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Geochemical characteristics, speciation and size-fractionation of iron (Fe) in two marine shallow-water hydrothermal systems, Dominica, Lesser Antilles

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A B S T R A C T

Marine shallow-water hydrothermal systems have so far largely been neglected with respect to trace metal fluxes and possible stabilizing complexation processes, even though they emit their fluids directly into the photic zone. The impact of stabilized dissolved metal input by shallow vents into surface waters as well as the effect on the transport and bioavailability of bioactive trace metals within the area of highest primary production rates in the world oceans is therefore, at present, mostly unknown.

In this study, we investigated the concentration, size fraction distribution (colloidal and soluble) as well as redox speciation and labile concentrations of the limiting micronutrient iron (Fe) at two marine shallow-water hydrothermal systems (Champagne Hot Springs and Soufriere) off the coast of Dominica, Lesser Antilles Island Arc, Caribbean.

Geochemical characterization of the two different vent sites showed that both are affected by meteoric and seawater influence, with a stronger meteoric influence at Soufriere than at Champagne Hot Springs. Measurements of soluble and labile Fe were performed using a modified competitive ligand exchange – adsorptive cathodic stripping voltammetry (CLE-AdCSV) with salicylaldoxime (SA) as the artificial ligand. Our results show that focused fluids discharging at the seafloor, as well as hydrothermal pore fluids are, despite a calculated theoretical oxidation half-life of only 6.4 min, highly enriched in Fe(II), indicating a strong complexation of Fe(II), strong enough to prevent Fe(II) from oxidation and precipitation. Since these fluids show enriched dissolved organic carbon (DOC) concentrations, and very low fractions of chemically labile Fe, complexation may occur by organic carbon, which was recently suggested to also be a factor in stabilizing particulate Fe(II) in deep-sea hydrothermal non-buoyant plumes.

Our results indicate that shallow-water hydrothermalism off the coast of Dominica releases high concentrations of stabilized, bioavailable Fe(II) into the photic zone, which influences the biogeochemical cycle of Fe in surface waters. Considering the abundance of marine shallow-water hydrothermal systems in many regions, such processes may even play a role in the global oceanic dFe cycle.

1. Introduction

Although more accessible than deep-sea hydrothermal systems, their shallow-water counterparts have so far not gained comparable scientific attention with respect to their dissolved metal concentration, speciation and possible metal-ligand complexation. By definition marine shallow-water hydrothermal systems are located in water depths <200 m (Tarasov et al., 2005) and therefore directly emit hydrothermal fluids into the photic zone, where they are most likely to influence primary production rates. Although fluid temperatures vary between 10 °C

and just above 100 °C in these shallow systems, far lower than those encountered at deeper vent sites, their fluids are enriched in concentrations of dissolved metals, compared to seawater. Phototrophic and chemotrophic organisms living in and around marine shallow-water vents in the photic zone are exposed to those high metal concentrations, with some of the metals being biologically essential micronutrients, such as iron (Fe), while others may be toxic at nanomolar concentrations, such as copper (Cu) or arsenic (As). Hence, marine shallow-water hydrothermal systems can be sources of trace metals to the ocean (e.g. Pichler et al., 1999b).

It is now globally accepted that not only atmospheric dust deposition and fluxes of material from continental margins are major sources of Fe to the ocean, but that deep-sea vents also contribute a large

fraction of dissolved Fe (dFe, <0.2 μm) to the global oceanic dFe budget; stabilized by organic molecules or as inorganic nanoparticles (Bennett et al., 2008; Gartman et al., 2014; Hawkes et al., 2013; Hsu-Kim et al., 2008; Kleint et al., 2016; Sander and Koschinsky, 2011; Yücel et al., 2011). However, in the distal open ocean, dFe concentrations are low, due to its poor solubility in seawater and microbial uptake (Johnson et al., 1997; Liu and Millero, 2002; Maldonado and Price, 2001). These low concentrations of Fe are known to limit primary production in 40% of the global surface ocean (Moore et al., 2004).

Since most shallow-water hydrothermalism is found in proximity to the coast, it might act as an additional Fe source to coastal oceans, in the same way as their deep-sea counterparts do for the distal ocean, while the bioavailability of Fe is controlled by its speciation, rather than by the concentration of Fe alone. However, to date, no studies about the speciation of Fe were carried out in shallow hydrothermal vent systems. Instead, their role in the ocean with respect to the biogeochemical cycle of metals and their bioavailability may have been underestimated. In contrast, hydrothermal Fe derived from deep-sea vents has found attention and is being considered in the global oceanic dFe cycle (e.g. Resing et al., 2015; Tagliabue et al., 2010).

Iron exists in two oxidation states in seawater: the bioavailable and very soluble Fe(II), occurring naturally in chemically reducing conditions, such as hydrothermal vent fluids or near oxygen minimum zones, and Fe(III) in well oxygenated waters (Landing and Westerlund, 1988). Since the bioavailable and soluble Fe(II) is rapidly oxidized to thermodynamically stable and highly insoluble Fe(III) in oxic waters (Kuma et al., 1996), microorganisms can adapt to the natural Fe limitation in the distal ocean by producing metal chelating molecules - so called organic ligands, such as siderophores (Kraemer, 2004). These organic ligands form stable complexes with Fe that increase Fe solubility and thereby facilitate its uptake (Vraspir and Butler, 2009). In surface and in oxic deep waters, such complexation dominates the speciation of Fe(III) and electrochemical measurements revealed that 99% of all dFe is strongly complexed by organic ligands, increasing Fe solubility and therefore also the total dissolved Fe concentration in the world's oceans as well as its bioavailability (Boyd et al., 2010; Gledhill and van den Berg, 1994; Rue and Bruland, 1995; Wu and Luther, 1995).

Most coastal areas are not considered to be Fe limited and the production of Fe(III) chelating molecules may not be crucial in such environments, however, such waters are mostly well oxygenated and the solubility of Fe(III) remains very low.

Together with other trace metals, the vent fluids off the coast of Dominica release high concentrations of Fe(II) into surface waters (McCarthy et al., 2005) but it is not known whether Fe(II) is stabilized or directly oxidized upon mixing with seawater. Both mechanisms will directly affect the biological cycle in the photic zone. Additionally, no data is available on, whether the introduced dFe (Fe(II)) is predominant in a dissolved colloidal form (0.2 μm to 0.02 μm) or the truly dissolved (soluble, <0.02 μm) fraction, and how much of the Fe is actually chemically labile and thereby available to marine organisms. Filtration through conventional membrane filters of different pore sizes provides the standard way of operationally defining different Fe size fractions, such as dissolved Fe (dFe <0.2 μm); whereby this dissolved fraction can be separated into two sub-fractions: colloidal Fe (cFe, 0.2 μm to 0.02 μm) and soluble Fe (sFe, <0.02 μm) (Landing and Lewis, 1991).

These different fractions have different environmental and biological mobility and may not be equally bioavailable. Since the soluble species of dFe is believed to be more bioavailable than colloidal Fe, it may control the community structure of primary producers (Boye et al., 2010; Chen et al., 2003; Chen and Wang, 2001; Cullen et al., 2006; Gledhill and Buck, 2012).

Another process that introduces Fe(II) to surface waters is the transformation of Fe(III) to Fe(II) by UV or microbial reduction (Kuma et al., 1992; Rijkenberg et al., 2005). However, if Fe(II) is not stabilized in its oxidation state, it will oxidize back to Fe(III) within a few minutes,

due to the very short oxidation half-life of Fe(II) in warm and oxic waters at natural seawater pH (Millero et al., 1987).

Recent research has shown that dissolved organic matter (DOM) has the ability to stabilize dFe (Gledhill et al., 2015; Stockdale et al., 2016) and that dissolved organic carbon (DOC) might stabilize hydrothermally vented Fe(II) (Toner et al., 2009). Additionally, the presence of Fe-binding ligands in rainwater and organic Fe(II) complexation in DOC rich rivers and estuaries have been reported (Cheize et al., 2012; Hopwood et al., 2015). Since shallow-water hydrothermal fluids can contain appreciable concentrations of DOC (Dittmar and Stubbins, 2014; Gomez-Saez et al., 2015; Hawkes et al., 2015; Rossel et al., 2015) they may play an important role in near shore Fe cycling. In order to examine the hydrothermal Fe fluxes at shallow-water hydrothermal vents and the potential role of DOC in stabilizing hydrothermal Fe(II), this study investigated hydrothermal vent fluids from two different locations off the coast of Dominica with respect to Fe speciation.

1.1. Location and geological setting

Dominica is located in the Caribbean Sea south of Guadeloupe and north of Martinique. It is one of the youngest islands on the Lesser Antilles archipelago, still being formed by volcanic activity (Fig. 1).

The Lesser Antilles is a double island-arc system that converges to form a single chain of islands just to the southeast of Dominica (Fink, 1972; Martin-Kaye, 1969). Quaternary volcanic activity on Dominica has been dominated by intermediate to felsic magmas, erupted as large volume ignimbrites and dome complexes. One of the largest concentrations of these deposits, and one of the currently most active areas in terms of shallow seismicity and hydrothermal activity, is the Plat Pays Volcanic Complex at the southern tip of the island (Lindsay et al., 2005). Most prominent submarine hydrothermal venting occurs in two areas south-west off the coast of Dominica; in Champagne Hot Springs (CHS) and Soufriere (SOU).

Two types of venting were observed: A focused discharge of a clear fluid and a diffuse discharge of vent fluids and streams of gas bubbles emerging directly through fractured volcanic rocks. Iron oxides cover these rocks in close proximity to the vent center. Precipitates occur in layers up to 5 cm thick (McCarthy et al., 2005). Another active hydrothermal vent site is located just south of Champagne Hot Springs, at Soufriere (Fig. 1). This setting is dominated by a much finer sediment bottom in approx. 5 m water depth close to the local beach. Diffuse venting is apparent by streams of gas bubbles discharging through the sediment (Fig. 2).

Apart from the marine hydrothermal venting, also land based activity exists. In our study the so-called "Soufriere Sulphur Springs" were sampled, located just west from Soufriere in the coastal mountains of Dominica.

2. Material and methods

2.1. Sampling and field measurements

In April 2013, a sampling campaign to Dominica, Lesser Antilles was conducted. SCUBA diving was carried out to collect all seawater and fluid samples. Temperatures were measured in-situ with a temperature probe, while pH, salinity and dissolved oxygen were measured on shore in sample aliquots using a WTW® multimeter. Since Dominica's hydrothermal fluids are reported to be relatively high in Fe compared to seawater, a first determination of total Fe and Fe(II) concentration was conducted directly in the field for all samples using a Fe CHEMets© field kit.

In Champagne Hot Springs, sample "CHS pore fluid" was sampled with a 60 mL syringe and attached tubing directly above the emerging point of the fluid between fractured rocks. In Soufriere, sample "SOU pore fluid" was collected using the same set-up but in 10 cm sediment depth. For both samples, the first 10 mL were discarded to decrease
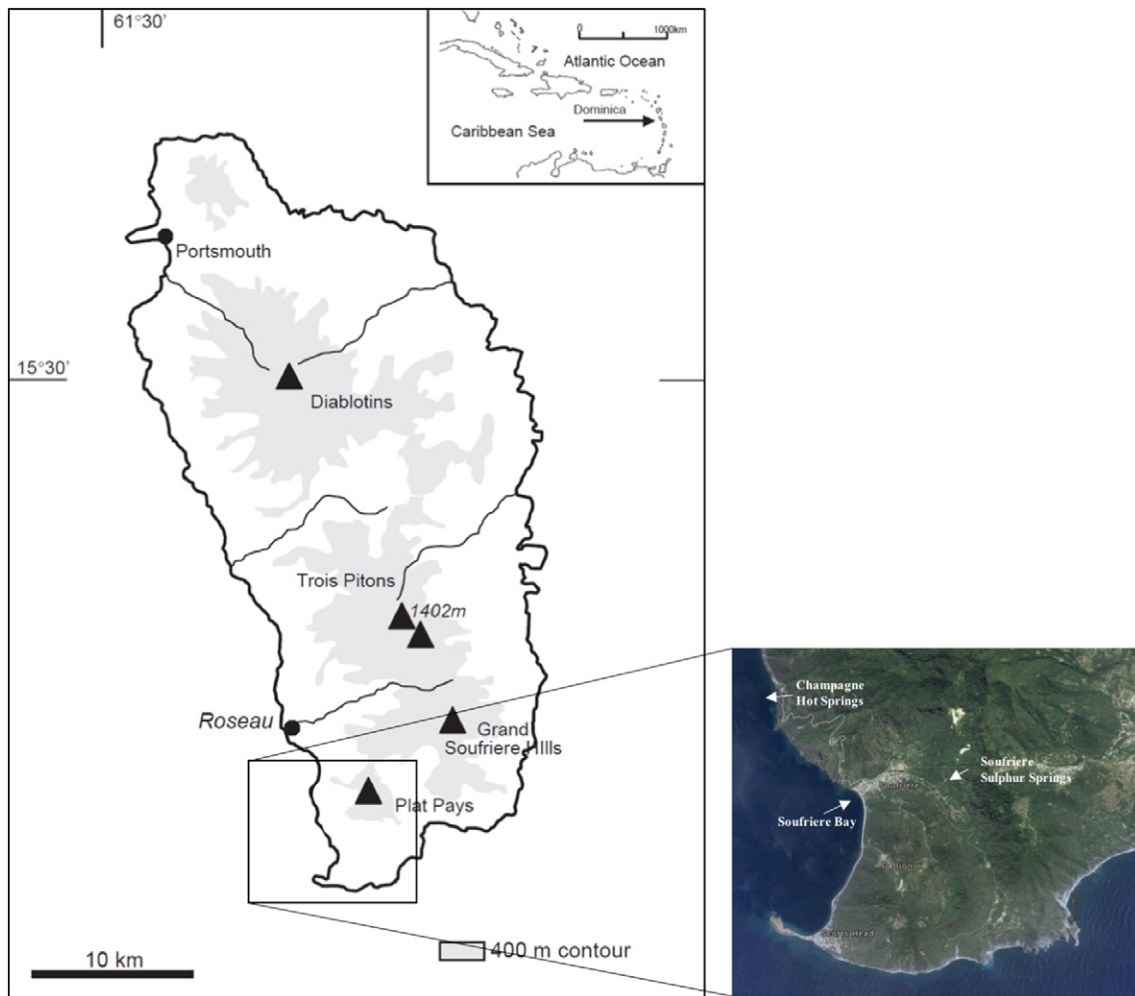
Fig. 1. Map of Dominica showing the location of the sampling sites Champagne Hot Springs, Soufriere and Soufriere Sulphur Springs. (Modified after McCarthy et al., 2005 and Google Maps).
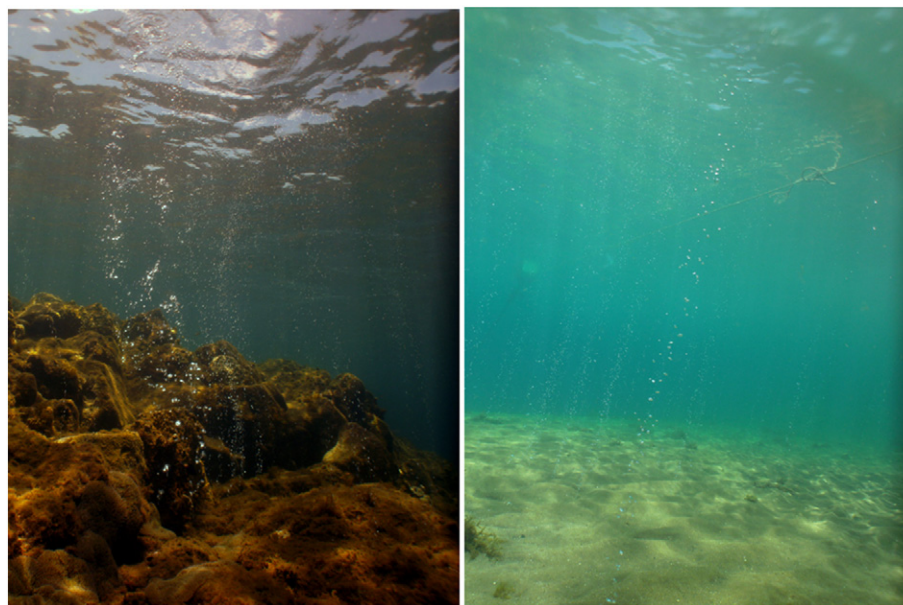
Fig. 2. Hydrothermal venting off the SW-coast of Dominica. Left: Champagne Hot Springs, in 3 m water depth, showing lots of rocks covered by iron oxides. Right: Soufriere, in 5 m water depth with much more sediments and less rocks. In both settings, hydrothermal venting is present by streams of gas bubbles and a diffuse discharge. Pictures were taken by A. Madisetti during the sampling campaign in 2013.

the amount of seawater contamination during sampling. Hydrothermal fluids (CHS and SOU fluid) were sampled with a custom built fluid collector, which consists of a funnel with an attached heat resistant collection bag that was placed over the hydrothermal vent outlet (Pichler et al., 1999b) and is described in more detail in Kleint et al. (2015). For comparison, a surface seawater sample was collected approximately 100 m away from the area of venting (Dominica Seawater) in areas with no hydrothermal emissions and two additional background pore water samples (CHS and SOU pore water) were collected using the syringe method from unaffected sediments from 10 cm sediment depth at both locations.

All samples were directly filtered (0.2 μm cellulose acetate (CA) membrane filters for metal analysis and 0.2 μm polyethersulfone (PES) filters for DOC analysis) and acidified to pH 2 (HCl 30% suprapure, NBS scale) if used for dFe and DOC determination or frozen at −20 °C if used for labile Fe determination and later filtration of the soluble fraction (0.02 μm Anotop membrane filters). Samples for metal analysis were stored in pre acid-cleaned LDPE or HDPE fluorinated bottles, while samples for DOC determination were stored in pre-combusted glass vials.

The Soufriere Sulphur Springs were reached by hiking. Samples from the source (on a top of a steep mountain) and the bottom of the springs were taken by direct sampling with acid cleaned PE bottles.

2.2. Methods

Dissolved Fe (dFe) concentrations in the 0.2 μm filtered and acidified samples, along with other major elements, except for As and Cu, were determined using a Spectro Ciros Vision ICP-OES (detection limit for Fe: 1 μM, filter blanks were below detection and the analytical error for the IAPSO standard seawater as well as internal standards was within the range of ±5% of the reference values). Arsenic was analyzed at the University of Bremen by atomic fluorescence spectrometry (detection limit for As: 0.3 nM, the analytical error for the standard reference material 1643e was within ±5% of the reference values), using a PS Analytical instrument and following the procedure of Price et al. (2007). Dissolved organic carbon (DOC) concentrations of 0.2 μm filtered and acidified samples were analyzed with a TOC analyzer (Analytic Jena, multi N/C 2100S, detection limit for DOC: 3.8 μM, filter blanks were below detection and the analytical error for the internal standard was ±2%). The determination of soluble Fe (sFe), labile Fe (Fe$_{labile}$) and Cu were performed by competitive ligand exchange–adsorptive cathodic stripping voltammetry (CLE-AdCSV) with salicylaldoxime (SA) as the artificial ligand using a 757 VA Computrace voltammetric system (Metrohm). The three-electrode configuration included a hanging mercury drop electrode (HMDE) as the working electrode, a double junction Ag/AgCl/3 M KCl reference electrode, and a glassy carbon counter electrode. Method details for the determination of Cu can be found in Kleint et al. (2015). Except for As, all measurements were conducted at Jacobs University Bremen.

2.2.1. Total and ferrous Fe

Total Fe as well as Fe(II) concentrations were determined directly on the island using a Fe CHEMets© field kit (detection limits: 1.8 μM to 180 μM Fe(II)) on unfiltered and non-acidified samples. The kit uses glass vacuum ampoules containing 1,10 phenanthroline that draw a defined volume of sample after breaking the tip of the ampoule. The phenanthroline reacts with Fe(II) and forms an orange colored complex, which corresponds to the Fe(II) concentration in the sample and can be visually compared to standard solutions contained in the CHEMets© field kit. For the determination of total Fe, an activator solution (containing thioglycolic acid and ammonia) is added to the original sample, which dissolves and reduces all particulate ferric Fe to Fe(II). Total Fe can now be determined using the same vacuum ampoules as described above.

2.2.2. Soluble Fe

For the determination of sFe, a frozen pre-filtered (0.2 CA membrane filters), but non-acidified sample was thawed at 4 °C overnight. Afterwards, the sample was gently shaken and 50 mL were directly sub-filtered through pre-cleaned (suprapure 0.1 M HCl and several times deionized (DI) water) 0.02 μm Whatman Anotop membrane syringe filters. The Anotop filters were chosen because they were successfully used for Fe fraction separation before (Fitzsimmons and Boyle, 2014a). The first 3 mL were discarded to decrease the risk of possible DI residue on the filter. Half of the filtrate was immediately acidified to pH 2 (HCl 30% suprapure, NBS scale) for sFe measurements while the other half was directly analyzed for labile Fe (Fe$_{labile}$). The concentration of soluble Fe was determined in 10 mL of the acidified sample, with the addition of an artificial ligand (SA; final concentration 25 μM). Due to high dFe concentrations, samples were first diluted with ultrapure NaCl solution in the same salinity as the sample. After the SA addition, the sample was allowed to stand for about 2 h, before the pH was adjusted to ~8.15 using suprapure NH$_3$ and the borate buffer (10 mM final concentration). DFe concentrations in each sample were then determined by adsorptive cathodic stripping voltammetry (AdCSV), which detects the electrochemically-active complex FeSA using standard addition method. All sample and titration vials were conditioned typically three times prior to each measurement. Voltammetric parameters were modified from Abualhaija and van den Berg (2014). This includes purging of the sample with compressed air (instead of N$_2$) at 1 bar, deposition at −0.05 V with an initial deposition time of 120 s (this was later adjusted to shorter times due to high Fe concentrations) and a cathodic scan from −0.05 to −0.8 V using the differential pulse (DP) mode.

2.2.3. Labile Fe

The chemically labile Fe that we measured is the fraction of Fe in the sample as a FeSA complex, including natural organic ligands that are weaker than the added ligand-Fe complex. This means that Fe dissociated from its previous complex with natural ligands to be available to our artificial ligand SA under these conditions, i.e. it is labile. For Fe$_{labile}$ measurements, 10 mL of the thawed sample were pipetted into an already conditioned PTFE titration vessel and equilibrated overnight at ~pH 8.15 and 100 μM SA. High dFe and DOC concentrations required a higher than normal SA concentration for out-competing all natural ligands in the samples, as also described in Kleint et al. (2016). For soluble Fe and also for measurements of labile Fe, samples were first diluted with an ultrapure NaCl solution in the same salinity as the sample. The next day, regular Fe standard additions were made with 10 min equilibration time after each addition, using the same voltammetric parameters as for sFe.

All voltammetric measurements were repeated three times for quality control and reproducibility, showing percentage standard deviations of below 6% for all samples. Additionally, reagent blanks as well as the seawater reference material for trace metals NASS-6 from the National Research Council Canada were measured together with the samples. The analytical error for NASS-6 was within the range of ±5% of the reference value.

3. Results and discussion

3.1. Geochemical characterization of hydrothermal fluids from Champagne Hot Springs, Soufriere and the land-based Sulphur Springs

In Champagne Hot Springs (CHS), as well as in Soufriere (SOU), two hydrothermal fluids, two hydrothermally influenced pore fluids and two non-affected background pore waters were sampled, resulting in three samples from each site as well as one reference background seawater sample. The general geochemical characterization of all samples taken at Dominica is given in Table 1.

Vent fluids of CHS and SOU had temperatures between 46 °C and 75 °C with the highest values in the both fluids compared to pore fluids

Table 1
Overview on all geochemical parameters measured for all derived samples in Champagne Hot Springs (CHS) and Soufriere (SOU). While the first five parameters were measured directly on the island, all others were determined in the home laboratories in Germany. (BG: background, b.d.: below the limit of detection, n.a.: not analyzed, Cu data from Kleint et al., 2015).

Sample		Dominica Seawater	CHS pore water (BG)	CHS pore fluid	CHS fluid	SOU pore water (BG)	SOU pore fluid	SOU fluid	Sulphur Springs source	Sulphur Springs bottom
Water Depth	[m]	0	3	3	3	5	5	5	On land	On land
Temperature	[°C]	28	28	46	75	28	55	70	n.a.	n.a.
pH		7.9	7.6	6.4	6.3	7.9	6.4	6.3	2.7	3
Salinity	[‰]	34	33	14.3	17.3	32.5	12.8	10.9	1.8	1.2
O$_2$	[%]	100	n.a.	n.a.	n.a.	71	65.1	60.6	94	96
DOC	[µM]	250	157	129	180	114	137	173	124	335
Mg	[mM]	64	60	25	28	62	23	21	3.29	2.30
Cl		613	572	240	269	538	209	181	b.d.	b.d.
K		11.4	10.4	4.9	5.6	10.6	3.9	3.0	0.19	0.18
Si		0.06	0.15	2.23	2.56	0.12	1.37	3.00	4.88	4.02
Sr		2.85	1.79	1.47	2.05	1.30	1.56	1.97	1.42	3.82
Ca		12.07	11.25	10.07	11.12	11.27	6.78	6.38	4.84	3.54
Br		0.93	0.88	0.39	0.49	0.85	0.34	0.31	0.03	0.02
B		0.49	0.44	1.00	1.03	0.44	0.68	0.70	0.12	0.22
Fe	[µM]	1.25	29.8	103	109	1.61	178	233	2089	464
As		0.03	0.50	0.78	1.25	0.13	0.16	0.22	0.05	0.13
Li		3.19	2.75	10.87	11.59	2.75	4.35	4.49	1.16	1.59
Mn		b.d.	2.55	21.13	10.02	8.56	7.29	8.20	111.5	38.4
Cu	[nM]	2.96	n.a.	21.53	3.04	0.57	0.78	1.59	971	25

and pore water, while the pH showed lowest values with 6.3 and the salinity decreased to 10.9‰. Additionally, the two land-based samples from the Soufriere Sulphur Springs were briefly characterized in the field, revealing acidic pH values (2.7) and a low salinity of only 1.2‰, which indicated that those fluids were of meteoric origin. This assumption was later confirmed by a full geochemical analysis.

Magnesium (Mg), which serves as a good tracer for seawater input, was with concentrations of 64 mM in seawater highly enriched compared to only 3.3 mM at the Sulphur Springs source and 2.3 mM at the bottom. This observation was also made for other elements such as potassium (K), which was lowest in the Sulphur Springs samples (0.18 mM) and highest in seawater (11.4 mM). To the contrary, silicon (Si), which serves as a good tracer for meteoric input, was highly enriched in the Sulphur Springs samples with 4.88 mM in the source compared to the ambient seawater (0.06 mM) at Dominica. All vent fluids from CHS and SOU were lower in Mg, K, as well as strontium (Sr) and bromine (Br) with respect to seawater. Observations that were made for Si, were similar for boron (B), manganese (Mn) and lithium (Li); all of which showed highest concentrations in the hydrothermal fluids compared to the pore fluid and pore water. Since Mg correlates with salinity data ($R^2 = 0.995$) and all four hydrothermally affected samples plot on the linear mixing line of ambient seawater and the meteorically derived Soufriere Sulphur Springs, we can assume that the four hydrothermally altered samples are influenced by both, seawater as well as by meteoric waters (Fig. 3), which is common for marine shallow-water hydrothermal systems and in agreement with previous studies about the Dominica fluids (Gomez-Saez et al., 2015; McCarthy et al., 2005). Calcium (Ca) concentrations were striking in the sense that all CHS samples had a concentration similar to seawater, while Ca was depleted relative to seawater in all SOU samples and even more depleted in the terrestrial Sulphur Springs samples. This may indicate that the Soufriere vent fluids are influenced to a greater extent by meteoric water than the CHS fluids, which seems plausible due to the proximity of the Sulphur Springs to Soufriere Bay and the steep mountains near the coast as seen in other shallow marine vent systems (e.g. Pichler et al., 1999a). Zinc (Zn) concentrations were below the detection limit (2 µM) in all samples except for Sulphur Springs source (13 µM) and Sulphur Springs bottom (8 µM), which is probably related to the high acidity of the Sulphur Spring samples.

Dissolved organic carbon (DOC) concentrations in the surface seawater of Dominica (250 µM) and the altered fluids (114–118 µM) were high, however, they lie within the range of reported values for coastal surface waters (80–300 µM) and diffuse, low temperature vents (50–750 µM) (Dittmar and Stubbins, 2014; Hawkes et al., 2015; Lang et al., 2010, 2006). These values are highly enriched compared to deep-sea water (35–48 µM) and higher than in most high-temperature hydrothermal vent fluids (15–200 µM). However, diffuse, low temperature vents are even reported to act as a source of DOC, mainly due to microbial productivity (Hsu-Kim et al., 2008). Since our fluid samples were collected only a few meters from shore, DOC transported by rivers and other terrestrial input will additionally affect and increase seawater DOC. Therefore, such high DOC values seem realistic.

Iron was more enriched in the Soufriere samples than in the Champagne Hot Springs samples, which might again be explained by the influence of the terrestrial Sulphur Springs that were high in Fe (2089 µM in the source sample). However, dissolved Fe might not only be supplied by hydrothermal venting in these coastal waters, but also by a dFe flux from the sediment (e.g., Elrod et al., 2004; Jones et al., 2011). Plotting concentrations of dFe, enriched in all hydrothermal fluids compared to seawater, against Mg or Si concentrations, results in a non-linear mixing curve between the Sulphur Springs samples and seawater, which is due to partial dFe loss (oxidation and precipitation) during hydrothermal endmember mixing with seawater. The mixing curve confirms that Dominica's vent fluids originate from seawater as well as meteoric water influence (Fig. 4). Sample CHS pore
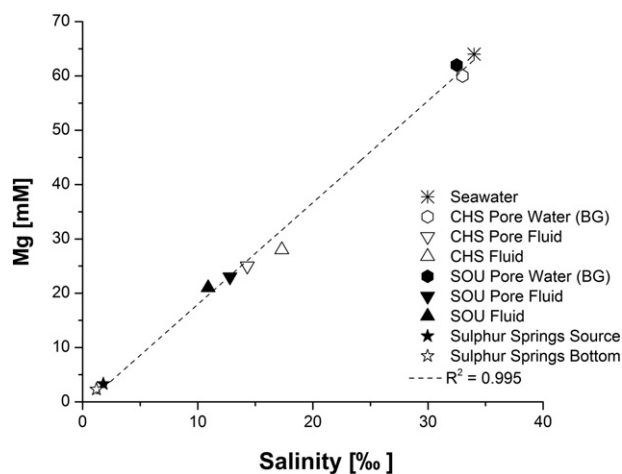
Fig. 3. Correlation between Mg and salinity, showing the four hydrothermally influenced samples from Champagne Hot Springs and Soufriere on a linear mixing line between the meteorically derived Sulphur Springs and seawater.
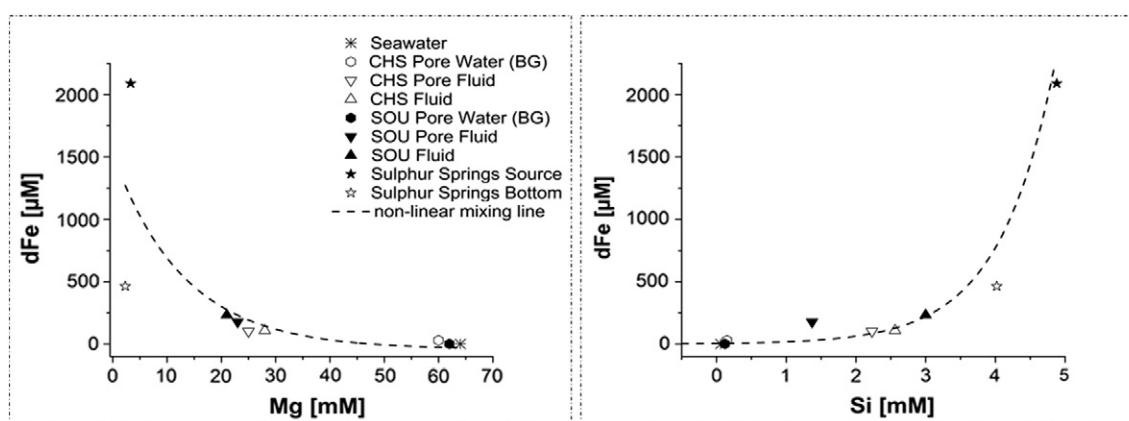
Fig. 4. dFe concentrations (<0.2 μm, determined by ICP-OES) plotted against Mg and Si, showing that all four hydrothermally influenced samples plot on the non-linear mixing curve between the Sulphur Springs sample and seawater.

water, thought to be a background pore water sample, showed elevated Fe concentrations, suggesting that it is partly hydrothermally affected. This is confirmed by slightly lower pH values of 7.6 compared to SOU pore water and Dominica seawater, having both a pH of 7.9.

The CHEMets© field kit allows the determination of total Fe and ferrous Fe (Fe(II)). Except for sample CHS pore water, in which only 50% of all Fe is Fe(II), all other samples showed about the same concentration for total Fe and Fe(II), indicating that in those samples all Fe is predominant in its reduced form, which was also observed for CHS by McCarthy et al. (2005). The higher concentration of total Fe compared to Fe(II) in sample CHS pore water indicates that oxic seawater, percolating through the coarse sediments at CHS, led to the precipitation of Fe oxy-hydroxide nanoparticles, which must, however, still be present in the dissolved phase, as the filtered sample measured with ICP-OES showed the same Fe concentration as the unfiltered sample measured with the CHEMets© field kit for total Fe (Table 2). This confirms that sample CHS pore water is only partly hydrothermally affected.

The good agreement (deviation below 7.4% for all samples, except for the Sulphur Springs source sample) between the Fe determination using the Fe CHEMets© field kit in the field and later analyzed dFe concentrations by ICP-OES is remarkable. This confirms that the kit represents a very easy and fast to use method, making it very suitable for the field (Table 2). Total Fe determination using the field kit was done using unfiltered samples, while Fe determination by ICP-OES was carried out on filtered samples. The fact that both results agree very well for all samples, indicates that any Fe is present in the dissolved phase, presumably as Fe(II), and not as particulate Fe(III).

Since the limit of detection for the used Fe CHEMets© field kit was between 1.8 and 180 μM, the seawater sample as well as the

background porewater sample in Soufriere could not be analyzed for Fe in the field. Although the Sulphur Springs samples were diluted, original Fe concentrations in the source of >2000 μM were too high to be measured accurately in the field, which explains the relatively high difference between the Fe concentrations measured on the island (1600 μM) compared the ones determined later by ICP-OES (2089 μM).

Copper (Cu) shows highest concentrations in the terrestrial Sulphur Springs samples, being 971 nM in the source sample and 25 nM in the bottom sample. For the three SOU samples, Cu is highest in the fluid (1.59 nM) and lowest in the pore water sample (0.57 nM), which is also in accordance with the related temperatures. CHS samples show an opposite trend. This Cu data together with its speciation is discussed in detail elsewhere (Kleint et al., 2015). Arsenic (As) concentrations reached up to 1.25 μM in the CHS fluid and was therefore highly enriched compared to ambient seawater, which had an As concentration of 0.03 μM. Additionally, CHS fluids showed higher As concentrations than SOU, suggesting that As was not derived from the Sulphur Springs hydrothermal system but rather from the volcanic basement rocks (andesite) in CHS. For CHS and SOU, As was highest enriched in the fluids (1.25 and 0.22 μM), followed by the pore fluids (0.78 and 0.16 μM) and lowest concentrations in the pore water samples (0.50 and 0.13 μM). While Soufriere seems to be influenced to a greater extent by the meteorically derived Sulphur Springs than CHS, CHS shows more influence by the volcanic basement rocks. Thus, CHS might be a productive site for metal-tolerant organisms, which can sustain high concentrations of potentially toxic metals, such as Cu and As. However, data by Kleint et al. (2015) indicated a stable complexation of Cu in most cases at CHS and SOU, probably lowering the toxic effect of Cu.

Table 2

Overview on the Fe speciation and fractionation data for all derived samples in Champagne Hot Springs (CHS) and Soufriere (SOU) (dFe: dissolved Fe (<0.2 μm), sFe: soluble Fe (<0.02 μm), cFe: colloidal Fe (0.2 μm–0.02 μm), BG: background, b.d.: below the limit of detection, n.a.: not analyzed). While dFe and sFe were measured using ICP-OES and CSV, respectively, cFe was calculated by the difference between dFe and sFe.

			Dominica Seawater	CHS pore water (BG)	CHS pore fluid	CHS fluid	SOU pore water (BG)	SOU pore fluid	SOU fluid	Sulphur Springs Source	Sulphur Springs Bottom
Fe(II)	[μM]	*FeKit*	b.d.	16	107	107	b.d.	190	230	1600	450
Total Fe	[μM]	*FeKit*	b.d.	32	107	107	b.d.	190	230	1600	450
dFe	[μM]	*OES*	1.25	29.8	103	109	1.61	178	233	2089	464
Deviation	[%]		–	7.4	3.9	1.9	–	6.7	1.3	30.6	3.1
sFe	[μM]	*CSV*	1.12	3.0	18.2	35.3	1.53	21.9	26.8	n.a	n.a
cFe	[μM]		0.13	26.8	84.8	73.7	0.08	156	206	–	–
sFe	[%]		89.6	10.1	17.6	32.4	95	12.3	11.5	–	–
cFe	[%]		10.4	89.9	82.4	67.6	5.0	87.7	88.5	–	–
dFe$_{labile}$	[μM]	*CSV*	0.01	0.7	19	5.2	0.02	8.6	15.8	n.a	n.a
sFe$_{labile}$	[μM]	*CSV*	0.01	0.2	1.3	2.1	0.02	1.3	1.2	n.a	n.a
dFe$_{labile}$	[%]		0.8	2.3	18.5	4.8	1.2	4.8	6.8	–	–
sFe$_{labile}$	[%]		0.9	6.7	7.1	5.9	1.3	5.9	4.5	–	–

3.2. The speciation of Fe

The high content of ferrous iron (Fe(II)) in the fluids appears reasonable at a first glance, since hydrothermal fluids are known to transport metals in their reduced oxidation state. However, considering the high dissolved oxygen content in the fluids and the rather neutral pH values of ≤6.3, usually leading to a short half-life if Fe(II), it is surprising that Fe was predominantly present as Fe(II) and thus not immediately oxidized to ferric Fe(III).

The oxidation half-life of Fe [$t_{1/2}$] is dependent on the ionic strength, the dissolved oxygen concentration, temperature and pH (Millero et al., 1987) and can be calculated by the following pseudo first order equation:

$$\frac{-d[Fe(II)]}{dt} = k_1[Fe(II)]$$

with

$$k_1 = k[O_2][OH^-]^2$$

$$\log k = \log k_0 - 3.29\, I^{1/2} + 1.52\, I$$

$$\log k_0 = 21.56 - 1545/T$$

and the half-life of Fe(II) being:

$$t^1/_2 = \ln 2/k_1.$$

where I is the ionic strength, O_2 is dissolved oxygen concentration, both expressed in M and T is the temperature in degrees Kelvin.

For the fluids off the coast of Dominica, the calculated Fe oxidation half-life was 6.4 min, which is very short. This can be explained by the high water temperature in these well oxygenated shallow Caribbean coastal waters, which also agrees with published Fe oxidation half-lives for a variety of oceanic settings (Field and Sherrell, 2000; Rudnicki and Elderfield, 1993; Statham et al., 2005; Wang et al., 2012).

A few studies suggested that the Fe(II) oxidation process is not only influenced by T, pH and oxygen, but can also be affected by complexation with dissolved organic matter (DOM), which would reduce the rate of Fe(II) oxidation enabling the dissolved Fe(II) to be exported into the surrounding waters (Santana-Casiano et al., 2000; Statham et al., 2005). A study by Rijkenberg et al. (2005) additionally showed that sunlight, especially the UVB (ultraviolet B), plays a major role in the photo-reduction of Fe in surface waters. In the Caribbean surface waters, which are exposed to high UV irradiation, the formation of Fe(II) would therefore be favored over Fe(III), which would also increase the half-life of Fe(II) as well as its bioavailability.

Size fraction measurements revealed that the majority of dissolved Fe in the vent fluids (67%–90%) was present as colloidal Fe (Table 2), which is in agreement with other studies for the open ocean (Boye et al., 2010; Cullen et al., 2006; Fitzsimmons and Boyle, 2014b; Wu and Luther, 1995; Wu et al., 2001). A high fraction of soluble Fe in the surface water and the unaffected pore water at Soufriere with 89.6% and 95%, respectively, seem unusual and since only a few studies on size fraction analysis are published and even less studies exist for hydrothermal vent fluids, there is no distinct explanation for these enriched concentrations of sFe over cFe (Table 2). However, it has been shown in the past that unexpected high dissolved concentration of soluble Fe(II) may be present in oxic surface waters and coastal waters in general (Elrod et al., 2004; Kuma et al., 1996; Willey et al., 2008). One explanation is that Fe(II) in these surface waters is produced by photo-reduction of Fe(III) (Kuma et al., 1992), which is then existent in the soluble fraction. This soluble Fe(II) might either be stabilized by strong ligands, such as organic substances, which are very abundant in all our samples (DOC concentrations of up to 250 μM) or be present as soluble free Fe^{2+}. However, as only 0.8% of dFe and 0.9% of sFe is actually chemically labile, it is more

likely that sFe is stabilized by strong soluble ligands, rather than being present as free soluble, labile Fe^{2+} (Table 2). Although sFe might be preferentially incorporated by marine organisms, sufficient and continuous Fe supply by hydrothermal venting at the studied sites is given. Within the shallow waters, any ferric Fe^{3+} from different sources, such as terrestrial input or oxidized hydrothermal Fe is subsequently reduced to soluble Fe(II) by photo-reduction. Bioavailable ferrous Fe is therefore not limited and detectable excess concentrations of sFe can be measured in surface water samples. It was additionally reported that Fe-ligand complexes occur in both fractions, colloidal and soluble, with excess ligands in the soluble fraction compared to the colloidal one, indicating that all sFe is complexed (Boye et al., 2010; Cullen et al., 2006; Wu et al., 2011). The very low fractions of dFe_{labile} and sFe_{labile} in the SOU pore water sample (1.2% and 1.3%, respectively, Table 2) and the ability of organic ligands to solubilize natural Fe gives further reason for the assumption that sFe is complexed by strong soluble ligands and may thereby explain the very high soluble fraction in the SOU pore water sample.

When plotting dFe vs dFe_{labile} and sFe vs sFe_{labile} (Fig. 5), all samples from CHS and SOU, except for sample CHS pore fluid, plot on one line. Soufriere shows higher dFe concentrations (dFe and dFe_{labile}) than CHS, while CHS shows higher soluble Fe concentrations than SOU. Generally, the more sFe, the higher is the sFe_{labile} concentration. The same trend can be observed for dFe and dFe_{labile}: the more dFe in the sample, the higher is the dFe_{labile} concentration, except for sample CHS pore fluid, which shows highest dFe_{labile} concentrations (19 μM/18.5%) for all samples. This demonstrates that the labile Fe contents are controlled by the total Fe concentrations of the respective fractions with very low labile fractions for dFe (0.8%–18.5%) and even less labile Fe in the sFe fraction (0.9%–7.1%).

3.3. Stabilization possibilities of Fe(II)

A common inorganic Fe stabilization process in hydrothermal fluids is the formation of Fe sulfide nanoparticles (such as pyrite) or Fe oxy-hydroxide nanoparticles (Hsu-Kim et al., 2008; Sands et al., 2012). Such colloids form rapidly after the reduced fluid is mixed with oxygenated seawater and Fe(II) is oxidized to Fe(III). Dominica, compared to other marine shallow-water hydrothermal systems, such as Milos, is very low in sulfide (Gomez-Saez et al., 2016) and the formation of sulfide nanoparticles will therefore be insignificant. The formation of Fe oxides in CHS is demonstrated by the presence of up to 5 cm thick rock coatings. However, since we still measured high concentrations of Fe(II) 1 to 2 h after recovery, despite the calculated very low theoretical oxidation half-life of only 6.4 min, Fe(II) must be stabilized in these fluids.

Recent work suggested that DOM or DOC have the potential to strongly bind Fe(II) in coastal waters as well as particulate Fe(II) in hydrothermal plumes, respectively (Hopwood et al., 2015; Toner et al., 2009) and that these complexes might even be strong enough to prevent Fe(II) from oxidization. The hydrothermal vent fluids off the coast of Dominica are high in DOC together with high Fe(II) concentrations. This combination gives reason for the assumption that Fe(II) being released by these diffuse vents is strongly complexed by organic carbon, which is further supported by our labile dFe and sFe measurements (Table 2). Our data implies that only a very small fraction of the available Fe in all size fractions (dFe and sFe) is actually chemically labile, mostly not >7%. Therefore, the presence of strong organic Fe-binding ligands in the hydrothermal fluids, such as humic substances and organic degradational products, would be the most probable explanation for these low labile fractions of Fe, while the Fe-ligand complex must be strong enough not to be degraded by the added highly concentrated artificial ligand (100 μM SA) during analysis.

Apart from DOC, produced biologically within the areas of diffuse discharge or introduced by rivers and other terrestrial sources, it was suggested that rainwater contains Fe-binding ligands that completely
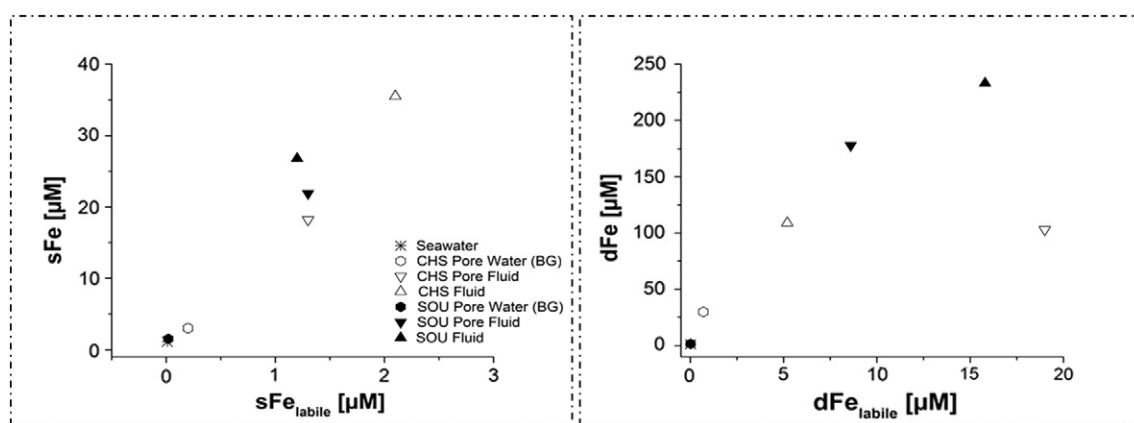
Fig. 5. sFe concentrations plotted against sFe$_{labile}$ concentrations (<0.02 μm, determined by CSV) and dFe concentrations (<0.2 μm, determined by ICP-OES) plotted against dFe$_{labile}$ concentrations (<0.2 μm, determined by CSV).

prevent Fe(II) oxidation for several hours after rain is mixed with sea-water (Cheize et al., 2012; Hopwood et al., 2015; Kieber et al., 2005, 2001; Willey et al., 2008). The authors further state that the rainwater ligands are among the strongest ligands observed in natural waters. Due to abundant rain, high amounts of Fe-binding ligands should be present in and be continuously supplied to the shallow coastal waters along the west side of Dominica. Such rainwater- and land-derived ligands could potentially also contribute to the pool of Fe-solubilizing ligands in the investigated systems through the influx of meteoric water.

4. Conclusion

The Champagne Hot Springs (CHS) and Soufriere (SOU) marine shallow-water hydrothermal systems at the southern tip of Dominica, Caribbean were investigated together with two samples from the terrestrial Soufriere Sulphur Springs. From the geochemical characteristics, we can conclude that the hydrothermal fluids at both marine vent sites are derived from a combination of seawater and meteoric water. Of the two sites, SOU showed a greater influence of meteoric water than CHS.

To date, Fe size fraction analysis and the determination of labile Fe within those size fractions was not carried out in any other marine shallow-water hydrothermal system and thus this dataset presented is the first one of its kind. The shallow vents at Dominica present an interesting geochemical environment in the sense that the hydrothermal fluids were highly enriched in DOC and Fe, particularly Fe(II), which is released into the photic zone. Due to the absence of sulfide, the formation of sulfide nanoparticles cannot be an important process to reduce bioavailable Fe after mixing with seawater. Instead, organic substances seem to stabilize Fe(II) within the fluids and photo-reduction may keep surface Fe(II) in its soluble and bioavailable species. Thus, our findings indicate that stabilized and bioavailable Fe(II) is introduced into the oxic waters off the coast of Dominica, which affects the biochemical cycle of Fe. If this process would also be active at other comparable settings, implications for the global marine dFe cycle should be considered. However, extrapolation to a global scale using data from this one site is not straightforward, given the geological and geochemical differences of the different shallow vent sites (Chen et al., 2005; Pichler et al., 1999a, 1999b; Pichler and Humphrey, 2001; Price et al., 2015, 2013; Prol-Ledesma et al., 2004). Therefore, it is essential to analyze other marine shallow-water hydrothermal systems with respect to Fe(II) fluxes, such as Milos (Palaeochori and Spathi Bay), Taiwan (Kueishantao) or Iceland (Hveravík Bay), all of which release their fluids into the photic zone (Gomez-Saez et al., 2016; Kleint et al., 2015; Price et al., 2013). These systems display different geochemical and physical characteristics, all of which may influence metal fluxes; including very high sulfide and Fe concentrations for example at Milos (Kleint et al., 2015; Price et

al., 2013), or DOC enrichment but lower Fe values at the Hveravík Bay, Iceland (Gomez-Saez et al., 2016).

Additionally, it will be of particular interest to analyze other important trace metals at shallow hydrothermal vents with respect to the oceanic biogeochemical cycle, such as Zn and Mn, which have gained much less attention in hydrothermal metal speciation studies thus far. Manganese and Zn, both being released in elevated concentrations from most hydrothermal vents, represent important micronutrients for marine organisms and display a complex speciation as well as organic stabilization, which may additionally lead to increased fluxes of these elements from different hydrothermal vent settings, as just recently reported for Zn at deep-sea vents (Roshan et al., 2016).

From our data, we conclude that marine shallow-water hydrothermalism may be a significant source of Fe to surface waters and should be included in any estimation of the hydrothermal Fe-fluxes and its role in the global dFe cycle.

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