

The Search for Organosulfur Compounds in the Tagish Lake Carbonaceous Chondrite.

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Introduction: Although the C2 ungrouped carbonaceous chondrite Tagish Lake (TL) has been extensively studied, a thorough analysis of the sulfur species it contains has not yet been completed. As part of a study aimed at determining the nature and abundances of the sulfur species present in TL, we have initiated a study of organosulfur compounds. The goal of this study is to place organosulfur compounds in the context of the Fe-Ni sulfide mineralogy of TL [1].

Initial soluble organosulfur extraction: We carried out chemical extractions for organosulfur species from powdered samples that had been previously leached using hot water and dichloromethane (DCM). These extractions employed a 1:1 solution of methanol and toluene, mixed with powders of TL11h and TL5b inside sealed vials. Subsequent GC-MS analysis of the concentrated samples did not reveal the presence of any organosulfur species, nor have either the previous hot water [2] or DCM [3] extractions. However, [4] identified ~20 ppm of methane sulfonic acid (MSA) within their examined sample of Tagish Lake (TL8a).

Petrography: To determine whether the presence of MSA in sample TL8a could be due to differences in sample lithology, a polished epoxy mount of several small fusion-crusted fragments of TL8a was made. The Fe-Ni sulfide minerals within this mount were examined by SEM and analyzed by EPMA to determine the degree of aqueous alteration relative to other samples; this was done using the Fe/S (at%) ratio of pyrrhotite-group Fe-Ni sulfides, following [5]. The results place the sample within the range of degree of alteration of previously described samples of TL [1], with an Fe/S ratio of 0.851 – similar to specimen 11h (Fe/S = 0.850) and specimen 5b (Fe/S = 0.867). This suggests that the degree of alteration in TL8a is not entirely dissimilar to those of previously examined samples, and likely not the main or sole reason for the difference in their reported organic contents. That TL8a has a similar degree of alteration to these other samples is also supported by the visual examination of its petrography by SEM, as the chondrules observed have similar morphologies to the moderately altered TL specimens 5b, 10a, and 11h.

Implications: The discrepancy between TL8a organic content and those of other TL samples could be explained in several ways: 1) Heterogeneity of organic content between different specimens of TL, including due to storage conditions; 2) Oxidation of any organosulfur compounds present during or prior to leaching with hot water; 3) Inability of the methods used to capture and analyse any organosulfur species present (e.g., below detection). A new phase of experiments was designed to reveal whether the apparent absence of organosulfur species within our examined samples is due to a failure of experimental methods or whether the sulfonic acid content of the samples is indeed below the detection limits of the instrument.

Experimental Design and future work: Several phases of experiments have been designed to determine the effectiveness of previously utilized methods at capturing organosulfur species, and to establish a more effective methodology. Because sulfonic acids are water-soluble, previous hot-water extractions [2] should have removed them from the powdered TL samples. However, due to the relatively high polarity of MSA and similar compounds it is possible that these species were not detected by the GC-MS, requiring the use of a derivatizing agent. To test the effectiveness of our chosen derivatizing agent, MTBSTFA, a three-fold excess of the MTBSTFA was added to lab-grade samples of each of three sulfur species - MSA, sulfuric acid, and NaHSO₄ - in dried, deoxygenated acetonitrile in glass ampules. The ampules were then sealed and heated, following which the contents were analyzed by GC-MS. Derivatized species of both MSA and sulfuric acid were recovered. Therefore, MTBSTFA will be used in future experiments to retrieve organosulfur species that contain acidic hydrogens.

It is also possible that the organosulfur compounds were oxidized during hot water leaching, as suggested by sulfate crystals recovered from the residue of a post-hot water extracted TL11h sample. To test this hypothesis, a new round of water extractions under anoxic conditions at ambient temperatures will be carried out. This new methodology, as well as the original methodology of [2] will be tested first on powdered samples of the meteorite Allende which have been artificially doped with MSA. These samples have been prepared under anoxic conditions, with 1.5 mL of 50ppm MSA solution added to 1g of powdered Allende. Two sets of the samples will be stored for several days for a short-term experiment, and approximately one month for a longer-term experiment to test the effects of temperature and anoxic storage on the stability of MSA.

[1] Holt M.C. & Herd C. D. K. (2022) *Meteoritics & Planetary Science* [2] Glavin D. P. et al. (2012) *Meteoritics & Planetary Science* 47(8):1347–1364. [3] Hilt R. W. et al. (2014) *Meteoritics & Planetary Science* 49(4):526-549. [4] Pizzarello S. et al. (2001) *Science* 293(5538): 2236-2239. [5] Schrader D. L. et al. (2021) *Geochimica et Cosmochimica Acta* 303:66-91.