



Intermediate sulfur oxidation state compounds in the euxinic surface sediments of the Dvurechenskii mud volcano (Black Sea)

Anna Lichtschlag^{a,1}, Alexey Kamyshny Jr.^{a,b,*}, Timothy G. Ferdelman^a,
Dirk deBeer^a

^a *Max Planck Institute for Marine Microbiology, Celsiusstrasse 1, 28359 Bremen, Germany*

^b *Department of Geological and Environmental Sciences, The Faculty of Natural Sciences, Ben-Gurion University of the Negev,
P.O. Box 653, Beer Sheva 84105, Israel*

Received 24 June 2011; accepted in revised form 15 November 2012; available online 5 December 2012

Abstract

The deep Black Sea is known to be depleted in electron-acceptors for sulfide oxidation. This study on depth distributions of sulfur species (S(II), S(0), S_n^{2-} , $S_2O_3^{2-}$, SO_3^{2-} , SO_4^{2-}) in the Dvurechenskii mud volcano, a cold seep situated in the permanently anoxic eastern Black Sea basin (Sorokin Trough, 2060 m water depth), showed remarkable concentrations of sulfide oxidation products. Sulfite concentrations of up to $11 \mu\text{mol L}^{-1}$, thiosulfate concentrations of up to $22 \mu\text{mol L}^{-1}$, zero-valent sulfur concentrations of up to $150 \mu\text{mol L}^{-1}$ and up to five polysulfide species were measured in the upper 20 cm of the sediment. Electron-acceptors found to be available in the Dvurechenskii mud volcano (DMV) for the oxidation of hydrogen sulfide to sulfide oxidation intermediates are iron-minerals, and probably also reactive manganese phases. Up to $60 \mu\text{mol g}^{-1}$ of reactive iron-minerals and up to $170 \mu\text{mol L}^{-1}$ dissolved iron was present in the central summit with the highest fluid upflow and fresh mud outflow. Thus, the source for the oxidative power in the DMV are reactive iron phases extruded with the mud from an ancient source in the deeply buried sediments, leading to the formation of various sulfur intermediates in comparably high concentrations. Another possible source of sulfide oxidation intermediates in DMV sediments could be the formation of zero-valent sulfur by sulfate dependent anaerobic microbial oxidation of methane followed by disproportionation of zero-valent sulfur. Sulfide oxidation intermediates, which are produced by these processes, do not reach thermodynamic equilibrium with rhombic sulfur, especially close to the active center of the DMV due to a short equilibration time. Thus, mud volcano sediments, such as in the DMV, can provide oxidizing niches even in a highly reduced environment like the abyssal part of the Black Sea.

© 2012 Elsevier Ltd. All rights reserved.

1. INTRODUCTION

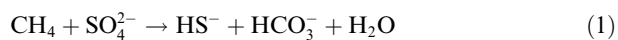
An important pathway for hydrogen sulfide formation in the marine environment is microbial sulfate reduction coupled to mineralization of organic matter buried in the seafloor, i.e. organoclastic sulfate reduction. Hydrogen sulfide may also be produced during the anaerobic oxidation of methane (AOM) with sulfate (Eq. (1)) (Martens and Berner, 1974; Barnes and Goldberg, 1976). AOM is one of the main pathways for the removal of methane derived from organic-rich sediments, where methane is produced

* Corresponding author at: Department of Geological and Environmental Sciences, The Faculty of Natural Sciences, Ben-Gurion University of the Negev, P.O. Box 653, Beer Sheva 84105, Israel.

E-mail addresses: alexey93@gmail.com, kamyshny@bgu.ac.il (A. Kamyshny).

¹ Current address: National Oceanography Centre, University of Southampton Waterfront Campus, European Way, Southampton SO14 3ZH, UK.

in situ (Jørgensen et al., 2004; Treude et al., 2005), as well as from cold seep structures such as microbial reefs, pockmarks and mud volcanoes, where methane is externally supplied from a deep reservoir (Michaelis et al., 2002; Haese et al., 2003; Joye et al., 2004; Niemann et al., 2005; Mau et al., 2006; Sauter et al., 2006). In both types of environments methanotrophic archaea and sulfate-reducing bacteria are thought to be responsible for the anaerobic turnover of the ascending methane with sulfate from the seawater (Boetius et al., 2000). Hydrogen sulfide is produced in equimolar amounts as methane is consumed.



Recent research suggests that zero-valent sulfur can also be an intermediate in sulfate dependent AOM and that the bacteria associated with the archaea perform polysulfide disproportionation to sulfide and sulfate (Milucka et al., 2012).

Hydrogen sulfide, whether formed through either organo-oclastic, methanotrophic, or disproportionating pathways, is oxidized by a complex net of microbiological and geochemical redox processes, with sulfate as the most oxidized product and pyrite as the dominant buried reduced product (Zopfi et al., 2004). Oxidation of hydrogen sulfide with oxygen or nitrate, which supports a rich chemolithotrophic community, is characteristic for most methane-rich cold seeps (e.g. Olu et al., 1997; Treude et al., 2003; Olu-Le Roy et al., 2004; de Beer et al., 2006; Lichtschlag et al., 2010a). Thiotrophic symbionts associated with macrobenthos and giant sulfur bacteria that form extensive mats on the sediment surface, either completely oxidize hydrogen sulfide to sulfate or transform it to elemental sulfur (Olu et al., 1997; Olu-Le Roy et al., 2004; de Beer et al., 2006; Niemann et al., 2006). In non-seep marine sediments, where chemolithotrophic microbiota are conspicuously absent, hydrogen sulfide is also completely re-oxidized either to sulfate or to sulfide oxidation intermediates (SOIs) usually by reaction with reactive iron and manganese oxides (Zopfi et al., 2004, and references therein).

Elemental sulfur is a common intermediate product of hydrogen sulfide oxidation by various electron-acceptors, and elemental sulfur content in sediments is usually greater than other SOIs (Zopfi et al., 2004). Elemental sulfur itself reacts with hydrogen sulfide, producing polysulfides (S_n^{2-}) and their protonated forms with $n = 2 - 9$ (Maronny, 1959; Cloke, 1963; Teder, 1971; Giggenbach, 1972; Boulegue and Michard, 1978; Kamyshny et al., 2003, 2004, 2007; Gun et al., 2004; Amrani et al., 2006). Thiosulfate and sulfite will form when hydrogen sulfide reacts with dissolved oxygen (Zhang and Millero, 1993), MnO_2 (Yao and Millero, 1993) or ferric iron oxides (Pyzik and Sommer, 1981; dos Santos Afonso and Stumm, 1992; Yao and Millero, 1996). Thiosulfate is known to be produced during the chemical and bacterial oxidation of pyrite by oxygen, Fe(III) and Mn(IV) (Burdige and Neilson, 1986; Luther, 1987; Edwards et al., 1999; Rimstidt and Vaughan, 2003; Balci et al., 2007). In many productive marine surface sediments giant sulfur bacteria (e.g. *Beggiatoa*, *Thiomargarita*, *Thioploca*) can oxidize sulfide using nitrate stored in liquid vacuoles inside the cell (Schulz and Jørgensen, 2001), which

leads to the formation of elemental sulfur and eventually sulfate.

Although the presence of sulfide oxidation intermediates such as elemental sulfur, thiosulfate and tetrathionate in anoxic marine sediments is well documented (Troelsen and Jørgensen, 1982; Podgorsek and Imhoff, 1999; Zopfi et al., 2004), the distribution of these compounds, and their sources and sinks, have never been studied in cold seep systems, where sulfur turnover plays a key role. With a variety of analytical techniques (Fahey and Newton, 1987; Zopfi et al., 2001, 2004; Rong et al., 2005; Kamyshny, 2009; Kamyshny et al., 2006, 2009), the speciation and concentrations of a range of hydrogen sulfide oxidation products, such as polysulfides (S_n^{2-}), colloidal and solid elemental sulfur (S^0), thiosulfate ($\text{S}_2\text{O}_3^{2-}$), sulfite (SO_3^{2-}) and polythionates ($\text{S}_n\text{O}_6^{2-}$) can be assessed. Methods for analysis of individual polysulfides (Kamyshny et al., 2004, 2006) are now available and allow calculation of how far the polysulfides are from equilibrium with zero-valent sulfur in the sediment (Kamyshny et al., 2008). Deviation from equilibrium would suggest ongoing conversion processes.

In the Black Sea electron-acceptors for microbiological and geochemical hydrogen sulfide oxidation, such as dissolved oxygen and nitrate, are depleted below the pycnocline. The absence of nitrate or dissolved oxygen as electron acceptors for chemolithotrophy is manifested in the lack of thiotrophic mats and macrobenthos at the deep-water Black Sea cold seeps. Sulfide oxidation processes should be limited by the small flux of settling particulate metal oxides. Here we show that even in such a reduced environment SOI formation can occur, driven by oxidants originating from the deep seafloor, in this case the Dvurechenskii mud volcano (DMV), a cold fluid seep situated in permanently anoxic waters of the Black Sea (Sorokin Trough).

2. MATERIALS AND METHODS

2.1. Sampling site

The Sorokin Trough in the northeastern part of the Black Sea is a 150 km long and 50 km submarine foredeep of the Crimean Mountains (Tugolesov et al., 1985). In the Sorokin Trough, diapiric mud volcanoes have formed as a result of SE-NW directed tectonic compression (Krastel et al., 2003). The DMV is located in the central part of the Sorokin Trough (N 44°17'; E 34°59') at a water depth of 2060 m in permanently anoxic waters (Fig. 1). The hydrogen sulfide concentration in the bottom water is around 378 $\mu\text{mol L}^{-1}$ (Neretin et al., 2001). Ambient bottom water temperature above the DMV is 9 °C (Bohrmann et al., 2003), and chloride and sulfate concentrations are 355 and 17 mmol L^{-1} in the Sorokin Trough (Aloisi et al., 2004). Morphologically, the DMV resembles a flat oval mud pie: 1200 by 800 m across and with steep outer edges that rise 80 m from the surrounding seafloor (Fig. 1).

Submarine mud volcanoes are tectonic windows where pore waters, gases and mud from a deep-seated source are released into the marine environment. At the DMV the expelled mud originates from the 4–5 km thick Maikopian

Download English Version:

<https://daneshyari.com/en/article/4702546>

Download Persian Version:

<https://daneshyari.com/article/4702546>

[Daneshyari.com](https://daneshyari.com)