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# A NEW METHOD FOR ORGANIC AND MINERAL SULFUR MULTI-ISOTOPE ANALYSIS OF SEDIMENTS AND PETROLEUM SOURCE ROCKS

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## Introduction

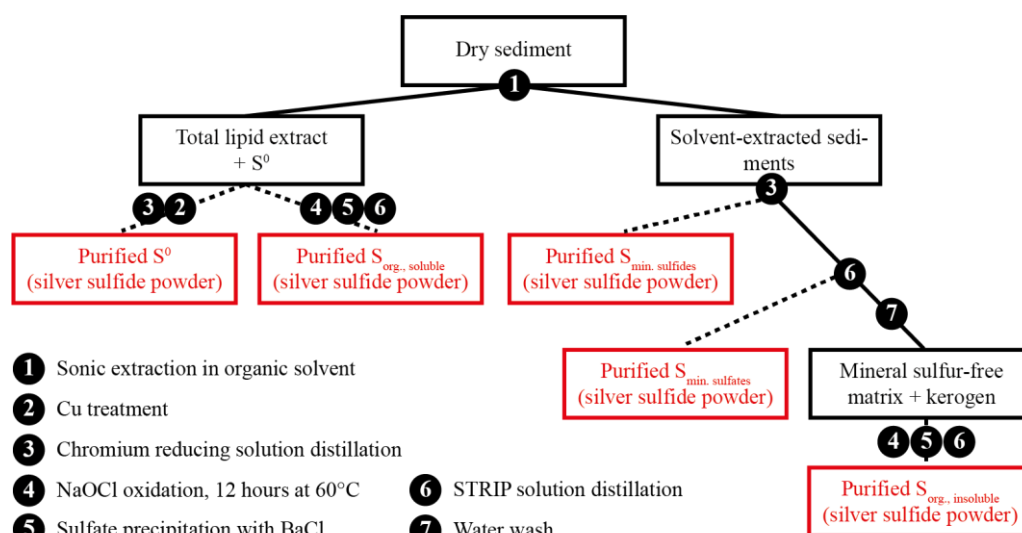
Sulfur (S) is a key element of biogeochemical cycles. Its four stable isotopes (<sup>32</sup>S, <sup>34</sup>S, <sup>33</sup>S, <sup>36</sup>S, in order of decreasing abundance) are subject to equilibrium and kinetic fractionations, which can be used as tracers to understand processes involved in the S cycle. However, the analytical procedure for the determination of the S multi-isotope composition requires the quantitative extraction and purification of S and its transformation into Ag<sub>2</sub>S, which can then be analyzed by Fluorination-GC-IRMS. If the specific extraction and purification of the various mineral S pools (sulfides, sulfates and elemental sulfur, S<sup>0</sup>) are well-known procedures, the quantitative extraction and purification of organic sulfur (S<sub>org</sub>) still requires further development. Indeed, existing procedures for the extraction of S<sub>org</sub> based on either Raney Nickel desulfurization (Oduro *et al.*, 2011), or Parr bomb oxidation (*e.g.* Marcano *et al.*, 2013), are not well adapted since the former is restricted to specific S species and is sensitive to steric hindrance, whereas the latter is technically restrictive.

Here we propose a new stepwise chemical procedure for the quantitative recovery and multi-isotope analysis of S<sub>org</sub> from both solvent soluble and insoluble fractions, which further allows the multi-isotope analysis of inorganic S species in the same samples. Its application to different well-known petroleum source rocks and to an oil demonstrates its great interest for disentangling the S biogeochemical cycle in these different settings.

## Results

The new procedure that was developed (Fig. 1) allows the quantitative and sequential recovery of all the mineral (sulfides, sulfates and S<sup>0</sup>) and organic (S<sub>org</sub> from soluble and insoluble organic matter, OM) S pools as analyzable Ag<sub>2</sub>S from the same sample (Jovovic *et al.*, in prep.). **Erreur ! Source du renvoi introuvable.** The extraction of S<sub>org</sub> is based on the quantitative oxidation of S bound either to soluble or insoluble OM into sulfates using hypochlorite solutions. Ag<sub>2</sub>S for multi-isotopic analysis can then be generated from these sulfates *via* classical procedures. The kinetics of the oxidative digestion of OM and its possible influence on the S isotopic composition of S<sub>org</sub> were investigated, allowing optimal conditions to be set up. The comparison of our new procedure with previous ones based on Raney Nickel desulfurization (Oduro *et al.*, 2011) showed extraction yields 3 to 200 times higher with the new procedure when applied to soluble and insoluble OM.

This procedure was validated on various samples with different S contents comprising recent sediments from an euxinic crater lake, petroleum source rocks from the Green River and Monterey formations and an oil (Rozel Point). We were able to purify and analyse the above-mentioned S pools from these samples with a good replicability, and to reconstruct their S mass-balance states. These mass-balances matched perfectly with the S-content and δ<sup>34</sup>S evaluated by elemental analysis of the same samples, demonstrating their reliability.



**Figure 1** Workflow for the sequential recovery and multi-isotope analysis of organic and mineral sulfur pools from sediments/oils.

The  $\delta^{34}\text{S}$  values of mineral S species retrieved from the different samples investigated showed large ranges of variation (*e.g.*  $+2.5\text{‰} < \delta^{34}\text{S}_{\text{sulfides}} < +35\text{‰}$ ) but were compatible with data previously published in the literature (when available). A  $^{34}\text{S}$ -enrichment of  $\text{S}_{\text{org}}$  relative to  $\text{S}_{\text{sulfides}}$  was observed in some samples, also matching literature data (*e.g.*  $\delta^{34}\text{S}_{\text{org}} - \delta^{34}\text{S}_{\text{sulfides}} = +3\text{‰}$  in the Monterey Fm; Zaback and Pratt, 1992). However, unprecedented  $^{34}\text{S}$ -enrichments of  $\text{S}_{\text{org}}$  were observed in Green River Fm samples, with a difference between  $\delta^{34}\text{S}_{\text{org}}$  and  $\delta^{34}\text{S}_{\text{sulfides}}$  ranging from  $-20$  to  $-25\text{‰}$  instead of the classical  $+5\text{‰}$  shifts reported previously (*e.g.* Tuttle and Goldhaber, 1993). Such differences might be explained by high heterogeneities of  $\text{S}_{\text{org}}$  in some source rocks. However, since our  $\text{S}_{\text{org}}$  recovery yields were significantly higher than those reported in previous studies for equivalent samples, it may be that earlier procedures used for determination of  $\delta^{34}\text{S}_{\text{org}}$  were not quantitative and that they led to isotopic fractionations (and thus to incorrect  $\delta^{34}\text{S}$  values). Interestingly, similar shifts between the  $\delta^{34}\text{S}$  of soluble and insoluble  $\text{S}_{\text{org}}$  and the  $\delta^{34}\text{S}$  of the different mineral pools (sulfides, sulfates and  $\text{S}^0$ ) were observed in sediments from an euxinic modern analogue of lacustrine source rocks, supporting the reliability and geochemical significance of such unusual  $\delta^{34}\text{S}$  differences.

## Conclusions

Our new procedure allows to recover separately, specifically and quantitatively all the S pools present in various types of samples, and to analyze them for S multi-isotopes. In addition to demonstrating the interest of an S multi-pool approach, some data lead to the reconsideration and to a new understanding of the S cycle in complex biogeochemical systems including important petroleum source rocks.

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