Arsenic in marine hydrothermal fluids and associated vent biota

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Christian Breuer

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1. Gutachter:	Prof. Dr. Thomas Pichler
2. Gutachterin:	Prof. Dr. Britta Planer-Friedrich

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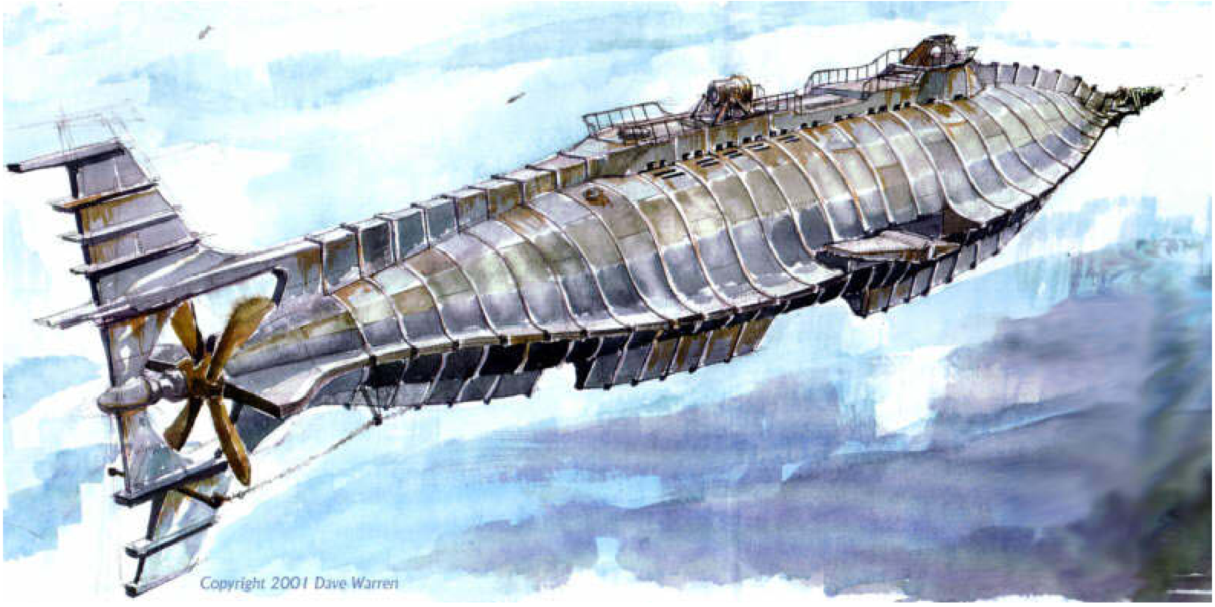
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"The sea is everything. It covers seven tenths of the terrestrial globe. Its breath is pure and healthy. It is an immense desert, where man is never lonely, for he feels life stirring on all sides. The sea is only the embodiment of a supernatural and wonderful existence. It is nothing but love and emotion; it is the living infinite."

Jules Verne,
Twenty Thousand Leagues Under the Sea

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Abstract

Arsenic (As) is a unique element, in terms of its chemical und physical characteristics and ubiquitously present in the terrestrial and marine environment. Despite its well-known toxicity and carcinogenicity and its reputation as the “king of poison”, several biogeochemical aspects are so far only rarely investigated and often poorly understood.

The concentration of As in river waters (0.62 µg L^{-1}) is lower than in seawater (1.7 µg L^{-1}), which is the first unique attribute, as rivers normally represent dominant elemental sources to the oceans. The main factors controlling the concentration of As in seawater are, in addition to the riverine input, the weathering of the seafloor, input of volcanic gases, atmosphere-seawater exchange, as well as sedimentation on the seafloor and anthropogenic input. Another important and likely underestimated source are hydrothermal fluids emanating at the seafloor, which could be greatly enriched in their As concentration. The most important factors affecting this concentration, varying from below seawater to several thousand µg L^{-1}, are the tectonic setting with its different physicochemical parameters like temperature, controlling phase separation processes, pH affecting As species, mobility and leaching capacity, pressure as a function of depth, the redox conditions and different adsorption and desorption reactions. Furthermore the H_2S, CO_2 and metal concentrations in the fluids, as well as the chemistry and mineralogy of the underlying host rocks are important parameters. In general, the higher the temperature and the amount of gases, and the lower the pH, the more As is leached from the host rock and transported with the hydrothermal fluids. However, the only slightly variable concentration of As in the underlying bulk rocks in the different

regimes cannot be responsible for the overall very variable concentrations observed in the hydrothermal fluids. The input of magmatic volatiles, which are able to transport a huge amount of metals and also As, has to be considered depending on the system and location and also the preferentially transport of one species over another during phase separation processes in the vapor or brine phase has to be taken into account. To get a deeper understanding about the influencing parameters from the different tectonic regimes, case studies were conducted during this thesis at the mid-ocean ridge, as well as in a typically back-arc basin environment and at an island-arc setting. In addition to this, the influence of the emitted As on the resident vent biota was investigated

Hydrothermal fluids from mid-ocean ridges reveal mostly pretty low As concentrations in the range of several tens of µg L^{-1}, most likely due to precipitation of As-bearing minerals in the subsurface or low leaching capacity. Clear hydrothermal fluids sampled at the Menez Gwen hydrothermal field at 37°N on the Mid-Atlantic Ridge were up to 285 °C hot with a pH between 4.0 and 5.1 and phase separation influenced. Concentrations of As^T were between 6 and 90 µg L^{-1} with only the two inorganic species arsenite (As^{III}) and arsenate (As^V) found in the hydrothermal fluids in variable proportions.

Higher fluid concentrations of mostly several hundred µg L^{-1} are reported from back-arc basin environments, where host rocks are more acidic, leading to low pH hydrothermal fluids. Samples taken at the PACMANUS and SuSu Knolls hydrothermal areas in the eastern Manus Basin revealed As^T concentrations of up to 376 µg L^{-1}. These were found in focused white smoker fluids bubbling liquid CO_2 with temperatures of around 100 °C and a very low pH. Much lower concentrations were measured in black smoker fluids, most likely due to the precipitation of As-bearing minerals or particles in the subsurface and immediately when mixing with cold oxygenated seawater. Concentrations in clear fluids were also lower, as they represent a mixture of seawater and the pure hydrothermal fluids. Again only the inorganic As^{III} and As^V species could be observed.

These elevated values compared to seawater concentrations are superpassed by fluids from shallow-water island-arc settings, which typically show concentrations of several thousand µg L^{-1}. Sediment cores of altered volcaniclastic sediments from the Palinuro volcanic complex in the Tyrrhenian Sea were taken in 630 m water depth. Pore fluids had temperatures of up to 58 °C, a minimum pH of 6.3 and maximum dissolved sulfide concentrations of up to 3.5 mM. These samples were extremely enriched in As^T concentrations with up to 18.3 mg L^{-1} and for the first time, considerable amounts of mono-, di- and trithioarsenates (up to 94 %) were measured in fluids from systems located in those depths. A crucial step for the investigation of thioarsenic species is sample preservation between sampling and measurements, as these species are only marginally stable under oxygen and can easily precipitate, and an appropriate method for sample conservation has to be developed.

Associated vent biota like mussels and snails living in the lower temperature zones where shimmering hydrothermal fluids discharge are able to bioaccumulate and biotransform the As emanating with the hydrothermal fluids. However, literature data is sparse, and only a few studies exist dealing with this topic despite this highly interesting and very special environment. The accumulated concentration depends on the characteristics of the fluids like As^T, As speciation, temperature and pH, as well as on the characteristics of the different vent animals like their metabolism, based on chemolithoautotrophic bacteria, and resistance against toxic metals. Hydrothermal vent snails like *Alviniconcha hessleri* from the Manus Basin are able to accumulate high concentrations of As^T with of up to 5580 mg kg^{-1} in the gill, 721 mg kg^{-1} in the digestive gland, and 43.3 mg kg^{-1} in their muscle tissue. This value is highly increased compared to snails living in the photic zone and accumulating several tens or a few hundred mg kg^{-1}. Lower concentrations could be found in the snails of the species *Ifremeria nautilei* living in colder fluids with a higher pH and lower As^T concentration, which accumulate up to 118.3 mg kg^{-1} in the gill, 107.6 mg kg^{-1} in the digestive gland, and 21.7 mg kg^{-1} in the muscle tissue. High amounts of As found in the gill are due to the accumulation of iron-zinc-sulfur particles rich in As, but also due to the activity of chemosynthetic sulfur- or methane-oxidizing symbionts. Furthermore high concentrations in the digestive gland could be explained as it acts as a pathway and storage organ for different metals. Overall lower concentrations could be found in mussels of the genus *Bathymodiolus* sampled at Menez Gwen (*Bathymodiolus azoricus*) and in the Manus Basin (*Bathymodiolus manusensis*), which only accumulate several tens of mg kg^{-1}, with the highest concentrations found in the digestive gland, followed by the gill and muscle tissues.

After uptake of the inorganic species As^V and As^{III} available in the surrounding seawater most likely via the essential phosphate transporter system, different methylation steps are following forming monomethylarsonic acid (MA) and dimethylarsinic acid (DMA). From these, different kind of arsenosugars are produced, which seem to be an endproduct in marine algae, but precursor for arsenobetaine in higher consuming marine animals, feeding from marine algae. Vent animals show a completely different metabolism carried out by chemolithoautotrophic bacteria located in their gill epithelial tissues. The snails and mussel from the deep situated Manus Basin hydrothermal system (1800 m), show no or only a very low concentration of arsenosugars, indicating that there might be other pathways of forming arsenobetaine, without the filtering and presence of marine algae. Compared to these, hydrothermal vent mussels from the Menez Gwen hydrothermal system (850 m) show an elevated amount of different arsenosugars and low arsenobetaine. Both organic species are present in the hydrothermal environment, where photosynthetic input is not or only very sparsely available, so that other pathways and mechanism for their formation may be possible, which could be connected to the very special chemolithoautotrophic nutrition.

Zusammenfassung

Arsen (As) ist ein einzigartiges Element, betrachtet man seine chemischen und physikalischen Eigenschaften. Es ist zudem im terrestrischen und marinen Milieu allgegenwärtig präsent. Trotz seiner großen Bekanntheit als Nervengift und Karzinogen, sowie seinem Ruf als „König aller Gifte“, sind verschiedene biogeochemische Aspekte nur wenig erforscht und schlecht verstanden.

Die Konzentration von As in Flüssen (0.62 µg L^{-1}) ist geringer als die im Meerwasser (1.7 µg L^{-1}), was eine erste Besonderheit darstellt, da normalerweise Flüsse eine maßgebliche Quelle für die verschiedenen Elemente im Ozean sind. Die dominierenden Faktoren für die Konzentration von As im Meerwasser sind neben dem Eintrag von Flüssen, die Verwitterung des Meeresbodens, der Eintrag von vulkanischen Gasen, der Austausch zwischen Atmosphäre und Meerwasser, die Sedimentation auf den Meeresgrund sowie der anthropogene Einfluss. Eine weitere wichtige und bis heute vielleicht unterschätzte Quelle sind hydrothermale Fluide, die am Meeresboden austreten und stark an As angereichert sein können. Die wichtigsten Faktoren für die Konzentration von As in diesen Fluiden, die zwischen unterhalb der Meerwasserkonzentration und mehreren tausend µg L^{-1} variieren kann, sind das tektonische Regime und dessen verschiedenen lokalen physikochemischen Bedingungen. Hierzu zählen die Temperatur, welche eine Phasenseparation hervorrufen kann, der pH-Wert, welcher die jeweilige As-Spezies, Mobilität und Lösungsprozesse beeinflusst, der Druck als Funktion der Tiefe, die Redox-Bedingungen und verschiedene Absorptions- und Desorptions-Reaktionen. Des Weiteren spielen die H_2S- und CO_2-Konzentration sowie das Auftreten anderer Elemente wie Eisen oder Mangan in den Fluiden, aber auch die Chemie und Mineralogie des Wirtsgesteins eine entscheidende Rolle. Je höher die Temperatur und die Konzentration der Gase und je niedriger der pH-Wert, desto mehr As kann

aus dem Wirtsgestein gelöst und mit den hydrothermalen Fluiden in den Ozean transportiert werden. Jedoch kann der nur geringe Unterschied in der As-Konzentration des Wirtsgesteins aus den verschiedenen tektonischen Regimen nicht allein für die stark variablen Konzentrationen in den hydrothermalen Fluiden verantwortlich sein. Der zusätzliche Eintrag von magmatischen Volatilen, die eine große Menge an verschiedensten Metallen sowie auch As transportieren können, muss hier in Abhängigkeit des tektonischen Regimes berücksichtigt werden, sowie auch der vorrangigen Transport verschiedener Spezies während der Phasenseparation. Um die jeweiligen Faktoren in den verschieden tektonischen Regimen besser zu verstehen, wurden Untersuchungen sowohl am Mittelozeanischen Rücken, als auch in einem Backarc-Becken und in einem Inselbögen-Milieu durchgeführt. Zusätzlich dazu wurde auch der Einfluss des As aus den hydrothermalen Fluiden auf die lokal ansässige Fauna untersucht.

Hydrothermale Fluide, die an Mittelozeanischen Rücken beprobt wurden, zeigen eine zumeist sehr geringe As-Konzentration, oft im Bereich von wenigen zehner µg L^{-1}. Dies geht wahrscheinlich auf die Ausfällung von As-reichen Mineralen im Meeresboden und einer geringen Lösungskapazität hervor. Klare hydrothermale Fluide, die am Menez Gwen Hydrothermalfeld bei etwa 37°N am Mittelatlantischen Rücken beprobt wurden, zeigten Temperaturen von bis zu 285 °C, einen pH-Wert zwischen 4.0 und 5.1 und As-Konzentrationen zwischen 6 und 90 µg L^{-1}. Weiterhin zeigten die Analysen das Vorkommen der anorganischen Spezies Arsenit (As^{III}) und Arsenat (As^{V}).

Höhere As-Konzentrationen, zumeist im Bereich von mehreren hundert µg L^{-1}, können in hydrothermalen Fluiden aus Backarc-Becken beobachtet werden. Hier sind zumeist saure Wirtsgesteine anzutreffen, welche Fluide mit einem sehr geringen pH-Wert zu Folge haben. Proben, die an den PACMANUS und SuSu Knolls Hydrothermalsystemen im östlichen Manus Becken gewonnen wurden, zeigten As-Konzentrationen von bis zu 376 µg L^{-1} in weißen Fluiden, die mit ca. 100 °C, einem pH von 1.2, sowie einer hohe Konzentration von gelöstem CO_2 austreten. Sehr viel geringere Konzentrationen wurden in Fluiden von schwarzen Rauchern gefunden, was auf die Ausfällung As-reichen Mineralen oder Partikeln im unterliegenden Gestein, aber auch während der Mischung mit dem umgebenden Meerwasser während des Austretens zurückzuführen ist. Auch klare und kältere Fluide zeigten eine eher geringe Konzentration aufgrund der Vermischung des reinen hydrothermalen Fluids mit dem kalten Meerwasser. In diesen Proben konnten wiederum nur die anorganischen As^{III} und As^{V} Spezies beobachtet werden.

Diese im Vergleich zum Meerwasser bereits stark erhöhten Konzentrationen werden von Fluiden, die an Hydrothermalsystemen in Inselbögen austreten und mehrere tausend µg L^{-1} zeigen können, übertroffen. Mittels Schwerelot wurden Sedimentkerne bestehend aus alteriertem vulkanoklastischen Material nahe des untermeerischen Palinuro Vulkankomplexes im Tyrrhenischen Meer aus 630 m Wassertiefe geborgen. Die daraus gewonnen Porenfluide zeigten Temperaturen von bis zu 58 °C, einen minimalen pH-Wert von 6.3 und eine maximale Konzertration an gelöstem Sulfid von 3.5 mM. Des Weiteren enthielten sie extrem erhöhte As-Konzentration von bis zu 18.3 mg L^{-1} und zum ersten Mal wurden hier beträchtliche Anteile von Mono-, Di-, und Trithioarsenaten (bis zu 94 %) in hydrothermalen Fluiden aus diesen Tiefen nachgewiesen. Ein wichtiger Schritt für die gute qualitative und quantitative Untersuchung dieser As-Schwefel-Spezies ist die Konservierung der Proben zwischen der Probennahme und der Analyse im Labor, da diese unter Sauerstoffeinfluss instabil sind und sich leicht Präzipitate bilden. Somit muss hier noch eine wirksame Konservierungsmethode gefunden werden.

Die an und von den hydrothermalen Quellen und Fluiden lebenden Muscheln und Schnecken sind in der Lage, das austretende As einzulagern und umzuwandeln. Obwohl dieses ein sehr interessantes Themengebiet und Milieu ist, gibt es nur wenige Studien, die sich damit befassen. Die Menge an As, welche eingelagert werden kann, hängt auf der einen Seite von den Charakteristiken der Fluide wie der Konzentration an As, der Verteilung der Spezies, der Temperatur und dem pH-Wert, aber auch von den Charakteristiken der Organismen, geprägt durch ihre Ernährung mittels chemolithoautotrophen Bakterien und ihrer Resistenz gegenüber toxischen Metallen, ab. Die an den hydrothermalen Quellen des Manus Beckens lebenden Schnecken der Spezies *Alviniconcha hessleri* sind in der Lage große Mengen an As von bis zu 5 580 mg kg^{-1} in ihren Kiemen, 721 mg kg^{-1} in ihren Mitteldarmdrüsen und 43.3 mg kg^{-1} in ihrem Muskelfleisch einzulagern. Verglichen zu Schnecken aus photischen Zonen, welche zumeist mehrere zehn bis wenige hundert mg kg^{-1} einlagern können, sind diese Werte extrem erhöht. Weniger hohe Konzentrationen zeigen Schnecken der Spezies *Ifremeria nautilei*, die in kälteren Fluiden mit einem höheren pH-Wert und geringeren As-Konzentrationen leben. Diese Schnecken lagern bis zu 118.3 mg kg^{-1} in ihren Kiemen, 107.6 mg kg^{-1} in ihrer Mitteldarmdrüse und 21.7 mg kg^{-1} in ihren Muskeln ein. Die extrem hohe Konzentration in den Kiemen kann auf die Einlagerung von Eisen-Zink-Schwefel-Partikeln, die viel As enthalten können, sowie auf die Aktivität der Sulfat- und Methan-reduzierenden Bakterien, zurückgeführt werden. Weiterhin lassen sich die hohen Konzentrationen in den Mitteldarmdrüsen auf ihre Eigenschaft als Durchgangs- und Einlagerungsorgan zurückführen. Insgesamt niedrigere Konzentrationen wurden in Muscheln der Gattung *Bathymodiolus* bei Menez Gwen (*Bathymodiolus azoricus*) und im Manus Becken (*Bathymodiolus manusensis*) gefunden, meist im Bereich von wenigen zehn mg kg^{-1}. Hier wurden die höchsten Konzentrationen jeweils in der Mitteldarmdrüse gefunden, gefolgt von den Kiemen und Muskeln.

Nachdem die im Meerwasser vorhandenen anorganischen As^{III} und As^{V} Spezies über das essenzielle Phosphattransporter-System aufgenommen werden folgt die Anlagerung von Methyl-Gruppen und die Bildung von Methylarsonsäure (MA) und Dimethylarsinsäure (DMA). Aus diesen werden im Weiteren verschiedene Arsenozucker gebildet, die als Endprodukt in Algen vorkommen, aber auch als Ausgangsstoff für Arsenobetain in höher konsumierenden Organismen, die sich von diesen Algen ernähren, angesehen werden können. Organismen, die an den Hydrothermalquellen leben, zeigen eine extrem unterschiedliche Ernährungsweise im Vergleich zu Organismen aus der photischen Zone. Die Ernährungsweise basiert hier auf den an den Außenseiten der Kiemen befindlichen chemolithoautotrophen Bakterien. Die Schnecken und Muscheln aus dem Manus Becken (1800 m) zeigen keine oder nur sehr geringe Mengen an Arsenozucker, und dies ohne die Präsenz von photosynthetischen Organismen. Im Vergleich dazu lassen sich bei Muscheln vom Menez Gwen Hydrothermalfeld (850 m) höhere Konzentrationen dieser Arsenozucker erkennen, im Gegensatz zu einem geringen Anteil von Arsenobetain. Das Vorkommen beider Spezies in dieser sehr speziellen Umgebung, wo photosynthetische Biomasse wie Algen gar nicht oder nur sehr wenig verfügbar ist, lässt auf andere Wege und Mechanismen schließen, wodurch Arsenozucker oder Arsenobetain gebildet werden kann, die vermutlich im engen Zusammenhang mit der sehr speziellen chemosynthetischen Ernährung stehen.

1 | Introduction

Arsenic (As) is a ubiquitous element ranking 14th in the elemental abundance of the seawater and is known for its toxicity and carcinogenicity. The average seawater concentration of As is 1.7 µg L^{-1} (Neff, 2002) and its cycling in the global ocean is controlled by different factors and sources of As. High amounts of As can be discharged into the oceans by riverine input, which can be affected by mining or industrial effluents and further by natural sources such as geothermal fluids, atmospheric precipitation, weathering of volcanic rocks and biological activity. A so far underestimated input is contributed by marine hydrothermal fluids emitting at the seafloor, which are able to provide a huge amount of different elements into the oceans. The most important factors controlling the hydrothermal systems and the concentration of As therein are the tectonic regime and different physicochemical conditions at and beneath the seafloor. The composition of the vent fluids has a strong influence on the surrounding ecosystem and allows unique organisms to dwell in this environment. Hydrothermal activity represents one of the fundamental processes involved in the transfer of energy and mass from the mantle and lithosphere into the oceans. Therefore, this thesis will focus on the fate and transport of the potentially toxic element As in hydrothermal fluids and the accumulation and transformation in the hydrothermal vent biota.

The introduction of my dissertation will provide an overview of the abundance and behavior of As in terrestrial and aquatic systems. Further it describes the processes taking place in hydrothermal systems and their impact on the vent biota. Chapter 2 with the title “Arsenic in marine hydrothermal fluids” will give an overview of important studies on hydrothermal fluid chemistry, that consider As in their measurements and the factors controlling the amount of transported As in the hydrothermal fluids. This chapter also presents thermodynamic calculations and modelling of the different As species and their precipitation as solid phases in shallow- and deep-water hydrothermal systems.

The following three chapters represent case studies for As concentration and speciation in hydrothermal fluids and associated vent biota of three different tectonic regimes: mid-oceanic ridges, back-arc basins and island arc settings. Chapter 3 will describe a study on the Menez Gwen system at the Mid-Atlantic ridge, followed by a study on the PACMANUS and SuSu Knolls hydrothermal systems located in the Eastern Manus Basin in chapter 4 and at last chapter 5 describes a study on the Palinuro volcanic complex at the Aeolian island arc in the Tyrrhenian sea.

1.1 Arsenic in the environment

The potentially toxic element As is ubiquitous present in the terrestrial and marine environment, whereas its concentrations can vary tremendously due to mobilization by natural and anthropogenic processes. Arsenic can be found in lithospheric rocks, soils and sediments, as well as in different types of water bodies such as rivers, lakes, oceans, groundwater and as well in high concentrations in acid mine drainage and industrial waste water.

1.1.1 Arsenic in the terrestrial environment

The average concentration of As in igneous rocks from the crust is estimated to be approximately 1.5 mg kg^{-1} with only small variations and in general below 5.0 mg kg^{-1} (Ure and Berrow, 1982; Plant et al., 2003). It behaves strongly chalcophile forming preferentially sulfide minerals in addition to oxides and phosphates. More than 300 As minerals are known to date and in more than 200 minerals As acts as a major constituent. Most of them are ore minerals or associated alteration products and As is preferably incooperated in sulfide minerals like pyrite (FeS_2) with up to 10% (Blanchard et al., 2007). Metamorphic rocks typically reflect concentrations measured in igneous rocks with only minor variations. Soils are generally more enriched in As compared to igneous and metamorphic rocks, with concentrations ranging between 5 and 13 mg kg^{-1} (Smedley and Kinniburgh, 2002) and originating from geological processes or anthropogenic contamination. Higher concentrations can be caused by the occurrence of sulfide minerals under reducing conditions or also due to the release during the oxidation of pyrite as observed in acid sulfate soils with As concentrations up to 50 mg kg^{-1} (Dudas, 1984). Anthropogenic contamination of soils by copper smelting, combustion of fossil fuels, or usage of agriculture pesticides is also highly relevant and can cause considerably higher As concentrations. Considering As concentrations in sedimentary rocks and unconsolidated sediments, which are typically in the range of 5 to 10 mg kg^{-1}, it becomes obvious that concentrations vary a lot with up to 3 000 mg kg^{-1} in organic-rich and sulfide-rich shales, or in high-iron and high-phosphate rocks (Smedley and Kinniburgh, 2002). This reveals again the impact of an increasing portion of sulfide minerals, organic matter, and clays on the concentration of As. Contamination of soils and sediments by industrial mining, especially from mine tailings and effluents, can result in highly increased concentrations of As (e.g. Sarmiento et al., 2009). One reason is the co-existence of As and gold and originates from the finding that the fate of both elements are closely bound together as gold is often found in arsenopyrite (FeAsS) and As is mobilized when the gold is leached out of the ore mineral. The release of As itself from different ore-forming minerals is mostly related to the oxidation and changes in solubility of primary and secondary sulfide minerals rich in As (Masscheleyn et al., 1991). The primary mineral arsenopyrite (FeAsS) releases As due to its oxidation during mining activity or redistribution of tailings in ponds and heaps (Plant et al., 2003). The oxidation reaction of FeAsS can be described as follows:

$$4FeAsS + 13O_2 + 6H_2O \rightarrow 4Fe^{2+} + 4AsO_4^{3-} + 4SO_4^{2-} + 12H^+ \qquad \text{(Eq. 1)}$$

1.1.2 Arsenic in the aquatic and marine environment

Arsenic is also often found in the aquatic and marine environment, with a mean seawater value of 1.7 µg L^{-1} and ranging between 0.5 µg L^{-1} and 3.0 µg L^{-1} (Neff, 2002). Rivers transport between 0.1 µg L^{-1} and 0.8 µg L^{-1} with an average of 0.62 µg L^{-1} (Gaillardet et al., 2003), which is typically in the same range or slightly higher than in lake waters. The As concentration in rivers, which might run into lakes or the oceans, depends mostly on the bedrock lithology with its As concentration and on the surface recharge and the groundwater flow (Smedley and Kinniburgh, 2002).

Extremely enriched values due to mobilization by weathering or dissolution were found in groundwater, geothermal waters and mine drainage waters, with up to several thousand µg L^{-1} of As. In addition to this, the disposal of industrial waste, smelting of As bearing minerals and burning of fossil fuels causes As enrichments and subsequent dramatic damages in the environment of rivers and the groundwater (Bissen and Frimmel, 2003). Significant problems are known especially from developing countries like Bangladesh, India, Argentina, Chile, Vietnam, Mexico and Taiwan, but since 2002, when the WHO set the United States drinking water standard from 50 µg $L^{-1}$of As down to 10 µg L^{-1}, a broad interest on the As geochemistry awoke again (Smith et al., 2002).

The release and mobilization of As into rivers and groundwater is mainly controlled by two processes, whereof the first is an elevated pH (> 8.5) in combination with a semi-arid or arid environment, leading to a desorption of adsorbed As from various mineral oxides (especially Fe-oxides) or prevents adsorption at all. The second major process is triggered under strongly reducing conditions in combination with circum-neutral pH, again resulting in desorption of As from mineral-oxides, but also during the reduction of iron and manganese oxides (Smedley and Kinniburgh, 2002).

The chemistry, toxicity, mobility, and behavior of As in the environment depends strongly on its oxidation state. In nature, the oxidation states +V (arsenate), +III (arsenite), 0 (arsenic), and –III (arsine) can be found, but in the aqueous environment, the inorganic As mostly occurs in the trivalent and pentavalent form (Mandal and Suzuki, 2002; Sharma and Sohn, 2009). Thereby, at the modern pH of the seawater, the most abundant form of inorganic pentavalent arsenate (As^{V}) is $HAsO_4^{2-}$ and some traces of $H_2AsO_4^{1-}$ and AsO_4^{3-} and in the case of arsenite (As^{III}) its neutral form H_3AsO_3. In oxidized aqueous solutions, As^{V} is the most stable form, while under more reducing conditions (from about + 300 mV at pH 4 to -200 mV at pH 9) the trivalent As^{III} species is more stable (Fig. 1). The most important species and structures found in aqueous systems are shown in Fig. 2.

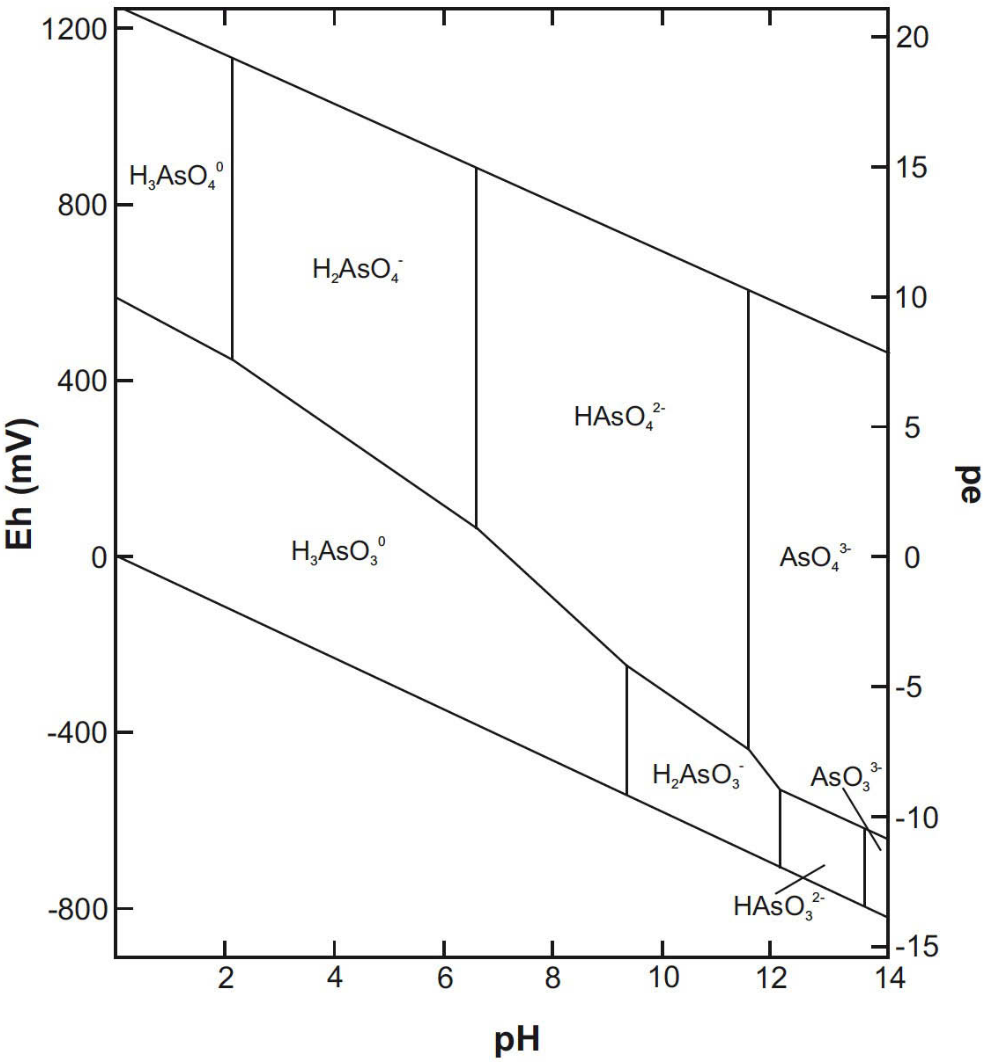


Fig. 1: Eh-pH diagram for aqueous arsenic species in the system As-O_2-H_2O at 25 °C and 1 bar pressure (after Lu and Zhu, 2011).

By examining the seawater for As species, it is striking that amounts of As^{III} can be found, that are higher than thermodynamically feasible. This is probably due to biotic and abiotic reduction of As^{V}, atmospheric deposits, as well as input from upwelling of anoxic waters and input of hypoxic river basins (Cutter, 1992). Both, the reduction of As^{V} into As^{III} and the reversible process, the oxidation of As^{III} to As^{V} are relatively rapid processes promoted abiotically and/or biologically and has to be taken into account while preserving aqueous samples during until the measurements (e.g. McCleskey et al., 2004).

In surface and coastal waters, where the biological activity is high and an impact of the industrial activity might be observed, organic forms of As have been frequently found, although in low concentrations. The two dominant organic As species in seawater are methylarsonic acid (CH_5AsO_3; MA) and dimethylarsinic acid ($C_2H_7AsO_2$; DMA). These two species are mainly generated by different reduction processes in combination with methylation by marine organisms like phytoplankton, bacteria and yeasts, followed by excretion into the seawater or during degradation of the biomass (Andreae and Klumpp, 1979; Vidal and Vidal, 1980). Overall, As^V, As^{III} and the methylated species MA and DMA can coexist in seawater, with the relative species distribution dominantly depending on the pH, the redox conditions additionally to the prevailing temperature and the overall availability of biomass.

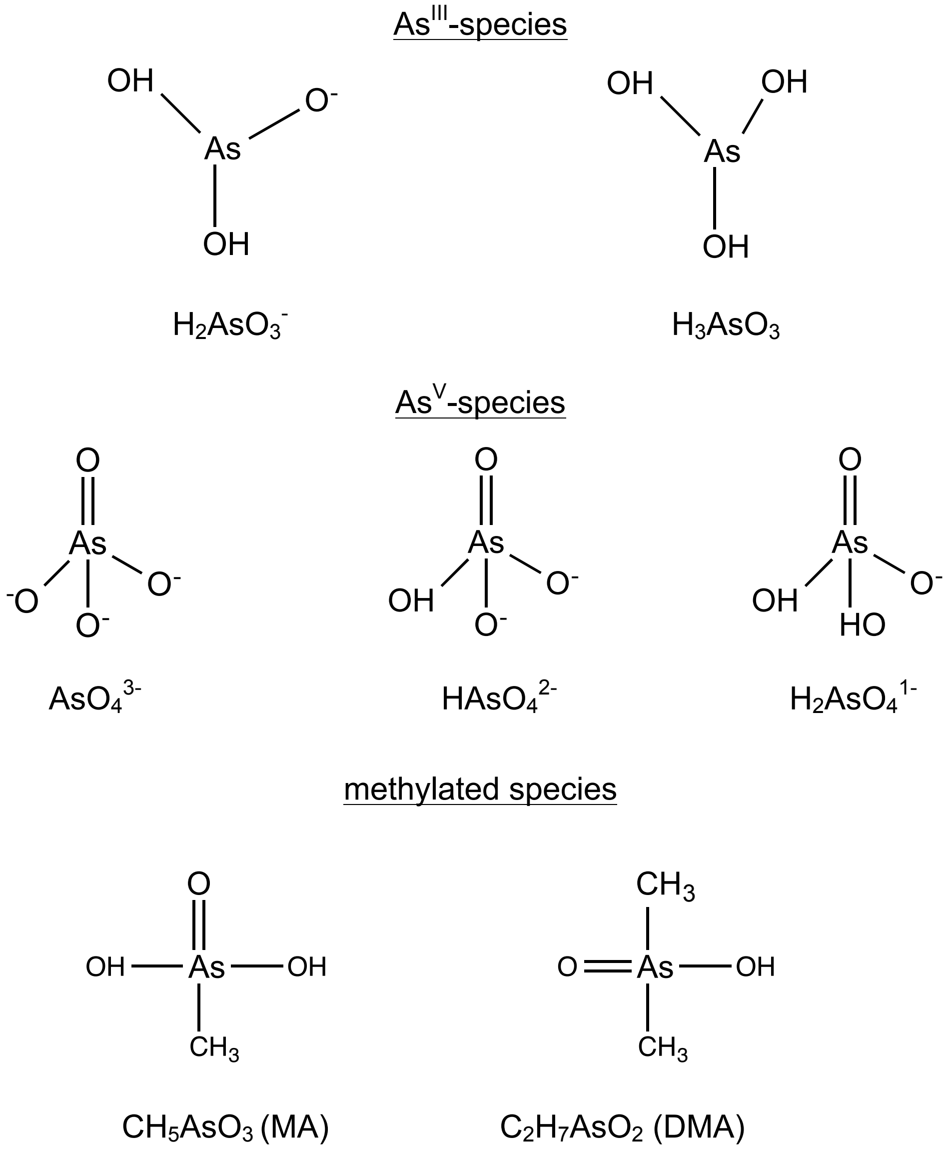


Fig. 2: Different As species found in aqueous systems.

In the last years, the presence of different thioarsenic species was monitored in solutions with high dissolved sulfide and high As concentrations and their environmental relevance had become apparent. These As species were found and studied for instance in geothermal waters from the Yellowstone National Park or in contaminated industrial waters (e.g. Stauder et al., 2005; Planer-Friedrich et al., 2007). Thioarsenic species exist as mono-, di-, tri- and tetrathioarsenates as well as mono-, di- and trithioarsenites. However, their preservation is highly challenging, because thioarsenates can quickly transform into As^{III} and As^{V} due to decomposition and by a stepwise ligand exchange of SH- and OH-groups. For preservation of thioarsenates especially in iron-rich waters, the addition of acids lowers the pH and promotes the precipitation of poorly crystalline As_2S_3 (Smieja and Wilkin, 2003) and flash freezing solely supports the formation of iron hydroxides. To date, the most efficient method that has been described for the preservation of thioarsenates in iron-rich waters is the addition of EDTA for iron-complexation in combination with flash freezing under anoxic conditions and a small headspace in the sampling vial, but this method needs a more careful development (Suess et al., 2011).

1.2 Arsenic in marine organisms

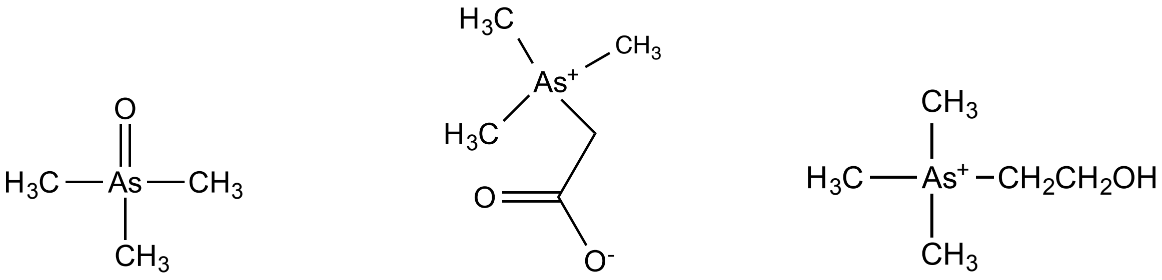
Organisms living in the marine environment are able to bioaccumulate and transform inorganic As from the surrounding seawater into their bodies reaching concentrations up to several hundred mg kg^{-1} and transfer it through the marine food web in different forms of organic As species. Marine plants and especially algae can only incorporate inorganic As from the surrounding seawater, whereas higher organisms are able to absorb it from the surrounding seawater as well as through the food chain by consumption of smaller organisms such as algae and phytoplankton (Edmonds and Francesconi, 2003). Several studies showed, that depending on the organisms and the availability of specific As species in the surrounding environment, variable amounts of As can be assimilated into the different tissues. Marine bivalves for instance are capable to accumulate up to 214 mg kg^{-1} of As (in average 10.4 mg kg^{-1}) and snails are able to accumulate even higher amounts with concentrations up to 530 mg kg^{-1} (in average 52 mg kg^{-1})

(Neff, 1997). In general, organisms living in polluted environments with high input of As reveal higher accumulation of As.

Marine bacteria, micro- and macroalgae, as well as plants assimilate via the cellular phosphate transporter system mainly inorganic pentavalent As^V, which is the dominant form of As in oxygenated sea- and freshwater. This is because As^V and phosphate are very similar to each other and thus As^V cannot be excluded from this essential mechanism performed by the organisms. However, differences between As^V and phosphate exist as As^V esters are less stable and can be reduced by different agents, whereas phosphate displays more inert properties (Benson et al., 1988). There are also different bacteria, which are able to excrete the As again in a more rapid way than it is assimilated, preventing a net accumulation in the cells (Silver and Misra, 1984). Due to the absence of a real competition between As^V and phosphate uptake in microbial experiments, there might be other mechanisms for the uptake and accumulation of inorganic As in algae possible (Andreae and Klumpp, 1979). After the assimilation of As^V, different steps of sequential reduction and oxidative methylation by microorganism are following. Thereby, As^V is first reduced to the much more mobile As^{III} and then further to MA, DMA and trimethylarsine oxide (C_3H_9AsO) as proposed by the Challenger pathway (Challenger, 1945; Challenger, 1955). The process inducing the reduction from As^V to As^{III} remains still unclear. However, as a source for the methyl groups, which are needed for processing the methylation, the S-adenosylmethionine ($C_{15}H_{23}N_6O_5S$; AdoMet) was identified as an active and universal donor (Qin et al., 2006). By adding one more reaction step to the last product trimethylarsine oxide (Fig. 3), the relatively volatile trimenthylarsine is produced, which was proposed to be the final product by Challenger et al. (1955). Another pathway for As methylation in algae is the transformation of the adenosyl group from the AdoMet to the As atom of the DMA molecule, instead of adding the last methyl group and before forming trimethylarsine oxide (Edmonds and Francesconi, 1983).

After processing the different methylated forms, algae are able to generate different ribose derivatives known as arsenosugars (As-sug), showing a comparably lower toxicity. After the first investigations, a total of 15 As-sug were identified and isolated from different algae families (Francesconi and Edmonds, 1993), whereof the most important groups are phosphate-, sulfate-, sulfonate- and glycerol-sugars (Fig. 3). The presence of dimethylarsinoyladenosine found in the kidney of a giant clam supported the formation of As-sug due to enzymatic removal of adenine and glycosidation of matching algal metabolites (Edmonds and Francesconi, 1987). However, As-sug, which were solely observed in the marine environment and in urine from people consuming seafood, can be considered as a by-product of the various detoxification processes carried out by algae (Francesconi and Edmonds, 1993). In addition to these processes, As-sug can be synthesized by microorganisms performing different steps of methylation and adenosylation (Edmonds and Francesconi, 2003). These described As-sug seem to be an endproduct of As transformation in algae, while the finding of arsenobetaine (AsBet) in some special algae species (Slejkovec et al., 2006; Grotti et al., 2008) could have been caused by incorrect sample treatment when epiphytes were not correctly removed.

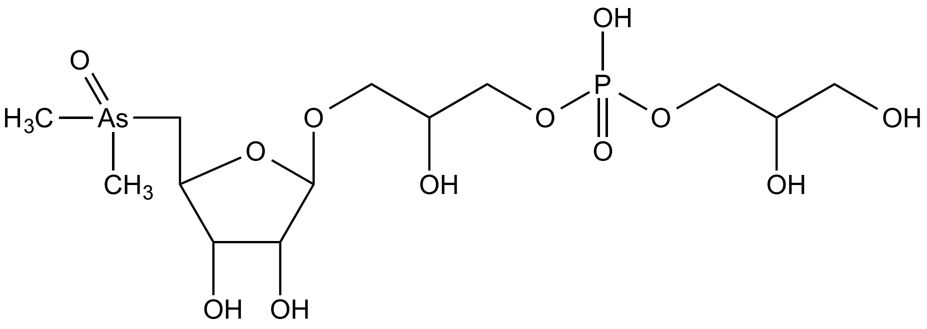
In general, AsBet ($C_5H_{11}AsO_2$; Fig. 3) could be detected and was reported as the dominant form of organoarsenic in higher marine organisms such as fish or snails with fractions sometimes higher than 95 % of the total As (As^T) found in the tissues. Additionally, other compounds such as MA, DMA, arsenocholine ($C_5H_{14}AsO^+$; AC; Fig. 3.) and various arsinylribosides were detected in these organisms. Both, the dimethylarsinylribosides and trimethylarsonioribosides, which are delivered by the food chain and ubiquitous present in marine algae, have been proposed to act as intermediates and to be precursors of AsBet (e.g. Francesconi and Edmonds, 1993; Edmonds and Francesconi, 2003). However, at least the direct transformation of dimethylarsinylribosides into AsBet in marine organisms seems to be highly unlikely (Edmonds and Francesconi, 1981) as this requires the cutting of the C3-C4 bond of the ribose ring, several oxidation steps, decarboxylation, and methylation. AsBet is in general metabolically stable and is thought to be the main endproduct of all metabolic and detoxification processes in higher marine animals and organisms.



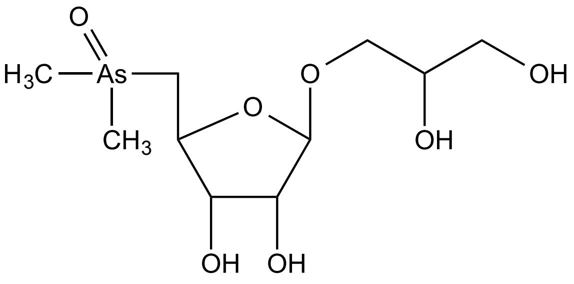
C_3H_9AsO
(trimethylarsine oxide)

$C_5H_{11}AsO_2^-$
(AsBet)

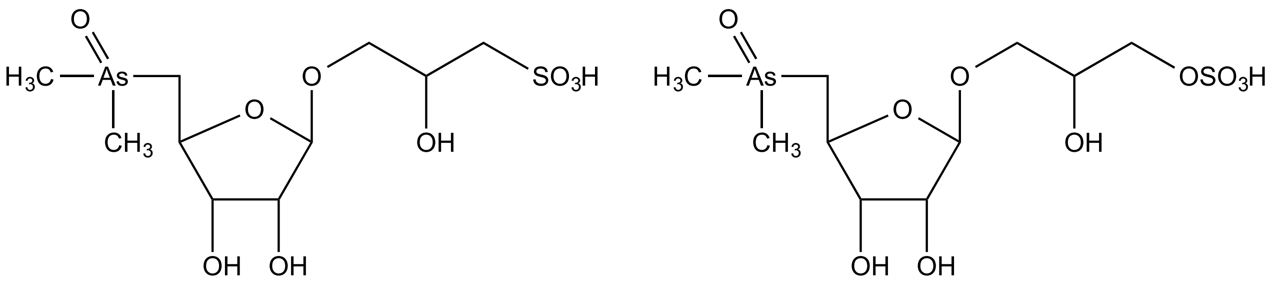
$C_5H_{14}AsO^+$
(AC)



phosphate-sugar



glycerol-sugar



sulfonate-sugar

sulfate-sugar

Fig. 3: Various important organoarsenic compounds found in marine organisms.

1.3 Hydrothermal systems

1.3.1 History of hydrothermal systems

The impressive feature of deep-sea hydrothermal vent systems also called thermal springs in former times, were first discovered near the Galápagos Islands in 1977 as published in *NATURE Geoscience* (Corliss et al., 1979). Hydrothermal systems have been the subject of many investigations since their discovery unraveling their very special geology, chemistry and biology. The convective circulation of cold seawater through the lithosphere near the Galápagos Islands was already proposed some years earlier, deduced from heat flow and bottom water temperature measurements (Williams et al., 1974). First speculations about thermal springs near the mid-oceanic ridges were already published in 1965 with the discovery of "thermal areas" showing elevated heat fluxes and energy sources at depth by penetrative convection from the upper mantle (Elder, 1965). Further speculations were based on investigations of ophiolite complexes of E. Liguria (Italy), where the mineral assemblages and metamorphic parageneses gave evidence for sub-seafloor hydrothermal convection and transport of solutions enriched in heavy metal (Spooner and Fyfe, 1973). After the first discovery by Corliss et al. (1979), several studies were conducted on seawater-basalt interaction, modeling of convective systems, as well as on calculating global energy and mass fluxes.

The investigations at the different Galápagos sites called Clambake, Dadelions, Garden of Eden and Oyster bed in February and March 1977 with the deep submersible *Alvin* showed the presence of shimmering discharge of warm hydrothermal fluids with temperatures between 10 to 17 °C and fluid flow rates between 2 and 10 cm sec^{-1}. The involved scientists discovered also the presence of different fascinating vent communities consisting mainly of crabs, mussels, limpets, and giant white tubeworms. The fluid geochemistry was characterized by an increased concentration of manganese, lithium, calcium, barium, silicon, carbon dioxide and a decreased concentration of magnesium with respect to the unaffected seawater. In addition to these observations, they discovered hydrothermal mound deposits with heights ranging from less than 1 m to over 20 m, which consisted mainly of iron, silica and manganese (Corliss et al., 1978;

Corliss et al., 1979). Only some years later (1979), impressive black smoker systems were discovered on the East Pacific Rise at 21°N, where hydrothermal fluids reached maximum temperatures of 350 °C and high fluid flow rates of 1 to 5 m sec^{-1} (MacDonald et al., 1980).

During the last 35 years of research following these sensational discoveries, many more hydrothermal vent systems and associated ecosystems were discovered and investigated with submersibles or remotely operating vehicles (ROV) at various seafloor spreading centers, back-arc basins and near island-arcs. It is now well know, that these systems play an important role in the transfer of energy and mass from the mantle and crust into the ocean. Thereby, the ecosystems at hydrothermal systems may give insights into the first development of live. Until today, more than 300 sites of active hydrothermal venting have been found (http://www.interridge.org), while it is expected that there must exist many more that still have to be discovered. This makes quantification of fluxes on a global scale pretty difficult. At these sites, more than 500 new species of hydrothermal vent biota were discovered until today (Desbruyères et al., 2006), living in this dark, potentially toxic and hostile environment.

1.3.2 Chemistry of hydrothermal fluids

The chemistry of hydrothermal fluids discharging at the seafloor as clear, black, or white smoker fluids is largely controlled by the interaction of seawater with the underlying mainly basaltic rocks at elevated temperatures in addition to phase-separation processes, when temperature and pressure conditions of the fluid approach the two-phase boundary. However, these two processes are inextricably linked to each other. Only insufficiently studied is the contribution of biological processes and magmatic degassing, whereas the contribution of the latter strongly depends on the tectonic setting, magma sources and maturity of the system (e.g. German and Von Damm, 2003).

The heat source, causing these elevated temperatures could be a shallow magma chamber or due to serpentinization processes, which is the dominant process at slow spreading ridges. The cold seawater percolates into the crust through faults and fissures, passing the down-flowing "**recharge zone**" at elevated temperatures before reaching the hot “**reaction zone**” near the axial heat source, where temperatures prevail exceeding 400 °C. After boiling, the fluids rise upwards again due to the difference in buoyancy compared to colder overlying seawater, and after passing the “**discharge zone**”, they are expelled at the seafloor (Alt, 1995).

During the reaction of the seawater with the surrounding rocks, chemical species are gained and others lost during all stages or zones described above. This depletion or enrichment processes depend on different factors such as the temperature and pressure, but also on the bulk rock composition and mineralogy of the host rock. In the lower temperature **recharge zone**, which can be several km long, the alteration of basaltic glass, olivine and plagioclase has been observed. Several elements such as potassium, rubidium, cesium and boron are early removed from the penetrating cold seawater and silica and sulfur added to the fluids by leaching of the surrounding rocks. When the seawater is heated to temperatures above 150 °C, two major processes occur: the precipitation of anhydrite ($CaSO_4$) where SO_4 is lost from the fluid, and the formation of Mg-OH silicates, where Mg is fixed in and at the rocks and the fluid gets depleted in Mg.

The formation of anhydrite, showing retrograde solubility, removes all the calcium and around one-third of the sulfate from the down-flowing seawater. If calcium is leached from the surrounding host rock, further anhydrite precipitation will occur and the fluid gets more depleted in sulfate. When temperatures are in excess of 250 °C, the sulfate could also be reduced to hydrogen sulfide (H_2S) when reacting with igneous pyrrhotite, resulting in slightly elevated $\delta^{34}S$ values as observed in different studies on sulfide deposits (Shanks, 2001).

Removal of Mg from the fluids and incorporation into clays can occur by the formation of Mg-rich smectite (T < 200 °C) or chlorite (T > 200 °C) as the following equation for the formation of chlorite shows:

$$4(NaSi)_{0.5}(CaAl)_{0.5}AlSi_2O_8 + 15Mg^{2+} + 24H_2O \leftrightarrow \\ 3Mg_5Al_2Si_3O_{10}(OH)_8 + SiO_2 + 2\,Na^+ + 2Ca^{2+} + 24H^+ \quad \text{(Eq. 2)}$$

The release of H^+ causes a decreasing pH value, and at the same time, H^+ is consumed by silicate hydrolysis reactions, acting as a weak buffer. If temperatures increase to values higher than 250 °C, different ion exchange reactions will influence the composition of the fluid. During albitization, basaltic anorthite is altered to albite, which strongly affects the concentration of calcium and sodium in the fluid as shown in Eq. 3, where these two elements replace each other in the plagioclase feldspars:

$$CaAl_2Si_2O_8 + 2Na^+ + 4SiO_2(aq) \leftrightarrow 2NaAlSi_3O_8 + Ca^{2+} \qquad \text{(Eq. 3)}$$

When the altered seawater finally reaches the **reaction zone** near the heat source, it is slightly acidic, anoxic, alkali-rich and Mg-poor. Near the heat source, large quantities of heavy metals like Fe, Mn, Cu and Zn are leached from the surrounding host rock and rise up within the boiling fluid. Additionally, if the crust is rich in sulfur (sulfide minerals, elemental sulfur), it will be dissolved from the corresponding minerals and supplied to the hydrothermal fluid.

Drastic changes in the chloride concentrations (< 6 % to 200 % of seawater concentration) or the concentration of other elements in the hydrothermal fluid can be caused by the phase separation process. This process is expected to be ubiquitous in the sub-seafloor at hydrothermal systems, as almost every investigated hydrothermal fluid is depleted or enriched in chloride concentrations relative to the seawater. Phase separation occurs when fluid temperatures reach the two-phase boundary at a specific pressure. The deeper the system, the higher is the temperature of the boiling hydrothermal fluid as depicted in Fig. 4. When the fluid reach the theoretical two-phase curve it forms two phases, one phase gets strongly enriched in chloride and the other phase *vice versa* gets depleted in chloride. Furthermore, an important point in the two-phase scenario is the critical point, a kind of threshold which is calculated for seawater to be at 407 °C and 298 bar (Bischoff and Rosenbauer, 1984). When fluids pass the two-phase boundary at lower P-T conditions than this critical point, a low chloride vapor phase containing salt is generated. In contrast to this subcritical phase separation, at P-T conditions above the critical point (supercritical phase separation), a high chloride brine phase will be produced (German and Von Damm, 2003). Generally, both phase separation processes are expected to occur in the underlying host rocks during hydrothermal convection, with minor amounts of halite precipitation. Most of the other cations in the fluids behave similar as chloride as they are partly present as chloride-complexes and thus follow the chloride trend during phase separation processes.

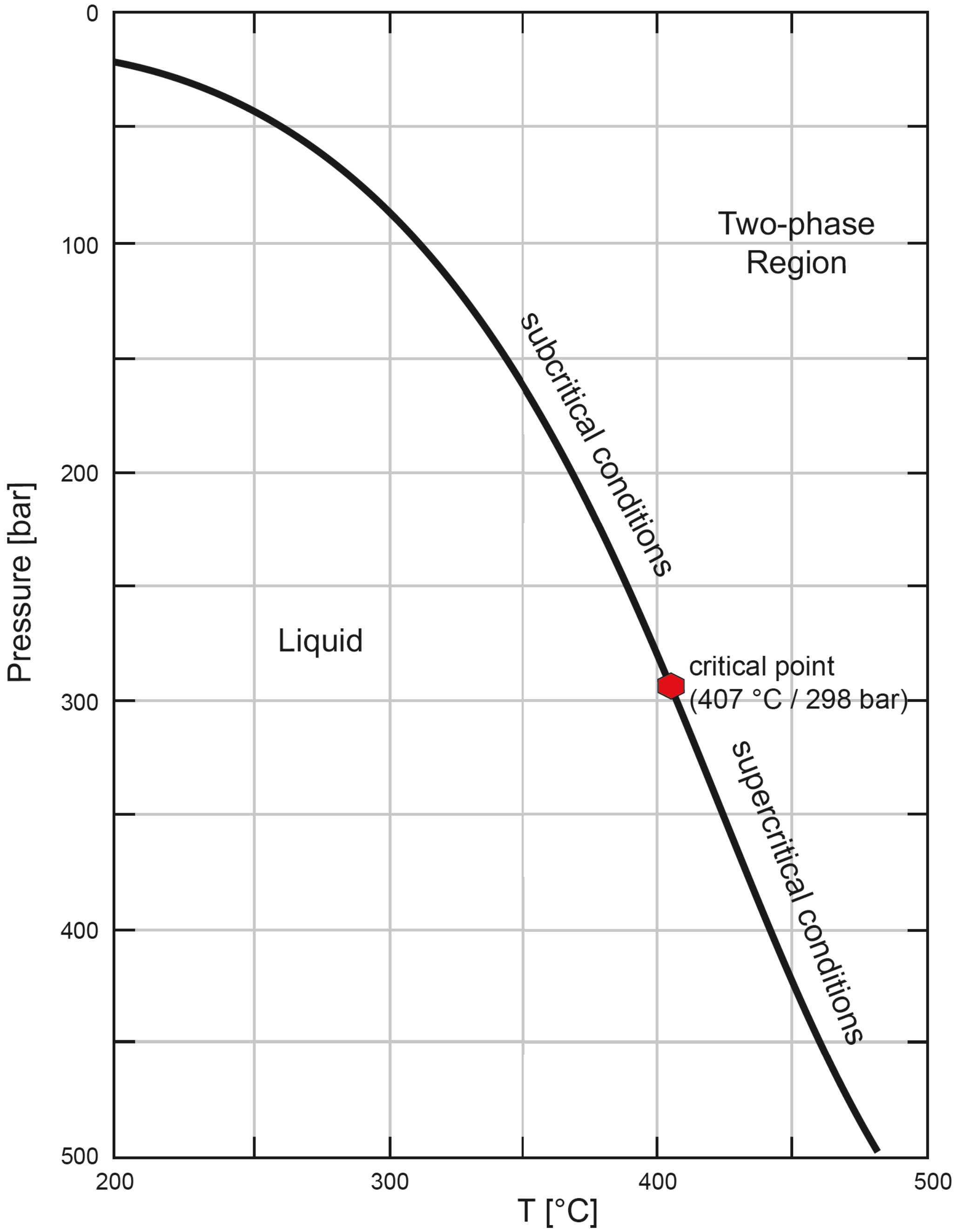


Fig. 4: Two-phase curve for seawater as a function of pressure and temperature (after Bischoff and Rosenbauer, 1984).

In the reaction zone, magmatic volatiles from the degassing of an underlying magma chamber might be supplied to the hydrothermal fluid, which is indicated by high concentrations of CO_2, CH_4, H_2, SO_2 and ^3He (Alt, 1995). In arc and back-arc settings, magmatic SO_2 was observed to disproportionate to H_2S and H_2SO_4, when it reacts with the entrained altered seawater (Giggenbach, 1992). These fluids can be as well enriched in various metals such as Cu, Zn, Fe, As and Au, that were supplied together with the magmatic volatiles (e.g. Yang and Scott, 1996; Gamo et al., 1997).

All these processes occur in a very buoyant fluid that rises rapidly through the **discharge zone** back to the surface of the oceanic crust, where the hydrothermal fluids expel. This rise can be so fast, that it is unclear to which extent chemical equilibrium with the surrounding rocks can be attained in the discharge zone. Some predictions were made by thermodynamic calculations as quartz becomes saturated; nonetheless it cannot precipitate due to the kinetics during rapid rise in contrast to sulfide phases. The various sulfide phases can be precipitated, but also re-dissolved (Reed and Palandri, 2006). Minerals such as pyrite (FeS_2), chalcopyrite ($CuFeS_2$), galena (PbS) and sphalerite ((Zn,Fe)S) can precipitate and thus create huge hydrothermal ore deposits or mounds.

After passing through the discharge zone, the hydrothermal fluid is expelled at the seafloor as focused flow through chimneys with elevated temperature or more diffuse as shimmering water through cracks and fissures. Thereby, lower temperature fluids represent a mixture between hot hydrothermal fluid and cold seawater penetrating and mixing in the shallow oceanic crust. During this mixing of hot, anoxic and more reductive hydrothermal fluid with entrained oxygenated seawater, the physical conditions change rapidly causing the precipitation of iron monosulfide particles. This can be observed in form of the characteristic black smoke discharged at some of the chimneys, but also other minerals can precipitate during this mixing and create huge chimney-like structures.

1.3.3 Hydrothermal ore deposits

Hydrothermal ore deposits form when minerals precipitate out of hydrothermal solutions due to rapid changes in physicochemical conditions such as temperature, pH, redox conditions, gas fugacity and pressure. The most important factors controlling the composition and formation of ore deposits are the chemical composition and temperature of the hydrothermal fluid itself, as well as the permeability and porosity of the oceanic crust. A wide range of different kinds of mineral deposits, mainly consisting of various types of sulfide minerals, were found at the different tectonic settings. In addition to massive mounds made of sulfide minerals from high-temperature discharge, precipitation of Fe-Mn-oxyhydroxides occurs from low-temperature fluid discharge and accumulation of fine grained particles settling from the black smoker plumes have been observed (German and Von Damm, 2003).

Hydrothermal chimneys can grow up to several cm per day and can be several tens of meters high, until they become unstable, collapse and form so called detritus or talus. Inside the orifice of the chimneys, where hottest temperatures were measured, sulfide minerals like chalcopyrite ($CuFeS_2$), pyrrhotite ($Fe_{1-x}S$; $x = 0$ to 0.2), cubanite ($CuFe_2S_3$) and bornite (Cu_5FeS_4) have been observed, surrounded by a low temperature zone with pyrite (FeS_2), sphalerite ($(Zn,Fe)S$), wurzite ($(Zn,Fe)S$) and anhydrite ($CaSO_4$). With decreasing temperatures towards the rim and top of the chimney, anhydrite, barite ($BaSO_4$) and amorphous silica (SiO_2) dominantly precipitate, in parallel to a decrease in the concentration of sulfide minerals. These chimneys are located on top of hydrothermal mounds, constructed of collapsed chimney material and different mineral precipitations, while the mineralogical composition of these mounds is also temperature-zoned. The hot inner zones ($T > 300$ °C) consists mainly of Cu-Fe-sulfides, whereas the low temperature more peripheral zones consist of Zn-Fe-sulfides in combination with barite, anhydrite and amorphous silica. A good example to get an idea about the dimension of such a complex is the TAG hydrothermal mound on the Mid-Atlantic Ridge at 26°N, which is the largest single hydrothermal mound known to date with 250 m in diameter and 35 m in height consisting of massive sulfide minerals (Rona, 2005). This mound alone contains about 3.9 million tons of sulfide-bearing material with in average 2.1 wt% copper and 0.6 wt% zinc (Petersen et al., 2000). These high concentrations reveal the economic potential of such submarine ore deposits, which will probably become of highest economic interest in the near future.

A lot of these sulfide deposits are also known to be rich in As, as shown by different minerals like orpiment (As_2S_3) or realgar (As_4S_4), which are frequently found in low-temperature hydrothermal veins. However, at temperatures between

250 and 300 °C, these two minerals are extremely soluble and the dominant As bearing mineral is arsenopyrite (FeAsS) (Pokrovski et al., 2002). The precipitation of various As-bearing minerals in combination with sulfur or metals such as manganese and iron can lower significantly the concentration of As in the sampled hydrothermal fluids before they get discharged into the seawater.

1.3.4 Hydrothermal vent biota

Since their discovery in 1977 near the Galápagos spreading center, hydrothermal vent fauna surprises and fascinates the scientific community every time a scientific dive is performed, because at these sites, the highest production rates of biomass on our planet were observed (Lutz et al., 1994). Over 500 new species have been found and described to date and it is expected that there are living much more still unknown species in the low-temperature zones, where hydrothermal fluids mix with the ambient seawater or at the outer walls of the high-temperature discharging chimneys, waiting for discovery and thorough investigations.

Compared to most ecosystems on earth, that rely on photosynthesis with light and carbon dioxide as energy source, the life of deep-sea vent communities is based on chemosynthesis. The main components and energy source for these processes are hydrogen sulfide (H_2S) and methane (CH_4), which are supplied by the hydrothermal fluids. The basic and principal reactions for the oxidation of hydrogen sulfide (Eq. 4) and methane (Eq. 5) can be described as in the following reactions:

$$CO_2 + 4H_2S + O_2 \rightarrow CH_2O + 4S^0 + 3H_2O \qquad \text{(Eq. 4)}$$

$$CH_4 + O_2 \rightarrow CO_2 + 4H^+ \qquad \text{(Eq. 5)}$$

The most important and well-investigated reaction for energy gain by hydrothermal vent biota is the oxidation of hydrogen sulfide (Eq. 4), which is the dominant form of emitted sulfur form hydrothermal fluids. The oxidation of sulfide is performed by free-living chemolithoautotrophic sulfur-oxidizing bacteria. Those are able to yield ATP (Adenosine triphosphate) and convert inorganic carbon into organic carbon for their metabolic processes where the hydrothermal fluids discharge into the cold seawater. In addition to this reaction, the reversible reaction is possible, where microorganisms reduce sulfate to hydrogen sulfide:

$$SO_4^{2-} + 2H^+ + 4H_2 \rightarrow H_2S + 4H_2O \qquad \text{(Eq. 6)}$$

Organisms, living mainly in the low-temperature discharge zones, can be either free-living as individuals in the water like shrimps or crabs, or on the surface of different substrates like at the sides of active hydrothermal chimneys. Some organisms are living in symbiotic relationships with other hydrothermal organisms. The structure of the vent community also depends on the depth and the prevailing pressure conditions. In general, systems located in deeper areas have a longer history, which can lead to a higher number of obligate species, a high rank of obligate taxa and more complicated morphological and physiological adaptions (Tarasov et al., 2005). Shallow water hydrothermal systems in contrast, which are mostly located near the shore, have a higher input of photosynthetic compounds like benthic organisms, phytoplankton and algae in comparison. This may play an important and additional role in nutrition cycle of the resident biota (Kharlamenko et al., 1995).

Most of the ecosystems in the deep-sea are comprised of bacterial mats, different species of snails and mussels, in addition to various tubeworms, crabs, fishes and shrimps. The exact composition depends on the tectonic setting, as well as on the physiochemical characteristics of the fluids. However, the upper temperature limit in which microbial live might be still possible was measured to be approximately 121 °C and was recorded for cultivated microbes from the Mothra hydrothermal field on the Juan de Fuca Ridge (Kashefi and Lovley, 2003).

Hydrothermal vent ecosystems are also often associated with theories concerning the origin of life, because they harbor rich microbial communities despite the discharge of chemically toxic, anoxic and acidic hydrothermal fluids in this hostile deep-sea environment, which was always shielded from the UV radiation by the deep-water column. Black smoker systems most likely represent primordial environmental conditions, reminding of the early earth having extreme chemical and thermal differences operating on a small scale, as well as the appearance of reactive gases and dissolved elements (Martin et al., 2008).

Especially the Lost City hydrothermal system, located on the Atlantic Massif several kilometers off-axis from the spreading zone, is extremely different compared to black smoker systems with respect to its fluid and host rock composition, and is a good example for the extreme early earth conditions. The underlying ultramafic rocks have a similar composition to lavas erupting in the early ocean made of magnesium- and iron-rich olivine with low silica content and hydrothermal fluids that are highly alkaline, 40 to 91 °C hot, enriched in H_2 and CH_4, but depleted in CO_2 (Kelley et al., 2005).

These hydrothermal vent systems represent a very special and complex but at the same time very interesting environment for studying As accumulation and transformation in marine vent biomass, because the foodweb is extremely different to organisms living in the photic zone. Despite this interesting area of research, only two studies were published dealing with As and As speciation in hydrothermal vent biota to date (Larsen et al., 1997; Taylor et al., 2012). In the first study, shrimps of the species *Rimicaris exoculata* and mussels of the species *Bathymodiolus puteoserpentis* from the TAG and Snake Pit hydrothermal site at the Mid-Atlantic Ridge were collected and investigated. Thereby, the shrimp displayed As^T concentrations of 13 mg kg^{-1}, whereof the As was mainly present as AsBet, and the mussels showed As^T concentrations of 40 mg kg^{-1}, with the major portion of As being present as As-sug and lower portions of AsBet (Larsen et al., 1997). This was somewhat surprising as algae can be hardly found in this environment and vent animals have a very special nutrition supplied by the chemoautotrophic bacteria. These bacteria are postulated by the authors to be responsible for the transformation of As into the organic species found here. The second and more recent study investigated shrimps of the species *Rimicaris exoculata*, mussels of the species *Bathymodiolus azoricus*, its commensal polychaete *Branchipolynoe seepensis*, as well as the gastropod *Peltospira smaragdina* from the TAG, Rainbow and Lucky Strike hydrothermal field on the Mid-Atlantic Ridge. The concentration of As^T in the shrimp was measured to be between 3.3 and 29.8 mg kg^{-1} with the As again almost exclusively present as AsBet, whereas *Bathymodiolus azoricus* showed concentrations up to 11.6 mg kg^{-1} with the As mostly present as As-sug. The same dominance of As-sug was also observed in *Branchipolynoe seepensis* with As^T concentrations of 18.2 mg kg^{-1}. No speciation analysis was performed for the gastropod *Peltospira smaragdina*, but showing As^T concentrations of up to 67.8 mg kg^{-1}(Taylor et al., 2012). The authors implied from the occurrence of organic As species, that there might be other pathways for the production of AsBet than the ones assumed known so far via As-sug delivered via the food-web. The source of present As-sug in the vent organisms also remains unclear, as there prevail no or only very little algae.

2 | Motivation and objectives

This study aims to contribute to a better and deeper understanding of arsenic (As) concentration, mobility and behavior in hydrothermal systems located in different tectonic settings and the influence on global ocean geochemistry. So far, only a few publications are dealing with the concentration and speciation of As in hydrothermal fluids. Even less publications are available dealing with As in hydrothermal vent biota, despite these are highly interesting and unique ecosystems. Furthermore, the preservation and conservation of the different kinds of samples showing high iron and dissolved sulfide was neglected and not considered critically at all. The main questions and objectives of my thesis are:

1) What is the concentration of As in hydrothermal fluids from different tectonic settings and what are the influencing parameters for the observed overall low and extremely high values? What is the influence of hydrothermal fluids on the global ocean geochemistry and cycling of As therein?
2) Which As species can be found in hydrothermal fluids and how can the speciation of hydrothermal fluids be preserved best with different matrixes of high iron or sulfur concentrations? Can thioarsenic species be found, preserved and measured in hydrothermal fluids from deep-water systems?
3) How much As^T can be bioaccumulated by different hydrothermal vent animals in their gill, digestive gland and muscle? How are they able to deal with this highly toxic input, and are there correlations with other elements?
4) Can speciation analysis help to understand the detoxification processes of As in the vent biota from this very special environment in a better way?
5) How can the geochemistry of hydrothermal fluids influence the amount and species of As found in the vent biota living in the adjacencies of the fluids?

To answer the different questions, the existing literature was reviewed and new samples collected and the gathered data evaluated. The different chapters of this thesis represent the different scientific papers submitted to the journals.

The first paper "Arsenic in marine hydrothermal fluids" by Breuer & Pichler (Chapter 3), which is already in press for *Chemical Geology*, gives an overview about all published data for As in marine hydrothermal fluids to date and also about the most important factors controlling the respective concentration in these fluids from the different tectonic settings like mid-ocean ridges, back-arc basins and island arcs. The overall different and highly variable As concentrations measured in hydrothermal fluids sampled at different locations makes it necessary to take a closer look at the systems, which differ greatly in their physicochemical conditions.

Chapter 4 with the submitted paper "Arsenic in fluids and biota of the Menez Gwen hydrothermal system" (*Deep-Sea Research Part 1*) represents the first field study conducted at a hydrothermal system located on a mid-ocean ridge system. During a research cruise in September and October 2010, hydrothermal vent fluids and biological samples from associated vent biota were collected at the Menez Gwen hydrothermal field on the Mid-Atlantic Ridge at 37° 51'N and afterwards investigated in the labs for As^T and As species.

The subsequent study "Arsenic in hydrothermal fluids and vent biota from the PACMANUS and SuSu Knolls hydrothermal fields, Manus Basin, Papua New Guinea" was conducted in a typical back-arc basins environment (Chapter 5). Sampling of black, white and clear discharging hydrothermal fluids as well as different vent animals like mussels and snails from the local ecosystem was performed during a research cruise with R/V Sonne in June and July 2011 and the help of the remotely operating vehicle QUEST 4000.

The third and last tectonic setting is represented by island arc systems. For this study, four hydrothermal influenced gravity cores made of altered mineralized volcaniclastic sediments and intercalated layers of sulfide precipitates were recovered in February 2012 during a research cruise on R/V Meteor in the Tyrrhenian Sea. Their hydrothermal pore fluids were investigated for As^T and the various As species including thioarsenic species at the University of Bremen and Bayreuth as presented as the last study "Thioarsenates in pore fluids from the Palinuro volcanic deep-water hydrothermal complex" in Chapter 6.

Because several scientist were participating and contributing to the different studies and papers, the following list gives my contribution:

Chapter 3: **“Arsenic in marine hydrothermal fluids”**

- literature research
- data collection and rework
- manuscript writing and editing

Chapter 4: **“Arsenic in the Menez Gwen hydrothermal system”**

- preparation for the sampling cruise
- measuring of hydrothermal fluids for As^T and As species on (HPLC-)ICP-MS
- processing of biological samples and measuring on (HPLC-)ICP-MS
- data evaluation for fluids and biota
- manuscript writing and editing

Chapter 5: **“Arsenic in the Manus back-arc basins hydrothermal system”**

- preparation for the sampling cruise
- participation in SO216 cruise, sampling and preservation of fluids and biota
- measuring of hydrothermal fluids for As^T and As species on (HPLC-)ICP-MS
- processing of biological samples and measuring on (HPLC-)ICP-MS
- data evaluation for fluids and biota
- manuscript writing

Chapter 6: **“Arsenic in pore fluids from the Palinuro hydrothermal system”**

- proposal writing for funding of the cruise for one scientist and one student
- preparation and organization of the sampling cruise
- participation in M86/4 cruise, sampling and preservation of pore-fluids
- measuring of fluid samples on ICP-MS for As^T
- data evaluation
- manuscript writing

3 | Arsenic in marine hydrothermal fluids

Christian Breuer [a,b] **& Thomas Pichler** [a,b]

[a] MARUM – Center for Marine Environmental Sciences

[b] Department of Geosciences, University of Bremen

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Abstract

Hydrothermal fluids emerging at the seafloor near mid-ocean ridges (MOR) or in back-arc basins (BAB) and island arc (IA) settings are known to contain a considerable amount of dissolved metals (e.g. Fe, Zn, Cu, Cd) due to water–rock interaction at elevated temperatures and potentially magmatic degassing. The chemical input from these fluids plays an important role for ocean chemistry and the cycling of elements. Despite its notoriety as an environmental toxin and its abundance in hydrothermal ore deposits in combination with gold, arsenic (As) is one of the few elements, which has been only rarely investigated.

Compared to the amount of As in open ocean seawater of around 1.7 µg L^{-1}, hydrothermal fluids can have significantly higher concentrations. Fluids from MOR hydrothermal systems such as the East Pacific Rise can contain up to 80.5 µg L^{-1} As and at the Mid-Atlantic Ridge the highest values were around 24 µg L^{-1}. Those values, although elevated are surpassed by As concentrations in BAB and IA hosted hydrothermal systems, which can be as high as 1386 µg L^{-1} in BAB settings and even higher with values up to 5 850 µg L^{-1} (~3900-times seawater) in IA shallow-water settings, occurring near shore hydrothermal systems.

The most important factors controlling the amount of As in hydrothermal fluids are the different – mostly physicochemical – conditions at and beneath the seafloor. These include temperature (controlling phase separation of the fluids and leaching processes in the host rock), pressure as a function of depth, pH directly influencing leaching processes, As mobility and speciation, reaction time and maturity of the system in combination with redox reactions and diverse chemical reactions like adsorption and desorption. The concentration of As in the underlying host rock may also play a role, although its mineralogical association may be more important than bulk rock concentration. Additional input of As could be caused by degassing magmatic metal-rich volatiles or sediment-fluid interaction in sediment covered hydrothermal systems. The contribution from magmatic volatiles is hard to quantify and therefore often neglected in calculations and discussions. Of the two As redox species, arsenate (As^{V}) and arsenite (As^{III}), arsenite is easier transported in the vapor phase. However, As speciation has not been traditionally part of chemical analyses. Prior to discharge at the seafloor, the concentration of As in hydrothermal fluids may decrease rapidly, if precipitation of As-bearing and As-scavenging minerals, such as pyrite, orpiment, claudetite and hydrous ferric/manganese oxides, occurs in the shallow subsurface as shown by thermodynamic calculations. This is consistent to the observation that those hydrothermal fluids high in Fe and Mn are often low in As.

Arsenic concentrations in fluids from shallow BAB/IA hydrothermal systems are higher than those in deep situated MOR hydrothermal systems most likely due to their different physicochemical conditions. Basaltic host rocks (MOR) and dacitic/andesitic host rocks (BAB/IA) have As concentrations which are more or less identical and cannot account for the huge differences in fluid As concentration.

Arsenic is one of the few trace elements whose concentration in seawater is higher than in river water, which could be caused by the flux of As from hydrothermal systems. Estimating that between 3.0×10^3 and 1.25×10^8 kg As could be discharged at the MOR annually, which is a substantial amount compared to 53.9×10^6 kg transported annually by rivers. Higher flux can be expected at BAB and IA settings, however data is sparse. A single IA system, confined to a very small area of 60 by 100 m (Tutum Bay, Papua New Guinea), discharges around 5.5×10^2 kg As annually.

Highlights:

► We present data for arsenic in marine hydrothermal fluids. ► The concentration of arsenic is related to different physicochemical parameters. ► Different host rocks can't be responsible for varying arsenic concentrations alone. ► Hydrothermal input likely exceeds the riverine input of arsenic into the ocean.

Keywords:

Arsenic; Metalloids; Hydrothermal; Fluids; Ocean; Chemistry

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 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, and 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 systems, 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 known as an environmental toxin (e.g. Ahmed et al., 2006). In gold deposits, for example, Au-As associations are common and As is known as a strictly ore-forming element, with 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 extremely 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 (e.g. 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).

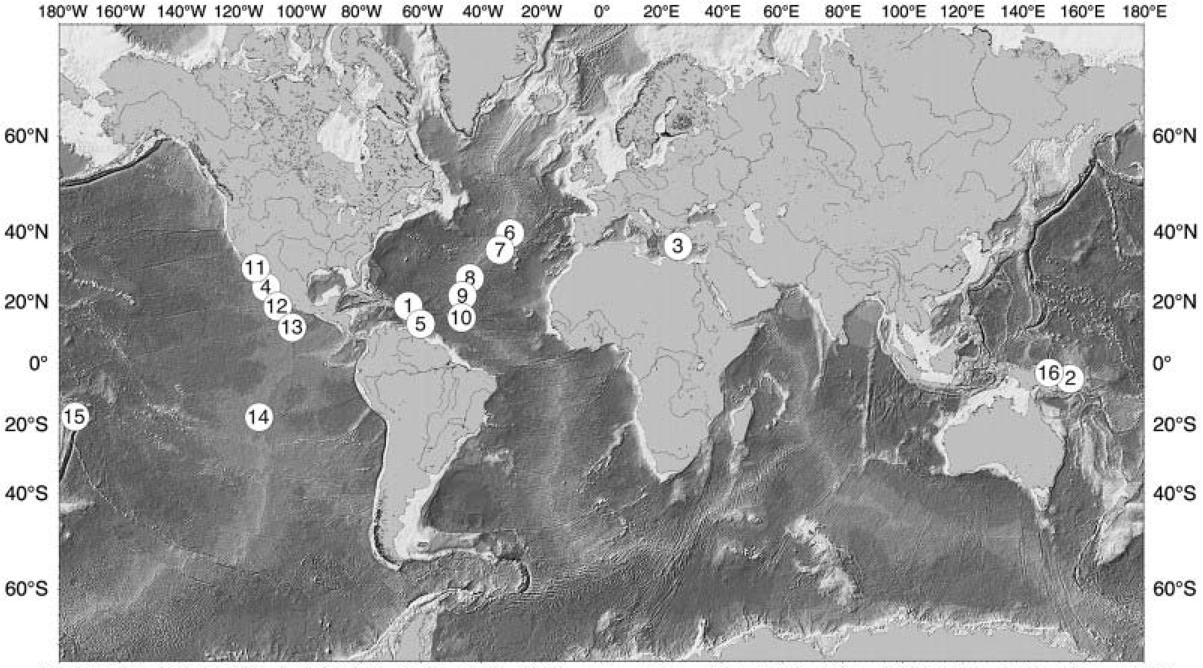

Fig. 1: Distribution of selected hydrothermal systems worldwide: 1 = Montserrat; 2 = Tutum Bay; 3 = Milos; 4 = Bahía Concepción; 5 = Champagne Hot Springs; 6 = Menez Gwen; 7 = Lucky Strike; 8 = TAG; 9 = Snakepit; 10 = Logatchev; 11 = Guaymas Basin; 12 = 21°N EPR; 13 = 13°N EPR; 14 = 17–19°S EPR; 15 =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

During water-rock interaction, the chemical composition of host rocks and water can change drastically, 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., 1999).

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, and at higher temperatures and pressures 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. 2 A-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. 3 A-C). At 100 °C and 200 °C (Fig. 3 D-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, but 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, and their existence is favored by thermodynamic studies of As sulfide solubility (Webster, 1990; Eary, 1992; Wilkin and Ford, 2006) and observations. Thioarsenates, for example, were reported for the geothermal waters of the Yellowstone National Park (Planer-Friedrich et al., 2007; Planer-Friedrich et al., 2010).

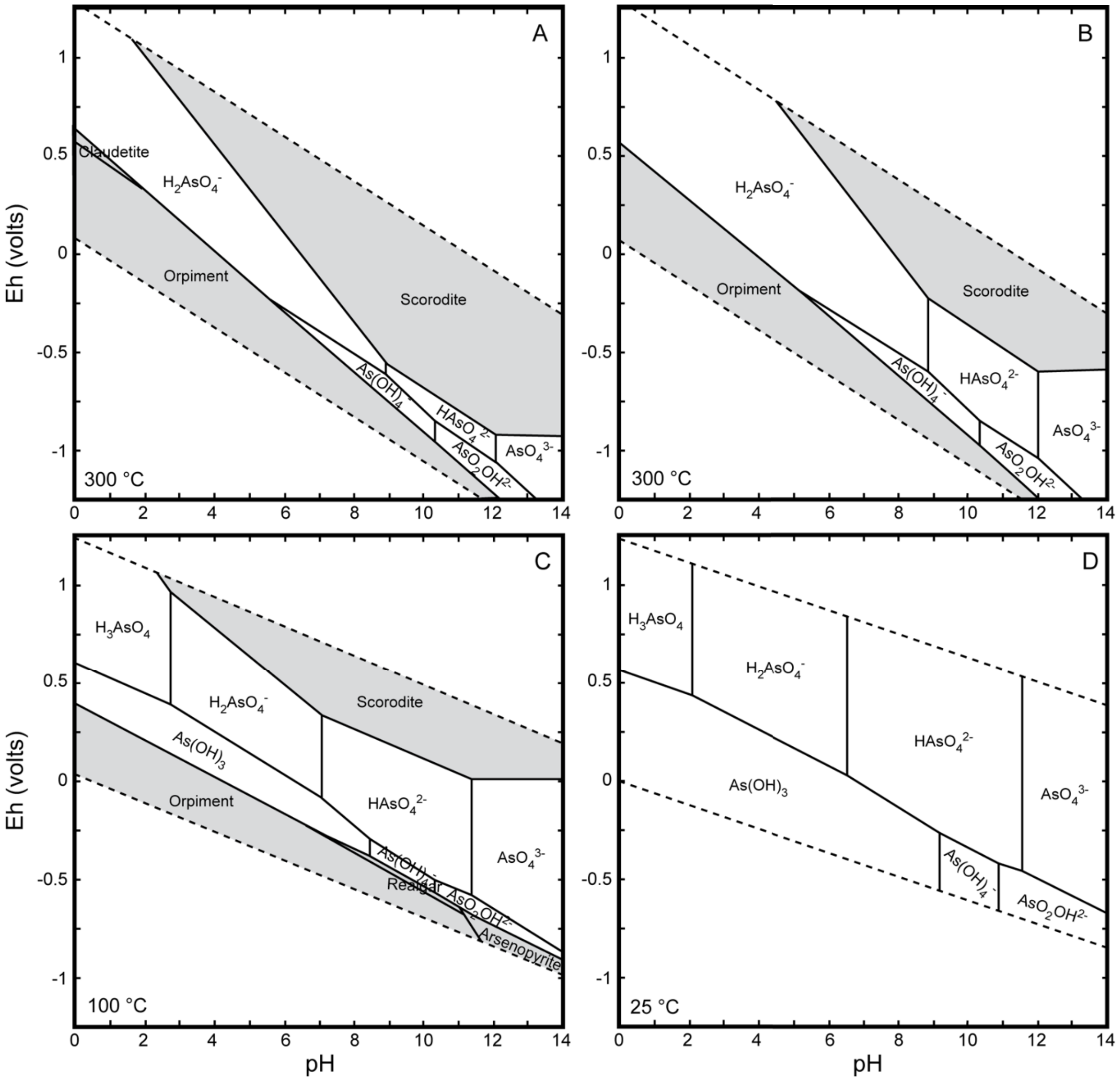

Fig. 2: Eh–pH diagrams for typical hydrothermal fluids from back-arc basins (A; Roman Ruins), mid-ocean ridges (B; Logatchev), island arcs (C; Tutum Bay) and for pure seawater at 25 °C (D). Grey shaded areas show solid phases.

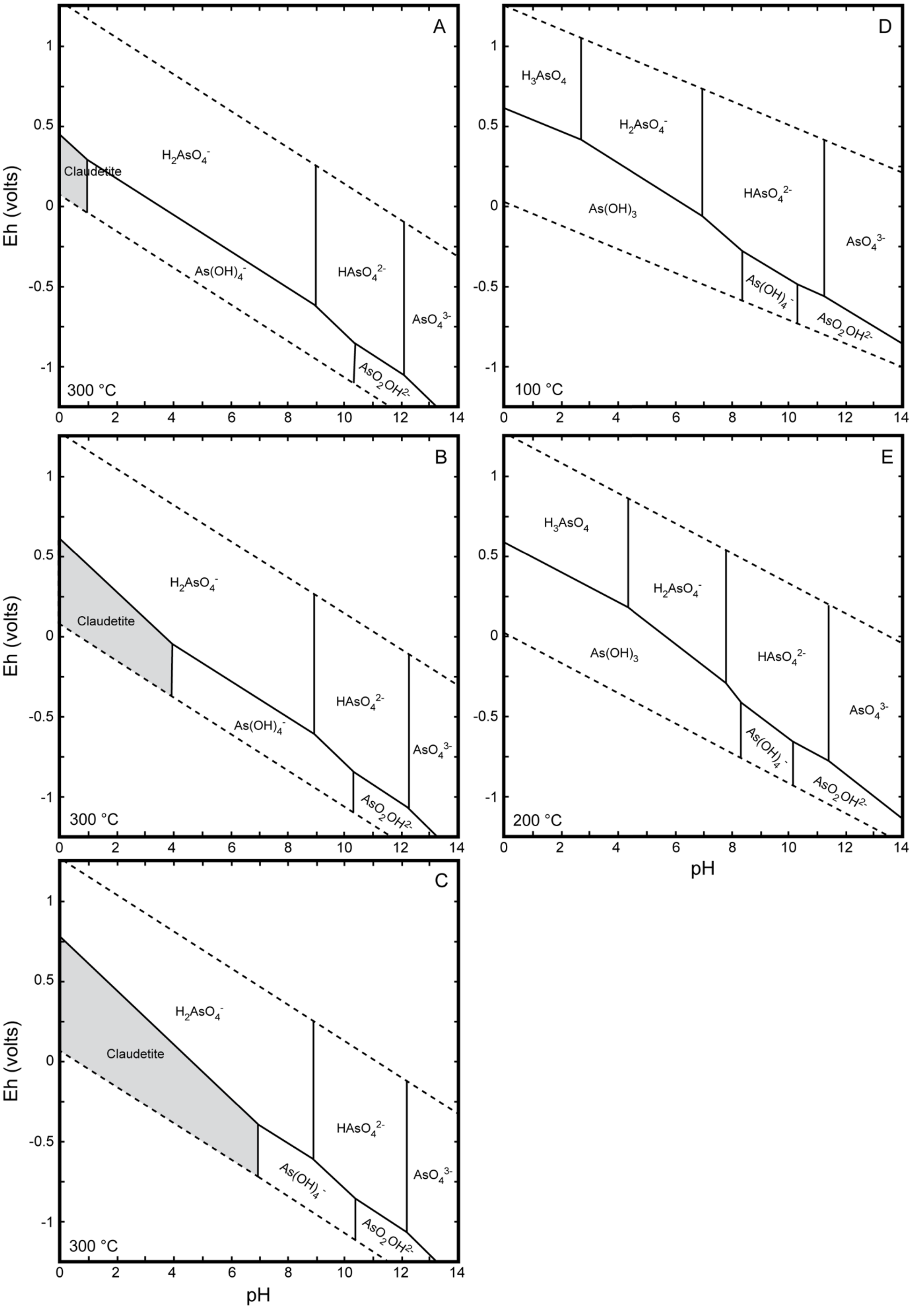

Fig. 3: Eh–pH diagrams for hydrothermal fluids from deep-water systems at different As activities at 300 °C (A–C). ΣAs is 1.0×10^{-8} (A), 1.0×10^{-5} (B), and 1.0×10^{-2} (C). Diagrams D and E were made for 100 °C and 200 °C respectively and ΣAs of 10^{-5}. Grey shaded areas show solid phases.

Tab. 1: Different species and minerals and their reactions for As speciation diagrams.

Species / mineral	Activity	Reaction	Log K$^+$
$As(OH)_4^-$	10^{-8}	$As(OH)_4^- = As(OH)_4^-$	0
$AsH_{3\,(aq)}$	10^{-8}	$AsH_{3\,(aq)} + 4H_2O = As(OH)_4^- + 6e^- + 7H^+$	9.3
AsO_4^{3-}	10^{-8}	$AsO_4^{3-} + 2e^- + 4H^+ = As(OH)_4^-$	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}	$H_2AsO_4^- + 2e^- + 2H^+ = As(OH)_4^-$	8.53
H_3AsO_4	10^{-8}	$H_3AsO_4 + 2e^- + H^+ = As(OH)_4^-$	4.15
$HAsO_4^{2-}$	10^{-8}	$HAsO_4^{2-} + 2e^- + 3H^+ = As(OH)_4^-$	16.31
arsenolite	1	arsenolite $+ 5H_2O + 4e^- + 2H^+ = 2As(OH)_4^-$	-16.86
As_2O_5	1	$As_2O_5 + 3H_2O + 4e^- + 2H^+ = 2As(OH)_4^-$	16.05
claudetite	1	Claudetite $+ 5H_2O = 2As(OH)_4^- + 2H^+$	-17.26

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 behaves strongly chalcophile and therefore, the most important As minerals in the mafic rocks from 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 Tab. 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).

Tab. 2: Concentration of As in different marine rocks and sediments.

Rock Type	**Location**	**Ø As** [mg kg^{-1}]	**As** $_{\text{range}}$ [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	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	

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 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 may still take 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 the 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 (e.g. Francesconi and Kuehnelt, 2004; Planer-Friedrich et al., 2007; Planer-Friedrich et al., 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, such as 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 3 600 µg L^{-1} (Tab. 3), approximately 2 400-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).

3.1.2 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 1 050 µg L^{-1}, which was up to 275-times local seawater enrichment (Tab. 3). Arsenic occurred more or less exclusively as the trivalent arsenite species (As^{III}; Pichler et al., 1999a; Price and Pichler, 2005). The host rock of the Tutum Bay hydrothermal system is made of andesite, dacite and basalt, covered with sandy to pebbly unconsolidated sediments. The sediments 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; Pichler et al., 1999b; Price and Pichler, 2005). Arsenic concentrations in HFO were in excess of 50 000 mg kg^{-1}.

3.1.3 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., 2005), where As concentrations were as high as 2 900 µg L^{-1}. In the neighbouring Spathi Bay, As concentrations were even higher, with values up to 5 850 µg L^{-1} (Tab. 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}, As^{V} and also mono-, di-, and trithioarsenates (Price et al., 2013). 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., 2005). 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).

3.1.3 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 (e.g. 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 2 000 µg L^{-1} (Tab. 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, with low Cl values leading 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)

Tab. 3: As endmember concentration and further characteristics for various shallow- and deep-water hydrothermal systems.

Location	**Type**	**As** [µg L^{-1}]	**pH**	**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, PNG	IA	749 – 1049	6.0	98	Alkaline volcano, andesirte, dacite	5 – 10	Pichler et al., 1999
		950		115	Sediment covered	5 – 20	Price and Pichler, 2005
Milos, Greece	IA	5850	5.0		Andesites and greenschist metamorphic rocks		Price et al., 2013
Bahía Concepción	IA	2016	5.9	87	Dacitic ti andesitic volcanic rocks, covered by sediments	15	Prol-Ledesma et al., 2004
Champaign Hot Springs	IA	104	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., 1999
Lucky Strike	MAR	14.9	3.8	324	E-MORB	1600 – 1740	Douville et al., 1999
TAG	MAR	< 0.8	3.1	366	MORB	3436 – 3670	Douville et al., 1999
Snakepit	MAR	3.2 – 14.2	3.7	350	MORB	3450 – 3500	Douville et al., 1999
Logatchev	MAR	2.8 – 4.7	3.3	350	MORB, serpentinite, gabbro, ultramafic	2925 – 3050	Douville et al., 1999
Guaymas area	EPR	50.5	5.1	315	MORB, sediment hosted	2000	von Damm et al., 1985
21 °N	EPR	2.6 – 33.9	3.3	405	MORB	2600	von Damm et al., 1985
13 °N		< 0.8 – 1.4	3.8	317	MORB	2600 – 2630	Douville et al., 1999
13 °N 17 – 19 °N	EPR	< 0.8 – 41.0	3.1	300	MORB	2600 – 2700	Douville et al., 1999
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, rhyolite	1707 – 1764	Douville et al., 1999
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., 1999
Satanic Mills, Manus Basin	BAB	1206 – 1386	2.3	358	BABB, MORB, med-K andesite, dacite	1650 – 1800	Douville et al., 1999
Desmos, Manus Basin	BAB	10.2	2.1	120	BABB, MORB, med-K andesite	2000	Douville et al., 1999

Note: IA = Island Arc; MAR = Mid Atlantic Ridge; EPR = East Pacific Rise; BAB = Back Arc Basins; n.a. = not available

3.1.4 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} (Tab. 3). The dominant species found in these fluids was As^{III} in addition to minor As^{V}. 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 1 880 mg kg^{-1} (McCarthy et al., 2005).

3.2 Deep-water hydrothermal systems

3.2.1 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 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} (Tab. 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} (Tab. 3). A reversed correlation with Fe and high As/Fe ratios and 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 et al., 1975; Rona, 1980), with the most impressive feature, an active mound, discovered in 1985 (Rona et al., 1986). Black smoker fluids with temperatures around 366 °C and white smoker fluids 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 smoker fluids 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., 1999). 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 3 000 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., 1999), 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).

3.2.2 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 2 000 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} (Tab. 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 2 600 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, as well as different alteration minerals (Haymon and Kastner, 1981). Concentrations of As in these fluids varied between 2.3 (LOD) and 33.9 µg L^{-1} (Tab. 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 2 600 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 of 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., 1999). 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., 1999). 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).

3.2.3 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 1 700 and 2 000 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} (Tab. 3), which is up to 550-times seawater. Similar concentrations between 480 and 630 µg L^{-1} (Tab. 3) were measured in samples from the high temperature Vai Lili hydrothermal field at the central Valu Fa Ridge (Douville et al., 1999). Phase separation is unlikely, because the hydrothermal fluids had Cl 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 1 650 to 2 500 m depth in the rapidly opening Manus Basin (Tregoning, 2002). At the New Britain Trench, 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 2 500 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., 1999). 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 1 200 and 1 390 µg L^{-1} (Tab. 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 also showing higher concentrations of Cl and Fe. The nearby located Desmos caldera is characterized by venting of hot and highly acidic (pH ≤ 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} (Tab. 3) much lower than at Satanic Mills. In general, the hydrothermal fluids were rich in Mg and poor in Fe and the host rock 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 5 850 µg L^{-1} (Tab. 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 5 850 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, and 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, and 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., 1999). 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 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 value of 80.5 $\mu g\ L^{-1}$ measured in fluids from the sediment hosted Guaymas basin on the EPR (Von Damm et al., 1985). 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 (Fig. 2 and Fig. 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 showed 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) showed 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., 1999).

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 µg 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 total As concentration 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 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 µg L^{-1} (Gaillardet et al., 2003), As is enriched in the global ocean with an average value of 1.7 µg 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 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 less data is available there. 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 potentially toxic 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 5 850 µg L^{-1}), followed by fluids from deep-water hydrothermal systems in back-arc basins (BAB; up to 1 386 µg L^{-1}) and mid-oceanic ridges (MOR), whose As concentration is comparably much lower (up to 80.5 µg 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 as observed in fluids from shallow-water hydrothermal systems.

III) The only slightly higher bulk rock concentration of As in 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 should 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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4 | Arsenic in fluids and biota of the Menez Gwen hydrothermal system

Christian Breuer [a,b], Maria José Ruiz-Chancho [b],
Eoghan Reeves [a,b], Andrea Koschinsky [c],
Thomas Pichler [a,b]

[a] MARUM – Center for Marine Environmental Sciences
[b] Department of Geosciences, University of Bremen
[c] Jacobs University Bremen

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Abstract

Hydrothermal vent fluids emanating at the seafloor can contain considerable amounts of the element arsenic (As), which may be incorporated into vent macrofauna. Here we present combined results for total As (As^T) and As speciation for both, vent fluids and biota from the Menez Gwen hydrothermal system located on the Mid-Atlantic Ridge. Concentrations of As in emanating hot spring fluids range between 6 and 90 µg L^{-1} and contain the inorganic arsenite (As^{III}) and arsenate (As^V) species in varying proportions. Mussels of the species *Bathymodiolus azoricus*, which are dominant in this hydrothermal ecosystem, were analyzed to study the effect of As concentration and speciation on bioaccumulation and biotransformation. Concentrations of As in *Bathymodiolus azoricus* were highest in the digestive gland (19.0 mg kg^{-1}), followed by gill (14.9 mg kg^{-1}) and muscle (6.4 mg kg^{-1}) tissue. Higher amounts of As in the digestive gland may be due to the fact that this organ stores As and other elements, which accumulate by filtration of Fe-oxyhydroxide particles, and in the gill may be due to the activity of chemosynthetic sulfur- or methane-oxidizing symbionts. In methanol/water extractions of the tissues, elevated amounts of arsenosugars (As-sug) were observed accompanying unusually low amounts of arsenobetaine (AsBet) relative to marine animals from photic zones. The inorganic As-species As^{III} and As^V were also detected in considerable proportions in the tissues. In general, marine algae have high concentrations of As-sug, whereas marine animals accumulate preferentially AsBet, with As-sug from algae possibly serving as precursors. The unusual high proportion of As-sug in *Bathymodiolus azoricus* from the Menez Gwen hydrothermal system could therefore be due to the presence of symbionts, or alternatively the exposure to elevated As input from hydrothermal fluids and overstressed detoxification processes.

Highlights:

► We present novel and combined data for arsenic and arsenic species in hydrothermal fluids and vent biota. ► Hydrothermal vent mussels are able to accumulate and transform arsenic from hydrothermal fluids. ► Concentration of arsenic in the hydrothermal fluids sampled at Menez Gwen is up to 90 µg L^{-1}. ► *Bathymodiolus azoricus* accumulates arsenic in the digestive gland (19.0 mg kg^{-1}), gill (14.9 mg kg^{-1}), and muscle tissue (6.4 mg kg^{-1}).

Keywords:

Arsenic; Hydrothermal; Vent biota; Metalloids; Fluids; Ocean; Chemistry

1. Introduction

Seafloor hydrothermal venting represents a fundamental process controlling the transfer of energy and mass into the oceans, and discharging fluids and associated biota have been extensively studied for their chemical composition, geologic setting and biological processes (e.g. Von Damm, 2001; German and Von Damm, 2003). Hydrothermal systems are typically driven by an underlying heat source (e.g. magma chamber), which progressively heats downward percolating cold seawater, before it rises upwards again due to the excess buoyancy (Alt, 1995). These systems can be located in diverse tectonic settings such as mid-ocean ridge axial zones, back-arc basins and submarine neovolcanic edifices, influencing the style and characteristics of venting. The potentially toxic element arsenic (As) was only rarely investigated during chemical analysis of hydrothermal fluids, what is surprising as it is known as an environmental toxin, strongly influences the biological environment and plays an important role in hydrothermal ore formation.

1.1 Arsenic in the marine aquatic system

The average concentration of arsenic (As) in the global ocean is estimated to be around 1.7 µg L^{-1} (Neff, 2002), with the main factors influencing its abundance being riverine input, weathering and sedimentation on the seafloor, as well as atmosphere-seawater exchanges and input of volcanic sources (Matschullat, 2000). Hydrothermal fluids represent an additional source of As in the oceans in which concentrations can be greatly enriched, depending on different physicochemical parameters like temperature, pH, pressure, redox reactions, Fe and H_2S content and the composition and mineralogy of the host rock (Breuer and Pichler, 2012)

Arsenic in aqueous systems is mostly present as inorganic arsenite (As^{III}) and arsenate (As^{V}), but also exists to a lesser extent as methylated forms like methylarsonic acid (MA) and dimethylarsinic acid (DMA) (Mandal and Suzuki, 2002; Neff, 2002).

1.2 Arsenic in marine organisms

Marine organisms like algae, seagrass, plankton, bivalves, fish and gastropods accumulate and transform As, with typically concentrations between 1 and 200 mg kg^{-1} dry weight. Accumulation and speciation depends mostly on the position in the food chain of the respective organism and on the amount of As available in the surrounding environment. Several studies were conducted regarding As accumulation in marine bivalves from coastal non-polluted areas with average values ranging between 4.2 and 7.8 mg kg^{-1} (e.g. Leatherland and Burton, 1974; Zingde et al., 1976; Lai et al., 1999), whereas bivalves from polluted areas are able to accumulate As in higher concentrations of up to 214 mg kg^{-1} (e.g. Neff, 1997; Valette-Silver et al., 1999; Whaley-Martin et al., 2012). The most abundant As compounds found in bivalves are As-containing ribofuranosides, commonly named arsenosugars (As-sug) and arsenobetaine (AsBet) (Shibata and Morita, 1992), with the latter form being the dominant organic As species in higher marine animals.

Our understanding of As variability and speciation in hydrothermal vent fauna is limited, however, with only a few studies in existence. Larsen et al. (1997) investigated As in shrimps and mussels from the TAG and Snakepit hydrothermal systems located on the Mid-Atlantic ridge. Shrimps contained around 13 mg As kg^{-1} and soft tissues of the mussels around 40 mg As kg^{-1}, with AsBet as the dominant species in the shrimps and As-sug dominating in the mussels (Larsen et al., 1997). A recent study also determined As concentration and speciation in shrimps (*Rimicaris exoculata*), mussels (*Bathymodiolus azoricus*, *Branchipolynoe seepensis*) and a gastropod species (*Peltospira smaragdina*) from the Rainbow, TAG and Lucky Strike hydrothermal fields (Taylor et al., 2012). Shrimp showed As concentrations between 3.3 and 29.8 mg kg^{-1}, mussels between 9.9 and 18.2 mg kg^{-1} and gastropods between 14.0 and 67.8 mg kg^{-1}. Arsenic was primarily present as AsBet in the shrimps and as As-sug in the mussels and gastropod. Stable isotope analysis ($\delta^{13}C$ and $\delta^{15}N$) showed that food sources originated at the vents, and Taylor et al. (2012) hypothesized that organic As compounds can also be generated in the absence of photosynthetic organisms. Another study from a shallow-water hydrothermal system near Milos (Greece) evaluated gastropods (*C. neritea*), which contained As in concentration ranging between 15 and 24 mg kg^{-1}. The dominant species were inorganic As species with low proportions of AsBet (Ruiz-Chancho et al., 2012).

However, these studies give As concentrations for the whole animal, without considering the different organs like gill, muscle and digestive gland, having entire different functions. Accordingly, they should accumulate different amount of As from the fluids and also process these in a different way.

Primary producers like marine algae accumulate As directly from the seawater – where it exists mainly as inorganic As – and transform it into organoarsenic compounds, mainly As-sug. Marine animals can take up As from both the surrounding seawater and through the food chain (Edmonds and Francesconi, 2003). The biosynthetic pathways of organically-bound As in marine organisms are described in several studies, but are still not completely understood. The first step, the incorporation of inorganic As into microorganisms like phytoplankton, occurs because of the chemical and structural similarity of As^{V} to phosphate (PO_4^{3-}) (Hellweger and Lall, 2004). The As^{V} is then reduced to As^{III}, which is more mobile in the cells, but at the same time also more toxic. Then, the inorganic As^{III} is further transformed to methylated As (MA and DMA) and/or higher organosarsenic compounds like As-sug (Francesconi and Edmonds, 1996). These processes are mostly followed by the excretion of the methylated or organic forms, which seems to be the main detoxification process. It is thought that As-sug produced from algae – if accumulated by higher organisms – are precursors of AsBet and Arsenocholine (AsC) (Hansen et al., 2003). AsBet is a less-toxic form of As that is also rapidly eliminated. The finding of a possible intermediate, referred to dimethylarsinoylethanol, supports this hypothesis (Edmonds and Francesconi, 2003). Moreover, other pathways for the formation of AsBet have been proposed (Edmonds and Francesconi, 2003), which do not involve As-sug. However, in the hydrothermal systems environment, located in the deep sea, photosynthetic algae are not or only sparsely available, so that As-sug produced by these do not play a key role in the biosynthesis of arsenobetaine in these systems.

2. The Menez Gwen hydrothermal system (37°50’N, MAR)

On the Mid-Atlantic ridge near the Azores, the Menez Gwen hydrothermal system is located in 840 to 865 m depth on a 700 m high and 17 km wide circular volcano, with a 6 km long and 2 km wide axial graben at its top, cutting the edifice in two symmetrical parts (Fouquet et al., 1995; Parson et al., 2000; Fig. 1). The hydrothermal system is influenced by the Azores plume and the underlying host rocks are of enriched-MORB type. Previously reported fluids emanating at Menez Gwen were devoid of ‘black smoke’ precipitates, and rich in methane and reduced sulfide (Charlou et al., 2000). Temperatures up to 285 °C (close to boiling) and varying Cl concentrations measured in the hydrothermal fluids suggest phase separation.

The mussel *Bathymodiolus* is common in hydrothermal systems worldwide forming extensive communities on the base and walls of hydrothermal vents. They preferentially live in the mixing zone between the high temperature anoxic and metal-rich hydrothermal fluid and the cold oxic seawater. The dominant fauna at Menez Gwen is represented by *Bathymodiolus azoricus* (Bivalvia: Mytilidae), a bivalve living in dual endosymbiosis with methane- and sulfide oxidizing bacteria (MOX and SOX), which are located in specialized epithelial cells and within the gill epithelial tissue where they produce nutrients (Fiala-Médioni et al., 2002; Duperron et al., 2006). The energy obtained by microbial oxidation of sulfur and methane species plays an important role in the nutrition of *Bathymodiolus azoricus*. The gained energy is further used by the bacteria for the fixation of organic carbon via the Calvin Benson cycle (Felbeck et al., 1981), which is in turn utilized by the host animal. It was suggested, that these symbiotic bacteria play a protective role concerning toxic metals and oxidative stress (Kádár, 2007). *Bathymodiolus azoricus* may also partly feed on particulate and dissolved organic matter sinking through the water column from the surface (Riou et al., 2010b).

3. Materials and methods

3.1 Reagents, standards and Certified Reference Materials (CRM)

All solutions were prepared with double deionized water from a MilliQ Advantage A10 water purification system (18 MΩ cm^{-1}). Hydrochloric acid (HCl) and nitric acid (HNO_3) were purified by sub-boiling distillation. Methanol of HPLC grade, and suprapure hydrogen peroxide (H_2O_2), were supplied by Merck.

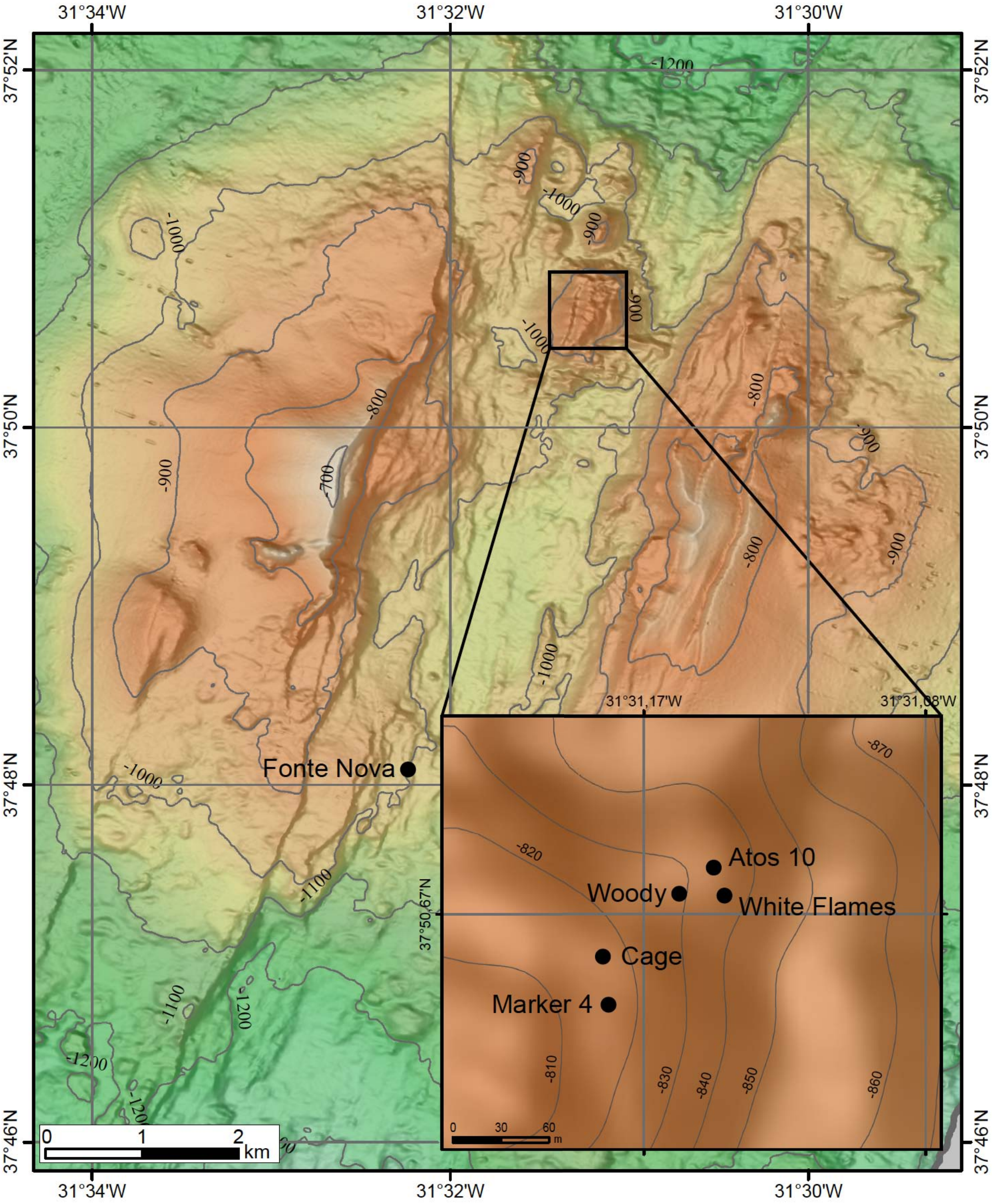

Fig. 1: The Menez Gwen hydrothermal system with the circular volcano and the new volcano at the northern end of the graben (black box). Black dots indicate the different sampling sites.

Arsenite (As^{III}) and arsenate (As^{V}) standard stock solutions were prepared from As_2O_3 (Sigma Aldrich) dissolved in 4 g L^{-1} NaOH (Merck) and from $Na_2HASO_4 \bullet 7H_2O$ (Sigma Aldrich) dissolved in water. Methylarsonate (MA) and dimethylarsinate (DMA) were prepared from $(CH_3)_2AsO(ONa)_2 \bullet 6H_2O$ (Chemservice) and from $(CH_3)AsO(ONa)_2 \bullet 6H_2O$ (Merck) respectively, both dissolved in water. Arsenobetaine (AsBet) and arsenocholine (AC) were purchased at Sigma Aldrich and Argus Chemicals, respectively, and dissolved in water. Standards for the total arsenic (As^{T}) measurements were prepared from a CertiPur® multi-element standard solution (XVI, 100 mg L^{-1}, Merck). All stock solutions were stored at 4 °C and further diluted standards for analysis were prepared daily.

Two certified reference materials were used for organic As quality control: a dogfish muscle, certified for trace elements (NRCC-DORM-2), with a certified concentration of As^{T} (18.0 ± 0.1 mg kg^{-1}), AsBet (16.4 ± 1.1 mg kg^{-1}), and Tetramethylarsonin (0.248 ± 0.054 mg kg^{-1}), as well as a tuna tissue (BCR-627) from the IRMM (Institute for Reference Materials and Measurements) with a certified As^{T} concentration of 4.8 ± 0.3 mg kg^{-1}. This material was also certified for AsBet (3.9 ± 0.2 mg kg^{-1}) and DMA (0.15 ± 0.02 mg kg^{-1}).

For the identification of arsenosugars (phosphate (PO_4-sug), sulfate (SO_4-sug), sulfonate (SO_3-sug) and glycerol (Gly-sug) sugars) an aliquot of a freeze dried extract of *Fucus serratus* containing the four sugars was used, which was kindly supplied by Prof. Dr. K. A. Francesconi from the Karl-Franzens University in Graz, Austria (Madsen et al., 2000).

3.2 Instruments

For digestion of the mussel tissues, a temperature controlled Milestone Ethos microwave digestion system was used with a power of 1000 W. Concentrations of As^{T} in the fluids and biota samples were determined by high resolution inductive coupled plasma mass spectrometry (ICP-(HR)MS) using a Thermo Scientific ELEMENT 2 instrument equipped with a microflow nebulizer. Speciation analyses were performed by coupling the ELEMENT 2 to a Thermo Scientific Accela 600 HPLC system system and using a “conical” nebulizer for sample introduction into the plasma. A Hamilton PRP-X100 column (250 x 4.1 mm, 10 µm; anion exchange) and a Zorbax 300-SCX column (250 x 4.1 mm, 5 µm; cation exchange), both protected by guard columns, were used for anion and cation exchange chromatography, respectively, whereas the chromatographic conditions are listed in Table 1. The ion intensity for m/z 75 ($^{75}As^+$) was monitored at both, low (LR) and high resolution (HR) to identify possible argon-chloride-interferences ($^{40}As^{35}Cl^+$).

3.3 Sampling and sample preparation

3.3.1 Sampling

Fluid samples and mussels were collected during *R/V Meteor* expedition M82/3 in September 2010 using the remotely operating vehicle (ROV) QUEST 4000 m (MARUM). For fluids, both isobaric-gas tight samplers (IGT) (Seewald et al., 2002) and the Kiel-Pumping-System (KIPS) (Garbe-Schönberg et al., 2006) were used, with a temperature probe attached to the respective fluid inlets for in situ temperature measurements. In total, 19 fluid samples were collected for chemical analyses. In addition, 8 mussels were collected from the hydrothermal area with nets manipulated by the mechanical arm of the ROV and stored in a sealed box during ascent to the surface. Fluid parameters measured onboard upon sampler recovery were pH (25 °C), Eh and sulfide by photometry.

Tab. 1: Chromatographic conditions for the coupled system HPLC-ICP-(HR)MS used in the present study.

	Anion Exchange	**Cation Exchange**
Column	Hamilton PRP-X100 250 x 4.1 mm, 10 µm	Zorbax 300-SCX 250 x 4.6 mm, 5 µm
Mobile phase	20 mM $NH_4H_2PO_4$ pH: 5.8 (adj. with NH_4 aq)	20 mM pyridine pH: 2.6 (adj. with HCOOH)
Flow rate	1.5 ml min^{-1}	1.5 ml min^{-1}
Injection volume	20 µl	20 µl
Arsenic species analyzed	As^{III}, As^{V}, MA, DMA, PO_4-sug, SO_3-sug, SO_4-sug	AsBet, AC, TETRA, TMAP, Gly-sug

3.3.2 Sample preparation and treatment

Fluid samples were filtered through a 0.22 µm unreactive cellulose acetate membrane filter. One sample aliquot was acidified with purified HCl for determination of As^T concentrations, while the remaining aliquot was stored cryofrozen at -80 °C for speciation analysis. Mussel samples were also stored cryofrozen during transport to the University of Bremen.

In the laboratory, frozen mussels were thawed under an Ar-atmosphere, then opened, cleaned with MilliQ water and dissected into gill, muscle and digestive gland. Gill, muscle and digestive gland samples were freeze-dryed and homogenized with mortar and pestle and afterwards stored at room temperature before analysis.

3.4 Analytical Procedures

3.4.1 Fluid major elements

Fluid samples were analyzed for the major elements Mg, Cl, Fe and Mn using either Inductively-Coupled-Plasma-Optic-Emission-Spectrometry (for Mg, Fe, Mn; ICP-OES) or ion chromatography (for Cl; IC). A seawater salinity reference material IAPSO K15 was used as a standard, in addition to a Certified-Reference-Material seawater standard (CRM-SW, High Purity Standards^{TM}) certified for major element composition.

3.4.2 Total Arsenic analysis

To determine As^T concentrations, a Thermo Scientific ELEMENT 2 was used in HR mode using ^{115}In as internal standard. Samples were quantified in triplicate with an external calibration. Procedure blanks and CRMs were analyzed in the same sequence.

For the digestions of the mussels, 0.2 g aliquots from the gill, muscle and digestive gland and also from the CRMs (DORM-2 and CRM627) were weighed into the digestion vessels and 5 ml of concentrated nitric acid (HNO_3) and 2 ml of hydrogen peroxide (H_2O_2) were added. Digestion of the samples was performed according to the following program: suspensions were heated for 2 min up to 80 °C, held there 1 min before heated further to 110 °C for 2 min. After that for 3 min from 110 to 140 °C, 4 min from 140 to 180 °C, 6 min from 180 to 190 °C and lastly maintained for 12 min at 190 °C. After cooling down to room temperature, samples were transferred into Falcon tubes and diluted up to 50 ml with double deionized water. Analyses of CRMs showed good agreement between the obtained and certified value.

3.4.3 Arsenic speciation analysis

For extraction of the different As species from the mussels, 50 mg from each freeze-dried and homogenized sample and also from the CRMs were weighed by triplicate in 20 ml PTFE (polytetrafluoethylene) vials and 5 ml of a MeOH/water mixture (1:1, v/v, purged with N_2) was added. Samples were extracted for 16 h at room temperature in an end-over-end shaker running at 20 rpm. Afterwards, mixtures were centrifuged at 4500 rpm for 10 min and the supernatants filtered through a 0.22 µm unreactive nylon filter before determination of As species by HPLC-ICP-(HR)MS within the next 24 hours after extraction by using 2 chromatographic separations (Tab. 1). Identification of the species was performed by comparison of the retention times with standards. External calibration curves were used to quantify As^{III}, As^{V}, MA, DMA and AsBet. Different As-sugars were identified by comparison of retention times with the As-sugars present in the *Fucus serratus* extract. They were quantified with the calibration curve of the closest As species in the chromatogram. Identification of TMAP and TETRA was made by comparing with the retention times in DORM-2. The presence of thio-arsenic species was investigated by addition of H_2O_2.

4. Results

4.1 Fluids

Fluid samples showed maximum temperatures of up to 297 °C and an acidic pH (25 °C) between 4.0 and 5.1. Chlorinity varied between 8 180 and 19 730 mg L^{-1} and magnesium concentrations between 72 and 1 240 mg L^{-1} (Tab. 2). All samples were extremely low in iron (< 9 mg kg^{-1}) and manganese (< 5 mg kg^{-1}) relative to most hydrothermal fluids (e.g. German and Von Damm, 2003), and no visible residual precipitates, also called the “dreg” fraction (Trefry et al., 1994), could be observed or recovered from either the fluid samplers or stored aliquots. Reported As^{T} concentrations and As species therefore reflect dissolved fractions only. Measured

As^T concentrations range from 6.1 to 89.1 µg L^{-1} (Tab. 2), the latter being up to 50-times the mean seawater concentration of 1.7 µg L^{-1} (Neff, 2002). While As is elevated in all hydrothermal fluid samples, concentrations do not trend consistently with Mg in a similar manner to Fe and Mn. This indicates non-conservative As behavior during sampling even without visible residual precipitate formation, and we therefore cannot discount loss of As to unrecoverable precipitates or uncharacterized colloids. Hence, we do not attempt to calculate end-member As concentrations here. During speciation, only the two inorganic species arsenite (As^{III}) and arsenate (As^V) were detected, with generally As^V more abundant than As^{III}, also the recovery with respect to As^T was partly rather bad, getting lower with higher temperature (Tab. 3).

4.2 Biota

Hydrothermal vent biota living near the warm hydrothermal fluids accumulated different portions of As in the different organs. The As^T concentration was highest in the digestive gland (19.0 mg kg^{-1}), followed by the gill (14.9 mg kg^{-1}) and muscle (6.4 mg kg^{-1}) tissues of the mussels *Bathymodiolus azoricus* (Tab. 4). In addition to these, also elevated concentrations of Sb, Cd, Mn and Fe could be observed, showing the same trend (Tab. 4).

Based on considerations of speciation analysis, extraction efficiencies for As in tissues (calculated as the ratio of the total concentration after digestion and total concentrations in the methanol-water extract) were between 43.2 and 65.7 %. Column recoveries calculated as the ratio between the sum of the different species and As^T in the extract, were between 65.1 and 76.8 % (Tab. 4). Six different species were detected in variable proportions: the inorganic species As^{III} and As^V, two As-sugars (PO_4-sug and Gly-sug), arsenobetaine (AsBet) and traces of DMA (Tab. 5). The fractions of the inorganic arsenic species ranged between 32.3 and 51.2 %, followed by As-sugars (28.2 to 55.0 %) and AsBet (8.0 to 23.0 %). One unknown species (UNK) was also detected at a retention time of 5.25 min during cation exchange chromatography.

Tab. 2: Characteristics of the different fluids emanating at Menez Gwen and sampled in 2010.

Location	pH	T_{max} [°C]	Type	As [µg L^{-1}]	Mg [mg L^{-1}]	Cl [mg L^{-1}]	Fe [mg L^{-1}]	Mn [mg L^{-1}]
White Flames	5.0	295	IGT	89.1	545	16026	1.15	3.38
37° 50’ 40.286’’ N	4.3	297	IGT	41.7	80	13627	2.29	5.63
31° 31’ 08.630’’ W	4.7	281	KIPS	24.7	296	13889	6.92	4.09
Woody	5.0	58	IGT	39.5	1243	19405	1.72	< DL
37° 50’ 40.214’’ N	4.7	91	IGT	8.7	1226	18897	1.15	< DL
31° 31’ 08.939’’W	4.7	61	IGT	6.5	1216	19732	< DL	< DL
Cage	4.1	294	IGT	31.7	87	8176	1.72	2.82
37° 50’ 39.372’’ N	5.1	260	KIPS	10.2	735	13940	3.34	1.01
31° 31’ 08.690’’ W	5.3	126	IGT	6.3	1298	19732	9.57	< DL
Atos 10	4.0	293	IGT	30.9	72	10720	1.72	3.38
37° 50’ 40.571’’ N	4.1	294	IGT	16.4	244	11956	1.15	3.38
31° 31’ 08.266’’ W	4.3	280	KIPS	11.5	147	11511	9.19	3.42
Marker 4	4.0	270	IGT	30.9	132	13009	1.15	5.06
37° 50’ 38.082’’ N	4.1	271	IGT	9.4	110	13119	2.29	5.06
31° 31’ 10.429’’ W	4.3	256	KIPS	21.4	249	13868	8.53	4.24
Fontenova	4.0	253	IGT	31.1	82	10211	2.29	3.95
37° 48’ 04.8’’ N	4.1	254	IGT	13.7	132	10575	2.86	3.38
31° 32’ 14.4’’ W	5.1	154	KIPS	6.1	1008	16851	6.08	0.73
	4.9	154	KIPS	6.7	941	16298	6.84	0.88
seawater	7.7	9.8	IGT	1.7	1341	20423	< DL	< DL

Note: IGT: isobaric gas tight sampler; KIPS: Kiel pumping system; < DL: below detection limit

Tab. 3: Concentration of As^T and the different As species, as well as maximum temperatures for selected cryofreezed KIPS hydrothermal fluid samples.

Location	**As^T** [µg L^{-1}]	**As^{III}** [µg L^{-1}]	**As^V** [µg L^{-1}]	**As^{III} + As^V** [µg L^{-1}]	**Recovery** [%]	**T$_{max}$** [°C]
White Flames	9.04 ± 0.06	1.43	0.0	1.43	16	280.5
Woody	1.84 ± 0.05	0	2.56	2.56	139	74.3
Atos 10	8.60 ± 0.15	1.95	2.40	4.35	51	279.6
White Flames	3.14 ± 0.11	1.12	2.43	3.55	113	117.0
Marker 4	8.06 ± 0.56	1.51	2.61	4.12	51	256.1
Fonte Nova	4.50 ± 0.14	0.96	2.51	3.47	77	154.1
Fonte Nova	3.77 ± 0.25	0.90	2.43	3.33	88	154.1

Tab. 4: Concentration of As^T (n=3), extraction efficiencies and column recovery for samples and CRMs as well as total antimony, cadmium, manganese and iron.

	As^T [mg kg^{-1}]	**Extraction efficiency** [%]	**Column recovery** [%]	**Sb** [mg kg^{-1}]	**Cd** [mg kg^{-1}]	**Mn** [mg kg^{-1}]	**Fe** [mg kg^{-1}]
Muscle	6.3 ± 0.2	65.7	69.6	0.08 ± 0.004	0.4 ± 0.02	4.7 ± 0.3	42 ± 3.8
Gill	14.9 ± 0.8	64.1	76.8	0.9 ± 0.06	2.8 ± 0.1	4.1 ± 0.3	105 ± 12.5
DG*	19.0 ± 1.4	43.2	65.1	1.1 ± 0.05	5.6 ± 0.3	22.2 ± 0.5	376 ± 11
DORM 2	16.8 ± 0.8	106.2	84.4	0.03 ± 0.006	0.04 ± 0.004	2.8 ± 0.3	112 ± 7.6
DORM2 *certified*	18.0 ± 1.1	-	-	-	0.043 ± 0.008	3.66 ± 0.34	142 ± 10
CRM 627	4.5 ± 0.3	88.2	73.9	0.01 ± 0.001	0.17 ± 0.032	0.8 ± 0.02	71 ± 5.8
CRM 627 *certified*	4.8 ± 0.3	-	-	-	-	-	-

* DG: Digestive Gland

Tab. 5: Concentration of the different species (n=3) and relative percentages with respect to he sum of the species for samples and CRMs.

		As^{III}	As^{V}	DMA	PO_4-sug	Gly-sug	AsBet	UNK
Gill	[mg kg^{-1}]	2.42 ± 0.15	1.11 ± 0.11	0.03 ± 0.006	1.84 ± 0.03	0.67 ± 0.01	0.82 ± 0.01	< DL
	[%]	35.1	16.1	0.5	26.7	9.7	11.9	
DG*	[mg kg^{-1}]	0.97 ± 0.15	0.79 ± 0.06	0.07 ± 0.003	1.0 ± 0.01	1.94 ± 0.12	0.43 ± 0.05	0.15 ± 0.01
	[%]	18.1	14.8	1.3	18.7	36.3	8.0	2.8
Muscle	[mg kg^{-1}]	0.82 ± 0.05	0.12 ± 0.03	0.02 ± 0.002	0.82 ± 0.03	< DL	0.67 ± 0.01	0.46 ± 0.03
	[%]	28.2	4.1	0.7	28.2		23.0	15.8
DOMR-2	[mg kg^{-1}]	< DL	< DL	0.26 ± 0.01	0.08 ± 0.01	< DL	14.68 ± 0.53	< DL
DORM-2 *certified*	[mg kg^{-1}]	n.a.	n.a.	n.a.	n.a.	n.a.	16.4 ± 1.1	n.a.
CRM 627	[mg kg^{-1}]	< DL	< DL	0.1 ± 0.004	< DL	< DL	2.86 ± 0.13	< DL
CRM 627 *certified*		n.a.	n.a.	0.15 ± 0.02	n.a.	n.a.	3.9 ± 0.2	n.a.

Note: DG: Digestive Gland; < DL: below detection limit; n.a.: not available; UKN: unknown species

5. Discussion

5.1 Fluids

Venting of submarine hydrothermal fluids can act as a substantial source for arsenic (As) to the oceans (e.g. Pichler et al., 1999; Price et al., 2012). The amount of As^T present in hydrothermal fluids evidently depends on a combination of tectonic setting and host rock composition, as well as various physicochemical parameters like temperature, pH, eH, as well as the hydrogen sulfide and iron concentrations (Breuer and Pichler, 2012).

Measured concentrations of As^T in hydrothermal fluids at Menez Gwen (6 to 90 µg L^{-1}; Tab. 2) are enriched compared to seawater, but generally similar to values for other hydrothermal systems at mid-ocean ridges, showing values between < 0.8 and up to 41 µg L^{-1} as observed on the East Pacific Rise at 17-19°S (Douville et al., 1999). Various other hydrothermal systems also show typically several tens of µg L^{-1} of As. A single concentration of As^T in Menez Gwen fluids of 18.5 µg L^{-1} (Douville et al., 1999) was previously reported. Arsenic concentrations in hydrothermal fluids from back-arc basins and island arc settings are generally much higher, with values up to 5 850 µg L^{-1} (Milos/Greece; Price et al., 2012). Given the non-conservative behavior, it is currently impossible to distinguish if the As is solely derived from leaching of the underlying host rock or if there is an additional input due to magmatic degassing, which may contribute considerable amounts of As to hydrothermal fluids (Yang and Scott, 1996)

No As speciation measurements are available from deep-water hydrothermal systems for comparison to this study. From a thermodynamic perspective, the prevalent conditions in many hydrothermal systems, such as low pH and Eh, favor the presence of the trivalent As^{III} (Smedley and Kinniburgh, 2002). However, thermodynamic modeling for deep-water systems performed by the authors also shows the presence of considerable amounts of the pentavalent As species H_2AsO_4, compared to shallow-water systems, which should be dominated by the trivalent As species $As(OH)_3$. These calculations also show the precipitation of different As-bearing minerals like orpiment and claudetite, which might be responsible for the overall low-As hydrothermal fluids in deep-water hydrothermal systems (Breuer and Pichler, 2012). Furthermore, fluids at Menez Gwen are more oxidizing favoring the presence of As^V (Charlou et al., 2000; Reeves et al., 2011a). In accordance with the thermodynamic modeling, also the analysis of fluids from the Menez Gwen hydrothermal system shows both inorganic species As^{III} and As^V.

The finding of As^V and the absence of organic As species is similar to observations from shallow-water hydrothermal systems in island-arc settings (e.g. Dominica and Ambitle Island) where hydrothermal fluids and pore waters were investigated (McCarthy et al., 2005; Price and Pichler, 2005; Price et al., 2007). However, compared to pore waters, deep-water hydrothermal systems are characterized by focused hydrothermal discharge, and fluids get immediately in contact with oxidized seawater, also favoring the oxidation of As^{III} to As^V. The occurrence of As^V could also be due to oxidation in the time between sampling and measurements, because samples cannot always be conserved in-time, and oxygen cannot always be excluded. However, portions were variable and column recoveries were low, and the low recovery might be due to the overall low As concentration encountered in the fluids and analytical challenges.

A mixture of meteoric water and seawater dominates shallow-water systems, which are mostly nearshore, in addition to a component of magmatic volatiles arising from a magma chamber, and this mixture of different types of fluids might strongly affect the As^T and species distribution. Compared to these shallow-water systems, however, hydrothermal fluids from mid-oceanic ridges are solely seawater derived, with minimal or no significant inputs of meteoric water (Shanks, 2001; German and Von Damm, 2003). The pore waters in the sediments surrounding the marine shallow-water hydrothermal system at Ambitle Island are dominated by As^V as a result of microbial oxidation (Akerman et al., 2011; Meyer-Dombard et al., 2011), which was also observed in areas of diffuse discharge of hydrothermal fluids. In contrast, focused fluids directly discharging from hydrothermal vents at Ambitle Island were dominated by As^{III}.

Thioarsenic species tend to transform quickly into As^{III} and As^V when they are oxidized. However, although Menez Gwen is a highly sulfidic environment, no thio-species were detected during such treatments or were rapidly oxidized during sample collection or handling. Spiking tests were performed with As^{III} and As^V and showed good correlations with the measured values, thus the low recovery could also represent an unknown As species, which can resist oxidation with peroxide.

Significant lower Mg concentrations compared to seawater in some fluids show that the samples were not exclusively hydrothermal fluids, whose Mg concentration should be zero due to Mg-fixation (Von Damm, 2001; German and Von Damm, 2003), but a mixture of hydrothermal fluid and seawater that likely formed in the subsurface (Reeves et al., 2011b). For most of the samples, “dilution” of As-rich hydrothermal fluid with low As seawater could be observed, but calculating an endmember concentration is not possible because of the non-conservative behavior of As during sample collection and handling. Varying Cl concentrations in the fluids, which were mostly lower than ambient seawater (20 420 mg L^{-1}), indicating that phase separation is likely occurring (Reeves et al., 2011a). It is widely speculated that As^{III}, also like Cu, Sb, B and Au, should partition into low salinity vapor phases because of neutral HS-complex formation, as indicated by fluid inclusion studies (Heinrich et al., 1999). However such partitioning behavior is still a matter of debate and the physico-chemical mechanisms are poorly understood (Pokrovski et al., 2005). In the case of Menez Gwen, all samples have lower Cl concentrations than seawater indicating a more vapor-like phase (Reeves et al., 2011a), but only a weak trend of increasing As with decreasing Cl could be observed (Fig. 2).

5.2 Biota

Bivalves of the species *Bathymodiolus azoricus* living in the vent fluid-seawater mixing zones of the Menez Gwen hydrothermal system are evidently able to bioaccumulate and transform high amounts of different metals in their tissues (Colaço et al., 2006; Charmasson et al., 2011). They live in symbiosis with sulfide- and methane-oxidizing *Gammaproteobacteria*, located in specialized epithelial cells within the gill epithelial tissue but also feed from particulate and dissolved organic matter, which originates from the chemolithoautotrophic bacterial activity produced by the local vent biota (Duperron et al., 2006; Riou et al., 2010a). The amount of uptake also depends on the abundance and bioavailability of As in the environment of the mussels, as well as on their very special nutrition (Cosson et al., 2008). Coastal bivalves, for example, are able to accumulate up to 214 mg kg^{-1} of As, with average values of lower than 10 mg kg^{-1} from non polluted areas (Neff, 2002).

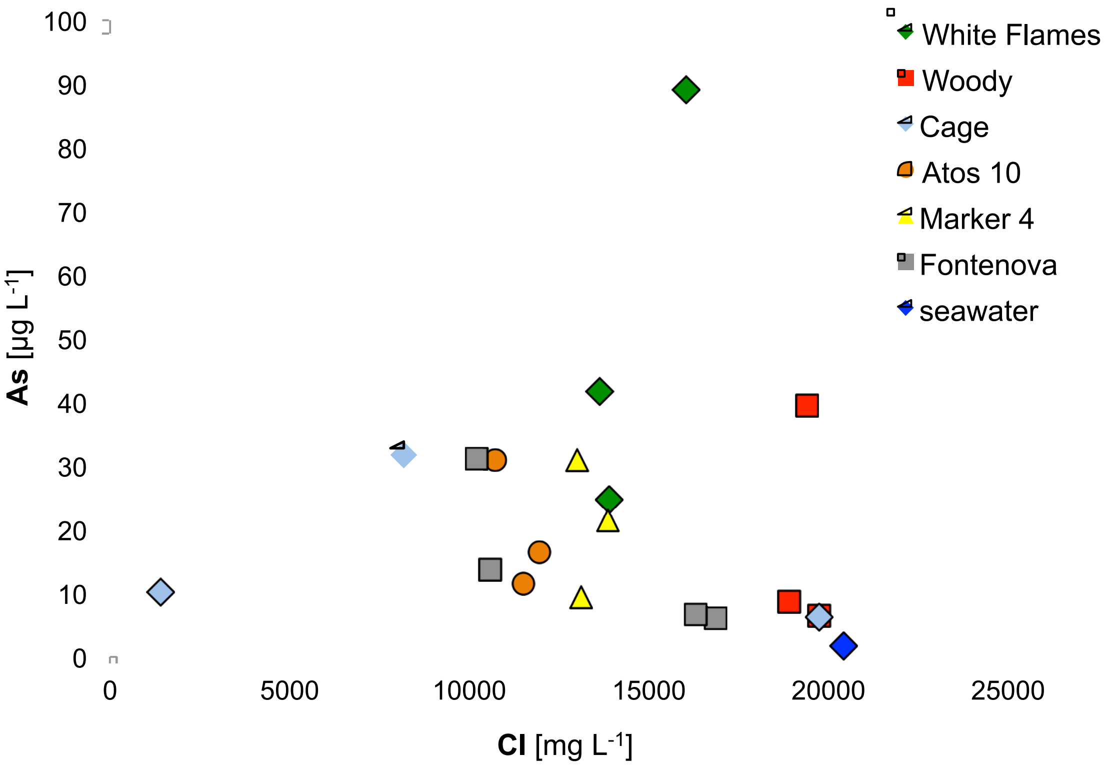

Fig. 2: As vs. Cl concentrations for the hydrothermal fluids from the different sampling locations.

The highest concentration of As^T was found in the digestive gland of *Bathymodiolus azoricus* (19 mg kg^{-1}), which is considered as an accumulation pathway and storage organ (Bennet-Clark, 1976). The gill of the mussels, consisting of fine filaments with symbiotic bacteria located inside, is directly exposed to the mixture of hydrothermal fluid and seawater, and shows As^T concentrations of 15 mg kg^{-1} dry weight. This may also reflect accumulation of oxyhydroxide particles during filtration, in addition to the activity of the symbiotic bacteria. Muscle tissues are less involved in such exchange and nutrition processes and not directly exposed to the high amount of As, and therefore contain a lower concentration of As^T (6.3 mg kg^{-1}). Similar distribution patterns of elemental concentrations were observed for other metalloids such as antimony (0.1 to 1.1 mg kg^{-1}), cadmium (0.4 to 5.6 mg kg^{-1}), manganese (4 to 22 mg kg^{-1}), and iron (42 to 376 mg kg^{-1}) (Tab. 4), indicating similar take-up and accumulation mechanisms as observed for As.

The extraction efficiency of approximately 60 % of As from tissues (Tab. 4) is low, but similar to numbers reported by others for coastal bivalves (e.g. Shibata and

Morita, 1992). Lower efficiency may due to the presence of different non-extractable polar arsenicals or precipitated As compounds like arsenic sulfides, which can form in this sulfide-rich environment. The latter forms may also explain the apparent non-conservative behavior of As during sample collection.

The cycling and transformation of As in this extreme environment relative to photic zone food webs can be better interpreted by investigating the As speciation. This shows the presence of different inorganic and organic As-species distribution in the different organs (Tab. 5), with the major As species observed are the two inorganic forms arsenite (As^{III}) and arsenate (As^{V}), in addition to two oxo-arsenosugars (phosphate- and glycerol-sugar) and lower but relatively constant portions of arsenobetaine (AsBet), as well as a very low amount of dimethylarsinic acid (DMA). This is comparable to results found by different authors in hydrothermal vent mussels of the genus *Bathymodiolus* from different hydrothermal fields on the Mid-Atlantic Ridge (Larsen et al., 1997; Taylor et al., 2012), and also comparable to different coastal bivalves from high As polluted environment (Whaley-Martin et al., 2012). Concerning the sugars, the digestive gland is dominated by the glycerol-sugar (Gly-sug), and the gill and the muscle show high amounts of phosphate-sugar (PO_4-sug). These two sugars were also the only one (but at low concentrations) observed in the gut of the gastropod *Cyclope nerita* living the As-rich hydrothermal system off Milos Island (Greece) (Ruiz-Chancho et al., 2012). In general, the major and dominant As compound in marine animals from photic zones is AsBet (Reimer et al., 2010), which is normally bioaccumulated to a larger degree than the other chemically similar organoarsenic compounds as for example shown by aquarium studies conducted on blue mussels (Gailer et al., 1995). Compared to this, As-sug are normally only present in low proportions in coastal bivalves from non-polluted areas and it is though that they might be precursors for AsBet. The high amount of inorganic As^{III} and As^{V} found in samples from this study might also reflect saturation and overstrain of the different biochemical pathways, which normally transform the inorganic species into organoarsenicals in high As environments. Very low DMA concentration may indicate that it is an intermediated product and fully utilized by producing higher complex species.

In marine algae, which are a primarily food source for marine organisms, As is present predominantly as complex carbohydrate derivatives like As-sug or *arsenoribosides*. It is unclear why algae absorb As^V from seawater, but a possible explanation could be the similarity between phosphate (P) and As^V, and that As cannot be excluded from the P uptake mechanism and is taken up by different P transporters (Maugh, 1979; Zhao et al., 2009). As^V from seawater is further converted to As^{III} because As^V is known to interfere with different metabolic processes in combination with phosphorylation (Slater, 1963), and the trivalent form is also more mobile within the cells. Regarding the food chain, some marine animals consume plants or exist in symbiotic relationships, allowing plant products to be incorporated in the marine animals. At Menez Gwen it seems more likely that As is directly accumulated from surrounding vent fluid-seawater mixtures where only the trivalent and pentavalent inorganic As forms are present, and the plant-stage of the food-chain is likely excluded because of depth below the photic zone and distance from terrestrial sources. However, other nutritional modes cannot be completely neglected, because *Bathymodiolus azoricus* also feeds from vent particulate and dissolved organic matter, with the amount of organic matter delivered to this depth being dependent on surface primary production. Another source of dissolved organic matter could be from the surrounding biological mats, which are present near and at the vent structures. The respective amount of energy delivered by filtering or by endosymbiosis also varies with the size of the mussel, with smaller mussels strongly dependent on filtering and larger ones obtaining relatively more energy from their symbiotic bacteria due to greater amounts of gill tissue (Martins et al., 2008). The detoxification of toxic metals in algae can be performed by different processes like binding to metallothioneins or incooperation to metabolically insoluble granules (Morgan et al., 2007). The “Challenger” pathway describes the methylation of As by microorganisms involving sequential oxidation and reduction methylation reactions with the relative volatile trimethylarsine as the end product (Challenger, 1945; Challenger, 1955). Another pathway was suggested in 1987 by Edmonds und Francesconi, who question the last step of the formation of a trimethylarsine and instead propose the transferring of an adenosyl group of the methylating agent to the As atom (Edmonds and Francesconi, 1987).

In the different parts of the mussels, only PO_4-sug and Gly-sug were found, and concentrations were anomalously high compared to AsBet which normally represents around 90 % of the As in marine animals. These sugars however are thought to be precursors for AsBet and get converted to dimethylarsinoylethanol before further transformation to AsBet due to different oxidation und reduction reactions in combination with methylation (Edmonds et al., 1982; Edmonds and Francesconi, 1987; Francesconi et al., 1999). This process is poorly understood and thus, other processes need to be considered, such as the generation of AsBet from other precursors or that certain steps do not occur during generation (Edmonds, 2000). Degradation of AsBet has to be taken into account. Overall, discussion of As compounds and their biochemical pathways is largely speculative and more research has to be conducted. The exceptional high proportion of As-sug may be of a different origin, either due to microbial activity of the methane- and sulfide oxidizing symbionts, or alternatively due to the high input of As in this extreme environment and overstressing of detoxification processes. Surprisingly, no thio-organic compounds (Schmeisser et al., 2004) were found during oxidation experiments by using H_2O_2, although this is a high sulfidic environment.

6. Conclusions

We presented novel and combined results for As^T and As speciation for fluids and vent biota from the Menez Gwen hydrothermal system and considered for the first time the different organs and their functions. Concentrations of As in the hydrothermal fluids were significantly higher than those in seawater and varied between 6 and 90 µg L^{-1}. Only the inorganic arsenite (As^{III}) and arsenate (As^V) species were found in the hydrothermal fluids during analysis.

Throughout the Menez Gwen hydrothermal system the mussel species *Bathymodiolus azoricus* was abundant, living in the mixing zones of hydrothermal fluid and seawater. Thus, these mussels were exposed to higher than normal As^T concentrations and therefore, accummulated As in their digestive gland (19.0 mg kg^{-1}), gill (14.9 mg kg^{-1}) and potentially muscle tissue (6.4 mg kg^{-1}). The concentration of As in coastal bivalves is mostly less 10 mg kg^{-1}. The high amount of As found in the digestive gland could be due to its function as an ingestion pathway and storage organ. The relatively higher amount of As in the gill compared to the digestive gland could be due to the presence of symbiotic bacteria, which are responsible for gaining energy, or alternatively by contamination of the biological matrix with As adsorbed on Fe-oxyhydroxide particles. The mussels show an unusual speciation pattern for the different organs with a particularly high amount of As-sugars and lesser amount of AsBet. Considering the low amount of dissolved organic matter present in 800 m depth and the occurrence of two different symbiotic bacteria, we propose that the high amount of As sugars is due to the activity of the methane- and sulfide oxidizing bacteria located in the gill.

Acknowledgments

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5 | Arsenic in hydrothermal fluids and vent biota from the PACMANUS and SuSu Knolls hydrothermal fields, Manus Basin, Papua New Guinea

Christian Breuer [a,b], Maria José Ruiz-Chancho [b],
Eoghan Reeves [a,b], Wolfgang Bach [a,b],
Thomas Pichler [a,b]

[a] MARUM – Center for Marine Environmental Sciences
[b] Department of Geosciences, University of Bremen

draft

not approved by all authors

Abstract

Hydrothermal activity taking place at the PACMANUS and SuSu Knolls hydrothermal fields located in the eastern Manus Basin is characterized by discharge of black, grey and white hydrothermal fluids and hydrothermal vent biota living as discrete habitats nearby. We present combined results for total arsenic (As^T) and As speciation in the different types of hydrothermal fluids, as well as for three different organisms living in the hydrothermal fluids. Sampled fluids from the Manus Basin were up to 348 °C hot with a pH between 1.4 and 7.0 (25 °C). Concentrations of As^T ranged between 1.5 and 376.0 µg kg^{-1}, with the inorganic arsenite (As^{III}) and arsenate (As^V) species in variable portions. Three different fluid trends could be distinguished: a low Cl vapor phase, a high Cl brine phase, both fairly enriched in As^T compared to seawater, in addition to a magmatic trend with Cl concentrations around seawater and highly enriched in As^T.

Gastropods of the species *Alviniconcha hessleri* and *Ifremeria nautilei* and mussels of the species *Bathymodiolus manusensis* were the dominant species living in the lower temperature zones at the PACMANUS und SuSu Knolls hydrothermal systems. The vent snail *Alviniconcha hessleri* was able to bioaccumulate up to 5 580 mg kg^{-1} of As in the gill, 721 mg kg^{-1} in its digestive gland and 43 mg kg^{-1} in its muscle tissue. In the gill of *Alviniconcha hessleri*, different small particles and coatings dominantly made of Fe, Zn, S and As were found, which were most likely responsible for the high concentrations of As^T. High concentrations measured in the digestive gland could be explained best by its activity as a pathway and storage organ. A similar pattern could be observed in the body parts of *Ifremeria nautilei* collected at the Roman Ruins site with 118 mg kg^{-1} in the gill, 108 mg kg^{-1} in the digestive gland and 22 mg kg^{-1} in the muscle tissue. Much lower concentrations were found in mussels of the species *Bathymodiolus manusensis* from the Fenway area, where the highest concentration was measured in the digestive gland (15.7 mg kg^{-1}), followed by gill (9.8 mg kg^{-1}) and muscle tissue (4.5 mg kg^{-1}). These concentrations are similar to values found in mussels from the Menez Gwen hydrothermal field (*Bathymodiolus azoricus*).

The concentrations measured in the organisms correspond to the characteristics of the fluids, which were collected at the places where the organisms were living. *Alviniconcha hessleri* lived in the hottest (T_{max} = 26.8 °C) fluid with the lowest pH (6.2), and highest concentration of As^T (12.7 µg kg^{-1}) and *Ifremeria nautilei* in surrounding hydrothermal fluid of T_{max} = 15.1 °C, a pH of 7.0 and an As^T concentration of 5.8 µg kg^{-1}. Mussels of the species *Bathymodiolus manusensis* with the lowest amount of As accumulated lived in fluids with a maximum temperature of 10.5 °C, a pH of 6.8 and the lowest As^T concentration of 3.3 µg kg^{-1}.

High percentages of the inorganic As^{III} and As^V species (Ø 60 % of sum of the species) were found, in addition to arsenobetaine (AsBet; Ø 33 %) and lower amounts of arsenosugar (As-sug). Marine algae have generally high concentrations of As-sug, which are thought to be precursors for AsBet in higher consuming organisms. These higher organisms have only limited ability to accumulate inorganic As from the surrounding seawater. The presence of As-sug and AsBet in a deep-sea hydrothermal environment, where the nutrition is strongly dependent on chemolithoautotrophic bacteria, is therefore unexpected and indicates that there might be other pathways forming these organic arsenicals than via the uptake of algae.

Highlights:

► We present novel and combined data for arsenic and arsenic species in hydrothermal fluids and associated vent biota from the Manus Basin. ► Arsenic concentration in hydrothermal fluids sampled at PACMANUS and SuSu Knolls are up to 376 µg L^{-1} depending on the style of venting. ► Hydrothermal vent mussels and snails are able to accumulate and transform arsenic from hydrothermal fluids. ► Investigations were performed on hydrothermal vent snails *Alviniconcha hessleri* and *Ifremeria nautilei* and mussels of the species *Bathymodiolus manusensis.*

Keywords:

Arsenic; Hydrothermal; Manus Basin; Vent biota; Metalloids; Fluids

1. Introduction

The geochemistry and style of emanating hydrothermal fluids is influenced by various physicochemical parameters and processes such as temperature, pressure, water-rock interaction, mixing with cold and oxygenated seawater and the possible input of magmatic volatiles arising from a deep magma chamber (e.g. Von Damm, 2001; German and Von Damm, 2003). These systems play an important role in transferring mass and energy from the crust into the oceans and have been the subject of many investigations concerning their geology, geochemistry and biology. They are mostly located at mid-ocean ridges, back-arc basins, or submarine neovolcanic edifices in arcs. Hydrothermal circulation is driven by a steep geothermal gradient, heating the downward percolating seawater up to temperatures in excess of 400 °C. During water-rock interaction at high pressure and temperature, the host rock composition, as well as the fluid chemistry changes dramatically. Fluids typically become acidic (pH (25 °C) of 2 to 3) and have low SO_4 and Mg concentrations, but are rich in metals, such as Fe^{II} and Mn^{II}, as well as magmatic CO_2, H_2S and dissolved H_2. Much less is known about the behavior of metalloids, including As, in these hydrothermal processes. This potentially toxic element was only rarely investigated in marine hydrothermal fluids, although it can be strongly enriched and plays and important role in the process of hydrothermal ore formation and furthermore can be found in many ore deposits in combination with gold (e.g. Barnes, 1997; Cepedal et al., 2008; Zhu et al., 2011)

In the immediate vicinity of the vents and commonly confined to the low-temperature turbulent mixing zones of seawater and hydrothermal vent fluids, unique communities of hydrothermal vent animals can be found. The basis of all hydrothermal vent faunae is energy harnessing from oxidation of reduced compounds such as sulfide and methane performed by chemolithoautotrophic microorganisms. These microorganisms comprise free-living ones, which may form bacterial mats, and those living in symbiotic relation with different species of snails and mussels, as well as various crabs, tubeworms and shrimps (Fisher et al., 2007). However, there is only little known about the diverse evolutionary processes and their metabolic cycles including As and the respective detoxification mechanism used by these kind of animals

1.1 Arsenic in the marine aquatic system

Arsenic (As) is ubiquitous in the terrestrial and marine environment with concentrations of around 0.62 µg L^{-1} in river waters (Gaillardet et al., 2003) and around 1.7 µg L^{-1} in seawater (Neff, 2002). This is somewhat uncommon, as normally rivers represent the main source for most elements into the oceans and rivers should be accordingly higher than seawater concentrations as it is observed for most of the elements. The main factors controlling the concentration of As in the oceans are in addition to the riverine input, the weathering and sedimentation on the seafloor, input from volcanic sources, atmosphere-seawater exchange and anthropogenic input due to industry by coal combustion and copper smelting (Matschullat, 2000; Deschamps and Matschullat, 2011). Another source are hydrothermal fluids emanating at the seafloor, which could be greatly enriched in As depending on different physicochemical parameters like temperature, pressure, pH, host rock composition and mineralogy, as wells as the concentration of CO_2, Fe and H_2S (Breuer and Pichler, 2012). The concentration of As in these fluids can vary between that of seawater to values several thousand times higher, with the highest values to date found in hydrothermal fluids from back-arc and island-arc settings (e.g. Douville et al., 1999; Price et al., 2012)

Under the pH and redox conditions in and around hydrothermal vents, As can occur in different oxidation states (+5, +3, 0 and -3), with the first two being the most common in aqueous systems (Smedley and Kinniburgh, 2002; Sharma and Sohn, 2009). Knowledge about As speciation is important, as toxicity, bioavailability as well as the physiological effects depend a lot on the chemical form (Bissen and Frimmel, 2003). In deep-water hydrothermal systems with high temperature, low pH and high iron und sulfur concentrations like in back-arc basins, the pentavalent arsenate species $H_2AsO_4^-$ should dominate as shown by thermodynamic calculations and minerals like orpiment (As_2S_3) and scorodite ($FeAsO_4 \cdot 2H_2O$) are preferentially precipitated (Breuer and Pichler, 2012). In addition to the inorganic forms, organic forms such as methylarsonic acid (MA) and dimethylarsinic acid (DMA) can also be found in seawater depending on the location and processes like upwelling of anoxic waters (Andreae, 1978; Cutter, 1992; Cabon and Cabon, 2000).

1.2 Arsenic in marine organisms

Marine organisms such as algae, plankton, bivalves, snails and fish are evidently able to bioaccumulate and transform As from the surrounding water and via the food chain. The most important factors controlling the accumulation are the concentration and chemical form of dissolved As, the position in the food web and the kind of nutrition. Marine bivalves are able to accumulate up to 214 mg kg^{-1} of As with an average value of 10.44 mg kg^{-1} (n = 151) and snails between 8.0 and 533 mg kg^{-1} with average 51.97 mg kg^{-1} (n = 41), with a strong correlation of high As found in marine animals living in environmental polluted areas (Neff, 1997).

Marine plants and algae are able to bioaccumulate inorganic As via the cellular phosphate transport system from the surrounding seawater and transform it from As^{V} via As^{III} (which is more mobile) and different methylated forms to arsenosugar (As-sug). In contrast to these photosynthetic organisms, higher consuming marine animals have only limited ability to accumulate inorganic As, and they prefer to take up and bioaccumulate the organic forms of As from marine algae via the marine foodweb (Neff, 2002; Azizur Rahman et al., 2012) and convert it to their endproduct arsenobetaine (AsBet; $(CH_3)_3As^+CH_2COO^-$) (Francesconi and Edmonds, 1993; Edmonds and Francesconi, 2003). This is the most abundant and important As species found in higher organisms.

Studies dealing with As accumulation in marine organisms living at deep-sea hydrothermal vent systems are rare and information about As speciation in these animals even more limited. Larsen et al. (1997) investigated As in shrimps and mussels from the TAG and Snakepit hydrothermal field, showing that the shrimp *Rimicaris exoculata* accumulated up to 13 mg kg^{-1} and the mussel *Bathymodiolus puteoserpentis* up to 40 mg kg^{-1} in their soft tissues (Larsen et al., 1997). The dominant species in the shrimps was AsBet, and in the mussels As-sug. Another recent study conducted on organisms from the TAG, Rainbow and Lucky Strike hydrothermal fields revealed concentrations between 3.3 and 29.8 mg kg^{-1} of As in shrimps, between 9.9 and 18.2 mg kg^{-1} in mussels and between 14.0 and 67.8 mg kg^{-1} in the snail *Peltospira smaragdina*. The dominant species in the shrimp *Rimicaris exoculata* was AsBet and in the mussels *Bathymodiolus azoricus* and *Branchipolynoe seepensis*, As-sug was primary present (Taylor et al., 2012). Taking that work a step further, our study shows the As concentrations in the different body parts such as the gill, muscle and digestive gland to get a more detailed picture of the metabolism and function of the organs. By sampling the matching hydrothermal fluids and vent biota, the influence of the different fluid parameters such as temperature, pH and As concentration on the organisms could be investigated.

2. Geological setting

The Manus Basin is a young (3.5 Ma) and rapidly opening (137 mm a^{-1}) back-arc basin located in the northeastern part of the Bismarck Sea (e.g. Taylor, 1979; Martinez and Taylor, 1996; Tregoning, 2002). It is bordered by the fossil inactive Manus Trench in the north and by the actively New Britain Trench in the south, where the Solomon microplate is subducted beneath the New Britain Arc (Fig. 1; Lee and Ruellan, 2006). Active spreading takes place along three major spreading centers: the western Manus spreading center (WMSC), the Manus Ridge spreading center (MSC) and the southeastern ridges (SER), with the spreading centers bounded by the Willaumez (WiT), Djual (DT) and Weithin transform faults. Venting occurs in the eastern Manus Basin (EMB) in water depths between 1200 and 1700 m at two main areas: the Papua New Guinea-Australia-Canada-Manus (PACMANUS) hydrothermal system and the SuSu Knolls hydrothermal area comprising North Su, South Su and Suzette.

PACMANUS, discovered in 1991, is located on the 500 m high and 20 km long dacitic to rhyodacitic Pual Ridge (Binns and Scott, 1993; Binns et al., 2007) with massive sulfide accumulations enriched in Au, Cu, As, Zn, Pb and Sb (Moss and Scott, 2001). Hydrothermal activity takes place at five main areas of discrete venting in depths between 1640 and 1710 m: Roman and Roger’s Ruins, Satanic Mills, Snowcap and Tsukushi. Focused black smoker fluids, lower temperature grey and white fluids, as well as low-temperature diffuse fluid flow could be observed in these areas (Fig. 2a-c). Another new site named Fenway was found during an expedition in 2006 located around 200 m south of Satanic Mills and in 1710 m water depth with a 40 m in diameter two-tiered mound in the center made of chimney debris, breccia of anhydrite and sulfide, as well as coarse anhydrite sand (Reeves et al., 2011).

The SuSu Knolls hydrothermal area located 45 km east of PACMANUS is markedly different to the ridge-hosted PACMANUS area and consists of three volcanic edifices forming a NNW-trending chain. Each of these edifices is 1.0 to

1.5 km in diameter and shows a great variability regarding its style of venting with hot black and white smoker vents and lower temperature diffuse discharge (Tivey et al., 2007). The cone-shaped North Su volcano rises up to 1150 m water depth and represents the most active area, with sulfide-rich black smoker fluids venting with temperatures of up to 325 °C near the summit, and very low pH white smoker fluids revealing a high amount of dissolved gases (Seewald et al., 2006).

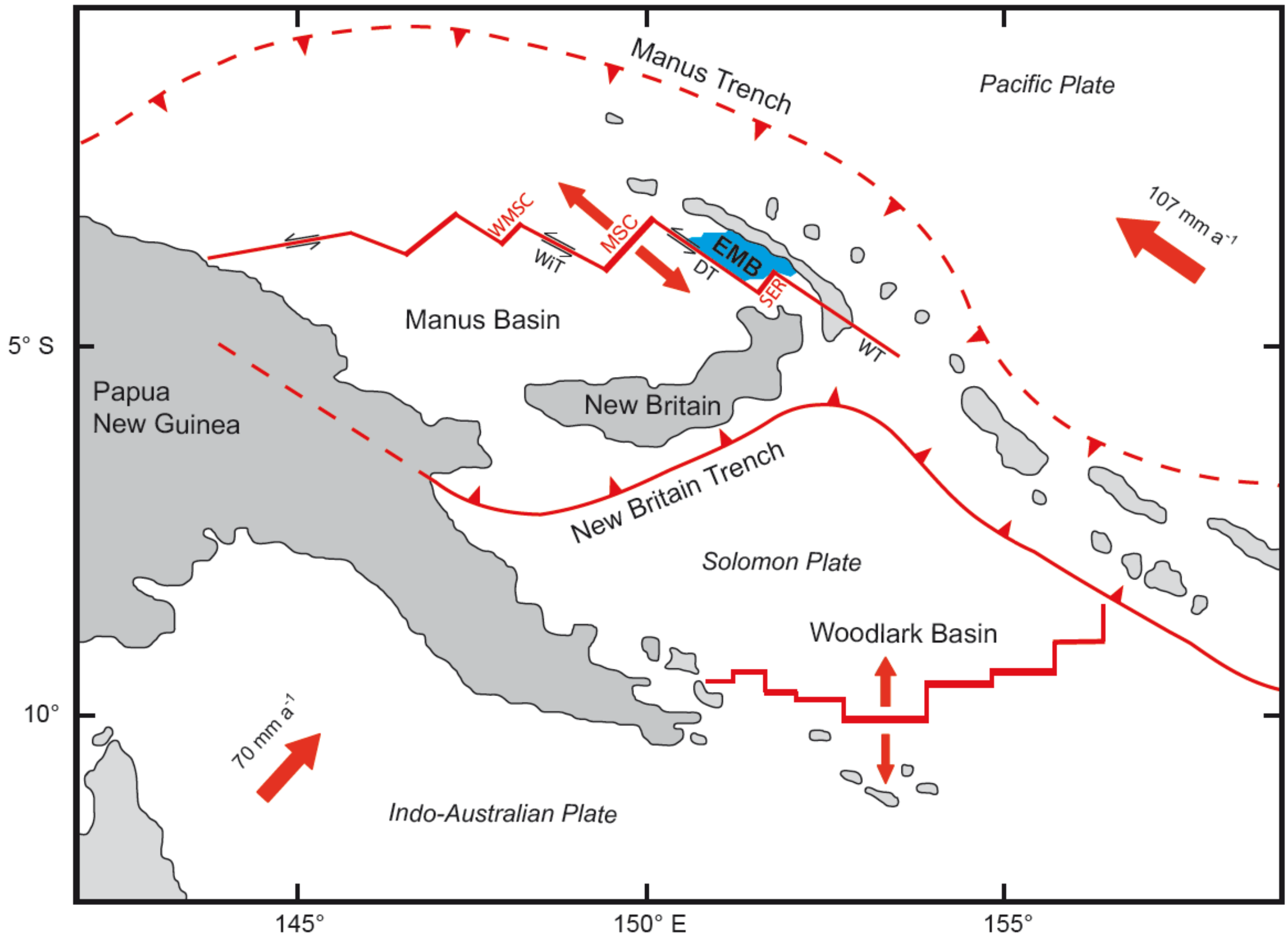

Fig. 1: Map of the tectonic setting of the Manus back-arc basin showing the major plates and their motions, as well as the different spreading centers and transform faults (WMSC: Western Manus Spreading Center; MSC: Manus Spreading Center; SER: Southeastern Ridges; WiT: Willaumez transform fault; DT: Djual transform fault; WT: Weitin transform fault).

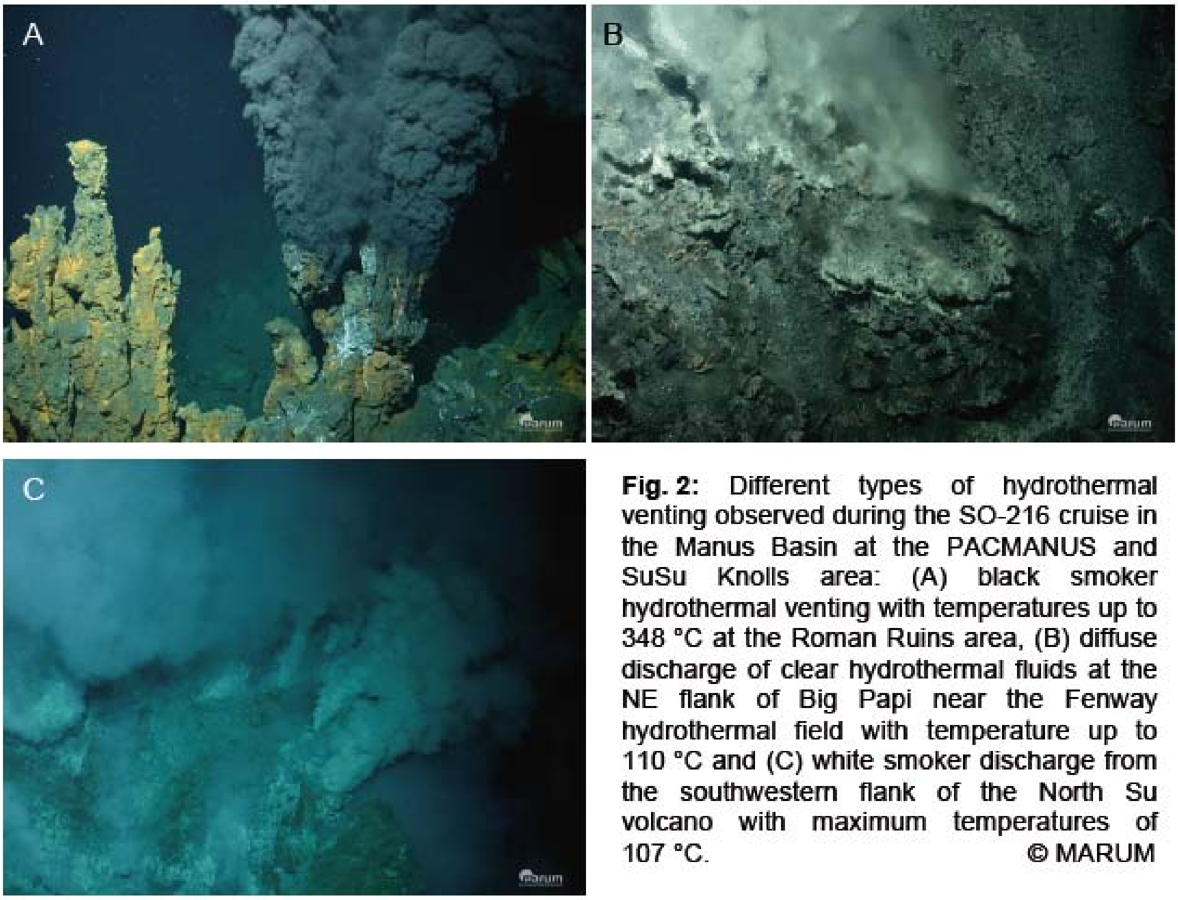

Fig. 2: Different types of hydrothermal venting observed during the SO-216 cruise in the Manus Basin at the PACMANUS and SuSu Knolls area: (A) black smoker hydrothermal venting with temperatures up to 348 °C at the Roman Ruins area, (B) diffuse discharge of clear hydrothermal fluids at the NE flank of Big Papi near the Fenway hydrothermal field with temperature up to 110 °C and (C) white smoker discharge from the southwestern flank of the North Su volcano with maximum temperatures of 107 °C. © MARUM

3. Hydrothermal vent fauna from the EMB

The hydrothermal vent fauna in the Manus Basin dominantly comprises of different gastropods, barnacles, bythograeid crabs, bresiliid shrimps, vestimentiferans, sea anemones and some new found species (Galkin, 1997). The most important and dominant primary consumers are snails of the species *Alviniconcha hessleri* and *Ifremeria nautilei* (also described as *Olgaconcha tufari*) from the family Provannidae, in addition to vent mussels of the species *Bathymodiolus manusensis* (Galkin, 1997; Desbruyères et al., 2006).

The hairy yellowish gastropod *Alviniconcha hessleri* (Fig. 3a) is widespread in the entire western Pacific back-arc basin and in the Indian Ocean (Warén and Bouchet, 2001), living in sulfide-rich (up to 750 µM) vent fluids with average temperatures between 10 and 25 °C. Within their enlarged gill filaments, which can contain elemental sulfur (Stein et al., 1988), these species harbor sulphur-oxidizing thioautotrophic endosymbiontic γ- and ε-proteobacteria (Suzuki et al., 2005; Suzuki et al., 2006a). Thereby, the ε-proteobacteria use a carbon metabolism pathway, which is different to the one used by γ-proteobacteria indicated by different $\delta^{13}C$-values (Suzuki et al., 2005). The ε-proteobacteria also use different sulfur compounds to act as electron-donors and electron-acceptors, and the γ-proteobacteria use two different sulfur-oxidizing pathways: a reverse sulfate reduction and a limited sulfur oxidation multienzyme system for their nutrition (Yamamoto and Takai, 2011). Radioisotope investigations from the gill showed an assimilation of CO_2, but no activity of CH_4 oxidizing bacteria (Galkin, 1997).

The black vent snail *Ifremeria nautilei* (Fig. 3b) is more widely distributed in the Pacific area, although it cannot be found in the Mariana Through. In the gill of these deep-sea provannid gastropod, methanotrophic and sulphur-oxidizing bacteria were found (Galchenko et al., 1992), showing that symbiotic bacteria may play a more significant role in the metabolism of this snail. Further investigations indicate, that they nutritionally dependent upon endosymbionts, which fall phylogenetically only into the lineage of γ-proteobacteria, maybe because of their dispersal capabilities (Suzuki et al., 2006b). They also show a high assimilation of CO_2, in addition to a high CH_4-oxidizing activity (Galkin, 1997).

Mussels of the genus *Bathymodiolus* (Mytilidae) are the common species in deep-sea hydrothermal vent systems worldwide (Van Dover et al., 2002), with the species *Bathymodiolus manusensis* (Fig. 3c) found in the Manus Basin (Hashimoto and Furuta, 2007). Their nutrition is also based on chemoautotrophic bacterial endosymbionts (Won et al., 2003), which also gain their energy from the oxidation of reduced compounds present in the hydrothermal fluids by sulphur- and methane-oxidizing bacteria located within the gill epithelial cells in the lateral zone of the gill filaments (Duperron et al., 2009; Duperron, 2010).

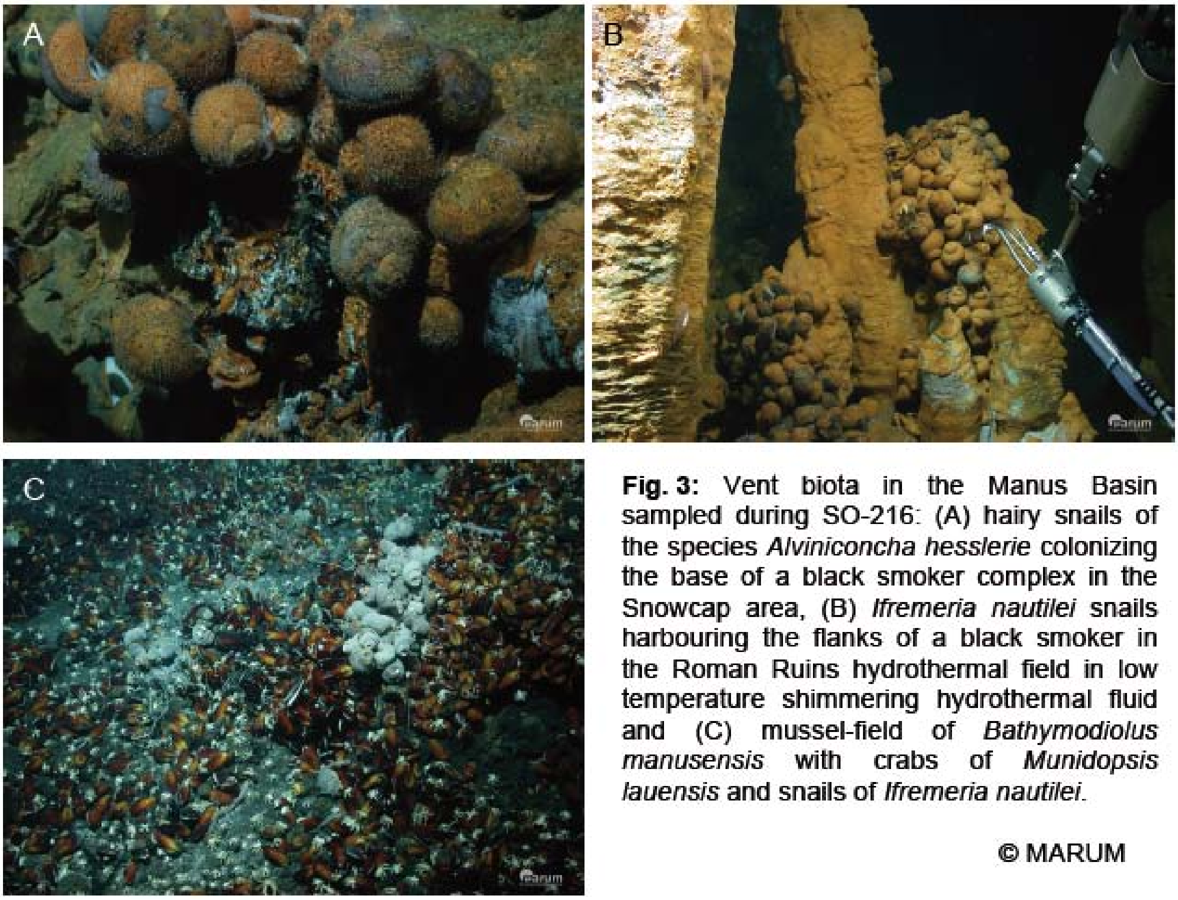

Fig. 3: Vent biota in the Manus Basin sampled during SO-216: (A) hairy snails of the species *Alviniconcha hesslerie* colonizing the base of a black smoker complex in the Snowcap area, (B) *Ifremeria nautilei* snails harbouring the flanks of a black smoker in the Roman Ruins hydrothermal field in low temperature shimmering hydrothermal fluid and (C) mussel-field of *Bathymodiolus manusensis* with crabs of *Munidopsis lauensis* and snails of *Ifremeria nautilei*.

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4. Materials and methods

4.1 Sampling and sample preparation

4.1.1 Fluids

Hydrothermal fluids from the PACMANUS and SuSu Knolls area were collected during *R/V Sonne* expedition SO216 in June and July 2011 using the remotely operated vehicle (ROV) QUEST 4000 m (MARUM) (Bach et al., 2011; Bach et al., 2012). Titanium isobaric gas-tight fluid samplers (IGT; Seewald et al., 2002) and the Kiel-Pumping-System (KIPS; Garbe-Schönberg et al., 2006) were mounted on and deployed from the ROV. An online temperature probe made of titanium was attached to the respective fluid inlets for in-situ temperature measurement during sampling (uncertainty ±2 °C) and an in situ mass spectrometer (ISMS; Wankel et al., 2010) was installed on the back of the ROV to gain real-time information of the different fluid characteristics like H_2S and CO_2 concentrations, as well as pH (at ambient seafloor conditions).

In total, 37 fluid samples were collected for chemical analysis, 24 by KIPS and 13 by IGT sampler, at the North Su, Fenway, Satanic Mills and Solwara 8 hydrothermal areas. The samples taken by IGT were recovered with gas tight syringes from the sampling device and samples from the KIPS were decanted into PET tubes avoiding headspace and immediately closed. Further processing was performed in a glove-bag under Ar-atmosphere, where the samples were filtered through an unreactive membrane filter (0.22 µm) and filled into 4 ml Polyvials® tubes (HDPE, Zinsser) avoiding headspace. One split from each sample was acidified with subboiled HCl for measuring As^T and another non-acidified for investigating As speciation. After carefully closing the tubes, they were removed from the glove bag and the split for As^T stored at 4 °C and the one for speciation immediately frozen at -80 °C. All samples were kept and transported cool or frozen and thawed shortly before the analysis started. Fluid parameters measured onboard upon sampler recovery were pH (25 °C, 1 atm), dissolved H_2 and Eh. Further splits were preserved by addition of HNO_3 for measuring major and trace elements.

4.1.2 Biota

Snails of the species *Alviniconcha hessleri* and *Ifremeria nautilei* and mussels of the species *Bathymodiolus manusensis* were collected from the hydrothermal areas with scoop nets manipulated by the mechanical arm of the ROV and transported in sealed boxes on the porch of the ROV during ascent and recovery of the ROV. Specimens were immediately opened onboard, cleaned with MilliQ and dissected into gill, muscle and digestive gland in the glove-bag under Ar-atmosphere. Samples were stored in 20 ml Polyvials® tubes under Ar-atmosphere and stored and transported frozen at -80 °C. In the laboratory, they were freeze-dried and homogenized with mortar and pestle and afterwards stored at room temperature until analysis.

4.2 Reagents, standards and Certified Reference Materials (CRM)

All solutions were prepared with double deionized water from a Millipore water purification system (MilliQ Advantage A10, 18 MΩ cm^{-1}), coupled to a Q-POD Element unit. Hydrochloric acid (HCl) and nitric acid (HNO_3) were purified with a Milestone acid sub-boiling system. Methanol (MeOH) and hydrogen peroxide

(H_2O_2, 30 %) of HPLC and suprapure grade were delivered by MERCK. Formic acid (CH_2O_2; p.a.), ammonium phosphate ($(NH_4)H_2PO_4$; s.p.) and pyridine (C_5H_5N; p.a.) were also purchased from MERCK.

Standard stock solutions (1000 mg L^{-1}) for arsenite (As^{III}) were prepared from As_2O_3 (Sigma Aldrich) dissolved in 4 g L^{-1} NaOH (Merck) and for arsenate (As^{V}) from $Na_2HAsO_4 \cdot 7H_2O$ (Sigma Aldrich) dissolved in water. Methylarsonate (MA) and dimethylarsinate (DMA) were prepared from $(CH_3)_2AsO(ONa)_2 \cdot 6H_2O$ (Chemservice) and from $(CH_3)AsO(ONa)_2 \cdot 6H_2O$ (MERCK), respectively, both dissolved in deionized water. Standards for arsenobetaine (AsBet) and arsenocholine (AC) were purchased from Sigma Aldrich and from Argus Chemicals. A CertiPur® multi-element standard solution (XVI, MERCK) containing 100 mg L^{-1} of several elements including As was used for measuring As^{T}. All stock solutions were stored at 4 °C and further dilutions were prepared on a daily base.

Two certified reference materials were used for quality control of the digestion, extraction and measurement procedure: a dogfish muscle (NRCC-DORM-2), certified for different trace elements, As^{T} (18.0 ± 0.1 mg kg^{-1}), AsBet (16.4 ± 1.1 mg kg^{-1}) and the tetramethylasonium ion (TETRA; 0.248 ± 0.054 mg kg^{-1}), in addition to a tuna fish tissue (BCR-627; Institute for Reference Materials and Measurements), certified for As^{T} (4.8 ± 0.3 mg kg^{-1}), AsBet (3.9 ± 0.2 mg kg^{-1}) and DMA (0.15 ± 0.02 mg kg^{-1}).

For identification of the phosphate- (PO_4-sug), sulfate- (SO_4-sug), sulfonate- (SO_3-sug) and glycerol-sugar (Gly-sug) by comparing retention times, an aliquot of freeze dried extract of *Focus serratus* containing these four sugars was used (Madsen et al., 2000), which Prof. Dr. K. A. Francesconi from the Karl-Franzens University in Graz (Austria) kindly provided.

4.3 Instruments

Sample digestion was performed using a temperature controlled Milestone Ethos digestion system with a microwave power of 1000 W. Concentrations of As^{T} was determined by using a Thermo Scientific iCAP Q inductive coupled plasma mass spectrometer (ICP-MS) and As speciation analysis were performed using a Thermo Scientific ELEMENT 2 high resolution inductive coupled plasma mass spectrometer (ICP-(HR)MS) coupled with an Accela 600 HPLC system. Performing anion exchange chromatography, a Hamilton PRP-X100 column (250 x 4.1 mm, 10 µm) was used, and for cation exchange, a Zorbax 300-SCX column (250 x 4.1 mm, 5 µm), both protected with guard columns, was used. Chromatographic conditions are given in Tab. 1. The ion intensity at m/z 75 ($^{75}As^+$) was monitored in low resolution (LR) and in high resolution (HR) mode to identify possible argon-chloride-interferences ($^{40}Ar^{35}Cl^+$). Scanning electron microscope (SEM) analyses were performed using a Zeiss SUPRA™ 40 FESEM with a XFlash® 6|30 EDX detector (BRUKER) and backscattered images taken at 15 and 20 kV.

Tab. 1: Chromatographic conditions for HPLC-ICP-(HR)MS measurments in the present study.

	Anion Exchange	**Cation Exchange**
Column	Hamilton PRP-X100 250 x 4.1 mm, 10 µm	Zorbax 300-SCX 250 x 4.6 mm, 5 µm
Mobile phase	20 mM $NH_4H_2PO_4$ pH: 5.8 (adj. with NH_4 aq)	20 mM pyridine pH: 2.6 (adj. with HCOOH)
Flow rate	1.5 ml min^{-1}	1.5 ml min^{-1}
Injection volume	20 µl	20 µl
Arsenic species analyzed	As^{III}, As^{V}, MA, DMA, PO_4-sug, SO_3-sug, SO_4-sug	AsBet, AC, TETRA, TMAP, Gly-sug

4.4 Procedures

4.1.1 Fluid major elements

Hydrothermal fluid samples were analyzed for Cl using ion chromatography (METHROM 883 IC Basic Plus) and for Mg using inductively coupled plasma optic emission spectrometry (Perkin Elmer Optima 3300 ICP-OES). A seawater reference material was used as internal standard (IAPSO K15), in addition to a certified reference material (CRM-SW).

4.4.2 Total Arsenic analysis

Concentration of As^T was measured using a Thermo Scientific iCAP Q ICP-MS and ^{115}In as internal standard. All samples were measured gravimetrically and in triplicate together with procedure blanks and CRMs. The different body parts of the mussels and snails were digested by giving 0.2 g aliquots of the samples and also from the CRMs (DORM-2 and CRM627) in digestion vessels and adding 5 ml of concentrated HNO_3 and 2 ml of H_2O_2. Samples were heated stepwise: for 2 min up to 80 °C, held there for 1 min, before heating to 110 °C for 2 min. Then, for 3 min from 110 to 140 °C, for 4 min from 140 to 180 °C, 6 min from 180 to 190 °C and as the final step, maintained for 12 min at 190 °C. Samples were cooled down, transferred into falcon tubes and diluted to 50 ml with double deionized water before storing at 4 °C. No visible residues were observed in the digestions vessels.

4.4.3 Arsenic speciation analysis

The different As species from the tissues were extracted by using 50 mg of each sample and also from the CRM materials and adding 5 ml of an N_2-purged MeOH/water mixture (1:1, v/v) in 20 ml PTFE tubes. Extraction was performed in triplicate and under Ar-atmosphere for 16 h at room temperature in an end-over-end shaker operating at 20 rpm. Afterwards, samples were centrifuged for 10 min at 4500 rpm and supernatants were filtered through a 0.22 µm unreactive nylon filter. All samples were stored at 4 °C and measured within hours by HPLC-(HR)ICP-MS. The different As species were identified by comparing the retention times with the prepared standards. TMAP and TETRA were identified by comparing with the retention times of the DORM-2 CRM and the different As-sug by comparison with the *Focus serratus* extract. The quantification was performed using the calibration curve of the closest As species in the chromatogram. The presence of thioarsenic species was investigated by adding hydrogen peroxide (H_2O_2).

Results for the standards DORM-2 and BCR-627 showed good agreement with the certified values. Extraction efficiency was above 90 % and the average column recovery in a good range between 78 and 86 %.

5. Results

5.1 Fluid samples

The fluid samples were collected at temperatures between 10.5 and 348 °C and yielded a pH (25 °C) between 1.35 and 7.02. Magnesium (Mg) concentrations for the hydrothermal fluids varied between 95 and 1 169 mg kg^{-1} and around 1 296 mg kg^{-1} for the local seawater (Tab. 2). The chloride (Cl) concentration revealed concentrations between 17 270 and 24 110 mg kg^{-1} with an average value of 18 840 mg kg^{-1} for the local seawater. Depending on the style of venting, i.e. black or white smoker, or shimmering clear fluids, the concentrations of iron (Fe), manganese (Mn) and sulfate (SO_4^{2-}) were either high or low. However, no "dreg" fraction (Trefry et al., 1994) could be observed, so that reported concentrations reflect the dissolved fractions only.

The concentration of total arsenic (As^T) ranged between 1.5 and 376.0 µg kg^{-1} (Tab. 2), with focused black smoker fluids from discrete orifices (Fig. 2a) revealing fairly low concentrations of As^T, between 1.5 and 12.5 µg kg^{-1} (n = 8; average 5.7 µg kg^{-1}). Clear fluids had As^T concentrations between 1.6 and 58.9 µg kg^{-1} (n = 18; average 15.1 µg kg^{-1}; Fig. 2b) and white hydrothermal fluids showed a wide range in As^T concentration between 2.3 and 376 µg kg^{-1} (n = 7; average 108 µg kg^{-1}; Fig. 2c). Because no trend with Mg could be observed, we assume a non-conservative behavior of As during water-rock interaction and fluid ascent and do not attempt to calculate endmember As concentrations.

Three different species were observed in 18 selected samples (11 KIPS, 7 IGT) with As^T concentrations between 1.5 µg kg^{-1} and 376.0 µg kg^{-1}: the two inorganic arsenite (As^{III}) and arsenate (As^V) in addition to one (or probably more) unidentified species with a broad peak and centered retention times between 5.08 and 6.72 min in six of these samples (Tab. 3). It could not be distinguished if this peak is neither always the same, nor if it is an artifact, but it was observed in the black and white smoker fluids, in addition to high proportions in two of the clear fluids. Recovery rates were in a good range between 45.8 and 113.4 %, with an average value of 90.5 % (Tab. 3).

Tab. 2: Characteristics and As^T concentrations of the different black, white and clear hydrothermal fluids.

Dive	Station	Sample	Fluid type	Location	T_{max} [°C]	pH	As [µg kg^{-1}]	Mg [mg kg^{-1}]	Cl [mg kg^{-1}]
301	19	IGT 7	black	North Su	332.0	3.27	12.45	371.9	24106
		KIPS 6	clear	North Su	58.1	4.73	32.70	1081.6	19391
302	21	IGT 3	clear	North Su	169.0	2.38	9.59	1057.3	20749
		KIPS 8	clear	North Su	39.6	7.02	3.95		19172
		KIPS 1	white	North Su	14.9	6.64	2.31		18795
304	23	IGT 3	white	North Su	90.0	1.35	341.63	1086.4	17273
		IGT 7	white	North Su	107.0	1.24	376.04	1037.8	16634
		KIPS 6		North Su	27.2	2.62	26.08	977.1	19275
306	27	IGT 7	clear	Snowcap/Tsukushi	224.0	3.96	23.53	648.9	19926
307	29	IGT 7	black	Fenway	304.0	2.38	1.51	228.2	22511
		KIPS 6	clear	Fenway	10.6	6.75	3.30	916.3	19702
308	31	KIPS 7	clear	Fenway	35.1	5.53	58.87	836.1	20700
		KIPS 5	clear	Fenway	10.5	6.00	3.38	1011.1	19220
		KIPS 2	clear	Fenway	15.1	5.89	5.57		19237
		IGT 7	black	Satanic Mills	345.0	2.99	4.39	345.1	13322
309	37	IGT 7	black	Roman Ruins	348.0	2.87	8.87	95.3	23442
		KIPS 6	clear	Roman Ruins	37.5	6.74	20.14		19478
		KIPS 3	clear	Roman Ruins	15.1	7.03	5.76	1156.9	
310	39	IGT 7	black	Roman Ruins	324.0	2.64	6.78	128.6	25603
311	41	IGT 7	black	Fenway	313.0	2.68	3.53	286.8	19371
		KIPS 8	clear	Fenway	87.7	5.22	5.10	1142.3	17570
		KIPS 6	clear	Fenway	22.0	6.19	2.14	1118.0	19708
		KIPS 1	clear	Fenway	110.0	5.07	8.64	1054.8	18326
312	43	IGT 7	black	Fenway	339.0	2.78	1.98	115.9	21711
		KIPS 8	clear	Fenway	21.6	6.12	1.58		19708
		KIPS 5	clear	Fenway	26.8	6.21	12.74		18538
313	45	KIPS 5	clear	North Su	73.2	3.53	26.38	1101.0	19780
314	47	IGT 7	white	North Su	100.0	1.86	8.85	991.6	20010
		KIPS 8	white	North Su	94.5	2.39	2.31	994.1	19500
		KIPS 5	white	North Su	63.8	2.87	8.22	1096.2	19748
		KIPS 1	clear	North Su	78.0	6.03	26.01		19444
315	49	IGT 3	black	Solwara 8/Fenway	305.0	2.95	6.45	172.1	20331
316	51	KIPS 8	clear	North Su	78.4	5.38	3.66	972.2	19657
		KIPS 5	white	North Su	42.6	2.16	16.95	1169.1	20025
298	12	KIPS 2	seawater	average	3.4	7.2	1.7	1295.5	18837

Tab. 3: Results for As^T and As species from selected hydrothermal fluids.

Dive	Station	Fluid	As [µg kg^{-1}]	As^{III} [µg kg^{-1}]	As^V [µg kg^{-1}]	UNKNOWN [µg kg^{-1}]	RT [min]	Σ SPECIES [µg kg^{-1}]	Recovery [%]
302	KIPS 1	white	2.31	0.17	1.95			2.12	91.7
304	IGT 3	white	341.63	168.95	218.53			387.48	113.4
	IGT 7	white	376.04	154.90	178.13			333.03	88.6
	KIPS 6	clear	26.08	15.29	3.45	9.90	5.08	28.65	109.8
306	IGT 7	clear	23.53	1.06	11.08	12.38	5.20	24.51	104.2
307	IGT 7	black	1.51	0.20	0.86			1.06	70.1
308	KIPS 7	clear	58.87	37.98	3.61			41.59	70.6
	KIPS 5	clear	3.38	1.19	2.22			3.41	100.9
	KIPS 2	clear	5.57	3.18	1.96			5.14	92.2
	IGT 7	black	4.39	1.12	0.90	0.64	5.65	2.65	60.4
309	IGT 7	black	8.87	2.04	1.03	0.99	6.73	4.06	45.8
	KIPS 6	clear	20.14	9.46	10.61			20.07	99.7
311	IGT 7	black	3.53	0.50	n.d.	2.25	6.04	2.75	77.8
	KIPS 1	clear	8.64	7.81	0.76			8.57	99.2
312	KIPS 5	clear	10.28	5.39	5.33			10.73	104.3
314	KIPS 8	white	2.31	0.65	0.61	0.92	5.70	2.18	94.2
	KIPS 1	clear	26.01	24.52	1.99			26.51	101.9
316	KIPS 8	clear	3.66	3.06	0.77			3.83	104.6

Note: n.d.: not detecable; RT: retention time

5.2 Hydrothermal vent biota

Hydrothermal vent animals accumulate different portions of As and other elements in the different organs as shown in Tab. 4. The highest concentration of As^T was found in the snail *Alviniconcha hessleri* (Fig. 3a) with 5 580 ± 14 mg kg^{-1} measured in the gill, 721 ± 7 mg kg^{-1} in the digestive gland and 43.3 ± 1.5 mg kg^{-1} in the muscle tissue. The snail *Ifremeria nautilei* (Fig. 3b) accumulated As^T concentrations of 118.3 ± 1.2 mg kg^{-1} in the gill, 107.6 ± 1.6 mg kg^{-1} in the digestive gland and 21.7 ± 0.4 mg kg^{-1} in the muscle tissue. Concentrations of As^T in the different parts of the mussel *Bathymodiolus manusensis* (Fig. 3c) were much lower with 15.7 ± 0.5 mg kg^{-1} in the digestive gland, 9.8 ± 0.2 mg kg^{-1} in the gill and 4.5 ± 0.1 mg kg^{-1} in the muscle tissue.

Selenium, lead and cadmium reflect this trend with the highest concentrations always found in the gill of *Alviniconcha hessleri*, in contrast to high concentrations of iron, manganese, chromium and copper found in the digestive gland. The snail *Ifremeria nautilei* and the mussel *Bathymodiolus manusensis* always revealed the highest concentrations of the different elements in the digestive gland, followed by the gill and the muscle tissue (Tab. 4). These showed good correlations when plotting the different elemental concentrations in the organs against each other (r^2: 0.85 – 0.99).

Speciation analysis revealed 8 different As species in variable proportions. In addition to the inorganic As^{III} and As^V species, smaller amounts of dimethylarsinic (DMA), SO_4-sugar, arsenobetaine (AsBet), trimethylarsoniopropionate (TMAP), arsenocholine (Ac) and tetramethylasonium ion (TETRA) were found (Tab. 5). The sum of the inorganic As^{III} and As^V species ranged between 32 and 99 % for the snails and between 8 and 33 % of total As species for the mussel. In addition, higher concentrations of AsBet were also observed in all samples along with smaller amounts of DMA, SO_4-sugar, TMAP, Ac and TETRA, which were not observed in all samples.

The extraction efficiencies (ratios of As^T in the digestions and As^T in the methanol-water extracts) were around 48 % for *Alviniconcha hessleri*, 22 % for *Ifremeria nautilei* and 51 % for *Bathymodiolus manusensis*. The column recoveries (ratios between As^T of the methanol-water extracts and the sums of the species) were generally higher and averaged 70 % for *Alviniconcha hessleri*, 89 % for *Ifremeria nautilei*, and 52 % for *Bathymodiolus manusensis*, respectively (Tab. 5).

Tab. 4: Concentrations of different elements for the two snails *Alviniconcha hessleri* and *Ifremeria nautilei* and the mussel *Bathymodiolus manusensis*, as well as for the two CRMs.

Vent animal/ Ref material	**organ**	**As** [$\mu g\ kg^{-1}$]	**Cr** [$mg\ kg^{-1}$]	**Mn** [$mg\ kg^{-1}$]	**Fe** [$mg\ kg^{-1}$]	**Co** [$mg\ kg^{-1}$]	**Cu** [$mg\ kg^{-1}$]	**Se** [$mg\ kg^{-1}$]	**Cd** [$mg\ kg^{-1}$]	**Pb** [$mg\ kg^{-1}$]
Alviniconcha	DG	721 ± 7	6.9 ± 0.3	262 ± 7	4627 ± 438	2.4 ± 0.3	11270 ± 130	23.7 ± 1.1	139 ± 6	6742 ± 308
hessleri	Gill	5580 ± 14	2.1 ± 0.04	56.0 ± 0.9	1081 ± 16	0.18 ± 0.01	2818 ± 53	27.1 ± 1.2	204 ± 2	11770 ± 650
	Muscle	43.3 ± 1.5	0.9 ± 0.05	11.1 ± 0.3	168 ± 7	0.6 ± 0.1	255 ± 3	7.2 ± 0.2	1.6 ± 0.1	125 ± 12
Ifremeria	DG	107.6 ± 1.6	39.6 ± 0.9	257 ± 17	2967 ± 336	0.09 ± 0.01	1993 ± 53	10.6 ± 0.7	476 ± 17	476 ± 17
nautilei	Gill	118.3 ± 1.2	13.7 ± 1.0	67.4 ± 1.8	1927 ± 25	0.1 ± 0.01	210 ± 2	5.0 ± 0.01	252 ± 3	252 ± 3
	Muscle	21.7 ± 0.4	7.4 ± 0.3	14.0 ± 0.2	1517 ± 16	0.1 ± 0.01	126 ± 6	4.95 ± 0.07	26.7 ± 0.6	26.7 ± 0.6
Bathymodiolus	DG	15.7 ± 0.5	2.4 ± 0.1	40.3 ± 2.5	498 ± 25	2.3 ± 0.5	84.1 ± 3.3	10.2 ± 0.3	3.4 ± 0.8	3.4 ± 0.8
manusensis	Gill	9.8 ± 0.2	1.1 ± 0.06	15.2 ± 1.8	150 ± 6	0.14 ± 0.01	50.8 ± 1.1	7.7 ± 0.1	3.0 ± 0.1	3.0 ± 0.1
	Muscle	4.5 ± 0.1	0.6 ± 0.07	3.8 ± 0.3	55.8 ± 2.8	0.13 ± 0.02	7.6 ± 0.6	5.2 ± 0.2	0.54 ± 0.04	0.54 ± 0.04
DORM 2		16.1 ± 0.4	29.4 ± 1.2	3.4 ± 0.2	148 ± 24	0.15 ± 0.01	2.11 ± 0.08	1.7 ± 0.3	0.043 ± 0.02	0.080 ± 0.013
DORM 2 *certf.*		18.0 ± 1.1	34.7 ± 5.5	3.66 ± 0.34	142 ± 10	0.18 ± 0.03	2.34 ± 0.16	1.4 ± 0.3	0.043 ± 0.08	0.065 ± 0.007
Tuna		4.1 ± 0.2	0.5 ± 0.1	1.02 ± 0.07	88 ± 10	0.05 ± 0.02	2.46 ± 0.11	2.6 ± 0.22	0.22 ± 0.03	0.58 ± 0.06
Tuna *certf.*		4.8 ± 0.3	n.c.	n.c.	n.c.	n.c.	n.c.	n.c.	n.c.	n.c.

Note: DG: Digestive Gland; n.c.: not certified

Tab. 5: Arsenic species distribution (n=3) for the two snails *Alviniconcha hessleri* and *Ifremeria nautilei* and the mussel *Bathymodiolus manusensis* and the two CRMs, as well as extraction efficiency and colum recovery.

Vent animal/ Ref material	**organ**	**As^T** [µg kg^{-1}]	**Extraction efficiency** [%]	**Colum recovery** [%]	**As^{III}** [mg kg^{-1}]	**As^V** [mg kg^{-1}]	**DMA** [mg kg^{-1}]	**So_4-sug** [mg kg^{-1}]	**AsBet** [mg kg^{-1}]	**TMAP** [mg kg^{-1}]	**Ac** [mg kg^{-1}]	**TETRA** [mg kg^{-1}]	**Σ SPECIES** [mg kg^{-1}]
Alviniconcha	DG	721 ± 7	30.1	86.4	153.24	29.41	0.0	1.41	3.46	0.0	0.0	0.0	187.52
hessleri	Gill	5580 ± 14	56.1	84.7	2580.37	60.07	0.0	6.71	4.04	0.0	0.0	0.0	2651.19
	Muscle	43.3 ± 1.5	58.3	38.4	4.65	0.95	0.0	0.0	4.09	0.0	0.0	0.0	9.69
Ifremeria	DG	107.6 ± 1.6	20.9	97.6	18.01	2.23	0.0	0.0	1.31	0.15	0.15	0.0	21.89
nautilei	Gill	118.3 ± 1.2	28.6	87.9	23.89	2.98	0.28	0.0	2.64	0.0	0.0	0.0	29.79
	Muscle	21.7 ± 0.4	17.1	80.6	0.94	0.0	0.0	0.0	1.84	0.20	0.0	0.0	2.98
Bathymodiolus	DG	15.7 ± 0.5	40.6	50.0	0.71	0.33	0.80	0.0	1.22	0.10	0.0	0.03	3.19
manusensis	Gill	9.8 ± 0.2	44.7	50.2	0.47	0.11	0.46	0.0	1.01	0.05	0.0	0.10	2.20
	Muscle	4.5 ± 0.1	66.4	55.9	0.14	0.0	0.0	0.0	1.53	0.0	0.0	0.0	1.67
DORM 2		16.1 ± 0.4	95.2	86.2					14.75			0.12	
DORM 2 *certf.*		18.0 ± 1.1							16.4				
Tuna		4.1 ± 0.2	91.3	77.9			0.26		3.15				
Tuna *certf.*		4.8 ± 0.3					0.15		3.9				

Note: DG: Digestive Gland

6. Discussion

6.1 Hydrothermal vent fluids

Hydrothermal fluids emanating at the seafloor are able to transport a considerable amount of the potentially toxic element arsenic (As) into the oceans (Breuer and Pichler, 2012) and can act as a – probably until today underestimated – substantial net source for this element in the ocean's As budget. The concentration of As^T in the hydrothermal fluids strongly depends on the tectonic setting, with the most important influencing parameters being temperature, pH, pressure, different redox reactions, composition and mineralogy of the host rock, as well as the metal, H_2S and gas concentration.

Concentrations of total arsenic (As^T) in hydrothermal fluids from the PACMANUS and SuSu Knolls areas ranged between 1.5 and 376.0 µg kg^{-1} (Tab. 2). These values are up to 200-times enriched relative to seawater, but similar to values from other hydrothermal systems investigated in the Manus back-arc basin such as at Vienna Woods (6.3 to 23.2 µg L^{-1}), Satanic Mills (1 210 to 1 390 µg L^{-1}) and Desmos (10.2 µg L^{-1}) (Douville et al., 1999). Various other hydrothermal fluids sampled in back-arc basins are in the same range, typically showing several hundred µg L^{-1} of As. Concentrations in fluids from mid-ocean ridges are generally lower with several tens of µg L^{-1} and hydrothermal fluids from island arc setting in general higher with several thousand µg L^{-1} (Breuer and Pichler, 2012).

The concentration of As^T in the hydrothermal fluids strongly depends on the style of venting. Black smoker fluids, mostly sampled in the PACMANUS area, contained large amounts of metals like Fe and Mn, and were mostly very low in As^T with values between 1.5 and 12.4 µg kg^{-1} (average 5.7 µg kg^{-1}, n = 8, Tab. 2). These low concentrations are very likely due to the formation and precipitation of Fe-Mn-S-As minerals like arsenopyrite (FeAsS) in the subseafloor and upon sampling, when the vent fluids mix with the ambient cold and oxygenized seawater, changing physicochemical conditions within seconds.

Clear fluids revealed much lower metal concentrations, but showed higher As^T concentrations between 1.6 and 58.9 µg kg^{-1} with an average value of 14.7 µg kg^{-1} (n = 18), because lesser minerals are precipitated and so, lesser As extracted from the fluids. Furthermore, the mixing of hydrothermal fluids with cold seawater as well as efficient zone refining (Pinto et al., 2005) with the precipitation of As could be reasons for the overall lower concentrations of As in the fluids.

Compared to these two kinds of fluids, sulfur-rich white smoker fluids, which were taken at the North Su site, revealed very variable As^T concentrations between 2.3 and 376 µg kg^{-1} (Tab. 2). The two white smoker samples showing the highest concentrations by far were collected at the newly found “Sulfur Candles” site in the North Su area (Dive 304, IGT 3 & 4) from a 90 and 107 °C hot and very low-pH focused white smoker. These data suggests that a high amount of dissolved gases and a very low pH and low concentration of metals leads to a high concentration of As^T in the hydrothermal fluids. A contribution of As-rich magmatic fluids rising from a deep magma chamber, which might also be responsible for the low pH and high gas concentrations, is very likely.

Calculations of As endmember concentrations in vent fluids are difficult, because of the non-conservative behavior of As during fluid ascent and sampling and the additional metal and As-rich component from magmatic degassing (Yang and Scott, 1996). Varying Cl concentrations in the fluids, higher and lower than in the surrounding seawater (18 837 mg L^{-1}), indicate phase separation and segregation of the fluids into a Cl-poor gas rich vapor phase and a Cl-rich and gas poor liquid phase. Arsenic, like Cu and Au, is predicted to portion into the vapor phase due to HS-complexation. Elements such as Na, K, Fe and Mn should portion into the brine phase as Cl-complexes (Heinrich et al., 1999). This portioning behavior is still a matter of debate and the underlying mechanisms are poorly understood (Pokrovski et al., 2005). However, when plotting the Cl against the As concentrations (Fig. 4), three different trends could be observed: a low Cl vapor phase and a high Cl brine phase, which were both fairly enriched in As^T compared to seawater, in addition to a magmatic trend with Cl concentrations around seawater and highly enriched in As^T. In both, the low and high Cl fluids, As might only be delivered by leaching from the basement, but the magmatic fluids might deliver volatile As directly from the underlying magma chamber, accounting for the high concentrations of As in the white smoker fluids.

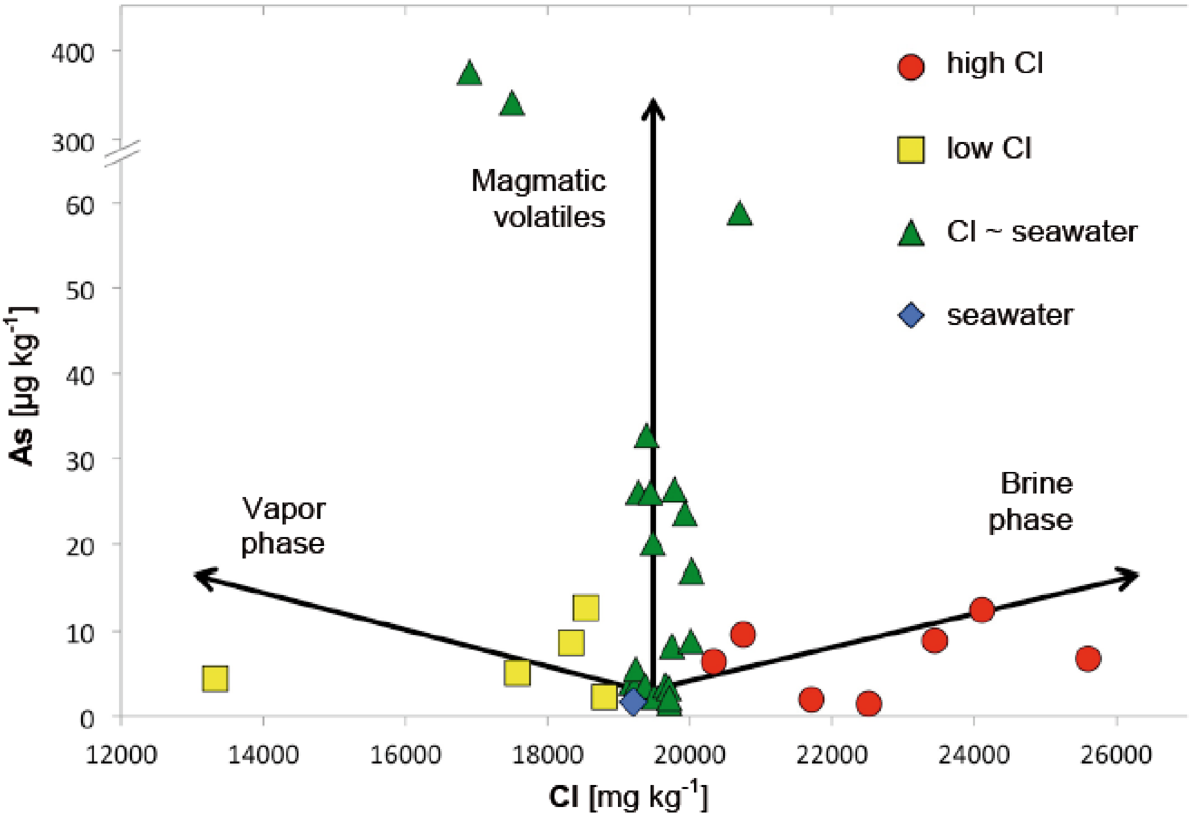

Fig. 4: As^T vs. Cl concentration for the hydrothermal fluids from the different sample locations showing a vapor, brine, and magmatic trend

Data for As speciation are not available for deep-water hydrothermal systems at all, but thermodynamic modeling showed that considerable amounts of the pentavalent As species $H_2AsO_4^-$ should be present despite low ph and Eh conditions (Breuer and Pichler, 2012). These calculations also show the preferential precipitation of orpiment (As_2S_3) and scorodite ($FeAsO_4 \cdot 2H_2O$), when H_2S and Fe are sufficient available. Speciation measurements revealed the two inorganic arsenite (As^{III}) and arsenate (As^V) species in variable proportions as predicted, in addition to one unknown species. However, no trend with temperature or other elements with species distribution could be observed. When the hydrothermal fluids mix with oxygenized seawater, thioarsenic species, which are potentially present in the hydrothermal fluids, quickly degrade into the inorganic As^{III}, which is then oxidized to As^V. No thioarsenic species could be found in these samples thought they were preserved in the best way possible and these are systems high in sulfide.

Recoveries of the species compared to As^T showed typical values for this kind of measurement between 46 and 113 %, with the recovery of the black smoker fluids being mostly very low. This was maybe because samples for speciation were just cryofrozen and not acidified compared to samples for As^T, as the pH directly influences the species distribution. The precipitation of small Fe-S-As particles could not be avoided before measurement during thawing, but anyway, this process was not observed visually in the lab during sample preparation, but could also happen in the column during separation.

6.2 Hydrothermal vent biota

6.2.1 Total As

Snails of the species *Alviniconcha hessleri* and *Ifremeria nautilei* as well as bivalves of the species *Bathymodiolus manusensis* living in the hydrothermal mixing zones are evidently able to bioaccumulate and transform high amounts of different metals and As in their tissues. The accumulated concentration strongly depends on the concentration and species in the fluids from the proximal environment, but also on the special metabolism performed by the organisms. This process is affected by chemosynthesis and different As and nutrient uptake mostly related to sulfide- and methane-oxidizing Gammaproteobacteria located in specialized epithelial cells within the gill (Duperron, 2010) compared to the mechanisms observed from animals living in photic zones. Coastal bivalves from non-polluted areas incorporate in general less than 10 mg kg^{-1} of As and snails less than 50 mg kg^{-1} (Neff, 1997; Neff, 2002).

The highest concentration of As^T was found in the gill of *Alviniconcha hessleri* (5 580 mg kg^{-1}) sampled in the Fenway area. These snails were living in clear fluids with the highest temperature (T_{max} = 26.8 °C), lowest pH of 6.2, as well as the highest concentration of As^T (12.7 µg kg^{-1}). Furthermore, up to 721 mg kg^{-1} were accumulated in its digestive gland and 43 mg kg^{-1} of As were detected in the muscle tissue (Tab. 5, Tab. 6). No comparable values were published to date for those kind of animals and only one hydrothermal snail (*Peltospira smaragdina*) was investigated before from the Lucky Strike hydrothermal field, showing As^T concentrations of up to 67.8 mg kg^{-1} (Taylor et al., 2012). The high amount of As in the gill, where other studies already revealed elemental sulfur (Stein et al., 1988), might be due to the formation of small suspended Fe-Zn-S-As-particles, which precipitate and accumulate when the hydrothermal fluid is filtered through the fine filaments of the gill. During scanning electron microscope analyses, those fine particles were found attached to the gill filaments, but also as coating on the organic material. These revealed a considerable amount of As most likely responsible for the high concentration of As^T found in the gill (Fig. 5, Fig. 6). Particles and coatings could be most likely sulfide minerals such as sphalerite (ZnS), pyrite (FeS_2), arsenopyrite (FeAsS), or orpiment (As_2S_3), all containing significant amounts of As. Furthermore, those particles cannot be leached during methanol-water washing, but they do get completely dissolved during acid digestion, explaining the low extraction efficiencies. Uptake of elements due to the dissimilatory activity of the chemolithoautotrophic bacteria in the gill or uptake via the essential phosphate transport system are alternative and additional explanations for the high As concentrations in the gill. The elevated amount of As in the digestive gland on the other hand, may be because as it acts as a pathway and especially storage organ for different elements and nutrients. However, the digestive gland is lesser involved in the nutrition cycle and metabolism because of the different symbiosis techniques and accordingly also reduced in size (Stein et al., 1988). Comparable low amounts of As^T in the muscle tissues is likely because of the lesser involvement in all these exchange and nutrition processes and the only indirect contact to the high As fluids.

Tab. 6: Sampling locations and concentration of As^T (n=3), for the two snails *Alviniconcha hessleri* and *Ifremeria nautilei* and the mussel *Bathymodiolus manusensis* as well as the characteristics of the fluids they live in.

Vent animal/ Ref material	Location/ depth	organ	$As_{ORGANISM}$ [mg kg^{-1}]	As_{FLUID} [µg kg^{-1}]	T_{FLUID} [°C]	pH_{FLUID}
Alviniconcha	Fenway area	DG	721 ± 7			
hessleri	003° 43.687’ S 151° 40.163’ E	Gill	5580 ± 14	12.7	26.8	6.21
	-1648 m	Muscle	43.3 ± 1.5			
Ifremeria	Roman Ruins	DG	107.6 ± 1.6			
nautilei	003° 43.238’ S 151° 40.519’ E	Gill	118.3 ± 1.2	5.8	15.1	7.03
	-1685 m	Muscle	21.7 ± 0.4			
Bathymodiolus	Fenway area	DG	15.7 ± 0.5			
manusensis	003° 43.699’ S 151° 40.347’ E	Gill	9.8 ± 0.2	3.3	10.6	6.75
	-1706 m	Muscle	4.5 ± 0.1			

Note: DG: Digestive gland

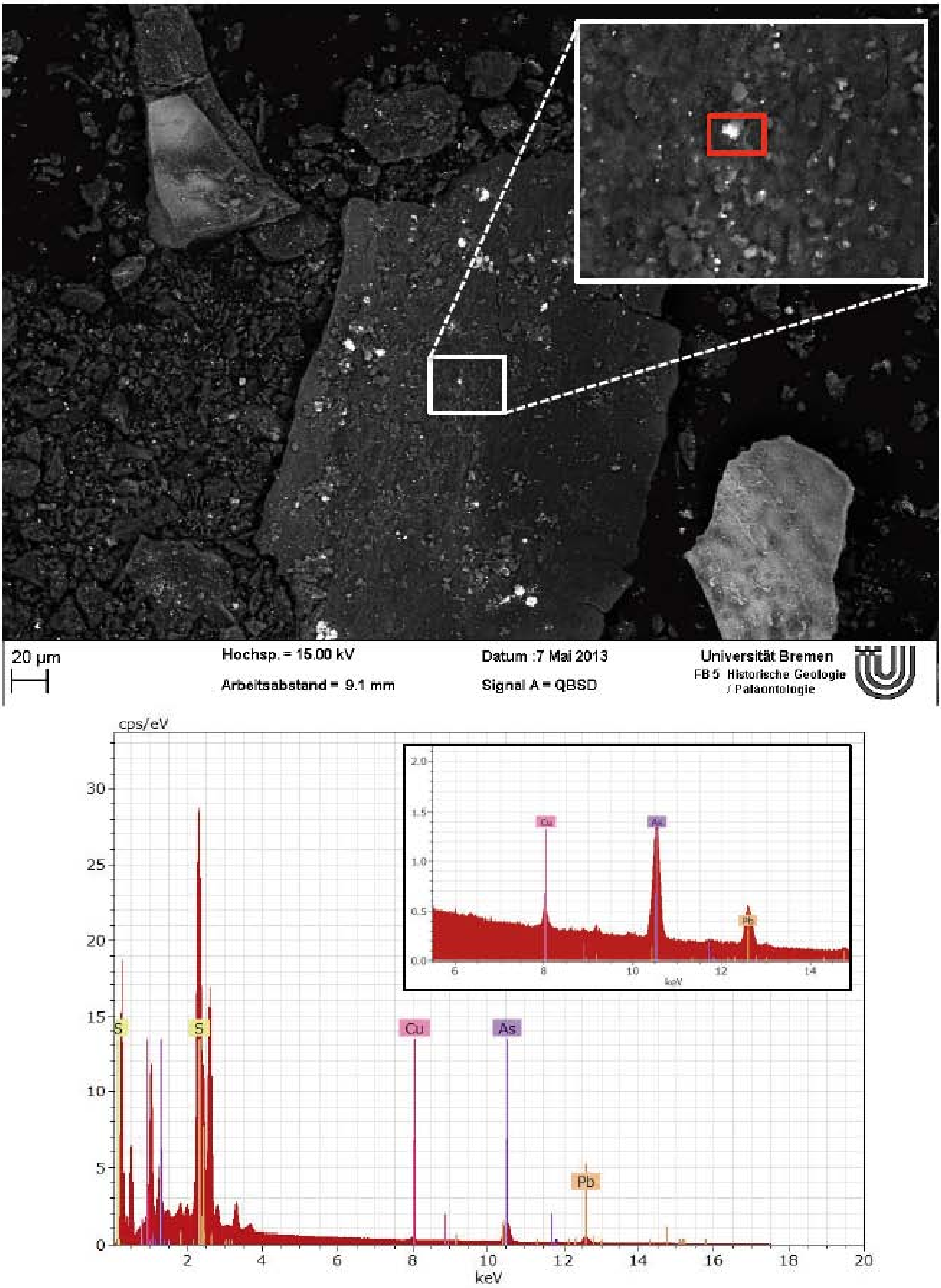

Fig. 5: Scanning electron microscopy analysis of the gill filaments from *Alviniconcha hessleri* showing different small and randomly distributed particles dominantly made of S and As (most likely orpiment, As_2S_3), as well as minor Cu and Pb, attached to the organic material. EDX analyses were performed from the white particle in the red box in the magnification above.

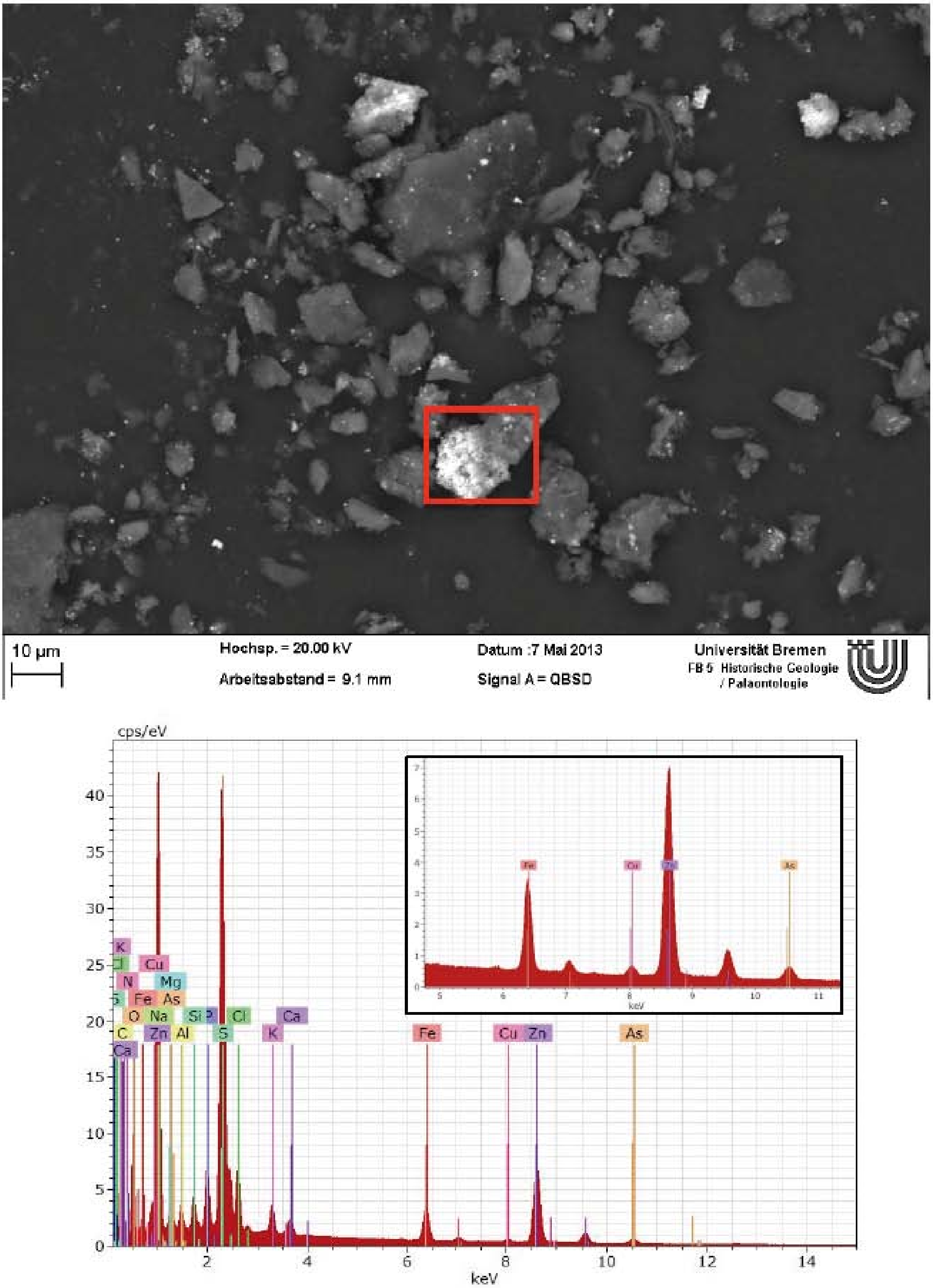

Fig. 6: Scanning electron microscopy analysis of the gill filaments from *Alviniconcha hessleri* showing a coating by high amounts of S, Zn, Fe and As (most likely sphalerite, (Zn,Fe)S) on the organic material in addition to smaller particles attached to the gill material.

The snails of the species *Ifremeria nautilei* were sampled at the Roman Ruins vent site living in lower temperature (T_{max} = 15.1 °C) and lower As (5.8 µg kg^{-1}) hydrothermal fluid. These accumulated lower concentrations of As^T, with 118.3 mg kg^{-1} in the gill, 107.6 mg kg^{-1} in the digestive gland and 21.7 mg kg^{-1} in the muscle tissue (Tab. 5, Tab. 6), showing the same pattern like *Alviniconcha hessleri*, resulting in the same explanation, but with lower amounts of accumulated particles. The hydrothermal vent mussel *Bathymodiolus manusensis* collected at the Fenway hydrothermal field showed significant lower As^T concentrations than the two snails with 15.7 mg kg^{-1} in the digestive gland, 9.8 mg kg^{-1} in the gill and 4.5 mg kg^{-1} in the muscle tissue. Also, the concentration of As^T (3.3 µg kg^{-1}) and the temperature (T_{max} = 10.6 °C) of the fluids the mussels lived in are lower (Tab. 6). The concentrations of As^T found in *Bathymodiolus manusensis* are similar to those in mussels of the species *Bathymodiolus azoricus* from the Menez Gwen hydrothermal field. These specimens had As^T concentrations of 19.0 mg kg^{-1} in their digestive gland, 14.9 mg kg^{-1} in their gill and 5.3 mg kg^{-1} in their muscle tissue (Breuer et al., in review for DSR1).

All in all, it can be shown that *Alviniconcha hessleri* seems to be more resistant against high concentrations of As^T in the fluids than *Ifremeria nautilei* and *Bathymodiolus manusensis*. Concerning the concentrations of Cr, Mn, Fe, Co and Cu, the highest amount was always found in the digestive glands acting as pathway and storage organ for these elements, contrasting Cd and Pb, where high concentrations were also found in the gills connected to the accumulation of different As-rich particles (Tab. 4). The reason for this overall selective accumulation remains unclear, but perfect correlations of Fe, Mn, Cr and Co for the different organs of the respective animals indicate that take-up mechanisms may be remarkably similar for these elements.

The extraction efficiency of approximately 48 % in tissues of *Alviniconcha hessleri*, 22 % in *Ifremeria nautilei* and 51 % in *Bathymodiolus manusensis* is low, but similar to other numbers reported for marine animals (e.g. Shibata and Morita, 1992; Lai et al., 2012). The overall lower efficiency might be also due to the presence of different non-extractable polar arsenicals or precipitation of different particles in the organs.

6.2.2. As speciation

Speciation analysis can help to interpret and understand the cycling and transformation of As in this extreme environment as the vent biota metabolism is different from organisms living in the freshwater and seawater photic zone. Results are given in Tab. 5, revealing that the major As components in the snails are the inorganic arsenite (As^{III}) and arsenate (As^{V}) species, in addition to smaller but constant amounts of arsenobetaine (AsBet). Furthermore, dimethylarsinic acid (DMA), sulfonate-sugar (SO_4-sug), trimethylarsoniopropionate (TMAP), arsenocholine (Ac) and tetramethylasonium ion (TETRA) could be observed in some of the samples. There are no comparable values reported in the literature for hydrothermal vent snails and mussels like the ones sampled here.

AsBet, which is known since 50 years, is preferentially bioaccumulated by higher marine organisms like fish, snails and mussels, and the dominant compound over other organoarsenic compounds in this organisms (e.g. Kaise et al., 1988; Ochsenkühn-Petropulu et al., 1997; Azizur Rahman et al., 2012). Derivates of dimethylarsinoylribisides and trimethylarsinoribosides, also called arsenosugars (As-sug), which are only present as sulfonate-sugar (SO_4-sug) in low proportions in the snail *Alviniconcha hessleri*, are the common and dominant species in marine seagrasses and algae. AsBet and As-sug are a lot less toxic than the inorganic forms As^{III} and As^{V} (Edmonds and Francesconi, 1981; Niegel and Matysik, 2010). Some recent studies also revealed low concentrations of AsBet in different algae (Slejkovec et al., 2006; Grotti et al., 2008), but this could be related to incorrect sample pre-treatment by not removing epiphytes.

Those algae play a key role in As cycling in the marine environment because they act as food source for higher organisms, but their exact mechanism for As uptake from the surrounding seawater is only poorly understood. A possible and general accepted way could be the uptake of As^{V} from the surrounding seawater via the essential phosphate transport system into the cell membranes (Rosenberg et al., 1977). Then, the As^{V} is reduced by arsenate reductases enzymes to As^{III} (Mukhopadhyay et al., 2002), because this form is more mobile in the cells and As^{V} is known to interfere with several metabolic processes like the oxidative phosphorylation (Slater, 1963). Further detoxification steps are characterized by multioxidative and sequential methylation and reduction due to microorganism to methylarsonic acid (MA) and further to dimethylarsinic acid (DMA) and trimethylarsine (TMA) as described by the “Challenger pathway” (Challenger, 1945; Challenger, 1955). However, since several years, it becomes clear, that this is not the only possible way forming organic As compounds in marine algae. Another pathway can be described by transferring the adenosyl-group of the methylation agent to the As-atom after forming DMA and eliminate the last step forming TMA (Edmonds and Francesconi, 1987). After that, different kinds of As-sug such as the sulfonate-, sulfate-, phosphate- and glycerol-sugar can be formed by adding methyl-groups, which are thought to be an endproduct in marine algae.

Even though primary producers like marine algae can accumulate their As from the surrounding seawater, consuming higher organisms such as bivalves and snails are theoretically able to take it up from both: the surrounding seawater and from algae through the food-chain (Edmonds and Francesconi, 2003). However, they have only limited ability to take up inorganic As from the seawater and prefer the accumulation mechanism via the foodweb (Azizur Rahman et al., 2012). It is thought that the As-sug produced, preconcentrated and transformed by marine algae are some kind of precursor for AsBet and arsenocholine (AsC) in higher marine organisms (Hansen et al., 2003). Algae are not or only sparsely available in this depth by filtering and chemolithoautothropic bacteria are the major nutrition for animals living in this environment. Only a small amount of As-sug could be observed in the gill of *Alviniconcha hessleri*, probably due to filtering of organic material, but in *Ifremeria nautilei* as well as *Bathymodiolus manusensis*, no sugars could be observed at all. So, there might be other pathways for the formation of organoarsenicals like AsBet found in the snails and mussels than via the accumulation of sugars delivered by algae, which could be connected to the autotrophic and symbiotic bacteria located in the gills of the organisms.

Another reason for the high amount of inorganic As, dominantly found as As^{III} and As^{V}, could be the high concentration of inorganic and reduced As in the low pH fluids and overstressing of detoxificaition processes and comparable slow methylation processes. Detoxification is normally performed by binding to metallothioneins or incooperation in metabolic insoluble granules (Morgan et al., 2007). DMA seems to be bypassed as an intermediate product and immediately and fully utilized to As-sug and/or AsBet.

Compared to mussels of the species *Bathymodiolus azoricus* from the Menez Gwen hydrothermal field, which have a high concentration of As-sug and a comparable low amount of AsBet, no As-sug could be observed in the mussels *Bathymodiolus manusensis*, despite their nutrition should be comparable. This might be due to the different depth of the mussels and the availability of organic material as Menez Gwen is located in around 850 m water depth and *Bathymodiolus manusensis* lives in around 1700 m water depth.

7. Conclusions

We presented novel and combined data for As^T and As speciation for black, white and clear hydrothermal fluids from the Manus Basin and three different vent organisms living in the immediate vicinity of these fluids, separated into gill, muscle and digestive gland. Hydrothermal fluids were up to 348 °C hot and revealed maximum As^T concentrations of 376 $\mu g\ kg^{-1}$ in low pH and white gas-rich fluids emanating with temperatures around 100 °C. Black smoker fluids had in general lower As concentrations because of precipitation of As-bearing minerals with high amounts of Fe, Mn and S transported with the fluids already in the subseafloor, but also immediately when mixing with the surrounding oxygenated seawater. The shimmering fluids as a mixture of hot hydrothermal fluids and cold seawater showed concentrations lower that the hot white fluids but higher that the black smoker fluids. Three different trends could be observed when plotting As against Cl concentrations with fairly enriched vapor and brine phases and a highly enriched magmatic phase with Cl concentrations close to seawater. Only the two inorganic arsenite and arsenate species could be observed in the fluids.

Hydrothermal vent fauna living in the warm mixture of hydrothermal fluids and oxygenated seawater are able to accumulate and transform As emanating with the fluids. Up to 5 580 $mg\ kg^{-1}$ could be found in the gill tissue of *Alviniconcha hessleri* due to the accumulation of inorganic Fe-Zn-S-As particles as observed during scanning electron microscope analysis, but also due to the very special nutrition performed by the chemolithoautothropic bacteria and uptake via the essential phosphate transporter pathway system. The accumulation of small inorganic particles could also be confirmed by low extraction efficiencies of around 50 % and lower, because these particles can only hardly be leached during methanol-water extraction. Higher amounts of As^T were also found in the digestive gland, which serves as a pathway and storage organ. *Alviniconcha hessleri*, accumulating the highest amount of As^T also lives in the hottest (26.8 °C) fluids with the highest concentration of As^T, (12.7 µg kg^{-1}), compared to *Ifremeria nautilei* and *Bathymodiolus manusensis*, living in 15.1 °C and 10.6 °C warm hydrothermal fluids with As^T concentrations of 5.8 µg kg^{-1} and 3.3 µg kg^{-1}, respectively. The concentration of As^T in *Bathymodiolus manusensis* is comparable to other hydrothermal vent mussels such as from the Menez Gwen hydrothermal system at the Mid-Atlantic Ridge. The two snails and the mussel dominantly show the inorganic species As^{III} and As^V and a constant but low amount of arsenobetaine and no or only a very low concentration of arsenosugars, without the presence of photosynthetic life or algae utilized during nutrition. This supports the theory, that there might be other pathways for the formation of organic arsenicals than the proposed traditional ones, where As-sug are accumulated in algae and are thought to be precursors for AsBet in higher, consuming marine animals.

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6 | Thioarsenates in pore fluids from the Palinuro volcanic deep-water hydrothermal complex

Christian Breuer [a,b], Britta Planer-Friedrich [c], Maximilian Halama [d], Harald Strauss [d], Dieter Garbe-Schönberg [e], Sven Petersen [f], Thomas Pichler [a,b]

[a] MARUM – Center for Marine Environmental Sciences
[b] Department of Geosciences, University of Bremen
[c] Environmental Geochemistry, University of Bayreuth
[d] Institut für Geologie und Paläontologie, WWU Münster
[e] Institut für Geowissenschaften, University of Kiel
[f] IFM Geomar - Helmholtz-Zentrum für Ozeanforschung, Kiel

draft

not approved by all authors

Abstract

Hydrothermal fluids emanating at shallow- and deep-water hydrothermal systems are naturally enriched in the potentially toxic element arsenic (As), strongly influencing the concentration and cycling of As in the oceans. Four hydrothermal influenced gravity cores made of altered mineralized volcaniclastic material and layers of sulfide precipitates were recovered from 630 m water depth at the western Palinuro volcanic complex in the Tyrrhenian Sea. Sampled pore fluids revealed a slightly acidic pH between 6.3 and 6.7 and elevated temperatures of up to 58 °C, as well as high concentrations of dissolved sulfide (H_2S, up to 3.5 mM) and low concentrations of dissolved iron. Total As concentrations were measured to be between 0.8 and 18.3 mg L^{-1}, due to hydrothermal leaching of As from the underlying host rocks and arising magmatic fluids, superpassing all concentrations measured in marine hydrothermal fluids to date. In addition to the inorganic arsenite and arsenate species, also up to 94 % of thioarsenates were found as mono-, di-, and trithioarsenates. Those species were never detected in deep-water systems > 200 m before. The concentration of thioarsenates and H_2S increased with depth, showing the influence of the downward penetrating cold seawater and warm advectively uprising hydrothermal fluid. Furthermore, a slight correlation with the appearance of sulfide crust could be observed.

Sample preservation is a crucial step for accurate measurements, because when fluids cool down and thermodynamic conditions change rapidly, different As-bearing minerals can precipitate in the sampled pore fluids, changing As speciation and total concentration. Commonly, those samples are filtered and cryofrozen to conserve the species distribution, because the common methods by adding acids to higher solubility would change the pH and influence the speciation. Precipitates were observed when unfreezing the samples leading to bad recoveries between 23 and 284 % (average 124 %), when comparing the sum of the species to the total amount of As and new methods have to be developed for preserving those kind of samples.

Highlights:

► We present data for arsenic and arsenic species in pore fluids from hydrothermal influenced sediment cores. ► Concentrations of As were up to 18.3 mg L^{-1} with up to 94 % of thioarsenate species. ► Increasing concentrations of arsenic, thioarsenate portion and dissolved sulfide with depth showed the increasing hydrothermal influence. ► Bad recoveries showed the importance of good sample preservation.

Keywords:

Arsenic; Hydrothermal; Pore fluids; Tyrrhenian sea; Palinuro volcanic complex; Thioarsenates

1. Introduction

Marine hydrothermal systems are driven by cold seawater penetrating downward into the oceanic crust through cracks, fissures and faults, which becomes progressively heated near an underlying magma chamber or due to serpentinisation processes, rises upwards again and expels at the seafloor due to excess buoyancy. This process and emanating fluids play a key role in ocean chemistry and cycling of elements from the oceanic crust into the oceans. The fluid chemistry strongly depends on different physicochemical parameters like temperature and pressure, causing phase separation, different water-rock reactions, magmatic degassing of an underlying magma chamber, as well as subsurface mixing with cold seawater and different biological processes, which are only poorly understood (e.g. Alt, 1995; German and Von Damm, 2003).

Hydrothermal fluids and pore-fluids from shallow-water hydrothermal areas are known to transport a high concentration of the potentially toxic element arsenic (As) in the range of several thousands µg L^{-1} into the oceans as shown by different studies from Tutum Bay or Milos (Pichler et al., 1999; Price et al., 2007; Price et al., 2012). These concentrations are superpassing those found in hydrothermal fluids emanating at mid-ocean ridges or back-arc basins. Despite this high concentration and the role of As known as an environmental toxin, only a few studies exist dealing with the investigation of As in hydrothermal fluids from the different tectonic regimes.

Contrasting to the high and very variable concentration of As in hydrothermal fluids, the average concentration of As in the global ocean is estimated to be constantly around 1.7 µg L^{-1} (Neff, 2002) and the concentrations in rivers even less around 0.62 µg L^{-1} (Gaillardet et al., 2003). This shows a paradox with a missing source of As, as normally rivers draining into the oceans reveal a higher elemental concentration than the oceans. The most important factors controlling the concentration of total arsenic (As^T) in hydrothermal fluids are the physicochemical parameters such as temperature and depth, controlling phase separation processes, pH, influencing As leaching and mobility, H_2S and CO_2 concentrations, as well as the amount of transported metals such as iron (Fe) and manganese (Mn). Furthermore different redox-, adsorption- and desorption-reactions and the mineralogy and crystallography of the underlying host rocks play an important role (Breuer and Pichler, 2012). In the aquatic environment, As can occur in different chemical oxidation states, but is mostly present in the inorganic form as the trivalent (oxo)arsenite (H_3AsO_3) and the pentavalent (oxo)arsenate ($H_2AsO_4^-$ and $HAsO_4^{2-}$). In hydrothermal systems rich in dissolved sulfide (H_2S) and As, also thioarsenic species should be present and constitute for a major fraction of the dissolved As as shown by thermodynamic modeling and experimental studies. These species are assumed to control As chemistry in reducing environments (Wilkin and Ford, 2006; Planer-Friedrich et al., 2007; Planer-Friedrich et al., 2010). Different thioarsenic species were already confirmed in shallow-water hydrothermal systems near Milos, where the highest concentrations of As^T were measured to date with up to 5.85 mg L^{-1} (Price et al., 2012), but were never detected in deep-water hydrothermal systems located in depths > 200 m.

Preservation of As and As speciation in hydrothermal fluids rich in H_2S and different metals like Fe or Mn is challenging but crucial. Wrong or inaccurate preservation can lead to precipitation of As-bearing minerals and lowering of As^T, as well as changes in species distribution. Several reviews exist, dealing with the critical consideration of this topic (Smieja and Wilkin, 2003; McCleskey et al., 2004; Gault et al., 2005; Suess et al., 2011) and the commonly used approach is filtering through a 0.22 µm unreactive membrane filter to remove microorganisms, the addition of reagents like HCl, EDTA, EtOH, or NaOH and cooling or freezing. However, changing the pH due to the addition of acids or other reagents can cause precipitation and changes of species distribution. Thioarsenate species are also unstable when oxygen is present and precipitate at acidic pH (Planer-Friedrich et al., 2007; Suess et al., 2009). Flesh freezing at -80 °C, which is already utilized, in combination with a low headspace in the vials to have low oxygen available, without adding reagents, seem to be the best method for sample preservation to date, though also this might not be the best and new techniques have to be investigated and tested for this very special kind of samples.

2. Geological and tectonic setting

The Tyrrhenian Sea as part of the western Mediterranean Sea represents a young and semi-closed extensional basin, surrounded by the Italian mainland in the east, Sicily in the south and Corsica and Sardinia in the west (Fig. 1a). The major tectonic process is characterized by the collision of the African and Eurasian plate, and the subduction of the oceanic part of the African plate below Europe, which is an ongoing process with a velocity of about 1 cm a^{-1} (Silver et al., 1998). The extension, which could be observed today, is caused by the subduction of the Adriatic slab and roleback motion of the northwestward dipping Ionian slab, pulling the edge of the overriding Tyrrhenian plate and extending it (Gvirtzman and Nur, 1999).

The southeastern part of the Tyrrhenian Sea comprises the volcanic cones of the Aeolian arc, the Marsili abyssal plain and the Palinuro volcanic complex (Fig. 1b). This complex represents an entirely submerged volcano, consisting of five coalesced volcanic edifices (Fig. 1c). It elongates along an east-west trending fault system with a size of 50 km in east-west direction and a maximum width of 25 km at the base. The edifices rise between 2 000 m (north) and 3 200 m (south) above the seafloor and the peaks of the volcanic cones are circular and may represent former eruption centers (Eckhardt et al., 1997; Monecke et al., 2009).

Investigations of the seafloor have shown large areas covered by sediments and underlain by massive sulfides and Mn-Fe-oxides, but volcanic rocks can only rarely be observed (Petersen and Monecke, 2008). Several colonies of tubeworms were found in areas of low-temperature hydrothermal discharge at Palinuro, which were not observed anywhere else in the Tyrrhenian Sea before, in addition to microbial communities hosted in the sediments (Monecke et al., 2009). The investigated cores were obtained in the western area of the Palinuro volcanic complex, with the top made of mineralized massive sulfides like pyrite (FeS_2), galena (PbS) and sphalerite (ZnS), in addition to minor phases of marcasite (FeS_2) and chalcopyrite ($CuFeS_2$), buried under a several meters thick layer of unconsolidated hydrothermally altered sediments (Marani et al., 1997; Dekov and Savelli, 2004).

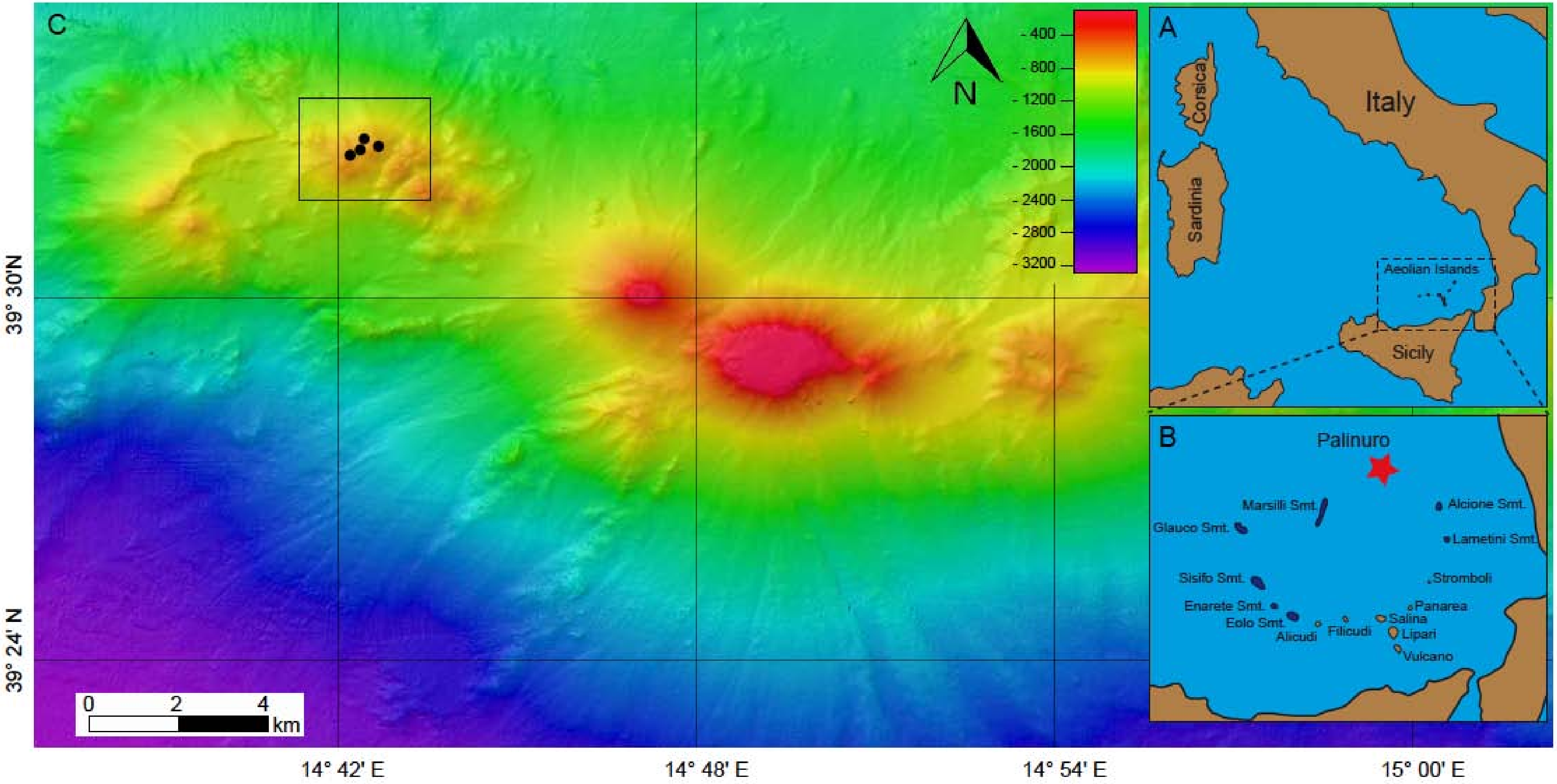

Fig. 1: (A) Location of the Tyrrhenian Sea in the western Mediterranean Sea surrounded by the Italian mainland, Sicily, Sardinia and Corsica and (B) the Aeolian Islands in the southeastern area with the location oft the different seamounts and islands, as well as (C) the submerged Palinuro volcanic complex with the five volcanic edifices. Black circles indicate sampling positions.

3. Sampling and Methods

3.1 Sampling, preservation and shipboard analysis

During *R/V Meteor* expedition M86/4 in February 2012, sediment coring was performed using a 3 m gravity corer with 125 mm inner diameter, 600 kg weight on top and a plastic liner inside the steel pipe. Temperature was measured immediately after recovery and the plastic liners filled with sediments were cut into 1 m long sections, before sealing the ends with plastic caps. Pore water sampling was performed by drilling holes into the plastic liner and using Rhizon Soil Moisture samplers every 10 or 20 cm, depending on the core and the assumed filling of the plastic liner. Rhizon samplers were made of a small microporous polymer tube (0.1 µm pore size) connected to a PVC-tube, which is again connected to a 10 mL syringe to produce low-pressure (Seeberg-Elverfeldt et al., 2005). Drilling small holes, immediately closing the liner sections and connecting the rhizon sampler to the syringes before sampling, minimized the oxygen contamination during sampling. After pore fluids were recovered, samples were immediately filled into 4 mL Polyvials® tubes (Zinsser) avoiding headspace and stored and transported cryofrozen at -80 °C until laboratory analysis.

Further sample splits were used for measuring the pH (WTW 191 and InLab Micro-D electrode) and concentration of H_2S via spectral photometry (Genesys 10) on board, as well as one split acidified with HNO_3 for major, minor and trace element analysis.

3.2 Lab analysis

Samples were analyzed for total As (As^T) and the inorganic As species arsenite, arsenate, mono-, di-, tri- and tetrathioarsenate at Bayreuth University. Sample and standard preparation before analysis was performed under anaerobic conditions in an atmosphere of 95 % nitrogen and 5 % hydrogen. All chemicals were of analytical reagent grade. Speciation was measured by IC (Dionex ICS 300 SP) coupled to ICP-MS (Thermo-Fisher XSeries2) and using an anion-exchange column (IonPac®, AG16/AS16, 4 mm, Dionex). The elution was performed by gradient using 0.02-0.1 M NaOH (Fluka, for IC, 50-52%) at a flow rate of 1.2 mL min^{-1} and an anionic self-regenerating suppressor (ASRS) at 13 psi. Arsenic was detected as AsO^+ (m/z 91) using the dynamic reaction cell technology with oxygen as reaction gas (10 % O_2, 90 % He) to avoid interferences of $^{75}As^+$ with $^{40}As^{35}Cl^+$. Arsenite and arsenate were quantified based on a five-point calibration curve from their standards ($NaAsO_2$ and $Na_2HAsO_4 \cdot 7H_2O$, Fluka). Thioarsenate peaks were quantified using the arsenate calibration due to a lack of commercial standards. This method has been previously validated by Planer-Friedrich et al. (2007).

Major elements (Cl, Fe, Mn, Mg) were measured either using Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES; SPECTRO CIROS ^{CCD} SOP) or Inductively Coupled Plasma-Mass Spectrometry (ICP-MS; Agilent 7500cs). The certified reference materials NIST 1643e and IAPSO K15 were used for validating the results.

4. Results

4.1 Gravity cores

The locations, water depths and recoveries, as well as temperature and pH of the four sediment cores recovered during the research cruise and investigated in the labs are given in Tab. 1. All cores showed elevated temperatures of up to 58.0 °C at their bottoms, decreasing to the top of the cores, with temperatures between 13.8 and 26.1 °C. Sediment cores were mostly made of altered mineralized volcaniclastic sediments consisting of fine-grained tuffaceous deposits and intercalated layers of dark sulfide precipitates as well as massive sulfide crusts and variable amounts of disseminated elemental sulfur. Pictures of the cores and location of the sulfide layers mostly consisting of irregular arranged black crusts are shown in Fig. 2.

Tab. 1: Characteristics of the different cores sampled during the M86/4 cruise in 2012.

Core	**Latitude**	**Longitude**	**Water depth** [m]	**Recovery** [cm]	**Temperature*** [°C]	**pH_{min}**
270 GC	39° 32.400’ N	14° 42.378’ E	630	290	58.0 / 48.1 / 37.7 / 26.1	6.4
277 GC	39° 32.410’ N	14° 42.404’ E	630	300	39.0 / 26.4 / 25.2 / 17.5	6.3
285 GC	39° 32.411’ N	14° 42.385’ E	629	285	38.1 / 28.4 / 20.3 / 13.8	6.7
287 GC	39° 32.437’ N	14° 42.390’ E	630	300	40.0 / 29.2 / 30.4 / 25.2	6.6

* measured when recovered on deck at the bottom / 2 m / 1 m / surface.

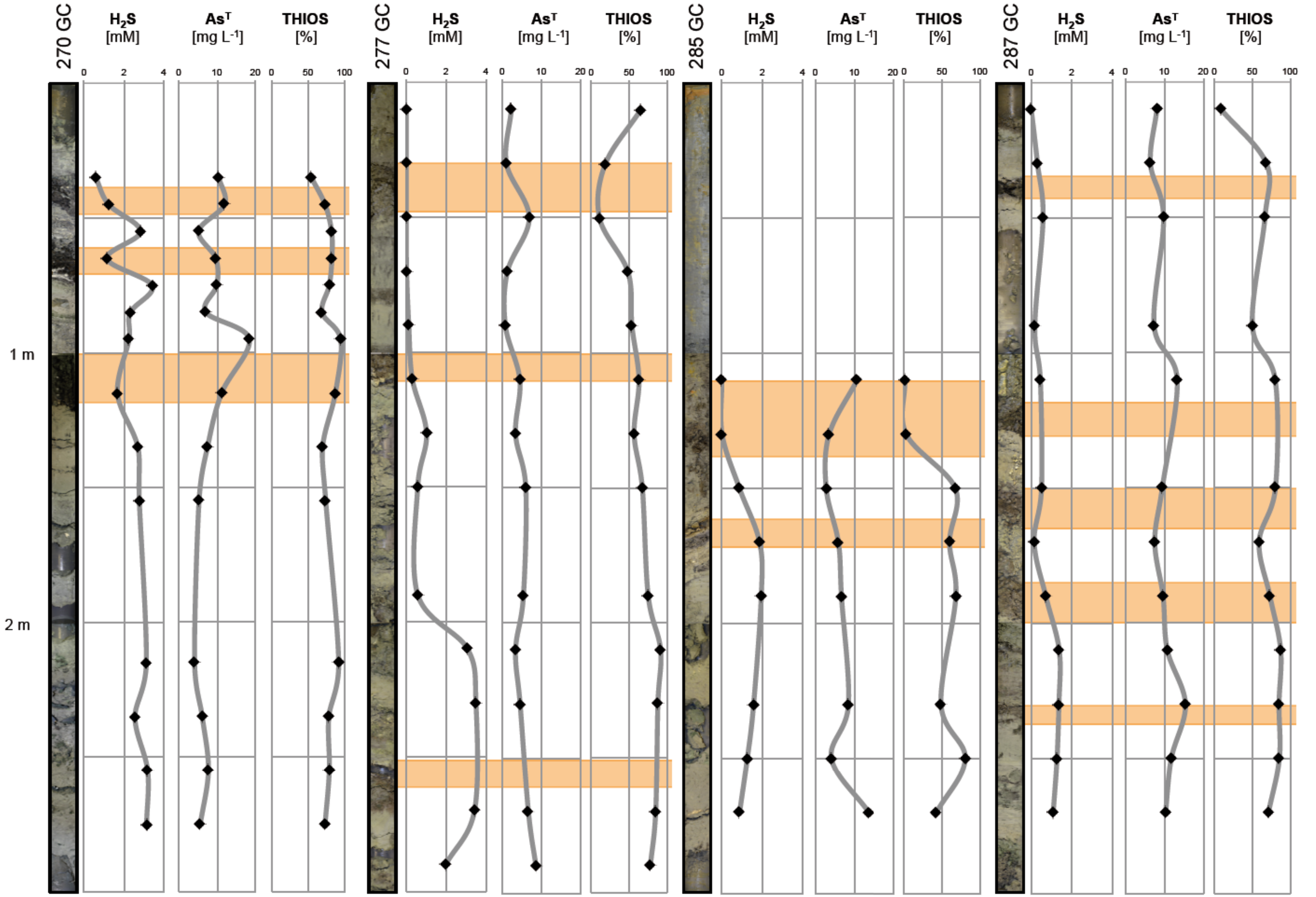

Fig. 2: Profiles of the four investigated cores 270 GC, 277 GC, 285 GC and 287 GC with concentrations of H_2S, As^T and sum of the thioarsenate species against depth. Sulfide layers are marked in orange.

4.2 Pore fluids

Pore fluids revealed a slightly acidic pH between 6.3 and 6.7 (Tab. 1) and a high concentration of dissolved sulfide (H_2S) with up to 3487 µM observed at the bottom of core 277 GC. The concentration of H_2S generally increased with sediment depth, but also to some extent correlating with the appearance of the sulfide crusts (Fig. 2, Tab. S1). Furthermore, the sampled pore fluids showed significantly elevated concentrations of chloride (Cl) with an average concentration of 26 625 mg L^{-1} when comparing to the ambient bottom seawater and background porewater samples (average Cl concentrations of 21 095 mg L^{-1}, unpub. data D. Garbe-Schönberg). The concentrations of iron (Fe) in the pore fluids were mostly below the limit of detection (< 0.28 mg L^{-1}) except for some samples near the sediment-seawater interface and the concentrations of manganese (Mn) varied between the limit of detection and 22 mg L^{-1}, revealing a slightly increasing trend with depth and correlating with decreasing magnesium (Mg) concentrations, which ranged between 591 and 1 390 mg L^{-1} (Tab. S2)

The concentrations of total Arsenic (As^T) were strongly enriched in the pore fluids compared to seawater and ranged between 810 and 18 315 µg L^{-1} (~ 10 000-times seawater concentration), with an average value of 7 350 µg L^{-1}. A general correlation of H_2S and As^T and increase with depth could be observed (Fig. 2, Tab. S1). Elevated concentrations of H_2S and As^T were also partly linked to the appearance of sulfide crusts layers. Speciation analysis showed the occurrence of the inorganic arsenite and arsenate species, as well as mono-, di- and trithioarsenic species in variable proportions (Fig. 3). The fraction of thioarsenic species dominates over the inorganic arsenite and arsenate with increasing depth, showing maximum values of up to 94.0 % in core 270 GC, 90.9 % in 277 GC, 80.0 % in 285 GC and 87.0 % in 287 GC (Fig. 3), with an average value of 65 % regarding all cores and all samples.

Recoveries calculated as the difference between As^T and the sums of the different species showed a big range between 23.4 and 284.0 % with an average value of 124.4 % (Tab. S1).

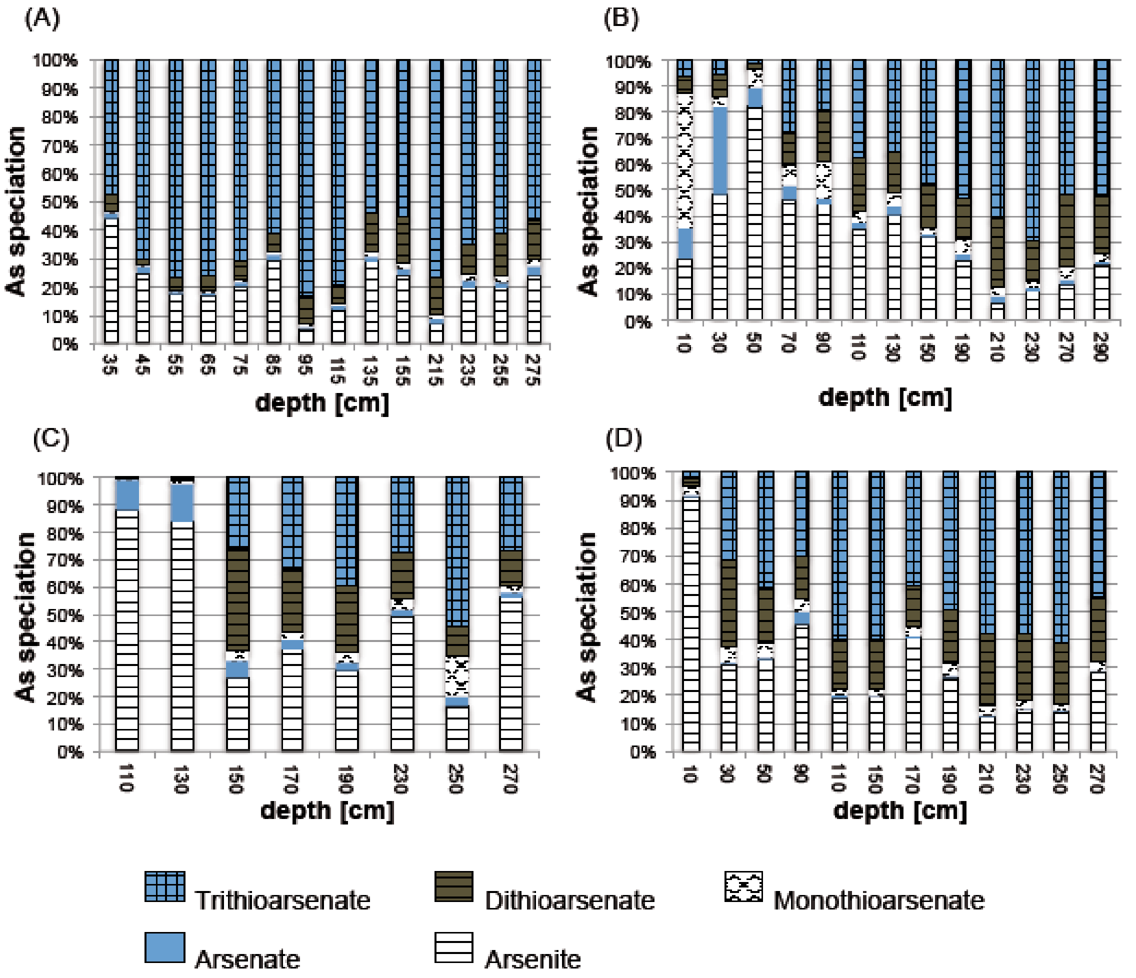

Fig. 3: Arsenic species distribution for the different cores vs. depth for 270 GC (A), 277 GC (B), 285 GC (C) and 287 GC (D).

5. Discussion

Shallow- and deep-water hydrothermal systems are known to act as a net source for arsenic (As) into the oceans (e.g. Pichler et al., 1999; Price et al., 2012) and play an important role in As transport and cycling therein. The concentration of total arsenic (As^T) present in emanating hydrothermal fluids and pore fluids from hydrothermal influenced sediment cores evidently depends on a variety of local physicochemical parameters such as temperature, pH, pressure, different redox, adsorption and desorption reactions, as well as the H_2S, CO_2 and metal concentration of the uprising fluids. Furthermore, the underlying host rocks and possible contribution of magmatic volatiles play important roles (Breuer and Pichler, 2012). Those hydrothermal fluids are able to transport a considerable amount of metals and also As from leaching of the underlying host rocks and the degassing of an underlying magma chamber (Heinrich et al., 1999).

Diffuse discharge is an ongoing process at the Palinuro volcanic complex located in the western Tyrrhenian Sea. The different physical and chemical parameters such as temperature, pH and H_2S concentrations showed an increasing hydrothermal influence with depth, as well as the influence of penetrating seawater in the upper parts of the sediment cores (Fig. 2, Tab. S1). This causes a distinct redox stratification, which could be observed in the chemical parameters of the pore fluids sampled from the sediment cores. Island-arc systems differ from those located at mid-ocean ridges or back-arc basins because of their shallow depth, favoring boiling and phase separation during fluid ascent, as well as different host rock composition and a major contribution of magmatic volatiles and metals as also observed in subaerial arc volcanoes (e.g. Giggenbach, 1992; Hannington et al., 2005).

Gravity cores from the Palinuro volcanic system showed extremely elevated concentrations of H_2S (up to 3.5 mM), increasing to the bottom of the cores and compared to a very low concentration at the sediment-seawater interface (Fig. 2, Tab. S1), going along with slightly acidic pH values. Microbial sulfate reduction and/or uprising hydrothermal fluids could be most likely the source for the high concentration of H_2S with decreasing values towards sediment-water interface due to the oxidation of the H_2S by the downward penetration seawater, responsible for shifting the oxic-anoxic boundary. The microbial sulfate reduction releases bicarbonate and increases the pH (Canfield, 2001), which otherwise would be more acidic. Furthermore, the presence of H_2S and also H_2SO_4 leading to those acidic fluids could be explained by the disproportionation of magmatic SO_2 arising with magmatic volatiles when these cool down and mix with penetrating seawater, as shown by the following equation (Giggenbach, 1992):

$$2SO_2 + 4H_2O = H_2S + 3HSO_4^- + 3H^+ \qquad \text{(Eq. 1)}$$

Magmatic fluids could also be responsible for transporting a considerable amount of certain metals including As (Gamo et al., 1997; Herzig et al., 1998). The bottom of the cores respective the last sample always showed lower H_2S concentrations most likely due to the contamination with oxygenated seawater during ascent of the gravity corer device.

Chloride (Cl) was significantly enriched with concentrations up to 26 625 mg L^{-1}, representing an emanating brine phase developed during phase separation when fluids encounter the two-phase boundary (Bischoff and Rosenbauer, 1984). The hypothetical hydrothermal endmember concentration of Cl was calculated to be around 31 945 mg L^{-1}, revealing almost twice the salinity of seawater averaging 21 095 mg L^{-1}. A brine or vapor phase portioning of As, which is still a matter of debate and only poorly understood (Pokrovski et al., 2005), could not be assumed as only the high-Cl brine phase was sampled. Furthermore, the concentration of iron was measured to be mostly below the limit of detection (Tab. S2) as the high concentrations of H_2S favor the precipitation of iron-sulfides such as pyrite (FeS_2) without remaining dissolved iron in the hydrothermal fluids. The concentrations of magnesium (Mg), which ranged between 591 and 1 390 mg L^{-1} (Tab. S2) decreased with depth, because the pure arising hydrothermal fluids should be free of Mg due to the precipitation of Mg-OH silicates when seawater temperatures is heated to temperatures higher than 150 °C. Increasing Mg concentrations towards the sediment-seawater interface showed the influence of the penetrating Mg-rich seawater.

Literature data for As^T and As speciation of marine pore fluids especially in hydrothermal influenced areas are very sparse. Several studies conducted at non-hydrothermal environments showed the presence of the inorganic arsenite and arsenate species in highly variable proportions. The ratio between them does not reflect the redox conditions solely, but is furthermore controlled by a combination of pH, the adsorption and release from different solid phases and organic matter, as well as microbial reactions (Andreae, 1979; Peterson and Carpenter, 1986). However, conditions at the Palinuro hydrothermal system are dramatically different as the concentrations of As^T delivered with the hydrothermal fluids is several times higher, in addition to a high amount of available H_2S and mixing of warm, reducing and slightly acidic hydrothermal fluids with penetrating cold oxygenated and slightly basic seawater. Sediments are made of intercalated layers of different sulfide minerals and also elemental sulfur could be observed. These favor different adsorption and desorption reactions with As, forming various As-bearing minerals like arsenopyrite (FeAsS) or orpiment (As_2S_3). An elevated concentration of As^T is to some extent connected to the appearance of these sulfide crusts as observed in the upper parts of core 270 GC and 277 GC. Core 285 GC and 287 GC by contrast showed constantly high concentrations, not linked to the appearance of sulfide crusts (Fig. 2).

Thioarsenic species dominate the pore waters with a maximum portion of 94 % measured in core 270 GC, which were already observed in various geothermal waters (e.g. Planer-Friedrich et al., 2007), followed by the inorganic arsenite and arsenate species (Fig. 3). The general increasing portion of thioarsenic species with depth also represents the increasing hydrothermal influence going along with increasing temperature and H_2S concentrations. A slight correlation with the appearance of the sulfide crusts, as well as between the concentration of H_2S and portion of thioarsenic species could be observed. Overall, these data showed, that thioarsenic formation most likely depends on a high concentration of As combined with a high concentration of available H_2S.

Those thioarsenates are fast degraded when they get in contact with the downward penetrating cold and oxygenized seawater, which could be observed in decreasing concentrations of trithioarsenate and increasing portions of arsenate towards the sediment-seawater interface (Fig. 4). This process includes the stepwise transformation of trithioarsenates into dithioarsenate, monothioarsenate and finally arsenite, which could then be oxidized to arsenate. Preservation is a crucial step for those kind of samples with this very special matrix, containing high concentrations of As and H_2S and under the influence of oxygen. The preservation for the inorganic arsenite and arsenate has been studied intensively and has been published in several publications (Smieja and Wilkin, 2003; McCleskey et al., 2004; Gault et al., 2005), but only a few studies exist focusing on preservation and measurement of thioarsenate species (Suess et al., 2009; Suess et al., 2011). However, thioarsenic species are even more unstable than the inorganic arsenite and arsenate species, where changes are mostly pretty slow, but depending on the pH, presence of oxidants, microbial activity and the concentration of As in the solution. Under oxidizing conditions, thioarsenates decompose with time due to a stepwise ligand exchange of SH- by OH-groups via arsenite to arsenate. In addition to this, also different iron and As-bearing sulfides such as pyrite (FeS_2) and orpiment (As_2S_3) can form, decreasing the concentration of As^T in the sampled solution and changing the original speciation. Because of inappropriate preservation of sulfidic waters and technical challenges, thioarsenic species were most likely overlooked in previous studies. The most common and successful approach is a combination of filtration to remove microorganisms, adding of reagents like HCl, H_2SO_4, EtOH, or EDTA to higher solubility and preventing precipitation of As with Fe or Mn, storing in the dark to avoid photooxidation and keeping the samples cool or frozen. However, decreasing the pH of sulfidic solutions can cause precipitation of poorly crystalline As_2S_3, going along with a major loss of As^T. Furthermore, changing the pH directly influences and changes the species distribution. Flash-freezing for sample preservation was published for the first time in the mid 1980s (Crecelius et al., 1986) and – also some disadvantages are known due to the formation of iron hydroxides – is the best method for preservation of sulfidic water samples with a low concentration of iron to date. Precipitates observed in the sampled hydrothermal pore fluids, which were most likely yellowish orpiment particles, and bad recoveries when comparing the sum of the species to As^T showed, that new methods for the preservation of those kind of samples have to be developed, tested and adapted.

6. Conclusions

We presented results for pore fluids from hydrothermal altered cores measured for As^T and As speciation, which showed for the first time the presence of thioarsenic species in deep-water hydrothermal systems from depths greater than 200 m. Samples taken at the Palinuro volcanic complex in the Tyrrhenian Sea at 630 m water depth were strongly enriched in As^T concentrations with up to 18.3 mg L^{-1} and revealed high concentrations of dissolved sulfide of up to 3.5 mM. Both increased with depth, reflecting the elevated hydrothermal influence, but were also partly linked to intercalated layers of sulfide crusts. In addition to the two inorganic arsenite and arsenate species, also mono-, di- and trithioarsenate were found in considerable proportions with up to 94 %, showing that thioarsenic species are a key species considering As redox chemistry in suldific aquatic hydrothermal systems.

Bad recoveries between 23 and 284 % observed when comparing As^T with the sum of the species showed that preservation is a crucial step for As geochemistry and speciation analysis as different precipitates were observed. New methods have to be developed for the preservation of thioarsenic species between sampling and measurements in the laboratories.

Acknowledgements

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SUPPLEMENTARY MATERIAL

Tab. S1: Concentration of As^T and As species measured in the pore fluids from the different cores.

Core	**Depth** [cm]	**As^T** [µg L^{-1}]	**As^{III}** [µg L^{-1}]	**As^V** [µg L^{-1}]	**Mono-** [µg L^{-1}]	**Di-** [µg L^{-1}]	**Tri-** [µg L^{-1}]	**Recovery** [%]	**H_2S** [µM]
270 GC	35	10321	4284	180	85	529	4633	94	573
	45	11915	6642	626	206	477	18700	224	1230
	55	5142	1982	130	40	530	8804	223	2820
	65	9586	2481	161	132	772	11180	154	1140
	75	9876	2081	150	97	693	7332	105	3400
	85	7013	2105	148	80	488	4379	103	2310
	95	18315	1173	182	260	2180	18880	124	2240
	115	11135	2012	241	158	1042	13540	153	1670
	135	7464	1915	121	124	911	3578	89	2690
	155	5251	1653	139	132	1134	3749	130	2760
	215	4098	492	127	98	942	5447	173	3110
	235	6084	2123	249	267	1112	6968	176	2540
	255	7689	1905	161	226	1427	5905	125	3179
	275	5580	2103	300	246	1181	4983	158	3120
277 GC	10	2378	901	437	1970	248	239	160	0.3
	30	1066	788	555	65	142	90	154	b.d.l.
	50	6863	4948	443	421	117	106	88	1.5
	70	1318	874	109	142	237	533	144	16,3
	90	808	415	22	133	183	182	116	125
	110	4475	901	62	120	523	964	57	303
	130	3389	1926	169	254	734	1694	141	1013
	150	5995	1912	72	143	1004	2869	100	573
	190	5386	1954	190	488	1336	4497	157	577
	210	3389	53	19	27	211	482	23	3064
	230	4553	893	125	209	1229	5615	177	3487
	270	6668	1024	159	369	2137	3955	115	3415
	290	8596	2135	116	299	2178	5274	116	1970
285 GC	110	10582	9437	1177	84	14	1	101	b.d.l.
	130	3477	3050	505	49	33	2	105	5.1
	150	2745	533	126	69	744	517	72	864
	170	5866	2422	219	180	1481	2196	111	1861
	190	6644	2711	284	346	2240	3682	139	1941
	230	8421	2871	140	215	1000	1586	69	1562
	250	4103	1938	388	1748	1245	6337	284	1251
	270	13689	4085	136	159	919	1949	53	868
287 GC	10	8081	7193	71	235	249	146	98	3
	30	6397	706	17	125	708	712	35	303
	50	9756	2859	71	436	1763	3586	89	577
	90	7333	3860	387	370	1312	2534	115	170
	110	13229	2807	166	357	2564	8828	111	444
	130	3725	1755	1494	423	1823	9370	399	654
	150	9426	2839	77	328	2678	8790	156	501
	170	7498	4386	75	369	1599	4364	144	137
	190	9619	3208	72	545	2302	5954	126	718
	210	10704	1806	78	486	3764	8411	136	1380
	230	15342	2751	68	567	4498	10710	121	1360
	250	11736	1737	46	309	2637	7457	104	1267
	270	10261	2929	53	320	2372	4608	100	1077

Note: b.d.l.: below detection limit

Tab. S2: Concentration of Fe, Mn and Mg measured in the pore fluids from the different cores.

Core	**Depth** [cm]	**Fe** [mg L^{-1}]	**Mn** [mg L^{-1}]	**Mg** [mg L^{-1}]
270 GC	35	b.d.l.	17.0	692.3
	45	b.d.l.	16.0	624.1
	55	b.d.l.	21.9	627.8
	65	b.d.l.	16.6	612.9
	75	b.d.l.	16.6	612.0
	85	b.d.l.	20.6	602.6
	95	b.d.l.	18.3	615.7
	115	b.d.l.	15.5	617.6
	135	b.d.l.	20.5	607.3
	155	b.d.l.	19.8	620.4
	215	b.d.l.	18.8	597.0
	235	b.d.l.	20.0	615.7
	255	b.d.l.	18.8	626.9
	275	b.d.l.	18.8	621.3
277 GC	10	1.81	b.d.l.	1390.2
	30	2.62	b.d.l.	1362.2
	50	0.54	b.d.l.	1306.1
	70	b.d.l.	b.d.l.	1387.4
	90	b.d.l.	0.7	1379.0
	110	b.d.l.	10.5	967.9
	150	b.d.l.	18.9	647.5
	190	b.d.l.	20.3	591.4
	210	b.d.l.	20.4	594.2
	230	b.d.l.	20.2	597.0
	270	b.d.l.	18.4	590.5
	290	b.d.l.	15.1	594.2
285 GC	110	2.44	b.d.l.	1383.7
	130	1.02	b.d.l.	1364.1
	150	b.d.l.	3.4	1265.0
	170	b.d.l.	12.1	834.3
	190	b.d.l.	16.9	669.9
	250	b.d.l.	17.2	597.9
	270	b.d.l.	18.0	597.9
287 GC	30	b.d.l.	2.0	1351.0
	50	b.d.l.	14.1	873.6
	110	b.d.l.	15.9	808.2
	130	b.d.l.	15.6	797.9
	150	b.d.l.	16.4	797.9
	170	b.d.l.	15.4	784.8
	190	b.d.l.	14.7	783.9
	210	b.d.l.	15.6	783.9
	230	b.d.l.	15.0	779.2
	250	b.d.l.	14.5	772.7
	270	b.d.l.	14.9	768.9

Note: b.d.l.: below detection limit

7 | Summary and conclusions

The different studies conducted and published during my dissertation revealed the importance of hydrothermal fluids emanating at the seafloor, which are able to act as a net source for arsenic (As) into the oceans and thus play an important role for As cycling therein. Hydrothermal fluids could act as the missing source of As in the oceans considering the low concentrations of As measured in rivers with respect to higher seawater values. The studies were performed at three different hydrothermal vent sites representing three highly distinct tectonic regimes characterized by different underlying host rocks, different physicochemical conditions and variable input of magmatic volatiles. Those magmatic volatiles are able to transport a huge amount of various metals and also As into the oceans (Heinrich et al., 1999). The concentration of As transported within the hydrothermal fluids strongly affects the surrounding ecosystem, as it is evidently accumulated and detoxified via different transformation processes by the hydrothermal vent biota mainly living in the low temperature discharging zones.

The concentrations and species distribution observed in the respective hydrothermal fluids depends on a variety of physicochemical parameters such as the depth of the system and the temperature, both influencing phase separation processes and portioning into brine and vapor phase. The pH can be directly related to the mobility and leaching capacity of As and further important parameters are the amount of H_2S, CO_2, metals, as well as different redox, adsorption and desorption reactions. All these parameters are furthermore influenced by the underlying host rock mineralogy, the maturity and the permeability of the system. Because only a very limited amount of data is available in the literature concerning total arsenic (As^T) and As speciation in hydrothermal fluids and the associated vent biota, the content of this thesis is an important contribution for the scientific community.

Hydrothermal fluids from systems located at mid-oceanic ridges, as shown by the first study conducted at the Menez Gwen hydrothermal system (37°50’N, Mid-Atlantic Ridge) show in general very low concentrations of As with only several tens of µg L^{-1}. This is most likely due to the precipitation of different As-bearing sulfide minerals such as arsenopyrite (FeAsS) or orpiment (As_2S_3) in the sub-seafloor, as well as when the hot and reducing fluids get in contact with the surrounding cold and oxygenated seawater, accompanied by a rapid change in the physicochemical conditions. Clear, hot (T_{max}: 285 °C) and slightly acidic fluids (pH: 4.0 to 5.1) collected during the M82/3 expedition of the German *R/V Meteor* in September 2010 displayed As^T concentrations between 6 and 90 µg L^{-1}. This is up to 50-times the average seawater concentration of 1.7 µg L^{-1} (Neff, 2002). No trend with other elements like Mg, Fe, or Mn could be observed, indicating a non-conservative behavior of As within these samples. Speciation analysis on cryofrozen preserved samples showed the presence of the inorganic arsenite (As^{III}) and arsenate (As^V) species in variable portions, but neither methylated species nor thioarsenic species were found, although we deal with an environment rich in dissolved H_2S (Charlou et al., 2000).

Mussels of the species *Bathymodiolus azoricus*, living in this very special environment near and in the discharging warm hydrothermal fluids, were collected and analyzed for the bioaccumulation, biotransformation and detoxification of As. These mussels are able to accumulate and transform the As emanating with the hydrothermal fluids in the various parts of their body. The highest concentration of As was detected in the digestive gland (19 mg kg^{-1}), which acts as a pathway and storage organ, followed by the gill (14.9 mg kg^{-1}) and the muscle tissue (6.4 mg kg^{-1}). The gill harbors chemosynthetic sulfur- and methane-oxidizing symbiotic bacteria for gaining energy (Duperron et al., 2006), which are most likely responsible for the As accumulation and transformation into the various organoarsenicals. The low concentration of As in the muscle tissues might be due to its lower involvement in exchange processes with the surrounding fluids. In contrast to higher organisms like mussels from the photic zone, which normally exclusively accumulate arsenobetaine (AsBet; e.g. Phillips, 1990; Francesconi and Edmonds, 1996), a high amount of arsenosugars (As-sug) and only low concentrations of AsBet could be observed in *Bathymodiolus azoricus*. The different As-sugars are generally considered as an end-product in marine algae, but are thought to be precursors for AsBet in higher marine consuming organisms (Francesconi and Edmonds, 1993; Edmonds and Francesconi, 2003). A reason for this unusual As species distribution might be the very special nutrient source and the activity of the different symbiotic bacteria located in the gill, which are responsible for the uptake of elements discharging from the fluids. Another reason could be the exposure to elevated amounts of partly reduced As in the acidic and hot hydrothermal fluids and subsequent overstressing of detoxification processes.

The second study was conducted in the eastern Manus Basin, a typical back-arc basin environment, where samples were taken during a research cruise in June and July 2011 at the hydrothermal areas of PACMANUS and SuSu Knolls. These hydrothermal fields at 1800 and 1200 m water depth are characterized by highly distinct fluid discharge as focused hot black, white and clear fluids through discrete chimneys, next to low temperature clear fluids emanating through cracks and fissures. The discharging hydrothermal fluids revealed maximum As^T concentrations of up to 380 µg L^{-1}. Samples of black smoker fluids were generally low in As^T and the highest concentrations of As^T among the analyzed samples were measured in a white smoker fluid with an extremely low pH of 1.2, high concentrations of CO_2 and temperatures of approximately 100 °C. Three distinct fluid trends could be identified from the analyzed samples: a low Cl vapor phase and a high Cl brine phase trend, both significantly enriched in As^T with respect to seawater, as well as a magmatic trend highly enriched in As^T showing Cl concentrations around seawater values. Again, only the inorganic As^{III} and As^V species were found in changing portions during speciation analysis.

Snails of the species *Alviniconcha hessleri* and *Ifremeria nautilei* as well as mussels of the species *Bathymodiolus manusensis*, which are the dominant species in the local hydrothermal ecosystem, revealed maximum As^T concentrations of 5 580 mg kg^{-1} found in the gill of *Alviniconcha hessleri*. This high concentration was due to the accumulation of inorganic As-bearing sulfide particles in the gill during filtering of the hydrothermal fluids. This was proven by scanning electron microscope analysis, but also supported by the low extraction efficiencies and elemental sulfur found in the gill (Beinart et al., 2012), as well as the overall presence of inorganic As^{III} and As^V. Another mechanism is represented by the uptake of As via the essential phosphate transporter system and the chemosynthetic symbionts located in the gill epithelial tissues. Additionally to inorganic species, low but constant amounts of AsBet were found, but As-sug was hardly detectable. Input of photosynthetic organisms in these deep-water systems such as the common As-sug source algae, which are thought to act as precursors for AsBet, could be nearly neglected. This implies, that there might be other pathways for the formation of organic AsBet and As-sug independent of the contribution of algae, probably caused by the activity of the symbiotic bacteria.

The final study was carried out on hydrothermal influenced sediments from the Palinuro volcanic complex in the Tyrrhenian Sea, representing a typical island arc environment. This study focused on thioarsenic species, which were already observed in shallow-water systems (e.g. Planer-Friedrich et al., 2007), but never in systems at water depths deeper than 200 m. The recovered sediment cores consisted of altered mineralized volcanoclastic sediments with intercalated layers of sulfide precipitates as well as elemental sulfur. Pore fluids sampled from these cores were slightly acidic with a pH between 6.3 and 6.7 and showed a high concentration of dissolved sulfide with up to 3.5 mM. Concentrations of As^T were in the range between 0.8 and 18.3 mg L^{-1}, generally increasing with depth. Furthermore, increasing H_2S concentrations and decreasing Mg concentrations also revealed the increasing hydrothermal influence with depth. The high concentrations of As^T could be due to the very different physicochemical conditions compared to mid-oceanic ridge or back-arc basin systems, but also due to an additional component of magmatic volatiles arising with the hydrothermal fluids. During As speciation analysis, considerable amounts of mono-, di-, and trithioarsenates were detected in addition to the inorganic As^{III} and As^V. The sum of the thioarsenic species increased with depth and concentration of dissolved H_2S (up to 94 %). Bad recoveries were observed when comparing As^T with the sum of the various As species, which showed once more the importance of correct sample preservation for a complex sample matrix with high amounts of As and H_2S.

In conclusion, this thesis elaborated, that hydrothermal fluids represent a substantial source of As into the oceans, with the concentrations depending a lot on the tectonic regime as demonstrated by the three studies conducted at highly distinct settings. As one of the few trace elements, As concentrations in river water are lower than in seawater, which could be caused by relatively higher contributions of As from hydrothermal systems. Because the global hydrothermal flux is difficult to estimate and the concentrations of As^T are highly variable, quantitative estimations for the global As discharge from hydrothermal fluids are hard to assess and need more investigations.

8 | Outlook

This thesis reports new insights on total arsenic (As^T) concentrations and As speciation in hydrothermal vent fluids and associated vent biota from different tectonic regimes. The results indicate that hydrothermally driven systems play an important role in the transport and cycling of As from the oceanic crust into the oceans. However, several aspects concerning the cycling of As at hydrothermal systems remain unclear and request further investigations. There are still various technical and analytical challenges to overcome and the research on hydrothermal vent systems in the deep sea is still in its infancy. To date, only a few studies exist on the hydrothermal vent biota living in symbiosis with bacteria that thrive from the supply of reduced methane and sulfide delivered by hydrothermal fluids. Since the first discovery 35 years ago, 300 new sites of active hydrothermal venting and 500 new species of hydrothermal vent biota have been reported (http://www.interridge.org) and it is expected that much more hydrothermal systems will be discovered in the near future.

Technical challenges have to be tackled to explore hydrothermal systems at greater depths and to perform long-term observations with repeated sampling campaigns. This would enable a more accurate estimate of fluxes discharging at hydrothermal systems. In the case of As for example, this could help to unravel if the hydrothermally supplied As acts as the missing source for As transported into the oceans, as the supply by rivers is to low to explain the As concentrations in the oceans. Especially hydrothermal systems along island-arcs as shown by the shallow-water hydrothermal system in Tutum Bay, Milos and Palinuro are large sources for As and should gain more attention in the future. The hydrothermal system at Tutum Bay alone discharges a minimum amount of As of $5.5\text{x}10^2$ kg a^{-1} in an area of 6 000 m^2 (Price and Pichler, 2005), which is worth to mention when considering a value of $23\text{x}10^6$ kg a^{-1} As delivered by rivers (Gaillardet et al., 2003).

For these flux-calculations, it is essential to sample more hydrothermal systems, as well as to get a deeper understanding for As-leaching from underlying host rocks and the parameters influencing this process. This data could be supported and better interpreted by performing leaching experiments at different pressure and temperature conditions on smaller scales using high-pressure flow-through cells.

Another important point, which has to be addressed in the next years and upcoming studies is the correct and suitable sample preservation, which is a crucial step for accurate measurements of the As^T concentration and the different As species. The precipitation of As-bearing minerals due to changes in temperature and pressure can significantly lower the concentration of As^T in the sample solutions. Furthermore, the influence of oxygen or shifts in pH e.g. due to acidification can cause changes and modify the original speciation. Various methods were tested for different kinds of aqueous samples (McCleskey et al., 2004; Kumar and Riyazuddin, 2010; Suess et al., 2011), nonetheless, a matrix of high As, Fe and H_2S is still challenging.

In summary, this thesis can be seen as a suitable instruction for the investigation of As in hydrothermal fluids and the hydrothermal vent biota, but it is still a long way to go to fully understand this highly interesting research field at such unique hydrothermal environments.

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Erklärung

Hiermit versichere ich, dass ich

i. die Arbeit ohne unerlaubte fremde Hilfe angefertigt habe,
ii. keine anderen als die von mir angegebenen Quellen und Hilfsmittel benutzt haben und
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