Acknowledgments

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A Natural Laboratory to Study Arsenic Geobiocomplexity

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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. 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.

Approximately 30 active marine shallow-water hydrothermal systems are currently known. They can introduce toxic elements, such as arsenic (As), antimony (Sb), mercury (Hg), and thallium (Tl) into the coastal ocean, as well as nutrients such as iron (Fe) and carbon (C). Thus, their discharge can have considerable impact on the chemical composition of the biologically important coastal ocean.

One such shallow-water hydrothermal system is in Tutum Bay, Ambitle Island, Papua New Guinea (Figure 1), and it provides an exceptional opportunity to study ecosystem response to elevated temperature, acidity, and As levels. Because of the peculiar chemical nature of the Tutum Bay system, As concentrations are extremely high, while other potentially toxic elements are approximately at background seawater levels [*Pichler et al.*, 1999]. The research presented here links As to microbial, foraminiferal, meiofaunal, and macrofaunal invertebrate diversity and community structure in pore fluids, the water column, and sediments, with high As levels correlating with low species diversity.

The study of As is particularly timely and has become the focus of the scientific community because of epidemic poisoning by As-rich groundwater in Southeast Asia and the enforcement of a new As drinking water standard of 10 micrograms per liter (down from 50 micrograms per liter) by the U.S. Environmental Protection Agency since January 2006.

Arsenic, pH, and Temperature in Tutum Bay

The submarine hydrothermal springs in Tutum Bay are located approximately 150 meters offshore at 5–10 meter water depth. Venting occurs as focused discharge of a clear hydrothermal fluid at discrete ports, 5–15 centimeters in diameter (Figure 2a), and as diffuse discharge of gas bubbles (94–98% carbon dioxide; Figure 2b). The hydrothermal waters are slightly acidic (pH ~6) and of predominantly meteoric origin. The concentration of As in the hydrothermal fluid is approximately 1000 micrograms per liter, and the combined As release into Tutum Bay is as much as 1.5 kilograms per day.

The sediments in Tutum Bay are mostly weathering products of volcanic rocks, and are heavily coated with hydrous ferric oxides (HFOs) near the vents, gradually decreasing with distance. Starting at approximately 200 meters away from the area of hydrothermal venting, the sediment composition is carbonate-dominated. At a reference site beyond the influence of hydrothermal venting (Figure 1), the sediments consisted entirely of calcium carbonate, thus providing a suitable 'non-hydrothermal' material for comparison with the Tutum Bay sediments.

Fieldwork was carried out in November 2003 and May 2005, the ends of the dry and wet seasons, respectively. To study the transition from hydrothermal to 'normal' marine conditions, a sampling transect was established that started at Vent Four in the northern portion of the hydrothermal area [*Pichler et al.*, 1999] and continued to the west for approximately 300 meters. A multitude of chemical, physical, and biological data were collected along the transect at a sediment depth of 10 centimeters, with emphasis on As in the sediment, and As, pH, and temperature in the pore water (Figure 3). Great care was taken to assure that measurements were made at exactly the same location where samples were collected, and that all team members worked on subsets of the same samples. With few exceptions, As concentration and temperature decreased with distance from the

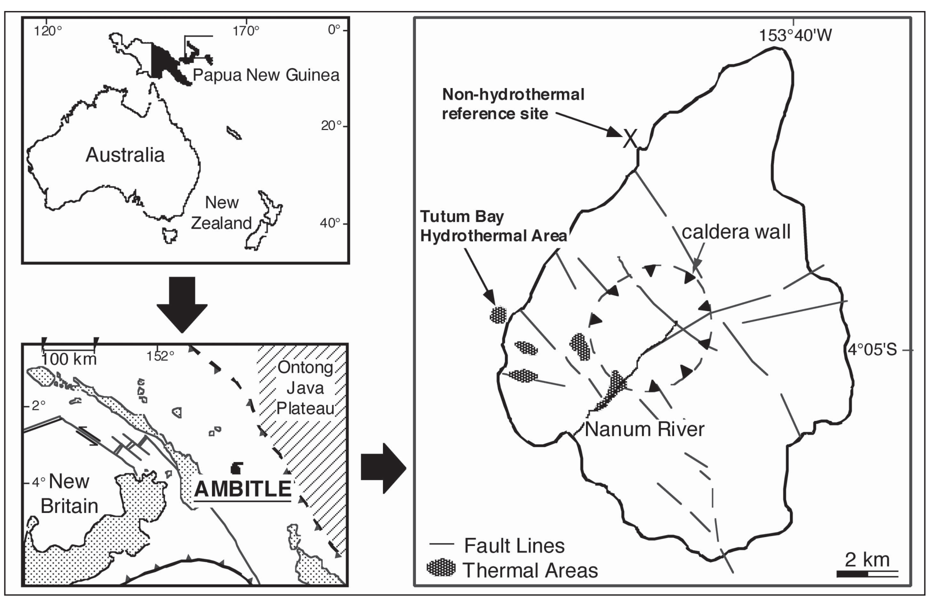

Fig. 1. Location of Ambitle Island and the shallow-water hydrothermal vents studied. Tutum Bay hydrothermal area and the control site are indicated [from Pichler et al., *1999].*

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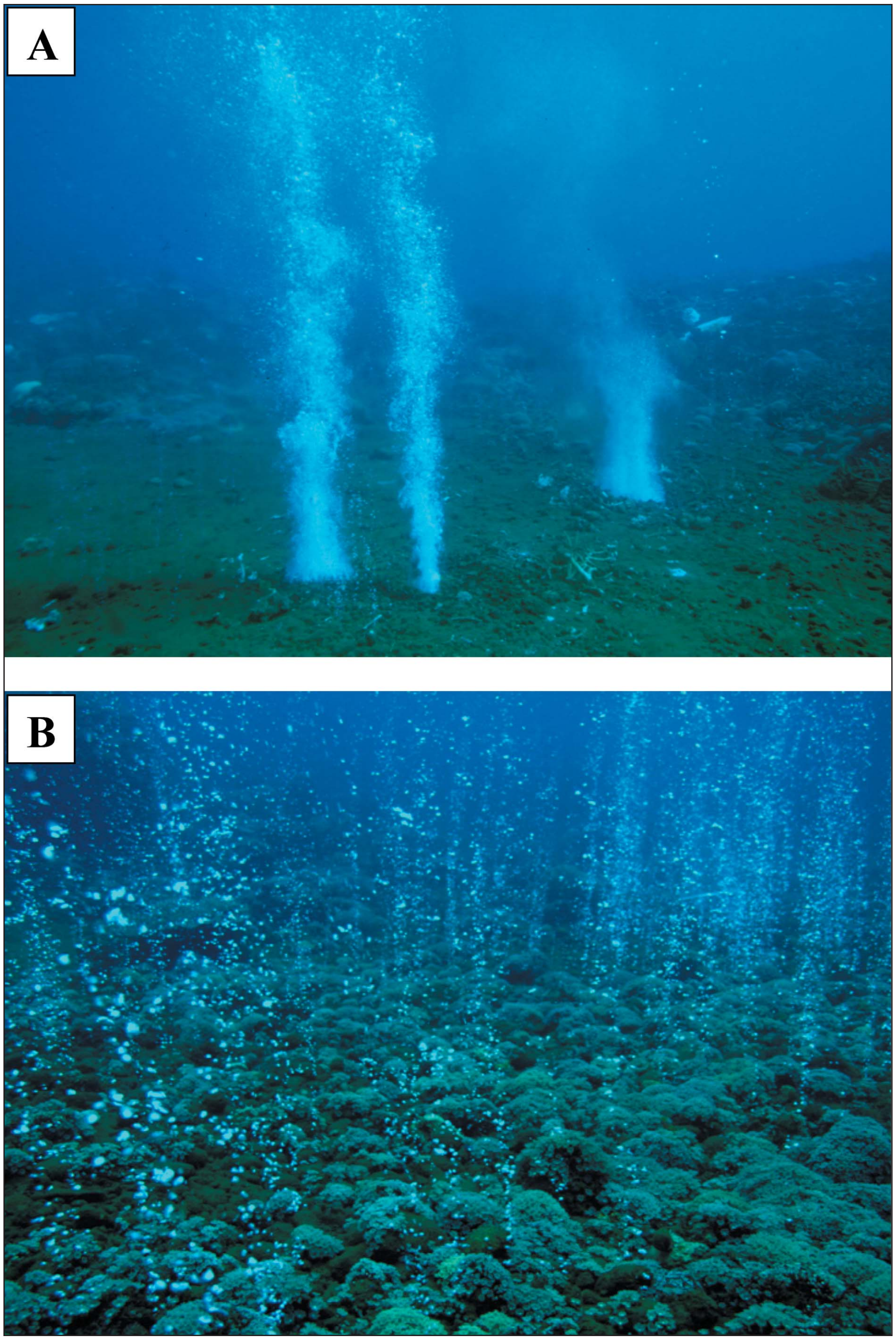

Fig. 2. (a) Underwater photograph of focused discharge in Tutum Bay. The field of view is approximately 10 meters at a water depth of eight meters. (b) Underwater photograph of the diffuse gaseous discharge. The field of view is approximately eight meters at a water depth of nine meters [from Pichler et al., *1999].*

hydrothermal area, whereas pH increased (Figure 3).

The total concentration of As in the sediment does not necessarily represent its biological availability or ecosystem toxicity; these are functions of the abundance, chemical form, oxidation state, and the nature of its binding to surfaces. Biological availability was estimated as the amount of As that could be extracted from the sediment using a potassium phosphate buffer at a pH of 7.2 [*Price and Pichler*, 2006]. A relatively small but significant proportion of between one and five percent of As appeared to be bioavailable (Figure 3). The mean bioavailable fraction of As in Tutum Bay was two orders of magnitude higher than the bioavailable portion at the reference site.

More than 90 percent of the As in Tutum Bay sediments is associated with the HFOs and should remain stable and immobile unless the physicochemical conditions change from oxic to anoxic. The surface seawaters of Tutum Bay contained up to four times the average seawater concentration of As. Thus, a significant amount of bioavailable As occurs throughout Tutum Bay by two major pathways: (1) easily exchangeable As from hydrothermally influenced sediments to as far away as 200 meters from focused venting, and (2) elevated As concentrations in surface seawater, which may allow for biological uptake by phytoplankton and transfer throughout the food web.

The Effect of Arsenic on Microfauna and Macrofauna

To begin to analyze the effects of arsenic on life and species diversity in this environment, several standard biological investigations were carried out. These included gene surveys, microbial culturing, and microscopy. The study confirmed the presence of microorganisms in the pore waters and near-surface sediments along the transect. In addition, green and red microbial mats covered rock and coral near sites of focused venting.

Bulk genomic DNA was extracted from these mats and from sediments at 30 and 150 meters away from Vent Four. Sequence analyses of archaeal DNA retrieved from these mats are represented as pie charts in Figure 3. In this order-level classification, uncultured Crenarchaeota (UC) dominated all three clone libraries, comprising 70 to 100 percent of the clones.

The archaeal community composition appears to broadly correlate with certain physicochemical parameters. For example, the archaeal diversity and total number of phylogenetic groups are lowest near the vent, where the temperature and As concentrations are highest and the pH is slightly acidic. It should also be noted that uncultured Euryarchaeota (UE), which are absent from the Vent Four mat clone library, are present in those from the sediments at 30 and 150 meters away.

Foraminifers, single-celled protists that feed upon bacteria and microalgae, are a critical link in the coastal ecosystem and were widely found in the study area. They are a useful group of paleoenvironmental indicators because their shells are abundant in sediments, different taxa have evolved to exploit most environments and nutritional modes in marine systems, and their shells geochemically record environmental conditions. Because of these characteristics, and because some taxa have the remarkable ability to survive in heavily polluted environments [*Alve,* 1995], there is an increasing use of foraminifers in environmental monitoring.

The biological effects of metal pollution are usually complicated and compounded in areas of anthropogenic pollution due to the presence of multiple co-occurring pollutants, such as other metals, nutrients, and pesticides. Tutum Bay is unique because there arsenic occurs in the absence of other pollutants. Although the hydrothermal venting also influences temperature, salinity, and pH, the Tutum Bay hydrothermal site provides a unique setting to study the isolated effects of

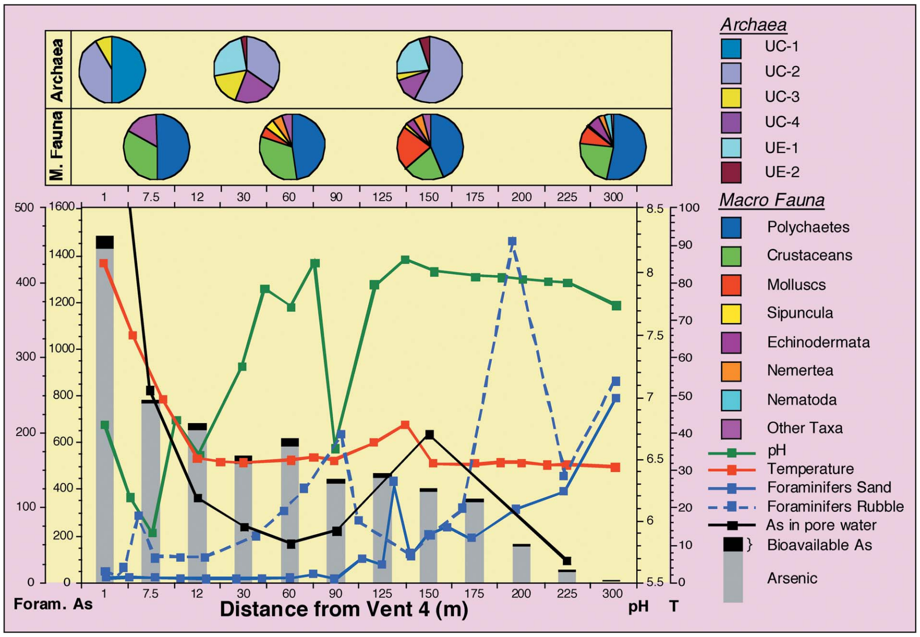

Fig. 3. Physical, chemical, and biological trends stepping away from the area of active venting in Tutum Bay. From left to right, the y-axes are number of foraminifera shells per gram of sediment, concentrations of As in milligrams per kilogram (sediment) and milligrams per liter (pore water), pH, and temperature in °C. The values for As in pore waters were multiplied by a factor of 10^4; the value at a distance of one meter is 0.9 milligrams per liter. The macrofauna pie at a distance of 300 meters represents a sample taken at the reference site. In the legend on the right side, UC and UE indicate 'uncultured Crenarchaeota' and 'uncultured Euryarchaeota,' respectively.

As on foraminiferal assemblages, populations, shell morphologies, and shell geochemistry.

Benthic foraminiferal assemblages within the surface sediments were examined along the transect (Figure 3). The abundance of foraminiferal shells in the sediment increased as sediment temperature, pH, and As concentrations approached those of ambient seawater. Thus, very few shells were found where the sediment was hotter and more acidic and had higher As levels (Figure 3). Further from the vents, sedimentary temperature, pH, and As concentrations approached background values, and foraminiferal shells were comparably abundant, as they were at reference sites.

Patterns of foraminiferal diversity—or the number of taxa present—showed trends analogous to abundance. The importance of pH as a controlling variable is indicated by the lack of globigerinid (planktic) shells in samples close to the vents. These shells should 'rain' down evenly along the transect and thus be found in similar numbers in all sediment samples. However, reference sites and transect sites further from hydrothermal venting show more globigerinid shells indicating that carbonate dissolution may be an important process acting on foraminifers closer to the hydrothermal area.

Benthic macrofauna also are commonly used indicators of environmental variations due to their sensitivity to physical and chemical changes in their habitat [*Zajac and Whitlatch,* 2003]. At the reference site and along the transect in Tutum Bay at 7.5, 60, and 150 meters, the structure of the benthic invertebrate community was examined to the lowest possible taxonomic level (Figure 3). The data show a strong trend of increasing species richness with distance away from the vent. The reference site samples contained twice as many individuals and species compared with the 150-meter site, suggesting that hydrothermal influence continues well past the 150-meter site.

Furthermore, the taxonomic composition becomes more complex as the distance from the vent increases. The most striking observation was that mollusks were completely absent near the vent and rare even at 60 meters, only becoming abundant at 150 meters (Figure 3). The vent fluids are low in pH, which apparently is an important factor in structuring members of the benthic community that rely on the precipitation of calcium carbonate shells and skeletons.

Future Directions

Initial results indicate that As appears to have an impact on the biodiversity in Tutum Bay. Molecular data suggest that high temperature and high As concentrations of the vent water limit archaeal biodiversity, which quickly increases a short distance from the vent. The absence of foraminifers and mollusks near the vents indicates that pH is the predominant factor for organisms that rely on calcium carbonate deposition. The increase of foraminiferal and macrofaunal diversity to a distance as far as 150 meters from the vents suggests that the hydrothermal influence is more far-reaching than was initially thought. Thus, As may be the key factor affecting the Tutum Bay ecosystem as pH and temperature stabilize with distance from the vents.

Many questions remain unanswered. For example, are microbial processes involved in the transformation of arsenite to arsenate? Are reef organisms bioaccumulating As into their tissues? Are organisms near the hydrothermal vents 'evolving' to become more As tolerant? Is phytoplankton, an essential link in the food chain, accumulating As, and thus providing the potential for bioaccumulation of As up the food chain? High As concentrations are the only metal pollutant in the system, but the ultimate challenge is to separate the pH, temperature, and As effects on biota.

Acknowledgements

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