SCIENTIFIC COMMUNICATIONS

Fe SULFIDE FORMATION DUE TO SEAWATER-GAS-SEDIMENT INTERACTION IN A SHALLOW-WATER HYDROTHERMAL SYSTEM AT LIHIR ISLAND, PAPUA NEW GUINEA

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Abstract

Fe sulfide minerals are forming in the shallow-water hydrothermal system in Luise Harbor, Lihir Island, Papua New Guinea, due to the interaction of hydrothermal gas + liquid, seawater, and Fe-rich sediments. Upon contact with oxygenated seawater, hydrothermal H₂S is oxidized and forms H₂SO₄ leading to the simultaneous dissolution of primary, Fe-rich sediment grains and the neoformation of mainly marcasite and pyrite. They are present as alternating colloform layers, as frambooidal aggregates in vugs, or they replace organic fragments, primary olivine and primary magnetite. Deposition of either marcasite or pyrite appears to reflect variations in acidity due to varying admixture of air-saturated seawater.

The gas phase is composed of mainly CO₂, N₂, and H₂S. Assuming equilibration of the gases dissolved in a liquid phase and preservation of equilibrium CH₄/CO₂, the CH₄-CO₂ equilibrium temperature is approximately 310°C ± 20°C.

Introduction

Fe sulfides are common secondary minerals in most marine sediments and sedimentary rocks where they form due to the reaction of bacterially produced H₂S with detrital iron minerals (e.g., Berner, 1984). The first crystalline phase to appear is generally metastable mackinawite, which subsequently transforms into stable pyrite (Rickard, 1968). Although pyrite and marcasite are the most abundant sulfide minerals in the Earth’s crust, the physicochemical conditions that lead to formation of one or the other are still not clearly understood. Precipitation is controlled by a variety of factors, in particular, total and relative concentration of sulfur-contributing species, pH, temperature, redox state, time, and Fe/S (e.g., Schoonen and Barnes, 1991a).

In this paper, the formation of Fe sulfides in submarine sediments in Luise Harbor, Lihir Island, Papua New Guinea, is interpreted to result from interaction of hydrothermal gas with seawater and detrital iron minerals. The formation of Fe sulfides at this location is of special interest because of its proximity to the world-class Ladolam Au deposit (Davies and Ballantyne, 1987).

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Location and Geologic Setting

The islands of the Tabar-Feni chain, Papua New Guinea, are Pliocene to Recent alkaline volcanoes in the fore-arc region of the former ensimatic New Hanover-New Ireland-Bougainville island arc (Fig. 1). The study area lies in Luise Harbor along the shore margin of Lihir (Fig. 1). Lihir is composed of the remnants of three Pliocene to Holocene volcanoes, Kinami, Huniho, and Luise, and common volcanic rocks, trachybasalt and alkali basalt (Wallace et al., 1983). Several thermal areas within the caldera of the Luise volcano consist of hot mud pools, springs of chloride and acid sulfate waters, and a few low-temperature fumaroles, with temperature and pH values ranging from 39°C to 99°C and 1.6 to 2.8, respectively (Wallace et al., 1983). Mineralization of the Ladolam deposit probably commenced 350,000 years before present (Davies and Ballantyne, 1987).

Field Observations

The hydrothermal area is located approximately 100 m offshore, along the north side of Luise Harbor in shallow water (3–10 m) within an area of approximately 5,000 m². Venting occurs through fine- to medium-grained volcaniclastic sand
Fig. 1. Location and tectonic setting of Lihir Island, one of the Feni islands in the Tabar-Feni island chain (redrawn from Wallace et al., 1983, and Davies and Ballantyne, 1987).

(Fig. 2), and oscillation ripples up to 10 cm high are ubiquitous, indicating that the area is above the fair-weather wave base (e.g., Walker and Plint, 1992).

Six locations of focused vigorous discharge of gas associated with a possible minor discharge of a clear liquid from vent orifices, 20 to 50 cm in diameter (Fig. 2), were observed. The discharge of liquid was inferred from observations of shimmering above the vent orifices. This discharge, however, was too small to be sampled. Temperatures at the point of discharge ranged from 60° to 96°C. Sites of gas exhalation are marked by small funnel-shaped indentations (i.e., conical pockmarks) in the sandy bottom. In addition to focused venting, gas bubbles emanate less vigorously all around the hydrothermal area through the sandy unconsolidated bottom without formation of a vent orifice or topographic edifice. Hydrothermal precipitates were not present around these bubble streams.

The sediment around the six locations of focused discharge is cemented due to hydrothermal precipitation, and the dominant hydrothermal precipitates are 1- to 2-cm-thick colloform bands of Fe sulfide, and Fe sulfides that coat and/or replace primary volcaniclastic sediment grains. The Fe sulfides precipitate 10 to 20 cm below the seawater-sediment interface and form a layer parallel to the seafloor up to 10 cm thick that extends up to several meters around discharge sites. The highest concentration of sulfide minerals occurs near the point of discharge as thick colloform bands of massive marcasite and pyrite. At greater distance from the center, Fe sulfides only partially replace and coat primary sediment grains. Four Fe sulfide bulk samples (LH-1, LH-3A, LH-3B, and LH-7) were taken from near the point of discharge for chemical and mineralogical analyses.

Analytical Methods and Results
The mineralogy and mineral composition was determined using standard X-ray diffraction (XRD), scanning electron microscope (SEM), and electron microprobe methods. Arsenic, Au, Hg, Sb, and Se were determined by neutron activation analyses (NAA) at Actlabs in Ancaster, Ontario. Copper was determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES), and Ag, Pb, Th, and Zn were determined by inductively coupled plasma-mass spectrometry (ICP-MS). XRD, SEM, ICP, and microprobe analyses were
carried out at the Geological Survey of Canada. Gases were analyzed at the Institute of Geological and Nuclear Sciences in Lower Hutt, New Zealand, following the method of Giggenbach and Coguel (1989).

Two groups of minerals are present in samples LH-1, LH-3A, LH-3B, and LH-7: primary minerals of detrital origin (modal abundance ~25%) and secondary minerals, formed due to gas-seawater-sediment interaction (modal abundance ~75%). Primary minerals are of detrital origin and include pyroxene and magnetite with an occasional grain of rutile, amphibole, feldspar, and olivine. Several euhedral pyrites are thought to be of a similar detrital origin (Fig. 3A). Secondary minerals include minor amounts of dolomite, native sulfur, and gypsum, but mainly Fe sulfides, of which, based on X-ray diffraction data, marcasite accounts for ~80 percent, pyrite for ~15 percent, and mackinawite for <5 percent of the Fe sulfides. Mackinawite, although present in XRD patterns, was not observed optically.

Secondary marcasite and pyrite display very complex growth textures (Figs. 3 and 4) and from microscopic observation alone, it is unclear what controls the preferential formation of either. They are deposited as alternating colloform layers on primary minerals or as frambooidal aggregates in vugs, and they replace organic fragments, primary olivine, and primary magnetite (Figs. 3 and 4). Based on thin section analyses (Fig. 3), the alteration of primary minerals in the sediment has been interpreted to proceed in the following sequence: (1) replacement of magnetite by hematite along cleavage (111) directions under oxidizing conditions prior to the influence of hydrothermal discharge (Fig. 3B); (2) Fe sulfide coating on primary mineral grains (Fig. 3); (3) complete breakdown and replacement of olivine by either Fe sulfides, smectite or chlorite; and (4) replacement of magnetite and hematite by Fe sulfide. Replacement of pyroxene by Fe sulfide was generally incomplete. Once a pyroxene grain is completely coated, it is protected from further hydrothermal attack. Within a given sample, this sequence of alteration and replacement events does not proceed along distinct alteration fronts, and all alteration stages as described above can be found in a single thin section. Unaltered magnetite grains are found next to completely replaced ones, and fragments of colloform Fe sulfide are often coated with later generations of Fe sulfide.

Representative structural compositions for Fe sulfide that were calculated from electron microprobe data are listed in

**Fig. 3.** Reflected-light thin section photomicrograph of (A) euhedral pyrite grains of a possible detrital origin coated with a later succession of marcasite and pyrite, and (B) martitized magnetite coated with a layer of marcasite. The scale bar in the lower right corners represents 20 um.

**Fig. 4.** A. Reflected-light (crossed polars) thin section photomicrograph of colloform layers of marcasite and pyrite. When viewed with crossed polars the marcasite layers become clearly visible. The scale bar in the lower right corners represents 300um. B. Scanning electron microscope image of coexisting dolomite (dol) and pyrite (py) at a magnification of 3600.
Table 1. Marcasite and pyrite have identical chemical compositions, and structural formulas are very close to FeS₂. The average of all microprobe analyses is 45.2 percent (±0.45) for iron and 53.2 percent (±0.56) for sulfur. Concentrations of selected trace elements in bulk sulfide samples are listed in Table 2, where they are compared to a sample (KB) that represents unaffected Luise Harbor sediment. Trace elements known to enter the vapor phase, such as As, Se, Sb, Hg, and Tl, are significantly enriched relative to Luise Harbor sediment, whereas Pb, Cu, Ag, Au, and Zn that are mainly transported in the liquid phase show a relatively lesser enrichment.

The chemical composition of two gas samples collected from submarine vents in Luise Harbor are listed in Table 3. Carbon dioxide is the predominant component, but both samples contain significant amounts of O₂, either an inherent component of these gases, dissolved air stripped from seawater by the rising gas bubbles, or introduced during sampling. In the absence of any information on the origin of O₂ and assuming contamination with atmospheric O₂, N₂ concentrations may be corrected by subtracting 2 – O₂ from measured values of N₂ to obtain N₂(c) (corrected). The factor of 2 is a value between the N₂/O₂ of air-saturated water of 1.9 and that of air of 3.7. Relative concentrations of N₂(c), He, and CO₂ suggest a predominantly magmatic origin, with some contribution from subducted sediments (Giggenbach, 1995). Assuming equilibration of the gases dissolved in a liquid phase and preservation of equilibrium CH₄/CO₂ (Giggenbach and Matsuo, 1991), the CH₄/CO₂ equilibria temperatures for the samples are 327°C and 296°C.

In order to better assess the conditions of sulfide formation, dolomite (coexisting with pyrite, Fig. 4B) was separated and analyzed for strontium, carbon and oxygen isotope. Carbon and oxygen isotope analyses were performed at the G. G. Hatch Isotope Laboratory, University of Ottawa, on a triple collector VG SIRA 12 mass spectrometer. The ⁸⁷Sr/⁸⁶Sr

Table 1. Representative Electron Microprobe Analyses of Marcasite and Pyrite (in wt %)

<table>
<thead>
<tr>
<th>Sample mineral</th>
<th>LH-1 Marcasite</th>
<th>LH-3 Marcasite</th>
<th>LH-7 Marcasite</th>
<th>LH-3 Pyrite</th>
<th>LH-7 Pyrite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>44.84</td>
<td>44.73</td>
<td>44.99</td>
<td>45.61</td>
<td>45.88</td>
</tr>
<tr>
<td>As</td>
<td>0.24</td>
<td>0.43</td>
<td>0.04</td>
<td>0.04</td>
<td>0.09</td>
</tr>
<tr>
<td>S</td>
<td>53.63</td>
<td>53.04</td>
<td>52.76</td>
<td>53.57</td>
<td>53.70</td>
</tr>
<tr>
<td>Bi</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Ni</td>
<td>0.02</td>
<td>0.08</td>
<td>0.04</td>
<td>0.04</td>
<td>0.06</td>
</tr>
<tr>
<td>Sb</td>
<td>0.07</td>
<td>0.13</td>
<td>0.04</td>
<td>0.04</td>
<td>0.03</td>
</tr>
<tr>
<td>Co</td>
<td>0.00</td>
<td>0.07</td>
<td>0.04</td>
<td>0.10</td>
<td>0.02</td>
</tr>
<tr>
<td>Mn</td>
<td>0.18</td>
<td>0.02</td>
<td>0.03</td>
<td>0.03</td>
<td>0.08</td>
</tr>
<tr>
<td>Zn</td>
<td>0.06</td>
<td>0.12</td>
<td>0.02</td>
<td>0.02</td>
<td>0.08</td>
</tr>
<tr>
<td>Pb</td>
<td>0.00</td>
<td>0.40</td>
<td>0.00</td>
<td>0.09</td>
<td>0.25</td>
</tr>
<tr>
<td>Total</td>
<td>99.04</td>
<td>98.97</td>
<td>98.05</td>
<td>99.56</td>
<td>100.12</td>
</tr>
</tbody>
</table>

Calculated structural formula

Fe 0.960 0.968 0.979 0.978 0.981 0.977
Sb 0.001 0.001 0.001 0.000 0.000 0.000
Co 0.000 0.002 0.000 0.002 0.001 0.001
Mn 0.004 0.001 0.000 0.001 0.000 0.000
Zn 0.001 0.002 0.000 0.001 0.001 0.000
Pb 0.000 0.002 0.000 0.001 0.001 0.000
As 0.004 0.007 0.001 0.001 0.001 0.005
Cation 0.970 0.983 0.982 0.984 0.984 0.985
S 2.000 2.000 2.000 2.000 2.000 2.000

Table 2. Concentrations of Selected Major and Trace Elements in Bulk Samples

<table>
<thead>
<tr>
<th>Sample type</th>
<th>LH-1 Massive sulfide</th>
<th>LH-3 A Massive sulfide</th>
<th>LH-3 B Massive sulfide</th>
<th>LH-7 Massive sulfide</th>
<th>KB Beach sand</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>4.7</td>
<td>3.0</td>
<td>4.6</td>
<td>0.7</td>
<td>29.8</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>51.2</td>
<td>50.9</td>
<td>50.6</td>
<td>52.5</td>
<td>21.2</td>
</tr>
<tr>
<td>Ag</td>
<td>0.2</td>
<td>0.2</td>
<td>0.3</td>
<td>0.6</td>
<td>0.3</td>
</tr>
<tr>
<td>As</td>
<td>2.3</td>
<td>1.2</td>
<td>2.2</td>
<td>4.9</td>
<td>100</td>
</tr>
<tr>
<td>Au</td>
<td>0.04</td>
<td>0.07</td>
<td>0.04</td>
<td>0.05</td>
<td>0.14</td>
</tr>
<tr>
<td>Cu</td>
<td>140</td>
<td>120</td>
<td>96</td>
<td>140</td>
<td>67</td>
</tr>
<tr>
<td>Hg</td>
<td>250</td>
<td>170</td>
<td>130</td>
<td>410</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Pb</td>
<td>13</td>
<td>12</td>
<td>8</td>
<td>10</td>
<td>6</td>
</tr>
<tr>
<td>Sb</td>
<td>110</td>
<td>14</td>
<td>60</td>
<td>160</td>
<td>2.2</td>
</tr>
<tr>
<td>Se</td>
<td>17.0</td>
<td>6.0</td>
<td>4.0</td>
<td>&lt;5</td>
<td>&lt;3</td>
</tr>
<tr>
<td>Tl</td>
<td>2.6</td>
<td>2.1</td>
<td>4.2</td>
<td>2.3</td>
<td>0.1</td>
</tr>
<tr>
<td>Zn</td>
<td>290</td>
<td>300</td>
<td>210</td>
<td>220</td>
<td>79</td>
</tr>
</tbody>
</table>

Note: SiO₂ and Fe₂O₃ are in wt%; all other analyses are in ppm

Table 3. Chemical Compositions of Gases from Luise Harbor, Lahr Island (T(°C) is the CH₄/CO₂ Equilibration)

<table>
<thead>
<tr>
<th>Sample</th>
<th>CO₂</th>
<th>H₂S</th>
<th>He</th>
<th>H₂</th>
<th>O₂</th>
<th>N₂(c)</th>
<th>CH₄</th>
<th>T(°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LH-G1</td>
<td>975</td>
<td>3.2</td>
<td>0.019</td>
<td>1.01</td>
<td>3.4</td>
<td>15.7</td>
<td>8.9</td>
<td>2.4</td>
</tr>
<tr>
<td>LH-G2</td>
<td>949</td>
<td>12.8</td>
<td>0.022</td>
<td>1.20</td>
<td>5.9</td>
<td>24.1</td>
<td>12.3</td>
<td>6.7</td>
</tr>
</tbody>
</table>

Note: N₂(c) = N₂-2O₂; all analyses are in mmole/mole

were measured on a five-collector Finnigan MAT 262 solid source mass spectrometer at the Institut für Geologie, Ruhr-Universität, Bochum, following Diener et al. (1996). The results for carbon and oxygen are δ¹⁸O, 20.8 and 21.8 per mil (VSMOW) and δ¹³C, 3.9 and 4.2 per mil (VPDB), respectively. Assuming heated seawater as the parent solution and following the procedure of Stout and Campbell (1983), the calculated temperature of formation (based on δ¹⁸O) ranges between 89°C and 107°C. The mean of five samples that were analyzed for ⁸⁷Sr/⁸⁶Sr is 0.70890 ± 0.00001.

Discussion

Before further investigating the precipitation of Fe sulfide in Luise Harbor sediments, it is necessary to determine the importance of gas vs. liquid discharge. It is unclear if the minor liquid discharge that manifests itself only in shimmering water right above the sediment is heated seawater or of a deeper origin. Based on laboratory experiments and field observations, O’Harra et al. (1994) concluded that due to a combination of gas seepage and increased heat flow, seawater convection can develop in permeable sediments around gas vents. The actual depth of such circulation is unknown but should be limited by the thickness of the sediment cover. The presence of dolomite in Luise Harbor samples is in clear favor of shallow circulation of seawater vs. a deeper source. Deeply circulating hydrothermal fluids are generally depleted in Mg²⁺ and have a very low Mg²⁺/Ca²⁺ (e.g., Nicholson, 1992; Von Damm, 1995), which would prevent the formation of dolomite (Morrow, 1982). Also, the ⁸⁷Sr/⁸⁶Sr of dolomite (0.70890) is different from local volcanic rocks (0.70398, M. Perfit, pers. commun.) but almost the same as contemporary
seawater (0.70918; e.g., Veizer, 1989). A dolomite that precipitated from a hydrothermal liquid of deeper origin would have values close or identical to the host rock because isotopic equilibrium for $^{87}$Sr/$^{86}$Sr between a hydrothermal fluid and its host rock is rapidly attained (Vutaz et al., 1988). The calculated $^{18}$O temperature of precipitation for dolomite, assuming precipitation from heated seawater, is in good agreement with temperatures measured in situ.

The physicochemical nature and origin of the Lihue Harbor hydrothermal area is best explained in a genetic scheme that was developed for the origin of thermal waters in geothermal systems. Conditions in Lihue Harbor can be compared to those responsible for the formation of superficial acid sulfate waters that are often found on the margins of thermal areas (e.g., Ellis and Mahon, 1977). Acid sulfate waters form by the condensation of hydrothermal gases, originally dissolved in the deep fluid but separated following boiling into near-surface oxygenated ground water (e.g., Ellis and Mahon, 1977; Nicholson, 1992). The equilibrium temperatures that were calculated with the CO$_2$/CH$_4$ thermometer also indicate possible boiling at depth which in turn is in agreement with observations from the deepest diamond drill hole (L63) in the Laddolam deposit (Davies and Ballantyne, 1987). Drill hole L63 is located approximately 1,000 m to the southwest of the Lihue Harbor hydrothermal area (Fig. 1). The surface expressions of acid sulfate springs are generally turbid pools or mud pools, such as the ones found onshore in the Lihue caldera (Wallace et al., 1983). In Lihue Harbor, conditions are different in that the hydrothermal gases condense into seawater instead of ground water.

The interplay of sedimentary and hydrothermal processes in Lihue Harbor continually modifies the physical features of the gas discharge sites. At water depths of less than 10 m, the vents are subject to the influence of wave action, as indicated by undulating ripple marks, causing constant sediment transport and mechanical enrichment of heavy minerals. This process affects mainly the top few centimeters of the sediments, preventing the formation of a permanent Fe sulfide layer due to constant reworking. Deeper (>10 cm) Fe sulfides are able to precipitate for extended periods, replacing and cementing the primary sediment. Here cementation continues uninterrupted until larger storm waves break up and rework these deposits. This process of daily and episodic reworking causes the observed textures, where unaltered minerals are found adjacent to completely replaced minerals and fragments of colloform Fe sulfide are coated with later generations of Fe sulfide.

Most observations on natural occurrences indicate that FeS$_2$ forms via metastable Fe sulfide precursors (e.g., Morse et al., 1987), although in sedimentary environments, FeS$_2$ may form via direct nucleation and growth (Raiswell, 1982). Experimental evidence by Schoonen and Barnes (1991b) suggests that direct precipitation of either pyrite or marcasite in hydrothermal systems is unlikely at temperatures $>60^\circ$C. According to Murowchick and Barnes (1986), marcasite will form in preference to pyrite at a pH <5.

The formation of Fe sulfide minerals in Lihue Harbor is in many ways similar to their formation in terrestrial marine sediments, where H$_2$S, produced via bacterial sulfate reduction, reacts with detrital iron-bearing minerals (e.g., Berner, 1984). The two limiting factors for the formation of Fe sulfide are the availability of iron and of sulfur. In the shallow-water hydrothermal system in Lihue Harbor, H$_2$S is a component of the gas and, therefore, readily available for reaction. The Fe necessary to form Fe sulfides is most likely derived from primary Fe-containing volcanioclastic components of the sediment because hydrothermal gases are unable to carry major amounts of Fe at temperatures $<300^\circ$C. Additional Fe may be derived from deeper within the Lihue Harbor sediments due to the circulation of heated seawater or from an upwelling hydrothermal liquid, whose presence cannot be completely ruled out. In terrigenous sediments that are deposited under normal oxygenated conditions, iron minerals are sufficiently abundant and reactive for the reaction to take place, and Fe sulfide formation is a common process during the low-temperature diagenesis of marine sediments (Berner, 1984). Around the vent sites in Lihue Harbor, elevated temperatures and acidity generated by the oxidation of H$_2$S are likely to accelerate this process.

The O$_2$ partial pressure of seawater is close to 0.2 bar causing O$_2$ to diffuse downward where it oxidizes H$_2$S (overall reaction: H$_2$S + 2O$_2$ $\rightarrow$ SO$_4^{2-}$ + 2H$^+$) followed by attack of H$^+$ on Fe-containing minerals in the sediment (2H$^+$ + FeO$^-$ $\rightarrow$ Fe$^{2+}$ + H$_2$O) and the precipitation of Fe sulfide (Fe$^{2+}$ + H$_2$S $\rightarrow$ FeS + 2H$^+$) and conversion to FeS$_2$ (FeS + H$_2$S + 0.5O$_2$ $\rightarrow$ FeS$_2$ + H$_2$O). A possible reaction governing mineral deposition in Lihue Harbor can be written as FeO + 2H$_2$S + 0.5O$_2$ $\rightarrow$ FeS$_2$ + 2H$_2$O, because the action of the hydrogen ions is largely catalytic. Some variations in local pH in response to variations in the exposure of the rising hydrothermal gas to aerated seawater is likely to be responsible for the alternating deposition of pyrite and marcasite (Fig. 4A).

Formation of elemental sulfur and gypsum requires much higher H$_2$S, or much lower H$_2$S fugacity than those indicated by the gases. As H$_2$S pressures are likely to be limited by those of the gas discharges, the presence of these phases points to the occurrence of more oxidizing conditions. Low H$_2$S fugacity is likely to result from oxidation of H$_2$S on contact with dissolved O$_2$ of air-saturated seawater, as observed at Whale Island, New Zealand (Propp et al., 1994). There in and in a similar shallow-water hydrothermal environment near White Island, New Zealand (T. Pichler, unpub. results, 1996), native sulfur forms around gas channels. The effects of variations in H$_2$S concentrations are illustrated by observations from other shallow-water hydrothermal systems where the conditions are more or less identical, i.e., temperature, discharge rate, gas composition (except H$_2$S), and sediment composition. For example, at Vulcano Island, Italy, H$_2$S concentrations are ~1 percent (Italiano and Nuccio, 1994), and Fe sulfides are present in the sediments. At Ambitile Island, Papua New Guinea, where H$_2$S concentrations are <0.1 percent (Pichler and Dix, 1996), Fe sulfides are absent.

**Summary and Conclusions**

In Lihue Harbor, on the eastern side of Lihue Island, Papua New Guinea, sedimentary and hydrothermal processes combine to form submarine, several centimeters thick, several meters wide, lenticular deposits of colloform Fe sulfide, largely marcasite and pyrite. The deposits are centered around hydrothermal vents that discharge gas + liquid. The gases
associated with their formation are likely to have attained gas-liquid equilibrium in an underlying hydrothermal system at a temperature between 250° and 350°C. Contact with aerated seawater leads to the oxidation of H₂S and H₂ and the generation of comparatively acid and oxidizing conditions conducive to the alteration of Fe-bearing minerals in the first few meters of the sediment. This process is likely to control also the geometry of the deposits. Temporal variations in local acidity, in response to variations in the exposure of the rising hydrothermal fluids to aerated seawater, is likely be responsible for the alternating deposition of pyrite or marcasite. There is no evidence for a seawater or meteoric-derived deep circulating hydrothermal solution. Therefore, the physicochemical processes that lead to the alteration of the bottom sediments in Luise Harbor are most likely identical to those producing subaerial acid sulfate water hot springs (e.g., Ellis and Mahon, 1977). These hot springs, although in close proximity to neutral chloride springs, are not connected to the deep circulating fluid. A simplified model is presented in Figure 5.

**Acknowledgments**

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**REFERENCES**


