Estuarine, Coastal and Shelf Science xxx (2014) 1–8

Contents lists available at ScienceDirect

Estuarine, Coastal and Shelf Science

journal homepage: www.elsevier.com/locate/ecss

Sulfur and oxygen isotope tracing of sulfate driven anaerobic methane oxidation in estuarine sediments

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ARTICLE INFO

Article history:
Received 7 November 2013
Accepted 1 March 2014
Available online xxx

Keywords:
sulfate
methane
estuaries
isotopes
pore-fluid

ABSTRACT

We use multiple stable isotope measurements in two highly stratified estuaries located along the Mediterranean coast of Israel (the Yarqon and the Qishon) to explore the consumption of sulfate through the anaerobic oxidation of methane (sulfate-driven AOM). At both sites, pore fluid sulfate is rapidly consumed within the upper 15–20 cm. Although the pore fluid sulfate and dissolved inorganic carbon (DIC) concentration profiles change over a similar range with respect to depth, the sulfur and oxygen isotopes in the pore fluid sulfate and the carbon isotopes in the pore fluid DIC are fundamentally different. This pore fluid isotope geochemistry indicates that the microbial mechanism of sulfate reduction differs between the studied sites. We suggest that in the Yarqon estuary, sulfate is consumed entirely through AOM, whereas in the Qishon, both AOM and bacterial sulfate reduction through organic matter oxidation coexist. These results have implications for understanding the microbial mechanisms behind sulfate-driven AOM. We compile data from marine and marginal marine environments that supports our conclusion that the intracellular pathways of sulfate reduction varies among environments with sulfate-driven AOM. The data can be used to elucidate new pathways in the cycling of methane and sulfate, and the findings are applicable to the broader marine environment.

1. Introduction

1.1. General

Organic carbon in marine and marginal marine sediments can be oxidized anaerobically through various electron acceptors (Froelich et al., 1979). These anaerobic electron acceptors are used in order of decreasing chemical potential, beginning with nitrate, and proceeding through manganese and iron oxides, and sulfate (Froelich et al., 1979). Any organic matter that is not oxidized aerobically or anaerobically can undergo further reduction, leading to the formation of methane (CH_4) in the process of methanogenesis (e.g. Whiticar et al., 1986). Marine sediments are the largest natural reservoir of methane on Earth (Kvenvolden, 1988).

Upwardly diffusing methane can be oxidized microbially (methanotrophy), both aerobically (via oxygen—e.g. Cicerone and Oremland, 1988) and anaerobically (anaerobic oxidation of methane —AOM—e.g. Martens and Berner, 1974; Hinrichs et al., 1999; Boetius et al., 2000; Milucka et al., 2012). In marine and marginal marine sediments, AOM has been identified as the main process consuming methane in the subsurface, and this methane oxidation is primarily coupled to sulfate reduction (hereafter called sulfate-driven AOM) (Eq. (1)—e.g. Martens and Berner, 1974; Barnes and Goldberg, 1976; Reeburgh, 1976):

$$SO_4^{2-} + CH_4 \rightarrow HCO_3^- + HS^- + H_2O \quad (1)$$

Sulfate-driven AOM often results in a geochemically detectable transition zone at the boundary between methane diffusing upwardly through the network of sedimentary pore fluids, intersecting with sulfate, diffusing downwardly from the overlying ocean (e.g. Niewöhner et al., 1998). Methane emissions from marine sediments are an order of magnitude smaller than those from rice paddies or terrestrial wetlands because of this sulfate-driven AOM, due to the large concentration of sulfate in the modern ocean (Wuebbles and Hayhoe, 2002). The fact that a high percentage of methane in marine sediments is oxidized through sulfate-driven AOM means that the earth's vast oceans are prevented from

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http://dx.doi.org/10.1016/j.ecss.2014.03.001
0272-7714/

becoming a major source of this potent greenhouse gas (Reeburgh, 2007).

Sulfate-driven AOM was first identified using evidence from sediment geochemical profiles (Martens and Berner, 1974; Barnes and Goldberg, 1976; Reeburgh, 1976). This process was initially controversial among microbiologists, because neither the responsible organism nor the mechanism was identified. About twenty years ago, field and laboratory studies demonstrated coupling between methanogens and sulfate reducers (Hoehler et al., 1994). Later, microbiologists and geochemists showed that consortia of archaea and bacteria are involved in AOM in some seep environments (Hinrichs et al., 1999; Boetius et al., 2000; Orphan et al., 2001), and that at least three groups of archaea may perform AOM (named ANME-1, ANME-2, and ANME-3) associated with sulfate reducing bacteria (Boetius et al., 2000; Orphan et al., 2002; Niemann et al., 2006). It was suggested that the archaea are responsible for the methane oxidation while the sulfate reducing bacteria separately reduce the sulfate. Recently it was shown that some ANMEs are able to oxidize methane and reduce sulfate alone and the bacteria-archaea consortia may not be required (Milucka et al., 2012).

Some specifics of sulfate-driven AOM and its link to the subsurface sedimentary sulfur cycle, however, remain enigmatic. For instance, if we consider the proposed consortia for sulfate-driven AOM, it is still unclear what drives the coupling between sulfate reducers and methane oxidizers and how this is energetically favorable for each. If we consider, on the other hand, that a single ANME performs both sulfate reduction and methane oxidation (Milucka et al., 2012), we do not yet know how prevalent this is in the natural environment and the role of key intermediate valence sulfur species in this pathway of Sulfate-driven AOM. Additionally, sulfate reducing bacteria can oxidize sedimentary organic matter, yet several studies have shown that when methane is present, all available sulfate is reduced through the less energetically favorable pathway of AOM (Niewöhner et al., 1998; Kasten and Jørgensen, 2000; Sivan et al., 2007). The lack of answers to these questions limits our understanding of the subsurface sulfur cycle and the crucial coupling to methanotrophy.

Carbon isotopes provide a good constraint on the depth distribution and location of methanogenesis and methanotrophy because of the large carbon isotopic fractionation associated with both methane production and consumption (e.g. Whiticar, 1999; Borowski et al., 2000). During methanogenesis, ^{12}C is strongly partitioned into methane; the $\delta^{13}C$ of the methane produced can be between −50‰ and −100‰. In contrast, the residual dissolved inorganic carbon pool becomes highly enriched in ^{13}C, occasionally by as much as 50–70‰. Oxidizing this methane during AOM on the other hand, results in ^{13}C-depleted dissolved inorganic carbon (DIC) and slightly heavier $\delta^{13}C$ values of the residual methane, due to both a fractionation of 0–10‰ during methane oxidation and to the initial $\delta^{13}C$ value of the methane itself (Alperin et al., 1988; Martens et al., 1999). Therefore, in sedimentary environments where methane is being produced and consumed, the $\delta^{13}C$ of dissolved inorganic carbon in the pore fluid typically follows a depth profile where it decreases from the surface to the zone of AOM and then increases below in the zone where methane is being produced (e.g. Blair and Aller, 1995; Sivan et al., 2007; Malinverno and Pohlman, 2011).

The sulfur and oxygen isotope ratios in dissolved sulfate in sedimentary pore fluids may also be a powerful tool for studying sulfate-driven AOM. Sulfur isotope fractionation during bacterial sulfate reduction, which partitions ^{32}S into the sulfide leaving ^{34}S behind in the residual sulfate, can be as high as 72‰ (e.g. Wortmann et al., 2001; Brunner and Bernasconi, 2005; Sim et al., 2011). As sulfate is reduced to sulfide via intercellular intermediates (Rees, 1973; Farquhar et al., 2003; Brunner and Bernasconi, 2005; Canfield et al., 2006), the magnitude of this sulfur isotope fractionation depends upon the isotope partitioning in each of the intercellular steps and on the ratio between the backward and forward sulfur fluxes within the bacterial cells (Rees, 1973; Brunner and Bernasconi, 2005).

Oxygen isotopes in sulfate, on the other hand, have been shown to be strongly influenced by the oxygen isotopic composition of water in which the bacteria are grown (e.g. Fritz et al., 1989; Brunner et al., 2005, 2012). The consensus is that, within the cell, sulfur compounds such as sulfite, and water exchange oxygen atoms; some of these isotopically equilibrated molecules return to the extracellular sulfate pool. As all the intercellular steps are considered to be reversible (Rees, 1973; Brunner and Bernasconi, 2005; Eckert et al., 2011; Holler et al., 2011), water-oxygen is also incorporated during the oxidation of these sulfur intermediates back to sulfate (Fritz et al., 1989; Brunner et al., 2006; Turchyn et al., 2006; Wortmann et al., 2007; Brunner et al., 2012; Antler et al., 2013; Wankel et al., 2013).

Thus, oxygen and sulfur isotopes in the residual sulfate during bacterial sulfate reduction are affected by the changes in the intercellular fluxes within the bacterial cells. However, these isotopes in the residual sulfate are affected in different ways, and therefore the relative change of one isotope vs. the other helps uniquely solve for the relative change in the flux of each intercellular step as sulfate is being reduced (Brunner et al., 2005, 2012; Antler et al., 2013). We term the relative changes in the fluxes at each intercellular step during bacterial sulfate reduction the 'mechanism' of bacterial sulfate reduction.

The sulfur and oxygen isotope composition of residual sulfate has been used to explore the mechanism of bacterial sulfate reduction during organic matter oxidation both in pure culture (e.g. Mangalo et al., 2007; Mangalo et al., 2008; Turchyn et al., 2010) and in the natural environment (e.g. Böttcher et al., 1998; Böttcher et al., 1999; Aharon and Fu, 2000, 2003; Turchyn et al., 2006; Wortmann et al., 2007; Antler et al., 2013). However, this isotope approach has not been used specifically to study sulfate-driven AOM, and to understand whether the intracellular mechanism of sulfate reduction is different when it is coupled to AOM as opposed to generic organic matter oxidation. This is partly because of the technical difficulty of measuring the isotopes of sulfate at the sulfate-methane transition, where the sulfate concentration is low.

In this study, we investigate sulfate-driven AOM at two different estuary sites using multi isotope measurements to further our understanding of the mechanism of this process. We report carbon isotopes in dissolved inorganic carbon ($\delta^{13}C_{DIC}$), sulfur and oxygen isotopes in pore fluid sulfate ($\delta^{34}S_{SO_4}$ and $\delta^{18}O_{SO_4}$ respectively) and carbon isotopes in pore fluid methane ($\delta^{13}C_{CH_4}$) as well as the concentrations of dissolved inorganic carbon, sulfate, and methane. Our samples were collected from off the Mediterranean coast of Israel (The Yarqon and the Qishon estuaries, Fig. 1). The Yarqon is the largest coastal river in Israel with a length of 27.5 km and a drainage basin area of 1800 km^2. The estuary contains high organic carbon load from up-stream of 20–60 mg L^{-1} (Gafny et al., 2000) and a lower water mass close to seawater salinity. The Qishon stream drainage area occupies 1100 km^2, with intensive agricultural activity and industry taking place within the basin. The 7-km long Qishon estuary is characterized by the penetration of seawater, thereby producing a highly stratified water column. Nearby industrial plants provide high nutrients/carbon load in the Qishon estuary (Eliani-Russak et al., 2013). The salinity of the pore fluids in the two estuaries is close to the salinity of the eastern Mediterranean (Antler et al., 2013; Eliani-Russak et al., 2013) with a $\delta^{18}O_{H_2O}$ of 2 ± 0.5‰, similar to previous measurements of the $\delta^{18}O_{H_2O}$ of the eastern Mediterranean (e.g. Sisma-Ventura et al., 2009). Thus the water at the boundary layer of the estuary sediments is predominantly saline

Please cite this article in press as: Antler, G., et al., Sulfur and oxygen isotope tracing of sulfate driven anaerobic methane oxidation in estuarine sediments, Estuarine, Coastal and Shelf Science (2014), http://dx.doi.org/10.1016/j.ecss.2014.03.001