

**SULFUR ISOTOPIC COMPOSITION OF HF/HCL RESIDUES FROM TYPE 1 AND 2 CARBONACEOUS CHONDRITES.** F. R. Orthous-Daunay and F. Gyngard. Laboratory for Space Sciences and Department of Physics, Washington University, St. Louis, MO 63130, USA. fdaunay@wustl.edu.

**Introduction:** Insoluble organic matter (IOM) consists of a carbon network made of aromatic cycles and aliphatic chains and includes oxygen (~10 at.%), nitrogen and sulfur (~2%) in the form of a large variety of organic functional groups [1]. The natural variability of the molecular compounds is expected to be a record of early processes occurring when the Solar System formed.

Molecular and isotopic studies, supported by astronomical observations, tend to conclude that this material cannot be formed by a single process. The identification of signatures of post-accretion processes and the mechanisms that modified the organic macromolecules is a key issue to build a plausible scenario of evolution through the interstellar, nebular and planetary history of this material. Isotopic anomalies in  $^{15}\text{N}$ ,  $^{13}\text{C}$ , and D have been recently invoked in favor of nebular/interstellar incorporation from several organic precursors [2]. Concurrently, strong alteration of these anomalies has been reported to be due to planetary hydrothermal processes [3]. From the molecular point of view, the mixture of  $\text{sp}^2$ ,  $\text{sp}^3$  carbon and heteroatoms finds no simple interstellar counterparts [4], to the point that some authors have proposed all IOM to be of planetary origin [5].

Sulfur is a minor element in the IOM which has the advantage of forming a large variety of bonds with C and having four stable isotopes. In the IOM, sulfur speciation has been previously investigated by X-ray Absorption Near Edge Structure spectrometry revealing that organics in Type-1 chondrites exhibit an excess of sulfonic acid groups compared those in Type-2 [6]. Independently, the sulfonic acids in the soluble fraction of Murchison (CM2) revealed a positive isotopic anomaly, interpreted as a photochemical effect [7]. We propose to determine the isotopic composition of organic relative to inorganic sulfur ( $\delta^{34}_{\text{IOM/Sulfide}}$ ) in several HF/HCl residues in order to investigate for differences between Type-1 and Type-2 chondrites as well as signatures of aqueous alteration.

**Experimental:** Orgueil (CI1), Mighei (CM2), Cold Bokkeveld (CM2), QUE97990 (CM2), Renazzo (CR2) and Tagish Lake (C2) were selected to cover a large range of aqueous alteration. The residues were produced by the technique described in [6]. This procedure has been proven to leave the organic matter with few recalcitrant minerals including micro-sulfides.

The certified IAEA-S1  $\text{AgS}_2$  standard ( $\delta^{34}_{\text{CDT}} = -0.3\%$ ) was selected as a mineral reference as well as

two organic compounds to investigate possible matrix effects due to different types of bonds involving sulfur. A lipoic acid sample ( $\delta^{34}_{\text{CDT}} = +16.6\%$ ) was selected as a reference compound to account for the reduced disulfide molecular group (-C-S-S-C-). A MES buffer sample ( $\delta^{34}_{\text{CDT}} = +5.6\%$ ) has been selected as an organic sulfonate salt for its oxidized organic function ( $\text{SO}_3^-$ ).

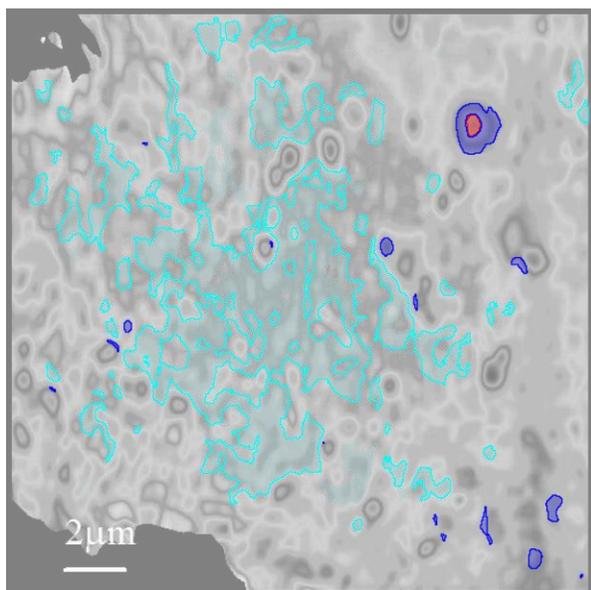
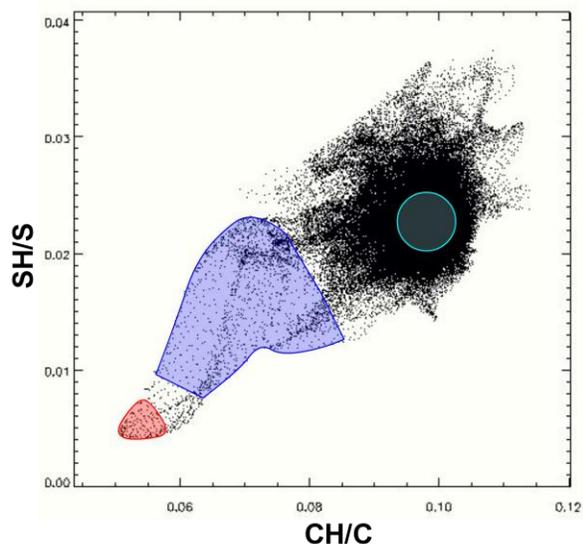
Special attention was paid to ensure planarity of samples and standards. Sample holders were hollowed out to provide smooth edges. Samples and references were deposited by pressing a glass slide on the steel, forming planar bevels on these edges. The sample mount was subsequently coated with 20 nm of gold.

The Washington University NanoSIMS50 was used to acquire secondary ion images of  $20 \times 20 \mu\text{m}^2$ . Primary  $\text{Cs}^+$  beam currents were kept around 1 pA. The detectors were set to simultaneously collect atomic and molecular anions of  $^{12}\text{C}^-$ ,  $^{12}\text{C}^1\text{H}^-$ ,  $^{32}\text{S}^-$ ,  $^{32}\text{S}^1\text{H}^-$  and  $^{34}\text{S}^-$ . The quasi simultaneous arrival (QSA) effect is expected to be non-negligible for sulfur anions and introduces a bias in isotopic measurements [8]. Each sample was measured 2 times with different aperture slits in order to introduce variability of count rates and, where possible, QSA corrections have been derived from the correlation between  $\delta^{34}\text{S}$  and count rates.

**Results:** QSA correction procedures for reference compounds highlighted that the correlation between  $\delta^{34}\text{S}$  values and count rates differ greatly from mineral to organic species. The correction factors we derived for the  $\text{AgS}_2$  standard are in good agreement with the expectation of the model used by [8]. For the organic references, the correction factors are greater and are more sensitive to the QSA effect. After QSA correction, we established  $\delta^{34}_{\text{CDT}}(\text{Lipoic acid}) = +43 \pm 3\%$  and  $\delta^{34}_{\text{CDT}}(\text{MES}) = +3 \pm 3\%$ . A direct comparison to the nominal values gives an anomaly of  $+27 \pm 3\%$  and  $-2 \pm 3\%$  that can be considered the matrix effect bias for the organic disulfide and the sulfonate, respectively. This effect is non-negligible for the reduced organic sulfur. Considering that the organic sulfur in the IOM is mostly in a reduced form and that the matrix effect is positive for the single reference we have, our isotopic values of  $\delta^{34}\text{S}$  for organics must be taken as upper limits.

Due to significant matrix bias and different QSA corrections, organic and sulfide areas within each image have been separated into regions of interest. CH/C and SH/S ratios measured for each pixel in an image

are used to distinguish inorganic sulfide from the IOM among different residue spots. By the use of scatter plots produced by Larry Nittler's "L'image" software (Fig. 1), we can isolate endmembers on the basis of hydride formation yields, assuming that hydride rich areas are associated with organics.



**Fig.1:** Top: sulfur and carbon hydride yields for each pixel of a 20×20 μm<sup>2</sup> image drawing mixing lines between chemical endmembers. Bottom: regions identified as mineral sulfide (red) and organics high (light blue). Intermediate (blue) hydride yields are likely mixed and rejected for this study.

For each image, sulfide and organic endmembers were found and their  $\delta^{34}\text{S}_{\text{CDT}}$  values were calculated. External reproducibility and instrumental drift introduced uncertainties of up to several tens of permil, preventing comparison with absolute values of inorganic

sulfides previously reported [9]. However, the relative isotopic enrichment of the organics with respect to the adjacent sulfides ( $\delta^{34}_{\text{IOM/Sulfide}}$ ) can be determined with better precision as shown in the following table:

Sample	( $\delta^{34}_{\text{IOM/Sulfide}}$ )
Orgueil (CI1)	+13±6‰
Mighei (CM2)	+7±2‰
QUE97990 (CM2)	-2±4‰
Renazzo (CR2)	-3±3‰
Tagish Lake (C2)	-8±8‰
Cold Bokkeveld (CM2)	-17±3‰

The  $\delta^{34}_{\text{IOM/Sulfide}}$  data show no obvious correlation or grouping consistent with aqueous alteration, with Orgueil (CI) having the most enriched organics while Cold Bokkeveld (CM) has larger depletions than both Renazzo (CR) and Tagish Lake. The variability reported here is greater than the variability reported in [9] concerning mineral sulfides which were possibly aqueous altered. According to [10], aqueous alteration can be responsible for an enrichment as high as 5‰ in some cases. If matrix effects are actually responsible for an overestimation of the reduced organic sulfur  $\delta^{34}_{\text{IOM/Sulfide}}$  by more than 20‰, none of the IOM shows evidence of an aqueous alteration isotopic enrichment of their organic sulfur. This tends to show that the natural sulfurization that would have covalently bound sulfur of mineral origin to organics [11] is not a major source of sulfur in the IOM. The global depletion and the variability among chondrites may have different causes such as heterogeneous sulfide/IOM assemblages, heterogeneous organics precursors that could have been more or less favorable to sulfur capture, or highly variable hydrothermalism conditions.

A complementary study based on the analysis of a larger number of reduced sulfur organic compound is required to refine the matrix effect on the isotopic measurements. This will confirm or not the global depletion of the IOM with respect to adjacent sulfides and put new constraints on the origin of sulfur in extra-terrestrial organic matter.

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