

ORIGIN OF SULFUR IN THE INSOLUBLE ORGANIC MATTER OF ORGUEIL, MIGHEI AND TAGISH LAKE.

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Introduction: Insoluble organic matter (IOM) refers to a macromolecular solid found in carbonaceous chondrites. Oxygen (~10 at.%), nitrogen and sulfur (~2%) [1] have been detected in a large variety of organic functional groups in meteoritic IOM [2].

The ability of post-accretion processes to form or modify these functional groups is a key issue to determine the source, interstellar/nebular or asteroidal, of heteroatoms in the IOM. Isotopic anomalies in ^{15}N , ^{13}C , and D have been invoked in favor of nebular/interstellar incorporation from organic precursors and ices [3, 4]. In parallel, substantial molecular growth during aqueous alteration has been suggested recently to explain oxygen atoms in the IOM structure [5].

Given that the sulfur speciation differs systematically between C1 and C2 chondrites [6], we propose to use the isotopic composition of organic relative to inorganic sulfur ($\delta_{\text{IOM/Sulfide}}^{\text{S}}$) in HF/HCl residues to investigate the impact of asteroidal aqueous alteration when compared to terrestrial sulfurization [7].

Experimental: Orgueil (C1), Mighei (C2) and Tagish Lake (C2-Ung.) were selected to cover a large span of aqueous alteration. The residues were produced by the technique described in [6], which preserves microscopic sulfides. The residues were crushed into steel for NanoSIMS measurements. For each residue, $^{12}\text{C}^-$, $^{12}\text{C}^1\text{H}^-$, $^{13}\text{C}^-$, $^{32}\text{S}^-$, $^{32}\text{S}^1\text{H}^-$, $^{33}\text{S}^-$ and $^{34}\text{S}^-$ secondary ion images of $20 \times 20 \mu\text{m}^2$ were acquired with a Cs^+ primary beam. Graphite and terrestrial kerogen (H/C=0.8) were used for $\delta^{13}\text{C}$ calibration. FeS, organic disulfide ($\text{C}_8\text{H}_{14}\text{O}_2\text{S}_2$), and a sulfonate ($\text{C}_6\text{H}_{13}\text{NSO}_4^-$) were used for $\delta^{34}\text{S}$ matrix effect estimation.

Results: CH/C and SH/H ratios are used to distinguish inorganic sulfide from the IOM among residues patches. By averaging isotopic ratios for organic-rich regions, we determined their $\delta^{13}\text{C}$ relative to our graphite standard: $\delta^{13}\text{C}_{\text{kero}} = -44 \pm 5\%$, $\delta^{13}\text{C}_{\text{Mighei}} = -25 \pm 6\%$ and $\delta^{13}\text{C}_{\text{TagishLake}} = -17 \pm 13\%$. All are in qualitative agreement with independent pyrolysis measurements [1]. Sulfur in the IOM seems to be systematically depleted in ^{34}S relative to the residual sulfides: $\delta^{34}\text{S}_{\text{IOM/Sulfide}}(\text{Orgueil}) = -20 \pm 4\%$, $\delta^{34}\text{S}_{\text{IOM/Sulfide}}(\text{Mighei}) = -67 \pm 19\%$ and $\delta^{34}\text{S}_{\text{IOM/Sulfide}}(\text{Tagish Lake}) = -75 \pm 36\%$. Such depletions are not expected to be produced by aqueous alteration [8] and are undoubtedly the result of matrix effects during the analysis. However, the significantly heavier sulfur in the C1 IOM than in the C2s may be due to a stronger alteration in Orgueil or a lower initial $^{34}\text{S}/^{32}\text{S}$ in the C2 sulfides [9]. Preliminary investigations indicate that instrumental fractionation between organics and sulfides can range up to 40%. Independent pyrolysis of our reference compounds are expected to provide corrections.

References: [1] Alexander, C.M.O'D. et al. 2007. *GCA* 71(17): p. 4380-4403. [2] Derenne, S. and Robert F. 2010. *M&PS* 45(9): p. 1461-1475. [3] Busemann, H. et al. 2006. *Science*. 312(5774): p. 727-730. [4] Okumura, F. and Mimura K. 2010. *GCA* 75(22): p. 7063-7080. [5] Cody, G.D. et al. 2011. *PNAS* 108(48): p. 19171-19176. [6] Orthous-Daunay, F.R. et al. 2010. *EPSL* 300(3-4): p. 321-328. [7] Werne, J.P. et al. 2008. *GCA* 72(14): p. 3489-3502. [8] Amrani, A. and Aizenshtat Z. 2004. *Org. Geochem.* 35(11-12): p. 1319-1336. [9] Bullock, E.S. et al. 2010. *M&PS* 45(5): p. 885-898.