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Molecular evidence for abiotic sulfurization of dissolved organic matter in marine shallow hydrothermal systems

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Abstract

Shallow submarine hydrothermal systems are extreme environments with strong redox gradients at the interface of hot, reduced fluids and cold, oxygenated seawater. Hydrothermal fluids are often depleted in sulfate when compared to surrounding seawater and can contain high concentrations of hydrogen sulfide (H_2S). It is well known that sulfur in its various oxidation states plays an important role in processing and transformation of organic matter. However, the formation and the reactivity of dissolved organic sulfur (DOS) in the water column at hydrothermal systems are so far not well understood. We investigated DOS dynamics and its relation to the physicochemical environment by studying the molecular composition of dissolved organic matter (DOM) in three contrasting shallow hydrothermal systems off Milos (Eastern Mediterranean), Dominica (Caribbean Sea) and Iceland (North Atlantic). We used ultra-high resolution Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR-MS) to characterize the DOM on a molecular level. The molecular information was complemented with general geochemical data, quantitative dissolved organic carbon (DOC) and DOS analyses as well as isotopic measurements (δ^2H, $\delta^{18}O$ and $F^{14}C$). In contrast to the predominantly meteoric fluids from Dominica and Iceland, hydrothermal fluids from Milos were mainly fed by recirculating seawater. The hydrothermal fluids from Milos were enriched in H_2S and DOS, as indicated by high DOS/DOC ratios and by the fact that >90% of all assigned DOM formulas that were exclusively present in the fluids contained sulfur. In all three systems, DOS from hydrothermal fluids had on average lower O/C ratios (0.26–0.34) than surrounding surface seawater DOS (0.45–0.52), suggesting shallow hydrothermal systems as a source of reduced DOS, which will likely get oxidized upon contact with oxygenated seawater. Evaluation of hypothetical sulfurization reactions suggests DOM reduction and sulfurization during seawater recirculation in Milos seafloor. The four most effective potential sulfurization reactions were those exchanging an O atom by one S atom in the formula or the equivalent + H_2S reaction, correspondingly exchanging H_2O, H_2 and/or O_2 by a H_2S molecule. Our study reveals novel insights into DOS

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dynamics in marine hydrothermal environments and provides a conceptual framework for molecular-scale mechanisms in organic sulfur geochemistry.

Keywords: Marine shallow hydrothermal systems; Dissolved organic matter (DOM); Dissolved organic sulfur (DOS); FT-ICR-MS; Milos (Eastern Mediterranean); Dominica (Caribbean Sea); Iceland (North Atlantic)

1. INTRODUCTION

Dissolved organic matter (DOM) is defined as the organic components in water that pass through a $\leqslant$0.7 μm filter. The importance of DOM in global geochemistry relies on the enormous amount of carbon that is dissolved in the oceans, quantified as more than 200 times the carbon of all living marine biomass (Hansell et al., 2009) and being similar to all atmospheric CO_2 (Hedges, 1992). Thus, changes in DOM dynamics may have implications for local and global carbon cycling processes (Battin et al., 2009; Dittmar and Stubbins, 2014; German et al., 2015). While molecular DOM characterization of a range of marine habitats has become available in the last years (e.g. Lechtenfeld et al., 2014; Hansman et al., 2015), there exists a striking scarcity of studies targeting specifically the role of organic sulfur species in DOM (e.g. Lechtenfeld et al., 2011; Pohlabeln and Dittmar, 2015). Sulfur plays a considerable role in the various transformations of organic matter, from early diagenesis to the late stage of catagenesis, due to its ability to exist in many different oxidation states (Aizenshtat et al., 1995; Sleighter et al., 2014). In marine sediments, organic sulfur is quantitatively the second most important sulfur pool only behind pyrite, frequently accounting for 35% of total sedimentary sulfur in many marine environments (Zaback and Pratt, 1992; Cutter and Kluckhohn, 1999; Werne et al., 2004; Zhu et al., 2014). Abiotic sulfurization can contribute to the stabilization of organic matter (Sinninghe Damsté et al., 1989; Sinninghe Damsté and de Leeuw, 1990) but whether it also contributes to the stability of DOM in the oceans is still an open research question (Dittmar, 2015).

A significant contribution to the understanding of dissolved organic sulfur (DOS) origin and fate may be achieved through the investigation of DOS biogeochemistry at hydrothermal systems. Hydrothermal activity has been operating for most of the Earth´s history, occurring over a wide depth range in the oceans, from intertidal to the abyss (Sander and Koschinsky, 2011). Hydrothermal vents have been postulated as possible sites for the first steps of organic chemical evolution, where sulfur reduction might have played a role in prebiotic chemical processes occurring in sulfide-rich environments (Russell and Hall, 1997; Cody et al., 2000; Hebting et al., 2006; McCollom and Seewald, 2007). The hydrothermal vents located at less than 200 m water depth are categorized as shallow-water hydrothermal systems (Tarasov et al., 2005). They are easily accessible extreme environments with strong redox gradients and unique biogeochemical conditions due to the interaction of hot, reduced fluids and cold, oxygenated seawater (e.g. Dando et al., 1999; Tarasov et al., 2005). The main group of solid phase extractable (SPE) DOS in the open ocean was recently identified as unreactive sulfonic acids (Pohlabeln and Dittmar, 2015). In hydrothermal systems, reduced sulfur compounds are expected to be released and quickly oxidized to form sulfonic acids once they reach the oxic sediment surface or water column. Some functional groups like thiols and thioethers could be produced by reaction of reduced inorganic sulfur compounds with organic matter (Sinninghe Damsté et al., 1989; Aizenshtat et al., 1995; Schneckenburger et al., 1998; Hertkorn et al., 2013; Sleighter et al., 2014) and then be rapidly oxidized to sulfonic acids as well (Pohlabeln and Dittmar, 2015). However, neither the pathways of sulfurization nor of oxidation of DOS at hydrothermal systems are well understood (Zhu et al., 2014; Pohlabeln and Dittmar, 2015).

Recent advances in mass spectrometry allow characterization of the complex mixture of DOM at a molecular level. Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR-MS) in combination with soft ionization techniques such as electrospray ionization (ESI) provides molecular information on individual compounds without prior chromatographic separation. Thousands of molecular formulas containing C, H, O, N, S or P can be attributed to a single water sample (e.g. Marshall et al., 1998; Kujawinski et al., 2002; Kujawinski and Behn, 2006; Schmidt et al., 2014; Zark et al., 2015), providing unique data sets to study the multitude of processes that affect the composition of the DOM pool in the oceans. The aim of this paper is to characterize at a molecular level DOS variations at the interface between hot, reduced hydrothermal fluids and cold, oxygenated seawater in three contrasting marine shallow-water hydrothermal systems off the coast of Milos (Eastern Mediterranean), Dominica (Caribbean Sea) and Iceland (North Atlantic) (Fig. 1). We hypothesize that in shallow hydrothermal systems (1) the reduced DOS released from hydrothermal fluids is oxidized upon contact with oxygenated seawater and (2) there is DOM reduction and sulfurization during seawater recirculation through the subsurface. Therefore, within a robust geochemical data set we specifically investigated (1) the impact of physicochemical properties on the DOM signature and (2) the molecular similarities and differences in DOS between shallow hydrothermal fluids and surrounding surface seawater samples.

2. STUDY SITES

2.1. Milos

Milos Island is located in the tectonically active region of the Hellenic Volcanic Arc in the Eastern Mediterranean