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Arsenic in marine hydrothermal fluids

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1. Introduction

Hydrothermal systems, discovered in 1977 near the Galápagos Islands (Corliss et al., 1979; Spiess et al., 1980), are mostly connected to thermal anomalies in the subseafloor at mid-ocean ridges (MOR) such as the Mid-Atlantic Ridge (MAR) and East Pacific Rise (EPR), back-arc basins (BAB) such as the Lau Basin and Manus Basin, sediment-hosted basins

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such as the Guaymas Basin and island arcs (IA) such as the Aeolian arc (Fig. 1). Hydrothermal fluid chemistry is largely controlled by physicochemical parameters in each system, such as depth and temperature in addition to host rock lithology, whereas systems are in general driven by a steep heat gradient, mostly due to an underlying magma chamber or serpentinisation processes. Cold and dense water percolates downward and is heated up to temperatures in excess of 400 °C near the heat source in the reaction zone, before rising upwards due to buoyancy. In the marine environment, hydrothermal systems can be divided based on their depth of occurrence in shallow and deep water, although the boundary is not clearly defined. Some authors draw the line at a water depth of 200 m on the assumption that deep water systems have a longer history, thus leading to a high number of obligate species and a high rank of obligate taxa, as well as more complicated morphological and physiological adaption (Tarasov et al., 2005). The depth of 200 m also coincides with a sharp change in the slope of the seawater-pressure boiling curve (Bischoff and Rosenbauer, 1984). In shallow-water systems of less than 200 m, the photosynthetic input from benthic organisms and phytoplankton may play an important role (Kharlamenko et al., 1995). Another difference is that seawater is the only fluid source for those hydrothermal systems located in deeper water, while hydrothermal systems in shallow water, near shore settings may also circulate meteoric water (Pichler, 2005). The temperature of the emanating fluids in both, shallow and deep systems, is limited by the boiling curve, so that shallow systems generally have temperatures of around 100 °C, while temperatures in deep systems can rise above 400 °C (Koschinsky et al., 2008; Devey and Garbe-Schönberg, 2011).

In general, the chemistry of hydrothermal fluids has been intensively studied for most elements because they play an important role in ocean chemistry (e.g. Von Damm, 2001). Arsenic (As) is an element, which has been rarely investigated in hydrothermal fluids. This is surprising, considering this element plays an important role in the formation of hydrothermal ore deposits (Cepedal et al., 2008) and is a known environmental toxin (e.g. Ahmed et al., 2006). In gold deposits, for example, Au – As associations are common and As is a strictly ore-forming element, whereas the most important factors causing changes in conditions and precipitation of gold are temperature, pressure and the fugacity of oxygen and sulfur (Zhu et al., 2011).

Elevated As concentrations in groundwater are responsible for the poisoning of almost 100 million people worldwide, particularly in the densely populated region of southeast Asia (Brammer and Ravenscroft, 2009). Those developments in conjunction with the lowering of the United States drinking water standard for As from 50 to 10 μg L^{-1} (Smith et al., 2002) has renewed the overall interest in the study of As. Findings of elevated concentration in marine shallow-water hydrothermal systems like Tutum Bay (Papua New Guinea), Milos (Greece), Bahía Concepción (Mexico) and several other locations sparked new interest in As cycling in the oceans and renewed interest of As in marine hydrothermal systems.

Another interesting aspect is the vent biota living in the mixing zone between seawater and hydrothermal fluid, like shrimps, mussels, and snails, as well as bacterial mats colonizing the areas of warm fluid discharge. Marine photosynthetic organisms like algae can absorb arsenate from the surrounding seawater because of its similarity to phosphate (Zhao et al., 2009) and convert it to arsenite and then further build up methylated species which are again converted and detoxified to different arsenosugars. These arsenosugars are postulated to be precursors for the less toxic arsenobetaine in higher marine organisms, which consume the photosynthetic organisms (Edmonds et al., 1977). However, several different pathways were proposed for this detoxification processes and are still under the matter of debate.

1.1. Chemistry of hydrothermal fluids

The general chemical composition of hydrothermal fluids depends on a multitude of factors, the most important being phase separation and water-rock interaction in addition to magmatic degassing and subsurface mixing (German and Von Damm, 2003). Biological processes also need to be considered, although their exact role remains unclear. Phase separation proceeds if the fluid encounters the two-phase boundary and a vapor phase and a brine phase are generated. Furthermore, the critical point (407 °C/ 298.5 bar) represents the boundary between subcritical conditions, when the separation takes places at pressures lower than the critical pressure, and supercritical conditions when separation takes place at pressures higher the critical pressure (Bischoff and Rosenbauer, 1988). When seawater is boiling under subcritical conditions, a gas-rich low Cl vapor phase and a high salinity brine phase are generated, while under supercritical conditions, condensation of small amounts of a dense brine phase occurs, leaving a relatively dense, low-Cl vapor phase (Koschinsky et al., 2008). An important factor is whether phase-separation is occurring in low-pressure systems, where the boiling can occur all the way from the heat source to the seafloor or in high-pressure systems, where phase-separation is mostly confined to the immediate vicinity of the hot magma chamber (Coumou et al., 2009).

During water–rock interaction, the chemical composition of host rocks and water can change and species are either lost (e.g. Mg, SO_4) or gained (e.g. Fe, Mn, Si) to the fluids depending on the water/rock ratio and reaction temperature. The ratio generally increases with increasing temperature and also increasing residence time. Seawater sulfate, for example, is removed via precipitation of $CaSO_4$ at temperatures higher than 130 °C. Magnesium is lost due to the formation of Mg – OH silicates, which results in H^+ generation contributing to low pH, mostly between 2 and 4 (German and Von Damm, 2003). Most metals and particularly trace and transition metals are generally enriched in hydrothermal fluids mainly due to complexation at low pH and high temperature (Douville et al., 2002). Fluid inclusion studies suggested that elements like Na, K, Fe and Mn preferentially partition into the brine phase during phase separation due to Cl-complexation, while trace elements like Cu, As and Au can accumulate in the vapor phase due to HS-complexation (Heinrich et al., 1999a).

1.2. Arsenic and arsenic species in aqueous systems

Arsenic is ubiquitously present in the aquatic environment with concentrations around 0.62 μg L^{-1} in river waters (Gaillardet et al., 2003) and between 0.5 and 3.0 μg L^{-1} with a mean of 1.7 μg L^{-1} in the oceans (Neff, 2002). Based on redox and pH, As can occur in the oxidation states +5, +3, 0 and -3 (Mandal and Suzuki, 2002; Smedley and Kinniburgh, 2002), whereas the first two are the dominant in aqueous systems (Sharma and Sohn, 2009). In hydrothermal fluids from shallow-water island arcs, the dominant species at a pH range between 5 and 7 and reducing conditions ($E_h<0$) should be the trivalent $As(OH)_3$ arsenite species, whereas at higher temperature and pressure like in deep-water systems from MOR and BAB, the $H_2AsO_4^-$ arsenate species should occur more often as shown in modeled speciation diagrams for the different regimes (Fig. 2A–C). These also show preferential precipitation of orpiment (As_2S_3) and claudetite (As_2O_3) at high temperature, and high iron and sulfur concentrations. Considering different concentrations for As, the stability field for claudetite expands with higher As concentration and the $H_2AsO_4^-$ field shrinks (Fig. 3A–C). At 100 °C and 200 °C (Fig. 3D–E), claudetite is no longer stable, but the most important species under these conditions is the trivalent $As(OH)_3$. Arsenite entering into aerobic seawater can be rapidly oxidized to arsenate due to abiotic and microbial reactions, and the trivalent form is more toxic than the pentavalent form. The most important species and minerals in these systems and their thermodynamic properties and reactions are given in Table 1.

Thioarsenic species are also possible in hydrothermal system rich in sulfide, where their existence is favored by thermodynamic studies of As sulfide solubility (Webster, 1990; Eary, 1992; Wilkin and Ford,

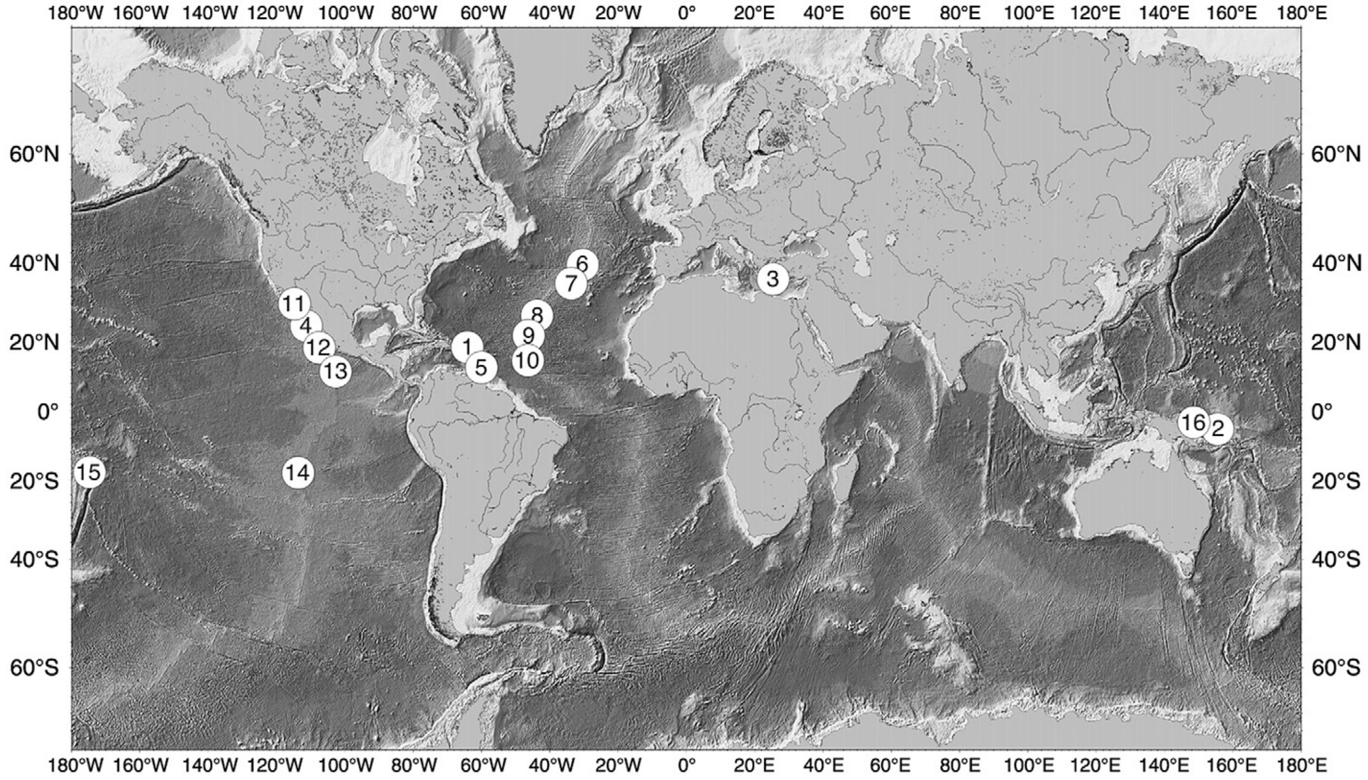

Fig. 1. Distribution of selected hydrothermal systems worldwide; 1 = Montserrat; 2 = Tutum Bay; 3 = Milos; 4 = Bahía Concepción; 5 = Champagne Hot Springs; 6 = Menez Gwen; 7 = Lucky Strike; 8 = TAG; 9 = Snakepit; 10 = Logatchev; 11 = Guaymas Basin; 12 = 21°N EPR; 13 = 13°N EPR; 14 = 17–19°S EPR; 15 = Lau Basin; 16 = Manus Basin.

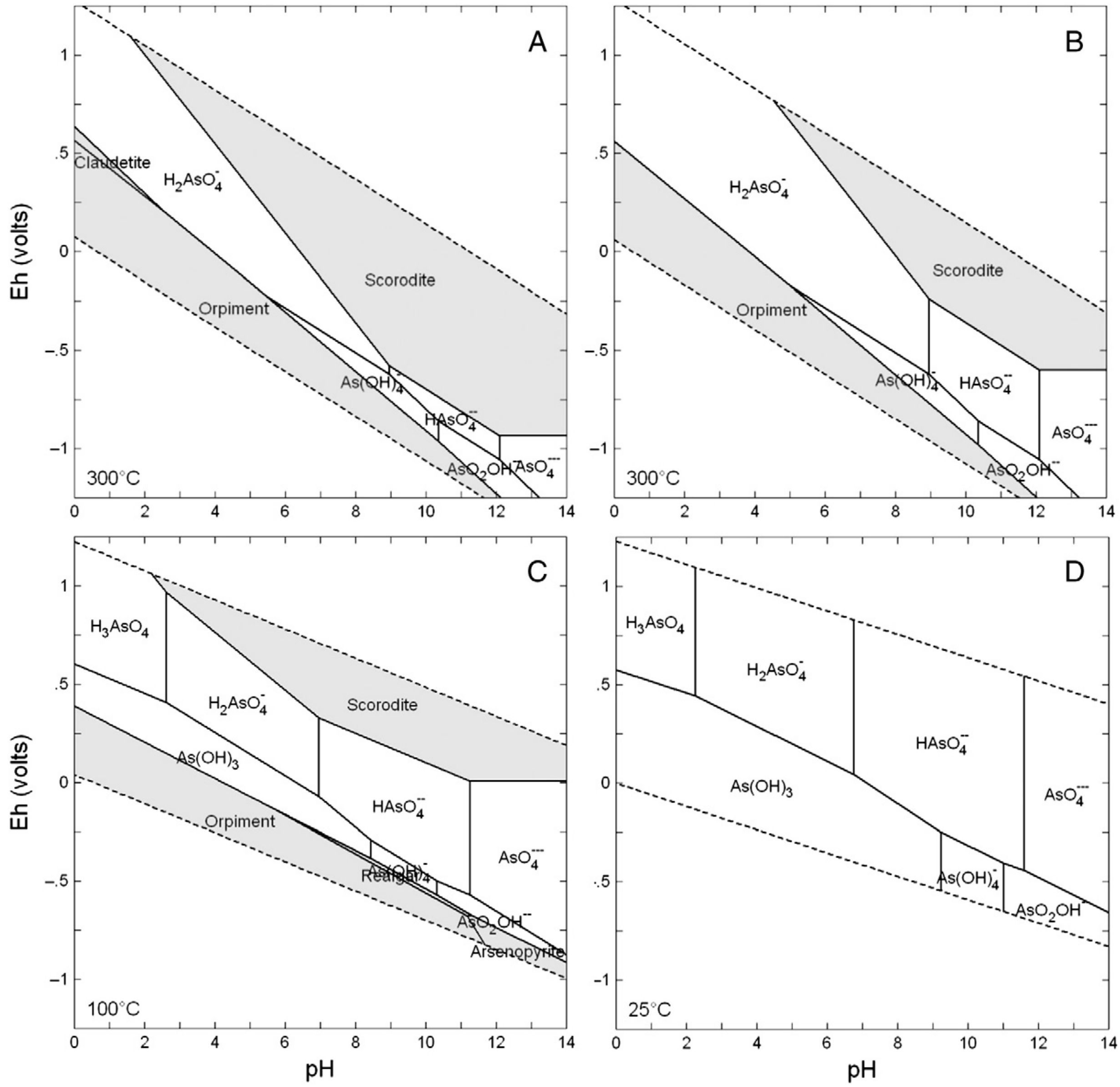

Fig. 2. Eh–pH diagrams for typical hydrothermal fluids from back-arc basins (A; Roman Ruins), mid-ocean ridges (B; Logatchev), island arcs (C; Tutum Bay) and for pure seawater at 25 °C (D). Grey shaded areas show solid phases.

2006) and observations. Thioarsenates, for example, were reported for the geothermal waters of the Yellowstone National Park (Planer-Friedrich et al., 2007, 2010).

1.3. Arsenic in rocks from the oceanic lithosphere

There is limited information about As in rocks from the oceanic lithosphere and overlying sediments. During rock forming processes, As is strongly chalcophile and therefore, the most important As minerals in the mafic rocks of the oceanic crust are cobaltite (CoAsS), loellingite-safflorite ($FeS_2(Co,Fe)As_3$), luzonite (Cu_2AsS_4), tennantite ($Cu_{10}(Fe,Zn)_2As_4S_{13}$), claudetite ($As_2O_3$) and elemental arsenic (As_0), mostly intergrown with elemental gold (Mozgova et al., 2005). In ocean ridge basalts, the average As concentration was estimated to be approximately 1.0 mg kg^{-1} (Matschullat, 2000). Data are rare, but available as shown in Table 2, for example, for ultrabasic rocks like abyssal peridotites from 15° 20'N MAR with average values of 0.94 mg kg^{-1} (Paulick et al., 2006), and serpentinized peridotites from the Kane area (MAR), varying around 0.91 mg kg^{-1} (Werner and Pilot, 1997). Magmatic rocks from island arc and back-arc settings, such as andesite, dacite, and rhyolite have generally slightly higher As concentrations than basic and ultrabasic rocks. In andesite, concentrations vary between 0.5 and 5.8 mg kg^{-1} and in rhyolite between 3.2 and 5.4 mg kg^{-1} (Mandal and Suzuki, 2002). The average concentration of As in deep-sea sediments was estimated to be approximately 40 mg kg^{-1} (Boström and Valdes, 1969). In oceanic sediments, As is mostly concentrated in fine-grained sediments, in particular those rich in organic matter, sulfide minerals, phosphates or iron oxides (Plant et al., 2003).

2. Sampling, preservation and determination of Arsenic in hydrothermal fluids

Sampling of hydrothermal fluids is difficult and challenging because most systems are located in great depths and either submarines or remotely operated vehicles (ROVs) are required in addition to specific fluid sampling devices. During discharge, the hydrothermal fluids mix immediately with ambient seawater, causing a rise in pH, cooling and the addition of oxygen, initiating mineral precipitation. Unfortunately mineral precipitation alters the fluid chemistry during and after sampling on the way to the surface. Gas tight samplers – at the moment the best

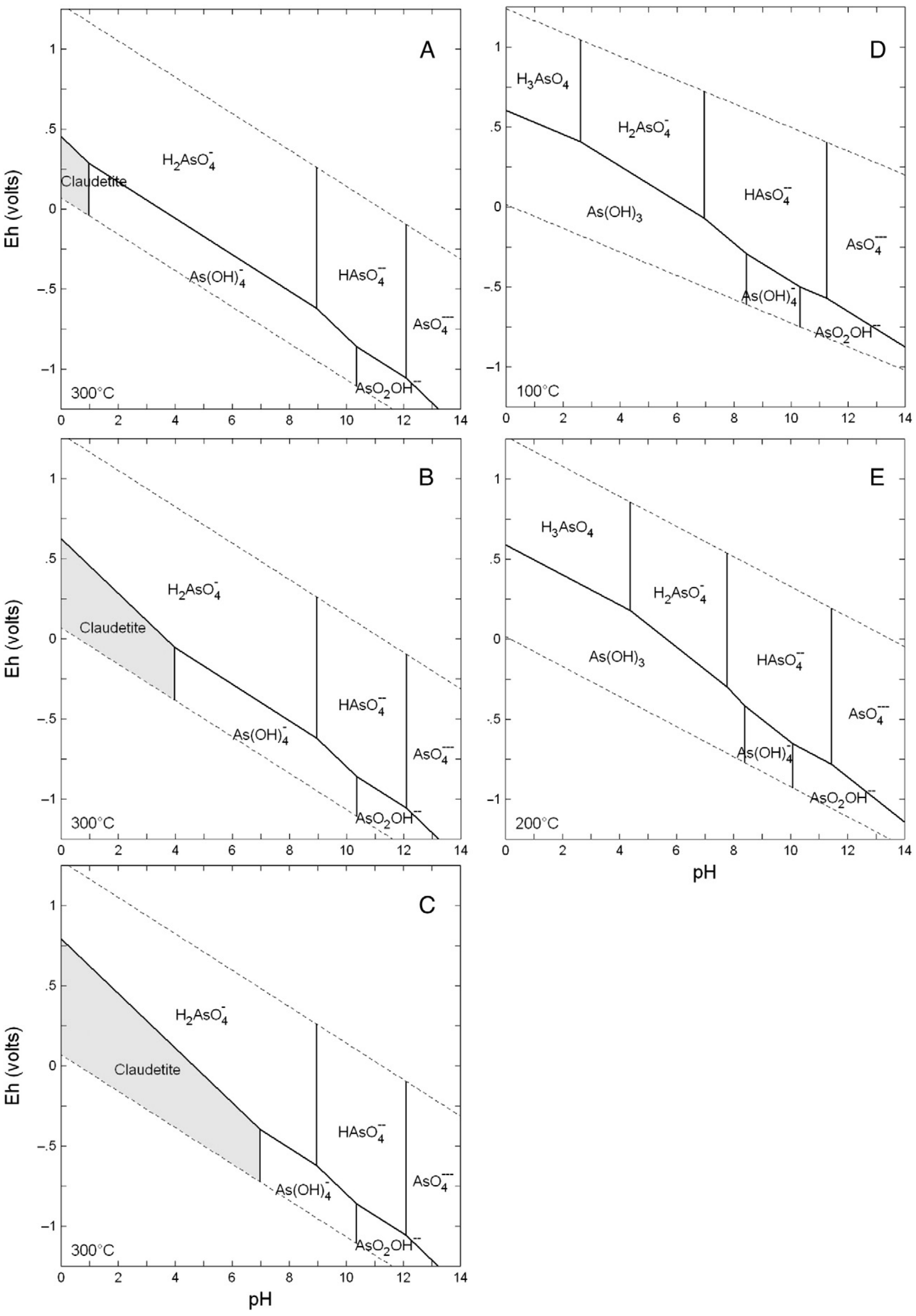

Fig. 3. Eh–pH diagrams for hydrothermal fluids from deep-water systems at different As activities at 300 °C (A–C). ΣAs is 1.0×10^{-8} (A), 1.0×10^{-5} (B), and 1.0×10^{-2} (C). Diagrams D and E were made for 100 °C and 200 °C respectively and ΣAs of 10^{-5}. Grey shaded areas show solid phases.

Table 1
Different species and minerals and their reactions for arsenic speciation diagrams.

Species / mineral	Activity	Reaction	Log K$^+$
$As(OH)_4^-$	10^{-8}	$As(OH)_4^- = As(OH)_4^-$	0.0
$AsH_{3\ (aq)}$	10^{-8}	$AsH_{3\ (aq)} + 4H_2O = As(OH)_4^- + 6e^- + 7\ H^+$	9.30
AsO_4^{3-}	10^{-8}	$AsO_4^{3-} + 2e^- + 4\ H^+ = As(OH)_4^-$	27.75
$AsOH_3$	10^{-8}	$AsOH_3 + H_2O = As(OH)_4^- + H^+$	−8.39
AsO_2OH^{2-}	10^{-8}	$AsO_2OH^{2-} + H_2O + H^+ = As(OH)_4^-$	10.07
$H_2AsO_4^-$	10^{-8}	$H_2AsO_4^- + 2e^- + 2\ H^+ = As(OH)_4^-$	8.53
H_3AsO_4	10^{-8}	$H_3AsO_4 + 2e^- + H^+ = As(OH)_4^-$	4.15
$HAsO_4^{2-}$	10^{-8}	$HAsO_4^{2-} + 2e^- + 3\ H^+ = As(OH)_4^-$	16.31
Arsenolite	1	$arsenolite + 5H_2O + 4e^- + 2\ H^+ = 2As(OH)_4^-$	−16.86
As_2O_5	1	$As_2O_5 + 3H_2O + 4e^- + 2\ H^+ = 2As(OH)_4^-$	16.05
Claudetite	1	$Claudetite + 5H_2O = 2As(OH)_4^- + 2\ H^+$	−17.26

in-situ sampling equipment for hydrothermal fluids – are needed to prevent oxidation and gas release (Seewald et al., 2002). Nevertheless, entrainment of seawater and mineral precipitation due to cooling still takes place.

Another important aspect of As measurements is sample treatment, with the goal to preserve the total concentration and species distribution once at the surface. A first step is filtration through an unreactive membrane filter (commonly 0.22 μm) to remove microorganisms that might cause changes in speciation. During filtration, newly formed sulfides and hydrous ferric oxides are also separated from the hydrothermal fluid, however they have to be dissolved and their As concentration later re-included with the amount determined in the fluids. Further precipitation during storage and transport can be inhibited by acidification with HCl, HNO_3, H_2SO_4 or H_3PO_4 (McCleskey et al., 2004). These methods however, are controversial: (1) HCl preserved samples have to be corrected due to the $^{40}Ar^{35}Cl^+$ molecular interference with $^{75}As^+$ when using ICP-MS and (2) H_2SO_4 is difficult to purify and leads (also like HNO_3 and H_3PO_4) to higher E_h-values, which could result in oxidation reactions and changes in species distribution. One possibility to preserve speciation is addition of EDTA, but this it is difficult, because too much EDTA can increase pH and cause precipitation, while too little can be ineffective (McCleskey et al., 2004; Gault et al., 2005). Flash freezing of the sample under anaerobic conditions seems to be the better solution to preserve speciation and is already utilized (Francesconi and Kuehnelt, 2004; Planer-Friedrich et al., 2007, 2009; Kumar and Riyazuddin, 2010).

There are different analytical techniques for measuring total As concentration and its species: (1) spectroscopic methods (hydride generation in combination with atomic absorption (HG-AAS) or with atomic fluorescence (HG-AFS) and graphite furnace atomic absorption (GFAAS)), (2) inductively coupled plasma (ICP) techniques where the ICP can be coupled to a mass spectrometer (ICP-MS) or atomic fluorescence spectroscopy (ICP-AFS), in addition to combination with hydride generation (HG-ICP-MS) or high pressure liquid chromatography (HPLC-ICP-MS) and (3) furthermore electrochemical methods (Hung et al., 2004).

The today commonly used method for determination of As and the different species is ICP-MS coupled to HPLC, which allows determination and quantification of As species even at low concentrations with detection limits down to 0.2 μg L^{-1} (Kohlmeyer et al., 2002; Ronkart et al., 2007).

3. Arsenic in hydrothermal fluids

To present As data, the hydrothermal systems were grouped into shallow-water systems, like those from island arcs (IA) settings and deep-water systems, such as mid ocean ridge (MOR) and back-arc basin (BAB). All As values are given as endmember concentrations, which were calculated to zero Mg, unless otherwise stated. This possibly neglects magmatic input, but allows overall comparability.

3.1. Shallow-water hydrothermal systems

3.1.1. Montserrat

The 800 km long Lesser Antilles IA results from the subduction of the North American plate below the Caribbean Plate. The island of Montserrat is located at the northern end of the inner arc, consisting of mostly andesitic rocks, younger than 20 Ma (Bouysse et al., 1990; Le Friant et al., 2004). After an eruption of the Soufriere Hills volcano on Montserrat in July 1995, large increases in shallow water (2 to 5 m) hydrothermal discharge near the western coast were observed. These springs were sampled for one year revealing a sharp increase in Mn, Fe and As concentrations immediately after the eruption, followed by a steady decline (Cronan et al., 1997). In July 1995 the fluid As endmember concentrations were up to 3600 μg L^{-1} (Table 3), approximately 2400-times the mean of global seawater with fluid temperatures 30 °C above ambient. In contrast to the As concentration, Na and Cl concentrations remained stable, indicating, that no phase separation occurred (Cronan et al., 1997).

3.2. Tutum Bay

The shallow-water hot springs in Tutum Bay are located 150 m offshore along the southwest part of Ambitle Island (Papua New Guinea), which is a quaternary stratovolcano with a central eroded caldera. Submarine venting occurs in 5 to 10 m water depth with fluid temperatures up to 98 °C (Pichler and Dix, 1996). Phase separation in the deep reservoir, which feeds the Tutum Bay hot springs is likely (Licence et al., 1987). In addition to this high temperature focused discharge of slightly reducing fluids with a pH around 6.0, also low temperature diffuse venting was observed. Endmember As concentrations ranged from 750 to 1050 μg L^{-1}, which was up to 275-times local seawater enrichment (Table 3). Arsenic occurred more or less exclusively as the trivalent arsenite species (Pichler et al., 1999a; Price and Pichler, 2005). The host rocks of the Tutum Bay hydrothermal system are andesite, dacite, and basalt, covered with sandy to pebbly unconsolidated sediments. The sediments

Table 2
Concentration of As in different marine rocks and sediments.

rock type	Location	Average As concentration [mg kg^{-1}]	As concentration range [mg kg^{-1}]	Reference
Basalts	Ocean ridges		1.0	Matschullat, 2000
Latite, andesite, trachyte			0.5–5.8	Mandal and Suzuki, 2002
Rhyolite			3.2–5.4	Mandal and Suzuki, 2002
Abyssal peridotites	15° 20′N	0.94	0.4–4.3	Paulick et al., 2006
Serpentinized peridotites	Kane area	0.91	0.2–2.3	Werner and Pilot, 1997
Sediments	Sea of Japan West Pacific	10.3	5.8–20.0	Onishi and Sandell, 1955
Sediments	East Pacific	30.7	2–104	Boström and Valdes, 1969
Pelagic sediments	Pacific Ocean	86	3.1–455	Boström and Valdes, 1969
	Atlantic Ocean	18	10.8–26.1	
	Indian Ocean and Red Sea	16	5.9–86.5	

consist mostly of feldspar, hornblende, pyroxene and magnetite as well as weathering products coated with hydrous ferric oxide (HFO), which precipitated due to mixing between hydrothermal fluid and seawater (Pichler and Veizer, 1999; Pichler et al., 1999a,b; Price and Pichler, 2005). Arsenic concentrations in HFO were in excess of 50 000 mg kg^{-1}.

3.3. Milos

Milos is situated in the central Hellenic Volcanic Arc and formed due to the subduction of the African plate under the Aegean microplate (McKenzie, 1970). Discharge of acidic (pH ~5) and highly sulfidic hydrothermal fluids with temperatures up to 115 °C could be observed at the southeast coast in Paleochori Bay (Valsami-Jones et al., 2005a), where As concentrations were as high as 2900 µg L^{-1}. In the neighbouring Spathi Bay, As concentrations were even higher, with values up to 5850 µg L^{-1} (Table 3). This is approximately 2925-times local seawater and currently the highest value for marine hydrothermal systems. Speciation results for diffuse venting fluids indicate As^{III} and As^{V}, and also mono-, di-, and trithioarsenates (Price et al., 2013-this issue). Two groups of hydrothermal fluids could be distinguished due to phase separation at Milos: high-Cl fluids containing less As and a group of low-Cl fluids more enriched in As (Valsami-Jones et al., 2005b). The host rock of the system at Milos consists of andesitic to dacitic volcanic rocks and greenschist facies metamorphic rocks. Overlying high carbonate sediments enriched in lead and zinc mostly consist of quartz, calcite, aragonite, feldspars, plagioclase, and different clay minerals like smectite kaolinite, and illite (Karageorgis et al., 1998).

3.3.1. Bahía Concepción

As one of the largest fault-bound bays, Bahía Concepción is located in the Gulf of California and its heat anomaly is connected to extensional and accommodation tectonics related to the extension during the Late Miocene (Angelier et al., 1981; Ledesma-Vázquez and Johnson, 2001; Negrete-Aranda and Cañón-Tapia, 2008). Hydrothermal activity was observed as diffuse and focused venting with temperatures between 50 °C (sea bottom) and 87 °C (at 10 cm below the water-sediment interface) with estimated As concentrations for the hydrothermal endmember of around 2000 µg L^{-1} (Table 3). Emerging fluids of the sodium chloride type sampled at 5 m depth represented a mixture between seawater and a maximum of 40 % thermal endmember, whereas low Cl values lead to the assumption of phase separation and sampling of a low-density vapor phase (Prol-Ledesma et al., 2004). Metamorphic basement is overlain by dacitic to andesitic rocks from the lower Cretaceous (Busby et al., 2006), covered by a marine and continental sedimentary layer (Morán, 1984). Bright red and yellow precipitates as coatings on volcanic cobbles and boulders observed near the vent sites, mostly contain HFO, significantly enriched in As with concentrations up to 50 000 mg kg^{-1} (Canet et al., 2005; Berquó et al., 2007).

3.3.2. Champagne Hot Springs

The Champagne Hot Springs shallow-water hydrothermal system is located along the southwest flank of the Morne Plat Pays volcanic system, near the island of Dominica. Hydrothermal activity is connected to the double island arc system of the Lesser Antilles, and Dominica is situated on the inner arc (Fink, 1972). Fluids were a mixture of seawater and meteoric water emerging at a depth of 1 to 5 m with temperatures up to 71.4 °C and a pH around 6.0 (McCarthy et al., 2005). Arsenic concentrations were between 18 and 80 µg L^{-1} leading to zero-Mg endmember concentrations between 50 and 190 µg L^{-1} with an average of 100 µg L^{-1} (Table 3). The dominant species found in these fluids was arsenite in addition to minor arsenate. The host rocks of the Champagne Hot Springs hydrothermal system consist mainly of medium-K calk-alkaline andesites (Lindsay et al., 2003), and hydrothermal HFO found nearby, enriched in As with concentrations of up to 1880 mg kg^{-1} (McCarthy et al., 2005).

3.4. Deep-water hydrothermal systems

3.4.1. Mid-Atlantic Ridge (MAR)

The two hydrothermal systems Menez Gwen and Lucky Strike occur in close proximity and are located at 37°50′N and 37°17′N, respectively. They are similar in host rock composition and fluid geochemistry. Local spreading rates are around 20 mm a^{-1} and both systems are influenced by the Azores plume resulting in enrichment of incompatible elements in the underlying E-MORB basalts (Marques et al., 2009). Sediment coverage is either poor or absent, indicating that the volcanic rocks are young, only years to decades old (Fouquet et al., 1995). Fluids were

Table 3
Arsenic endmember concentration and further characteristics for various shallow and deepwater hydrothermal systems.

Location	Area/Type*	As [µg l^{-1}]	pH$_{min}$	T$_{max}$ [°C]	Host Rock	Depth [m]	Reference
Montserrat, Lesser Antilles	IA	3600	n.a.	43	Low K andesites	2–5	Cronan et al., 1997
Tutum Bay, Ambitle Island, PNG	IA	749–1049 950	6.0	98	Alkaline volcano, andesite, dacite, sediment covered	5–10	Pichler et al., 1999a,b Price and Pichler, 2005
Milos, Greece	IA	5850 *(no endmember)*	5.0	115	Andesites and greenschist metamorphic rocks	5–20	Price et al., 2013-this issue, in review for GCA
Bahía Concepción		2016	5.9	87	Dacitic to andesitic volcanic rocks, covered by sedimentary series	15	Prol-Ledesma et al., 2004
Champagne Hot Springs, Dominica	IA	104 (50.6–193.4)	6.0	71	Medium-K calc-alkaline andesites	1–5	McCarthy et al., 2005
Menez Gwen	MAR	18.51	4.4	285	E-MORB	840–865	Douville et al., 1999b
Lucky Strike	MAR	14.9 (4.3–23.9)	3.8	324	E-MORB	1600–1740	Douville et al., 1999b
TAG	MAR	<0.8	3.1	366	MORB	3436–3670	Douville et al., 1999b
Snakepit	MAR	3.2–14.2	3.7	350	MORB	3450–3500	Douville et al., 1999b
Logatchev	MAR	2.8–4.7	3.3	350	MORB, serpentinite, gabbro, ultramafic	2925–3050	Douville et al., 1999b
Guaymas area	EPR	50.8 (21.2–80.5)	5.1	315	MORB, sediment-hosted	2000	von Damm et al., 1985b
21°N	EPR	<2.6–33.9	3.3	405	MORB	2600	von Damm et al., 1985a
13°N	EPR	<0.8–1.4	3.8	317	MORB	2600–2630	Douville et al., 1999b
17-19°S	EPR	<0.8–41.0	3.1	300	MORB	2600–2700	Douville et al., 1999a, 1999b
Valu Fa Ridge, Lau Basin	BAB	449.5–824.1	2.0	342	Basalt-hosted/tholeiitic	2000	Fouquet et al., 1991
Vai Lili, Lau Basin	BAB	480.3–631.6	5.2	121	BABB, MORB, low-K andesite, rhyolithe	1707–1764	Douville et al., 1999b
Tui Malila, Lau Basin	BAB	157.3	4.2	312	BABB, basaltic andesites	1880	Mottl et al., 2011
Vienna Woods, Manus Basin	BAB	6.3–23.2	4.5	285	MORB, minor BABB	2500	Douville et al., 1999b
Satanic Mills, Manus Basin	BAB	1206.2–1386.1	2.3	358	BABB, MORB, med-K andesite, dacite	1650–1800	Douville et al., 1999b
Desmos, Manus Basin	BAB	10.2	2.1	120	BABB, MORB, med-K andesite	2000	Douville et al., 1999b

Note: * IA = Island Arc; MAR = Mid Atlantic Ridge; EPR = East Pacific Rise; BAB = Back Arc Basins; n.a. = not available measured to be poor in Cl (<18 440 mg kg^{-1}) and Fe (<44 mg kg^{-1}) but gas-rich (Charlou et al., 2000).

Menez Gwen is characterized by the absence of a central rift, with the main system being a 17 km in diameter and 700 m in high, circular volcano in the central part of the segment, which has a 6 km long, 2 km wide and 300 m deep axial graben at its top. The area of active hydrothermal discharge is located in a depth of 840 to 865 m on the northern end of this graben, covering around 200 m^2 (Fouquet et al., 1994). Clear fluids emerge with temperatures around 285 °C (Charlou et al., 2000) and calculated endmember As concentrations were around 18.5 μg L^{-1} (Table 3). Topographically, anhydrite chimneys and barite-rich mounds characterize the system.

Lucky Strike has a well-developed 15 km wide and up to 905 m deep rift valley, but without an axial graben. Three circular volcanic cones are located at the summit with the on-going hydrothermal activity in the depression between them (Langmuir et al., 1997). Hydrothermal chimneys surround a lava lake, 300 m in diameter with fresh lavas, while the cones are old and consist of highly vesicular volcanic breccia (Fouquet et al., 1994). Metal-poor fluids discharged with temperatures between 170 and 324 °C and pH values between 3.8 and 4.5 (Charlou et al., 2000). The As endmember concentrations of the fluids were between 4.3 and 24 μg L^{-1} with an average value of 15 μg L^{-1} (Table 3). A reversed correlation with Fe and high As/Fe ratios and also variable Cl-concentrations (Pester et al., 2012) indicate that phase separation is occurring.

The TAG hydrothermal field at 26°N on the MAR was discovered in 1972 during the NOAA Trans-Atlantic Geotraverse (Rona, 1980; Rona et al., 1975), with the most impressive feature, an active mound, discovered in 1985 (Rona et al., 1986). Black smokers with temperatures around 366 °C and white smokers with temperatures lower than 300 °C were observed, next to large areas of low temperature diffuse discharge (Edmond et al., 1995). Further south, at 23°22′N, the Snakepit hydrothermal system is located atop a neovolcanic ridge, also showing high temperature (350 °C) black smokers and lower temperature (270 °C) discharge of white fluids (Lalou et al., 1990). Fluids from both locations were Cl-rich and had As concentrations below the limit of detection of 0.8 μg L^{-1} for the two samples from TAG and 3.2 and 14.2 μg L^{-1} for the two samples from Snakepit (Douville et al., 1999b). Both systems are underlain by typical MORB, depleted in incompatible elements (Bryan et al., 1981).

At the Logatchev hydrothermal field (14°45′N) hot black smoker fluids (350 °C) and lower temperature diffuse fluids discharge in about 3000 m depth. Chlorinity was measured similar to seawater or slightly lower, which lead to the conclusion that there was no effect of phase separation (Douville et al., 2002). Fluids contained As concentrations of 2.8 and 4.7 μg L^{-1} (Douville et al., 1999b), lower amounts of Si, Li, and H_2S, as well as, elevated dissolved H and CH_4 due to serpentinization reactions (Schmidt et al., 2007). The basement consists dominantly of ultramafic rocks made of serpentinized harzburgites, with intruding gabbros (Petersen et al., 2009).

3.4.2. East Pacific Rise (EPR)

The 9000 km long EPR located in the Pacific Ocean has comparatively higher spreading rates than the MAR (Rea and Scheidegger, 1979). Areas of hydrothermal activity on the EPR were found and investigated in different sections like in the Guaymas basin at 27°N and in regions at 21°N, 13°N, and at 17° to 19°S.

The spreading center of the Guaymas Basin is located in the central Gulf of California in around 2000 m water depth and characterized by a high sedimentation rate of 1 to 5 m ka^{-1} (Fisher and Becker, 1991). Discharging black smoker fluids were up to 315 °C in temperature, highly reducing (Soto, 2009) and contained As endmember concentrations between 21.1 and 80.5 μg L^{-1} with an average value of 50.8 μg L^{-1} (Table 3). The high sedimentation rate results in a thick (>300 m) coverage of unconsolidated organic- and carbonate rich sediments of diatomaceous oozes and mud turbidites above the underlying basalts, intruded by dolerite sills (Einsele et al., 1980; Simoneit et al., 1984). Due to the sediment cover, the hydrothermal solution reacts with sediments in addition to the water-rock interaction at depth, and because of the pyrolysis of sedimentary organic matter, an enrichment of NH_4^+ was observed in the hydrothermal fluids (Sturz et al., 1996).

Further south, at 21°N where the EPR exhibits an intermediate spreading rate of around 60 mm a^{-1}, several fields of black smokers are situated in 2600 m depth, with fluid temperatures measured up to 405 °C (Dekov, 2007). Chimneys are 20 m high and made of anhydrite, iron-, zinc-, and copper-sulfides and different alteration minerals (Haymon and Kastner, 1981). Concentrations of As in these fluids varied between 2.3 (LOD) and 33.9 μg L^{-1} (Table 3), which is up to 17-times enriched in comparison to local seawater. The underlying rocks are composed of MORB with fresh basalt flows, talus and calcareous metalliferous sediments on the surface (Bäcker et al., 1985).

Another hydrothermal area linked to an axial graben (Ballard et al., 1984; Gente et al., 1986) exists near 13°N at 2600 m water depth in a region of fast spreading of up to 120 mm a^{-1} (Klitgord and Mammerickx, 1982). Recent lava flows were observed (Fouquet et al., 1988) as well as black and white smoker fluids with temperatures up to 317 °C and a minimum pH of 3.8 (Michard et al., 1984). Of the two samples, which were analyzed for As, one was below the detection limit (<0.8 μg L^{-1}) and the other had a concentration of 1.4 μg L^{-1} (Douville et al., 1999b). Further characteristics of the fluids were a high concentration of H_2 (Merlivat et al., 1987) and Cl (around 25 500 mg kg^{-1}) leading to the assumption that phase separation is occurring.

Along the southern EPR, where spreading is ultra-fast (143 to 147 mm a^{-1}), a hydrothermal area exists between 17° and 19°S. This area is characterized by abundant faults and fissures and has a 50 m deep and several hundred meter wide graben (Urabe et al., 1995). During the Naudur Cruise in 1993 several fluid samples were collected and two different hydrothermal fluids could be distinguished: one set with low Cl, gas enrichment and low content of dissolved metals and another set with high Cl, lesser gas enrichment and a high concentration of metals (Charlou et al., 1996). Samples from three black smokers with temperatures up to 300 °C were analyzed for As and endmember concentrations ranged from below the LOD (<0.8 μg L^{-1}; high Cl) up to 41.0 μg L^{-1} (low Cl) (Douville et al., 1999b). Volcanic eruptions were ongoing, occurring every few years as indicated by a very thin layer of sediments (<1 mm) leading the hydrothermal system to discharge diffuse low temperature to hot shimmering water and black smoker fluids (Renard et al., 1985; Auzende et al., 1996).

3.4.3. Back-Arc Basins (BAB)

Hydrothermal activity also occurs in back-arc spreading centers, where subduction leads to extension of the overriding plate due to roll-back and/or anchor behavior of the slab causing a high temperature gradient (Martinez et al., 2007). The chemical composition of the hydrothermal fluids is different from those at mid-ocean ridges because of the different geologic setting. Fluids are mostly very low in pH (~2) and contain a high amount of dissolved metals like Mn, Zn, Cu, and Pb due to the interaction of seawater with the host rocks, composed of dacites and andesites at elevated temperatures (Taylor and Martinez, 2003).

A typical example for an active BAB is the Lau Basin in the SW Pacific, located between the remnant Lau Ridge and the active Tofua volcanic arc (Mottl et al., 2011). In the southern segment of the Lau Basin from 21° to 23°S and in depths between 1700 and 2000 m, the 150 km long Valu Fa Ridge consists of (basaltic) andesite and rhyodacite, showing a clear influence of the subducted slab (Jenner et al., 1987; Vallier et al., 1991). Fluids from black and white smokers sampled during the Nautilau cruise on R/V Nadir in 1989 ranged between 240 and 342 °C in temperature, showed a pH of 2 and high Cl concentrations between 23 000 and 28 400 mg kg^{-1} (Fouquet et al., 1991). The amount of dissolved metals in these fluids were considerably higher than those measured at mid-ocean ridges and showed endmember As concentrations between 450 and 825 μg L^{-1}

(Table 3), which is up to 550-times seawater. Similar concentrations between 480 and 630 μg L^{-1} (Table 3) were measured in samples from the high temperature Vai Lili hydrothermal field at the central Valu Fa Ridge (Douville et al., 1999b). Phase separation is unlikely, because the hydrothermal fluids had chloride concentrations similar to seawater. Only 26 km further north, the Tui Malila hydrothermal field, sampled in 2005, showed maximum As values of 160 μg L^{-1} (Mottl et al., 2011), which is around 4-times lower than previous results at Vai Lili hydrothermal field. However, these measurements were made on not acidified samples, potentially resulting in lower As concentrations due to precipitation.

Other hydrothermal systems are active in 1650 to 2500 m depth in the rapidly opening Manus Basin (Tregoning, 2002). At the New Britain Trench to the south the Solomon Plate is being subducted, causing the formation of the New Britain arc. Back-arc spreading is occurring along the Manus Ridge, which is bounded by the Willaumez transform fault in the west and the Djaul transform fault in the east. Another strongly active hydrothermal area with active spreading is located in the Eastern Manus Basin (EMB), bounded by the Djaul and Weitin transform fault (Taylor, 1979; Martinez and Taylor, 1996; Lee and Ruellan, 2006). Underlying host rocks show variations from arc-like character with BAB basalts close to the New Britain arc to MORB-like character with increasing distance from the spreading center (Sinton et al., 2003).

The basalt hosted and sparsely sediment covered Vienna Woods hydrothermal field is located near the Manus Spreading center in 2500 m water depth and comprises diffuse fluid flow as well as hot clear, black and grey smokers reaching temperatures up to 285 °C and a pH around 4.5 (Craddock et al., 2010; Reeves et al., 2011). Two fluid samples were taken during the Manusflux cruise in 1995, which had As endmember concentrations of 6.3 and 23.2 μg L^{-1} respectively (Douville et al., 1999b). Fluids were also sampled in the EMB at the PACMANUS and the approximately 20 km northeast-located Desmos hydrothermal area. At the PACMANUS site, several chimney fields were observed on the felsic and only slightly sedimented Pual Ridge. The fluid temperatures were up to 358 °C, which is close to the phase boundary, and had a pH between 2.3 and 2.8, in addition to indications of involvement of magmatic fluids with acid-volatile constituents (Reeves et al., 2011). Emerging hydrothermal fluids had As concentrations of 1200 and 1390 μg L^{-1} (Table 3) for samples from the Satanic Mills field, which is part of PACMANUS. Both samples were rich in Cl and Fe (90 and 250 mg l^{-1}, respectively), with the second one showing higher As concentration and higher concentrations of both. The nearby located Desmos caldera is characterized by venting of hot and highly acidic ($pH \leq 2.1$) white fluids with temperatures between 88 and 120 °C. Fluids were rich in sulfate due to a magmatic component rich in SO_2, exsolving from a shallow intrusion (Gamo et al., 1997). One fluid sample from this location was analyzed for As and showed a concentration of 10 μg L^{-1} (Table 3), much lower than at Satanic Mills. In general, the hydrothermal fluids were rich in Mg and poor in Fe, and the host rock is composed of basaltic andesite and hyaloclastite deposits (Gena et al., 2001).

4. Discussion

The concentration of Arsenic (As) measured in marine hydrothermal fluids shows a broad range, from below detection (LOD) to 5850 μg L^{-1} (Table 3). In general, As concentration in hydrothermal fluids from shallow-water hydrothermal systems show higher concentrations than those in deep-water, whereas in the latter, hydrothermal systems from back-arc basins (BAB) show higher values than those from mid-ocean ridges (MOR).

Shallow-water hydrothermal systems mostly found in Island Arc (IA) settings like Tutum Bay, Milos, Bahía Concepción or Champagne Hot Springs, show the highest As concentrations of up to 5850 μg L^{-1}. The basement is dominantly made of andesitic and/or dacitic volcanic rocks with bulk rock As concentrations between 0.5 and 5.8 mg kg^{-1} (Mandal and Suzuki, 2002). These hydrothermal systems are often covered by sediments due to their close proximity to land masses. Important differences between the different shallow-water systems are temperature (leading to phase separation), pH, and H_2S content, which seem to be responsible for the broad range of observed As concentration. In addition, other physicochemical parameters like reaction time and maturity of the system, fluid pressure, redox state, iron concentration, and gas fugacity can affect the amount of As leached from the host rocks and transported in the hydrothermal fluid. Those fluids, which are higher in temperature, more acidic and high in H_2S (e.g. Milos), show the highest amount of As, probably due to the higher leaching capacity and phase separation and low amount of precipitated As-bearing minerals in the subsurface, whereas systems with lower temperature, more alkaline pH and low H_2S are also lower in As (e.g. Champagne Hot Springs). It seems that phase separation is one of the more important factors controlling the concentration of As in hydrothermal fluids. Phase separation produces a gas rich low-Cl vapor phase and a high-Cl brine phase, whereas As should partion into the vapor phase, due to the domination of the uncharged arsenite species ($H_3AsO_3^0$) at the prevailing pH and redox conditions in shallow-water systems, additional to HS^- complexation (Heinrich et al., 1999b). There is no consensus if partioning is occurring (Pokrovski et al., 2005) and further research is needed, because the effect of sulfur ligands like H_2S and SO_2 was neglected with respect to the volatility of As (Pokrovski et al., 2008). An additional cause for As enrichment could be leaching from As-rich sediments in the shallow sub seafloor, prior to discharge (McCarthy et al., 2005; Price and Pichler, 2005). Although conceptually likely, there is currently no evidence for leaching of As from sediments. Concentrations of As in hydrothermal fluids, which discharge from discrete orifices in the bedrock from areas of low sedimentation, are similar or sometimes even higher than those which discharge diffusively through sediments (McCarthy et al., 2005).

The system offshore in Montserrat showed higher As values during volcanic activity but did not show any temperature increase or variations in Na and Cl, which would be indicative that phase separation occurred. Thus, the observed enrichment of As here may be caused by enhanced magmatic input (in the form of magmatic volatiles) during the eruptive cycle. Unfortunately it is impossible to distinguish which proportions of As were leached from the host rocks due to water-rock interaction or added by magmatic volatiles.

Considering values from the MOR, As concentrations are significant lower with the highest values of 80.5 μg L^{-1} measured in fluids from the sediment hosted Guaymas basin on the EPR (Von Damm et al., 1985b). MOR host rocks are made of E-MORB and MORB due to different sources, melting styles and depth of melt formation (Perfit, 2001), whose As concentrations are roughly around 1.0 mg kg^{-1} (Matschullat, 2000) and often only sparsely covered with sediments. The slight difference in As concentration between andesites and dacites from the IA systems and the MORBs should not account for the overall lower values of the hydrothermal fluids from the MOR, leading to the conclusion that physicochemical parameters are more important than bulk As concentration of the host rock. A huge sink for As in these hydrothermal fluids could be a high amount of dissolved Fe transported with the fluids, leading to precipitation and incorporation of As into Fe-sulfides as observed in various hydrothermal ores where arsenopyrite or orpiment for example are common minerals. Eh–pH diagrams also show this where preferably minerals like orpiment and claudetite precipitate at low Eh and pH and high temperature (Figs. 2 and 3). Hypogene origin of orpiment was also suggested earlier by different experimental studies at high temperatures (Weissberg et al., 1966). Different samples from the TAG hydrothermal mound show As concentrations of up to 210 mg kg^{-1} (Hannington et al., 1995) and up to 100 mg kg^{-1} were found in a sediment core in 13 to 16 cm depth from Lucky Strike (Dias et al., 2008). For BAB settings, massive sulfide deposits from the Jade Hydrothermal field (Okinawa Trough) show As concentrations of up to 9.3 % and realgar (As_4S_4)

and orpiment (As_2S_3) minerals were found (Halbach et al., 1989). The possible amount of As lost prior to discharge due to precipitation has not been quantified yet but could be huge as shown above and responsible for the overall lower values in deep-water systems compared to the shallow-water systems. Considering that the As concentration in the oceanic rocks from IA and MOR show only little variations, it is probably also not the bulk quantity that is responsible for the large variation of As, but rather where the As is bound in the rocks in addition to the various physical and chemical parameters.

Data from the MOR tentatively verify the partioning of arsenite into the vapor phase during boiling and phase separation. Phase separation generally causes the vapor phase to be more enriched in As and the brine phase depleted, as observed in As enriched samples from Menez Gwen and Lucky Strike and depleted samples from TAG, Snakepit and 13°N EPR. At 17° to 19°S EPR two vapor phase samples showed higher values than the assumed liquid brine phase sample (Douville et al., 1999a).

In comparison to the alkaline basalts at the MOR, hydrothermal systems in BAB are hosted in acidic host rocks like at IA. Values for As are in general higher, varying between 450 and 1390 $\mu g\ L^{-1}$ for the usual BAB fluids because As seems to be strongly mobile during the interaction of seawater with the acidic rocks at greenschist-facies conditions (250 to 450 °C; 1 to 8 kbar). Exceptions are Vienna Woods, showing MORB-like host rock composition and low As values and Desmos caldera underlain by basaltic rocks and with very unique sulfate-rich fluids also showing low values. This may also be due to lower temperatures and the absence of phase separation or co-precipitation of As with Fe prior to discharge, resulting in low-Fe fluids.

As observed for two different measured values in the same area of the Lau Basin, the methods of As preservation and determination have to be reconsidered. The sampling strategy is a factor, affecting the quality of measurement and data. It would be the best to sample the pure fluid and keep it at bottom pressure to avoid oxygenation and precipitation with other elements, which can lower the original concentration and change speciation, and to acidify the samples for As_{total} to higher solubility and avoid precipitation. Most of the reviewed papers do not say anything about how the samples were taken and totally neglect errors in sampling strategy. Also different preservation methods make it hard to compare different data sets. Another important difficulty is the $^{40}Ar^{35}Cl^{+}$-interference during ICP-MS measurements with $^{75}As^{+}$, where results have to be corrected carefully.

The total concentration of As in the global ocean is mainly controlled by factors like riverine input, weathering of seafloor and sedimentation on the seafloor in addition to atmosphere-seawater exchange and input of volcanic gases and hydrothermal fluids. The residence time of As in the global ocean was assumed to be between 32,000 years (Matschullat, 2000) and 63,000 years (Turner, 1987), and compared to average river water values of around 0.62 $\mu g\ L^{-1}$ (Gaillardet et al., 2003), As is enriched in the global ocean with an average value of 1.7 $\mu g\ L^{-1}$ (Neff, 2002; Smedley and Kinniburgh, 2002; Plant et al., 2003). This is poorly understood, but hydrothermal input of As could be a possible explanation for the higher values.

The input of As by hydrothermal fluids into the global ocean is difficult to estimate, but can be constrained for individual sources. Estimations of the fluid flux from MOR hydrothermal systems, for example, range from 6.0×10^{10} to 2.5×10^{15} kg a^{-1} (Mottl and Wheat, 1994; Elderfield and Schultz, 1996; German and Von Damm, 2003). Based on these fluxes and available As data for MOR hydrothermal systems, the total flux of As can be estimated to be between 3.0×10^{3} and 1.25×10^{8} kg annually. However, this calculation neglects subsequent As removal through flocculation and precipitation within the hydrothermal plume and subsequent sedimentation. Nevertheless, in comparison to the annual input of As by rivers, which is around 23×10^{6} kg (Gaillardet et al., 2003) this amount is substantial. In addition the flux from BAB and IA systems has to be taken into account, although there less data is available. The hydrothermal system in Tutum Bay, for example, where sufficient data for the determination of As flux exists, discharges a minimum amount of 5.5×10^{2} kg per year (Pichler et al., 1999a). This value alone is similar to the minimum estimate of the total annual flux from the MORs (see above). Unfortunately there are no other reliable flux measurements for hydrothermal systems in shallow water or from BAB hydrothermal systems, which prevents a better estimation. Nevertheless, considering the high As concentrations in many of these systems the overall hydrothermal flux may be the answer why As is higher in seawater than in river water.

5. Conclusions

Discharge of hydrothermal fluids with significant fluxes of heat and chemicals occurs at shallow- and deep-water hydrothermal systems due to the interaction of cold seawater with heated rocks and/or hot magma. Hydrothermal fluids contain variable amounts of the element arsenic (As), due to dissolution and mobilization at elevated temperatures in addition to magmatic degassing of a deep magma chamber. The most important factors controlling the specific amount are the physicochemical parameters like temperature, pH, the amount of H_2S, reaction time, fluid pressure, redox reactions, iron and gas chemistry, in addition to the underlying host rocks mineralogy and crystallinity. Probably overlying sediments, the maturity and also the permeability of the different systems may play a role.

All these factors seem to be important, but most of them are hard to quantify and vary substantially between the hydrothermal systems, nevertheless it can be concluded that:

I. Hydrothermal fluids from shallow-water island-arc (IA) settings are mostly very high in As (up to 5850 $\mu g\ L^{-1}$), followed by fluids from deep-water hydrothermal systems in back-arc basins (BAB; up to 1386 $\mu g\ L^{-1}$) and mid-oceanic ridges (MOR), whose As concentration is comparably much lower (up to 80.5 $\mu g\ L^{-1}$).
II. The higher the temperature and the amount of H_2S, and the lower the pH, the more As is leached and transported with the fluids in shallow-water hydrothermal systems.
III. The only slightly higher bulk rock concentration of underlying acidic dacites and andesites from IA systems cannot be responsible for the overall much higher values of As compared to deep-water systems underlain by MORB. The efficiency of leaching should mostly dependent on the physicochemical parameters, but also on the As mineralogy of the host rocks. Precipitation of As-bearing minerals like orpiment and claudetite could be a huge sink for As in deep-water hydrothermal fluids as shown by thermodynamic calculations and diagrams. Different As-bearing minerals were also observed in drill cores from hydrothermal areas.
IV. Phase separation occurring when the hydrothermal fluid encounters the two-phase boundary leads to separation into a gas rich Cl-poor vapor phase and a Cl-rich liquid phase and causes major variations in fluid composition. Based on low pH and low E_h conditions in most of the moderate and high temperature systems, $H_3AsO_3°$ is the dominating As species, which should be preferentially transported in the vapor phase.
V. Additional input of As due to magmatic volatiles has to be considered and could also be linked to eruptive cycles.
VI. Changes in concentration and speciation due to incorrect sampling and storage have to be taken into account in addition to the analytical uncertainty.
VII. An important upcoming question concerning As in hydrothermal systems will be to understand how hydrothermal flux affects the As concentration in the ocean. First estimates showed, that large amounts are released by shallow IA and deep BAB systems, which may explain why the As concentration in seawater is higher than its concentration in river water.

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