

SULFUR SPECIATION IN CARBONACEOUS CHONDRITES HF/HCl RESIDUES BY S K-EDGE XANES MICROSCOPY. F. R. Orthous-Daunay¹, E. Quirico¹, L. Lemelle², P. Beck¹, V. De Andrade³, A. Simionovici⁴, S. Derenne⁵ ¹LPG Université Joseph Fourier CNRS/INSU BP53 38041 Grenoble Cedex9 France forthous@ujf-grenoble.fr, ²Université de Lyon, CNRS UMR5570-USR3010, Ecole Normale Supérieure de Lyon, 46 allée d'Italie, 69007 Lyon France, ³ID21 Beamline ESRF, 6 rue J. Horowitz, BP220 38043 Grenoble Cedex France, ⁴LGIT, OSUG, BP53 38041 Grenoble Cedex9 France, ⁵LCBOP, CNRS UMR7573, ENSCP, 11 rue Pierre et Marie Curie, 75231 Paris Cedex5, France.

Introduction: Sulfur is relatively abundant in carbonaceous chondrites and is distributed in several phases. In meteorites, bulk abundances of sulfur have been previously correlated with the petrochemical classification. Indeed, CI chondrites are more than 50 % richer in sulfur than CM which are richer than CO or CV [1]. Seven different sulfur species were described by Burgess et al.[2], that can be grouped into two types: i) organic sulfur and sulfides that evaporates below 500°C ii) oxidized sulfur like sulfates that evaporates at higher temperature.

This diversity in sulfur chemistry might be related to the complex history of chondrites. Sulfides are thought to be the major sulfur-bearing phases that condensed from the solar nebula. Sulfates formation seems to be due to sulfide aqueous alteration on the final parent body [3] or on planetesimals [4]. Some sulfates could also have formed during terrestrial alteration [5].

Because sulfur is affected by aqueous alteration, we decided to study sulfur speciation for different chondrites of different classes, that display increasing alteration degrees. We used S K α X-ray absorption near edge structure (XANES) spectroscopy to characterize sulfur speciation in organic matter which seems to be sensitive to parent body fluids [6].

In this study, the sulfur oxidation state of insoluble organic matter IOM (HF/HCl residues) from CI1 (Ivuna, Orgueil and Alais), CM2 (QUE97990 (2.6), Murchison (2.5), Murray (2.4), QUE99355 (2.3) and Cold Bokkeveld (2.2)), CR2 (Renazzo) and C2(Tagish Lake) was determined by S K-Edge XANES to investigate the main sulfur-rich minerals, organic functions and redox ratios within each group.

Materials and methods: IOM were produced at the LPG using a homemade demineralization device based on continuous filtration. The wet chemical attack consists of silicates, carbonates and sulfates removal by hydrofluoric and hydrochloric acids flow during 10 hours, under an oxygen-free atmosphere at 25°C, preceded and followed by an organic solvent wash. This avoids experimental oxidation and the loss of thermo labile organics. Kerogen embedded sulfides and sulfates are known to resist this protocol. IOM grains (~200 μ m diameter) were flattened to about

20 μ m between two foils of 4 μ m-thick Ultralene® (sulfur-free polymer). Spectra were acquired at the ESRF ID21 beamline with a defocused beam reduced to a 50 μ m diameter beam by use of a pinhole. The beam energy was tuned by a [111] silicon monochromator from 2.450 keV to 2.500 keV with a <0.3eV step. We recorded both absorption and fluorescence with on-axis and 90°off-axis Ge energy dispersive detectors. The sample was positioned at 60° from the beam/absorption axis, under vacuum. Each raw spectrum point is the area of the S K α peak on the EDS detector versus probe beam energy.

Spectra were normalized by setting pre-edge signal to 0 and post-edge signal to 1. We assume that the spectrum of a bulk sample is a linear combination of each sulfur specie spectrum weighted by its relative abundance. We use a least square routine to retrieve sulfur speciation that combines standard spectra from a 40 sulfur species database.

Results and discussion: Figure 1 shows the normalized fluorescence spectra of each measured chondrites. Table 1 summarizes the main features of the oxidation state of sulfur [7,8].

W.L.	Occurrences	Standards	O.S.
2.4703	All. Low in CIs. Very high in C.B.	Sulfides	<-1
2.4727	All. Low in C.B.	Elemental Disulfides	0 0.2
2.4739	CIs and C.B. only	Thiophenes ?	1 ?
2.4746	CIs and C.B. only	Thianthrene ?	0.5 ?
2.4762	CIs only	Sulfoxides	4
2.4783		unassigned	
2.4810	CIs only	Sulfonates	6
2.4828	C.B., Murray and QUE97990 only	Sulfates	6

Table 1: Spectral features assignment. W.L. is for white line energy (in keV), O.S. is for oxidation state and C.B. is for Cold Bokkeveld.

The broad feature starting at 2.4783 keV in every IOM, certainly a combination of secondary spectral features, could not be assigned.

Fitting shows that 8 standards (chosen among 40) are necessary and sufficient to fit the spectra. They are: pyrrhotite (-2), sulfur (0), Glutathione dimer (0.2), Glutathione (0.5), Dimethylsulfoxide (+4), Methionine sulfone (+5), Taurine (+6 sulfonate) and romerite (+6 sulfate). It can be noted that pyrrhotite was found in stardust grains [9] and is often associated with pentlandite in natural samples. Romerite is a highly hydrated iron sulfate. It appeared that C2 best fits did not include other organic sulfur species than Glutathione dimer contribution. On the contrary, C11 chondrites fits required 3 distinct oxidized organics. Even if thiophene and thianthrene were initially identified from the peaks position (and were previously reported in the literature [10,11]) they were not found by our linear fit procedure. The 2.4739 keV and 2.4746 keV peaks could be due to secondary features of sulfur species.

This study shows that the most altered chondrites show highly oxidized organic sulfur and the lowest sulfides contribution. This is consistent with the fact that alteration fluids might be responsible of oxidation processes involving oxygen addition.

Sulfoxide, and sulfone are in-chain organic sulfur species. Whilst they are absent in C2 chondrites, they were observed in the three CI. This testifies of chemical differences between CI chondrites kerogens and the others.

Conclusion: Sulfides, sulfur and sulfates were identified in all studied chondrites IOM. Organic sulfur speciation is very different between C11 group, Cold Bokkeveld and the other meteorites. Sulfonates are only observed in the 3 studied C11 chondrites. On the contrary, CM2 do not show any evidence for sulfonates, and they display a stronger sulfide peak. The one exception is Cold Bokkeveld, which presents both oxidized organic sulfur and an important reduced sulfide content.

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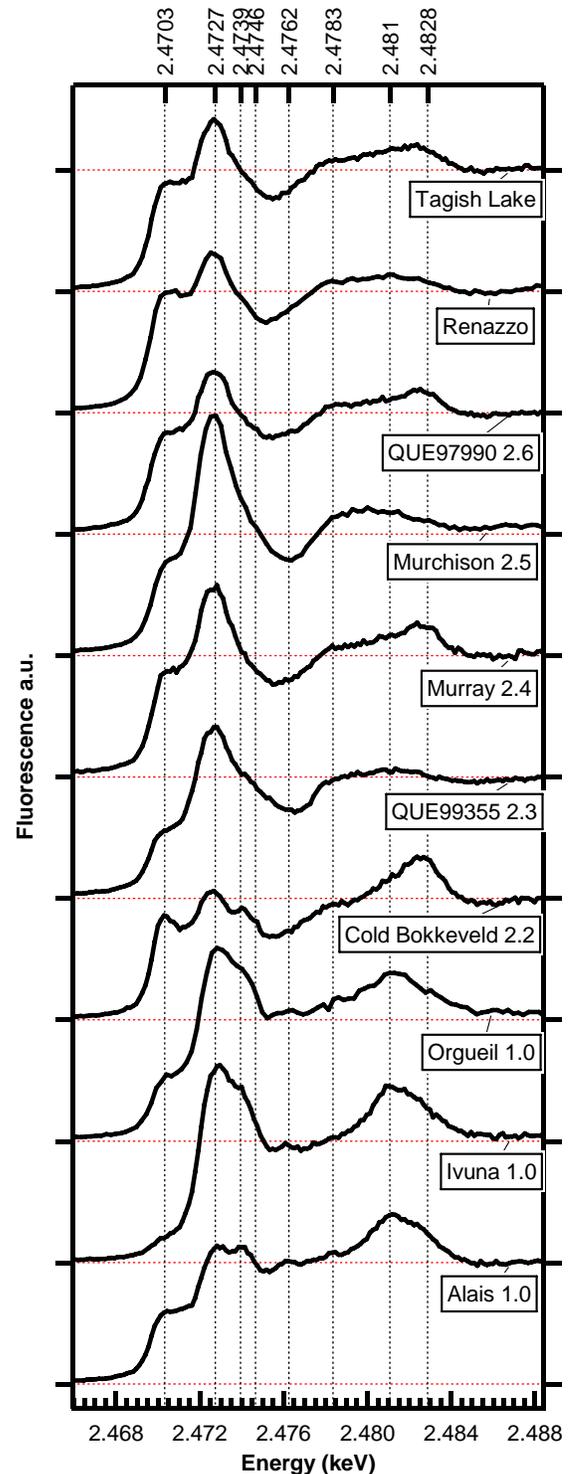


Figure 1: S K-Edge Xanes normalized fluorescence spectra of 3 CI1, 5 CM2, 1 CR2 and Tagish Lake. Every features positions are reported on top. See assignment in Table 1.