42. HYDROGEOCHEMISTRY IN THE LAU BACKARC BASIN

Gérard Blanc,2 Peter Stille,2 and Frédéric Vitali2

ABSTRACT

Interstitial water samples from Sites 834 through 839, drilled during Ocean Drilling Program Leg 135 in the backarc Lau basin (Southwestern Pacific), have been analyzed for major elements, manganese, copper, strontium, barium, vanadium, and 87Sr/86Sr isotopic composition values. The concentration-depth profiles of the major chemical components show almost straight concentration gradients at all sites, and seem to reflect slight alteration of volcanic material. However, the lower part of the sedimentary cover, where volcanogenic material is abundant and where diagenetic minerals occur, systematic decreases in calcium, strontium, manganese, copper, and vanadium concentrations are observed. A downwelling flow of bottom seawater, which affected the diagenetic chemical signature of the interstitial water, is probably responsible for the recorded chemical features. This hypothesis is supported by strontium isotope data obtained from interstitial water samples at Site 835. It is also in accordance with data from heat flow and physical properties.

INTRODUCTION

The Lau basin is a typical example of an active backarc basin situated between a remnant (Lau Ridge) and an active (Tofua) volcanic arc. Hydrothermal activity and ore deposits in backarc environments have been previously described in the Okinawa (Halbach et al., 1989), Manus (Both et al., 1986), Mariana (Craig et al., 1987), and North Fiji (Auzende et al., 1989) basins. For the Lau basin, witnesses of hydrothermal activities have been observed in the northern part of the basin (Hawkins and Helu, 1986), at the Peggy Ridge (Bertine and Keene, 1975), and near the Valu Fa Ridge (von Stackelberg and Shipboard Scientific Party, 1985, 1988; von Stackelberg and von Rad, 1992; Fouquet and the Nautilau Group, 1990; Fouquet et al., 1991). Data obtained during the Nautilau diving cruise suggest that the Valu Fa Ridge is one of the most active hydrothermal areas of the oceans (Fouquet and the Nautilau Group, 1990). The metal contents (Zn, Cd, As, Pb) and the pH (~2) are, respectively, the highest and the lowest ever measured in hydrothermal fields of oceanic ridges (Fouquet et al., 1991).

Leg 135 of the Ocean Drilling Program (ODP) drilled and cored six sites (Sites 834–839) located in the west of the Lau spreading centers (Central Lau [CLSC] and Eastern Lau [ELSC] spreading centers and Valu Fa Ridge [VF]; Fig. 1). These sites were drilled within smaller and narrower (<10 km) north-south fault basins and provide an ideal location to study fluid circulation and alteration of the interstitial water chemistry within a shallow sedimentary column situated at the flanks of the active spreading centers.

SAMPLING AND ANALYTICAL PROCEDURES

Shipboard Analyses

The shipboard analytical program for Leg 135 included analyses of interstitial water samples for pH, alkalinity, salinity, SO42−, Cl−, Ca2+, Mg2+, K+, Sr2+, H2SiO3, NH4+, PO43− and Mn2+. The method for obtaining interstitial water from the sediment, using a stainless-steel squeezer, was described in detail by Manheim and Sayles (1974). For interstitial water analyses, 10-cm-long, whole-round sediment core samples were collected immediately after the core arrived on deck. The sediment was extruded from the core liner, the outer layer of the sediment was removed by scraping with a spatula, and the sample was placed in a Carver laboratory press to remove the interstitial water. The press operated at a pressure of about 30,000 psi (2.11 kg/m²). The sediment remained under these pressure conditions until no more water could be squeezed out the sample. Interstitial water was collected in 50-cm³ syringes and filtered with a 0.45-μm Millipore filter. International Association for the Physical Sciences of the Ocean (IAPSO) standard seawater P99 was the primary standard for the water analysis on board. Individual inorganic species were analyzed according to procedures outlined by Gieskes and Peretsem (1986). Alkalinity and pH were determined using a Metrohm autotitrator with a Brinkmann combination pH electrode. Alkalinity reproducibility was better than 5%; data are given in millimoles of acid equivalent per liter of solution. Salinity was determined using a Goldberg optical hand refractometer measuring the total dissolved solids. Chloride was measured by silver nitrate titration of a 0.1 mL sample diluted in 5 mL of deionized water using potassium chromate as an indicator. The reproducibility on different dilutions of the IAPSO standard is better than ±1%. Sulfate was quantified using a Dionex-2120 ion chromatograph. Reproducibility on different diluted aliquots of the IAPSO standard is better than ±2%. Calcium was determined by complexometric titration of a 0.5-cm³ sample with EGTA using GHA as an indicator. To enhance the determination of calcium, calcium-GHA complex was extracted onto a butanol layer (Gieskes, 1973). Magnesium was determined by EDTA titration for total alkaline earth, and subsequent subtraction of the calcium and strontium values yielded the magnesium concentration in the interstitial water sample. Ammonia, silica, and phosphate determinations were performed with a Gifford spectrophotometer as well as by means of the colorimetric methods described by Gieskes and Peretsem (1986).

Precisions of the analytical data generally are better than 2%, but artefacts of squeezing may cause systematic offsets in the data. However, concentration-depth trends are not significantly affected. Atomic absorption measurements were performed using a Varian SpectrAA-20 spectrophotometer to determine K, Na, Mg, Sr, and Mn. All measurements were done in absorption mode using an oxidizing acetylene flame. The relative precision for all these elements is lower than 5%. Sodium concentrations were also determined by charge balance; the difference between the calculated and measured Na data never exceeded 5%. Similar accuracies were obtained between the two methods of the Mg determination.

Shore-based Analyses

The shore-based analytical determinations of the interstitial water samples include dissolved trace elements and the strontium isotopic
compositions. Determinations of Si, Mn, Cu, Ba, V, Zn, Ni, Co, Cr, Se, Y, and Zr were performed on interstitial water samples using an ARL inductively coupled plasma-atomic emission spectrometer (ICP-AES). The interstitial water samples were diluted with MilliQ-dionized water acidified with HNO₃. Dissolved Zn, Ni, Co, Cr, Sc, Y, and Zr concentrations were below the detection limits of the ICP-method (Zn < 40 ppb, Ni < 40 ppb, Cr < 20 ppb, Se < 2 ppb, Y < 4 ppb, and Zr < 20 ppb). The general precision is between 2% and 5% for Si, Mn, Cu, Ba, and V. The difference between shipboard and shore-based Si and Mn data never exceeded the analytical error of the methods. The elementary composition of the interstitial water samples is given in Table 1. Results are expressed in millimole or micromole per liter (mM or µM).

The ⁸⁷Sr/⁸⁶Sr ratios were measured for Site 835 interstitial water samples using a VG Sector mass spectrometer. A ⁸⁷Sr/⁸⁶Sr value of 0.710266 ± 0.000011 (2σ, N = 18) was measured for the NBS 987 standard. The results are given in Table 2.

### SITE DESCRIPTIONS AND RESULTS

#### Site 834

The sedimentary sequence has been divided into four lithologic units, as follows.

Unit I, from 0 to 42 m below seafloor (mbsf), is essentially composed of clayey nannofossil ooze stained by iron-oxyhydroxide and sporadically interbedded with graded foraminiferal sands and oozes. Its age ranges from late Pleistocene to late Pliocene (2.6 Ma). Its average sedimentation rate is 18.2 mm/k.y.

Unit II, from 42 to 78 mbsf, is late Pliocene in age and consists of clayey nannofossil ooze mixed sediment interbedded with vitric ash layers. Its clayey nannofossil ooze is more stained by iron-oxyhydroxide than that of Unit I. Downcore, foraminifera decrease whereas clay contents increase. The volcaniclastic sediment represents 20% of the total bulk sediment.

Unit III, from 78 to 112.5 mbsf, is early Pliocene in age and consists of up to 40% of vitric ashes interbedded with iron-oxyhydroxide-stained nannofossil clayey mixed sediments and nannofossil clays.

Unit IV, from 131.5 to 162.6 mbsf, is primarily composed of indurated claystones, vitric tufts, and calcarenites intercalated between vesicular basalt interpreted as a lava flow or sill.

Nine interstitial water samples were collected in Hole 834A. They were sampled from every core in the uppermost 55 mbsf. Below this depth, samples were taken only from every third core. One sample originates from the clayslones of the Unit IV.

In Hole 834A, the concentration-depth profiles of the dissolved major constituents (chloride, sodium, calcium, magnesium, potassium, and sulfate) are characterized by fairly uniform values from the mud line to 135 mbsf (Fig. 2). The Na/Cl ratios in all the interstitial water samples are constant (i.e., 0.857 ± 0.005). Calcium, magnesium, potassium, and sulfate concentrations determined in the interstitial water samples are almost equal to the average seawater concentration. The average concentration values from Hole 834A are sulfate = 27.8 ± 0.4 mM, calcium = 10.37 ± 0.54 mM, magnesium = 52.3 ± 1.07 mM, and potassium = 11.1 ± 0.31 mM. The observed deviations from these concentrations do not exceed the analytical uncertainty of the analytical methods (Gieskes and Peretseman, 1986). These values are similar to the average concentrations in free seawater (e.g., 28, 10, 53, and 11 mM, respectively; Broecker and Peng, 1982) and suggest that the elementary composition of the interstitial water is not affected by diagenetic processes. However, diagenetic processes are established by the occurrences of clays and zeolites (phillipsite, analcime) in this hole (Blanc, 1992, this volume). Hence, another mechanism must be involved to explain the uniform concentration values in dissolved major constituents.

Dissolved silica concentrations range between 200 and 400 µM, which is expected from sediments with little or no biogenic silica (Fig. 2). Because the influence of the squeezing effect dependent temperature on the dissolution of silica is not controlled, the absolute silica concentrations cannot be determined (Gieskes, 1973, 1974). However, relative changes in silica concentration may reflect changes in the mineralogical composition. Therefore, the slight increase in silica with depth is related to the increasing ash contents within the hole.

Concentrations of dissolved strontium gradually increase with depth to reach a maximum of about 130 mM at 82 mbsf (Fig. 2). Increasing strontium is generally related to carbonate recrystallization processes (Gieskes et al., 1986). However, in the lower part of Unit III and in Unit IV, a decrease in strontium concentrations is observed, even though calcarenite has been described for Unit IV. Concentrations of dissolved barium and vanadium are very low and uniform throughout the sedimentary column, with respective average concentrations of 0.239 ± 0.02 µM and 0.652 ± 0.07 µM.

In contrast to barium and vanadium, concentrations of dissolved manganese are not uniform along the sedimentary column (Fig. 2). From the mud line to 40 mbsf, manganese concentrations scatter around 40 µM. Between 40 and 50 mbsf, however, manganese concentrations increase up to more than 80 µM. These increased concentration values can be related to the occurrence of interbedded ash layers. Manganese concentrations decrease below 50 mbsf and reach a value of only 0.4 mM (Fig. 2). This decrease downhole cannot be explained by diagenetic processes.

From 5.9 to 32.5 mbsf, copper concentrations decrease from 5.98 to 1.13 µM. Copper release from a solid phase, like oxyhydroxides, may be responsible for the higher concentrations in the upper part of the hole. Another copper maximum reaching 3.18 µM has been de-
tected at 80.0 mbsf. Below this depth, the copper concentration-depth profile shows the same trend as that of manganese and stronblum.

Site 835

The sedimentary sequence recovered was divided into two units, as follows.

Unit I, from 0 to 130 mbsf, consists of iron-oxhydroxide-stained, clayey nanofossil ooze with sporadic interbeds of thin vitric volcanic silts, thin foraminifer sands, foraminifer nanofossil oozes, and thick mud-clast conglomerates. Vitric volcanic silty layers are present, volcaniclastic material is only rare in the sediment column between 135-839A-5R-5 and 135-839A-6R-5.

The decrease in ammonia below 53.5 mbsf could be related to clay uptake (Rosenfeld, 1979; von Breymann and Suess, 1988).

The barium concentration-depth profile is uniform in value over the whole profile (average = 0.262 ± 0.02 μM). The increase in vanadium concentrations downhole is probably related to the increases in volcanic silts, and is characterized by a content in volcanic material, especially glass, higher than that of Unit I.

Below 155.1 mbsf, vesicular basalts were cored.

A total of 10 interstitial water samples was collected. They were retrieved in the uppermost 35 mbsf from every core. Below this depth, interstitial water samples were only taken every second core.

The concentration-depth profiles of the dissolved major constituents (chloride, sodium, calcium, magnesium, potassium, and sulfate) are characterized by fairly uniform values from the mud line to the bottom of the sedimentary column (Fig. 3). This result is identical to that obtained in Hole 834-A.

Table 2. Strontium isotope data, Site 835.

<table>
<thead>
<tr>
<th>Core, section, interval (cm)</th>
<th>Depth (mbsf)</th>
<th>δ87Sr/δ18Sr</th>
</tr>
</thead>
<tbody>
<tr>
<td>11H-4, 140-150</td>
<td>6.0</td>
<td>0.709155</td>
</tr>
<tr>
<td>31H-4, 140-150</td>
<td>2.50</td>
<td>0.709094</td>
</tr>
<tr>
<td>2H-4, 140-150</td>
<td>2.20</td>
<td>0.709015</td>
</tr>
<tr>
<td>12H-4, 140-150</td>
<td>1.37</td>
<td>0.709065</td>
</tr>
<tr>
<td>14H-4, 140-150</td>
<td>0.87</td>
<td>0.708990</td>
</tr>
<tr>
<td>16H-4, 140-150</td>
<td>0.87</td>
<td>0.709156</td>
</tr>
</tbody>
</table>
Figure 2. Lithologic summary column and interstitial water chemistry, Site 834.
Figure 3. Lithologic summary column and interstitial water chemistry, Site 835.

The values of the dissolved silica concentrations in Hole 835A are comparable to those obtained at Site 834 (Fig. 3). The manganese concentration-depth profile shows an almost linear increase with depth. Below 110.5 mbsf, a linear decrease is observed. The concentration maximum of manganese (134.2 µM at 110.5 mbsf) implies a release of manganese from solid phases. A copper maximum of about 3.18 µM is reached at 34 mbsf in the weathered, pumice-rich, mud-clast conglomerate layer. Enhanced copper concentrations were not detected at the base of Unit I, where another thick layer of pumice-bearing conglomerates has been observed. Furthermore, dissolved copper concentrations decrease in Unit II, whereas the volcanic glass content increases drastically.
Site 836

A lithostratigraphic unit of 21 m thickness overlies vesicular basalt breccia. This unit comprises a sequence of generally thick-bedded, clayey nannofossil oozes with interbeds of volcaniclastic sediment. The hemipelagic deposits of Subunit IA contain up to 25 vol% of dispersed glass shards and are separated by rare ash layers. In Subunit IB, the number of volcaniclastic layers increases markedly. The sediments are middle to late Pleistocene in age. Only two interstitial water samples were collected. They show the same chemical characteristics as those obtained for Holes 834A and 835A.

Site 837

The 82.1-m-thick sedimentary sequence consists of clayey nannofossil ooze and vitric volcaniclastic rocks ranging in age from the Holocene to the late Pliocene. It was divided into two lithostratigraphic units.

Unit I, from 0 to 13.5 mbsf, is of Holocene to middle Pleistocene age (0.5–0.6 Ma). The sedimentation rate is about 25 mm/k.y. and is composed of iron-oxyhydroxide-stained, clayey nannofossil ooze containing rare beds of graded foraminifer oozes and thin vitric silts. Unit II, from 13.5 to 82.1 mbsf, is of middle Pleistocene to late Pliocene age. The average sedimentation rate is about 38 mm/k.y. It consists of thick volcaniclastic sands and silts interbedded with clayey nannofossil ooze.

Below 82.1 mbsf, igneous rocks were recovered.

Six interstitial water samples were collected from Hole 837A. They were collected from every core in the uppermost 32 mbsf; below this depth, samples were taken from every second core.

The chemical data in Hole 837A are comparable with those obtained in Holes 834A, 835A, and 836A (Fig. 4). Comparison between the low and uniform ammonia concentrations and the scatter of phosphate concentrations indicates that only small amounts of phosphate are released by organic matter degradation. The manganese concentration-depth profile at Site 837 shows a regular increase of manganese with depth. The manganese maximum reaches a value of about 87 µM at 71 mbsf. Slight decreases in strontium, copper, and vanadium are observed in the lower part of this hole.

Site 838

The sedimentary sequence consists of 98.7 m of volcaniclastic sediments and clayey nannofossil ooze, ranging in age from the middle Pleistocene to the upper Pliocene. It was divided into two lithologic units.

Unit I, from 0 to 23.04 mbsf, is of early to middle Pleistocene age (0.02–1.44 Ma). An average sedimentation rate of 21 mm/k.y. can be calculated. It is composed of homogeneous iron-oxyhydroxide-stained, clayey nannofossil oozes interbedded by four volcaniclastic layers.

Unit II, from 23.04 to 98.7 mbsf, is of late Pliocene to early Pleistocene age (1.4–1.9 Ma). An average sedimentation rate of 47 mm/k.y. can be calculated for the sedimentary column between 23.04 and 55 mbsf, and an average rate of 177 mm/k.y. for the sediments accumulated between 55 and 98.7 mbsf. This unit is dominated by very thick (up to 20 m), massive vitric sands and silts, and pumiceous gravels.

At 98.7 to 260 mbsf, indurated volcanic sediments were recovered. Only four interstitial water samples were collected in Hole 838A; three of them were sampled in the uppermost 32 mbsf of clayey nannofossil ooze and the fourth was collected from an interbedded clayey nannofossil ooze layer within the volcanic tuffides. In Hole 838A, interstitial water chloride, sodium, sulfate, and strontium concentrations are indistinguishable from the calculations of average seawater (Fig. 5).

Values of dissolved ammonia and phosphate concentrations in Hole 838A interstitial waters are comparable with those obtained in samples from the other Leg 135 sites drilled in the Lau Basin and are consistent with the sulfate data (Fig. 5).

The concentration-depth profiles of dissolved calcium and magnesium show slight deviations from average seawater compositions with increasing depth (Fig. 5). From the mud line to 67 mbsf, these deviations include a relative depletion in magnesium concentration of about −4.4 mM and a relative increase in calcium concentration of about +4.5 mM. These variations are greater than the analytical error, and linearly correlated concentration changes occur in calcium and magnesium. These changes follow the relationship ΔCa/ΔMg = −0.94 ± 0.09 (the Δ concentration used is Δ = interstitial water concentration - standard sea water concentration). A linear ΔCa vs. ΔMg correlation implies conservative behavior for these elements, at least over the thickness of the sedimentary column studied (Melfi et al., 1981). The observed changes of calcium and magnesium in the interstitial waters might be the result of exchange by diffusion with the underlying and alternating Layer 2 of the oceanic crust, as suggested for many other DSDP/ODP sites (Gieskes et al., 1975; Kastner and Gieskes, 1976; McDuff and Gieskes, 1976; Gieskes and Lawrence, 1981). The absence of a sulfate concentration gradient suggests that the slight increase in alkalinity with depth is independent of the bacterially mediated sulfate reduction (Fig. 5). Downhole temperatures between 30 and 70 mbsf (ranging from 2.5° to 6°C) are probably too low to consider the volcanic turbidites as a source for calcium and as the sink for magnesium. However, volcaniclastic sediments poorly recovered below 98 mbsf suggest that vitric silts and gravel may dominate the sequence at least at the base of the core section (260 mbsf). In this case, diagenetic processes involving the alteration of volcanic materials of this sedimentary sequence could contribute to calcium release and magnesium uptake.

The nature of the dissolved potassium profile (Fig. 5) implies an almost linear ΔCa/ΔK relationship and is probably also related to the alteration of volcanic material of the upper oceanic crust and of the base of the sedimentary column.

Dissolved silica concentrations increase gradually with depth to reach a maximum value of about 610 µM at 28.7 mbsf (Fig. 5). The increase in silica with depth, therefore, could be related to the occurrence of thick vitric sand and gravel layers characteristic for this hole. Below this depth, silica concentration remains constant, although volcanic material is the major component in the sedimentary column. This can be explained by dilution of the silica concentration toward the bottom of the hole.

The concentrations of copper, barium, and vanadium measured in this hole are comparable with those determined for the holes described previously.

The manganese concentration-depth profile for Hole 838A (Fig. 5) shows an increase with depth. The manganese maximum (about 55 µM) was reached at 19 mbsf in the upper nannofossil ooze unit and, as mentioned for the previously studied holes, suggests a release of manganese during diagenetic processes. Below this depth, a slight decrease is observed in the vicinity of the volcanic turbidite unit. Manganese concentrations decrease to low values near the boundary between hemipelagic sediments and basalts and within volcaniclastic sediments. This general pattern was also observed in Holes 834A through 836A.

Site 839

The sedimentary sequence ranges in age from the middle Pleistocene to the late Pliocene. It was divided into two lithologic units.

Unit I, from 0 to 17.85 mbsf, is of middle Pleistocene age. An average sedimentation rate of 9 mm/k.y. can be calculated. It is composed of iron-oxyhydroxide-stained, clayey nannofossil ooze containing rare volcaniclastic ash layers.

Unit II, from 17.85 to 256.7 mbsf, is of middle Pleistocene to late Pliocene age. An average sedimentation rate of 51 mms/k.y. has been calculated. In comparison with Unit I, Unit II shows much higher contents in volcaniclastic material.

From 99.5 to 214 mbsf, volcanic indurated sediments were poorly recovered, and 10 m of intralava sediments were recovered between 256.7 and 266.7 mbsf in Hole 839B.
Table 1. Chemical composition of interstitial waters at Site 837.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>[µM]</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH₄</td>
<td>0-20</td>
</tr>
<tr>
<td>PO₄</td>
<td>0-1</td>
</tr>
<tr>
<td>Cu</td>
<td>0-1</td>
</tr>
<tr>
<td>Si</td>
<td>0-20</td>
</tr>
<tr>
<td>Ba</td>
<td>0-1</td>
</tr>
<tr>
<td>V</td>
<td>0-1</td>
</tr>
<tr>
<td>Sr</td>
<td>0-1</td>
</tr>
<tr>
<td>Mn</td>
<td>0-1</td>
</tr>
<tr>
<td>pH</td>
<td>6-8</td>
</tr>
<tr>
<td>Alk. (mM)</td>
<td>2-3</td>
</tr>
<tr>
<td>Na (mM)</td>
<td>460-580</td>
</tr>
<tr>
<td>Cl (mM)</td>
<td>500-540</td>
</tr>
<tr>
<td>Ca (mM)</td>
<td>2,0-2,5</td>
</tr>
<tr>
<td>Mg (mM)</td>
<td>2,5-3,5</td>
</tr>
</tbody>
</table>

Figure 4. Lithologic summary column and interstitial water chemistry, Site 837.
Figure 5. Lithologic summary column and interstitial water chemistry, Site 838.
A total of seven interstitial water samples were collected. Samples were taken from every core in the uppermost 31 mbsf. Below this depth, samples were taken every second core.

Chloride, sodium, calcium, magnesium, potassium, sulfate, and strontium concentrations are indistinguishable from average seawater concentrations (Fig. 6) and are comparable with those obtained in Holes 834A through 837A.

As for the other Leg 135 sites, values of ammonia and phosphate concentrations in interstitial water samples from Hole 839A are very low and consistent with the fairly uniform sulfate data.

Silica, strontium, barium, and vanadium concentrations are characterized by nearly uniform values from the mud line to the bottom of the sedimentary column.

The manganese concentration-depth profile is comparable with those obtained at Sites 834, 835, 837, and 838. Manganese concentrations increase with depth, reaching a maximum of 88 µM at 48.5 mbsf. Below this manganese maximum, the concentrations decrease to value of 21 µM at the base of Unit II. The copper concentration-depth profile at Site 839 shows the same trend as the manganese profile, with a copper maximum of 3.12 µM at 48.5 mbsf followed by a decrease in copper concentration below this depth.

**DISCUSSION**

At all sites, the main features revealed by the interstitial water chemistry data are the extremely low gradients in the concentration-depth profiles of the major chemical components (sodium, calcium, magnesium, potassium, chloride, and sulfate). This feature suggests that diagenesis has a negligible effect upon interstitial water composition in the Lau Basin. At numerous DSDP and ODIP sites, alteration of the upper crustal basalts and of volcanogenic sediments into clays and zeolites leads to a depletion in dissolved magnesium, potassium, sodium, sulfate, and alkalinity and an enrichment in calcium (Kastner and Gieskes, 1976; Mcduff, 1981; Gieskes et al., 1990). However, the occurrence of zeolites (phillipsite, analcime) and Fe-Mn-rich clays in the sedimentary column at Sites 834–839 probably reflect alteration of the volcanogenic material in the sediment of the Lau Basin (Blanc, 1992, this volume). Diagenetic processes cannot, therefore, be ruled out. We postulate that the low concentration gradients recorded by the major components suggest an open system for local seawater circulation throughout the sedimentary column. This hypothesis is supported by the relatively uniform patterns of the concentration-depth profiles throughout the column, which range between 0.7º and 8.7ºC/100 m (Parson, Hawkins, Allan, 1992).

The calculated heat-flow values, ranging between 9.3 and 50.6 mW/m², are much lower than the theoretical heat-flow values of 175–200 mW/m² predicted for young oceanic crust (Anderson et al., 1977). The chemical and thermal gradients suggest that fluid flow exchanges between sediment and seawater occur locally, and that fluid circulation in the backarc is sufficient to dissipate large amounts of heat. Similar chemical results were obtained on the flanks of the Galapagos Spreading Center in a low heat-flow area (Maris et al., 1984; Becker and Von Herzen, 1983; Baker et al., 1991). Considering the small changes in Ca-C and Sr/Sr isotopic values, the alteration of the volcanogenic material in the sediment or underlying basalts, the concentration of calcium as a function of depth for the upper crustal basalts and of volcanogenic sediments into clays and zeolites leads to a depletion in dissolved magnesium, potassium, sodium, sulfate, and alkalinity and an enrichment in calcium (Kastner and Gieskes, 1976; Mcduff, 1981; Gieskes et al., 1990). However, the occurrence of zeolites (phillipsite, analcime) and Fe-Mn-rich clays in the sedimentary column at Sites 834–839 probably reflect alteration of the volcanogenic material in the sediment of the Lau Basin (Blanc, 1992, this volume). Diagenetic processes cannot, therefore, be ruled out. We postulate that the low concentration gradients recorded by the major components suggest an open system for local seawater circulation throughout the sedimentary column. This hypothesis is supported by the relatively uniform patterns of the concentration-depth profiles throughout the column, which range between 0.7º and 8.7ºC/100 m (Parson, Hawkins, Allan, 1992).

The calculated heat-flow values, ranging between 9.3 and 50.6 mW/m², are much lower than the theoretical heat-flow values of 175–200 mW/m² predicted for young oceanic crust (Anderson et al., 1977). The chemical and thermal gradients suggest that fluid flow exchanges between sediment and seawater occur locally, and that fluid circulation in the backarc is sufficient to dissipate large amounts of heat. Similar chemical results were obtained on the flanks of the Galapagos Spreading Center in a low heat-flow area (Maris et al., 1984; Becker and Von Herzen, 1983; Baker et al., 1991). Considering the small changes in Ca-C and Sr/Sr isotopic values, the alteration of the volcanogenic material in the sediment or underlying basalts, the concentration of calcium as a function of depth for the entire data set of the Lau Basin sites reveals information about the fluid flow pathways (Fig. 7). These Ca profiles exhibit a systematic trend with a slight increase in calcium in the upper part of the sedimentary column. Toward the bottom of the sedimentary cover, a decrease in the interstitial water calcium concentration was observed at Sites 834, 835, 837, and 839.

At Site 838, below 30 mbsf, the Ca concentration gradient is lower than observed above. Note that the maximum increase in calcium concentration is recorded in Hole 838A, which also yields the highest temperature gradient. Furthermore, small but significant magnesium and potassium anomalies are linearly correlated to the calcium anomalies in this hole, indicating the conservative behavior of these elements in the sedimentary column. We postulate that these features can be related to two major processes that probably varied in intensity, space, and time: (1) alteration of the volcanogenic material involving diffusive transport between basement rock and overlying seawater and (2) advection of seawater at the boundary between hemipelagic sediments and basaltic basement (Sites 834–837) or indurated volcanoclastic sediments (Sites 838 and 839). In-situ reactions of volcanoclastic sediments into clays and zeolites have probably worked in the past, but they did not affect the present major element concentration-depth profiles.

Trace metals such as manganese and copper are more useful than major elements for discriminating advection effects and diffusion processes caused by the interstitial water-sediment exchanges. This is clearly shown in the general diagram of Figure 8, in which manganese concentrations are plotted vs. depth. At all sites, manganese increases with depth and manganese maxima occur within the hemipelagic sediments. At Sites 834, 835, 838, and 839, interstitial water manganese gradients decrease below these maxima, with manganese concentrations reaching the lowest values toward the bottom of the holes, where hemipelagic sediments are characterized by high portions of volcanogenic sediments. We postulate that the variation in the manganese concentration data probably results from seawater-sediment interactions causing a manganese increase with depth in the past as well as from a dilution effect that caused an interstitial water manganese decrease more recently in the lower part of the sedimentary cover. However, at Site 837, the deepest sample analyzed shows the highest manganese concentration in this hole. This could be related either to a higher manganese release by diagenetic processes or to a diluting downwelling flow located in the deeper horizon of the hemipelagical sedimentary column. All the copper concentration-depth profiles also show a slight copper decrease in the deeper part of the holes (Fig. 8) and, therefore, support the assumption of a diluting downwelling flow toward the bottom of the sedimentary column. Conversely to the manganese profiles, the high copper concentrations determined at the top of Holes 834A, 836A, 837A, 838A, and 839A suggest that diagenetic processes removed copper from the solid phases. However, the copper concentration of 1.92 µM detected at 60 mbsf in Hole 835A seems to indicate a small exchange with seawater in the upper part of this hole.

The relative uniform patterns of the concentration-depth profiles suggest that molecular diffusion through the sedimentary column is probably responsible for the mixing between the two end-members. They are the interstitial water initially affected by the diagenetic processes and the diluting downwelling flow of seawater. The seawater probably circulates through structural pathways bounding the elongated sub-basins of the Lau Basin, and its initial chemical composition is probably slightly modified during its downward advection.

Advection of seawater at the hemipelagic sediment/volcanogenic basement boundary is also supported by the strontium concentration data and the preliminary results of strontium isotope measurements on interstitial waters (Fig. 9). The strontium concentration-depth profiles at Sites 834 and 835 show patterns similar to those of the manganese data sets. The relation among the interstitial water strontium concentrations, 87Sr/86Sr isotopic composition values, and depth (at Site 835) suggests that volcanicogenic strontium is released during alteration that lower the strontium isotope ratios. In the sedimentary column at Site 835, carbonate content ranges from 50% to 70%, and predominantly originated from biogenic tests having a radiogenic strontium signature close to that of contemporaneous seawater. Thus, the dissolution-recrystallization processes of biogenic tests may explain the increase in interstitial water strontium concentrations and, probably, helped limit the lowering of the strontium isotopic signature of the interstitial water from that of the ancient seawater. Therefore, the slight deviation of the strontium isotope ratios from contemporaneous seawater values more probably reflects volcanic material alteration in this hole.

However, diagenetic processes cannot explain the 87Sr/86Sr ratio determined at 148.5 mbsf, which is comparable with the present 87Sr/86Sr seawater ratio, and higher than that of Pliocene seawater.
Figure 6. Lithologic summary column and interstitial water chemistry, Site 839.
HYDROGEOCHEMISTRY IN LAU BACKARC BASIN

Figure 7. Geochemical profiles for dissolved calcium at the Lau Basin Leg 135 sites.

Figure 8. Generalized composite of copper and manganese concentration-depth profiles from Sites 834-839.

Figure 9. $^{87}\text{Sr}/^{86}\text{Sr}$ of dissolved strontium of Site 835. Shaded zone represents contemporaneous seawater range. Generalized composite of strontium concentration-depth profiles from Sites 834-839.

CONCLUSION

Studies of the chemical composition of interstitial waters from sediments recovered at the drilling sites cored during Leg 135 in the backarc Lau basin revealed two major features explaining the concentration-depth profiles of the constituents: (1) a very low gradient of the major chemical constituents in the sedimentary columns, and (2) a systematic decrease in calcium, strontium, manganese, and copper concentrations toward the bottom of the sedimentary covers. These features suggest that the sedimentary system is probably recharged by a downwelling flow of young seawater along the major structural pathways bounding the elongated sub-basins of the Lau basin. This recent seawater input at the sediment/basalt boundaries affected the diagenetic chemical signature of the pore water, first by dilution at the base of the sedimentary column, and second by...
ACKNOWLEDGMENTS

G.B. would like to thank J. Samuel and R. Rouault (Centre de Géochimie de la Surface, C.G.S.) for their analytical determinations of major and trace chemical composition. G.B. would like to thank Giona Baker on early drafts. This research was supported by INSU Grant GEO 91 3922, “Geosciences marines” (GB).

REFERENCES


