The use of $^{87}\text{Sr}/^{86}\text{Sr}$ ratios to document physico-chemical changes in shallow-water hydrothermal systems

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ABSTRACT: The dominant precipitates in the hydrothermal system at Ambitle Island are aragonite and hydrous ferric oxide (HFO). Their precipitation occurs due to a change in Eh, pH, temperature and chemical composition when the hydrothermal fluids discharge and mix with ambient seawater. The amount of seawater-hydrothermal fluid mixing during their precipitation was calculated using strontium isotopes. Based on a $^{87}\text{Sr}/^{86}\text{Sr}$-mixing model, aragonite precipitates up to a maximum seawater admixture of 11%, while above 11% and up to 57% HFO is the prominent precipitate. Thus, lamination of aragonite and HFO signals abrupt, short-term changes in the physical and chemical conditions at and near vents. These changes are most likely directly related to the rate at which Tutum Bay vents discharge and ultimately they are caused by changes in the hydrology of the hydrothermal system.

1 INTRODUCTION

The physico-chemical conditions in hydrothermal systems change through time and, therefore, observations made and samples analyzed represent only a point in time. Over the last decade we have made great progress understanding the physico-chemical conditions that control hydrothermal processes. At present, however, our greatest unknown with respect to hydrothermal systems is time. The chemical composition of hydrothermal precipitates and the skeletons or shells can record changes in fluid chemistry, temperature and discharge rate through time. If we are able to read those records then they can provide us with important information about the history of a hydrothermal system and we are no longer limited to in-situ observation.

The shallow-water hydrothermal springs in Tutum Bay, Papua New Guinea, provide us with an opportunity to investigate the chemical fingerprint in hydrothermal precipitates that is caused by a change in discharge rate. The purpose of this paper is to qualitatively assess the changes in physico-chemical conditions that lead to the distinct mineralogical and chemical zonation in Tutum Bay hydrothermal deposits.

2 LOCATION AND GEOLOGICAL SETTING

The study area lies along the southwest margin of Ambitle Island, one of the Feni islands in the southernmost island group of the Tabar-Feni chain (Figure 1). The island is part of a Quaternary stratovolcano with a central eroded caldera built on poorly exposed Oligocene marine limestone (Wallace et al. 1983). Volcanic strata (interbedded lava flows, lahar deposits, tuffs, and scoriae) dip radially from the island, presumably extending beneath the shelf. Several geothermal areas are located primarily along the western coast and in the western part of the caldera near breaches in the caldera wall (Figure 1).

2.1 The Tutum Bay hot springs

Submarine hydrothermal venting occurs at Tutum Bay (Figure 1) in shallow (5-10 m) water along the inner shelf that contains a patchy distribution of coral-algal reefs (Pichler & Dix 1996). Two types of venting are observed. (1) Focused discharge of a clear, hydrothermal fluid occurs at discrete ports, 10-15 cm in diameter. Fluid temperatures at vent orifices are between 89 and 98 °C. (2) Dispersed or
diffuse discharge consists of streams of gas bubbles emerging directly through the sandy to pebbly unconsolidated sediment and through fractures in volcanic rocks. The hydrothermal fluids are of meteoric origin and possess a salinity (TDS) of approximately 3.5 ‰ (Pichler et al. 1999). A more detailed description of Tutum Bay has been provided elsewhere (Pichler & Dix 1996, Pichler et al. 1999) and color images can be found at http://chuma.cas.usf.edu/~pichler.

2.2 Hydrothermal precipitates

Hydrothermal precipitates accumulate on dead coral substrate and rock fragments surrounding vent portals and include macrocrystalline aragonite, microcrystalline aragonite and hydrous ferric oxide (HFO).

Aragonite forms isopachous rims, massive monomineralic layers and splays of euhedral (pseudo-hexagonal) crystals up to 2 cm long. The growth direction of individual crystals is parallel to each other and normal to their substrate, and they can be up to 2 cm long. HFO is present throughout Tutum Bay, forming very thin layers on sediment grains in areas of high seafloor temperature. Massive layers and extensive filling of sediment pore space, however, are restricted to the vicinity of vent sites.

2.3 Precipitation Sequence

Hydrothermal precipitates generally occur in the succession: macrocrystalline aragonite, microcrystalline aragonite and HFO. Other successions, however, have been observed. Figure 2A (lower left corner) shows a change in precipitation from HFO to microcrystalline aragonite and again to HFO. Considering an accumulation rate of approximately 1 cm/year (Pichler & Veizer 1999), the period of HFO deposition may have been as short as 7-8 days.

A direct transition from large pseudo-hexagonal aragonite crystals to HFO is documented in Figure 2B. This transition is extraordinary in the sense that it happened without the formation of a layer of mi-
cocrystalline aragonite, as generally observed (Figure 2A). The transition must have been abrupt and rapid because the crystal faces of the aragonite are still smooth and do not show dissolution or recrystallization features. The relatively thin layer of material indicates a relatively short period of HFO accumulation. The sequence of precipitation continues with a layer of fine-grained aragonite followed by a layer of HFO and finally terminates with a layer of aragonite (Sequence a, b, c, d, e in Figure 2B).

3 ANALYTICAL METHODS

Bulk HFO material was separated from its substrate, rinsed with deionized water to remove halite and carefully crushed in an agate mortar. Sample powders were dried at room temperature to prevent goethite to hematite conversion. The mineralogy was confirmed by scanning electron microscope (SEM), transmission electron microscope (TEM) and powder and single-crystal X-ray diffractometry (XRD).

$^{87}\text{Sr}/^{86}\text{Sr}$ ratios of aragonite and HFO were measured on a five collector Finnigan MAT 262 solid source mass spectrometer at the Institut für Geologie, Ruhr Universität, Bochum. The average of 100 repeat measurements for the NBS 987 standard was 0.710224±0.000008.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mineralogy</th>
<th>$^{87}\text{Sr}/^{86}\text{Sr}$ ± 2 Std. Errors</th>
</tr>
</thead>
<tbody>
<tr>
<td>V-2D</td>
<td>Aragonite (macro)</td>
<td>0.704142 ±13</td>
</tr>
<tr>
<td>V-2D</td>
<td>Aragonite (macro)</td>
<td>0.704097 ±10</td>
</tr>
<tr>
<td>V-3A</td>
<td>Aragonite (micro)</td>
<td>0.704475 ±08</td>
</tr>
<tr>
<td>V-4.1 (x)</td>
<td>Aragonite (macro)</td>
<td>0.704131 ±14</td>
</tr>
<tr>
<td>V-4.1 (m)</td>
<td>Aragonite (micro)</td>
<td>0.704551 ±08</td>
</tr>
<tr>
<td>FV-1A</td>
<td>HFO</td>
<td>0.704580 ±09</td>
</tr>
<tr>
<td>V-1B</td>
<td>HFO</td>
<td>0.707010 ±09</td>
</tr>
<tr>
<td>V-2B I</td>
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</tr>
<tr>
<td>V-2B II</td>
<td>HFO</td>
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<td>HFO</td>
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</tr>
<tr>
<td>V-4.1D</td>
<td>HFO</td>
<td>0.706040 ±09</td>
</tr>
</tbody>
</table>

4 RESULTS AND DISCUSSION

$^{87}\text{Sr}/^{86}\text{Sr}$ values for aragonite and HFO are presented in Table 1. Values for aragonite are lower, but are very close to those of Tutum Bay vent fluids. Values for HFO vary, but are consistently higher than those for aragonite. A closer look at the aragonite samples that were collected by microdrilling reveals that micrococrystalline and macrococrystalline aragonite have distinctively different $^{87}\text{Sr}/^{86}\text{Sr}$ values (Table 1), with micrococrystalline having the higher ratios.

The precipitation of a carbonate phase from solution is primarily controlled by $\text{pCO}_2$, $\text{pH}$, temperature, ion activity and microbial activity. These factors are closely related and they often compete with each other. Hydrothermal fluids in Tutum Bay are $\text{CO}_2$-rich ($\text{pCO}_2 > 2$ atm) and are either boiling or close to boiling as they enter seawater; this combined with a drop in pressure causes a rapid loss of $\text{CO}_2$. Mixing with seawater causes a drop in temperature and an increase in $\text{pH}$, the latter favoring carbonate precipitation.

The precipitation of HFO from Tutum Bay hydrothermal fluids compared to aragonite precipitation is relatively straightforward. Mixing of the hydrothermal fluid with seawater causes an increase in $\text{Eh}$ and $\text{pH}$ and a decrease in temperature, all of which are in favor of HFO precipitation (Pichler & Veizer 1999). To further investigate the precipitation process, it is necessary to assess the amount of mixing between hydrothermal fluid and seawater prior to and during precipitation.

4.1 The $^{87}\text{Sr}/^{86}\text{Sr}$ mixing model

$^{87}\text{Sr}/^{86}\text{Sr}$ ratios are a widely used tracer in mixing processes (e.g. Faure 1986). The mass difference between the two strontium isotopes, $^{87}\text{Sr}$ and $^{86}\text{Sr}$, is too small to cause a measurable fractionation during precipitation. Thus the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio in aragonite and HFO can be used as a direct measure of the ratio in the parent fluid.

Most binary mixtures follow a simple mathematical expression:

$$M_{AB} = x*A + y*B$$  \hspace{1cm} (1)

where $M_{AB}$ is the composition of a mixture of A and B, and x and y are the respective fractions ($x + y = 1$). $^{87}\text{Sr}/^{86}\text{Sr}$ values in a binary mixture, however, depend not only on the ratios in the two endmembers, but also on their respective elemental Sr concentrations. This can be accounted for and the composition of a mixture can be calculated using the following equation:
\[
\left( \frac{^{87}Sr}{^{86}Sr} \right)_M = \left( \frac{^{87}Sr}{^{86}Sr} \right)_{HF} \left( \frac{Sr_{HF} \cdot (1-x)}{Sr_M} \right) \\
+ \left( \frac{^{87}Sr}{^{86}Sr} \right)_{SW} \left( \frac{Sr_{SW} \cdot x}{Sr_M} \right)
\]

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). \(Sr_M\) has to be calculated for each mixture using equation (1). Equation (2) is generally a hyperbola in coordinates of \(^{87}Sr/^{86}Sr\) (x-axis) and x (y-axis), unless the Sr values for the two endmembers are equal. For Tutum Bay, where hydrothermal fluid and seawater have similar Sr concentrations, the curvature is very small (Figure 3). Based on this \(^{87}Sr/^{86}Sr\) mixing model, it is evident that the change in precipitation mineralogy from macro to microcrystalline aragonite and finally to HFO is due to increasing admixture of seawater to the hydrothermal fluid.

Assuming seawater and hydrothermal fluid to be 30°C and 100°C, respectively, the temperature of the precipitation temperatures for aragonite and HFO can be calculated with equation (1), where A and B are the temperatures for hydrothermal fluid and seawater, respectively and x is the hydrothermal fluid fraction. The calculated maximum seawater fraction is 11%, which corresponds to a maximum temperature drop by approximately 7°C, resulting in a 93°C mixture. The conductive loss or gain of heat may perturb the use of Sr to calculate temperature, but precipitation is assumed to be very rapid. The calculated extent of mixing, although very small, may prevent precipitation if one of the mixing partners is dramatically undersaturated with respect to calcium carbonate. In Tutum Bay, however, both seawater and hydrothermal fluid are supersaturated with respect to calcium carbonate and the relatively elevated activity of Ca\(^{2+}\) in seawater may actually be the trigger that initiates nucleation (Dandurand et al. 1982).

Figure 3. Mixing curve between the hydrothermal fluid and seawater endmember. \(^{87}Sr/^{86}Sr\) ratios of macrocrystalline aragonite (open diamonds), microcrystalline aragonite (open circles) and HFO (filled squares) plotted vs. their respective amount of seawater fraction at the time of precipitation. Above 11% seawater addition (dashed line) to the hydrothermal fluid HFO precipitates instead of aragonite.

The calculated minimum and maximum seawater fractions during HFO precipitation are approximately 11% and 57%, respectively (Figure 3). Thus, precipitation of Tutum Bay HFO takes place within a temperature range between approximately 60° and 93°C. This model, however, cannot be used without reservation, because HFO is a mixture of different minerals and the mineral phases represent slightly different physico-chemical conditions. Post-depositional absorption of Sr or exchange with seawater or hydrothermal fluid cannot be excluded due to the extreme reactivity of the HFO surface (e.g. Davis & Kent 1991). Thus, through time, HFO may lose the chemical signature that represents the conditions during precipitation. Nevertheless, the temperatures that were estimated with the \(^{87}Sr/^{86}Sr\) mixing model are in good agreement with precipitation temperatures reported in the literature (e.g. Chukhrov et al. 1973, Puteanus et al. 1991).

5 SUMMARY AND CONCLUSIONS

The observed changes in mineralogy seem to be a direct response to changes in redox conditions that, in turn, must be closely controlled by the extent of mixing between seawater and hydrothermal fluid. A plot of \(^{87}Sr/^{86}Sr\) ratios in aragonite and HFO (Figure 3) demonstrates the control of seawater mixing on the observed mineralogy. \(^{87}Sr/^{86}Sr\) ratios and, therefore, seawater mixing is always lower for aragonite. At greater than 11% seawater admixed to the hydrothermal fluid, HFO precipitation commences.

If mixing between seawater and hydrothermal fluid is the sole process responsible for the observed mineralogy, then the sequence of precipitation would give a clue to changes in the hydrology of the hydrothermal system. A change in discharge rate of the hydrothermal fluid is the only plausible explanation for the observed physico-chemical changes. Without changing the hydrothermal systems as a whole, supply of groundwater must be the controlling factor to explain a change in discharge rate. Thus, extreme changes in local weather conditions may be recorded in Tutum Bay hydrothermal pre-
cipitates and long term monitoring may provide an answer.

REFERENCES


