how that speciation was captured and evolved over time. Tracking sulfur (S) chemistry will improve our understanding of nebular condensation and accretion, as well as small-body alteration and redox processes. Sulfur processes are ubiquitous in the formation of prebiotic organic compounds. S is then an essential nutrient for the formation and sustenance of life on early Earth and possibly elsewhere in the Solar System. The bioavailability of S is strongly dependent on the specific composition of sulfur species.

Carbonaceous chondritesare composed of primitive material that was later modified by aqueous and thermal processing. Their characteristic composition includes phyllosilicates, olivine and pyroxene, with oxides, sulfides, and carbonates making up < 5% of the meteorites volume [1]. The meteorites used for this study include Tagish Lake and Tarda, both of which are C2-ungrouped carbonaceous chondrites, while Murchison, Cold Bokkeveld and Northwest Africa 12748 are CM2 meteorites. The Tarda specimen fell in 2020, Tagish Lake fell in 2000, Murchison, , one of the most studied CM2 meteorites, fell in 1969, Cold Bokkeveld fell in 1838, and NWA 12748 was found in 2019.

The identification of the sulfur species in these meteorite specimens were analyzed using the Tender Energy Micro Spectroscopy beamline (TES) at the National Synchrotron Light Source II, which is specialized for X-ray fluorescence (XRF) imaging, X-ray absorption spectroscopy (XAS), and speciation imaging application in the 2-5 keV energy range and at 2 to 10 µm resolution [2]. The abundance of S, P, Mg, Ca, Al, Si, and other elements of the samples were mapped along with speciation imaging focused on sulfur species.

Methods and Materials: Thin sections of the Tarda, Murchison, NWA 12748, and Tagish Lake were prepared using a water-free and inert atmosphere polishing process to reduce alteration during sample preparation. The XRF imaging highlighted different sulfur species in a whole sample map (fig. 1). An area at the center of Tarda was selected for further measurements while areas boxed in white were selected for further measurements on the Tagish Lake sample. Then select pixels were analyzed by X-ray absorption near edge spectroscopy (XANES) to identify the S oxidation state (sulfide vs. Sulfate) and specific chemical species such as troilite (FeS).

Results: The speciation images at two energy levels (fig. 1) show a varied distribution of sulfide and sulfate throughout each meteorite on both the Tarda and Tagish Lake sections. Specifically, on the Tarda, sulfides mostly populate the edge region while on the Tagish Lake an abundance of sulfates and sulfides can be observed throughout. Microbeam S XANES showed sulfate and sulfide peaks at energies 2483 eV and 2471 eV respectively (fig. 2). These energies were chosen to map sulfide *vs* sulfate during XRF mapping (fig. 1). Heterogeneity of sulfur species are observed.

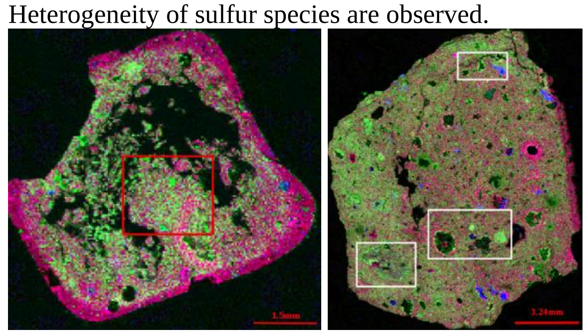

Figure 1. *Map of sulfide (red), sulfate (green), and phosphorus (blue). Left XRF map is of Tarda, while the right is of Tagish Lake. Tarda shows a distinct sulfide boarder with a thickness of around 0.6 mm to 0.7mm while toward the center we see an abundance sulfate with some sulfide. A more finely grained mixture of sulfide and sulfate species can be observed on Tagish Lake with some highlighted sulfide and sulfate spots.*

Even within sulfides, different species are observed within each meteorite and between them. In comparison to troilite (FeS) reference measured in Seymchan, one of the Tagish Lake sulfides shows a close resemblance in terms of the sulfide peak and the remaining features (fig. 3). The Tarda sulfide is a different sulfur species than that of Tagish Lake and Seymchan (fig. 4). Some sulfide spots of Murchison have been identified to be troilite, by matching XANES spectra (fig. 5). These four meteorites collectively show at least four different sulfide species so far. Identification of all these species is under way using XANES fingerprints and, as necessary, extended X-ray absorption spectroscopy (EXAFS), which can provide information about local structure.

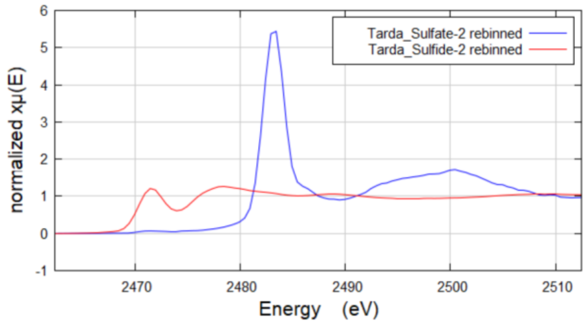

***Figure 2**. Microbeam S XANES (normalized absorbance vs. incident energy in eV) of two sulfur species in Tarda. Both sulfide and sulfate can be observed. Sulfate is identified by the distinct peak at 2483 eV while sulfide is characterized by a peak near 2471 eV. Primary peak positions, spectral shape, and minor features of peaks and troughs are all diagnostic fingerprints of species.*

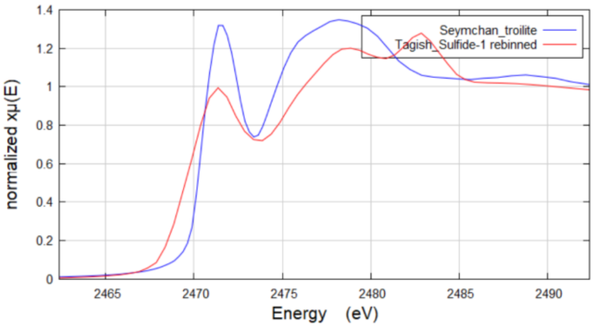

***Figure 3**. Microbeam S XANES of one sulfide species found in Tagish compared with troilite in Seymchan. Tagish sulfide shows an overall resemblance to troilite, but with some sulfate present in that spot as well.*

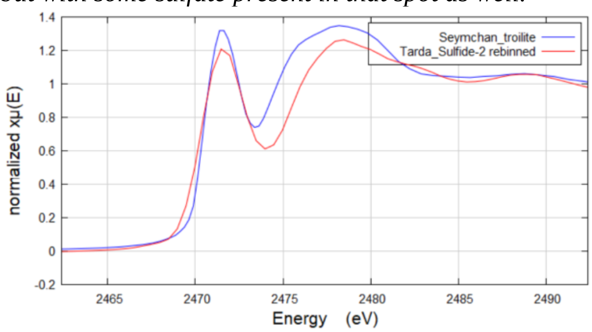

***Figure 4**. Microbeam S XANES of Tarda sulfide species in comparison to Seymchan troilite. The sulfide peaks line up at 2471 eV but vary in their other features, particularly the trough at 2473-2474 eV. The two are different species with Tarda sulfide-2 yet to be identified.*

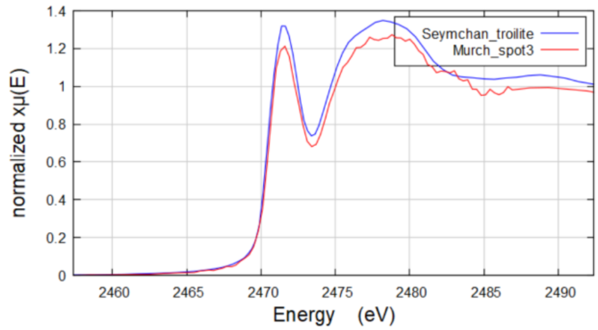

***Figure 5**. Microbeam S XANES of one Murchison sulfide in comparison to Seymchan troilite. The sulfide species in Murchison spot 3 match very closely the Seymchan troilite.*

In addition, we compared sulfur XANES spectra from components of other meteorites. As previously shown in [3], NWA 12748 contains components of troilite and at least two other sulfide species. Further comparisons are under way with NWA 12748 and Cold Bokkeveld.

Conclusions: Observation of various carbonaceous meteorites exhibit heterogeneity in sulfur chemistry, both within one specimen and between different meteorites. The two possible explanations for this heterogeneity are that either 1) the initial material itself was highly heterogeneous in its sulfur species, or 2) subsequent processing was locally heterogeneous, or both. Initial assemblage of material during condensation and accretion reflects differences in materials formed and their accretion processes. After accretion, alteration processes in the parent body may have acted locally or incompletely resulting in the current heterogeneity.

Similar work is underway looking at phosphorus speciation and heterogeneity in these carbonaceous chondrites [3]. We hope the combination of grain-scale P and S chemistry will improve our understanding of how this heterogeneity in carbonaceous chondrites came about.

Acknowledgments: This work was supported by NASA LARS grants 80NSSC21K0612 to T. D. Glotch and 80NSSC19K0940 to P. Northrup, and by the Frances Velay Women and Science Research Fellowship to J. Jung.

References: [1] Fujiya W. et al. (2012) *Nat. Comm.*, *3*, 627. [2] Northrup P. (2019) *J. Synch. Rad.*, 26, 2064-2074. [3] Northrup P. et al. (2021) *LPSC 52*.