Hydrothermal venting within a coral reef ecosystem, Ambitle Island, Papua New Guinea

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ABSTRACT
Shallow-water (5–10 m) hydrothermal venting in a nearshore coral reef environment at Ambitle Island in the Tabar-Feni island arc, east of Papua New Guinea, occurs as focused discharge of boiling fluid from discrete ports 10–15 cm in diameter, and as dispersed discharge of diffuse bubble streams that issue through the sandy mixed carbonate-volcaniclastic sea floor. Abiotic aragonite and microcrystalline ferroan, low-Mg calcite, interlaminated with Fe-oxhydroxides, are the prominent hydrothermal precipitates. Geochemical attributes of aragonite (δ18O, δ13C, and fluid inclusions) suggest that cements formed from a solution with salinities <5%e at temperatures of ~100 °C, with probable contribution of hydrothermal CO2. Sr isotope ratios in abiotic (hydrothermal) aragonite (~0.70415) are similar to those in island-arc basalt and denote considerable subsurface water-rock interaction of meteoric water derived from the adjacent volcanic island. The Sr isotope ratio of a coral sample (0.70746) collected adjacent to a vent portal suggests coral growth within a mixed seawater-hydrothermal environment.

INTRODUCTION
Previous research on sea-floor hydrothermal activity has focused primarily on deepsea, polymetallic sulfides found along volcanically active portions of the mid-ocean ridges or in deep back-arc basins. Additional submarine hydrothermal activity and hydrothermal alteration of oceanic crust can be found in much shallower water along the flanks of volcanic islands and on the tops of seamounts (e.g., Sedwick et al., 1992). There is, however, little known about either hydrothermal venting or its petrologic definition within shallow-water (nearshore or shallow shelf) carbonate settings associated with volcanic islands.

Our paper reports a reconnaissance study of newly discovered vents on a tropical, shallow-water carbonate shelf near Ambitle Island, Papua New Guinea (Fig. 1). It defines significant differences in petrologic and chemical properties of marine abiotic and biogenic carbonate compared to well-known submarine carbonate diagenesis in shallow-water tropical environments (Tucker and Wright, 1990). Such differences arise from mixing of hydrothermal fluids and seawater, creating additional physical and chemical factors to expected oceanographic controls that regulate biological productivity and sedimentation (Tucker and Wright, 1990). This “new” carbonate environment may be more applicable to the understanding of submarine diagenesis in ancient shallow-water carbonates from tectonically active regions, oceanic islands, or basins with high heat flow.

LOCATION AND GEOLOGIC SETTING
The islands of the Tabar-Feni chain, Papua New Guinea, are composed of Plio-

cene to Holocene alkali volcanoes that occur in the fore-arc region of the former New Hanover–New Ireland–Bougainville island arc (Fig. 1). They are geologically and economically significant because of their proximity toward Au mineralization as epitomized by the world-class Laidolam Au deposit on Lihir Island (Davies and Ballantyne, 1987).

Our 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 (Fig. 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 (Fig. 1). Hot mud pools, springs of chloride and acid sulfates waters, and a few low-temperature fumaroles are present, with temperature and pH values ranging from 67 to 100 °C and 1.9 to 9.1, respectively (Wallace et al., 1983).

FIELD OBSERVATIONS
Submarine, hydrothermal venting occurs at Waramung Bay in shallow (5–10 m) water along the inner shelf, which contains a patchy distribution of coral-algal reefs surrounded by medium to coarse-grained mixed carbonate-volcaniclastic sand and gravel. The site is located along a fault trace that intersects several of the onland geothermal areas (Fig. 1).

Two types of venting are observed. (1) Focused discharge of a clear, two-phase fluid occurs at discrete ports, 10–15 cm in diameter (Fig. 2); (2) there is phase separation (boiling) at the sea floor. There is no associated topographic edifice. This type of discharge produces a roaring sound underwater and...
Figure 2. Underwater photograph of focused and diffuse discharge. Scleractinian coral is adjacent to vent portal; surrounding biota are largely soft corals. Field of view is ~10 m at water depth of 8 m. (Additional color images can be viewed at http://www.amr.ca/~tpichler/)

has an estimated flow rate as high as 300 to 400 L/min (i.e., fire hose). Shimmering, indicative of hot water, extends several meters above vent portals, and the gas phase is completely condensed within 2 to 3 m above the sea floor. Fluid temperatures at portal entrances are between 94 and 98 °C. Hydrothermal precipitates have accumulated on dead coral substrate and rock fragments surrounding vent portals and include euhedral aragonite crystals (Fig. 3a) and microcrystalline crusts of Fe-oxyhydroxide, aragonite, and ferroan calcite. (2) Dispersed or diffuse discharge consists of streams of gas bubbles emerging directly through the sandy to pebbly unconsolidated substrate without formation of a port or topographic edifice (Fig. 2). This type of venting appears to be itinerant, with shifts in locations on the order of tens of centimetres, possibly related to tortuous migration through the surface sediment. Hydrothermal precipitates were not obvious around these vent streams.

The gas phase in both types of hydrothermal discharge is assumed to be mainly CO₂ as found in other hydrothermal systems (Giggenbach, 1995), because no H₂S was detected (smelled) in a fluid sample brought up to the surface. The general chemistry of the fluid, however, has yet to be studied.

ANALYTICAL PROCEDURES

Polished thin sections were examined using standard light, cathodoluminescence, and fluorescence microscopy. Mineral identification was aided by powder and single-crystal X-ray diffractometry, and mineral compositions were determined with a Camcera SX-50 electron microprobe (Table 1). In addition to the standard elements for carbonates—Ca, Mg, Fe, Mn, Sr, Ba, and Zn—we analyzed for S and As, two elements that are common in hydrothermal systems.

Splits of uncontaminated hydrothermal precipitates (FV-3a, FV-4a, and FV-4b) and one sample from a dead coral (FV-3b) were analyzed for C, O, and Sr isotope ratios at the University of Ottawa on a VG SIRA 12 mass spectrometer following the procedure of McCrea (1950). C and O were analyzed similarly for ferroan calcite. Strontium isotopes were determined at Carleton University on a Finnigan MAT 261.5 collector mass spectrometer following conventional ion-exchange techniques to isolate Sr. Standard errors for C and O are 0.1%, and standard error for Sr is 0.000002. Temperature and salinity of fluid inclusions were determined using a Fluid Inc. gas-flow heating-freezing stage.

ANALYTICAL RESULTS

Aragonite forms spalls of euhedral crystals (Fig. 3a) that encrust dead coral and volcaniclastic boulders and pebbles. It also fills secondary fracture and remaining primary intergranular porosity (Fig. 3b) within volcaniclastic arenite, cemented by ferroan calcite, that is exposed at the sea floor or is shallowly buried. Episodes of fracturing and cementation appear to be characteristic near these vents. Microcrystalline (0.1 mm) ferroan, low-Mg calcite occurs as crusts most commonly inter laminated with Fe-oxyhydroxides (Fig. 3b) and also appears to locally replace aragonite adjacent to Fe-oxyhydroxides (Fig. 3b).

Aragonite shows no anomalous concentrations of trace elements compared to normal marine aragonite (Table 1). In contrast, ferroan, low-Mg calcite has anomalously high Sr concentrations relative to Mg when compared to other marine calcite cements (Carpenter and Lohmann, 1991). Ferroan calcite also contains elevated concentrations of sulfur and arsenic (Table 1), probably representing impurities. Arsenic is also found in high concentrations in Fe-oxyhydroxide precipitates.

C and O isotope values of aragonite crystals and microcrystalline crusts form a single population (Fig. 5). Collectively, δ¹⁸O and δ¹³C values are more negative than those expected for abiogenic aragonite precipitated at low (25 °C) temperatures characteristic of shallow-water, tropical settings (Fig. 5). δ¹³C values, however, are within the ranges expected for both marine carbon (Anderson and Arthur, 1983) and known for abiotic aragonite from Lake Tanganyika that is interpreted to have incorporated hydrothermal CO₂ (Stollers and Botz, 1994). Ferroan calcite has an oxygen isotope composition similar to those of aragonite samples, but its δ¹³C value is depleted relative to aragonite by about 1‰. This is near to the shift predicted and observed between low-temperature aragonite and Mg-calcite cements (Gonzalez and Lohmann, 1985). The δ¹⁸O value of a dead scleractinian coral skeleton is distinct from the value of encrusting microcrystalline aragonite and falls just below the lower limit of the field defined by hemeatitic corals (Fig. 5).

87Sr/86Sr values for hydrothermal aragonite are similar to values for submarine volcanic rocks that were dredged ~2 km southeast of Kermadec Bay (Johnson et al., 1988). Skeletal aragonite of a dead scleractinian coral, however, has a value intermediate between values of oceanic crust and modern seawater (Table 2; Fig. 6).

Few fluid inclusions appear within aragonite crystals, and no measurable inclusions were found in calcite. Inclusions are elongate (5-10 μm) and oriented parallel to the crystal’s c-axis. From three crystals, six inclusions have high liquid to vapor ratios, no daughter products, and define a homogenization temperature range of 80–110 °C. These values are similar to field measurements (see above). Freezing experiments show ice-melting temperatures between –2.5 and 0 °C. Eutectic temperatures could not be determined.

PRELIMINARY HYDROLOGIC MODEL

Fluids in shallow-water hydrothermal systems located on the flanks of active volca-
TABLE 1. REPRESENTATIVE ELECTRON MICROPROBE ANALYSES FOR HYDROTHERMAL PRECIPITATES

<table>
<thead>
<tr>
<th>Sample</th>
<th>FV-4A Aragonite</th>
<th>FV-4A Aragonite</th>
<th>FV-4A Calcite</th>
<th>FV-4A Calcite</th>
<th>Fe-oxhydroxide</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaO</td>
<td>55.04</td>
<td>54.83</td>
<td>43.83</td>
<td>37.45</td>
<td>1.26</td>
</tr>
<tr>
<td>MgO</td>
<td>0.00</td>
<td>0.04</td>
<td>1.04</td>
<td>1.14</td>
<td>0.39</td>
</tr>
<tr>
<td>FeO</td>
<td>0.00</td>
<td>0.20</td>
<td>5.26</td>
<td>7.66</td>
<td>59.40</td>
</tr>
<tr>
<td>MnO</td>
<td>0.09</td>
<td>0.14</td>
<td>2.23</td>
<td>3.64</td>
<td>0.07</td>
</tr>
<tr>
<td>SrO</td>
<td>1.14</td>
<td>0.81</td>
<td>0.11</td>
<td>0.16</td>
<td>0.06</td>
</tr>
<tr>
<td>BaO</td>
<td>0.00</td>
<td>0.09</td>
<td>0.01</td>
<td>0.18</td>
<td>0.13</td>
</tr>
<tr>
<td>ZnO</td>
<td>0.00</td>
<td>0.04</td>
<td>0.07</td>
<td>0.18</td>
<td>0.00</td>
</tr>
<tr>
<td>SO₃</td>
<td>0.08</td>
<td>0.09</td>
<td>0.94</td>
<td>0.76</td>
<td>0.11</td>
</tr>
<tr>
<td>As₂O₅</td>
<td>0.01</td>
<td>0.02</td>
<td>0.00</td>
<td>0.10</td>
<td>7.68</td>
</tr>
</tbody>
</table>

Note: All analyses are reported in wt%, CO₂ by difference.

Table entries are in wt%.

TABLE 2. ISOTOPE SIGNATURE OF HYDROTHERMAL PRECIPITATES, CORAL ARAGONITE, SEAWATER, AND ISLAND-ARC BASALT

<table>
<thead>
<tr>
<th>Sample Type</th>
<th>δ¹⁸O (SMOW)</th>
<th>δ¹³C (PDB)</th>
<th>δ²⁶Sr/⁶⁰Sr</th>
</tr>
</thead>
<tbody>
<tr>
<td>FV-3a Aragonite crystal</td>
<td>14.94</td>
<td>2.16</td>
<td>0.704149 ± 17</td>
</tr>
<tr>
<td>FV-3b Coral aragonite</td>
<td>24.68</td>
<td>1.79</td>
<td>0.707464 ± 14</td>
</tr>
<tr>
<td>FV-4a Euhedral aragonite crystal</td>
<td>14.64</td>
<td>2.13</td>
<td>0.705150 ± 17</td>
</tr>
<tr>
<td>FV-4b Aragonite crystal</td>
<td>14.76</td>
<td>2.07</td>
<td>N.D.*</td>
</tr>
<tr>
<td>FV-4b Fe-calcite crystal</td>
<td>14.70</td>
<td>1.14</td>
<td>N.D.</td>
</tr>
<tr>
<td>FV-4b Euhedral aragonite crystal</td>
<td>14.54</td>
<td>2.25</td>
<td>N.D.</td>
</tr>
<tr>
<td>Seawater†</td>
<td>0</td>
<td>1 - 3</td>
<td>0.709234 ± 09</td>
</tr>
<tr>
<td>DR12§ Basalt</td>
<td>5.97</td>
<td>N.D.</td>
<td>0.704075 ± 20</td>
</tr>
</tbody>
</table>

* N.D., No data.
† Sr value, Faure (1986); δ¹³C value, Anderson and Arthur (1983).
§ Sr value is an average, Johnson et al. (1988); δ¹⁸O value, Faure (1986).

noes, such as the one at Ambitie island, may have three possible sources (i.e., magmatic, meteoric, and marine). On the basis of fluid-inclusion data, oxygen isotope ratios in aragonite, and hydrogeologic constraints, we propose that venting at Waramung Bay is the result of subsurface heating of meteoric water, with the center of recharge being Ambitie Island. Ice melting temperatures in aragonite suggest that, for a NaCl system, salinities vary between seawater (3.5 wt% NaCl) and fresh water (Lyman and Fleming, 1940). Transforming melting temperatures into salinities is difficult when the chemistry of the fluid remains unknown, yet the near 0 °C values strongly suggest vent fluid salinity to be ~5‰.

Following Faure (1986) and assuming isotopic equilibrium, a δ¹⁸O value of ~2.5‰ was calculated for the hydrothermal fluid, using the mean δ¹⁸O of aragonite (14.7‰) and a fluid temperature of 373 K (100 °C). In the absence of any fractionation factor for abiotic aragonite at temperatures above 40 °C, we used the calcite-water fractionation factor from Friedman and O'Neil (1977), because the differences between fractionation factors for aragonite and calcite appear to be insignificant above 30 °C (Anderson and Arthur, 1983). A more negative value than ~2.5‰ may be a better approximation due to the isotopic effect of phase separation. For example, a separation into 75% liquid and 25% vapor yields a δ¹⁸O value of ~−4‰ for the parent hydrothermal fluid (Friedman and O'Neil, 1977). Both values lie between the values for seawater (0‰) and rainfall (~6‰) in the region (e.g., Truk, Yap, and Madang; International Atomic Energy Agency, 1983). This suggests that meteoric recharge may be a possible fluid source, assuming that the positive shift relative to rainwater is due to subsurface isotopic exchange (Craig, 1966). A similar intermediate δ¹⁸O value, however, may also be the result of simple mixing between meteoric water and seawater, but low Sr-isotope ratios in hydrothermal aragonite relative to seawater indicate subsurface isotopic exchange between meteoric water and volcanic rock (Fig. 6).

Combined with the steep island topography and the geometry of the volcanic stratigraphy dipping toward and beneath the carbonate shelf, Ambitie Island represents a prominent meteoric recharge zone for the Waramung Bay vents. A strong circulation cell must extend beneath the shallow shelf, causing considerable fluctuation in the seawater-meteoric water boundary and establishing artesian conditions with subsurface fluids moving laterally and vertically along fault- and fracture-dominated conduits west of Ambitie Island (Fig. 1).

GEOLOGIC IMPLICATIONS

Substantial input of hydrothermal fluids within a reef environment adds to the expected biological, climatic, and oceanographic factors that influence coral growth and carbonate diagenesis in tropical, shal-

Figure 4. Sr concentrations in ferroan calcite are higher than expected when compared to average (black line) and general range (stippled area) of Sr concentrations in marine low-temperature abiotic calcite (Carpenter and Lohmann, 1991).

Figure 5. Carbon and oxygen isotope values for abiotic aragonite, coral aragonite, and ferroan calcite at Ambitie Island. Sources for other data are as follows: hermatypic corals (HC) (Tucker and Wright, 1990); low-temperature aragonite (LTA), experimentally determined (Tarantini et al., 1969); aragonite (A) and Mg-calcite (MgC) cements (Gonzalez and Lohmann, 1985); and Lake Tanganyika hydrothermal aragonite (LTC) and Mg-calcite (Stoffers and Botz, 1994). DDB, Peedee belemnite; SMOW, Standard Mean Ocean Water.

Figure 6. ⁶⁷Sr/⁶⁰Sr ratios for abiotic aragonite crystal, crust, and coral aragonite. Samples of crust and coral are from same hand specimens. Heavy stippled area is present-day seawater, and lighter stippled area is approximate range of seawater compositions through Phanerozoic time. Sources for volcanic rock are given in Table 2.
low-water carbonate settings (Tucker and Wright, 1990). Ambitle Island therefore offers a natural laboratory to evaluate the short- and long-term adaptation and/or mortality of biota related to changes in temperature, salinity, and carbonate saturation state (Thompson and Newton, 1988; Smith and Buddemeier, 1992).

The region defines several important implications for interpretation of diagenetic records in carbonates of tectonically active regions, oceanic islands, and basins with high heat flow.

1. Precipitation of aragonite rather than calcite is a common process in tropical shallow-water submarine environments (Tucker and Wright, 1990). In hydrothermal systems, however, calcite is the primary carbonate precipitate, and the presence of aragonite is usually attributed to rapid precipitation rates, elevated Mg/Ca, and stabilizing effects of Ba, Sr, and possibly Mg on the orthorhombic crystal structure (Brown, 1973; Folk, 1994). Hydrothermal fluids at Ambitle Island are boiling as they enter seawater; this causes a rapid loss of CO₂ and may cause supersaturation with calcium (Pentecost, 1995), subsequently leading to precipitation of aragonite rather than calcite: Ca²⁺ + 2HCO₃⁻ → CaCO₃ (aragonite) + H₂O + CO₂↑.

Thus, intercalation of aragonite and ferroan calcite probably signals abrupt, short-term changes in the physical and/or chemical conditions at and near vents. The presence of ferroan calcite contradicts the well-established paradigm that Fe is not incorporated within the submarine realm due to its oxidation state in seawater. Such calcite might form when vent fluids are poorly mixed with seawater, allowing Fe-rich, anoxic fluids to envelope the sea floor adjacent to vent portals.

2. Elevated concentrations of Sr²⁺ relative to Mg²⁺ in ferroan calcite are anomalous compared to "normal-marine" shallow-water abiogenic cements (Fig. 3). Three factors may be important. First, an elevated Sr distribution coefficient may arise adjacent to the vents due to increased temperature (Lorens, 1981). Second, Sr may be retained during local aragonite replacement by calcite (e.g., Sandberg, 1985), as observed for some of our samples (Fig. 2B) and as expected under hydrothermal conditions (Metzger and Barnard, 1968). Third, the Sr concentration of the hydrothermal fluids may be elevated relative to seawater due to Sr uptake during water-rock interaction in the subsurface.

3. The ⁸⁷Sr/⁸⁶Sr of marine carbonates has varied between 0.7067 and 0.7092 during the Phanerozoic, and this variation can be used to date marine carbonates (Faure, 1986). According to its ⁸⁷Sr/⁸⁶Sr, sample FV-3b (coral aragonite) would have an improbable age of at least Late Cretaceous. Rather than indicating a Cretaceous age, the unusual ⁸⁷Sr/⁸⁶Sr reflects fluid mixing above and adjacent to the vent portals resulting in O and Sr isotope gradients in skeletal carbonate controlled by the dissipation rate of the hydrothermal plume. Mixing is also supported by the slightly negative δ¹⁸O of coral skeletons compared to the general field for corals in similar low-temperature environments (Fig. 5). From this interpretation, we suggest that Sr-isotope records in corals from vents may preserve a record of changing vent activity.

4. Island arcs are favorable environments for the formation of epithermal ore deposits, and identification of anomalous strontium isotope signatures in marine limestones may be used to explore for paleohydrothermal systems in ancient island-arc settings.

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