A carbonate-based proxy for sulfate-driven anaerobic oxidation of methane

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ABSTRACT

Sulfate-driven anaerobic oxidation of methane (SD-AOM) supports chemosynthesis-based communities and limits the release of methane from marine sediments. Formation of authigenic carbonates at active methane seeps is promoted by SD-AOM stoichiometry. While distinctively small δ18O/δ34S slopes of pore fluid sulfate have been shown to typify modern methane-rich environments, identification of such environments has been difficult for the geological past due to the lack of sedimentary pore fluids. However, if the isotopic composition of sulfate were archived in authigenic carbonate during early diagenesis, carbonate-associated sulfate (CAS) should display the characteristic δ18O-δ34S pattern. To test this hypothesis, we investigated the δ18OCAS/δ34SCAS and 87Sr/86Sr signatures of authigenic carbonate minerals from three modern and two ancient methane-seep provinces. The data obtained demonstrate that all deposits regardless of age or location display consistently small δ18O/δ34S CAS slopes (~0.3) and CAS does not represent ambient seawater but pore-water sulfate. This finding confirms the utility of CAS as a recorder of SD-AOM in methane-rich environments. In addition, we report that aragonites bear higher CAS contents, ~Sr/86Sr ratios closer to that of contemporary seawater, and a larger δ18OCAS/δ34SCAS slope than calcites, reflecting the shallower formation depth of aragonite where pore-water has a composition close to that of seawater with high concentrations of sulfate. The new proxy can be used to constrain the record of SD-AOM through most of Earth history by measuring the δ18O and δ34S values of CAS of methane-derived diagenetic carbonates including but not limited to seep carbonates.

INTRODUCTION

Sulfate-driven anaerobic oxidation of methane (SD-AOM) has been shown to consume 90% or more of the methane produced in subsurface seafloor environments (e.g., Niewöhner et al., 1998; Knittel and Boetius, 2009). In methane-rich marine sediments, methane oxidation is primarily coupled to sulfate reduction, which is mediated by a consortium of anaerobic methanotrophic archaea and sulfate-reducing bacteria (Boetius et al., 2000). Although other electron acceptors are known to be able to sustain anaerobic oxidation of methane, SD-AOM sustains some of the richest marine ecosystems along modern continental margins at sites referred to as methane seeps (e.g., Boetius and Wenzhöfer, 2013). It has been shown that rates of sulfate reduction in methane-seep sediments can be several orders of magnitude higher than in non-seep sediments (Aharon and Fu, 2000; Joye et al., 2004). Sulfate, the electron acceptor, can change its concentrations, fluxes, and stable sulfur and oxygen isotope compositions during SD-AOM (Aharon and Fu, 2000; Joye et al., 2004; Bowles et al., 2014). However, SD-AOM processes could have been insignificant in the geological past when sulfate concentration was low (Bristow and Grotzinger, 2013). Thus, a geological record of SD-AOM can provide information on the evolution of Earth’s surface environments and specifically the sulfate concentration in paleo-oceans.

Oxygen and sulfur stable isotope compositions of dissolved sulfate (δ18O/δ34S) in modern sedimentary pore fluids affected by both organotrophic and methanotrophic microbial sulfate reduction have been analyzed to explore the respective operation modes (e.g., Böttcher et al., 1998, 2001; Aharon and Fu, 2000; Antler et al., 2013, 2014, 2015; Deusner et al., 2014; Rennie and Turchyn, 2014). Antler et al. (2015) discovered that SD-AOM in methane-rich environments results in distinctively small δ18O/δ34S sulfate slopes (0.24–0.4), which differ from the larger slopes typifying organotrophic sulfate reduction or sites of diffusive flux of methane within marine sediments. It has been put forward that barite deposits might be a potential proxy to look into the geological record of AOM (e.g., Böttcher and Parafiniuk, 1998; Torres et al., 2003). However, authigenic barite is relatively sparse in contrast to carbonate at modern seeps and in ancient seep deposits (Peckmann and Thiel, 2004; Campbell, 2006). Authigenic carbonate commonly forms under both methane diffusion–controlled and methane-rich conditions (Luff and Wallmann, 2003), and carbonate minerals can preserve pore-water sulfate as carbonate-associated sulfate (CAS; Staudt and Schoonen, 1995). Methane-seep carbonates have been reported to occur throughout much of Earth history (e.g., Peckmann and Thiel, 2004; Campbell, 2006), and their carbon and oxygen isotope signatures reflect the involvement of methane in sulfate reduction–driven authigenesis.

To examine if the isotopic composition of CAS from seep carbonates indeed reveals a specific, characteristically small δ18O/δ34S slope, we conducted a survey of δ18OCAS/δ34SCAS data pairs from three modern (Gulf of Mexico; Black Sea; South China Sea) and two ancient (Neogene, northern Italy; Paleogene, western Washington State, USA) seep provinces (Fig. 1). The focus is on seep carbonates from the Gulf of Mexico where a great number of samples representing different types of seepage were available and the presence of both aragonite and calcite mineralogies allowed for a mineral-specific analysis of CAS composition.

MATERIALS AND METHODS

Authigenic carbonates used for this study have been previously shown to represent marine hydrocarbon-seep deposits (see the GSA Data
RESULTS

The overall $\delta^{34}S_{CAS}/\delta^{18}O_{CAS}$ slopes are more or less parallel among the modern samples (Gulf of Mexico and Black Sea), the Neogene samples, and the Paleogene samples with slopes of 0.28 ($R^2 = 0.81$, n = 52), 0.29 ($R^2 = 0.89$, n = 5), and 0.32 ($R^2 = 0.94$, n = 5), respectively (Fig. 2). On a plot of Gulf of Mexico samples that distinguishes aragonite and calcite mineralogy, the CAS isotope data for aragonite and for calcite have slopes of 0.53 ($R^2 = 0.81$, n = 12) and 0.30 ($R^2 = 0.80$, n = 38), respectively, with the aragonite array falling on a line with open-ocean seawater sulfate ($\delta^{18}O = 8.7‰$, $\delta^{34}S = 21.2‰$; Johnston et al., 2014; Fig. 3), whereas the calcite array projects to higher $\delta^{18}O$ and $\delta^{34}S$ values.

The CAS contents in Gulf of Mexico aragonite and calcite vary widely and without an apparent pattern, clustering around averages of 249 ppm ($\pm 145$, 1 standard deviation [SD], n = 12) and 188 ppm ($\pm 141$, 1 SD, n = 38), respectively (Table DR2 in the Data Repository). The experimental procedures used ensured that the observed CAS stable isotope patterns represent primary signatures reflecting pore-water sulfate at the respective seep sites.

DISCUSSION

The $\delta^{18}O_{CAS}/\delta^{34}S_{CAS}$ plots of modern and ancient methane-seep carbonates reveal not only strong correlations, but more importantly, a characteristic slope of ~0.3. This slope is at the lower end of the $\delta^{18}O/\delta^{34}S$ slope range (0.29–0.47) observed from pore-water sulfate in modern methane-rich environments and is considerably different from a slope of 0.4 for GSA Data Repository item 2016336, description of samples and analytical methods, results of pyrite-rich samples (Figure DR1 and Table DR1), plot of isotope values of seep and non-seep carbonates (Figure DR2), and summary of geochemical data (Table DR2), is available online at http://www.geosociety.org /pubs/f2016.htm or on request from editing@geosociety.org.

Figure 1. Global map showing five study areas.

Figure 2. $\delta^{18}O_{CAS}$ (CAS—carbonate-associated sulfate) versus $\delta^{34}S_{CAS}$ values of seep carbonates from modern seafloor (Gulf of Mexico and Black Sea), Neogene deposits (Northern Italy), and Paleogene deposits (western Washington State, USA). VCDT—Vienna Canyon Diablo troilite; VSMOW—Vienna standard mean ocean water. Black cross corresponds to $\delta^{18}O$ and $\delta^{34}S$ composition of modern seawater (SW) sulfate.

Figure 3. $\delta^{18}O_{CAS}$ (CAS—carbonate-associated sulfate) versus $\delta^{34}S_{CAS}$ values of Gulf of Mexico seep carbonates grouped by dominant mineral composition (aragonite dominated versus calcite dominated). VCDT—Vienna Canyon Diablo troilite; VSMOW—Vienna standard mean ocean water. Black cross corresponds to $\delta^{18}O$ and $\delta^{34}S$ composition of modern seawater (SW) sulfate.

Figure 4. Strontium isotope data for Gulf of Mexico aragonite and calcite. Dashed line corresponds to $\delta^{87}Sr/\delta^{86}Sr$ ratio of modern Gulf of Mexico seawater (0.709175; Fu and Aharon, 1998).
pore-water sulfate in methane diffusion–controlled or methane-devoid environments (cf. Antler et al., 2015). Antler et al. (2015) concluded that the slope is independent of physical parameters in the environment (e.g., temperature, water pressure, salinity, and sulfate concentration), and our results support this conclusion. All types of seep carbonates analyzed in this study, regardless of location or age, exhibit small and constant $\delta^{18}O_{\text{CAS}}$ and $\delta^{34}S_{\text{CAS}}$ slopes (0.28–0.32; Fig. 2) with the exception of pure aragonite (0.53; Fig. 3). This observation suggests that the extracted CAS from seep carbonates preserved the primary isotope signals of the pore-water sulfate.

During sulfate reduction, $^{34}S$ and $^{18}O$ behave differently. The $\delta^{34}S_{\text{CAS}}$ value typically increases as the $^{32}S$ isotope is distilled into the reduced (0.53; Fig. 3). This observation suggests that the extracted CAS from seep carbonates originated from pore fluids rather than seawater. Depending on the flux of methane, the sulfate-methane transition zone is placed at different sediment depth. If SD-AOM occurs at shallow sediment depth in pore water of a seawater-like composition, a resulting small slope of $\delta^{34}S_{\text{CAS}}$ and $\delta^{18}O_{\text{CAS}}$ values lies on a line with the composition of coeval seawater sulfate. If SD-AOM occurs deeper in the sediment, the even smaller slope lies on a line with the composition of pore-water sulfate at the lower left end, corresponding to higher $\delta^{34}S$ and $\delta^{18}O$ values than those of seawater. Differences in the CAS patterns of aragonite and calcite from the Gulf of Mexico seep carbonates support this interpretation, revealing that the new proxy can also be used to reconstruct flow intensities and identify different redox environments at seeps or other sites where SD-AOM has occurred. Periods of enhanced methane flux may have occurred repeatedly in modern and ancient oceans. The new CAS stable isotope proxy will help to identify and better constrain SD-AOM activity throughout the geological record.

CONCLUSIONS

Oxygen and sulfur isotope analyses of CAS in carbonates from three modern and two ancient methane-seep provinces revealed that CAS faithfully records the characteristic isotope fingerprint of SD-AOM, i.e., a small slope of the $\delta^{18}O_{\text{CAS}}$ vs. $\delta^{34}S_{\text{CAS}}$ data array. The sulfate in seep carbonates originated from pore fluids rather than seawater. Depending on the flux of methane, the sulfate-methane transition zone is placed at different sediment depth. If SD-AOM occurs at shallow sediment depth in pore water of a seawater-like composition, a resulting small slope of $\delta^{34}S_{\text{CAS}}$ and $\delta^{18}O_{\text{CAS}}$ values lies on a line with the composition of coeval seawater sulfate. If SD-AOM occurs deeper in the sediment, an even smaller slope lies on a line with the composition of pore-water sulfate at the lower left end, corresponding to higher $\delta^{34}S$ and $\delta^{18}O$ values than those of seawater. Differences in the CAS patterns of aragonite and calcite from the Gulf of Mexico seep carbonates support this interpretation, revealing that the new proxy can also be used to reconstruct flow intensities and identify different redox environments at seeps or other sites where SD-AOM has occurred. Periods of enhanced methane flux may have occurred repeatedly in modern and ancient oceans. The new CAS stable isotope proxy will help to identify and better constrain SD-AOM activity throughout the geological record.

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