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# Enhanced geochemical gradients in a marine shallow-water hydrothermal system: Unusual arsenic speciation in horizontal and vertical pore water profiles

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## 1. Introduction

Most research on marine hydrothermal activity has focused on deep, mid-ocean ridge and back-arc basin systems; shallow-water hot springs (<200 m), which occur in coastal environments, have been largely overlooked. Like their deep-sea counterparts, these shallow-water hydrothermal

systems are characterized by steep physicochemical gradients, which can drastically affect surrounding biology, particularly microbial community composition (Amend et al., 2003; Brinkhoff et al., 1999; Rogers and Amend, 2006; Rusch et al., 2005; Tarasov et al., 1986). They can be found worldwide, commonly on the flanks of active volcanoes, near the tops of seamounts, or in areas of tectonic activity (Dando et al., 2000; Johnson and Cronan, 2001; Pichler et al., 1999a; Pichler and Dix, 1996; Tarasov et al., 1986; Vidal et al., 1978). The chemical dis-

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equilibria that are caused by hydrothermal venting may have large impacts on coastal biota, including corals (Pichler et al., 2000; Price and Pichler, 2005), and steep geochemical gradients (e.g., for As speciation) may allow for microbial communities similar to those found in terrestrial hot springs or hydrothermal lakes (Langner et al., 2001; Oremland and Stolz, 2003). Considering their occurrence in coastal waters, which are the breeding grounds for many species of fish, marine shallow-water hot springs may be of greater importance than their restricted geographical occurrence suggests.

Marine shallow-water hydrothermal systems are often characterized by gradients in temperature, pH,  $\text{HCO}_3^-$ , and an array of biologically toxic elements such as As, Sb, Pb, Cd and Hg (e.g., Price and Pichler, 2005; Johnson and Cronan, 2001). This article explores the geochemical gradients associated with the hydrothermal system in Tutum Bay, Ambitle Island, Papua New Guinea where As (as  $\text{As}^{\text{III}}$ ) was demonstrably enriched in the hydrothermal fluid, sediments and hydrothermal precipitates (Pichler et al., 1999b). Here, data are presented for total As abundance ( $\text{As}^{\text{T}}$ ), As speciation ( $\text{As}^{\text{III}}$  and  $\text{As}^{\text{V}}$ ), aqueous silica ( $\text{H}_4\text{SiO}_4$ ),  $\text{Mg}^{2+}$ , and other physicochemical parameters related to the hydro-

thermal system. Analyses are presented first for pore water samples collected at 10 cm sediment depth along a 300 m horizontal transect, and second for pore water profiles down to 100 cm, which were collected at distances of 2.5, 30, 60, 140 and 300 m along the same transect. The organoarsenicals, DMA and MMA, were not detected in any of the pore water samples.

## 2. Site description

Ambitle Island is part of the Feni Island group and is located NE of New Ireland Province, Papua New Guinea. The island is of volcanic origin, and several geothermal areas exist (Fig. 1). One of these areas occurs submerged on the west side of Ambitle Island, within Tutum Bay in 5–10 m of water (Figs. 1 and 2). Tutum Bay contains a patchy distribution of coral–algal reefs surrounded by medium to coarse-grained mixed carbonate–volcaniclastic sand and gravel. The hydrothermal activity consists of four main vent sites, along with diffuse venting throughout the area. The hydrothermal fluids are of meteoric origin and, compared to seawater, vent fluids are about 10 times less saline. A more detailed description of Tutum Bay hydrothermal vent fluids

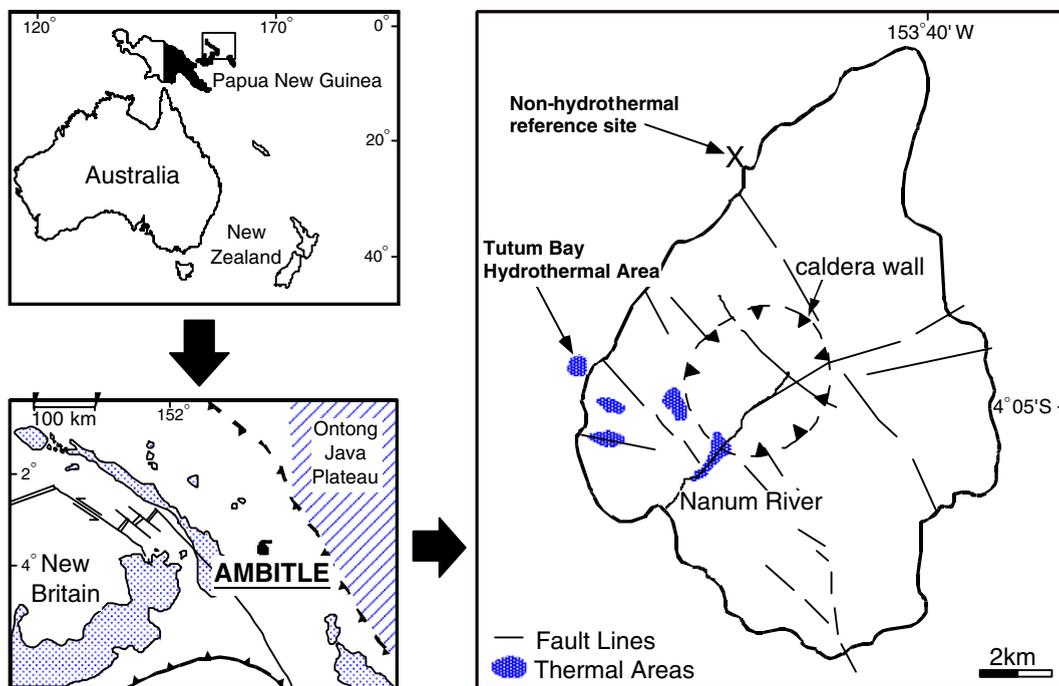


Fig. 1. Location of Ambitle Island and the shallow-water hydrothermal vents studied. The Tutum Bay hydrothermal area and the reference site are indicated (modified from Pichler and Dix, 1996).

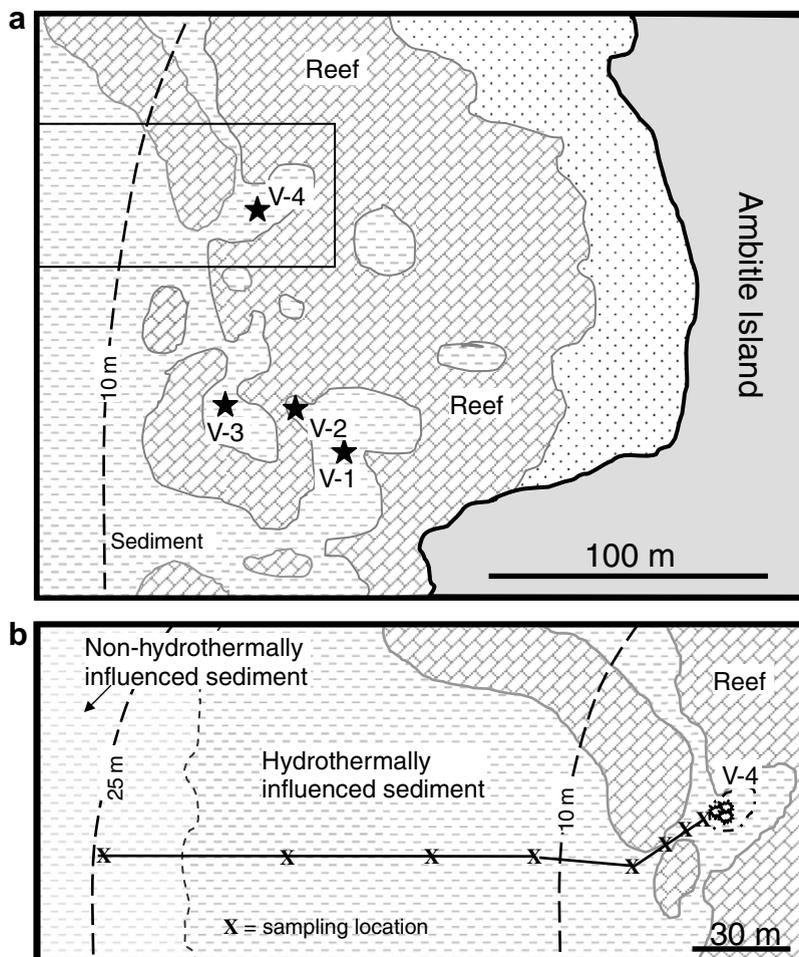


Fig. 2. (a) Location of the main venting areas of the hydrothermal system at Ambitle Island. The box in the upper left is enlarged in (b) (modified from Pichler et al., 1999c). (b) Location of transect along which pore waters were collected for this study. Vent fluids were also collect at the area of focused venting.

and precipitates has been provided elsewhere (Pichler and Dix, 1996; Pichler et al., 1999b; Price and Pichler, 2005).

Of all potentially biologically toxic elements, As is the only one that was significantly enriched compared to seawater (~500 times). It has been estimated that the main hydrothermal vents discharged as much as 1.5 kg per day of As directly into the coral-reef ecosystem (Pichler et al., 1999b; Pichler et al., 1999c). However, diffuse venting also played a critical role on the distribution of As throughout Tutum Bay (Price and Pichler, 2005).

In order to compare the Tutum Bay area to a “normal” marine coral reef a reference site was established several kilometers to the north (Fig. 1). That site was well beyond the influence of present

or past hydrothermal venting. The sediments at the reference site consisted entirely of  $\text{CaCO}_3$ , thus providing a suitable end-member for comparison.

### 3. Methods

#### 3.1. Field

To investigate the transition from hydrothermal to “normal” marine conditions a sampling transect was established, which began at Vent 4 of (Pichler et al., 1999c) and extended out to beyond 300 m (Fig. 2). Pore water temperature and pH were measured every meter at a sediment depth of ~10 cm, using an IQ Scientific Instruments® #IQ 150 pH/mV/temperature probe, with automatic temperature

compensation to 100 °C, in an underwater housing. Vent fluids were collected by placing an inverted Teflon<sup>®</sup> funnel over focused venting. The temperature from the top of the funnel, along with the appearance of density fronts, indicated that the flow of hydrothermal fluid discharge had displaced all seawater from the funnel. Syringes (60 mL) were attached to the funnel, and the vent fluid was slowly drawn into the syringe at a rate slower than vent discharge to decrease seawater entrainment.

The collection of pore waters in Tutum Bay required specialized, easy to use and reliable equipment designed to endure high temperatures (~100 °C), low pH (2–6), and it must be submersible and light-weight for transport to remote areas. With those requirements in mind a 10-port pore water sampler (10 cm spacing), which consisted of a 1 in. (25.4 mm) diameter Al pipe with Teflon<sup>®</sup> tubing extending through the pipe to all individual sample ports was developed. Up to 10 syringes could be attached and filled simultaneously to ensure equal flow to all ports. In situ temperatures for the pore water profiles were measured by using a Fisher Scientific Traceable<sup>®</sup> digital thermometer in an underwater housing with a probe that extended up to 1 m into the sediment. In addition to the vertical profiles pore waters were also collected at 10 cm sediment depth at 16 sites along the transect. Those samples were collected using a small plastic tube connected via Tygon<sup>®</sup> tubing to a 60 mL syringe. A pipette tip with small holes punched into the end served as a filter to prevent sediment entrainment.

Vent fluids, pore waters, and surrounding seawater were collected and brought on-board for immediate measurement of sensitive field parameters such as pH and alkalinity. Total alkalinity was measured as equivalent CaCO<sub>3</sub> using a HACH digital titrator, titrated to an endpoint of pH 4.5 and is expressed as HCO<sub>3</sub><sup>-</sup>. Onboard, the pH was measured using a Myron-L pH meter with temperature compensation. Onboard pH was very similar to in situ pH measurements using the underwater-housed pH meter. Water samples were preserved by following two procedures for later laboratory analysis. The first procedure was for preservation of major cations, total As abundance (As<sup>T</sup>), and As species (As<sup>III</sup> and As<sup>V</sup>). This consisted of syringe filtering the water sample through 0.45 µm filters into 30 mL nalgene bottles and acidifying to a pH <2 using 1% optima HCl. All Nalgene<sup>®</sup> bottles used for As speciation were capped tightly without headspace. Decreasing the pH to less than 2 prevents Fe

from precipitating and thus helps to preserve As speciation (McCleskey et al., 2004). The second procedure was for preservation of major anions, and consisted of syringe filtering the water sample through 0.45 µm filters into 30 mL Nalgene<sup>®</sup> bottles without acidification. All water sample bottles were sealed with electrical tape and kept cool and away from light until laboratory analysis.

Sample collection for As speciation analysis specifically consisted of the following step by step procedure:

- (1) Sample collection into 60 mL syringes using the pore water sampler with multi-syringe puller described above.
- (2) Transporting syringes to the ship, disconnecting them from the sampler, immediately attaching to syringe filters (0.45 µm) and filtering into 30 mL Nalgene<sup>®</sup> bottles containing 0.3 mL optima HCl.
- (3) The lids were screwed on tightly with no headspace by slightly squeezing the bottle.
- (4) Sample bottles were immediately placed in a refrigerator until it was time to leave the ship.
- (5) For transport from the ship to the lab, samples were placed into a cooler with ice packs, which maintained a low temperature until reaching the laboratory, at which time they were transferred to the refrigerator.
- (6) Arsenic speciation was then performed in the lab following the methods described below.

### 3.2. Laboratory

Magnesium and silica were analyzed by inductively coupled plasma-optical emission spectrometry (ICP-OES) on a Perkin-Elmer Optima 2000 DV. Arsenic abundance and speciation was determined by hydride generation-atomic fluorescence spectrometry (HG-AFS) on a PSA analytical 10.055 Millennium Excalibur system (Cai, 2000). In preparation for the determination of As<sup>T</sup>, 10 mL of sample were combined with 15 mL concentrated HCl and 1 mL saturated KI solution to reduce As<sup>V</sup> to As<sup>III</sup>, and diluted with deionized water (DI) to a final volume of 50 mL. Arsenic speciation analysis was carried out by high pressure liquid chromatography (HPLC) separation of As<sup>III</sup>, DMA, MMA and As<sup>V</sup> prior to detection by HG-AFS. A sample volume of 200 µL was injected without pretreatment and separated in a Hamilton

PRP-X100 cation exchange column using a  $\text{KH}_2\text{PO}_4/\text{K}_2\text{HPO}_4$  buffer at a pH of 6.00. Analytical and instrumental quality assurance and quality control (QA/QC) was evaluated for all laboratory analyses by including sample duplicates and certified reference standards from NIST and Fisher Scientific®, which indicated a precision of better than 5% for HG-AFS and ICP-OES. Background signal drift was consistently <1% for all instruments. Because the  $\text{As}^{\text{T}}$  analysis is considered to be more accurate, the ratio of the concentration obtained from the As speciation analysis was used and applied to the  $\text{As}^{\text{T}}$  concentration to get a final concentration of each As species.

## 4. Results

### 4.1. Horizontal profile (10 cm pore water samples)

With increasing distance from the vent, temperature,  $\text{HCO}_3^-$ ,  $\text{As}^{\text{T}}$  and  $\text{H}_4\text{SiO}_4^0$  decreased considerably, although occasional spikes were observed (Table 1). The temperature decreased from 90.5 °C close to the vents (0.5 m) to near ambient seawater temperature (~30 °C) at 300 m. Bicarbonate decreased from 683 mg/L in the vent fluids to near seawater concentration (~140 mg/L) at 300 m.

$\text{H}_4\text{SiO}_4^0$ , a very good indicator of hydrothermal fluid mixing, dropped from 100 mg/L in the vent fluid to ~2 mg/L both at the end of the transect and at the Picnic Island reference site. On the other hand, pH and  $\text{Mg}^{2+}$  concentrations increased with distance from the vent (Table 1); pH values from 6.1 to 8.0, and  $\text{Mg}^{2+}$  from ~130 mg/L to ~1200 mg/L.

In the vent fluid and in pore waters near the area of focused venting (<2.5 m),  $\text{As}^{\text{III}}$  was the dominant valence state (Table 1). However,  $\text{As}^{\text{III}}$  levels decreased rapidly, leveling off to near ambient values of less than 10 µg/L at a distance of 12 m. One notable spike in  $\text{As}^{\text{III}}$  (51 µg/L) was observed at 150 m. At distances from 2.5 to 300 m, As was, with one exception, predominantly in the oxidized,  $\text{As}^{\text{V}}$  form (Table 1). Although the  $\text{As}^{\text{V}}$  levels fluctuated considerably, they were higher than those of ambient seawater and the control site (1–2 µg/L). With increasing distance from the vent,  $\text{As}^{\text{T}}$  decreased exponentially from ~900 µg/L at the source to <20 µg/L beyond 150 m. Those gradients correlate well with those of  $\text{H}_4\text{SiO}_4^0$ , and inversely with those of  $\text{Mg}^{2+}$ .

### 4.2. Pore water profiles

The  $\text{As}^{\text{T}}$  concentration in pore water profiles generally increased with sediment depth, although only

Table 1  
Arsenic,  $\text{H}_4\text{SiO}_4^0$ ,  $\text{Mg}^{2+}$  and other physicochemical parameters measured in 10-cm pore waters for the Tutum Bay hydrothermal system, sorted by distance from focused venting

Distance (m)	$T$ (°C)	pH	$\text{HCO}_3^-$ (mg/L)	$\text{As}^{\text{III}}$ (µg/L)	$\text{As}^{\text{V}}$ (µg/L)	$\text{As}^{\text{III}}/\text{As}^{\text{V}}$	$\text{As}^{\text{T}}$ (µg/L)	$\text{H}_4\text{SiO}_4^0$ (mg/L)	$\text{Mg}^{2+}$ (mg/L)
Vent 4	98.0	6.0	683.2	950.0	<1	~945.6	945.6	100.0	130
0.5	90.5	6.2	610.0	1031.2	<1	~1031.2	1031.2	85.2	230
1	77.6	6.1	610.0	900.0	<1	~900	900.0	97.0	220
2.5	81.0	6.1	439.2	95.2	160.3	0.59	255.5	61.5	710
12	90.1	6.1	197.4	2.3	34.3	0.07	36.6	n.a.	144
17	33.8	6.5	218.2	8.6	11.4	0.75	20.0	7.9	1290
18	33.1	6.5	233.1	1.2	27.1	0.04	28.3	10.7	1220
20	29.7	7.6	156.2	4.2	2.3	1.79	6.5	13.6	1100
30	31.7	6.1	385.5	1.7	23.0	0.07	25.0	21.0	1090
60	33.3	6.8	244.0	3.1	13.0	0.23	16.4	15.0	1140
90	31.1	7.5	122.0	2.4	20.0	0.12	21.9	2.0	1320
140	34.0	6.1	244.0	1.8	45.4	0.04	47.2	16.4	1075
150	n.a. <sup>a</sup>	7.2	244.0	51.0	12.0	4.22	62.8	2.0	1310
180	32.8	7.8	141.5	4.9	14.7	0.33	19.6	2.0	1260
225	n.a.	7.8	122.0	1.3	3.2	0.39	4.5	2.0	1330
240	n.a.	7.9	153.7	5.1	2.7	1.86	7.8	0.4	1260
300	n.a.	7.1	167.1	2.0	12.1	0.17	14.1	1.0	1305
Picnic Island control	n.a.	7.6	186.2	1.9	1.4	1.30	3.4	2.0	1289
Ambient Seawater	30.2	8.1	139.7	1.3	1.1	1.12	2.4	1.0	1330

<sup>a</sup> n.a. = not available.

the two profiles at 30 and 60 m showed a continuous increase (Table 2). However  $\text{As}^{\text{T}}$  correlated well with  $\text{H}_4\text{SiO}_4^0$  and  $\text{Mg}^{2+}$ , indicating that mixing between hydrothermal fluid and seawater controlled its abundance. Unexpectedly, however,  $\text{As}^{\text{V}}$  was the dominant oxidation state at all depths from 10 to 100 cm in all Tutum Bay profiles (Table 2). The  $\text{As}^{\text{III}}/\text{As}^{\text{V}}$  ratio ranged from 0.01 to 0.23, with one anomalous value of 0.59 (2.5 m at 10 cm depth). In contrast, the pore water profile at the reference site had an  $\text{As}^{\text{III}}/\text{As}^{\text{V}}$  ratio  $> 1$  (Table 2).

## 5. Discussion

### 5.1. Are the $\text{As}^{\text{III}}/\text{As}^{\text{V}}$ ratios in vertical pore water profiles unusual?

The measurements of  $\text{H}_4\text{SiO}_4^0$ ,  $\text{Mg}^{2+}$ ,  $\text{HCO}_3^-$ , temperature, and pH (Table 1) demonstrated (1) the increase of hydrothermal influence with sediment depth on pore water chemistry and (2) the decrease of that influence with distance from the vent area. The changes in  $\text{As}^{\text{T}}$  concentration along the transect and with depth told the same story. On the other hand, the As speciation data did not seem to reflect hydrothermal influence, because As in the vent fluid was predominantly  $\text{As}^{\text{III}}$ . Hence, in pore waters with elevated temperatures and at sites with obvious diffuse venting, a relatively high  $\text{As}^{\text{III}}/\text{As}^{\text{V}}$  ratio might be expected.

Unfortunately, literature on As speciation in marine pore waters, whether hydrothermally influenced or not, is surprisingly sparse. One of the first publications describing As speciation in marine pore waters reported an  $\text{As}^{\text{III}}/\text{As}^{\text{V}}$  ratio of 0.25 for samples from the Santa Barbara Basin, California (Andreae, 1979). The sedimentary environments studied spanned a wide range of redox conditions and biological activity. Nevertheless,  $\text{As}^{\text{V}}$  dominated  $\text{As}^{\text{III}}$  even in the reducing sediments, but not to the extent of the Tutum Bay hydrothermal system. Reimer and Thompson (1988) reported  $\text{As}^{\text{III}}/\text{As}^{\text{V}}$  ratios, ranging from 0.3 to 1.8 (mean = 0.9), for pore waters from two British Columbia coastal sites which were influenced by mine-tailings discharge. Peterson and Carpenter (1985), reported  $\text{As}^{\text{III}}/\text{As}^{\text{V}}$  ratios between 0.21 and 1.5 for pore waters in Puget Sound (estuary), 0.026–0.76 for the Washington coast (coastal ocean), and 2.8–5.0 for Saanich Inlet (intermittently anoxic fjord), but controls on the As speciation were unclear. These investigations suggest that pore water  $\text{As}^{\text{III}}/\text{As}^{\text{V}}$

are highly variable, and that they are controlled by a combination of redox conditions, pH and adsorption/release from solid phases, such as Fe and Mn (hydr)oxides. Andreae (1979) suggested that As was released (due to  $\text{As}^{\text{V}}$  desorption) to the pore water during organic matter degradation or Fe and Mn dissolution.

The conditions in Tutum Bay differ from those of the previous studies in that  $\text{As}^{\text{T}}$  concentrations in the pore waters were much higher and that mixing between an  $\text{As}^{\text{III}}$ -dominated hydrothermal fluid and seawater occurred. Also, the sediments of Tutum Bay contain substantial amounts of hydrous ferric oxides (HFO). At the reference site the  $\text{As}^{\text{III}}/\text{As}^{\text{V}}$  ratios in 10-cm pore waters and ambient seawater were 1.3 and 1.1, respectively. These ratios are similar to those previously reported for non-hydrothermally influenced sediments. The  $\text{As}^{\text{III}}/\text{As}^{\text{V}}$  ratio for pore waters from the reference site at 20 cm depth however is 7.36, indicating predominance of  $\text{As}^{\text{III}}$  and reducing conditions. Freshly deposited carbonate sediments, however, have a high organic matter content, which causes a rapid change from oxidizing to reducing conditions (Lyons et al., 1973). This could explain the observed dominance of  $\text{As}^{\text{III}}$  deeper in the sediment at the reference site. Along the transect in Tutum Bay the  $\text{As}^{\text{III}}/\text{As}^{\text{V}}$  ratios in pore water at 10 cm depth are similar (0.76), if the 0.5 and 1 m samples are excluded. These two samples were almost identical to the hydrothermal fluid (Table 1). To better illustrate the As speciation at Tutum Bay, the  $\text{As}^{\text{III}}/\text{As}^{\text{V}}$  ratio has been plotted represented as % species versus distance away from focused venting in 10-cm pore waters and vertical pore water profiles (Figs. 3 and 4).

Unexpectedly, the As speciation ratio in the vertical pore water profiles (i.e., below 10-cm depth) is an order of magnitude lower than the control site, with values consistently below 0.1 (range = 0.01–0.59; Fig. 4; Table 2). Comparing previously reported ratios and reference site ratios to Tutum Bay pore waters, the As speciation ratios in hydrothermally influenced pore waters below 10-cm were clearly skewed towards  $\text{As}^{\text{V}}$  (Fig. 4). If mixing with oxygenated seawater led to oxidation of  $\text{As}^{\text{III}}$  to  $\text{As}^{\text{V}}$ , the  $\text{As}^{\text{III}}/\text{As}^{\text{V}}$  ratio should be somewhere between that of the hydrothermal fluid and seawater. However, in the hydrothermal system at Tutum Bay, the  $\text{As}^{\text{III}}/\text{As}^{\text{V}}$  ratio is far below that found in local seawater. Mixing between hydrothermal fluid and seawater is demonstrated by pH and tempera-

Table 2

Arsenic,  $\text{H}_4\text{SiO}_4^0$ ,  $\text{Mg}^{2+}$  and other physicochemical parameters in all pore waters for the Tutum Bay hydrothermal system, sorted by distance from focused venting, then by depth into sediment

Distance (m)	Depth (cm)	$T$ ( $^{\circ}\text{C}$ )	pH	$\text{HCO}_3^-$ (mg/L)	$\text{As}^{\text{III}}$ ( $\mu\text{g/L}$ )	$\text{As}^{\text{V}}$ ( $\mu\text{g/L}$ )	$\text{As}^{\text{III}}/\text{As}^{\text{V}}$	$\text{As}^{\text{T}}$ ( $\mu\text{g/L}$ )	$\text{H}_4\text{SiO}_4^0$ (mg/L)	$\text{Mg}^{2+}$ (mg/L)
Vent 4	–	98	6.0	683	950.0	<1	~945.6	945.6	100	129
2.5	10	81.0	6.1	439	95.2	160.3	0.59	255.5	61.5	710
2.5	20	73.6	5.9	561	21.3	599.6	0.04	620.9	68.2	592
2.5	30	69.5	5.9	561	77.3	430.5	0.18	507.8	63.7	678
2.5	40	63.5	5.8	537	12.8	358.4	0.04	371.1	67.8	864
30	10	31.7	6.1	386	1.7	23.0	0.07	25.0	21.0	1090
30	20	33.0	6.2	312	1.1	42.0	0.03	42.9	21.0	1010
30	30	34.5	6.2	322	1.2	61.0	0.02	62.6	19.0	987
30	60	37.9	6.1	440	4.5	355.0	0.01	359.5	81.0	582
30	100	40.8	n.a.	205	0.6	95.0	0.01	95.5	27.0	1170
60	10	33.3	6.8	244	3.1	13.0	0.23	16.4	15.0	1140
60	20	34.9	6.2	220	1.5	38.0	0.04	39.2	12.0	1150
60	30	36.6	6.2	249	2.0	63.0	0.03	65.2	16.0	1130
60	60	40.5	n.a.	260	1.2	65.0	0.02	66.5	16.0	1350
60	100	n.a. <sup>a</sup>	n.a.	473	20.0	130.0	0.15	150.0	56.0	1314
140	10	34	6.1	244	1.8	45.4	0.04	47.2	16.4	1075
140	20	n.a.	6.2	278	1.9	21.7	0.09	23.6	12.4	1190
140	30	n.a.	6.1	185	2.1	31.8	0.07	33.9	13.2	1225
140	40	n.a.	6.3	254	2.0	15.9	0.12	17.8	11.2	1180
140	50	n.a.	6.1	190	1.7	29.4	0.06	31.1	9.2	1215
140	60	n.a.	6.3	100	2.3	14.4	0.16	16.6	8.4	1200
140	90	n.a.	6.5	166	2.4	20.0	0.12	22.4	6.7	1220
300	10	n.a.	7.1	167	2.0	12.1	0.17	14.1	1.0	1305
300	20	n.a.	7.2	151	1.2	11.5	0.11	12.8	0.9	1260
300	30	n.a.	6.7	137	1.6	11.6	0.13	13.2	0.7	1280
300	40	n.a.	6.6	83	1.2	14.1	0.09	15.4	1.4	1300
300	50	n.a.	6.8	205	2.5	17.9	0.14	20.4	1.5	1310
300	60	n.a.	7.1	146	2.5	15.2	0.16	17.7	1.9	1290
300	70	n.a.	6.9	156	2.2	12.4	0.18	14.6	2.2	1280
Ambient seawater	–	30.2	8.1	139.7	1.3	1.1	1.12	2.4		1289
Picnic Island reference site	10	n.a.	7.6	186.2	1.9	1.4	1.30	3.4	2.0	1330
Picnic Island reference site	20	n.a.	7.8	187.8	1.8	0.3	7.36	2.1	2.0	1300

<sup>a</sup> n.a. = not available.

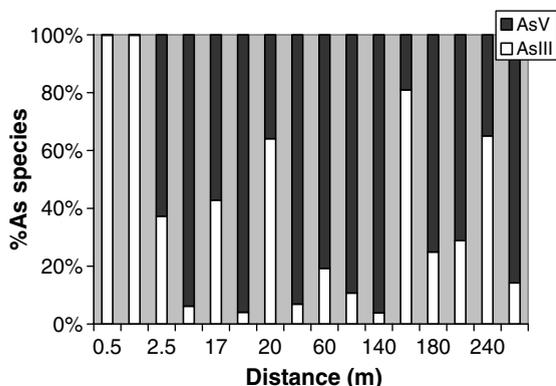


Fig. 3. The distribution of the two inorganic As species, arsenite (As<sup>III</sup>) and arsenate (As<sup>V</sup>) in pore waters collected at 10 cm sediment depth, stepping away from the area of hydrothermal venting.

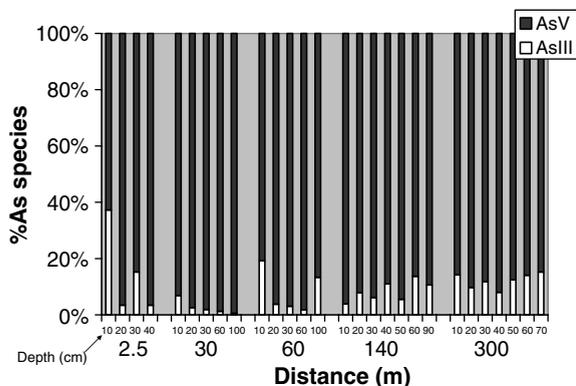


Fig. 4. The distribution of the two inorganic As species, arsenite (As<sup>III</sup>) and arsenate (As<sup>V</sup>) in vertical pore water profiles that were collected at a distance of 2.5, 30, 60, 140 and 300 m away from the area of hydrothermal venting.

ture, and by increasing/decreasing concentrations of  $\text{HCO}_3^-$ ,  $\text{H}_2\text{SiO}_4^0$ ,  $\text{Mg}^{2+}$  and  $\text{As}^{\text{T}}$  in the pore water profiles (Tables 1, 2). Thus one would expect  $\text{As}^{\text{III}}/\text{As}^{\text{V}}$  ratios to increase with sediment depth, i.e., greater sediment depth leads to higher hydrothermal fluid/seawater ratio, more reducing sediments, and thus greater  $\text{As}^{\text{III}}$  (Fig. 5). That scenario was not encountered in the Tutum Bay pore water profiles. All profiles showed the expected increase in As with sediment depth, but unexpectedly  $\text{As}^{\text{V}}$  was always the dominant As species. The depth profiles of sample locations 30 m and 60 m are good examples of this enigma (Fig. 6). In those profiles  $\text{As}^{\text{III}}$  is more or less absent and  $\text{As}^{\text{V}}$  is equal to  $\text{As}^{\text{T}}$ , decreasing towards the sediment–seawater interface.

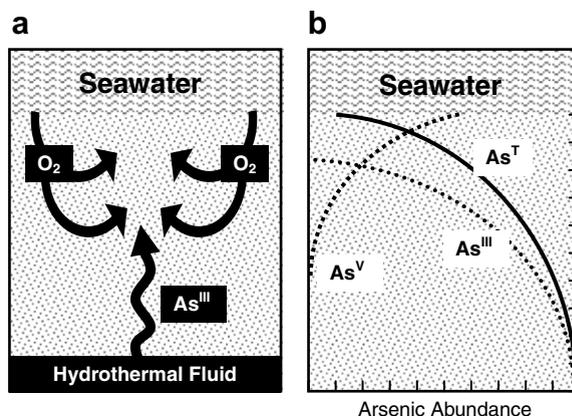


Fig. 5. Conceptual model of the expected As gradients in Tutum Bay pore water profiles exclusively invoking the assumption of seawater mixing and abiotic oxidation.

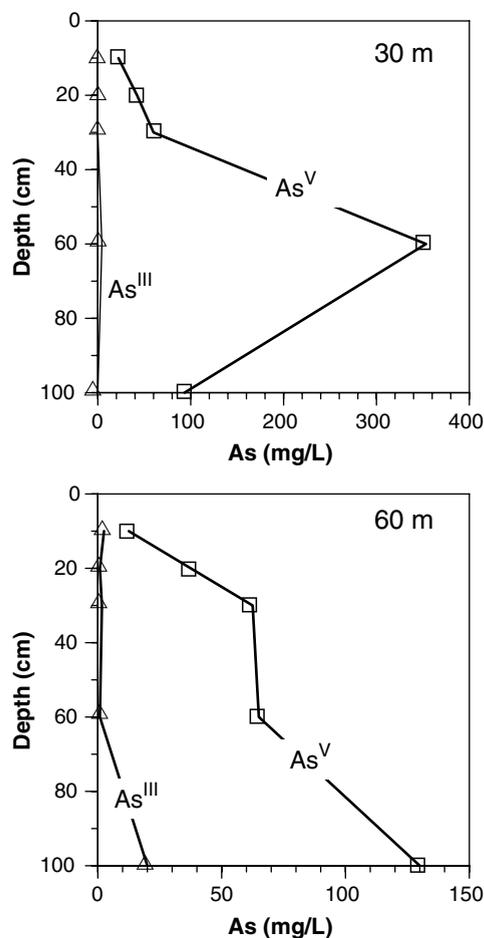


Fig. 6. Observed vertical pore water profiles in Tutum Bay sediments at a distance of 30 and 60 m away from the main area of hydrothermal venting.

## 5.2. Thermodynamic and kinetic considerations

Smedley and Kinniburgh (2002) suggest burial of organic matter and slow diffusion of  $O_2$  out of the sediment can lead to reducing conditions just below the sediment–water interface, thus facilitating the reduction of  $As^V$ . Other studies have shown that ‘typical’ coastal waters become reducing just below the sediment–water interface, and that in organic-rich sediments it is common to observe  $O_2$  reduction at the sediment surface,  $NO_3^-$ , Mn and Fe reduction within the next few centimeters, and  $SO_4^{2-}$  reduction over another meter or so (e.g., Berner, 1980). These reactions are almost certainly microbially mediated. Cullen and Reimer (1989) provide an excellent review on As speciation in ocean environments, and thermodynamic calculations suggest that under slightly reducing conditions and/or lower pH,  $As^{III}$  is stable, mainly as neutral  $H_3AsO_3^0$ .

Based on thermodynamic data alone however, it is widely accepted that  $As^V$  should strongly dominate over  $As^{III}$  in “normal” seawater (pH  $\sim 8$ ,  $O_2 \sim 8$  mg/L) with predicted  $As^{III}/As^V$  ratios as low as  $10^{-26}$  (Cullen and Reimer, 1989). However, thermodynamic predictions of  $As^{III}/As^V$  ratios assume equilibrium, which, of course, may not be obtained. The oxidation kinetics for  $As^{III}$  in seawater are slow. Johnson and Pilson (1975) report a half-life on the order of weeks to months for various temperatures and salinities. Thus, in the pore waters of the hydrothermal system at Tutum Bay the oxidation of  $As^{III}$  by  $O_2$  cannot be completely ruled out, but according to the observed  $As^{III}/As^V$  ratios, oxidation must have happened at a sediment depth of more than 1 m (Fig. 5). Considering results from previous studies of marine pore waters (e.g., Berner, 1980; Lyons et al., 1973) it is very unlikely that sufficient dissolved  $O_2$  (DO) would be available at that depth, neither from downward circulating seawater nor some other mechanism. Additional analyses (not included here) show that the hydrothermal fluids and pore waters from Tutum Bay contain several other reduced species (e.g., Fe(II) and sulfide), which are much more easily oxidized by seawater DO (e.g., Millero et al., 1987). It is therefore inferred that little to no abiotic oxidation of  $As^{III}$  by seawater derived DO has occurred.

## 5.3. Possible microbial metabolisms

Thermodynamic calculations can be used effectively to predict potential microbial metabolisms

(e.g., Broda, 1977), but not to assess whether a reaction proceeds biotically or abiotically. The oxidation rate described above was empirically derived, ignoring the potential role of microbial catalysts. In fact, slow abiotic reaction kinetics permit microorganisms to harness chemical energy by catalyzing redox reactions that are far from equilibrium, such as the  $As^{III}$ – $As^V$  couple at Tutum Bay.

In a recent paper, Oremland and Stolz (2003) reviewed available data on microbially mediated As redox reactions, and several studies confirmed the presence of a microbial As cycle, where  $As^{III}$  oxidation in the oxic zone is coupled to arsenate reduction in the anoxic zone (Macur et al., 2004; Oremland et al., 2005; Rhine et al., 2005). While dissimilatory arsenate reducing prokaryotes have received far more attention (e.g., Hoefft et al., 2004; Hollibaugh et al., 2006; Niggemeyer et al., 2001; Saltikov and Newman, 2003), several bacterial strains are known to gain metabolic energy from  $As^{III}$  oxidation (e.g., Santini et al., 2000). The terminal electron acceptor is generally  $O_2$ , but  $NO_3^-$  has also been implicated (Oremland et al., 2002). Several studies have shown that the rates of As oxidation increase dramatically when catalyzed by microorganisms (e.g., Salmassi et al., 2002; Weeger et al., 1999). As an example, the oxidation of  $As^{III}$  was 100 times faster in an experiment with the bacterium *Thermus* HR13 than in the abiotic control (Gihring and Banfield, 2001). A similarly enhanced biotic rate for  $As^{III}$  oxidation was reported by Skudlark and Johnson (1981). Wilkie and Hering (1998) showed that in the presence of submerged macrophytes that hosted oxidizing bacteria, the half-life for As oxidation was 0.3 h. For comparison, Langner et al. (2001) reported a half-life for As oxidation of 1 min in the presence of a brown Fe/As-rich microbial mat in a hot spring at Yellowstone National Park. The data presented in the current study support the interpretation that microorganisms played a major role in oxidizing the  $As^{III}$  found in the vent fluid. It is proposed that microorganisms, perhaps including yet unidentified thermophilic archaea and bacteria, use  $As^{III}$  as an electron donor in a respiratory process, as the vent fluid and seawater mix in the water column and in the shallow subsurface. For example, microorganisms in Tutum Bay sediments could use  $O_2$  or  $NO_3^-$  as terminal electron acceptors.

Mapping of redox reaction energetics can be used to help identify and even target specific

potential metabolisms, and perhaps show to which reduction half-reaction  $\text{As}^{\text{III}}$  oxidation can be coupled. However, computations of such reaction energetics require additional chemical analyses and extensive geochemical modeling, which is beyond the scope of the present communication, but will be addressed in a future study. In addition, microbial community structure studies and enrichment culturing are currently underway, with cultivation efforts targeting putative arsenite oxidation.

## 6. Summary and conclusions

The pore waters in Tutum Bay seemed to be influenced by hydrothermal venting out to more than 300 m away from the main area of venting. With respect to total As concentration ( $\text{As}^{\text{T}}$ ) two general trends could be observed: (1) an  $\text{As}^{\text{T}}$  increase with sediment depth and (2) an  $\text{As}^{\text{T}}$  decrease with distance from the main area of venting. Those trends were caused by mixing between the hydrothermal fluid and seawater, which was corroborated by the abundance of  $\text{H}_4\text{SiO}_4^0$  and  $\text{Mg}^{2+}$ , two excellent tracers of hydrothermal influence (Bischoff and Dickson, 1975; Pichler et al., 1999c). The  $\text{As}^{\text{T}}$  concentrations in seawater and in pore waters at the reference site fell into the range expected for “normal” marine conditions (e.g., Smedley and Kinniburgh, 2002). In contrast, the distribution of the two inorganic As species,  $\text{As}^{\text{III}}$  and  $\text{As}^{\text{V}}$  showed neither the expected influence of hydrothermal venting nor what could be expected for “normal” marine conditions (e.g., Cullen and Reimer, 1989; Smedley and Kinniburgh, 2002). The oxidized As species,  $\text{As}^{\text{V}}$  was always dominant, except at the reference site.

There may be several factors controlling the oxidation state of As in Tutum Bay pore waters. These include, but are likely not limited to, microbial interactions, mixing with seawater, and the influence of Fe-rich sediments. It is proposed that microorganisms likely play a role in the transformation of  $\text{As}^{\text{III}}$  to  $\text{As}^{\text{V}}$  in pore waters of Tutum Bay. Possible microbial metabolic reactions include the use of  $\text{O}_2$  or  $\text{NO}_3^-$  as electron acceptors and  $\text{As}^{\text{III}}$  as the electron donor. Research continues which will hopefully allow a full understanding of the role microbes play in affecting the redox chemistry of pore waters throughout Tutum Bay and other shallow marine hydrothermal systems.

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