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ABSTRACT

Deciphering the role of sulfur in biogeochemical cycles strongly relies on its stable isotope composition, which ultimately depends on the ability to quantitatively recover different sulfur species from geological samples. For decades most studies have been restricted to the $^{34}S/^{32}S$ composition of bulk samples, using simple methods based on the analysis of SO_2 released by sample combustion combined to mass spectrometry. The wet chemistry procedures required to selectively extract specific sulfur species were generally avoided due to their tediousness and inefficiency for some complex matrices, especially when targeting organic sulfur. With the recent advent of multi-isotope studies (investigating the minor sulfur stable isotopes ^{33}S and ^{36}S) which rely either on the analysis of sulfur as SF_6, or on the use of secondary ion or multi-collector inductively coupled plasma mass spectrometry, wet chemistry-based

preparation procedures were brought back to the stage with a renewed interest in developing procedures better adapted to the investigation of specific sulfur species.

Here we propose a new stepwise chemical procedure for the quantitative recovery and multi-isotope analysis of organic sulfur from both solvent soluble (total lipid extract) and insoluble (kerogen) fractions, based on a wet oxidation by sodium hypochlorite. This procedure also allows the multi-isotope analysis of inorganic sulfur species (elemental sulfur, sulfates and sulfides) in the same sample. Its application to different well-known petroleum source rocks and to an oil demonstrates its relevance for disentangling the interactions between the different sulfur pools and for shedding new light on the sulfur biogeochemical cycle.

Keywords : sulfur (multi-)isotopes; organic and mineral sulfur; source rocks; chemical oxidation of organic sulfur; S biogeochemical cycle

1. INTRODUCTION

Sulfur (S) is a key element of biogeochemical cycles, being both an essential component of living cells and involved in major geological processes. The proportions of its four stable isotopes (^{32}S, ^{34}S, ^{33}S, ^{36}S, in order of natural abundance) vary upon equilibrium and/or kinetic conditions, and can be used as tracers of S biogeochemical cycles and processes (Passier et al., 1999; Canfield, 2001; Johnston, 2011). S-isotope compositions are expressed as per mil (‰) differences relative to the isotopic composition of the Vienna Canyon Diablo Troilite international standard (V-CDT), and presented in standard δ notation: $\delta^{A}S = {}^{A}R_{sample}/{}^{A}R_{CDT} - 1$ where $^{A}R = {}^{A}S/{}^{32}S$ and A = 33, 34 or 36 (note however that there is not yet any international standard for the $^{33}S/^{32}S$ and $^{36}S/^{32}S$ ratios).

The three isotope ratios ($\delta^{33}S$, $\delta^{34}S$ and $\delta^{36}S$) primarily scale on their relative mass differences and their fractionation can be predicted using an approximation of their partition function

(Bigeleisen and Mayer, 1947; Young et al., 2002). This is known as mass-dependent fractionation: $\delta^{33}S \approx 0.515 \times \delta^{34}S$ and $\delta^{36}S \approx 1.89 \times \delta^{34}S$ (see thereafter for more formal and rigorous equations). However, most studies solely focus on ^{34}S fractionation, which is the easiest to measure. Such measurements have become common with the development of elemental analysis coupled to isotope ratio mass spectrometry (EA-IRMS), in which S is oxidized to SO_2, and the $^{34}SO_2/^{32}SO_2$ ratio subsequently measured (Giesemann et al., 1994). EA-IRMS analyses of $\delta^{34}S$ are low cost, easy and fast to operate. Though, the oxygen interferences inherent to the use of SO_2 gas forbid reliable multi-isotope approaches (Rees, 1978).

More recently, multi-isotope studies have enlightened previously poorly constrained atmospheric and (bio)(geo)chemical processes (Farquhar et al., 2000; Farquhar and Wing, 2003; Luo et al., 2018). For instance, the specific ^{32}S, ^{33}S, ^{34}S and ^{36}S signatures of ancient rocks led to a new understanding of Archean and Paleoproterozoic atmospheric chemistry and S cycling (Farquhar et al., 2000; Philippot et al., 2007). The analysis of ^{33}S and ^{36}S isotope compositions was also a key factor in achieving a better understanding of hydrothermal processes (Ono et al., 2007) and microbial metabolic pathways such as sulfate reduction, S oxidation and S disproportionation (*e.g.* Farquhar et al., 2003; Johnston et al., 2005; Ono et al., 2006). The interpretations rely on both the (small) deviations in the behavior of each S-isotope and mass-conservation effects which are expressed using the conventional Δ notation: $\Delta^{33}S = \delta^{33}S - [(\delta^{34}S + 1)^{0.515} - 1]$ and $\Delta^{36}S = \delta^{36}S - [(\delta^{34}S + 1)^{1.89} - 1]$. As for any isotope method, the determination of the multi-isotope composition of specific S species in a given sample (*e.g.* sulfates, sulfides, elemental sulfur (S^0), organic sulfur; Table 1) requires the quantitative recovery and purification of the different S pools. Sulfides (and/or acid volatile S), sulfates and S^0 are typically recovered as Ag_2S using distillation methods and reducing solutions (Thode et al., 1958; Pepkowitz and Shirley, 1950; Forrest and Newman, 1977;

Canfield et al., 1986). Each targeted S-pool is first converted into H_2S by an adapted acid treatment, and subsequently recovered as a solid metal sulfide (typically as Ag_2S, sometimes as ZnS or CdS). The obtained metal sulfide is then transformed into either SO_2 or SF_6 (*e.g.* Thode et al., 1961; Thode and Rees, 1971, respectively) and analyzed by IRMS. Contrary to oxygen, fluorine has only one stable isotope. Because it avoids the need for ^{17}O or ^{18}O corrections (Rees, 1978), IRMS analysis of SF_6 is more precise and accurate and, accordingly, has been preferentially used to investigate all four S stable isotopes (Hulston and Thode, 1965). This, however, requires a non-automated conversion of Ag_2S into gaseous SF_6 and the purification of the latter. Alternatively, the use of secondary ion mass spectrometry (SIMS) has been proposed for the *in-situ* analysis of ^{32}S, ^{33}S and ^{34}S (*e.g.* Thomassot et al., 2009; Whitehouse, 2012), and multi-collector inductively coupled mass spectrometry (MC-ICPMS) has been used for the determination of ^{32}S, ^{33}S and ^{34}S contents in small purified samples (*e.g.* Albalat et al., 2016). SIMS is however less available and requires specific standards. Though high precision measurements of ^{34}S can be obtained with MC-ICPMS (*e.g.* Paris et al., 2013), this technique is hardly as precise as IRMS analysis of SF_6 for ^{33}S-measurements and cannot provide ^{36}S data.

Organic sulfur (S_{org}) is, after pyrite, the second most abundant reduced S pool in sediments (Anderson and Pratt, 1995), where it usually occurs as a complex mixture of monomeric and polymeric organosulfur compounds (OSC). Sedimentary S_{org} can be further divided into a soluble (solvent-extractable) and an insoluble (non-extractable or residual) OSC-pools. Biosynthetic S_{org} mainly occurs as chemically labile proteins and amino acids that are expected to be quickly degraded during diagenesis (Tissot and Welte, 1984 ; Kutuzov et al., 2019) though, in some cases, they could contribute their sulfur atoms to the kerogens (Raven et al., 2018). On the other hand, S_{org} in recent sediments typically increases with depth. For example, Werne et al. (2003) showed an increase from 0.05 to 0.12 of the organic S/C ratio in

the Cariaco Basin with sediment depth. This increase reflects a diagenetic S-enrichment of organic matter by sulfurization processes (natural vulcanization) which involve reduced S species produced by microbial sulfate reduction (MSR; Sinninghe Damsté et al., 1989; Adam et al., 1993). The idea of a common source of sedimentary S_{org} and mineral S (usually pyrite) is further supported by their respective $\delta^{34}S$ signatures generally depleted relative to sulfates (*e.g.* Thode et al., 1958; Zaback and Pratt, 1992; Tuttle and Goldhaber, 1993; Canfield et al., 1998; Werne et al., 2003). However, S_{org} is still often ^{34}S-enriched relative to pyrite (*e.g.* 10-20‰ in marine sediments, Orr, 1986; 5-8‰ in Cariaco Basin, Werne et al., 2003). Tuttle (1991), then Werne et al. (2003) explained this relative enrichment by a delayed sulfurization of organic matter relative to the formation of pyrite, but this simple view likely overlooks the fact that different organic molecules may react with reduced species at different rates depending on the context (*e.g.* Amrani, 2014, Raven et al., 2016a, Raven et al., 2016b, Shawar et al., 2020).

Thus, our understanding of the biogeochemical S cycle still remains incomplete and could clearly benefit from S_{org} multi-isotope analyses, but only few dedicated studies have been performed so far (*e.g.* Oduro et al., 2011, Labidi et al., 2017, Siedenberg et al., 2018). Reasons are linked to the structural diversity and distinct solubilities of biological and geological OSC, and to their difficult clear-cut separation from the inorganic S pools, which make them more arduous to recover specifically and quantitatively. In this respect, an adapted procedure for the specific and quantitative recovery of S_{org} would also be useful for studies dedicated to $^{34}S_{org}$ signatures. Most existing procedures for the release of S_{org} rely on its oxidation into sulfates by combustion methods such as Eschka fusion (using a 2:1 mixture of MgO and Na_2CO_3 at *ca.* 900°C, Eschka, 1874), or Na_2O_2 Parr bomb and Br_2 oxidations, with yields close to 100% and a good replicability (Selvig and Fieldner, 1927; Siedenberg et al.,

2018). However, those methods are tedious, dangerous and difficult to apply routinely to large sets of samples.

More recently, some studies have introduced the use of specific methods to improve S_{org} recovery for (multiple) S-isotope measurements (Table 1). For instance, Oduro et al. (2011) used Raney nickel as a catalyst for the desulfurization of volatile OSC and the recovery of S_{org} as nickel sulfide. Though they showed yields close to 100% for the desulfurization of many volatile OSC, this method did not appear suitable for the recovery of sulfones. Moreover, Raney nickel is a solid which poorly reacts with insoluble OSC from kerogens. To our knowledge, none of the presently available procedures allows a simple, selective and quantitative recovery of both mineral S and S_{org} pools.

Here we propose a new stepwise chemical procedure for the selective and quantitative recovery as Ag_2S of solvent-extractable and non-extractable S_{org} from sediments and oils, applicable for a specific and reliable determination of either ^{34}S or the multiple S-isotope composition of distinct S_{org} pools. It relies on oxidation of organic matter with sodium hypochlorite (NaOCl), which was previously shown to release organic-bound S as sulfates (*e.g.* Li and Cho, 2005). This procedure is further compatible with the analysis of sulfides, sulfates and S^0 in the same samples. The complete optimized procedure was carefully tested on an oil and sediment samples from lacustrine and marine environments of various ages (from modern to 50 Myr), validating its suitability for the (multi-)isotope analysis of geological organic and mineral S and allowing a new model of the S cycle to be considered for some depositional environments.

2. MATERIAL AND METHODS

2.1. Samples

Due to the large diversity of S forms in nature, their distinct reactivity and potential interaction with natural matrices, our method was developed and tested on several natural samples rather than pure minerals and OSC. These samples were selected among organic matter- and S-rich sediment formations from various locations, and complemented with a S-rich oil (Table 2).

We selected sediments from the Eocene Green River Fm Mahogany Zone (Utah, USA, Bradley, 1964; Smith and Carroll, 2015; Tuttle, 1991), and sub-superficial sediments from the modern Lake Dziani Dzaha (Mayotte, Indian Ocean, Leboulanger et al., 2017; Milesi et al., 2020). A marine shale sample from the Miocene Monterey Fm (California, USA, Orr, 1986; Zaback and Pratt, 1992) was added to the sample set. Lastly, we used a sample from Rozel Point seeps (Utah, USA, Thode et al., 1958; Eardley, 1963; Mauger et al., 1973) to evaluate the efficiency of the new method on pure organic matter. A non-referenced sample from the Limagne Basin (Massif Central, France, Wattinne et al., 2003; Seard et al., 2013) was added to compare the yields of S_{org} obtained with Raney nickel (Oduro et al., 2011) and the newly developed method (Table 3).

None of these samples was thermally mature except for the Rozel Point oil seep sample for which maturity was hardly defined (Eardley, 1963); thermal maturation effects on S_{org} recovery is therefore not discussed in this study.

2.2. Analytical steps

Samples were freeze dried, ground to <100 µm, and homogenized. Subsamples (*ca.* 1 g) were then subjected to a sequence of chemical extractions in order to specifically recover the different organic (soluble and insoluble) and mineral (S^0, sulfates, sulfides) S pools (Fig. 1).

Only Pyrex glassware was used and all chemicals were reagent-grade. Dilutions and washes were performed in 100 mL centrifuge tubes using deionized water. S-purity of all reagents

was regularly checked and considered as acceptable when less than 5 µg of S was recovered in a whole blank procedure.

2.2.1. Solvent extraction and S^0 precipitation

The soluble organic matter was extracted by multiple sonication cycles (10 minutes each) with methanol (MeOH, twice), dichloromethane (DCM):MeOH (1:1, v/v, twice) and DCM (twice) at room temperature (*ca.* 20°C). The total lipid extract (TLE) was treated with activated copper curls to precipitate S^0 as Cu_xS_y (Blumer, 1957).

2.2.2. Reducing distillations

The acidic $CrCl_2$ (Canfield et al., 1986) and STRIP (Forrest and Newman, 1977; Pepkowitz and Shirley, 1950; Thode et al., 1961) solutions have been extensively used for the extraction of mineral S compounds in samples from a wide range of natural settings and laboratory experiments. Gröger et al. (2009) have shown that the $CrCl_2$ solution typically converts 99±1 % of both sulfides and S^0 into H_2S, but hardly reacts with individual OSC and sulfates (typical yields <0.2 %). However, since the reactivity of the $CrCl_2$ solution has never been tested against very fresh natural OM, the eventuality of a reaction with some OSC, *e.g.* organic polysulfides cannot be totally excluded. Moreover, Arnold et al. (2014) have shown that the STRIP solution typically yields close to 100 % of both sulfides and sulfates, but hardly converts OSC to H_2S. Therefore, the $CrCl_2$ solution was used to selectively recover sulfide-S and Cu_xS_y-S, whereas the STRIP solution was used to recover sulfate-S from sulfide-free samples.

Due to its sensitivity towards oxidation, the $CrCl_2$ solution was prepared daily according to Fossing and Jorgensen (1989). A glass bottle closed with a teflon-coated rubber cap was filled with a an acidic $CrCl_3$ solution (80 ml of 3 % HCl and 21.15 g $CrCl_3$, 6 H_2O). The Cr(III)

198 solution was then reduced to Cr(II) by the addition of zinc granules (14 g). The solution was
199 stirred under a nitrogen flush until the initial dark green color had completely turned to bright
200 blue.
201 The STRIP solution is more stable and was used within 6 months after preparation. A glass
202 Erlenmeyer flask was filled with 523 ml of 37 % HCl, 321 ml of 57 % hydriodic acid (HI)
203 and 156 ml of 50 % hypophosphorous acid (H_3PO_2). The solution was heated under a nitrogen
204 flush and gently refluxed, for 6 hours.
205 The apparatus that was used for S distillation is represented in Fig. 2. We ensured that the
206 treated sample did not contain more than *ca.* 125 µmol S to guarantee a large excess of
207 reagents and allow the reaction to be quantitative. The targeted S pool was converted to H_2S
208 with either 10 mL of 37 % HCl and 25 mL of $CrCl_2$ solution (sulfides/S^0) or 25 mL of STRIP
209 solution (sulfates), and refluxed for 3 hours. Produced H_2S was purged and precipitated as
210 Ag_2S in a silver nitrate trap (20 ml of 2.48 % $AgNO_3$). A few drops of a 25 % ammonia
211 solution were added to the the Ag_2S precipate, which was then centrifuged, washed three
212 times with 30 ml of deionized water, and lyophilized. The dry Ag_2S powder was stored out of
213 sunlight before fluorination and S multi-isotope analysis.
214
215 *2.2.3. Oxidation of organic matter*
216 The mineral S-free sediments/oils and S^0-free TLE were heated at 60 °C under stirring with a
217 10-15 % NaOCl solution in a 100 mL centrifuge Pyrex tube. It is noteworthy that, even under
218 reflux and stirring, concentrated NaOCl easily tends to evaporate, resulting in a poor
219 reactivity, especially over long reaction times. Therefore, the solution was kept under 70 °C.
220 To guarantee a large excess of hypochlorite ions, we introduced no more than *ca.* 125 µmol S
221 and *ca.* 25 mmol C from each sample for 25 ml of NaOCl solution. Various treatment times
222 (6, 12, 24 and 48 hours) were tested to evaluate the reaction kinetics. This oxidative digestion

of organic matter resulted in the liberation of S_{org} from solvent-soluble or insoluble organic matter as sulfates. After reaction, the solution was carefully acidified with 37 % HCl, until pH <2, to allow the consumption of excess hypochlorite ions and carbonate by-products, and to facilitate the precipitation of sulfates. Sulfates were precipitated as $BaSO_4$ using 20 mL of a saturated $BaCl_2$ solution (>360 $g.L^{-1}$). The resulting precipitate was centrifuged and rinsed twice with 20 mL of the saturated $BaCl_2$ solution, than freeze dried and homogenized before distillation as illustrated in 2.2.2.

2.2.4. TOC and GC-MS analyses

The evolution of total organic carbon (TOC) contents in residual sediments during digestion was monitored using an elemental analyzer (Vario ISOTOPE Select, Elementar) equipped with a Thermal Conductivity Detector. The accuracy of the measurements was evaluated using an international sediment standard, namely IVA33802151 (TOC = 9.15 %).

Residual aqueous phases after oxidation with NaOCl were extracted with DCM and ethyl acetate, successively, to investigate the potential soluble organic compounds freed by the process. The extracts were then derivatized with diazomethane and analyzed by gas chromatography coupled to mass spectrometry (GC-MS), using a Thermo Trace gas chromatograph coupled to a Thermo TSQ Quantum mass spectrometer operating in the electron ionization mode (70 eV) and scanning *m/z* 50 to 700. The temperature of the source was set to 220 °C. Gas chromatographic separations were performed on a HP5-MS column (30 m length with 0.25 mm diameter and 0.1μm film thickness) with helium as carrier gas (1.1 $mL.min^{-1}$). The temperature program was: 40°C (10 min), 40-300 °C (6 $°C.min^{-1}$), isothermal at 300 °C (25 min).

2.2.5. Isotope analyses

The Ag_2S powders corresponding to the different organic and mineral S pools were freeze dried, homogenized and weighed in aluminum boats before being fluorinated overnight in Nickel bombs with excess fluorine gas at 350°C. The produced SF_6 was purified cryogenically and by subsequent gas chromatography prior to the determination of its $\delta^{33}S$, $\delta^{34}S$ and $\delta^{36}S$ values using a Thermo Scientific MAT 253 dual-inlet IRMS (Au Yang et al., 2016). The accuracy of the measurements was evaluated using an international Ag_2S standard, namely IAEA-S1 (also known as Vienna-CDT), with a $\delta^{34}S$ value = -0.3 ‰. Typical analytical deviations were below 0.01 ‰ and 0.1 ‰ for $\delta^{33}S$ or $\delta^{34}S$ and $\delta^{36}S$ values, respectively, and ≈ 0.005 ‰ and 0.1 ‰ for $\Delta^{33}S$ and $\Delta^{36}S$ values, respectively (1σ).

Total sulfur contents (TS) and associated $\delta^{34}S$ values were measured with a VarioPYROcube elemental analyzer (Elementar) in NCS combustion mode interfaced in continuous-flow mode with an Isoprime 100 IRMS (Fourel et al., 2014). The accuracy of those measurements was evaluated using the aforementioned international Ag_2S standard and one international $BaSO_4$ standard (NBS-127, $\delta^{34}S$ value = +20.3 ‰). Typical analytical deviations were below 0.05 % and 0.3 ‰ for the TS and $\delta^{34}S$ values, respectively (1σ).

3. RESULTS AND DISCUSSION

3.1. Procedure validation

Subsamples were first used to test and optimize the oxidation procedure of S_{org} with NaOCl. Then, triplicates of most samples were treated with the full stepwise procedure (Fig. 1 and Table 2). Using a mass balance calculation, the results of the triplicate analyses were compared to those obtained by direct EA-IRMS analysis of the dry sediments as a quantitative validation of the overall analytical workflow.

3.1.1. S_{org} oxidation to sulfates and recovery

Figure 3 shows the evolution of the carbon- and sulfate-contents in TLE and mineral-S free kerogens during 48 hours of NaOCl oxidation at 60°C. Within 24 hours, less than 7 ±3 % of the initial carbon remained in the sample, and more than 95 ±5 % of S_{org} was recovered as sulfates. The GC-MS analysis of residual organic compounds in aqueous phases after 4 and 12 hours of oxidation showed the occurrence of carboxylic diacids (> 4 carbons), chlorinated carboxylic monoacids as well as chlorinated and non-chlorinated benzene carboxylic polyacids (up to hexa-acids). Those products are expectable during the oxidation of organic matter with NaOCl (Wang et al., 2014). More importantly, no OSC (*e.g.* thiols, thiophenes, sulfoxides, sulfones, sulfonic acids, thioesters, polysulfides) was identified in any aqueous phase, showing an efficient oxidation of S bound to organic matter into recoverable sulfates. It cannot be excluded, however, that some OSC in other matrixes may react less efficiently, thus requiring a longer reaction time to be entirely oxidized.

The remaining S_{org} recovered after 6, 12, 24 and 48 hours revealed no significant isotope evolution associated with the oxidation process (Fig. 4). This suggests that the progressive organic matter digestion is not associated with significant isotope effects, and that an incomplete oxidation of S_{org} in samples would not impact S isotopes measurement –though quantitative aspects should not be considered in this case.

For some samples, the yield of S_{org} obtained with our new method was compared with that obtained with the Raney nickel desulfurization method used by Oduro et al. (2011). Much higher yields were obtained with the new method for soluble S_{org} (7 to 200 times, Table 3), which can be explained by a possible high steric hindrance of S_{org} in these specific samples. Unsurprisingly, due to the low kinetics of unfavorable solid-solid reactions, the new method was also significantly more efficient for the insoluble S_{org} present in kerogens, compared with the 4-times lower recovery of this S pool using Raney nickel (Table 3). None of the quantities

297 of S_{org} recovered with Raney nickel were sufficient for the determination of S isotopic
298 composition with Fluorination-IRMS.
299
300 *3.1.2. Mass balance validation*
301 The TS content and bulk $\delta^{34}S$ value measured for each bulk sample were compared to those
302 calculated from the S multi-pool analysis of the same sample (triplicate analyses), using the
303 following mass balance equation : $\%S_{total} \times \delta^{34}S_{total} = \Sigma(\%S_i \times \delta^{34}S_i)$, where *i* is in {soluble
304 S_{org}, insoluble S_{org}, S^0, sulfides, sulfates}.
305 The results are presented in Figure 5. The very good consistency between the two approaches
306 ($RMSE_{TS}$ = 0.13 % and $RMSE_{\delta 34S}$ = 1.07 ‰) and the good replicability of the new method (as
307 shown by the error bars) demonstrate that this new method indeed allows the reliable and
308 quantitative recovery of both soluble and insoluble S_{org}.
309
310 *3.1.3. Suitability for multi-isotopes analyses*
311 In addition to the selective and quantitative recovery of different mineral (sulfates, sulfides
312 and S^0) and organic (solvent-extractable and non-extractable) S pools, the new stepwise
313 procedure developed allows the reliable determination of their S (multi-)isotope composition
314 by IRMS (^{32}S, ^{33}S, ^{34}S, ^{36}S) or MC-ICPMS (^{32}S, ^{33}S, ^{34}S). In the present case, the S multi-
315 isotope composition of the investigated samples (from IRMS analysis of SF_6 gas) showed
316 mass-dependent fractionation of all S-isotopes with small but significant $\Delta^{33}S$ and $\Delta^{36}S$
317 values, within the range of $\Delta^{33}S \approx \pm 0.10$ ‰ and $\Delta^{36}S \approx \pm 1.50$ ‰ (Fig. 6 and Table 4) that are
318 expected for sediments younger than 2 Ga (see review by Johnston, 2011).
319
320 *3.1.4. Suitability for pure organic substrates*

The Rozel Point oil was primarily used here to test our oxidation procedure on 'pure' S-rich (> 90 mg S/g oil) organic matter. The ^{34}S composition of soluble S_{org} as obtained from the new method ($\delta^{34}S$ = -6.05 ±0.11 ‰, Table 4) differed by ≈ 1.5 ‰ from the EA-IRMS measurement ($\delta^{34}S$ = -7.5 ±0.3 ‰). Still, most of S_{org} could be recovered with the new method (with TS estimated to 9.18 ±0.1 % against 9.29 ±0.2 % with EA-IRMS), supporting the applicability of our procedure to 'pure' petroleum mixtures of OSC (possibly with a longer reaction time).

Yet, the efficiency of the method on fresh biological OSC and on very mature OSC (*e.g.*, Precambrian organic matter) remains to be established but should not be problematic.

3.2. Comparison with literature data and further interpretation of the geological record

Though the source rocks considered in this study have already been largely studied, the S stable (multi-)isotope composition of their different S pools remains poorly documented. A comparison between our ^{34}S data and those reported in previous studies of the Monterey and the Green River Formations is illustrated in Figure 7. This is complemented by data obtained for the present-day Lake Dziani Dzaha. Our multi-pool and multiple S-isotope data (Table 4), although still limited, were further used to bring new insights on our present understanding of the S isotope signatures observed in these settings (Fig. 8).

3.2.1. Monterey Formation

The investigated sample of the Monterey Fm mainly contained sulfides and insoluble S_{org} (4.73 ±0.30 and 3.57 ±0.22 mg/g of dry sediment, respectively; Table 4). Sulfates and soluble S_{org} were also present but their concentrations were *ca*. ten times lower than those of sulfides and insoluble S_{org}, respectively (Table 4). S^0 was not detected, in accordance with the

literature (Zaback and Pratt, 1992). The presence of sulfates (which are only 2-4 ‰ ^{34}S-enriched relative to sulfides; Table 4) was not described as primary in previous literature and could either correspond to artifactual oxidation products formed after sampling (likely during transport and storage) from sulfide minerals and potential organic polysulfides, or to secondary gypsum possibly derived from oxidation of S associated to migrating hydrocarbons (personal communication A.L. Sessions). Sulfides appeared 3-5 ‰ depleted in ^{34}S ($\delta^{34}S$ = +2.79 ±0.61 ‰) relative to soluble ($\delta^{34}S$ = +6.01 ±0.20 ‰) and insoluble ($\delta^{34}S$ = +8.73 ±0.04 ‰) S_{org}. This is consistent with literature data (Zaback & Pratt, 1992, Fig. 5) and with classical biogeochemical models of the S cycle in 'open' sedimentary systems (Fig. 8a).

Indeed, despite a large heterogeneity of sedimentary facies in the Monterey Fm, most of them are described as marine-influenced deposits (Orr, 1986; Zaback and Pratt, 1992). In these environments, S mainly derives from marine sulfates ($\delta^{34}S \approx +20$ ‰) which, in anoxic porewaters, can be reduced to H_2S by MSR (Canfield and Des Marais, 1993). This major microbial process is associated with a large depletion in ^{34}S, typically with $\delta^{34}S_{porewater\ sulfate}$ - $\delta^{34}S_{H2S}$ = 30 to 50 ‰ (Habicht and Canfield, 1997; Canfield, 2001). ^{34}S-depleted H_2S can then react with sedimentary iron or organic matter to produce iron sulfides or OSC, respectively. While the formation of iron sulfides only induces small S isotope fractionations, the sulfurization of organic matter seems to induce a slight ^{34}S-enrichment (generally < 5 ‰) of S_{org} relative to sulfides (Orr, 1986; Werne et al., 2003; Amrani, 2014). This is classically explained by a different timing of sulfurization, with the formation of iron sulfides (classically pyrite) occurring faster than the sulfurization of organic matter (Tuttle, 1991; Tuttle and Goldhaber, 1993; Werne et al., 2003). As schematized in Figure 8a, the delayed sulfurization of organic matter likely involves sulfates/reduced sulfur species enriched in ^{34}S by Rayleigh fractionation of the residual inorganic S pool. With time, this may result in a continuous enrichment of the $\delta^{34}S$ signatures of sulfides and S_{org} until the source of mineral S is totally

depleted (Thode et al., 1961; Zaback and Pratt, 1992; Tuttle and Goldhaber, 1993; Fig 8a), as supported by the large range of $\delta^{34}S$ values of sulfides (between ≈ -9 ‰ and ≈ +20 ‰) reported for the Monterey Fm (Fig. 7; Zaback and Pratt, 1992). However, upon Rayleigh fractionation, one would predict positive $\Delta^{33}S$ (> 0.1 ‰) and strongly negative $\Delta^{36}S$ (< 1.0 ‰) (see Ono et al., 2006b; Sansjofre et al., 2016) which would result from mass-conservation effects (*e.g.* Farquhar et al., 2007). These values are however not observed in the present study, which deserves further investigation with a larger set of samples.

3.2.2. Green River Fm and Lake Dziani Dzaha

As for the Monterey Fm, the main S pools in the selected samples from the Mahogany Zone of the Green River Fm and from the sub-surface sediments of Lake Dziani Dzaha were sulfides and S_{org} (Table 4). This latter, however, essentially occurred as solvent insoluble S_{org} in Lake Dziani Dzaha (0.34 ±0.05 and 3.69 ±0.18 mg/g of dry sediment for soluble and insoluble S_{org}, respectively), whereas the amount of soluble S_{org} in the sample from the Green River Fm was of the same order of magnitude as insoluble S_{org} (2.32 ±0.02 and 3.79 ±0.25 mg/g of dry sediment, respectively). Sulfides (essentially iron sulfides) were also present in a *ca.* four times higher concentration in the Green River Fm than in Lake Dziani. Variable relative abundances of the main S pools between both samples might reflect varying organic matter source or nature, sulfurization mechanisms, iron availability and depositional and diagenetic (e.g., ageing) histories (Table 2). A significant amount of S^0 (0.66 ±0.04 mg/g of dry sediment) was also detected in Lake Dziani Dzaha sediments while only traces (< 0.005 mg/g of dry sediment) were detected in the Green River sample. Low amounts of sulfates (< 5.5 % of total S) were recovered in both samples, which likely are artifactual oxidation products of mineral sulfides and eventual organic polysulfides. A strong argument for the absence of native sulfates in sediments from Lake Dziani Dzaha is the very low content of

sulfates (< 3 µM) in the present-day partially anoxic water column (Leboulanger et al., 2017) which is far from their supersaturation threshold. Despite differences in S content and speciation, the selected samples from the Green River Fm and from Lake Dziani showed striking similarities in their S multi-isotope compositions (Table 4 and Figure 7), with sulfides exceptionally enriched in heaviest S-isotopes (*i.e.*, $\delta^{34}S \approx +35$ ‰), while solvent soluble and insoluble S_{org} being strongly depleted (by -25 to -30 ‰ for ^{34}S) relative to sulfides (Table 4). Highly-^{33}S, ^{34}S and ^{36}S-enriched S^0 was also observed in Lake Dziani Dzaha with values of $\delta^{34}S$, $\delta^{33}S$ and $\delta^{36}S$ slightly above those of sulfides (≈ +4, +2 and +7 ‰, respectively, *i.e.* ≈ +5.5 % of their values). Such uncommon S isotope features suggest strong similarities between these two ecosystems and a biogeochemical functioning clearly distinct from that of marine systems such as the Monterey Fm (Figs. 7 and 8).

^{34}S highly-enriched sulfides have already been reported in samples from the late stages of the Green River Fm (Thode et al., 1958; Mauger et al., 1973; Tuttle and Goldhaber, 1993). The authors suggested that this enrichment was the result of a long-term Rayleigh fractionation process in past Green River lakes, driven by MSR and the diagenetic precipitation of depleted sulfides. According to Tuttle and Goldhaber (1993), a main difference with 'open' marine systems is that Green River lakes behaved as 'closed' systems, *i.e.* with no renewing of sulfate from the water column. Lake Dziani Dzaha can actually be considered similarly. This hypersaline tropical and insular stratified phreatomagmatic crater lake has no present-day connection to seawater, but its high S content most likely originates from initial marine sulfates (Leboulanger et al., 2017). In such 'closed' and stratified systems, the presence of a large anoxic water layer favors the production of sulfides by MSR and their subsequent precipitation as iron sulfides or their reaction with of organic matter, inducing a progressive enrichment in heavy isotopes of the residual S pool (Fig. 8b). It is noteworthy, however, that the geological record of the Green River Fm is the result of multiple long-scale sedimentary

421 evolutions over 100,000 years (Tuttle and Goldhaber, 1993), whereas the sedimentary story of
422 Lake Dziani Dzaha is less than 9000 years (Zinke et al., 2003). Different mechanisms could
423 have been involved in the temporal evolution of isotopic signature recorded in both systems.
424 Remarkably, as mentioned above, "closed"-system (Rayleigh-type) model predicts positive
425 $\Delta^{33}S$ and negative $\Delta^{36}S$ signatures which, again, were not observed here, possibly pointing
426 towards yet unkwnown specific S fractionation mechanisms.
427 The second remarkable feature observed for the Green River Fm and Lake Dziani Dzaha was
428 the strong depletion in heavy S isotopes of S_{org} relative to sulfides (by -25 to -30 ‰ for ^{34}S).
429 Such an isotopic shift has been previously reported in some studies of the Green River Fm,
430 but the values were not discussed further than the fact that they were out of range compared to
431 usual marine and euxinic environments (Mauger et al., 1973; Tuttle and Goldhaber, 1993).
432 Interestingly, a recent compound-specific $^{34}S/^{32}S$ analysis of organic matter from the Cariaco
433 Basin showed a *ca.* 10 ‰ depletion of several OSC (*e.g.*, triterpenoid thianes, and acyclic
434 isoprenoid thiophenes and thiolanes) relative to pyrite and to total extractable and residual S_{org}
435 (Raven et al., 2015). The authors suggested that total S_{org} likely contains a mixture of OSC
436 with distinct S-isotopic compositions formed by different sulfurization pathways (reversible
437 vs irreversible sulfurization processes). Shawar et al. (2018) further suggested that ^{34}S-
438 depletion of OSC relative to pyrite could be the result of competitive reactions between iron,
439 sulfur and organic matter, in particular in iron-limited environments. Under these specific
440 conditions, contrary to the 'open' marine systems described above, organic compounds might
441 react with reduced sulfur species at the earliest stage of burial more efficiently than iron, thus
442 recording the $\delta^{34}S$ signature of reactive sulfides whereas the formation of iron sulfides might
443 be delayed due to complexation or sorption of iron by the organic matter (Fig. 8b). S-isotopic
444 shifts between S_{org} and mineral sulfides might thus result from a predominant kinetic isotope

445 effects occurring during the fast sulfurization of organic matter by different pathways that
446 remain to be characterized.
447
448 **4. CONCLUSIONS**
449 We validated a new stepwise chemical procedure for the quantitative recovery and multi-
450 isotope (^{33}S, ^{34}S and ^{36}S) analysis of S_{org} present in both solvent-extractable (bitumen) and
451 residual (kerogens) organic matter. This method is further compatible with the analysis of
452 different inorganic S species (S^0, sulfates and sulfides) in the same samples. The most
453 distinguishing feature of this procedure is the use of NaOCl as an oxidative agent for the
454 degradation of organic matter and release of S_{org} as recoverable sulfates. The efficiency of this
455 analytical oxidation step was demonstrated with geological samples of various age and S-
456 content (contemporary anoxic sediment, source rocks and oil), noticeably showing that it does
457 not introduce any artificial fractionation of S_{org} multi-isotopes. This method can be used either
458 for the determination by EA-IRMS of the S-content and $\delta^{34}S$ of different S-pools recovered as
459 Ag_2S powders, or for the high-precision multi-isotope analysis of these Ag_2S powders by
460 IRMS ($\delta^{33}S$, $\delta^{34}S$ and $\delta^{36}S$ from SF_6) or MC-ICPMS ($\delta^{33}S$, $\delta^{34}S$).
461 The application of this S multi-pool approach to samples from the Mahogany zone of the
462 Green River Fm and the contemporaneous Lake Dziani Dzaha revealed striking and similar
463 features of their S isotope composition, including highly-enriched mineral sulfides (with
464 values of $\delta^{34}S$ around +35‰), and pools of S_{org} depleted in ^{34}S by *ca.* -27 ‰ relative to
465 sulfides. This depletion contrasts with the typical (+5/+10 ‰) enrichment in ^{34}S of S_{org}
466 relative to sulfides observed in marine sediments and confirmed in the present study with a
467 sample from the Monterey Fm (for which we report a +4.9 ‰ enrichment in ^{34}S of S_{org}
468 relative to sulfides). Such uncommon S isotopic characteristics probably point to fast

sulfurization of organic matter (with a kinetically controlled S fractionation) from ^{34}S-enriched sulfides/sulfates, leading to a strong $^{34}S_{org}$ depletion.

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Table 1 Methods previously used for studying the ^{34}S composition of organic and mineral S. For further details about STRIP and $CrCl_2$ distillations, see 3.2. * Studies in which ^{33}S and/or ^{36}S were also measured. n/i: not investigated.

Table 2 Origin, nature and use of samples. O = oxidation tests (Figs. 3 and 4), N = Raney nickel tests (Table 3), W = complete workflow procedure (triplicate analyses, Table 4), L = comparison with literature data and biogeochemical interpretation.

Table 3 Comparison of S_{org} contents (mg/g of dry sediment) released with the Raney nickel method (Oduro et al., 2011) and the new method from selected samples. TLE = solvent-soluble organic matter.

Table 4 S content (mg/g of dry sediment) and multiple-isotope composition (‰ vs CDT) of the different S pools from the investigated samples. n/d: non determined or excluded value, due to either a lack of material (under limit of detection) or mass spectrometry issues/contaminations. *The 4^{th} replicate of Lake Dziani Dzaha was sampled in a different part of the core than the three others. It was therefore not used in the mass balance calculations. TLE S_{org} = solvent-soluble S_{org} and Kerogen S_{org} = solvent-insoluble S_{org}.

Table 1

Study	Sample type	Total S	Sulfides	Sulfates	S^0	S_{org}
Thode et al. (1958)	Oil	Calculated	Bubbled out	Centrifuged out	n/i	Br_2, HNO3 oxidation to sulfates, STRIP distillation, SO_2 IRMS
	Bulk sediment	n/i	Br_2, HNO_3 oxidation to sulfates, STRIP distillation, SO_2 IRMS	Dissolution + precipitation, STRIP distillation, SO_2 IRMS	n/i	n/i
Mauger et al. (1973)	Organic extract from tar sand	n/i	n/i	n/i	n/i	Br_2 oxidation + STRIP distillation, SO_2 IRMS
Orr (1986)	Solvent-extracted sediment	Calculated	HNO_3 oxidation to sulfates, EA-IRMS	n/i	n/i	Parr bomb oxidation to sulfates, EA-IRMS
	Oil/organic extract from sediment					Parr bomb oxidation to sulfates, EA-IRMS
Zaback and Pratt (1992)	Solvent-extracted sediment	Calculated	$CrCl_2$ distillation, SO_2 IRMS	Dissolution + precipitation, SO_2 IRMS		
	Organic extract from the sediment	Calculated			Combustion, SO_2 IRMS	Parr bomb oxidation, SO_2 IRMS
Tuttle and Goldhaber (1993)	Bulk sediment	Calculated	$CrCl_2$ distillation, SO_2 IRMS analysis	SO_2 IRMS analysis	n/i	Eschka oxidation, SO_2 IRMS
Werne et al. (2008, 2003)	Solvent-extracted sediment	EA-IRMS on bulk sediment	$CrCl_2$ distillation, EA-IRMS	EA-IRMS on pore water precipitates	n/i	EA-IRMS
	Organic extract from the sediment		$CrCl_2$ distillation, EA-IRMS		n/i	EA-IRMS + compound-specific EA-IRMS
Amrani et al. (2012, 2009)	Oil/Organosulfur standard	EA-IRMS	n/i	n/i	n/i	Compound-specific MC-ICPMS
Oduro et al. (2011)	Solvent-extracted sediment	Calculated	$CrCl_2$ distillation, SF_6 IRMS*	STRIP distillation, SF_6 IRMS* on pore water precipitates		n/i
	Organic extract from the sediment	Calculated			$CrCl_2$ distillation, SF_6 IRMS*	Raney Ni desulfurization + $CrCl_2$ distillation, SF_6 IRMS*
Raven et al. (2018, 2016a, 2016b, 2015)	Solvent-extracted sediment	Calculated	HNO_3 oxidation to sulfates, ion chromatography, ICPMS/EA-IRMS	Dissolution + precipitation, ion chromatography, ICPMS/EA-IRMS		n/i
	Organic extract from the sediment	Calculated			Oxidation, ion chromatography, ICPMS/EA-IRMS	H_2O_2 oxidation, ion chromatography, ICPMS/EA-IRMS + compound-specific MC-ICPMS
Siedenberg et al. (2018)	Solvent-extracted sediment	n/i	$CrCl_2$ distillation, SF_6 IRMS*	n/i		Eschka powder oxidation + STRIP distillation, SF_6 IRMS*
	Organic extract from the sediment	n/i			n/i	Eschka powder oxidation + STRIP distillation, SF_6 IRMS*
This study	Solvent-extracted sediment	EA-IRMS on bulk sediment	$CrCl_2$ distillation, SF_6 IRMS*	STRIP distillation, SF_6 IRMS*		NaHClO oxidation + STRIP distillation, SF_6 IRMS*
	Oil/Organic extracts from the sediment				$CrCl_2$ distillation, SF_6 IRMS*	NaHClO oxidation + STRIP distillation, SF_6 IRMS*

Table 2

	Sample source	*Sediment type*	*Age*	*TOC (%)*	*Use*
Lake Dziani Dzaha (Mayotte, Indian Ocean)	Sub-superficial sediment	Euxinic lake sediment	Modern (0-1 kyr after Milesi et al., 2020)	9.2 ±0.3	O + N + W + L
Green River Fm (UT, USA)	Outcrop & core sediments	Microbialite	Eocene (ca. 50 Myr)	31.8 ±0.4	O + N + W + L
Monterey Fm (CA, USA)	Outcrop sediment	Shale	Miocene (5-17 Myr)	7.1 ±0.5	O + W + L
Rozel Point oil (UT, USA)	Oil seep	Crude oil	Tertiary	49.3 ±0.5	O + N + W
Limagne Basin (Massif Central, France)	Outcrop sediment	Microbialite	Oligo-Miocene (5-34 Myr)	13.4 ±0.1	N

Table 3

	New method	*Raney nickel*
Lake Dziani Dzaha TLE	0. 33 ± 0.05 (n=3)	0.047 ± 0.01 (n=3)
Green River Fm TLE	2.32 ± 0.02 (n=2)	0. 11 ± 0.05 (n=2)
Limagne Basin kerogen	1.11 ± 0.03 (n=2)	0.32 ± 0.02 (n=2)
Rozel Point oil	91.78 ± 1.05 (n=3)	0.46 ± 0.12 (n=2)

Table 4

Sample	*Pool*	*Replicate*	*S quantity*	$\delta^{34}S$	$\delta^{33}S$	$\delta^{36}S$	$\Delta^{33}S$	$\Delta^{36}S$
Monterey Fm	Sulfides	1	4.759	2.666	1.465	5.67	0.028	-0.53
		2	5.015	2.251	1.252	4.89	0.029	-0.51
		3	4.416	3.454	1.874	7.16	0.032	-0.53
	Sulfates	1	0.560	4.739	2.573	9.22	0.070	-0.89
		2	0.534	5.868	3.126	11.47	0.043	-0.790
		3	0.642	7.370	3.920	14.29	0.065	-0.84
	S^0	1	< 0.005	n/d	n/d	n/d	n/d	n/d
		2	< 0.005	n/d	n/d	n/d	n/d	n/d
		3	< 0.005	n/d	n/d	n/d	n/d	n/d
	Kerogen S_{org}	1	3.428	8.768	4.623	17.20	0.051	-0.60
		2	3.462	8.691	4.586	16.97	0.055	-0.68
		3	3.829	8.732	4.615	17.02	0.062	-0.71
	TLE S_{org}	1	0.339	5.871	3.145	11.62	0.061	-0.65
		2	0.269	n/d	n/d	n/d	n/d	n/d
		3	0.285	6.151	3.295	11.86	0.067	-0.94
Rozel Point	Sulfides	1	< 0.005	n/d	n/d	n/d	n/d	n/d
		2	< 0.005	n/d	n/d	n/d	n/d	n/d
		3	< 0.005	n/d	n/d	n/d	n/d	n/d
	Sulfates	1	< 0.005	n/d	n/d	n/d	n/d	n/d
		2	< 0.005	n/d	n/d	n/d	n/d	n/d
		3	< 0.005	n/d	n/d	n/d	n/d	n/d
	S^0	1	< 0.005	n/d	n/d	n/d	n/d	n/d
		2	< 0.005	n/d	n/d	n/d	n/d	n/d
		3	< 0.005	n/d	n/d	n/d	n/d	n/d
	Kerogen S_{org}	1	< 0.005	n/d	n/d	n/d	n/d	n/d
		2	< 0.005	n/d	n/d	n/d	n/d	n/d
		3	< 0.005	n/d	n/d	n/d	n/d	n/d
	TLE S_{org}	1	92.836	-6.165	-3.034	-11.58	0.081	-1.07
		2	90.728	-6.025	-2.963	-11.33	0.079	-1.08
		3	91.765	-5.960	-2.924	-11.18	0.085	-1.06
Lake Dziani	Sulfides	1	2.363	35.143	18.027	69.07	0.014	0.37
		2	2.485	35.651	18.278	69.86	0.008	0.17
		3	2.382	35.528	18.216	70.14	0.009	0.67
		4*	2.522	37.126	19.027	72.71	0.011	0.14
	Sulfates	1	0.353	n/d	n/d	n/d	n/d	n/d
		2	0.409	n/d	n/d	n/d	n/d	n/d
		3	0.484	n/d	n/d	n/d	n/d	n/d
		4*	0.387	33.216	17.077	64.86	0.040	-0.08
	S^0	1	0.647	n/d	n/d	n/d	n/d	n/d
		2	0.632	n/d	n/d	n/d	n/d	n/d
		3	0.709	n/d	n/d	n/d	n/d	n/d
		4*	0.556	39.583	20.245	77.67	-0.014	0.29
	Kerogen S_{org}	1	3.768	6.701	3.491	13.82	-0.019	-0.06
		2	3.478	5.933	3.119	12.05	0.003	-0.35
		3	3.812	6.781	3.546	14.05	-0.006	0.02
		4*	3.603	8.228	4.290	16.69	-0.004	-0.09
	TLE S_{org}	1	0.300	9.613	5.001	19.64	-0.003	0.21
		2	0.385	10.169	5.277	20.80	-0.012	0.30
		3	0.319	10.548	5.474	21.56	-0.010	0.34
		4*	0.256	9.070	4.705	18.17	-0.020	-0.21
Green Riv. Fm	Sulfides	1	10.002	34.714	17.733	68.98	-0.062	1.08
		2	9.960	35.337	18.050	69.98	-0.061	0.88
		3	9.303	35.266	17.999	69.78	-0.076	0.82
	Sulfates	1	0.905	27.832	14.248	n/d	-0.055	n/d
		2	< 0.005	n/d	n/d	n/d	n/d	n/d
		3	0.924	25.349	12.971	n/d	-0.070	n/d
	S^0	1	< 0.005	n/d	n/d	n/d	n/d	n/d
		2	< 0.005	n/d	n/d	n/d	n/d	n/d
		3	< 0.005	n/d	n/d	n/d	n/d	n/d
	Kerogen S_{org}	1	3.821	9.002	4.644	n/d	-0.047	n/d
		2	4.013	8.690	4.497	17.78	-0.034	0.11
		3	3.527	10.069	5.209	n/d	-0.029	n/d
	TLE S_{org}	1	2.302	5.848	3.062	12.03	-0.010	-0.22
		2	< 0.005	n/d	n/d	n/d	n/d	n/d
		3	2.331	5.718	3.001	12.98	-0.005	0.94

Fig. 1. Proposed workflow for the sequential recovery of organic and mineral S from sediments/oils as Ag_2S powders, prior to their fluorination and S multi-isotope analysis.

Fig. 2. Experimental setup used for S distillation; **a**, sample with gentle reflux, **b**, reducing solution ($CrCl_2$/STRIP), **c**, nitrogen flush, **d**, water acid-trap, **e**, silver nitrate sulfur-trap.

Fig. 3. Organic carbon content (**a**) and S_{org} recovery (**b**) of selected samples along 48 hours of NaOCl oxidation at 60°C.

Fig. 4. $\delta^{34}S$ of recovered S_{org} as a function of NaOCl oxidation time at 60°C.

Fig. 5. Comparison of S mass balances between bulk EA-IRMS and multi-pool SF_6-IRMS (new method) analyses; **a**, TS content calculated from Ag_2S weighing as a function of EA-IRMS bulk evaluation; **b**, bulk $\delta^{34}S$ calculated with mass-balance equations from multi-pool SF_6-IRMS analyses, as a function of EA-IRMS bulk evaluation. Error bars show the standard deviation between triplicate analyses.

Fig. 6. Multi-isotope data from the samples of this study; open diamonds, sulfides, open circles, sulfates, open triangles, S^0, black diamonds, soluble S_{org}, black circles, insoluble S_{org}. **a** and **c** show mass-dependent fractionation of all S-isotopes. **b** and **d** show the interest of the Δ notation to enhance the variability between samples.

Fig. 7. Comparison between $\delta^{34}S$ in sedimentary sulfides and kerogens. Data for the Green River Fm is from Tuttle & Goldhaber (1993), data for the Monterey Fm is from Zaback and Pratt (1992). The expected range for marine sediments is extrapolated after Orr (1986).

Fig. 8. Two possible models for S geochemistry and organic matter sulfurization during sediment deposition and diagenesis. **A** shows S fractionation associated with organic matter sulfurization in the anoxic part of the sediments in 'open' marine environments such as the Monterey Fm. The inflow S derives from marine sulfates. **B** shows S fractionation associated with organic matter sulfurization in a partially sulfidic stratified water column with a high H_2S/sulfates ratio from a 'closed' system such as some Green River Fm members and Lake Dziani Dzaha. The inflow S derives from enriched sulfates resulting from the Rayleigh fractionation of marine sulfates in a closed system (as suggested by Tuttle, 1991). MSR = Microbial Sulfate Reduction.

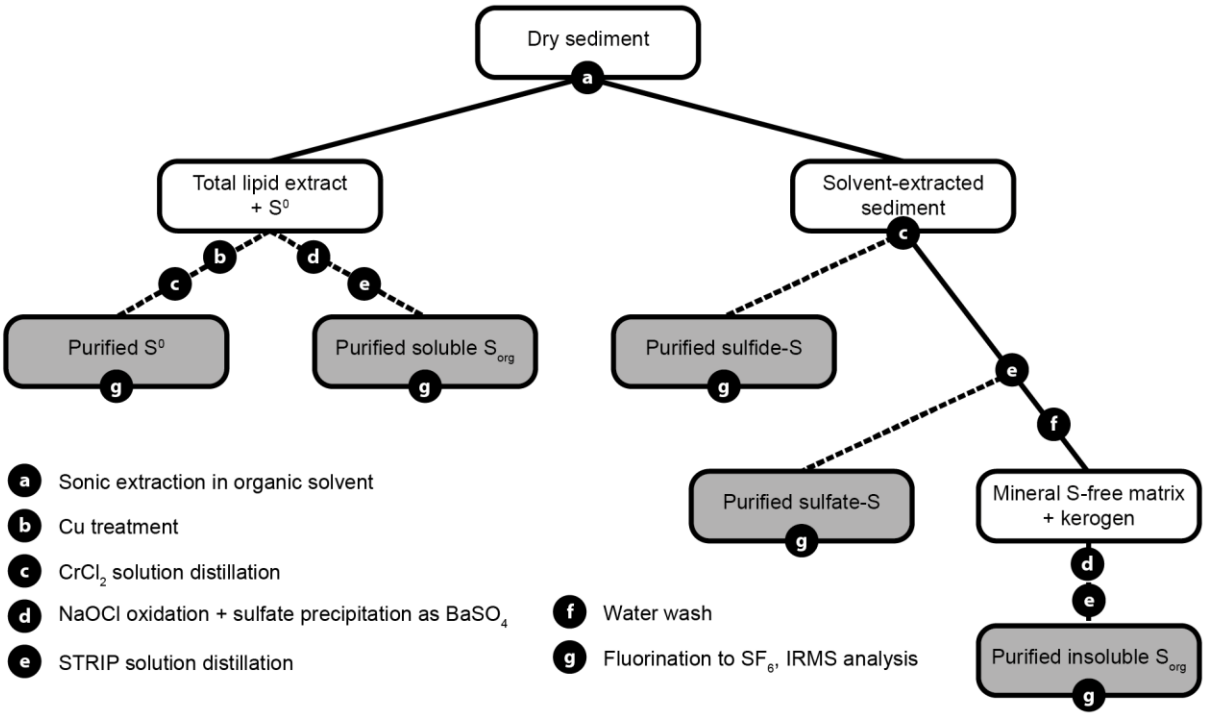
Dry sediment
a
Total lipid extract + S0
Solvent-extracted sediment
b
c
d
e
c
Purified S0
Purified soluble Sorg
Purified sulfide-S
g
g
g
e
f
Purified sulfate-S
Mineral S-free matrix + kerogen
d
e
Purified insoluble Sorg
g
a Sonic extraction in organic solvent
b Cu treatment
c CrCl2 solution distillation
d NaOCl oxidation + sulfate precipitation as BaSO4
e STRIP solution distillation
f Water wash
g Fluorination to SF6, IRMS analysis

Figure 1

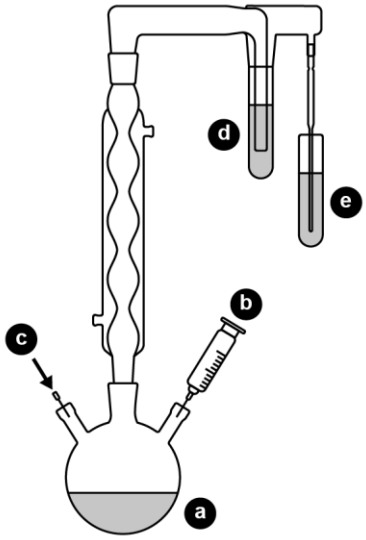

Figure 2

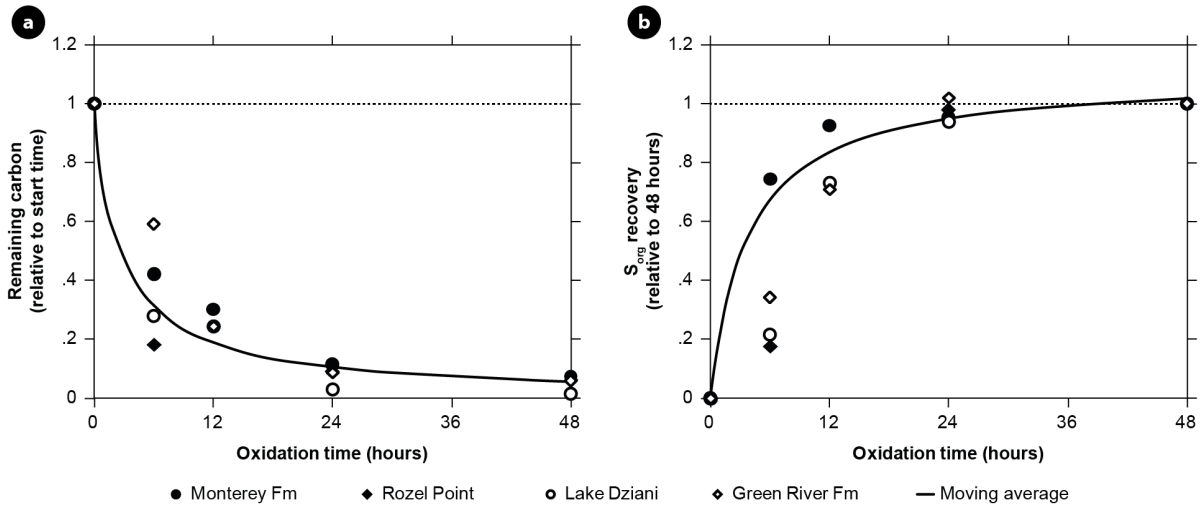
a
b
Remaining carbon
(relative to start time)
S_{org} recovery
(relative to 48 hours)
1.2
1
.8
.6
.4
.2
0
0
12
24
36
48
Oxidation time (hours)
Monterey Fm
Rozel Point
Lake Dziani
Green River Fm
Moving average

Figure 3

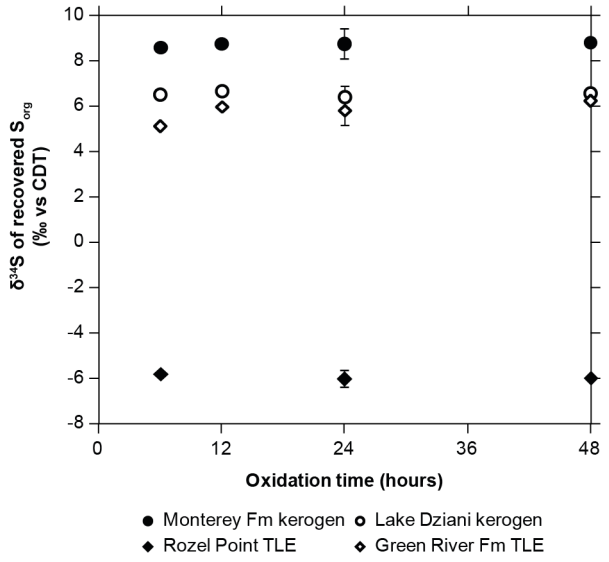
10
8
6
4
2
0
-2
-4
-6
-8
0
12
24
36
48
δ34S of recovered Sorg
(‰ vs CDT)
Oxidation time (hours)
Monterey Fm kerogen
Lake Dziani kerogen
Rozel Point TLE
Green River Fm TLE

Figure 4

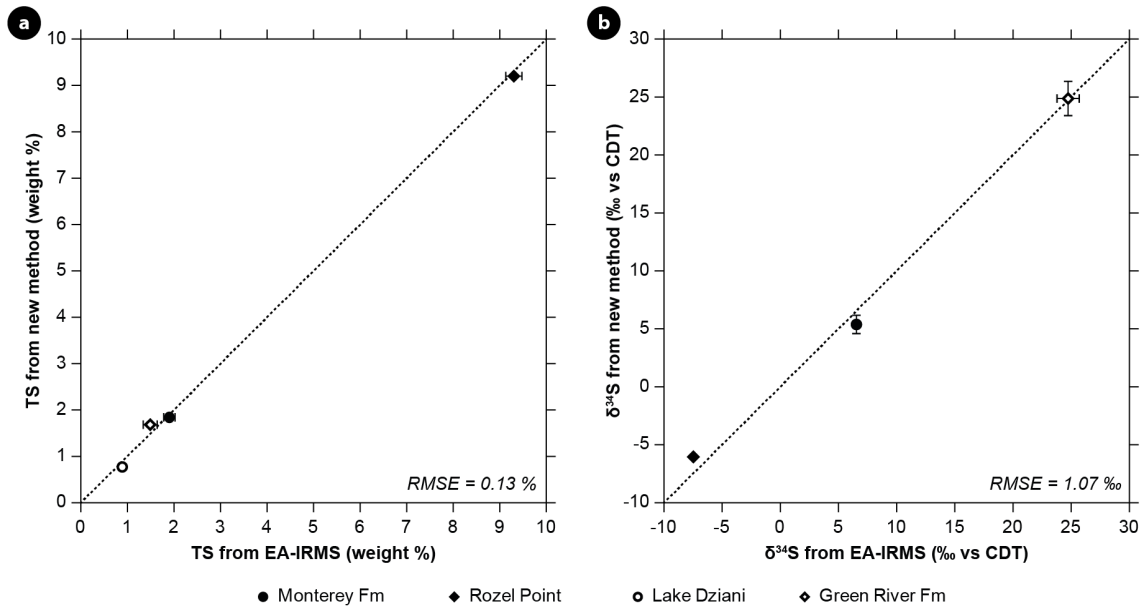
a
TS from new method (weight %)
TS from EA-IRMS (weight %)
RMSE = 0.13 %
b
δ³⁴S from new method (‰ vs CDT)
δ³⁴S from EA-IRMS (‰ vs CDT)
RMSE = 1.07 ‰
Monterey Fm
Rozel Point
Lake Dziani
Green River Fm

Figure 5

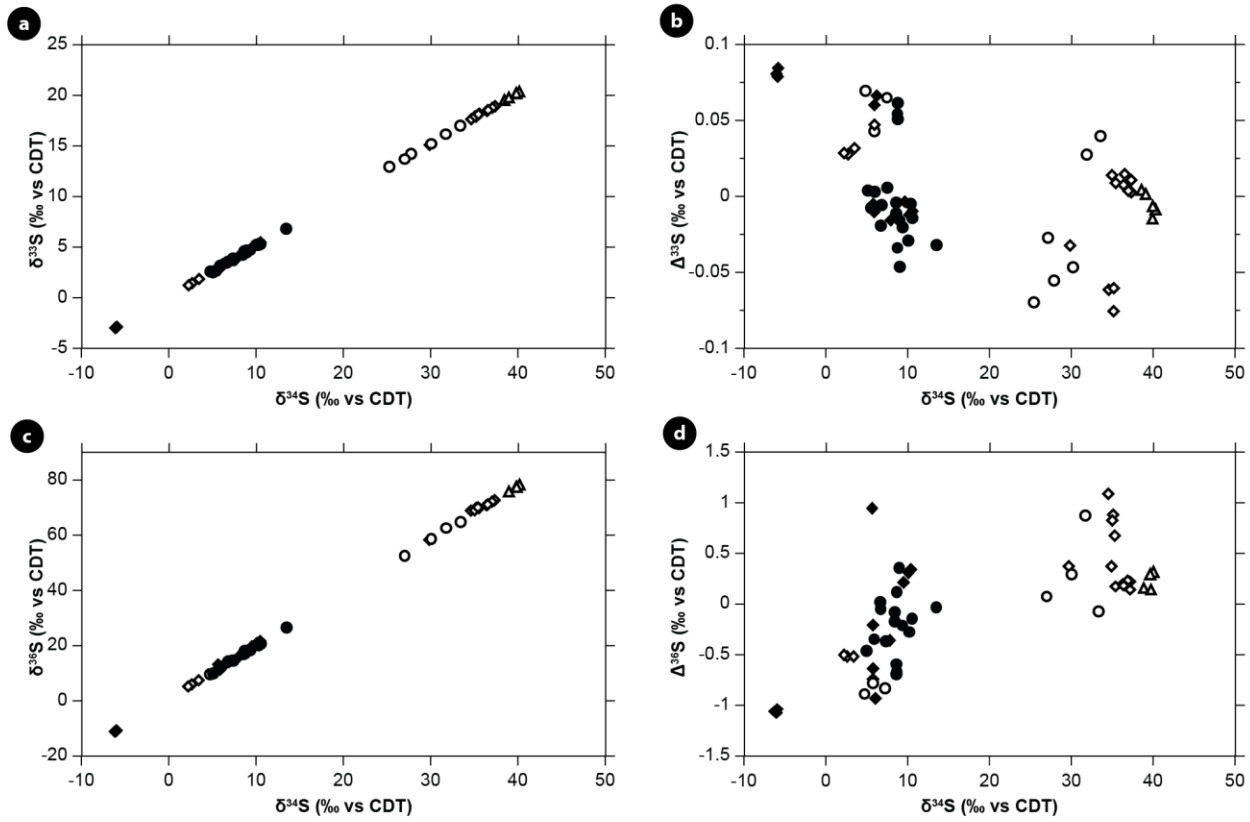

Figure 6

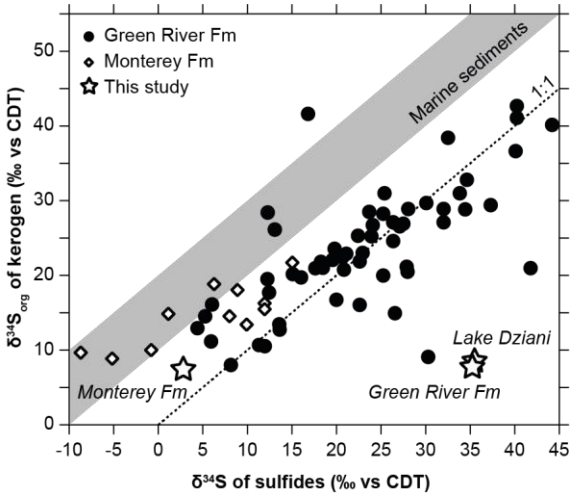
Green River Fm
Monterey Fm
This study
Marine sediments
1:1
Lake Dziani
Monterey Fm
Green River Fm
δ34Sorg of kerogen (‰ vs CDT)
δ34S of sulfides (‰ vs CDT)
0
10
20
30
40
50
-10
-5
0
5
10
15
20
25
30
35
40
45

Figure 7

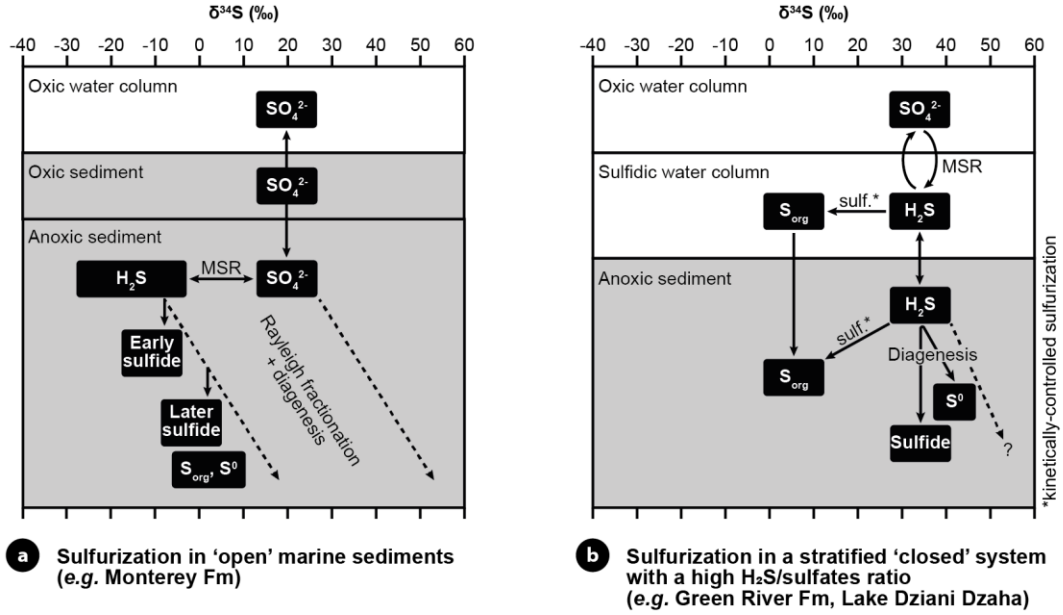
δ³⁴S (‰)
-40 -30 -20 -10 0 10 20 30 40 50 60
Oxic water column
SO4 2-
Oxic sediment
SO4 2-
Anoxic sediment
H2S
MSR
SO4 2-
Early sulfide
Later sulfide
Sorg, S0
Rayleigh fractionation + diagenesis
a
Sulfurization in 'open' marine sediments (e.g. Monterey Fm)
δ³⁴S (‰)
-40 -30 -20 -10 0 10 20 30 40 50 60
Oxic water column
SO4 2-
MSR
Sulfidic water column
Sorg
sulf.*
H2S
Anoxic sediment
H2S
sulf.*
Diagenesis
Sorg
S0
Sulfide
?
*kinetically-controlled sulfurization
b
Sulfurization in a stratified 'closed' system with a high H2S/sulfates ratio (e.g. Green River Fm, Lake Dziani Dzaha)

Figure 8