



Interaction between iron and dissolved organic matter in a marine shallow hydrothermal system off Dominica Island (Lesser Antilles)



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ABSTRACT

Shallow submarine hydrothermal systems are extreme environments with unique biogeochemical conditions, originating from the interaction of hot, reduced fluids and cold, oxygenated seawater. Hydrothermal fluids represent one of the marine sources of essential trace elements like iron, the flux of which is controlled by dissolved organic matter (DOM) in and between terrestrial and marine ecosystems. However, the selectivity of the DOM with iron in marine environments is not well understood. Here we characterized at a molecular level the marine hydrothermal iron–DOM interaction using Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR-MS). Our study site was a shallow-water hydrothermal system off Dominica Island (Lesser Antilles, Caribbean Sea), where reduced fluids were strongly enriched in dissolved Fe and Si as compared to surface seawater. The dissolved organic carbon (DOC) concentration was lower in the hydrothermal fluids, most likely due to low-DOC meteoric water influence, but also suggesting biotic or abiotic processes consuming or depleting DOC when seawater is re-circulated through the sediment. The formation of hydrous ferric oxides upon aeration of the hydrothermal fluids for 10 h leads to an 8% decrease in DOC, indicating co-precipitation of iron and DOM. Resolubilization of iron precipitates revealed increased relative abundance of aromatic compounds in co-precipitated DOM, which is in accordance with iron-coagulation observed in terrestrial environments. In conclusion, we provide evidence of co-precipitation of DOM with iron at hydrothermal systems as a selective process, which characteristically alters the molecular composition of DOM released with hydrothermal fluids.

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1. Introduction

Dissolved organic matter (DOM) plays a major role in key biogeochemical cycles. DOM conducts the flux of carbon, nutrients and trace elements in and between terrestrial and marine ecosystems (Dittmar and Stubbins, 2014). It is defined as the organic components in water that pass through a 0.2–0.7 μm filter (Dittmar and Stubbins, 2014). The global DOM pool contains more than 200 times the carbon than all living marine biomass (Hansell et al., 2009) and similar amounts of carbon as all the atmospheric CO₂ (Hedges, 1992). Due to its enormous pool size, changes in DOM dynamics have implications for local and global carbon cycling processes (Battin et al., 2009; Dittmar and Stubbins, 2014; German et al., 2015). Recent advances in mass spectrometry allow characterization of the complex mixture of DOM at a molecular level. The use of Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR-MS) in combination with soft ionization techniques such as electrospray ionization (ESI) provides molecular

formulas of thousands of individual compounds in a DOM sample without prior chromatographic separation (e.g. Marshall et al., 1998; Koch et al., 2005; Kujawinski and Behn, 2006). This technique has been used extensively in recent years to understand the multitude of processes that affect the composition of the DOM pool in the oceans, such as microbial degradation and production (e.g. Kim et al., 2006; Kujawinski et al., 2009; Rossel et al., 2013), input and selective degradation of terrestrial DOM (e.g. D'Andrilli et al., 2013; Riedel et al., 2013) or light-dependent transformations (e.g. Gonsior et al., 2009; Stubbins et al., 2012; Gonsior et al., 2013). Furthermore, FT-ICR-MS is considered one of the most promising techniques to isolate and unequivocally identify dissolved metal–organic complexes in diverse natural water samples (Waska et al., 2015).

Iron is an essential trace element and frequently acts as a limiting micronutrient (Martin and Fitzwater, 1988). Iron can exist in seawater in two oxidation states, Fe²⁺ and Fe³⁺, free or complexed with inorganic and organic ligands (Liu and Millero, 2002). In the ancient anoxic Ocean of the Archean Eon, iron was abundantly present in the form of dissolved Fe²⁺ likely derived from hydrothermal systems (Jacobsen and Pimentel-Klose, 1988; Bau and Möller, 1993). At a certain point in

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the Earth's history, large scale oxidation of Fe^{2+} to Fe^{3+} occurred, leading to the formation of massive deposits of iron-rich minerals known as banded iron formations (e.g., Konhauser et al., 2007). In modern oxic oceans, iron sources include aeolian deposition, continental runoff and hydrothermal fluid discharge (Moore et al., 2002). It is estimated that about 9% of deep-ocean iron is introduced by hydrothermal fluids (Sander and Koschinsky, 2011). However, iron oxidizes slowly in hydrothermal plumes due to the presence of natural organic ligands that are bound to nearly all dissolved iron (Rue and Bruland, 1995; Toner et al., 2009; Benner, 2011; Sander and Koschinsky, 2011). In addition to acting as organic ligands and keeping iron in solution, DOM also has a large affinity to co-precipitate with Fe^{3+} , which is why ferric salts are widely used as coagulants in waste water treatment (e.g. Duan and Gregory, 2003). It is known that freshly precipitated Fe^{3+} oxides react with sulfides and other dissolved elements from seawater (Poulton and Canfield, 2006; Toner et al., 2009; Wang et al., 2012). In deep ocean hydrothermal vents, the presence of sulfide may create pyrite nanoparticles (FeS_2) increasing the probability that vent-derived iron will be transported over long distances in the water column (Yücel et al., 2011). In terrestrial environments, such as in iron-rich peatlands, redox interfaces have been proposed as selective intermediate barriers for land-derived DOM (Riedel et al., 2013). However, the selectivity of DOM interacting with iron and trace metals in marine environments is not well understood (Gledhill and Buck, 2012; Bennett et al., 2011; Dittmar and Stubbins, 2014).

Shallow-water hydrothermal systems are easily accessible marine environments with strong redox gradients (e.g. Pichler et al., 1999a; Price et al., 2013). They are considered extreme environments with unique biogeochemical conditions, originating from the interaction of hot, reduced fluids and cold, oxygenated seawater (e.g. McCarthy et al., 2005; Tarasov et al., 2005). The study of organic carbon at hydrothermal systems is also of particular interest for those investigating the chemical environment of the early Earth and other planetary bodies (e.g. Lang et al., 2010). In deep-sea hydrothermal plumes, evidence for a close coupling between organic carbon and Fe^{3+} oxides fluxes has been reported, but it remains to be determined whether this is as a result of biotic or purely abiotic geochemical processes (Bennett et al., 2011). In this context, the understanding of the iron–DOM interaction

occurring in shallow hydrothermal systems may improve the general understanding of DOM cycling and the role of iron and hydrothermal vents in marine ecosystems. Here, we hypothesize that co-precipitation of DOM with iron at hydrothermal systems is a selective process, which characteristically alters the molecular composition of DOM released with hydrothermal fluids. Applying ultra-high resolution mass spectrometry, we characterized the molecular composition of (1) DOM in fluids from a shallow hydrothermal system and (2) the DOM fraction that co-precipitates with Fe^{3+} .

2. Materials and methods

2.1. Study site

We explored a shallow hydrothermal vent system located at 5 m water depth on the south-west Coast of Soufrière Bay at Dominica Island (Caribbean Sea) (Fig. 1). Dominica Island belongs to the Lesser Antilles archipelago, which represents one of only two active arc systems in the Atlantic Ocean. Although most of the Lesser Antilles islands have a single main vent (e.g. Saba, Statia, Nevis, Montserrat, Guadeloupe and Saint Vincent), Dominica has nine potentially active volcanic centers (Lindsay et al., 2005; Joseph et al., 2011; Fig. 1). Therefore, Dominica has been the most volcanically productive island in the Lesser Antilles arc over the last 100,000 years and one of the highest worldwide (Wadge, 1984; Lindsay et al., 2005). Dominica marine shallow hydrothermal systems located on the south-west of the island belong to the flank of the Morne Plat Pays volcanic complex (Lindsay et al., 2005; Fig. 1). They are characterized by high concentrations of ferrous iron in the hot vent fluids of up to 75 °C. Upon contact with seawater, the ferrous iron is rapidly oxidized leading to precipitation of hydrous ferric oxides (McCarthy et al., 2005).

2.2. Field sampling and co-precipitation experiment

The hydrothermal fluids and seawater samples for this study were taken during the field expedition to Dominica Island (Fig. 1) between 9th and 24th of April 2013. Identification of hot-fluid spots in the area were carried out by SCUBA diving using the same *in situ* temperature

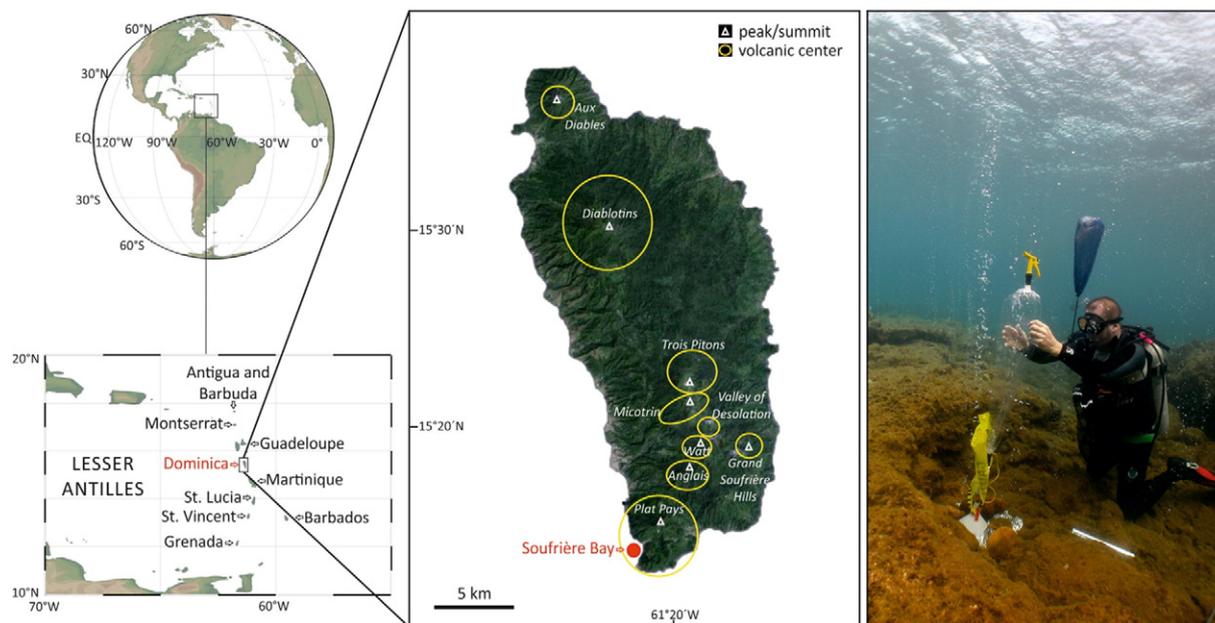


Fig. 1. Study area in Soufrière Bay, south-west of Dominica Island (Lesser Antilles, Caribbean Sea). Maps were created using Ocean Data View (R. Schlitzer, <http://odv.awi.de>) and Google Earth (<http://earth.google.com>). Submarine photo courtesy of A. Madisetti showing the visible iron-precipitation in Dominica sediment and the hydrothermal fluid sampling procedure with a funnel opened into food-grade large volume nylon bags where hot fluids were collected. Summits and volcanic centers adapted from Lindsay et al. (2005); Joseph et al. (2011).

probes as previous geochemical studies of marine shallow-water hydrothermal systems (e.g. Price et al., 2013; Kleint et al., 2015). Fluid samples were collected with a funnel placed on the vent orifice which opened into food-grade large volume nylon bags (Fig. 1). On shore, 2 L polycarbonate bottles (Nalgene, USA), previously cleaned with ultrapure pH 2 water, were filled with the hydrothermal fluids, immediately closed and kept in the dark until filtration and acidification. Surface seawater samples were taken directly into the 2 L bottles. Samples were filtered using precombusted glass microfiber filters (GF-F, pore size: 0.7 μm , diameter: 47 mm; Whatman, USA), acidified to pH 2 (HCl 25% p.a., Carl Roth, Germany) and kept at 4 °C in the dark until extraction. The filters were stored separately in polystyrene tubes (15 mL, Sarstedt, Germany) at -20 °C. For the co-precipitation experiment, 1 L from a 2 L bottle (Nalgene, USA) was immediately acidified, filtered and extracted, and the remaining liter was left in contact with the headspace air for 10 h before filtration, acidification and DOM extraction.

2.3. Geochemical parameters

Temperature, pH and salinity were measured directly in the field. The pH and salinity were determined using a WTW pH meter 3210 with Mic-D electrode. Aliquots of 4 mL of filtered vent fluids were kept sealed in cold storage at approximately 3 °C for transport to the laboratory. Inorganic geochemical analyses were performed at the University of Bremen (Germany) following established procedures for hydrothermal fluids from marine shallow hydrothermal systems (e.g. McCarthy et al., 2005; Reeves et al., 2011). The anions Br, Cl, F and SO_4 were determined by ion chromatography using a Metrohm system (USA). The cations of As, Ca, Fe, K, Li, Mg, Mn, Na, Si and Sr were measured by inductively coupled plasma-optical emission spectroscopy (ICP-OES) using a Perkin Elmer Optima 7300 (USA). Micro images of hydrous ferric oxides were generated in secondary and backscatter electron mode using a Zeiss Supra 40 scanning electron microscope (SEM). Energy dispersive X-ray (EDX) spectra were used to obtain semi-quantitative chemical compositions using a Bruker X-Flash 6/30 instrument at the University of Bremen (Germany).

2.4. Dissolved organic matter

Aliquots of 20 mL fluids (triplicates per sample), filtered (0.7 μm) and acidified to pH 2, were analyzed for DOC via high temperature catalytic combustion using a Shimadzu TOC-VCPH/CPN Total Organic Carbon Analyzer at the University of Oldenburg (Germany). Accuracy of DOC determination was checked daily by analyzing the deep-sea reference provided by D. Hansell (University of Miami, USA). DOM was extracted by solid phase extraction (SPE) using divinyl benzene polymer cartridges (PPL, volume: 6 mL, Agilent, USA) according to Dittmar et al. (2008). Acidification of the sample to pH 2 is recommended for DOM extraction of natural water samples in FT-ICR-MS analysis, because the majority of natural DOM is assumed to consist of organic acids (Dittmar et al., 2008). Although low pH may decrease binding strengths, protonation of the binding sites is not high enough to completely dissociate Fe from acid-stable metal-organic complexes (Waska et al., 2015). Prior to extraction, the cartridges were soaked with methanol for 24 h and rinsed afterwards twice each, with ultrapure water, methanol (VWR, USA) and ultrapure water at pH 2. After loading DOM onto the SPE cartridge, the remaining salts were removed by rinsing with ultrapure water at pH 2, dried by pressing air through the cartridge with a clean air-syringe (20 mL, Braun, Germany) and eluted with 6 mL of methanol (HPLC-grade, Sigma-Aldrich, USA). The SPE-DOC extracts were stored in amber vials at -20 °C. The DOM trapped in the precipitates on the filters was extracted by treating the filters for 48 h with ultrapure water at pH 2 in the dark. Blank duplicates with only filters and ultrapure water at pH 2 were prepared simultaneously. Then the same DOM extraction process was performed (Dittmar et al., 2008) using PPL cartridges. Afterwards, the SPE-DOC

extracts were concentrated at room temperature via evaporation in a centrifugal evaporator system (Christ, Germany) by a factor of >5 prior to measurements on the FT-ICR-MS in order to yield DOC concentrations >20 mg L^{-1} .

Mass spectra were obtained in negative ionization mode using the 15 tesla FT-ICR-MS at the University of Oldenburg (Germany) (Solarix, Bruker Daltonics, USA) combined with an ESI device (Bruker Apollo II) with a needle voltage set to -4 kV. All extracts were analyzed at a DOC target concentration of 20 mg L^{-1} in 1:1 volumetric water to methanol mixture. A total of 500 scans were accumulated per run. The mass-to-charge window was set to 150–2000 Da. Internal calibration of the spectra was performed using the Bruker Daltonics Data Analysis software package with help of an established calibration list for marine dissolved organic matter, consisting of >100 mass calibration points of known molecular formulae. The data was processed using in-house Matlab routines (Riedel et al., 2012) and molecular formulae with C_{1-100} , H_{1-250} , O_{1-100} , N_{0-4} , S_{0-2} or P_{0-1} were assigned to peaks with a minimum signal-to-noise ratio of four according to Koch et al. (2007). In the case of DOM extracted from the precipitates, only those molecular formulas detected in both analytical replicates were considered, which efficiently removed non-analytes from the data set that result from noise in the mass spectra (Riedel and Dittmar, 2014). For control of overall mass spectrometry quality and reproducibility, twice a day an in-house reference of DOM from North Equatorial Pacific Intermediate Water (NEQPIW) was analyzed (Green et al., 2014; Riedel and Dittmar, 2014). Peak identification was done according to Riedel and Dittmar (2014).

Molecular formulas were used to calculate two indexes: the Double Bond Equivalence Index ($\text{DBE} = 1 + 1/2(2\text{C} - \text{H} + \text{N} + \text{P})$) in order to evaluate the degree of unsaturation, and the modified aromaticity index ($\text{AI}_{\text{mod}} = (1 + \text{C} - 1/2\text{O} - \text{S} - 1/2\text{H}) / (\text{C} - 1/2\text{O} - \text{S} - \text{N} - \text{P})$) to estimate the presence of aromatics ($\text{AI}_{\text{mod}} \geq 0.5$) and condensed aromatics ($\text{AI}_{\text{mod}} \geq 0.666$) taking in consideration the abundance of carboxyl groups in natural organic matter (Koch and Dittmar, 2006). Condensed aromatics containing nitrogen, sulfur or phosphorus were excluded for data interpretation as they were not specifically confirmed by the presence of the respective ^{13}C isotopologous due to their low abundance in the mass spectra. Signal intensities of individual signals were converted into percentages relative to total signal intensity in a sample. These relative signal intensities were used to calculate intensity weighted averages of DBE index, AI_{mod} and molar ratios (H/C, O/C) (e.g. Schmidt et al., 2009; Seidel et al., 2014).

3. Results and discussion

3.1. Hydrothermal fluids imprint on general geochemistry

The shallow hydrothermal vents in Soufrière Bay (south-west Dominica Island) released fluids of 55 °C temperature and a slightly acidic pH of 6.33 (Table 1). In contrast, surface seawater samples were 28 °C and had a pH of 7.90 (Table 1). Previous studies on Dominica marine shallow hydrothermal systems in Champagne Hot Springs (~2 km North from Soufrière Bay) reported a similar range of fluid temperatures from 44 to 71 °C with a pH ranging from 5.95 to 6.27 (McCarthy et al., 2005). However, not just submarine venting occurs at this island. Dominica has been reported as the most volcanically productive island in the Lesser Antilles arc with several areas of geothermal activity (Lindsay et al., 2005; Fig. 1). Some ponds or lakes can reach up to 97 °C and strongly acidic pH of 1.4 has been reported (e.g. Boiling Lake, Valley of Desolation; Joseph et al., 2011). The strong difference in temperature and pH between terrestrial and marine vents is due to the fact that Dominica submarine fluids are meteorically influenced and mixed with seawater (McCarthy et al., 2005). Meteoric influence plays a key role in the composition of the fluids at shallow hydrothermal systems, generating variations in fluids temperature and geochemical composition (Pichler, 2005; Tarasov et al., 2005). In our study, the

Table 1

Chemical composition of Dominica surface seawater, Soufrière shallow hydrothermal vent fluids, and the hydrothermal fluids analyzed in the co-precipitation experiment before and after 10 h aeration. The elements As, F and Mn are not shown as their values were always below detection limit (b.d.).

	Dominica surface seawater	Soufrière Bay hydrothermal fluids	Co-precipitation experiment	
			Initial hydrothermal fluids	Hydrothermal fluids after 10 h aeration
Temperature (°C)	28	55	55	n.a.
Water depth (m)	0	5	5	5
pH	7.90	6.33	n.a.	n.a.
Salinity	30.8	10.9	n.a.	n.a.
DOC (µM)	99	27	25	23
<i>Major elements (mM)</i>				
Br	0.83	0.20	0.26	0.28
Ca	11.0	3.97	2.43	4.12
Cl	569.6	141.8	190.8	199.3
K	10.6	3.19	3.46	3.63
Mg	60.3	18.2	18.5	20.3
Na	513.6	149.3	154.9	174.0
SO ₄	26.1	7.42	7.65	9.27
<i>Trace elements (µM)</i>				
B	409.7	543.2	448.4	499.1
Fe	b.d.	214.7	186.4	105.5
Li	45.5	64.3	55.2	61.2
Si	b.d.	665.9	268.1	351.3
Sr	88.3	26.4	24.4	29.5

salinity of the fluids (10.9) suggests a mixture of meteoric water and seawater (Table 1).

The chemical composition of Soufrière Bay hydrothermal fluids differed from surface seawater (Fig. 2). Br, Ca, Cl, K, Mg, Na, SO₄ and Sr were depleted in the fluids as compared to seawater, probably due to mixing with meteoric waters (McCarthy et al., 2005). Potential interactions of hot fluids with minerals in the subsurface might be another explanation (Pichler, 2005). In contrast, dissolved Fe and Si were strongly enriched in the fluids (Fig. 2). Previous studies on Dominica marine shallow hydrothermal systems demonstrated that concentrations of Fe²⁺ were similar to the concentration of total dissolved Fe as determined by ICP-OES (McCarthy et al., 2005; Kleint et al., 2015), indicating that the predominant dissolved species in the vent fluids of our study was ferrous iron as well. In surface seawater, dissolved Fe is rapidly removed due to insolubility of Fe(OH)₃ after oxidation of Fe²⁺ (Fig. 3). Fe³⁺ precipitates typically form spherical particle aggregates often enriched in Si (e.g. Boyd and Scott, 1999, 2001). They commonly form in the oceans (von der Heyden et al., 2012), usually associated to volcanic areas (e.g. Franklin Seamount at Papua New Guinea; Boyd and Scott, 2001). SEM microscopic images of hydrous ferric oxides precipitates, which precipitated around the shallow hydrothermal vents off Dominica also showed spherical particles of successively smaller spheres containing Fe and Si (Fig. 3). The energy-dispersive X-ray (EDX) spectrum indicated up to 20% SiO₂ in the structure, which is common for ferrihydrite precipitated abiotically from hydrothermal fluids (Pichler and Veizer, 1999; Pichler et al., 1999a).

3.2. DOC depletion in the hydrothermal fluids

The DOC concentration of Soufrière Bay shallow-water hydrothermal fluids (27 µM on average) was less than 30% compared to that of Dominica surface seawater (99 µM on average; Table 1). The surface seawater DOC concentration was higher than typical for the open ocean, but representative for coastal regions (Dittmar and Stubbins, 2014). In our case, given the close proximity to the island with intensive biomass production an input of terrigenous organic matter is a likely explanation for the enhanced DOC concentration in the surface seawater. Lignin-derived phenols are representative compounds of terrigenous

DOM (Dittmar and Stubbins, 2014). In our study, we identified ~2% more aromatics in the surface seawater of Dominica compared to North Equatorial Pacific Intermediate Water (NEqPIW) supporting the possibility of terrigenous enrichment. Furthermore, the hydrothermal system of Dominica is located in a shallow and continuously mixed water column, influencing benthic–pelagic coupling and subsequent production of DOC by plankton. Therefore, high DOC concentrations in the surface seawater of Dominica could be explained by both terrigenous enrichment and/or microbial production.

One likely explanation for the low DOC concentration in the hydrothermal fluids (27 µM DOC; Table 1) could be the influence of low-DOC meteoric water. Fluids in a shallow-water hydrothermal system may be derived from any or a combination of the following sources: meteoric water, seawater, connate water and magmatic water (Pichler, 2005; McCarthy et al., 2005). In our study, the salinity, seawater major elements (Br, Ca, Cl, K, Mg, Na, SO₄) and DOC concentration in the hydrothermal fluids accounted approximately for 30% of seawater values, respectively. The DOC concentration in the fluids was 27% compared to seawater, the salinity of the fluids was 35% compared to seawater salinity and seawater major elements concentration in the fluids was 29 ± 4% of surface seawater concentrations (Table 1; Fig. 2). This suggests that seawater accounted for approximately one third of the fluids and the other two thirds were from meteoric origin although discharging in a submarine environment, along with possible magmatic contributions (e.g. Giggenbach, 1992; McCarthy et al., 2005). However, biotic consumption or abiotic depletion of DOC during seawater re-circulation through the sediment cannot be ruled out as an additional reason for the low DOC concentrations (Bennett et al., 2011). In deep waters, active processes in hydrothermal systems should actively sequester organic carbon and play an important role globally in the delivery of particulate organic carbon (POC) to the seafloor (German et al., 2015). During hydrothermal circulation within the Earth's crust, seawater DOC can be removed though the exact mechanism is still unknown. This removal is estimated as 4% of the global rate of refractory DOC removal (Lang et al., 2006; Hansell et al., 2009; Hansell, 2013). Potential explanations of DOC removal are microbial consumption driven by deep-sea vent communities, interaction with minerals in the subsurface leading to DOC sorption or direct abiotic thermal degradation of DOC (Lang et al., 2006; Santelli et al., 2008; Bennett et al., 2011; Hawkes et al., 2015).

The possibility of potential subsurface heterotrophic consumption in the shallow hydrothermal system of Dominica should be further investigated. However, abiotic processes such as organic matter adsorption to mineral surfaces favored by high porosity of the sediment or thermal degradation of DOC are potentially feasible in Dominica. An increase in temperature may affect the ability of water to react with organics (Siskin and Katritzky, 1991), though the temperature difference between fluids and seawater is less severe in shallow hydrothermal systems than in deep-sea vents (Tarasov et al., 2005; Table 1). Nevertheless, DOC concentration of Dominica fluids was in between the averaged DOC concentrations of high temperature deep-sea hydrothermal fluids (200–350 °C; 15–17 µM of DOC) and low temperature diffuse fluids (20–85 °C; 47–48 µM of DOC) (Juan de Fuca Ridge; Lang et al., 2006). Therefore, similar abiotic processes in DOC depletion may be taking place at shallow-water and deep-sea hydrothermal systems.

3.3. Hydrothermal fluids imprint on the DOM signature

A total of 2840 molecular formulas were identified in the DOM of the hydrothermal fluids from Soufrière Bay, 2538 in Dominica surface seawater and 2418 in NEqPIW. We applied a common detection limit on the relative signal intensity scale to facilitate maximum comparability among samples, and this explains the relatively low number of compounds detected in NEqPIW compared to previous studies (Riedel and Dittmar, 2014). In the DOM of the hydrothermal fluids, the largest fraction (45.3%) of all assigned formulas were organic compounds

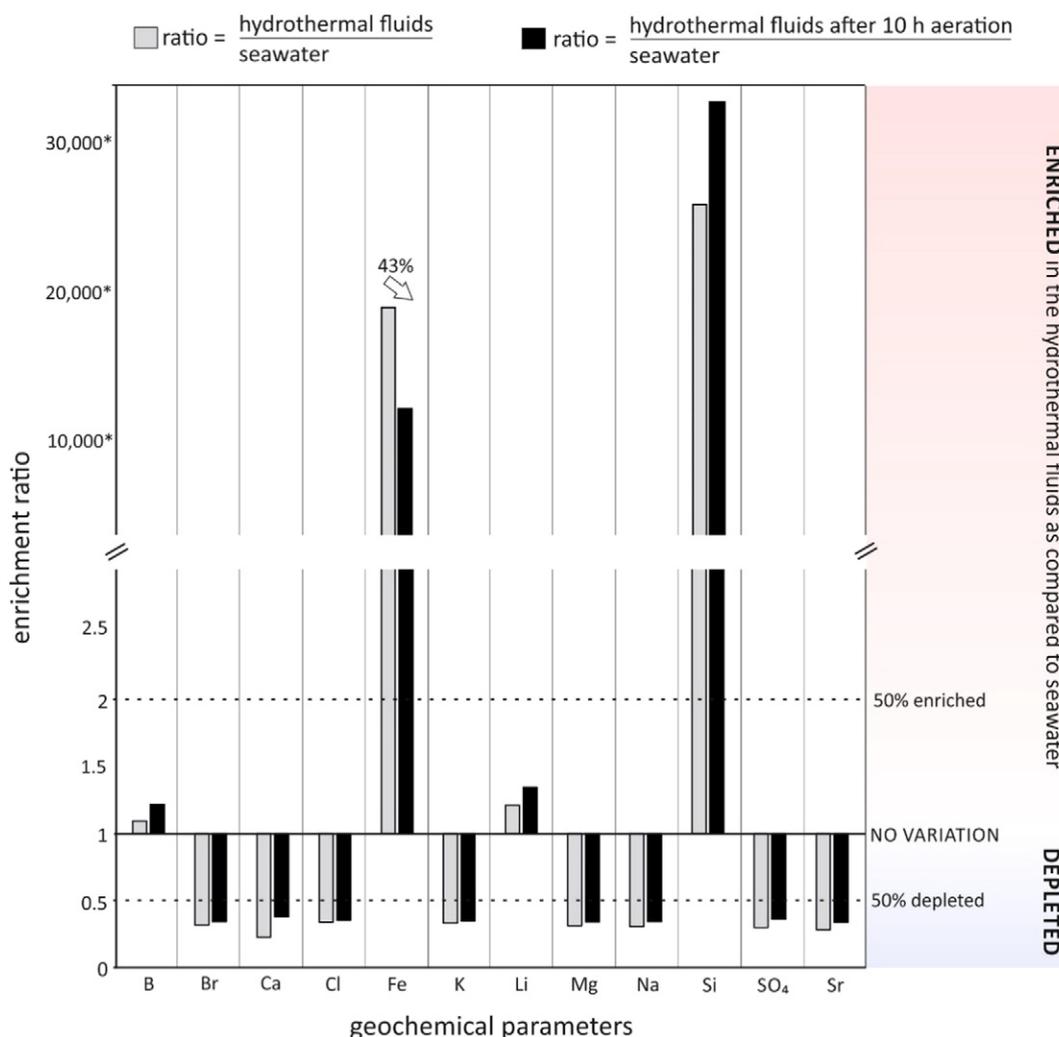


Fig. 2. Geochemical enrichment ratios of the hydrothermal fluids as compared to the seawater before and after induced 10 h aeration, being initial hydrothermal fluids (gray) and hydrothermal fluids after 10 h aeration (black). The value of the detection limit (0.01 mg L^{-1}) was attributed to the seawater values of Fe and Si (both b.d.) in order to calculate the minimum enrichment ratios (*). The elements As, F and Mn were not showed as their values were always b.d. in both hydrothermal fluids and seawater.

containing only carbon, hydrogen and oxygen atoms (CHO), followed by compounds containing also nitrogen with or without sulfur and phosphorus (39.5%; CHON, Table 2). In the surface seawater DOM, the CHO compounds represented the most abundant group of formulas (44.6%), closely followed by CHON (42.8%). However, in NEqPIW the nitrogen-containing compounds were more abundant (45.3%) than CHO compounds (42.4%). Formulas containing sulfur with or without nitrogen and phosphorus were 14.2% in the hydrothermal fluids, 11.7% in surface seawater and 11.1% in NEqPIW (CHOS, Table 2). The abundance of phosphorus-containing formulas with or without nitrogen and sulfur was always below 1.5% in hydrothermal fluids, close to 2% in Dominica seawater and 3.2% in NEqPIW (CHOP; Table 2).

The DOM from the fluids had higher DBE (9.26 compared to 8.37 or 8.89) and lower H/C ratio (1.18 versus 1.25) intensity-weighted averages than surface seawater or NEqPIW (Table 2), indicating more unsaturated compounds in the hydrothermal fluids than in the seawater. Compared to other environments, DOM from Dominica hydrothermal fluids was more unsaturated than Svalbard fjords water samples (8.43 DBE; 1.27 H/C; Osterholz et al., 2014), glaciers from Austrian Alps (1.22–1.64 H/C; Singer et al., 2012) or pore water from sediments of the northwest Iberian shelf (8.40–8.95 DBE; 1.24–1.29 H/C; Schmidt et al., 2009). The degree of unsaturation from Dominica fluids was similar to pore water from intertidal sediments of the southern North Sea (1.00–1.25 H/C; Seidel et al., 2014) or rivers from northwest Spain

(8.92–10.18 DBE, 1.13–1.19 H/C; Schmidt et al., 2009), but lower than fen ponds from northern Germany (1.05–1.17 H/C; Riedel et al., 2013). The O/C ratio average of Dominica hydrothermal fluids was lower than the surface seawater or NEqPIW (0.43 versus 0.49; Table 2), and also compared with other environments like Svalbard fjord water samples (0.46 O/C; Osterholz et al., 2014), glacier DOM from Austrian Alps (0.38–0.62 O/C; Singer et al., 2012), rivers or pore water from the northwest Iberian shelf (0.49–0.52 O/C; Schmidt et al., 2009) or pore water from intertidal sediments of the southern North Sea (0.45–0.50 O/C; Seidel et al., 2014). A similar O/C ratio was found in fen ponds from northern Germany (0.41–0.44 O/C; Riedel et al., 2013). Thus, our data indicated potential input of unsaturated and reduced DOM compounds from Dominica shallow hydrothermal fluids into the surrounding seawater. These compounds likely originate from decomposition of vascular plant biomass (Dittmar and Stubbins, 2014).

Lower H/C ratios could also be indicative of increasing aromaticity. Applying the aromaticity index (Koch and Dittmar, 2006), we detected more aromatic compounds in the hydrothermal fluids than in surface seawater or NEqPIW (16.2 to 13.3 and 11.7%; Table 2). The relative abundance of condensed aromatics was also higher but below 2% in all the samples (1.6 to 1.3 and 0.3%; Table 2). Potential explanations for the variations in aromatic compounds between shallow-water hydrothermal fluids and seawater might be photooxidation due to light irradiation, microbial degradation, or a coagulation together with iron-

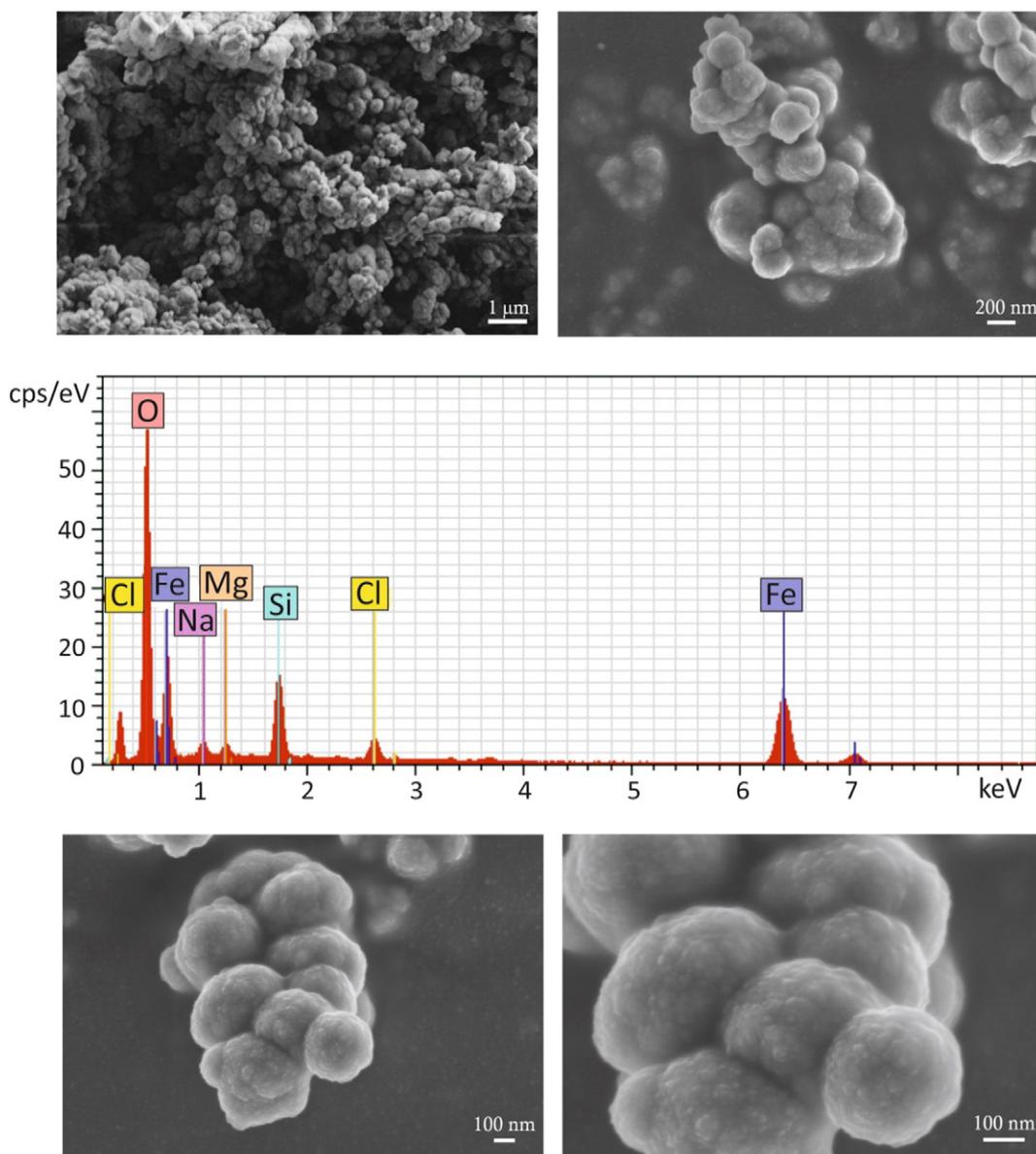


Fig. 3. Scanning electron micrographs of hydrous ferric oxide (2-line ferrihydrite), which precipitated in the vicinity of the shallow hydrothermal vents and the associated energy dispersive X-ray (EDX) spectrum indicating the chemical composition to be mainly O, Fe and Si. The minor peaks for Cl, Na and Mg are a preparation artifact. During drying of the ferrihydrite, seawater evaporates and those elements remain in quantities detectable by EDX.

Table 2
Summary of molecular composition of the DOM samples of seawater, hydrothermal fluids and co-precipitated DOM in the iron precipitates given in percentages of the relative abundances of the total DOM, and as intensity-weighted average values, where indicated.

	NEqPIW	Dominica surface seawater	Soufrière Bay hydrothermal fluids	Co-precipitation experiment			
				Initially		After 10 h aeration	
				Hydrothermal fluids	Iron precipitates	Hydrothermal fluids	Iron precipitates
Total formulas	2418	2538	2840	2673	292	2524	185
H/C ratio, average	1.25	1.25	1.18	1.19	1.33	1.20	1.28
O/C ratio, average	0.49	0.49	0.43	0.44	0.40	0.44	0.41
DBE index, average	8.89	8.37	9.26	9.01	5.77	8.94	6.00
AI _{mod} index, average	0.25	0.25	0.31	0.31	0.23	0.31	0.26
CHO, %	42.4	44.6	45.6	46.1	57.2	46.4	73.0
CHON, %	45.3	42.8	39.5	38.8	13.0	38.6	2.7
CHOS, %	11.1	11.7	14.2	14.4	29.8	14.5	23.8
CHOP, %	3.2	1.9	1.4	1.3	1.0	1.1	0.5
Aromatics, %	11.7	13.3	16.2	17.2	13.4	17.4	20.0
Condensed aromatics, %	0.3	1.3	1.6	1.6	3.8	1.7	5.9

oxidation in a similar way as occurs in terrestrial iron-rich ponds (Riedel et al., 2012, 2013). Photodegradation decreases the abundance of aromatics and is accompanied by an increase in compounds with higher O/C ratios, because aromatics should be transformed to more saturated and oxidized compounds (Schmitt-Koplin et al., 1998; Gonsior et al., 2009). Our results showed an increase in the O/C ratio average from 0.43 to 0.49 comparing fluids with seawater. Photo-labile compounds in marine DOM have been reported frequently (e.g. Stubbins et al., 2012; Gonsior et al., 2013) and photo-degradability was reported as varying with the degree of condensation of the molecule and, therefore, with the aromaticity (Stubbins et al., 2012). Dominica hydrothermal fluids were taken at shallow waters (5 m water depth) where solar irradiation may reach, so that photodegradation of the surface seawater or of the hydrothermal fluids when they were collected immediately after being released from the shallow hydrothermal vents (Fig. 1) might be a possible explanation. That could explain the low abundance of aromatics (13–16%) and condensed aromatics (1–2%) in the marine hydrothermal system of Dominica compared to terrestrial environments with limited penetration of light. For instance, turbid fen waters presented aromatics relative abundances between 20 and 35% and condensed aromatics up to 11% (Riedel et al., 2013). The second possible explanation for the variations in aromatic compounds between hydrothermal fluids and seawater might be microbial degradation of aromatics. However, aromatic moieties are generally less susceptible to microbial attack (Riedel et al., 2013). Thus, the third possibility of iron-coagulation of DOM is a potential explanation due to the depletion of dissolved iron and the precipitation of hydrous ferric oxides in this specific environment (McCarthy et al., 2005; Fig. 3). We tested the hypothesis that DOM is co-precipitating with Fe^{3+} oxides forming upon oxidation of the hydrothermal fluids from Dominica by artificially inducing such a precipitation under laboratory conditions.

3.4. Co-precipitation modulates DOM composition

After inducing 10 h aeration of the hydrothermal fluids, an 8% decrease in DOC co-occurred simultaneously with a 43% depletion of dissolved iron (Fig. 2). Fe was the only detected element that was depleted in solution after precipitation, while most others did not show variations (Fig. 2). Calcium and Si were enriched in the filtrate after 10 h most likely due to the crystals dissolving when the hydrothermal fluids cooled down during the oxygenation, as for instance occurs due to the retrograde solubility of calcite or aragonite (Morse and Mackenzie, 1990). Previous studies on iron-precipitation in deep-sea hydrothermal plumes estimated Fe^{2+} oxidation rates with Fe^{2+} half-lives ranging from 15 min in North Atlantic Ocean to ~6 h in North East Pacific Ocean (Field and Sherrell, 2000). In deep-sea hydrothermal plumes from vents of the Indian Ocean, the average half-life of Fe^{2+} was 2.31 h (Statham et al., 2005). That more than 50% of the dissolved iron still remained in solution after 10 h of contact with air suggests Dominica shallow hydrothermal system as a promising site to study potential complex formation with iron binding ligands as proposed for deep-sea hydrothermal plumes (Bennett et al., 2008; Sander and Koschinsky, 2011; Hawkes et al., 2013). The apparently slow Fe^{2+} oxidation rate of Dominica hydrothermal fluids might be caused by the precipitation of Fe^{3+} colloids, which equivalent diameter (~50 nm; Field and Sherrell, 2000) may count them to the dissolved pool because colloids are smaller than filters pore size (e.g. Wu et al., 2001; Hawkes et al., 2013, 2014). The possibility of Fe^{3+} colloids rapidly clumping together prior to the initial stage of the co-precipitation experiment was consistent with the spherical particles of successively smaller spheres observed in the SEM microscope images (Fig. 3). This could be an explanation of the minor differences observed in the molecular DOM composition between the initial and aerated hydrothermal fluids during the co-precipitation experiment (Table 2).

However, we observed clear trends in the re-solubilization of the iron precipitates. 2673 formulas were detected originally in the filtrated

hydrothermal fluids, 292 sorbed onto particles in co-precipitated DOM, and these numbers of formulas decreased to 2524 and 185 after 10 h aeration, respectively (Table 2). The samples were stored under dark conditions during re-solubilization, and so photodegradation cannot explain the decrease in DOC concentration associated to the 10 h aeration. Consequently, the observed molecular changes did not match those that would be expected for photo-degradability (Gonsior et al., 2009; Stubbins et al., 2012; Table 2). Instead, we propose that DOM was co-precipitated with Fe^{3+} oxide particles as previously demonstrated in other environments (e.g. Riedel et al., 2013). Combining both initial and aerated samples, we observed evidence for selective alteration of the DOM molecular composition. If there would be no selectivity, the relative abundances, molar ratios and index averages should remain similar in the co-precipitated DOM. However, the DOM fraction in the iron precipitates contained more reduced and saturated compounds than the DOM in the filtrated hydrothermal fluids (co-precipitated DOM: 0.40 ± 0.01 O/C; 1.31 ± 0.03 H/C; 5.89 ± 0.12 DBE; hydrothermal fluids: 0.44 ± 0.00 O/C; 1.19 ± 0.01 H/C; 8.98 ± 0.04 DBE; Table 2). The DOM compounds category preferentially co-precipitating with iron were those containing only CHO (co-precipitated DOM: $65.1 \pm 7.9\%$ CHO; hydrothermal fluids: $46.3 \pm 0.2\%$ CHO; Table 2; Fig. 4), followed by compounds containing sulfur most likely due to the affinity of iron to form metal sulfides in hydrothermal fluid precipitates (Pichler et al., 1999b) (co-precipitated DOM: $26.8 \pm 3.0\%$ CHOS; hydrothermal fluids: $14.5 \pm 0.1\%$ CHOS; Table 2; Fig. 4). In contrast, the compounds containing nitrogen or phosphorus preferentially remained in solution (co-precipitated DOM: $7.9 \pm 5.2\%$ CHON; $0.8 \pm 0.3\%$ CHOP; hydrothermal fluids: $38.7 \pm 0.1\%$ CHON; $1.2 \pm 0.1\%$ CHOP; Table 2; Fig. 4).

In marine environments, iron availability is mainly limited by the solubility of Fe^{3+} that is determined as a function of pH, temperature and ionic strength (Johnson et al., 1997; Liu and Millero, 1999, 2002). In our study, the mixing of hydrothermal fluids with seawater may have increased the pH and decreased the temperature favoring the precipitation of Fe^{3+} oxides, as in other shallow hydrothermal systems (e.g. Tutum Bay, Papua New Guinea; Pichler and Veizer, 1999). Some compounds may precipitate faster than others (Fig. 4d). After 10 h aeration, compounds containing nitrogen, sulfur or phosphorus decreased in abundance in the co-precipitated DOM, but the relative proportion of only CHO compounds increased (Table 2; Fig. 4a). Consequently, there was an increase of 6.6% of aromatics associated with the re-dissolved precipitates (13.4 compared to 20.0%; Fig. 4a) supporting the iron-coagulation theory of Riedel et al. (2013). In terrestrial environments, the coagulation of DOM by iron depends on the DOC/metal ratio (Riedel et al., 2012). At ratios ~9, preferential removal of aromatic compounds is observed while at lower ratios ~1 additionally more oxidized and highly aromatic compounds disappear. In our case, the DOC/ Fe^{2+} ratios were ~0.3 (Table 1), which is much lower than required for quantitative co-precipitation of iron and DOM (Nierop et al., 2002). Therefore, marine hydrothermal DOM may also be subject to preferential precipitation with Fe^{3+} similar to terrestrial environments (Riedel et al., 2012, 2013). Our data showed the potential of FT-ICR-MS to perform molecular characterization of the DOM associated with hydrothermal fluids and iron precipitates.

4. Conclusions

Here we applied FT-ICR-MS to characterize the molecular composition of DOM in hydrothermal fluids from a shallow-water system and of the DOM fraction that co-precipitates with Fe^{3+} . Hydrothermal fluids were strongly enriched in dissolved Fe and Si, but DOC concentrations were less than 30% compared to the surface seawater. The DOC depletion in the fluids was most likely due to low-DOC meteoric water influence but also suggested biotic or abiotic processes consuming or depleting DOC when seawater entrained the sediment. Dominica fluid DOC concentration was in between the average of high temperature deep-sea hydrothermal fluids and low temperature diffuse fluids DOC

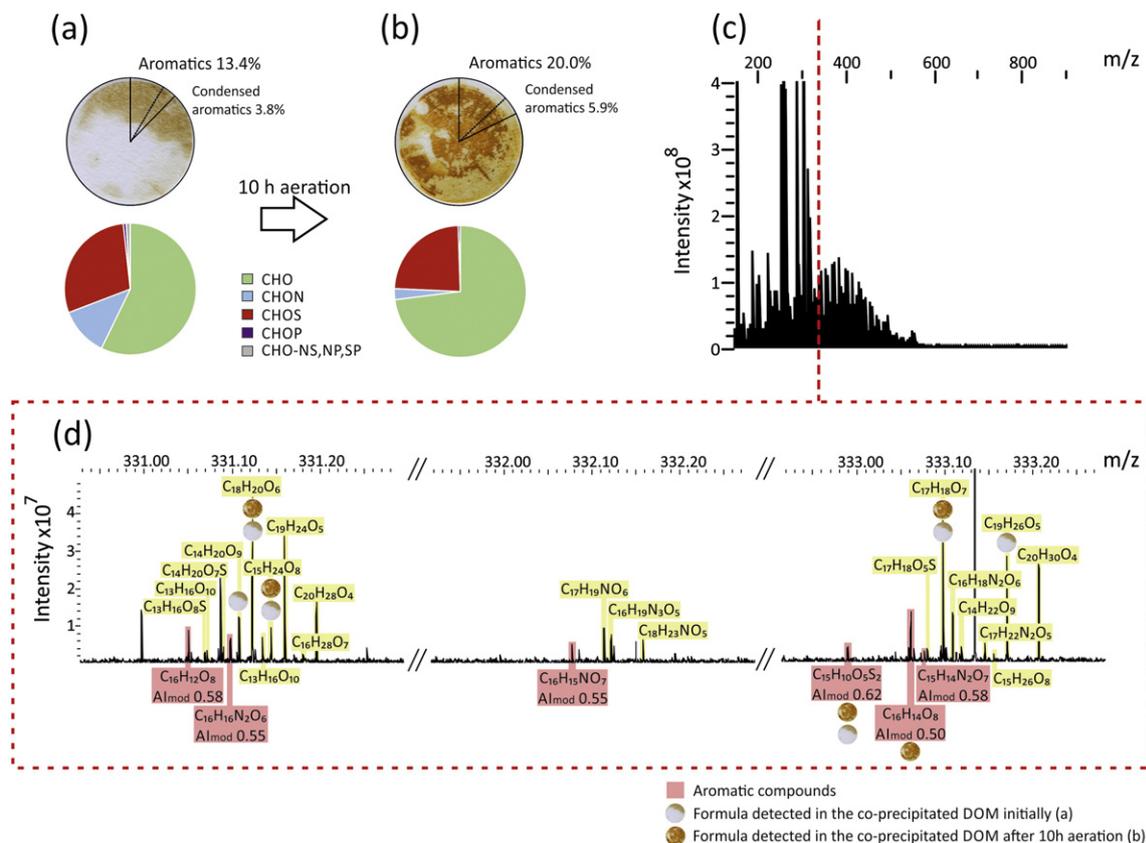


Fig. 4. Co-precipitation experiment summary, showing the percentage of aromatic compounds and different formula groups of total DOM from iron precipitates re-solubilization, overlaying the original photography of the filters where the iron-precipitation was visible. Being: (a) initial hydrothermal fluids filters; (b) the same hydrothermal fluids filters after 10 h aeration; (c) FT-ICR mass spectra (ESI negative mode) of the initially filtrated hydrothermal fluids. (d) expanded section of the mass spectra at 331–333 Da with the identified molecular formulas, the compounds classified as aromatics and those formulas detected in the co-precipitated DOM initially and/or after 10 h aeration (e.g. $C_{14}H_{20}O_9$ was identified in the co-precipitated DOM initially, $C_{16}H_{14}O_8$ only after 10 h aeration and $C_{18}H_{20}O_6$ in both, initially and after 10 h aeration co-precipitated DOM).

concentrations. Thus, similar abiotic processes in DOC depletion may be taking place at shallow-water and deep-sea hydrothermal systems.

Formation of hydrous ferric oxides by aeration of the hydrothermal fluids for 10 h lead to an 8% decrease in DOC, indicating co-precipitation of iron and DOM. Due to the fact that 50% of the Fe^{2+} still remained in solution after 10 h aeration, we propose Dominica iron-rich hydrothermal system as a suitable marine environment to perform further investigation on iron binding organic ligands. Re-solubilization of iron precipitates revealed co-precipitated DOM with more reduced and saturated compounds than the filtrated hydrothermal fluids. The main category of DOM compounds co-precipitating with iron were those containing only CHO followed by sulfur-containing compounds. In contrast, compounds containing nitrogen or phosphorus preferentially remained in solution. After 10 h aeration we detected increased relative abundance of aromatic compounds in the co-precipitated DOM, which is in accordance with iron-coagulation in terrestrial environments.

In conclusion, we provide evidence for selective alteration of DOM molecular composition in shallow hydrothermal systems, which are linked to the special abiotic processes occurring in these extreme environments. We showed the potential of studying the hydrothermal fluids and iron precipitates with ultra-high resolution mass spectrometric techniques to improve the general understanding of DOM and the role of iron and hydrothermal vents in marine ecosystems.

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