

# Marine shallow-water hydrothermal systems as natural laboratories

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**Abstract.** Marine shallow-water hydrothermal systems were discovered at more than 40 locations. The discharge of hot mineralized fluids into near shore marine environments creates dramatic physical, chemical and biological gradients. This, combined with easy accessibility, makes them excellent “natural” laboratories to study a wide range of chemical, physical, and biological processes. Studies can be performed in the form of passive thought experiments or actively by inserting experiments into the system. These types of experiments possess the potential to overcome several of the limitations of „normal“ laboratory environments.

## Introduction

Research on seafloor hydrothermal activity has focused primarily on deep-sea black smoker-type locations, which are found along volcanically active portions of the mid-ocean ridges and in deep back-arc basins. Submarine hydrothermal activity, however, is not confined to deepwater environments. Hydrothermal vents have been documented on the tops of seamounts, on the flanks of volcanic islands, and in other near-shore environments characterized by high heat flow (e.g., Dando and Leahy, 1993; McCarthy et al., 2005; Prol-Ledesma et al., 2004). Their easy accessibility, relative to deep-sea hydrothermal systems, makes them excellent “natural” laboratories to study a wide range of chemical, physical, and biological processes.

The purpose of this contribution was not to give an all-encompassing account of the use of marine shallow-water hydrothermal systems as natural laboratories. Rather the intent is to introduce the idea and to demonstrate their utility on hand of select examples. In addition some basic information about the relationship between, geology, water source, heat source and discharge depths are given to aid in the search of marine shallow-water hydrothermal systems with desired physico-chemical conditions.

### **Abundance of marine shallow-water hydrothermal systems**

Approximately 40-50 sites are presently known. However considering that many are found in remote, poorly explored areas of the globe it is likely that for every known there will be several unknown localities. Their occurrence is closely controlled by geologic and tectonic conditions, because a large heat differential is needed to initiate hydrothermal circulation (Fehn and Cathles, 1986). This heat differential is generally caused by heat released from intruding magma bodies or by the generation of frictional heat along fractures. As a result, most marine shallow-water hydrothermal systems are found near ocean island volcanoes (mantle hot spots), island arc volcanoes (subduction zones) and large active faults (transform faults).

### **Characteristics of marine shallow-water hydrothermal systems**

Unfortunately there is no clear definition of what marine shallow-water hydrothermal systems are, nor is there any clear agreement how to call these phenomena. This author defines them as: the submarine discharge of a hydrothermal fluid into the shallow ocean (<200 m); they can have characteristics of sub aerial hot springs or that of deep-sea hydrothermal systems; the hydrothermal fluid source can include any fraction of meteoric water; phase separation (boiling) during or immediately prior to discharge is likely; they discharge into the photic zone and may contain appreciable amounts of dissolved oxygen.

The term “marine shallow-water hydrothermal systems” was used consistently throughout the manuscript and conforms to what is currently used in the scientific literature (Aliani et al., 1998; Ishibashi et al., 2008; Miwako Nakaseama, 2008; Pichler et al., 2006; Price et al., 2007; Price and Pichler, 2005). This terminology seems to be the most appropriate to avoid possible confusion. The term marine is necessary to separate these systems from their lacustrine counterparts. The term shallow-water, hyphenated, is necessary to indicate that these systems are at a shallow water depth, rather than that their subsurface circulation is shallow.

A simple approach to classify marine shallow-water hydrothermal systems could be based on the chemical composition of their liquid and gaseous discharge, geologic setting and physico-chemical parameters, such as temperature, pH, etc. Climate, however, may also play an important role. For example, their occurrence in a desert climate such as Bahia California should prevent the presence of meteoric water in the hydrothermal system (Forrest et al., 2005; Prol-Ledesma et al., 2004). In other areas, such as Dominica (McCarthy et al., 2005), large annual variations in rainfall may force large annual variations in salinity of the hydrothermal fluid.

### ***Gas chemistry***

The chemical composition of gas in marine shallow-water hydrothermal systems is closely controlled by a combination of heat source and host rock. Nevertheless,

generally CO<sub>2</sub> is the main component (Botz et al., 1996; Capasso et al., 1997; Forrest et al., 2005; McCarthy et al., 2005; Pichler et al., 1999). Systems in volcanic areas may have a chemical composition very close to that of volcanic gases discharging directly from active volcanoes in the vicinity. The source of such gases is likely phase separation in the magma chamber. Such gases can be high in H<sub>2</sub>S, SO<sub>2</sub> and He (Giggenbach, 1996). Marine shallow-water hydrothermal systems whose heat source is frictional may be much higher in N<sub>2</sub> or CH<sub>4</sub>, for example (Forrest et al., 2005). Large concentrations of CO<sub>2</sub> and CH<sub>4</sub> may also indicate carbonate rocks in the subsurface (Pichler et al., 1999).

### ***Solution chemistry***

The source and therefore, initial chemical composition, of a hydrothermal fluid is an important factor controlling the final chemical composition. While the determination of fluid sources is relatively straightforward in deep marine and inland settings, the subject becomes more complex in coastal regions (offshore and onshore) where marine and terrestrial sources may both be involved (Pichler, 2005). A fluid in a hydrothermal system may be derived from any, or any combination, of the following sources: meteoric water, seawater, connate water, magmatic water and juvenile water. Mixing of waters from different sources affects many aspects of the geochemistry of a hydrothermal system, such as its chemical composition, isotopic composition, temperature profile or gas content.

Marine shallow-water hydrothermal systems, which circulate seawater or mixed seawater-meteoric water, have abundant complexing ligands in the form of Cl<sup>-</sup> and SO<sub>4</sub><sup>2-</sup> to transport metals, such as Pb, Zn, Cu and Cd (Vidal et al., 1978). On the other hand, fluids from marine shallow-water hydrothermal systems, which circulate mainly water of meteoric origin generally transport metals, which form oxyanions, such as, As, Sb, Tl, etc. (Pichler et al., 1999).

### ***Physico-chemical parameters***

The two most important physico chemical parameters to categorize marine shallow-water hydrothermal systems are temperature and pH. The discharge temperatures of hydrothermal fluids range from just above ambient up to approximately 130°C. They largely depend on water depth (i.e., the pressure curve) gas content (i.e., CO<sub>2</sub> curve) and salinity (i.e., the NaCl curve) (e.g., Henley and Ellis, 1983; Nicholson, 1992). Therefore the fluid with the least gas content, highest salinity and deepest discharge point has potentially the highest discharge temperature.

The pH values can range from as low as 1-2 up to 8-9. This range is controlled by a combination of water-rock interaction, initial buffer capacity and near surface conditions. Based on pH and chemical conditions we can group many marine shallow-water hydrothermal systems using the same classification used for on land thermal springs: acid sulfate, bicarbonate and neutral chloride (Giggenbach, 1997).

## Examples of “natural” laboratory studies

The use of marine shallow-water hydrothermal systems as natural laboratories is comprised of two fundamentally different approaches, passive or active. The difference is that the passive approach relies on already generated data, while the active approach generates new data as part of the experiment.

A passive approach consists of a thought experiment, which can be tested with data generated as part of the chemical, physical, biological, etc. description of the system. An active approach consists of inserting an experiment into the system and observing a reaction, change or response.

The passive approach involves the following steps: (1) generation of a thought experiment (identification of a scientific problem), (2) complete description of the site – or at least of those parameter, which pertain to the problem, (3) extraction of data from desired parts or locations of the system, and (4) data evaluation and interpretation. The active approach on the other hand consists of: (1) design of an experiment, (2) complete description of the site – or at least of those parameter, which pertain to the experiment, (3) insertion of the experiment at desired location(s), (3) extraction of data from the experiment, and (4) data evaluation and interpretation. Concrete examples for both types are given below.

### Determination of oxidation rates (passive approach)

Mixing of the hot mineralized hydrothermal fluid with ambient seawater causes chemical and physical gradients in sediments surrounding marine shallow-water hydrothermal systems and in the water column above. If these gradients can be mapped, they present an exceptional opportunity to study a wide variety of reactions. Particularly the influence of redox and temperature changes on precipitation, dissolution and adsorption. The gradients can be readily mapped with the help of flow meters and the careful determination of mixing between hydrothermal fluid and seawater (see also the section on Isotopes below).

The scientific problem to be studied is that the oxidation rates of iron and arsenic in seawater proceed at different rates; Fe(II) being much faster oxidized by seawater derived O<sub>2</sub> than As(III). To cover a wide range of physico-chemical conditions (i.e., flow rate, temperature, salinity, oxygen content) the four sites at Tanga (Pichler, unpubl. data), Ambitle (Pichler et al., 1999), Bahia Concepcion (Prol-Ledesma et al., 2004) and Dominica (McCarthy et al., 2005) are ideal “natural” laboratories. Although physico-chemically quite different, all of these sites have elevated arsenic and the precipitation of hydrous ferric oxide (HFO) in common.

A first step would be to sample the hydrothermal discharge at five locations stepping away from the vent orifice. This will provide a time sequence and concentration gradient, similar to the sampling along an out flow channel from an on-land hot spring. The measurement of flow velocity and change in Fe(II)/Fe(III) and As(III)/As(V) will allow to compute an approximate oxidation rate. The computation of oxidation rates ( $R = (\partial\text{Fe}^{2+}/\partial t)$ ) for these field experiments can now follow the approach of Johnson and Pilson (1975).

### Determination of oxidation rates (active approach)

The active approach to measure oxidation rates would be to force precipitation at a controlled site and to measure precipitate accumulation. To achieve this several small (1 cm<sup>2</sup>) ceramic plates can be positioned at the vent orifices directly in the hydrothermal discharge as close as possible to the locations of ferrihydrite deposition. Ceramic plates are an ideal substrate for ferrihydrite precipitation. By installing them on the first day of fieldwork, one can collect precipitation information for the duration of fieldwork and by installing another set at the end of fieldwork, one may be able to collect precipitation information for the duration between two field seasons. The amount of precipitation can be determined by weighing the plates before and after the experiment. In conjunction with a measurement of hydrothermal flow, chemical composition of the vent fluid (Fe(II)/Fe(III) and As(III)/As(V)), and chemical composition (Fe and As) of the ferrihydrite, this will allow the calculation of an approximate *in situ* oxidation rate for Fe and As.

### Determination of isotope fractionation factors (passive approach)

One of the dominant precipitate in the hydrothermal system at Ambitle Island is aragonite. Its precipitation occurs due to a change in Eh, pH, temperature and chemical composition when the hydrothermal fluids discharge and mix with ambient seawater. The aragonite, however, is not homogenous and shows a distinct layering of different colors, crystal sizes and chemical/isotopic composition. It can be hypothesized that the layering is a result of changing physico-chemical conditions during precipitation, particularly discharge rate and thus seawater mixing. This has an impact on precipitation temperature, saturation and precipitation velocity. The amount of seawater-hydrothermal fluid mixing during precipitation was calculated using strontium isotopes (Pichler, 2001):

$$\left(\frac{{}^{87}\text{Sr}}{{}^{86}\text{Sr}}\right)_M = \left(\frac{{}^{87}\text{Sr}}{{}^{86}\text{Sr}}\right)_{HF} \left(\frac{\text{Sr}_{HF} * (1 - x)}{\text{Sr}_M}\right) + \left(\frac{{}^{87}\text{Sr}}{{}^{86}\text{Sr}}\right)_{SW} \left(\frac{\text{Sr}_{SW} * x}{\text{Sr}_M}\right)$$

where M is the mixture, HF is the hydrothermal fluid, SW is seawater and x is the degree of mixing (or fraction of hydrothermal fluid present in the mixture). Sr<sub>M</sub> has to be calculated for each mixture using equation (1). Based on the <sup>87</sup>Sr/<sup>86</sup>Sr-mixing model, the aragonite layers precipitate at different temperatures and precipitation ceases at a seawater admixture of 11%, which corresponds to a temperature drop of up to 7°C. Thus, the lamination of aragonite signal changes in the physical and chemical conditions at and near vents.

The δ<sup>13</sup>C of Tutum Bay hydrothermal aragonite ranges from 1.9 to 2.2‰ (VPDB). This range of values is in good agreement with experimental data (Bottinga, 1968; Kim and O'Neil, 1997), indicating that C-13-equilibrium has been reached during its formation. Values for δ<sup>18</sup>O range from 14.2 to 14.7‰ and calculated isotopic equilibrium temperatures are approximately 20°C lower than directly measured vent fluids and those temperatures obtained from fluid inclusion

measurements and the  $^{87}\text{Sr}/^{86}\text{Sr}$  mixing model. This indicates that either oxygen isotope equilibrium was not attained or that the calcite-water fractionation factor for oxygen isotopes is not applicable to the precipitation of Tutum Bay hydrothermal aragonite. Apparently, carbon isotopic equilibrium was reached, while for oxygen complete equilibrium was not attained.

An alternative explanation for the discrepancy between the measured and calculated could be that the assumption of identical fractionation factors for aragonite and calcite at higher temperatures is not correct. Assuming that the aragonite in Tutum Bay precipitated in equilibrium with its parent fluid, the isotope values here can be used for a  $\delta^{18}\text{O}$  aragonite-water fractionation factor between 90 and 100°C.

### **Determination of arsenic toxicity (active approach)**

Laboratory experiments measured the effects of  $[\text{As}^{3+}]$  and  $[\text{As}^{5+}]$  on foraminiferal growth and survivorship. Exposure of foraminifers to  $\text{As}^{3+}$  and  $\text{As}^{5+}$  at concentrations of 0 to 1000  $\mu\text{g}/\text{kg}$  showed that  $\text{As}^{3+}$  is approximately 2.2× more toxic to foraminifers than  $\text{As}^{5+}$ , that concentrations of 600-1000  $\mu\text{g}/\text{kg}$   $\text{As}^{3+}$  is sufficient to kill or severely impair *Amphistegina gibbosa* specimens on approximately two-week timescales, and that concentrations of 1000  $\mu\text{g}/\text{kg}$   $\text{As}^{5+}$  or 200  $\mu\text{g}/\text{kg}$   $\text{As}^{3+}$  are sufficient to retard their growth (McCloskey et al., 2009).

To test these results in a more realistic (natural) setting growth experiments were positioned at increasing distances from the marine shallow-water hydrothermal systems in Tutum Bay, PNG, thus exposing foraminifers to a range of  $\text{As}^{3+}$  concentration. The foraminifers, together with some natural substrate were, enclosed in mesh bags and positioned at the sediment-seawater interface. Following extraction the data collection procedures were identical to those of the laboratory experiment.

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