

# FORMATION OF DOLOMITE IN RECENT ISLAND-ARC SEDIMENTS DUE TO GAS-SEAWATER-SEDIMENT INTERACTION

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**ABSTRACT:** Dolomite occurs as a primary precipitate that cements Recent volcanoclastic sands in the shallow-marine environment of Luise Harbor, Lihir Island, Papua New Guinea. Field observations and geochemical data suggest that dolomite precipitates through complex mineral reactions in response to discharge of gas (> 90% CO<sub>2</sub>) and heated seawater from hydrothermal vents in the seafloor. Gas discharge causes the formation of shallow circulation cells, and cold seawater is drawn into the sediment, where it is heated to approximately 100°C. Reaction between hydrothermal CO<sub>2</sub> (g), primary sediment grains, and heated seawater causes the precipitation of primary dolomite. Once temperatures are above 70°C the Mg/Ca ratio in seawater increases because CaSO<sub>4</sub> precipitates, while at the same time the dissolution of iron oxide minerals increases the pH; both reactions favor dolomite precipitation. Ferrous iron reacts with H<sub>2</sub>S to form co-precipitated Fe-sulfide minerals. The dolomite is nearly stoichiometric and occurs as zoned inclusion-rich and inclusion-poor spherulitic cements, many of which are present as coalesced composite spherules. Oxygen isotope values for dolomite of -8.8 to -10.2‰ VPDB constrain the temperature of precipitation to be between about 77 to 110°C. Strontium isotope ratios for dolomite (average 0.70886) are close to those of modern seawater; their slightly less radiogenic compositions implicate minor addition of magmatic strontium. Hydrothermal dolomite may develop in shallow, near-surface sediments in active tectonic settings.

## INTRODUCTION

On the basis of their mode of formation, dolomites can be broadly divided into two groups. Primary dolomite is directly precipitated from solution either as sediment or cement, whereas secondary dolomite is formed via replacement of precursor CaCO<sub>3</sub> in the presence of Mg<sup>2+</sup>-bearing fluids. Primary dolomite is comparatively rare, forming in saline lakes and sabkhas (e.g., Patterson and Kinsman 1982), from pore fluids during early and late stage diagenesis (e.g., Humphrey 1988; Kaldi and Gidman 1982), and in certain hydrothermal environments (e.g., Magenheimer and Gieskes 1992; Baker et al. 1994; Plumlee et al. 1994). Most Recent dolomites forming in surficial sediments are Ca-rich and far from perfectly ordered (e.g., Land 1980).

In this paper we report the presence of primary dolomite in shallow-water, nearshore Recent sediments in Luise Harbor, Lihir Island, Papua New Guinea, where magmatic and hydrothermal gases, containing up to 98% CO<sub>2</sub>, percolate constantly through the sediment cover (Pichler et al. 1999a). Modification of the seawater contained in seafloor sediment pores creates a chemical microenvironment within which mineral reactions, including dolomite precipitation, are taking place. In comparison with massive dolomitization of carbonate platforms, the Lihir dolomite represents a volumetrically insignificant contribution to the sedimentary record of dolomite. However, epigenetic, metal-sulfide mineral deposits have the common association with dolomite. Understanding the origin of dolomite in this study thus provides clues to early, epigenetic mineralization.

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## LOCATION AND GEOLOGICAL SETTING

Islands of the Tabar-Feni chain, Papua New Guinea, are Pliocene to Recent alkaline volcanoes located in the fore-arc region of the New Hanover-New Ireland-Bougainville island arc (Fig. 1). The study area lies in Luise Harbor along the eastern margin of Lihir (Fig. 1). Lihir comprises remnants of three Pliocene to Holocene volcanoes (Kinami, Huniho, and Luise) and common volcanic rocks are quartz trachyte, trachybasalt, and alkali basalt (Wallace et al. 1983). Several geothermal areas are located principally within the caldera of Luise volcano and include hot mud pools, springs of chloride and acid sulfate waters, and a few low-temperature fumaroles, with temperature and pH values ranging from 39 to 99°C and 1.6 to 2.8, respectively (Wallace et al. 1983).

Submarine, hydrothermal venting occurs 100 m offshore, along the north side of Luise Harbor in shallow water (3–10 m) over an area of approximately 5000 m<sup>2</sup> (Pichler et al. 1999a). Oscillation ripples up to 10 cm high are ubiquitous throughout the area, indicating that venting occurs in sediments located above fair-weather wave base (Walker and Plint 1992).

Focused, vigorous discharge of gas from vent orifices, 20–50 cm in diameter, was observed at six locations. A possible discharge of clear liquid associated with the gases is inferred from observations of shimmering above vent orifices. This discharge, however, is volumetrically small and could not be sampled. Temperatures at the point of discharge range from 60 to 96 °C. Sites of gas exhalation are marked by small funnel-shaped indentations (i.e., conical depressions) 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 are not present around these bubble streams.

Two types of hydrothermal precipitates are predominant around the submarine vents: (1) Fe-sulfides forming 1–2 cm thick colloidal bands, coating and/or replacing primary sediment grains (Pichler et al. 1999a), and (2) dolomite, present as cement in sediment pore spaces and as massive veinlets that crosscut already cemented sediment. Other minerals of hydrothermal origin include smectites, chlorite, and Ca-sulfate.

## ANALYTICAL METHODS

Samples for this study were collected in the shallow underwater setting of Luise Harbor. Samples LH-2C and LH-8 were collected as hand samples, using hammer and chisel. Sample LH-6 was collected as drill core (2.5 cm diameter) and represents consolidated volcanoclastic-dolomitic sediment that was exposed above the seafloor (Fig. 2A). LH-2C represents a layer of massive dolomite that was located approximately 10 to 20 cm below the sediment-water interface. LH-8 was taken from a layer of consolidated volcanoclastic-dolomitic sediment (Fig. 2B) that was also covered by approximately 10 to 20 cm of volcanoclastic sediment. All samples were taken in the immediate vicinity of points of extensive gas discharge.

Mineralogy and mineral composition were determined using standard X-ray diffraction (XRD), scanning electron microscope (SEM), and electron microprobe methods. Structural compositions were calculated from electron probe microanalysis data and are based on 6 oxygen atoms. Cu, Ba, Rb and Sr were determined by ICP-AES, and Be, Cs, V, Y and Zn were determined by ICP-MS. Major elements were analyzed by X-ray fluorescence (XRF) and wet chemical methods. XRF, XRD, SEM, ICP, and mi-

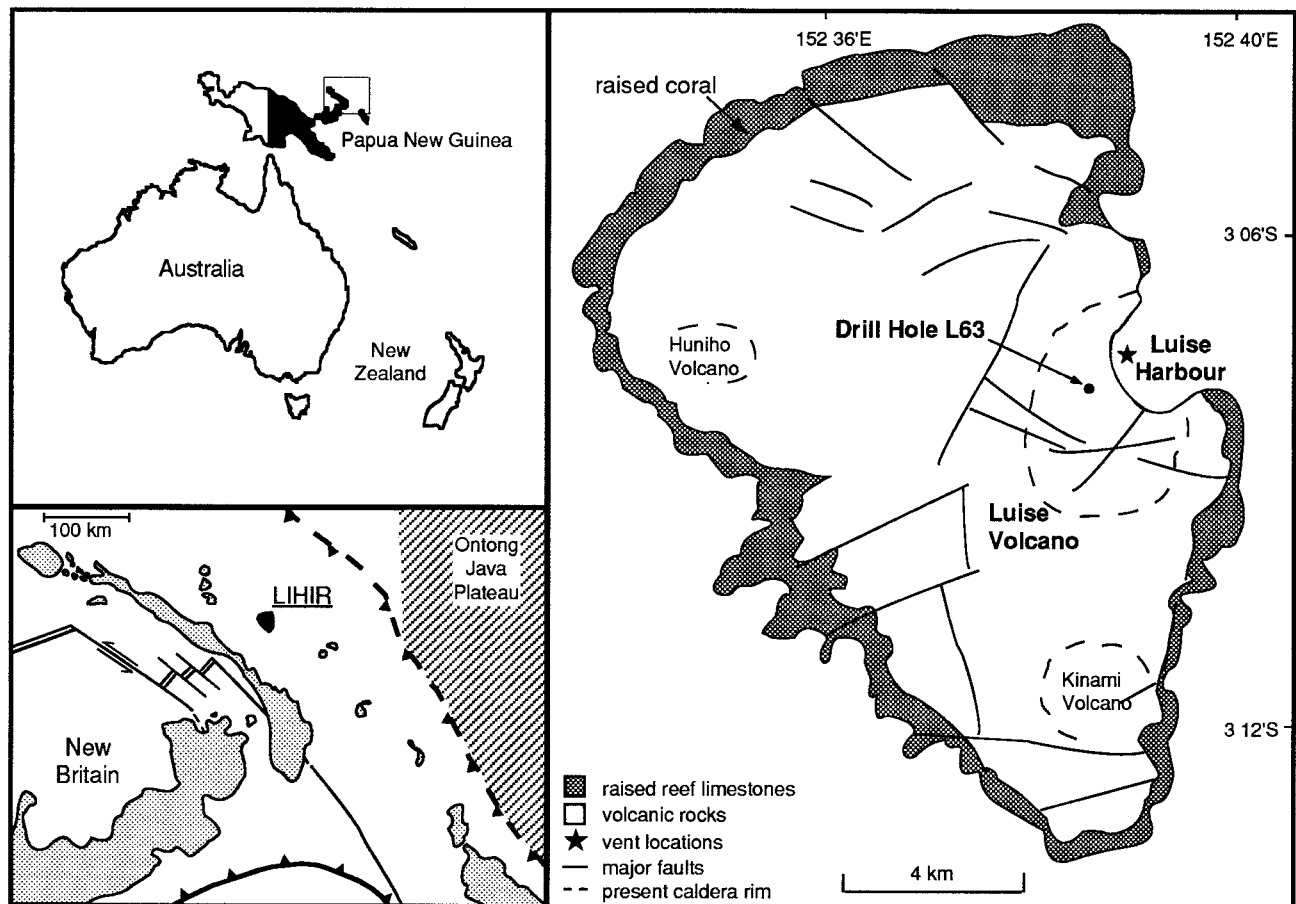


FIG. 1.—Location and tectonic setting of Lihir Island, one of the Feni islands in the Tabar–Feni island chain (modified from Wallace et al. 1983; Davies and Ballantyne 1987).

croprobe analyses were carried out at the Geological Survey of Canada and at the Colorado School of Mines.

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 using standard techniques. Dolomite samples were reacted at 50°C and corrected using the fractionation factor from Rosenbaum and Sheppard (1986). Strontium isotope samples were collected using a micro-drill to avoid contamination with nondolomitic material, and digested in ultrapure HCl.  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios were measured on a five-collector Finnigan MAT 262 solid-source mass spectrometer at the Institut für Geologie, Ruhr Universität, Bochum, following the procedures of Diener et al. (1996). The average of 100 repeat measurements for the NBS-987 standard was  $0.710224 \pm 0.000008$ .

## RESULTS

### Petrology

Hydrothermal precipitates, consisting of Fe-sulfide minerals and dolomite, cement volcanoclastic sediments near vent sites in Luise Harbor. Consolidated and lithified sediments occur as seafloor outcroppings and as layers below the current sediment–water interface (10 to 20 cm below). Constant reworking of loose and consolidated sediments proximal to shallow (less than 10 m water depth) vent sites results in sediment transport and disruption of cemented layers.

Sample LH-2C consists almost entirely of dolomite, except for minor amounts of pristine to slightly altered olivine and pyroxene sand-size de-

trital grains. The dominant rock fabric in LH-2C is a massive-to-laminated dolomiticite to dolomicrospar breccia. Breccia clasts have been generated through multiple episodes of *in situ* fracturing, cementation, and brecciation (Fig. 3A). Pore-rimming and pore-occluding dolomite cements are commonly subhedral, equant, zoned crystals ranging from 10 to 80  $\mu\text{m}$  across, with an average size of about 50  $\mu\text{m}$ . These equant dolomite cements are relatively inclusion-free, except for thin growth zones demarcated by sub-micron fluid and solid inclusions (Fig. 3B), the composition of which has yet to be determined. Some growth zones occur as euhedral rhombic outlines, although many show evidence of rounding through dissolution. These cements are the dominant intergranular precipitate and constitute approximately 20% of the rock fabric. Rounding of crystal terminations, etching of crystal faces, and the presence of rounded and crosscut growth zones within crystals imply that dolomite dissolution occurred intermittently throughout precipitation of these cements (Fig. 3C).

Crosscutting relations indicate that precipitation of Fe-sulfide minerals is coeval with precipitation of dolomite cement (Fig. 3B–D). Iron sulfide minerals are mainly marcasite and minor amounts of pyrite, and these minerals provide a substrate for dolomite crystal growth, occur as solid inclusions within dolomite, and grow on dolomite substrates. Throughout this sample, euhedral marcasite crystals grow on a dolomite substrate in voids and fractures. These marcasite crystals have a distinctive tarnish caused by a thin oxidation layer of Fe-sulfate on the crystal surface.

Another abundant type of cement present in LH-2C is pore-filling spherulitic dolomite cement (Fig. 3D) that occurs as cloudy, inclusion-rich composite crystals ranging from 200 to 400  $\mu\text{m}$  in diameter. Composite crystals

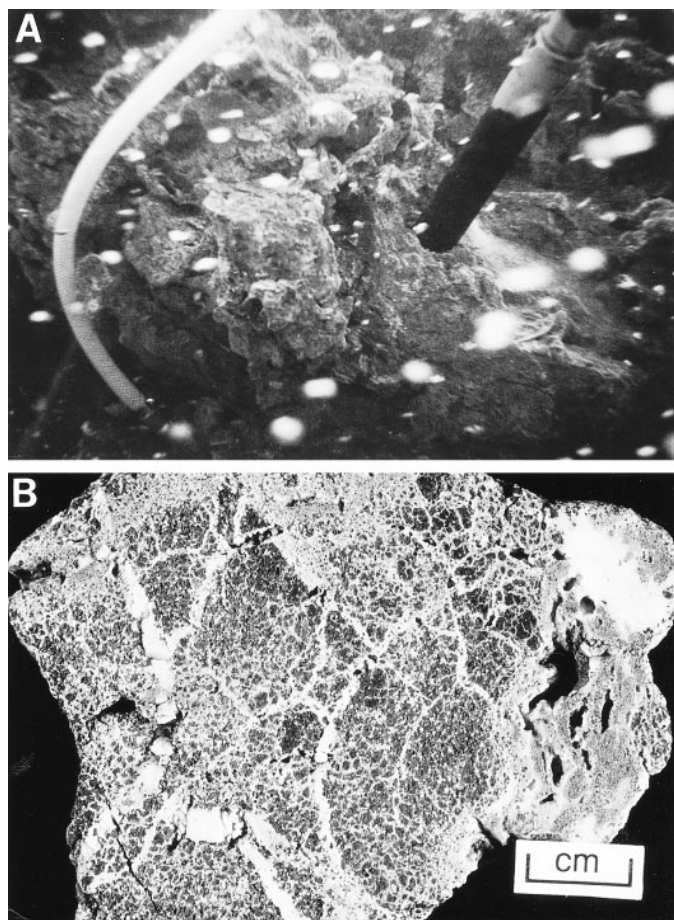


FIG. 2.—A) Underwater photograph of outcropping dolomitic sediment in Luise Harbor. Note the abundant gas bubbles emanating from the rock and sediment. The drill bit is approximately 50 cm long. Sample LH-6 was taken at this location. B) Photograph of a polished slab that was cut from sample LH-8. Dolomite veins (white) crosscut volcaniclastic material.

are composed of a radial arrangement of perhaps thousands of elongate, bladed crystallites. Pseudo-uniaxial crosses are developed under crossed-polarized light, indicating a dominant radial *c*-axis orientation of crystallites within the composite crystals. The resulting sweeping style of extinction superficially resembles that produced by baroque dolomite; however, in all cases it is merely an artifact of spherulitic construction. Undifferentiated solid and fluid inclusions create a cloudy appearance to the spherulitic crystals and also define concentric growth zones. Inclusion-rich zones alternate with inclusion-poor zones. Radial and/or dumbbell inclusion patterns (Nielsen et al. 1997) have not been observed.

Sample LH-6 contains a substantial amount (about 50%) of primary volcanic minerals (pyroxene and olivine, with minor amphiboles and plagioclase and potassium feldspar) and volcanic rock fragments cemented by minor dolomite. Most of the olivine is partly or completely replaced by either chlorite or smectite. The remaining 50% of the rock is composed of spherulitic dolomite cement, similar to that described above for sample LH-2C. These spherules show a slightly wider range of diameters, ranging from 100 to 500  $\mu\text{m}$ . Spherules are commonly poikilitopic, partially to completely incorporating volcaniclastic grains. They are extremely cloudy and inclusion rich and show concentric growth zones. Dolomite spherules serve as substrates for sulfide minerals, incorporate sulfides as solid inclusions, and grow on sulfide substrates, indicating the intimate chemical association between dolomite and sulfide precipitation.

Sample LH-8 also contains about 50% altered volcaniclastic material

(Fig. 2B). Much of this material occurs as resedimented clasts of smectite- and dolomite-cemented grains. Volcaniclastic grains are highly altered. Dolomite occurs almost entirely as coalesced, inclusion-rich, zoned spherules. Individual spherules are rare but occur disseminated throughout the sample. Individual dolomite cement crystals are likewise rare but occur as mosaics of equant, anhedral, and inclusion-poor crystals. These likely represent precipitation late in the paragenesis, because the only other inclusion-poor dolomite cement in this sample occurs as epitaxial terminations on spherulitic crystals.

### Geochemistry

Representative chemical and structural compositions from electron probe microanalysis for Luise Harbor dolomites are listed in Table 1. Most dolomite crystals approach ideal stoichiometric compositions of  $\text{Mg}/\text{Ca} = 1$ . Departures from stoichiometric composition are within the precision of the analytical method. Only analysis LH-6 shows a moderate Ca excess (Table 1). Dolomite stoichiometry was also analyzed by XRD analysis of *d*-spacing offset of the [104] peak. Near-stoichiometric compositions were confirmed, with the mole percentage of  $\text{MgCO}_3$  in samples LH-2C, LH-6, and LH-8 equal to 48.3%, 49.5%, and 49.8%, respectively. Trace-element concentrations are generally low, and only Mn is slightly enriched. There is no correlation between trace elements and major elements, and  $\text{Mg}/\text{Ca}$  ratios likewise show no correlation with trace-element concentrations.

Concentrations of major elements and selected trace elements for the bulk samples determined by XRF, ICP, and wet-chemical methods are listed in Table 2. All elements listed correlate with  $\text{CO}_2$ , which in turn is controlled by the modal abundance of dolomite (LH-2C > LH-8 > LH-6). Elements that are enriched in dolomite relative to Luise Harbor sediments (Pichler et al. 1999a) are positively correlated, whereas all others are negatively correlated.

The results of isotope analyses for LH-2C are  $\delta^{13}\text{C} = 4.2\%$ ,  $\delta^{18}\text{O} = -8.8\%$ , and  $^{87}\text{Sr}/^{86}\text{Sr} = 0.708960$ . Isotope analyses for LH-8 yielded  $\delta^{13}\text{C} = 3.9\%$ ,  $\delta^{18}\text{O} = -10.2\%$ , and  $^{87}\text{Sr}/^{86}\text{Sr} = 0.708718$ . Values for  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  are different from those expected for sedimentary dolomites (e.g., Land 1980; Tucker and Wright 1990). Two strontium isotope analyses of LH-6 yielded ratios of 0.708858 and 0.708897. The mean of the four dolomite samples analyzed for  $^{87}\text{Sr}/^{86}\text{Sr}$  is 0.70886, a value close to that of present day seawater in the Tabar-Feni island arc (Pichler et al. 1999b).

### DISCUSSION

Near vent sites, Luise Harbor sediment is cemented due to hydrothermal precipitation dominantly of Fe-sulfides (Pichler et al. 1999a) and spheroidal dolomite. The highest concentration of sulfide and dolomite, and therefore, degree of consolidation and lithification is near the points of hydrothermal discharge. The interplay of sedimentary and hydrothermal processes in Luise Harbor continually modifies the physical features of the gas discharge sites. At water depths of less than 10 m, vents are subject to the influence of wave action, as indicated by symmetrical ripple marks, causing constant sediment transport and mechanical enrichment of heavy minerals. This process affects mainly the top few centimeters of sediment, preventing the formation of a permanent dolomite layer because of constant reworking. Deeper (> 10 cm), dolomite and Fe-sulfides are able to precipitate for extended periods, replacing and cementing primary sediment. It is not possible to resolve a spatial relation between dolomite and sulfide precipitation, because episodic storm events result in disruption of seafloor sediment.

Luise Harbor dolomite is interpreted to have formed by gas-sediment-seawater interaction. The simultaneous processes of gas discharge, seawater convection, and mineral precipitation and dissolution create the necessary physicochemical conditions for dolomite precipitation. The Luise Harbor shallow-water hydrothermal system discharges mainly gas and a minor

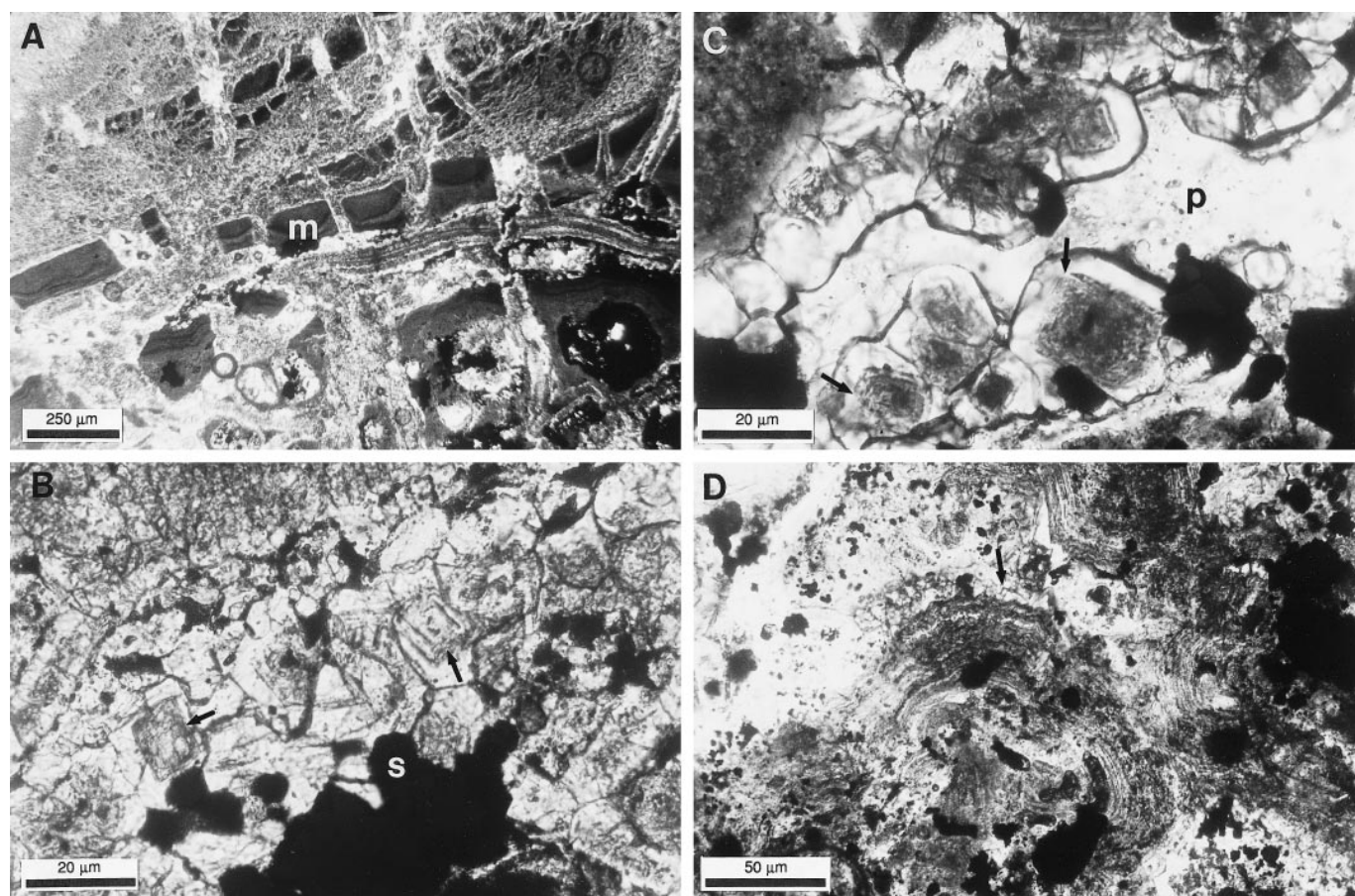


FIG. 3.—Thin-section photomicrographs of dolomite fabrics from Luise Harbor. **A**) Multiple episodes of dolomite cementation and brecciation of dolomite micrite (m). Sample LH-2C. Plane light. **B**) Zoned dolomite showing inclusion-rich (arrows) and inclusion-poor growth layers. Note opaque iron-sulfide minerals (s) co-precipitated with dolomite cement. Sample LH-2C. Plane light. **C**) Zoned dolomite showing evidence for intermittent dissolution. Note rounding of interior rhombic zones (arrows) and rounded crystal faces and terminations facing open pore space (p). Sample LH-2C. Plane light. **D**) Spherulitic dolomite cement showing micron-scale alternations of inclusion-rich and inclusion-poor growth layers. Some spherules mantled by euhedral, inclusion-poor crystal terminations (arrow). Iron-sulfide minerals appear black. Sample LH-6. Plane light.

component of heated seawater (Pichler et al. 1999a). From laboratory experiments and field observations, O'Hara et al. (1994) concluded that seawater convection can develop in permeable sediments around vent sites as a result of a combination of gas seepage and increased heat flow. The actual depth of such circulation is unknown, but it should be limited by the downward extension of the sediment cover.

Most Luise Harbor dolomites are present as spheroidal precipitates. Other examples of spheroidal carbonate cements have been documented in the literature. For example, a recent study by Nielsen et al. (1997) reported the occurrence of spheroidal dolomite in a Lower Carboniferous karstified sequence in eastern Belgium. Interpreted as bacterially induced precipitates, the spheroidal nature of their dolomite is similar to that described for other carbonates by Buczynski and Chafetz (1991), who suggested that spheroidal and dumbbell habits imply bacterially mediated precipitation. Although the dolomite of Nielsen et al. (1997) contains co-precipitated framboidal pyrite, its presence is interpreted to be the result of local bacterial sulfate reduction. Sulfide minerals (predominantly marcasite with lesser amounts of pyrite), co-precipitated with spheroidal dolomite in Luise Harbor sediments, occur through hydrothermal processes. We cannot entirely rule out the involvement of bacteria in dolomite nucleation and/or growth. Indeed, dense inclusion-rich zones in spheroidal dolomite may suggest microscale involvement of bacteria; however, the presence of dolomite in these sediments is more likely the result of complex inorganic mineral reactions.

Bacterial sulfate reduction of organic matter liberates bicarbonate ion strongly depleted in  $^{13}\text{C}$ , and diagenetic precipitates tend also to have depleted compositions (e.g., Irwin et al. 1977). Luise Harbor dolomites have  $\delta^{13}\text{C}$  values around 4‰, and thus argue against any major bacterial contribution of carbon isotope fractionation.

Compared to pencontemporaneous sedimentary dolomites,  $\delta^{18}\text{O}$  values for Luise Harbor dolomites ( $-10.2\text{‰}$  to  $-8.8\text{‰}$  VPDB) are extremely low (e.g., Budd 1997; Carballo et al. 1987; Mitchell et al. 1987; Swart et al. 1989). Budd (1997) reported a much more enriched range of  $\delta^{18}\text{O}$  values ( $+1.5\text{‰}$  to  $+2.8\text{‰}$  PDB) for Holocene pencontemporaneous dolomites in tropical to subtropical settings. Depleted oxygen isotope values in dolomites may derive from precipitation at high temperatures, or be due to precipitation from waters containing a significant admixture of meteoric water. Inasmuch as the depositional and diagenetic environment of Luise Harbor sediment is entirely in marine waters, the influence of meteoric water can be discounted. These values can be explained only by precipitation at temperatures higher than those of tropical seawater. Assuming heated seawater ( $\delta^{18}\text{O} = 0\text{‰}$  SMOW) as the parent solution, minimum and maximum precipitation temperatures were calculated (based on  $\delta^{18}\text{O}_{\text{dol}} = -10.2$  to  $-8.8\text{‰}$  VPDB) to be between 77 and 110°C (Fig. 4). These temperatures are in good agreement with, though slightly higher than, those measured *in situ* at the point of discharge (60 to 96°C). Temperatures at the site of dolomite precipitation, within the sediment column,

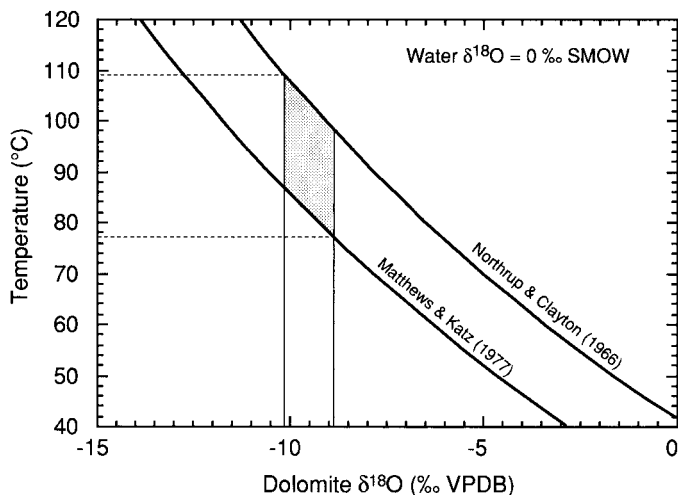


FIG. 4.—Oxygen isotope equilibrium plot of  $\delta^{18}\text{O}$  of dolomite vs. temperature of precipitation. Fluid  $\delta^{18}\text{O}$  composition is assumed to be 0‰ SMOW (i.e., seawater).

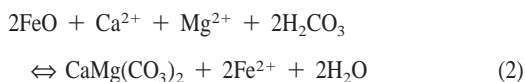
are likely higher than those at vent discharge sites, but were not directly measured.

Precipitation of dolomite in this hydrothermal environment is controlled by a combination of lowered fluid  $\text{SO}_4^{2-}$  concentration, increased fluid  $\text{Mg}^{2+}/\text{Ca}^{2+}$  ratio, and competing mineral reactions. Although surface seawater ( $\text{Mg}^{2+}/\text{Ca}^{2+} = 5$ ) is supersaturated with respect to dolomite, recent marine carbonate is rarely dolomitized, most likely because of a variety of kinetic inhibitors (e.g., Land 1980; Budd 1997). Dolomitization of precursor calcium carbonate in seawater solutions proceeds rapidly at higher temperatures and  $\text{Mg}^{2+}/\text{Ca}^{2+}$  ratios (e.g., Sibley et al. 1987). Additionally, the presence of  $\text{SO}_4^{2-}$  in seawater may be a kinetic inhibitor of dolomite precipitation (Baker and Kastner 1981).

In the Luise hydrothermal system, seawater is drawn into the sediment, where it is heated. Once temperature rises above 70°C,  $\text{CaSO}_4$  begins to precipitate because of its retrograde solubility (Fig. 5). The resulting decrease in  $\text{SO}_4^{2-}$ , increase in  $\text{Mg}^{2+}/\text{Ca}^{2+}$  ratio, and higher temperatures all favor dolomite precipitation. However, addition of hydrothermal  $\text{CO}_2$  ( $f\text{CO}_2 \sim 1.7$ ) will lower the seawater pH from approximately pH = 8 to pH = 4, thus preventing the precipitation of dolomite (Fig. 5). The process that produces the necessary increase in pH is dissolution of primary volcanogenic Fe-bearing minerals, such as magnetite, pyroxene, and ilmenite. The reduced form of the reaction is



Such dissolution rapidly increases the pH to about pH = 6 and, once the stability field of dolomite is reached (Fig. 5), the overall reaction may be similar to



Dissolved  $\text{Fe}^{2+}$  reacts with hydrothermal sulfur ( $\text{H}_2\text{S}$ ) to form coexisting Fe-sulfides (Fig. 3B–D), and further increasing the pH. Iron sulfide minerals form the substrate upon which some dolomite precipitates, occur as solid inclusions within dolomite cement crystals, and use dolomite cement as a substrate upon which to grow. This intimate association of Fe-sulfide minerals and dolomite implies complex buffering and mineral precipitation reactions in the hydrothermally affected sedimentary environment. While the above equations are not intended to demonstrate mass balance, mainly due to the lack of fluid geochemistry, field and petrographic evidence in-

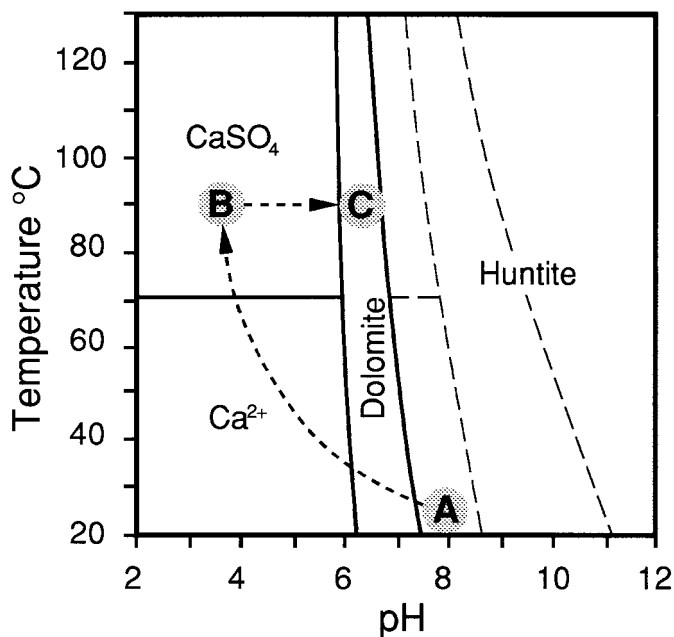


FIG. 5.—Temperature-pH diagram for the system  $\text{Mg-Ca-Fe-SO}_4\text{-CO}_2$  at 90°C (solid lines) at a pressure of 1.7 bars, and at normal seawater conditions (dashed lines): 25°C,  $[\text{HCO}_3^-] = 10^{-4}$ . Activities for  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{SO}_4^{2-}$ , and  $\text{HCO}_3^-$  are assumed to be  $10^{-3}$ ,  $10^{-3.7}$ ,  $10^{-5}$ ,  $10^{-2.6}$  and  $10^{0.23}$ , respectively.  $\text{Mg}/\text{Ca} = 5$ . Thermodynamic data are from Brookins (1988) and references therein. Arrows indicate the approximate evolution of the system. **A**) Cold seawater, dolomite and/or huntite do not precipitate because of kinetic inhibition. **B**) Addition of heat and  $\text{CO}_2$  causes a temperature increase and decrease in pH. Precipitation of  $\text{CaSO}_4$  commences once temperatures are above 70°C, resulting in a constant increase of the  $\text{Mg}/\text{Ca}$  ratio. **C**) Dissolution of Fe-bearing minerals increases the pH until dolomite precipitates.

dicates that approximately the same amounts of Fe-sulfides and dolomite precipitate, suggesting some kind of mass balance.

Calcian and poorly ordered hydrothermal dolomite has been observed at several locations where marine sediment is subject to hydrothermal alteration (e.g., Stout and Campbell 1983; Goodfellow and Blaise 1988; Magenheimer and Gieskes 1992; Baker et al. 1994). Formation of dolomite in such an environment occurs throughout the upper few meters of sediment at temperatures up to 100°C. It is unclear, however, if there is a direct contribution from a deep circulating hydrothermal fluid or if the dolomite formed entirely by interaction between sediment and heated seawater. Stout and Campbell (1983) reported  $^{87}\text{Sr}/^{86}\text{Sr}$  values ranging from 0.7060 to 0.7091 for hydrothermal interstitial waters in the Gulf of California. Although 0.7060 indicates at least some contribution of magmatic Sr, the value of 0.7091 is nearly the same as contemporary seawater (e.g., Veizer 1989).

Dolomite in Luise Harbor sediment formed presumably, if not entirely, by interaction between sediment and heated seawater, and its presence is in clear favor of shallow circulation of seawater versus a deeper source. Deeply circulating hydrothermal fluids are generally depleted in  $\text{Mg}^{2+}$  and have very low  $\text{Mg}^{2+}/\text{Ca}^{2+}$  ratios (e.g., Nicholson 1992; Von Damm 1995), which would preclude the formation of dolomite (e.g., Morrow 1982). Also, the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of Luise Harbor dolomite (0.70886) is dramatically different from local volcanic rocks (0.70398, M. Perfit, personal communication), but almost the same as contemporary seawater (0.70918) (e.g., Veizer 1989). Dolomite that precipitated from a hydrothermal fluid of deeper origin would have values closer to the host rock because isotopic equilibrium for  $^{87}\text{Sr}/^{86}\text{Sr}$  between a hydrothermal fluid and host rock is rapidly attained (Vuataz et al. 1988).

## SUMMARY AND CONCLUSIONS

In Luise Harbor, on the eastern side of Lihir Island, Papua New Guinea, sedimentary and hydrothermal processes combine to form Recent dolomite in a shallow-water environment. The deposits are located near hydrothermal vents that discharge a combination of hydrothermal gas and heated seawater. Dolomite precipitates at temperatures of 77 to 110°C, comparable to *in situ* measured temperatures. The physicochemical conditions for dolomite precipitation are attained through a combination of several processes that modify Luise Harbor seawater. Gas discharge and magmatic heat input drive seawater convection in shallow (< 10 m water depth) volcanoclastic sediment. Cold seawater is drawn into the sediment and heated. Once temperatures reach about 70°C, CaSO<sub>4</sub> precipitates, thereby increasing and decreasing Mg<sup>2+</sup>/Ca<sup>2+</sup> ratio and SO<sub>4</sub><sup>2-</sup> concentration, respectively. Simultaneous dissolution of volcanogenic Fe-bearing minerals buffers the pH, and both dolomite and Fe-sulfide minerals precipitate. This occurrence of Recent dolomite precipitation indicates that hydrothermal dolomite may develop in shallow, near-surface sediments in active tectonic settings.

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