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Multiple sulfur isotopes ($\delta^{34}S$, $\Delta^{33}S$) of organic sulfur and pyrite from Late Cretaceous to Early Eocene oil shales in Jordan

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ABSTRACT

We present the first multiple sulfur isotope study (^{32}S, ^{33}S, ^{34}S, ^{36}S) of bulk kerogen sulfur (KS) and disulfides ('chromium-reducible sulfur', CRS) from the oil shale of the Umm Rijam Chert-Limestone and Muwaqqar Chalk Marl Formation, Jordan (Late Cretaceous to Early Eocene, appr. 50–70 Ma).

Analysis of the sulfur isotopic composition of KS ($\delta^{34}S_{KS}$) shows values ranging from 0.3 to 17.9‰, which are ^{34}S-enriched compared to the $\delta^{34}S_{CRS}$ ranging from −23.5 to −3.7‰. Values for CRS and KS are significantly ^{34}S-depleted compared to seawater sulfate sulfur which suggests a major input of early-diagenetic, microbially-generated sulfide. A minor contribution of assimilated seawater sulfate to KS is assumed. The ^{34}S-enrichment of KS compared to CRS can be partly explained by (1) sulfide oxidation to intermediate sulfur species prior to its incorporation into organic material, by (2) fractionations during organic sulfur generation, as well as by (3) a post-depositional timing of formation.

Additionally, we hypothesize, based on parallel depth trends of maturity parameters (e.g., vitrinite reflectance) and $\delta^{34}S_{CRS}$ and $\delta^{34}S_{KS}$ values, that the sulfur isotopic compositions were influenced by thermal maturation (catagenesis). We suggest that the CRS pool comprises a contribution of sulfide released during the thermal decomposition of KS.

Overall, our study highlights the importance of organic sulfur in sulfur isotopic studies and the potential of multiple sulfur isotope analyses in maturated sedimentary successions.

1. Introduction

Organic sulfur (OS) is the second most abundant reduced sulfur fraction in the sedimentary environment after pyrite sulfur and it has been reported to account for up to 80% of the total reduced sulfur pool (e.g. Monterey Fm; Zaback and Pratt, 1992). Sulfur isotope studies often focus on pyrite sulfur and neglect OS, despite its important role. Thus, mode and timing of OS formation are still poorly constrained (Anderson and Pratt, 1995; Brüchert and Pratt, 1996; Hartgers et al., 1997; Werne et al., 2003, 2008; Raven et al., 2015). In this study, we investigate the timing of OS generation and, moreover, the impact of thermal maturation on the sulfur species by analyzing multiple sulfur isotopes of chromium-reducible sulfur (CRS) and kerogen sulfur (KS).

The sulfur isotopic composition of organic sulfur depends on (1) the isotopic signature of the sulfur source (2) the isotopic fractionation accompanying the reduction of sulfate to sulfide, a possible re-oxidation to intermediate sulfur forms and any subsequent sulfur processing, (3) the reaction of the sulfur species with organic matter and (4) the thermal decomposition of OS during maturation. For (1), two main sulfur sources can be distinguished by different sulfur isotopic signatures: the assimilation of seawater sulfate and the incorporation of microbially-derived porewater sulfide. The assimilation of seawater sulfate, which is the active uptake into cell constituents (e.g. cysteine), is assumed to have only a small isotopic fractionation effect of −1 to −3‰ (Kaplan and Rittenberg, 1964). Thus, the sulfur isotopic composition of this organic sulfur would be quite similar to the $\delta^{34}S$ of seawater sulfate. Organic sulfur generated from microbially-derived porewater sulfide, in contrast to bio-synthetic sulfur, has a considerably ^{34}S-depleted isotopic signal. During microbial sulfate reduction (MSR), microbes preferentially reduce the isotopically lighter $^{32}SO_4$ to sulfide, which can induce a large isotopic fractionation between seawater sulfate and sulfide of up to 65.6‰ (*Desulfovibrio* sp.; Sim et al., 2011). The resulting sulfide either reacts with iron to form iron sulfides, is incorporated into organic matter forming OS or is again oxidized to intermediate sulfur species. Microbes can

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disproportionate these intermediate sulfur species (elemental sulfur, thiosulfate and sulfite, produced by sulfide oxidizers) to sulfide and sulfate (microbial sulfur disproportionation; MSD). Repeated cycles of MSD followed by sulfide oxidation can, thus, lead to a large cumulative isotopic fractionation between sulfide and the initial seawater sulfate (Canfield and Teske, 1996). Past studies often report that organic sulfur is enriched in ^{34}S compared to their corresponding pyrite sulfur (e.g. Zaback and Pratt, 1992; Anderson and Pratt, 1995; Werne et al., 2008) which was attributed to the late timing of formation and/or the fractionation during the sulfur incorporation into organic material. In general, the reaction of iron is kinetically favored over the reaction with organic matter, especially when there is an excess of highly-reactive iron relative to sulfide (Hartgers et al., 1997). This process produces a progressively ^{34}S-enriched sulfide pool that can react with organic matter after iron sulfide formation has ceased. However, several studies have shown that pyrite formation and organic matter sulfurization can occur simultaneously in sedimentary environments (Ferdelman et al., 1991; Brüchert and Pratt, 1996; Werne et al., 2003; Dale et al., 2009).

There is an isotopic fractionation associated with OS generation. Amrani and Aizenshtat (2004) suggest an isotopic fractionation of 4–5‰ during the incorporation of polysulfides and sulfides into carbonyl functional groups. Moreover, an equilibrium fractionation is proposed, where polysulfide is enriched in ^{34}S by 2–4‰ compared to sulfide (Amrani et al., 2006). The addition of both effects can already account for a ^{34}S-enrichment of about 10‰ in OS compared to coeval inorganic sulfur pools (Werne et al., 2008).

Another factor that can influence the isotopic composition of reduced sulfur species is thermal maturation. During maturation, macromolecular structures are breaking apart due to the cleavage of weaker S—S and C—S bonds of aliphatic structures (e.g. sulfides and thiols) in the beginning, followed by the cleavage of C—C bonds and finally the fusion of aromatic heterocyclic molecules (e.g. benzothiophenes and dibenzothiophenes; for an overview see Sinninghe Damsté and de Leeuw, 1990; Amrani, 2014). Each degradation step is accompanied by the release of sulfur as H_2S that can either re-react with organic material, react with iron to iron disulfides, or is released into an open system (Amrani et al., 2005). Thus, thermal maturation can highly influence the isotopic composition of the bulk OS and possibly the sedimentary sulfide if new iron disulfides are formed subsequently. In experimental studies it was shown that thermal maturation led to a ^{34}S-enrichment of the residual bulk (i.e. kerogen, bitumen, oil) samples due to the loss of isotopically light H_2S (pyro-bitumens are ^{34}S-enriched by +5 to +8‰ compared to the original kerogen (Aizenshtat and Amrani, 2004), organic sulfur is ^{34}S-enriched by 2‰ compared to its initial value before the hydrous pyrolysis experiment (Amrani et al., 2005)) and decreases the variability of sulfur isotopic signals between specific organic sulfur compounds (Rosenberg et al., 2017). Recently, Ellis et al. (2017) demonstrated that the difference in sulfur isotopic values of benzothiophenes (BTs) and dibenzothiophenes (DBTs) in crude oils of the Phosphoria Formation in the Bighorn Basin decreases with increasing thermal maturity. However, to our knowledge, there is no study so far that deals with the influence of thermal maturation on the multiple sulfur isotopic composition of bulk OS in naturally matured samples.

Multiple sulfur isotopes (^{32}S, ^{33}S, ^{34}S, and ^{36}S) are successfully applied to reveal paleoredox conditions (Shen et al., 2011; Zhang et al., 2015) and microbial processes in experimental (e.g. Johnston et al., 2007; Bradley et al., 2011; Leavitt et al., 2014, 2015; Antler et al., 2017) and field studies (e.g. Canfield et al., 2010; Tostevin et al., 2014; Wu et al., 2014; Zerkle et al., 2016). Process-specific differences are discernible in $\delta^{34}S$ vs $\Delta^{33}S$ correlations, i.e. sedimentary sulfide derived from MSR displays a distinct multiple sulfur isotopic composition ($-\delta^{34}S$ vs $+\Delta^{33}S$). Up to date, the multiple sulfur isotopic composition of bulk organic sulfur species has not been investigated. However, minor sulfur isotopes might provide critical information with respect to the mode of sulfur incorporation into organic matter.

We have conducted the first multiple sulfur isotope study of bulk kerogen sulfur of the Jordan Shale in order to identify its sulfur source and reveal the timing of its formation. Moreover, we examine the influence of maturation on the sulfur isotopic compositions of the reduced sulfur species CRS and KS. We propose that a new generation of pyrite was formed from sulfide that was released during the thermal decay of OS and this can alter the primary sulfur isotopic signal of CRS and KS.

2. Material and methods

2.1. Sulfur and carbon contents

The abundances of total sulfur (TS), total carbon (TC) and total inorganic carbon (i.e., carbonate carbon, TIC) were determined by IR spectroscopy of SO_2 and CO_2 with a CS-MAT 5500 (Ströhlein Instruments). For TS and TC, sample powder was mixed with a V_2O_5 catalyst and combusted at 1350 °C in an oxygen supply flow to SO_2 and CO_2. For TIC, 3 mL of 25% hydrochloric acid was added at 70 °C, liberating CO_2.

Accuracy and precision was monitored by repeated measurements of standard materials yielding 1.0 ± 0.1 wt% for sulfur in coal (NIST 2692b, n = 67) and 12.0 ± 0.6 wt% for inorganic/total carbon in calcium carbonate (Merck reagent grade $CaCO_3$, n = 72). Total organic carbon contents were calculated as the difference between TC and TIC.

2.2. Iron speciation

Iron speciation was performed following the extraction scheme described in Poulton and Canfield (2005), quantifying the abundances of total iron (Fe_T), Fe bound in carbonates (Fe_{carb}), in reducible oxides (Fe_{ox} including easily reducible oxides) and in magnetite (Fe_{mag}). Iron bound in pyrite (Fe_{Pyr}) is calculated from the yield of chromium-reducible sulfur (iron disulfides, CRS) during the sequential sulfur extraction (see Section 2.4). Highly-reactive iron (Fe_{HR}) is defined as the sum of Fe_{carb}, Fe_{ox}, Fe_{mag} and Fe_{Pyr}.

For the quantification of total iron, 100 mg of sample powder were placed in a porcelain crucible and combusted for 8 h at 450 °C. Subsequently, total iron was extracted with 1 mL of 6 N hydrochloric acid at 70 °C for 24 h.

For the sequential iron extraction, 100 mg of sample powder were extracted with 25 mL of sodium acetate at 50 °C for 48 h. The extract (containing Fe_{carb}) was separated from the residual powder. Then, 10 mL of 5% sodium dithionite solution buffered to pH 4.8 with 0.35 M acetic acid/0.2 M sodium citrate was added to the residue. After 2 h, the supernatant containing Fe_{ox}, was collected and immediately used for photometric analysis. Subsequently, Fe_{mag} was extracted from the residue with 10 mL of a 0.2 M ammonium oxalate/0.17 M oxalic acid solution for 6 h.

For the photometric analysis, 500 µL of the sample extract, 1000 µL ascorbic acid, 2500 µL phenantrolic and 5000 µL ammonium acetate solution were placed in a 50 mL volumetric flask and filled up with deionized water. After 30 min, the solution was analyzed at 515 nm using a Genesys Spektrophotometer Serie 10.

The following two parameters were calculated:

$$Fe_{Pyr}/Fe_{HR} = \frac{Fe_{Pyr}}{Fe_{carb} + Fe_{ox} + Fe_{mag} + Fe_{Pyr}} \quad (1)$$