



Refining the extraction methodology of carbonate associated sulfate: Evidence from synthetic and natural carbonate samples



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ABSTRACT

Sulfur and oxygen isotope analyses of trace and whole mineral sulfate are valuable in investigating diagenetic processes and the microbial communities that produced them, seawater anoxia, and paleoclimate. Oxygen isotopes are particularly useful in that they may also record alterations to the original isotope ratio, be it from post-depositional processes or oxidation of sulfide minerals during the chemical extraction procedure. Here we rigorously test several common methodological procedures of extracting carbonate associated sulfate (CAS) for sulfur and oxygen isotope analyses in order to generate a method that will extract only the CAS, while preserving associated organic reduced sulfur and sulfides for analysis. The results of these experiments on synthetically generated carbonates demonstrate that our proposed protocol sufficiently removes all non-CAS sulfate and does not result in oxidation of included sulfides. Analytical reproducibility (standard deviation) of synthetic carbonates is 0.1‰ (1 σ) for $\delta^{34}\text{S}$ and 0.3‰ (1 σ) for $\delta^{18}\text{O}$. Extractions of low pyrite, high organic matter geologic samples from the Monterey Formation across a range of facies types demonstrate a reproducibility (1 σ) of 0.4‰–0.7‰ for $\delta^{34}\text{S}$ and 0.8‰–1.3‰ for $\delta^{18}\text{O}$, resulting from sample heterogeneity. $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ from Monterey Formation samples do not demonstrate oxidation of organic matter, suggesting our proposed protocol will preserve organic sulfur. A high pyrite-concentration Jet Rock concretion demonstrates that additional sulfate can be produced during the non-CAS leaching processes from oxidation of pyrite. We show that pyrite from the Jet Rock concretion ceases to oxidize when the sample is leached under an anoxic environment.

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1. Introduction

Marine $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ are powerful parameters for characterizing seawater anoxia, perturbations in the global sulfur cycle, and productivity of microbial communities (e.g. $\delta^{34}\text{S}$: Thode et al., 1951; Burdett et al., 1989; Strauss, 1999; Hurtgen et al., 2002; Kamschulte and Strauss, 2004; Paris et al., 2014; Rennie and Turchyn, 2014a, $\delta^{18}\text{O}$: Claypool et al., 1980; Newton et al., 2004; Brunner et al., 2005; Bottrell and Newton, 2006; Rennie and Turchyn, 2014a). $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ of seawater sulfate are particularly useful in that the target isotope systems are coeval. Due to the long residence time of sulfate in seawater (~20 My) with respect to the oceanic mixing time (~1000 year), seawater sulfate will reflect a well-mixed system (Holland, 1984; Paytan et al., 1998), and these residence/mixing times are considered stable throughout much of the Phanerozoic. Exceptions to this stable system include the latest Permian/early Triassic (Luo et al., 2010) and the Early Jurassic (Newton et al., 2011), both demonstrating very low seawater sulfate concentrations that significantly decreased typical seawater sulfate

residence times. Perturbations in seawater sulfate $\delta^{34}\text{S}$ specifically will reflect changes in the global sulfur cycle, and characterize local productivity of microbial communities in the depositional environment and post-burial alteration, all of which will strongly fractionate seawater sulfate $\delta^{34}\text{S}$. Seawater sulfate $\delta^{18}\text{O}$ will reflect changes in riverine input and global climate regimes, as well as local bacterial or inorganic sulfide reoxidation (Fritz et al., 1989; Van Stempvoort and Krouse, 1994; Krouse and Mayer, 2000; Turchyn and Schrag, 2004). Given the power of seawater sulfate isotopes to characterize the cycle of weathering of continental material, burial, and preservation, there is a strong need to differentiate clearly between primary and diagenetic seawater sulfate $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$.

Early studies of paleoseawater sulfate focused on evaporite deposits (gypsum, barite, etc.) (e.g. Claypool et al., 1980; Nielsen, 1989; Holser, 1992). Due to the poor spatial and temporal continuity of evaporites and their preferential deposition in shallow water, evaporitic deposits are confined to studies characterizing oxic systems or tracking turnover of stratified systems (Strauss, 1997). Carbonate associated sulfate (CAS), which is structurally bound in the calcite lattice and substitutes for carbonate (Takano, 1985; Staudt et al., 1994), is pervasive spatially and temporally in marine deposits. Burdett et al. (1989) demonstrate a remarkable similarity between seawater sulfate $\delta^{34}\text{S}$ (20.80‰ \pm 0.36‰)

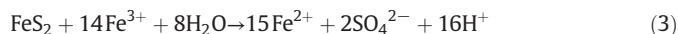
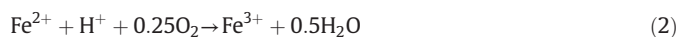
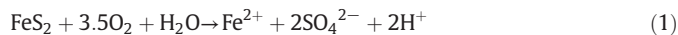
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and foraminiferal sulfate ($20.64\% \pm 0.39\%$), suggesting that CAS is an accurate reflection of seawater sulfate. Recent analyses of CAS using multicollector inductively coupled plasma mass spectrometry (MC-ICP-MS) demonstrate extraordinary accuracy for CAS $\delta^{34}\text{S}$ ($\sim 0.1\%$) on extremely small samples (nmol) of foraminiferal calcite (Paris et al., 2014). Biogenic carbonate shells, including foraminiferal calcite, are ideal given their high concentrations of sulfate (hundreds to thousands of ppm as opposed to tens of ppm for whole rock limestones) (Burdett et al., 1989; Kampschulte et al., 2001; Paris et al., 2014), yet have a few drawbacks. First, these recent advances using MC-ICP-MS cannot differentiate between $\delta^{18}\text{O}$ from carbonate versus $\delta^{18}\text{O}$ from sulfate. Therefore, carbonate shell $\delta^{18}\text{O}$ analyzed via MC-ICP-MS will reflect some combination of seawater and seawater sulfate $\delta^{18}\text{O}$. Second, relying on the presence of carbonate shells imposes a limitation to the depositional environments in which these shells are generated. For example, if a foraminifera species only calcifies under oxic conditions, foraminiferal CAS from an anoxic depositional environment will only record the global seawater sulfate $\delta^{34}\text{S}$, and will omit the isotopic fractionations associated with anaerobic microbial ecosystems of the depositional environment. Therefore, only foraminifera that can calcify under anaerobic conditions will be useful for describing the depositional environment and early burial conditions. To date, only a few foraminifera have been shown to calcify under anoxic conditions, carefully controlled in a laboratory (Nardelli et al., 2014). As a result, whole rock CAS $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ are the most versatile in application, being useful from abyssal to coastal and lagoonal systems (Hurtgen et al., 2002; Kampschulte and Strauss, 2004; Loyd et al., 2012; Wotte et al., 2012a,b).

One of the greatest limitations of whole-rock CAS analyses of $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ lies in isolating primary and diagenetic values from isotopic artifacts generated during analytical extraction of CAS. Bacterial sulfate reduction will increase $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ of CAS substrate during early diagenesis due to preferential uptake of ^{32}S and ^{16}O by sulfate reducing bacteria (e.g. $\delta^{34}\text{S}$: Thode et al., 1951; Strauss, 1997, $\delta^{18}\text{O}$: Mitzutani and Rafer, 1973; Fritz et al., 1989; Brunner et al., 2005; Antler et al., 2013). However, oxidation of sulfides (e.g. H_2S , pyrite, galena, sphalerite, marcasite), whether by microbial oxidation or inorganic oxidation, generate lower $\delta^{34}\text{S}_{\text{CAS}}$ and may increase or decrease $\delta^{18}\text{O}_{\text{CAS}}$ values (Taylor et al., 1984; Böttcher and Thamdrup, 2001). Additional non-CAS sulfate can be introduced to surface outcrops and may produce a distinctive positive $\Delta^{17}\text{O}$ (Peng et al., 2014). Oxygen isotope compositions of CAS therefore serve as a measure of both the primary and early diagenetic conditions, as well as an additional check on possible sample contamination or isotopic artifacts generated during analytical extractions.

The typical CAS extraction procedure follows three phases: 1) leaching of soluble, non-CAS sulfur compounds, 2) dissolution of carbonate minerals to liberate lattice-bound SO_4^{2-} , and 3) precipitation of liberated SO_4^{2-} as BaSO_4 . Therefore, it is imperative first to remove all soluble, non-CAS sulfate, then remove associated sulfides without oxidizing sulfides to sulfate. Sulfides can oxidize via the following reactions (shown for pyrite):



where Fe^{2+} production by microbially mediated sulfide oxidation (Eq. (1)) promotes further inorganic oxidation of sulfides (Eq. (3)) when Fe^{2+} is oxidized to Fe^{3+} (Eq. (2)). Sulfides can also be inorganically oxidized (Eq. (3)), which may be more common in laboratory processing of samples. Of these reactions, microbial sulfide oxidation, initiated by the use of atmospheric oxygen as the oxidant, is orders of magnitude more rapid as a process for generating sulfate (Eqs. (2) and (3)) (Nordstrom and Southam, 1997). If associated sulfides are oxidized

during extraction, $\delta^{34}\text{S}$ will reflect a mixture of $\delta^{34}\text{S}_{\text{CAS}}$ and $\delta^{34}\text{S}_{\text{sulfide}}$, whereas $\delta^{18}\text{O}$ will reflect mixing between $\delta^{18}\text{O}_{\text{CAS}}$ and $\delta^{18}\text{O}$ derived from the extraction procedure (Eq. (3)).

In their pioneering study, Burdett et al. (1989) used sodium hypochlorite (NaOCl) to remove organic and non-CAS sulfate and sulfides (e.g., organic sulfur, sulfides, sulfate salts). This method has been utilized in many CAS extraction methodologies, with several modifications. The leaching step to remove non-CAS sulfur and sulfides varies from soaking in NaOCl , NaCl , H_2O_2 , rinsing in deionized water for 12–24 h, or a combination of all four (Burdett et al., 1989; Ohkouchi et al., 1999; Kampschulte et al., 2001; Hurtgen et al., 2002; Fike et al., 2006; Fike and Grotzinger, 2008; Marenco et al., 2008; Gill et al., 2011; Shen et al., 2011; Loyd et al., 2012; Xiao et al., 2012). NaOCl is used to remove organic sulfur and H_2O_2 to remove pyrite (Eqs. (1) and (3)) (Shen et al., 2011). However, in many cases, we wish to preserve the organic sulfur and associated sulfides so that they may be analyzed from the insoluble residue resulting from CAS extraction. As a result, several researchers have adopted the use of a NaCl solution, which will not remove organic sulfur or pyrite, but will leach soluble sulfate minerals such as gypsum, epsomite, and surface-adsorbed sulfate. Still others use deionized water as a leachate solution. However, Peng et al. (2014) has recently shown that deionized water will not adequately leach non-CAS phases.

Therefore, the difficulties in preserving the sulfides, organic sulfur, and CAS are to a) remove all non-CAS sulfate-bearing phases without adding to the sulfate pool and b) avoid oxidizing the remaining sulfides, which will produce sulfate. As an additional measure, some researchers attempt to reduce the possibility of pyrite oxidation to sulfate (Eqs. (1) and (3)) by varying the strength of HCl used to liberate lattice-bound SO_4^{2-} (e.g. Burdett et al., 1989; Newton et al., 2004; Fike et al., 2006; Marenco et al., 2008). Likewise, some researchers have completed acidification under anoxic or N_2 conditions to further reduce the possibility of oxidation (Fike et al., 2006; Fike and Grotzinger, 2008) or by adding HCl slowly using a dropping funnel in an unsealed vessel (Marenco et al., 2008). A few recent studies have added SnCl_2 during the acidification step to reduce associated Fe^{3+} that may oxidize pyrite (Planavsky et al., 2012; Rennie and Turchyn, 2014a) based on the experimental monosulfide extractions of Chanton and Martens (1985). If sulfides are oxidized during CAS extraction, $\delta^{34}\text{S}$ will reflect a mixture of sulfide and CAS $\delta^{34}\text{S}$. Similarly, oxidation of sulfides during extraction will produce $\delta^{18}\text{O}$ values that reflect a mixture of CAS $\delta^{18}\text{O}$ and atmospheric or water $\delta^{18}\text{O}$ (with associated isotopic fractionations) used in the leaching and/or dissolution steps (Eq. (3)).

Our goal is to identify the extraction techniques that will preserve organic sulfur and sulfides in the resulting residue, while maintaining the original $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ of CAS. Therefore, here we test the most common methods of CAS extraction on synthetically generated CAS-carbonates. We compare synthetic CAS that are leached and unleached using a NaCl solution, with and without the presence of pyrite, and under atmospheric and N_2 headspace conditions. By testing various methods on synthetic CAS-carbonates in which pyrite concentrations can be controlled, we establish a refined protocol for CAS extraction. In addition, we compare $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ analyses from the proposed procedure to samples in which we anaerobically and abiotically forced associated pyrite to oxidize. We evaluate the purity of several BaSO_4 precipitates by comparing chromatography and energy dispersive x-ray spectroscopy (EDX). Our proposed protocol is then applied to several natural, geologic samples from different facies types of the mid-Miocene Monterey Formation to test the reproducibility of extraction and analysis of natural samples.

2. Development of analytical methods

2.1. Synthetic CAS precipitation

Synthetic CAS-carbonates were generated for these experiments so that leaching and CAS extraction techniques could be compared based

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