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Distribution and size fractionation of elemental sulfur in aqueous environments: The Chesapeake Bay and Mid-Atlantic Ridge

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Abstract

Elemental sulfur is an important intermediate of sulfide oxidation and may be produced via abiotic and biotic pathways. In this study the concentration and size fractionation of elemental sulfur were measured in two different sulfidic marine environments: the Chesapeake Bay and buoyant hydrothermal vent plumes along the Mid-Atlantic Ridge. Nanoparticulate sulfur (<0.2 μm) was found to comprise up to 90% of the total elemental sulfur in anoxic deep waters of the Chesapeake Bay. These data were compared with previous studies of elemental sulfur, and represent one of the few reports of nanoparticulate elemental sulfur in the environment. Additionally, a strain of phototrophic sulfide oxidizing bacteria isolated from the Chesapeake Bay was shown to produce elemental sulfur as a product of sulfide oxidation. Elemental sulfur concentrations are also presented from buoyant hydrothermal vent plumes located along the Mid-Atlantic Ridge. In the Mid-Atlantic Ridge plume, S^0 concentrations up to 33 μM were measured in the first meter of rising plumes at three different vent sites, and nanoparticulate S^0 was up to 44% of total elemental sulfur present.

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1. INTRODUCTION

Zero-valent sulfur (ZVS) species, meaning compounds in which sulfur is in a neutral oxidation state, can form via a variety of biotic and abiotic pathways. As a (meta)stable intermediate of sulfide oxidation, elemental sulfur (S^0), and other ZVS species such as polysulfides (S_x^{2-}) may be important components of microbial (Schauder and Muller, 1993; Franz et al., 2007) and geochemical (Luther, 1990) processes in natural waters.

The oxidation of sulfide to elemental sulfur by molecular oxygen requires a two electron oxidation of sulfide. The one electron transfer from sulfide to oxygen is thermodynamically unfavorable (Luther, 2010). The two electron transfer from sulfide to oxygen, although thermodynamically favorable, is kinetically inhibited. In order for a two electron transfer from sulfide to oxygen to occur, the electrons from sulfide must first be unpaired, (Luther, 1990) which poses a kinetic barrier to the oxidation (Luther et al.,

Abbreviations: ZVS, zero-valent sulfur; AVS, acid volatile sulfides; CRS, chromium reducible sulfide; MAR, Mid-Atlantic Ridge; TAG, trans atlantic geotraverse; ROV, remotely operated vehicle; CTD, conductivity temperature and depth; SEM, scanning electron microscopy; EDX, energy dispersive X-ray spectroscopy

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2011). Oxidation of sulfide by oxygen can be facilitated with the aid of a bridging metal catalyst (Yao and Millero, 1996), which facilitates the transfer of electrons from sulfide to oxygen. Elemental sulfur has been observed as an oxidation product of sulfide oxidation by manganese oxides (Herszage and dos Santos Afonso, 2003) and iron (oxy)hydroxides (Pyzik and Sommer, 1981; Luther, 1991; Poulton, 2003).

Due to these thermodynamic and kinetic constraints on abiotic sulfide oxidation in the absence of metal catalysts, micro-organisms play an important role in mediating sulfide oxidation environmentally, forming elemental sulfur as the first stable oxidation product (Taylor and Wirsen, 1997; Frigaard and Dahl, 2008). Biotic sulfide oxidation kinetics are orders of magnitude more rapid than abiotic pathways (Luther et al., 2011). The exact composition of elemental sulfur produced by different types of bacteria is a matter of debate; however, in general, microbially produced elemental sulfur is hydrophilic and of lower density than inorganically produced sulfur (Kleinjan et al., 2003). Microbially produced sulfur can be intracellular, such as that produced by purple sulfur bacteria, or extracellular, as in green sulfur bacteria (Van Gemerden, 1986; Frigaard and Dahl, 2008), and may have a protein coating. The actual globules are not the more crystalline orthorhombic sulfur, but rather a more hydrated form of S_8 rings or chains (Prange et al., 2002). In addition to bacteria that produce elemental sulfur as a product of sulfide metabolism, many bacteria, such as *Sulfurospirillum arcachonense*, *Desulfurella acetivorans*, and *Shewanella putrefaciens* utilize elemental sulfur and polysulfides as an energy source (Schauder and Muller, 1993; Franz et al., 2007; Sievert et al., 2007). Elemental sulfur is also an important source of energy for many archaea, and can be utilized as either an electron donor for aerobic archaea such as the *Acidianus* and *Sulfolobus* species, or an electron acceptor for anaerobic archaea (Kletzin et al., 2004).

Zerovalent sulfur species have been observed in a variety of natural environments, and nanoparticulate elemental sulfur has been synthesized and characterized in the laboratory (Steudel, 2003; Guo et al., 2006; Deshpande et al., 2008; Ghosh and Dam, 2009). Elemental sulfur has been found in the water columns of stratified lakes (Zerkle et al., 2010; Kamyshny et al., 2011), and in marine environments, including tidal pools (Kamyshny and Ferdelman, 2010), inland bays (Ma et al., 2006), the Black Sea (Jørgensen et al., 1991; Luther et al., 1991; Trouwborst et al., 2006), and the Cariaco Basin (Hastings and Emerson, 1988; Li et al., 2008). Sulfur has also been found in sediments (Yücel et al., 2010; Lichtschlag et al., 2012) and in sediment porewaters (Luther et al., 1986; Rozan et al., 2000; Wang and Tessier, 2009).

The size of elemental sulfur affects its chemical reactivity (Steudel, 2003) and thus its availability to micro-organisms as a substrate (Franz et al., 2007). Despite the influence of particle size on chemical and biological processes, the size distribution of elemental sulfur in the environment has not yet been widely studied. Elemental sulfur measured in sediments is reported as unfiltered extractions (Troelsen and Jorgensen, 1982; Wang and Tessier, 2009; Lichtschlag et al., 2012). In the water column, reports of elemental sulfur have been presented as unfiltered totals (Zopfi et al., 2001), as the fraction caught on a 0.2 μm filter (Ma et al., 2006), and only a few studies have investigated the fraction passing through a filter. Kamyshny and Ferdelman (2010) measured S^0 in the filtrate passing a 5 μm filter, Kamyshny et al. (2011) passing a 1.2 μm filter, Zerkle et al. (2010) passing both a 0.45 and a 0.2 μm filter, and Li et al. (2008) in that passing a 0.2 μm filter.

In this study, we operationally define the portion of sulfur passing through a 0.2 μm filter as nanoparticulate and the fraction caught on the filter as particulate. Total elemental sulfur refers to the sum of these two fractions. We present data on the presence and distribution of particulate and nanoparticulate elemental sulfur in two distinct marine environments (the Chesapeake Bay and the Mid-Atlantic Ridge), as well as in cultures of anoxygenic phototrophic sulfide oxidizing bacteria. In particular we show that nanoparticulate elemental sulfur exists in both the Chesapeake Bay and the Mid-Atlantic Ridge, and we highlight the importance of nanoparticulate elemental sulfur as a component of biotic and abiotic cycling in these different systems.

1.1. Study sites

The Chesapeake Bay is a partially mixed and seasonally anoxic estuary. An oxic upper layer and an anoxic deep layer develop in the spring and summer due to temperature and salinity gradients (Officer et al., 1984). The deep layer can become sulfidic, typically resulting in a suboxic zone in which neither oxygen nor sulfide is detected (Lewis et al., 2007). The study site on the Chesapeake Bay is a hole south of the Chesapeake Bay bridge (Station 858; 38°58.8′ N; 76°22′ E) that is 25 m deep, measures 0.4 km in length, and 0.8 km in width (Lewis et al., 2007).

The Rainbow, Trans-Atlantic Geotravers (TAG), and Snakepit vent sites were sampled along the Mid-Atlantic Ridge (MAR), a slow spreading plate boundary moving at rates less than 3 cm/year (Schmidt et al., 2007). The vent fluid at these three sites has the highest trace metal content of vent fields along the MAR (Douville et al., 2002) and iron and sulfide data from each site are given in Table 1. The Rainbow vent site (36°14′ N, 33°54′ W) at 2300 m depth is comprised of serpentinised peridotite and contains high temperature vents (up to 365 °C) characterized by low shipboard pH (2.8), high iron concentrations, and high chlorinity (Marques et al., 2006). The vent fluid at Rainbow is enriched in metals and organics, and is relatively low in sulfide. TAG (26°8′ N, 44°50′ W) at 3600 m depth ($T < 365$ °C, $pH > 3.14$) and Snakepit (23°22′ N, 44°57′ W) at 3500 m depth ($T < 358$ °C, $pH > 3.2$) are basalt hosted massive sulfide deposits and contain high temperature black smokers at depths approximately 1000 m deeper than Rainbow (Desbruyères et al., 2001) with iron concentrations an order of magnitude lower and sulfide concentrations approximately five times higher than those of Rainbow (Douville et al., 2002; Gartman et al., 2014). The TAG vent field is located on a large sulfide deposit approximately 50 m high and is located 1500 m from the

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