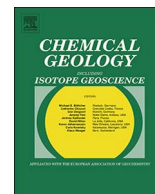




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Diagenesis of carbonate associated sulfate

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ABSTRACT

Carbonate associated sulfate (CAS) is a proxy for the seawater redox conditions of ancient oceans. Despite its frequent utilization from altered carbonate archives, the impact of diagenetic and anchimetamorphic overprint on CAS itself has not yet been calibrated in a systematic manner. In the present study, CAS abundances and sulfur and oxygen isotopic compositions from early diagenetic sabkha type dolomiticrites (Triassic Dolomia Principale Formation) were compared with geochemical ($^{87}\text{Sr}/^{86}\text{Sr}$, $\delta^{13}\text{C}_{\text{carb}}$, $\delta^{18}\text{O}_{\text{carb}}$), optical (cathodoluminescence), and crystallographical data to assess the impact of burial alteration. Data shown here document that $\delta^{34}\text{S}_{\text{CAS}}$ withstands burial diagenesis or anchimetamorphosis (350 °C) and reliably preserves a record of ambient seawater sulfate and early diagenetic redox processes. In contrast, $\delta^{18}\text{O}_{\text{CAS}}$ ratios of early diagenetic dolomites exposed to burial temperatures of 200 °C and more are enriched in ^{18}O likely due to exchange between $\delta^{18}\text{O}_{\text{CAS}}$ and $\delta^{18}\text{O}_{\text{carb}}$. Carbonate associated sulfate concentrations are directly affected by burial conditions: Under increasing burial depth, temperature, and cation order in the increasingly stoichiometric dolomite crystal lattice, CAS concentration decreases linearly from a mean value of 470 ppm in samples that experienced a burial temperature of 100 °C to values below analytical detection in samples exposed to burial fluids with temperatures in excess of 350 °C. Significant variations of $\delta^{34}\text{S}_{\text{CAS}}$ in samples from the northern Alps are further attributed to local sulfide oxidation triggered by the influence of meteoric water as based on the $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ values of the water soluble sulfate (WSS). The data shown here are of significance for those concerned with the chemical parameters of ancient oceans and shed light on processes during dolomite formation and diagenetic pathways.

1. Introduction

Carbonate associated sulfate (CAS) is sulfate that is liberated by dissolving the host carbonate rock and/or biogenic carbonate. Previous studies have proven that sulfur isotope values in CAS are similar to those from more traditional sulfate proxies, i.e. evaporites and barites. Hence, $\delta^{34}\text{S}_{\text{CAS}}$ reflects the sulfur isotopic composition of ambient seawater sulfate (Balan et al., 2014, but see Present et al., 2015 for an alternative view). Carbonate associated sulfate is used for reconstructing the evolution of the marine sulfur cycle, for characterizing redox conditions and for identifying biological activity in former oceans. Thus, temporal variations in $\delta^{34}\text{S}_{\text{CAS}}$ reflect changes in marine sulfur cycling during Earth's history (Kampschulte and Strauss, 2004; Newton et al., 2004; Fike and Grotzinger, 2008; Song et al., 2014; Wu et al., 2014; Schobben et al., 2015). When investigating the marine sulfur cycle, CAS provides some advantages over barite and evaporites: carbonate rocks are present throughout the entire geological record, their age can often be constrained, and their origin is not related to

specific environmental conditions such as progressive evaporation. However, during diagenesis carbonates are prone to alteration and recrystallization providing opportunities for changing the CAS concentration and the $\delta^{34}\text{S}_{\text{CAS}}$ and $\delta^{18}\text{O}_{\text{CAS}}$ signals.

Bacterial sulfate reduction (BSR) and pyrite oxidation are the two principal processes that control the $\delta^{34}\text{S}$ value of marine sulfate (Claypool et al., 1980; Bottrell and Newton, 2006). In times of enhanced microbial sulfate reduction and subsequent pyrite burial, the dissolved marine sulfate becomes enriched in ^{34}S due to the preferential turnover of isotopically light sulfate sulfur by sulfate-reducing bacteria (i.e. $^{32}\text{SO}_4$) (Harrison and Thode, 1957; Kaplan and Rittenberg, 1964). The $\delta^{18}\text{O}$ value of CAS exhibits only limited fractionation compared to the $\delta^{18}\text{O}$ values of dissolved sulfate (Cortecci and Longinelli, 1971; Newton et al., 2004). Yet, it is more complex than the $\delta^{34}\text{S}$ values of CAS and can also display signals from other processes (Cortecci and Longinelli, 1973; Rennie and Turchyn, 2014). Similar to $\delta^{34}\text{S}_{\text{CAS}}$, the $\delta^{18}\text{O}$ value of residual sulfate increases during BSR, but with a smaller fractionation factor (Mizutani and

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Rafter, 1973). In contrast, sulfide oxidation can result in different oxygen isotopic compositions for the resulting sulfate depending upon the respective oxygen source (Lloyd, 1968). Notably, oxygen can either be of atmospheric origin or come from the ambient water, depending on the redox conditions and the biological activity (Lloyd, 1967; Balci et al., 2007).

In addition to CAS, i.e. the carbonate assumed to be part of the crystal lattice, another sulfate phase is present in carbonates. Water soluble sulfate (WSS) is the first sulfate phase that is liberated during a sequential wet chemical CAS extraction (Wotte et al., 2012). This phase represents a trace to minor constituent in most carbonate rocks and can result either from syndimentary evaporative processes (i.e. co-precipitation of a true evaporative sulfate mineral) or from sulfide oxidation during diagenesis. Frequently, the $\delta^{34}\text{S}_{\text{WSS}}$ is lower than the $\delta^{34}\text{S}_{\text{CAS}}$ indicating an influence of oxidized sulfides (Kampschulte, 2001). Thus, depending on its origin, the $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ values of WSS reflect the sulfur and oxygen isotopic compositions of ambient seawater or the oxidized ^{34}S -depleted sulfide sulfur that originated from BSR. The $\delta^{18}\text{O}$ value of WSS reflects the oxygen source that fostered sulfide oxidation.

Disagreement exists with regard to the environmental conditions that control sulfate incorporation into (biogenic) carbonates, the exact mode of incorporation, and the structural position of CAS in the carbonate (Takano, 1985; Cuif et al., 2003; Dauphin et al., 2005; Tamenori et al., 2014; Perrin et al., 2017). These uncertainties in our understanding are also caused by significant differences in CAS concentration in biogenic carbonates and bulk rocks. CAS concentration in modern biogenic carbonates usually varies around an average of 600 ppm (Staudt and Schoonen, 1995; Kampschulte and Strauss, 2004). In contrast, most carbonate rocks show CAS concentrations below 100 ppm (Kampschulte and Strauss, 2004). Moreover, a direct and quantitative correlation between the CAS concentration in carbonate rocks and the sulfate concentration of their ambient aquatic environment at precipitation is not apparent. At present, only few studies have addressed the effects of early diagenetic processes on CAS (Takano, 1985; Loyd et al., 2012; Rennie and Turchyn, 2014; Swart, 2015). A link between the $\text{SO}_4^{2-}/\text{CO}_3^{2-}$ ratio in the diagenetic fluid and the sulfate concentration in carbonates was reported by Staudt and Schoonen (1995) and Swart (2015). These authors also proposed that low ratios of sulfate-to-carbonate will lead to low sulfate concentrations in carbonates formed during marine diagenesis (Swart, 2015) as well as in burial dolomites (Staudt and Schoonen, 1995). This implies a strong control of fluid composition on the CAS concentration during progressive diagenesis.

Presumably, increasing burial temperature results in an increase in intensity of water-rock-interaction. Consequently, a series of differently altered carbonate rocks would offer a way for reconstructing past seawater sulfate concentration via back-extrapolation of present CAS concentrations. Early diagenetic processes, including BSR can alter the concentration and isotope ratios of CAS (Loyd et al., 2012). The low ratio of dissolved sulfate to CAS during meteoric diagenesis, for example, causes a decrease in CAS concentration without changing $\delta^{34}\text{S}_{\text{CAS}}$ (Gill et al., 2008). In contrast, early marine diagenesis has been documented to alter the sulfur and oxygen isotope signal by processes such as recrystallization, and incorporation of sulfate from (^{34}S enriched) pore waters affected by BSR (Rennie and Turchyn, 2014). A change in the sulfur isotopic composition in CAS during diagenetic loss has only been described as a result of BSR in early diagenetic environments (Swart, 2015).

During burial diagenesis, anchimetamorphism (i.e. the temperature range between 200 and 350 °C), and low grade metamorphism (i.e. at temperatures moderately above 350 °C), $\delta^{18}\text{O}_{\text{CAS}}$ is likely to exchange with oxygen isotopes of diagenetic and/or metamorphic fluids or carbonate oxygen ($\delta^{18}\text{O}_{\text{carb}}$). This could be visible by enriched CAS oxygen isotope values. With progressing burial depth, water soluble sulfates such as gypsum and anhydrite are successively dissolved

starting with dewatering of gypsum and crystallization to anhydrite and later aragonite (Carulli and Colussi, 1974; Scheffler et al., 2015). During the nucleation and precipitation of diagenetic carbonate phases, water soluble sulfate with probably lower $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ values than the primary CAS could be incorporated. Consequently, late diagenetic recrystallization could result in an isotope exchange between CAS and WSS. Thermochemical sulfate reduction (TSR) starts at temperatures between 100 °C and 200 °C, provided sufficient organic matter is available. Enrichments in ^{34}S of up to 10‰ in the residual sulfate have been reported (Machel, 2001).

This paper reports on the effects of burial diagenesis and low-grade metamorphism on CAS concentration and its sulfur and oxygen isotopic compositions in a natural laboratory, the Upper Triassic Hauptdolomit Formation (Dolomia Principale) in the Eastern and Southern Alps. The aims of this study are twofold: First, the hypothesis is tested that with increasing burial, a potential loss in CAS concentration is commonly found whereas $\delta^{34}\text{S}_{\text{CAS}}$ values remain unchanged. The $\delta^{18}\text{O}_{\text{CAS}}$ values may change to either lower or higher isotope ratios, depending on the dominant source of oxygen (commonly a burial brine). Second, the isotope exchange between different sulfate phases (CAS and WSS) and the relationship between CAS concentration and progressive diagenetic stabilization of dolomites is tested and discussed. The outcome of this study is of relevance for those applying carbonate associated sulfate and its isotope ratios to ancient carbonate rocks. It serves as an important baseline against which proxy data can be tested and calibrated.

2. Geotectonic setting, sample material and study sites

The Upper Triassic Hauptdolomit (Norian; Dolomia Principale) facies expands over large parts of central Europe (Pfiffner, 2010). The Hauptdolomit is composed of early diagenetic dolomite, minor proportions of limestone and calcite cements, and bituminous carbonate (Müller-Jungbluth, 1970; Fruth and Scherreiks, 1984). The stratigraphic thickness varies substantially and reaches a maximum of 2300 m. The calcitic (and aragonitic) sediments that originally formed the Hauptdolomit were deposited in sub- to supratidal environments along the northern passive margin of the Adriatic plate (Ziegler, 1988; Zorlu, 2007). The Hauptdolomit represents an example of the sabkha-type model including seepage reflux and evaporative pumping promoting dolomite precipitation (McKenzie et al., 1980; Warren, 2000; Meister et al., 2013). Evidence for hypersaline, sabkha environment with temporary surface exposure and sporadic influence of meteoric waters include paleosols, vadose features, sheet cracks, evaporite layers and silicified sulfate nodules (Fruth and Scherreiks, 1984; Frisia and Wenk, 1993; Mastandrea et al., 2006; Zorlu, 2007). For a detailed description and facies type analysis of the Hauptdolomit please refer to Müller-Jungbluth (1970), Gianolla et al. (2003), Zorlu et al. (2007), and Meister et al. (2013).

During Alpine orogeny, the Hauptdolomit in the Eastern Alps experienced burial and overprint caused by intense tectonic deformation while in the Southern Alps, tectonic activity only led to weak deformation (Zorlu, 2007). Because of its rather homogenous dolomite facies and regionally variable diagenetic overprint, the Hauptdolomit facies has been in the focus of a series of previous studies (e.g., Kürmann and Richter, 1989; Iannice and Frisia, 1994; Geske et al., 2012). Burial temperatures at different study sites were assessed by conodont color alteration index, vitrinite reflectance, and calcite thermometry (Dietrich, 1983; Kürmann and Richter, 1989; Gawlick and Königshof, 1993). Geske et al. (2012) reported geochemical ($^{87}\text{Sr}/^{86}\text{Sr}$, $\delta^{18}\text{O}_{\text{carb}}$, $\delta^{13}\text{C}_{\text{carb}}$, trace metal concentrations, cathodoluminescence imaging), and crystallographic parameters (mol% CaCO_3 , degree of cation order) and observed a homogenization of the data with increasing burial overprint.

Five sampling locations throughout the Eastern and Southern Alps were chosen for their different degrees of diagenetic alteration and burial temperatures (Fig. 1). Across all sampling locations, the recon-

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