42. GEOCHEMISTRY OF ROCKS ABOVE TRACHYTE BASEMENT AT DEEP SEA DRILLING PROJECT SITE 465, SOUTHERN HESS RISE¹

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ABSTRACT

Samples of laminated limestone above trachyte basement in Deep Sea Drilling Project Hole 465A were analyzed for 27 major, minor, and trace elements, to test for contributions of metals from hydrothermal sources. These samples are slighty enriched in several elements, especially Mo, Ni, V, and Zn. However, the relatively high concentration of Al in these samples and the lack of significant enrichment in Fe, Mn, B, and Ba indicate that introduction of metals by hydrothermal solutions venting at the sea floor is unlikely.

INTRODUCTION

Sediments containing high concentrations of certain elements (particularly Fe, Mn, Ba, B, As, Cd, V, Cu, Ni, Co, Cr, and Zn) have been reported in association with active crustal-spreading centers such as the East Pacific Rise and adjacent Bauer Deep (e.g., Boström and Peterson, 1969; Boström et al., 1969; Boström, 1970; Dymond et al., 1973; Sayles and Bischoff, 1973; Sayles et al., 1975; Heath and Dymond, 1977; Spiess et al., 1980) and the Mid-Atlantic Ridge (Rona, 1976; Rona et al., 1976; Varentsov, 1978). The most spectacular examples of metal concentrations associated with an active spreading center are the massive polymetallic sulfide deposits on the East Pacific Rise at about 21° north latitude (Corliss et al., 1978; Natland et al., 1979; Hekinian et al., 1980). Studies of these sediments have shown that significant amounts of metals are contributed by hydrothermal solutions. Hydrothermal metal enrichment in sediments not associated with active spreading centers has also been reported from the western Philippine Basin (Bonatti et al., 1979) and Parece Vela Basin (Scott and Bolger, in press) of the Philippine Sea, and in the northeast-Pacific manganese-nodule area between the Clipperton and Clarion fracture zones (Bischoff and Rosenbauer, 1977).

Hess Rise, a large, mid-ocean plateau, possibly formed at a spreading center. If so, the basal rocks of the plateau should show evidence of the type of metal enrichment commonly found near active mid-ocean spreading centers.

METHODS

Eleven samples of laminated limestone (Lithologic Unit II; see Site 465 report, this volume) were collected over a distance of 2 meters immediately above trachyte basement in Core 40, Hole 465A, to test for contributions of metals from hydrothermal sources. A summary of lithologies in Core 40 and locations of samples are shown in Figure 1.

Samples were air-dried and ground in a ceramic mill to pass a 100-mesh (149- μ m) sieve. One split of each of the 11 samples was

analyzed in the analytical laboratories of the U. S. Geological Survey for 27 major, minor, and trace elements, by a combination of optical emission spectroscopy, X-ray fluorescence, and atomic-absorption spectrophotometry. Details of the analytical methods are described in the analytical sections of a report by Miesch (1976).

A second split of each sample was analyzed for Al, Fe, Mg, Mn, Cu, Co, and Ni by atomic-absorption spectrophotometry at Texas A&M University. Aliquots of 0.3 to 0.5 grams were weighed to the nearest 10 µg in teflon beakers and dissolved in concentrated reagentgrade HC1, HNO3, and HF. The samples were then dried, redissolved in concentrated HCl, and diluted to 100 ml final volume with distilled water (1% HC1 matrix). Additional samples of USGS standards JB-1 (basalt) and MAG-1 (marine mud) were digested concurrently for accuracy determinations. The analyses were performed with an air-acetylene flame for Mg, Fe, Mn, and Cu, a nitrous-oxide-acetylene flame for Al, and flameless atomic absorption for Co and Ni. Concentrations were determined by comparison with appropriate dilutions of standards, with a precision of better than $\pm 5\%$ for all elements. Comparison of experimental results with published values for JB-1 (Flanagan, 1973) and MAG-1 (Manheim et al., 1976) showed that recoveries were within $\pm 6\%$ of the published values for Mg, Fe, and Cu, and within $\pm 10\%$ of the published values for Co and Ni.

RESULTS

Results of analyses for 27 elements in 11 samples from Core 40, Hole 465A, are plotted versus sub-bottom depth in Figure 2. Mean concentrations of elements in laminated limestone of Lithologic Unit II are indicated by arrows on the plots in Figure 2 and are listed in Table 1. Plots of element concentrations above Core 40 and a list of element concentrations for samples from Core 40 and above are given in a report by Dean (this volume).

The top six samples from Core 40, to a depth of 410.63 meters sub-bottom, are laminated, olive-gray limestone typical of Lithologic Unit II (Fig. 1; see Site 465 report, this volume). A zone of obvious mineralization begins with the seventh sample (410.89 m sub-bottom), which is laminated limestone like the top six samples, but with large, euhedral calcite crystals. The eighth sample (411.01 m sub-bottom) is laminated volcanic ash. The ninth sample (411.32 m sub-bottom) is dolomite with barite and pyrite. The tenth and eleventh samples (411.56 and 411.65 m sub-bottom) are volcanic ash.

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Figure 1. Lithologic summary of Core 40, Hole 465A, from 409.5 to 412 meters sub-bottom, showing locations of samples discussed in this report.

Most of the elements charted in Figure 2 show one of two patterns of concentration versus depth. The first pattern, illustrated by Cr, Cu, Mo, Ni, Sc, Sr, V, and Zn, is a decrease in concentration in laminated limestone down to the mineralized zone (~410.6 m subbottom), with low concentrations in the three samples of volcanic ash (samples 8, 10, and 11). However, concentrations of these elements at the top of Core 40 are higher than average for the laminated limestone of Lithologic Unit II (indicated by arrows in Fig. 2), and decrease to values that are about average for Unit II. This pattern shows particularly well in plots or Ni, V, and Zn in Figure 2.

The second pattern, illustrated by Si, Al, Na, K, Ti, B, Be, Ga, La, Li, and Zr, is the result of higher concentrations of these elements in volcanic ash than in laminated limestone. Concentrations of these elements in the laminated limestone above the mineralized zone (top six samples) are more or less constant and about average for the laminated limestone; they then increase in the mineralized laminated limestone (sample 7) and volcanic ashes (samples 8, 10 and 11). The plots for Si, Al, B, and Li show this pattern particularly well.

The concentration of Mg shows a pattern similar to the second pattern, except that the lowest two laminated-limestone samples (samples 5 and 6) are enriched in Mg, with concentrations similar to those in the volcanic-ash layers. The concentration of Mn shows a pattern similar to that for Mg, except that the ash samples are not enriched, and enrichment of Mn in the laminated limestone occurs to a higher stratigraphic level (above 410 m sub-bottom).

Concentrations of Fe are only high in those samples that contain pyrite. The concentration of Ba is very high in the barite-bearing dolomite bed (411.32 m subbottom), and slightly elevated in the lower two ash layers. Concentrations of Pb are only slightly elevated in the lower two ash layers.

DISCUSSION

The element-concentration patterns shown in Figure 2 and discussed above indicate that laminated limestone is enriched in some elements relative to average laminated limestone of Lithologic Unit II, for as much as 2 meters above trachyte basement. This enrichment is particularly evident for Mo, Ni, V, and Zn, and to a lesser extent for Mg and Mn.

The laminated limestone is enriched in organic matter throughout Lithologic Unit II and contains up to 9% organic carbon (see Dean et al., this volume). Some trace-element enrichment may be due to concentration of these elements in organic matter, but if so we would expect high concentrations throughout Unit II, not the marked decrease above 410 meters sub-bottom. In fact, some elements concentrated in the bottom 1.5 meters of Unit II—especially Mo, Mn, Ni, and V—are suspected of being enriched by bioconcentration in most of the organic-carbon-rich limestone of Unit II (see Dean, this volume).

Sediments affected by hydrothermal solutions tend to be particularly enriched in Fe and Mn and depleted in Al and Ti (Boström and Peterson, 1969; Boström, 1970; Bischoff and Rosenbauer, 1977). Data on relative enrichment or depletion of various elements are usually based on carbonate-free concentrations. Our samples were not analyzed for CaCO₃, so we were unable to compute concentrations of elements on a carbonate-free basis, but this problem can be eliminated by using ratios or by expressing relative concentrations on a triangular diagram. The base of the laminated-limestone unit does not show the enrichment in Fe, Mn, B, or Ba that is characteristic of hydrothermal sediments and rocks (Boström et al., 1969; Heath and Dymond, 1977; Bischoff and Rosenbauer, 1977). Figure 2 shows ratios of several metals to aluminum, derived from the atomicabsorption data, in comparison with the same ratios for average Pacific pelagic clay. The upper part of the section studied in Hole 465A appears to be enriched in Ni and slightly enriched in Cu and Co relative to average Pacific pelagic clay. However, the diagnostic Fe and Mn enrichments are absent.

| Element | Observed Range | Arithmetic Mean | Standard Deviation |
|----------|-------------------|--------------------|-----------------------|
| Si (%) | 0.47-6.5 | 2.6 | 1.7 |
| Al | 0.21-2.1 | 0.83 | 0.59 |
| Fe | 0.046-1.6 | 0.34 | 0.34 |
| Mg | 0.24-1.9 | 0.50 | 0.40 |
| Na | 0.001-0.42 | 0.15 | 0.14 |
| K | < 0.017-0.78 | 0.15 | 0.20 |
| Ti | < 0.013-0.16 | 0.033 | 0.038 |
| Ba (ppm) | 8-230 | 56 | 58 |
| Co | < 0.7-1.9 | 1.0 | 0.38 |
| Cr | 3.6-62 | 18 | 15 |
| Cu | 1.6-34 | 9.2 | 9.1 |
| La | <7.0-92 | 25 | 25 |
| Li | <7.0-20 | 8.9 | 3.4 |
| Mn | 22-3700 | 700 | 1100 |
| Mo | <1.5-80 | 24 | 19 |
| Ni | 4.5-120 | 36 | 34 |
| Sc | < 0.70-6.7 | 4.5 | 1.9 |
| Sr | 190-2300 | 1300 | 600 |
| v | 55-1000 | 430 | 310 |
| Y | 1.0-55 | 17 | 13 |
| Yb | 0.30-8.0 | 3.0 | 2.0 |
| Zr | 11-370 | 110 | 110 |

Table 1. Summary statistics for total element concentrations in 24 samples of laminated limestone from Lithologic Unit II, Hole 465A.

Figures 3 and 4 compare the chemistry of rocks above basement in Hole 465A with the chemistry of sediments from both hydrothermal and normal pelagic areas. The laminated limestone and volcanic ash samples from Hole 465A are more enriched in Al relative to Fe and Mn than metalliferous sediments from either the Bauer Deep or the East Pacific Rise, and more enriched in Al



Figure 3. Triangular diagram showing relative concentrations of Al, Fe, and Mn in samples taken above trachyte basement at Site 465. Numbers correspond to sample numbers in Figure 1. Areas representing ranges of concentrations of Al, Fe, and Mn in sediments from the Bauer Deep, East Pacific Rise, and Pacific pelagic sediments are from Bischoff and Rosenbauer (1977).



Figure 4. Plot of the ratios Fe/Ti and Al/(Al + Fe + Mn) for samples taken above trachyte basement at Site 465. Numbers correspond to sample numbers in Figure 1. Curves show mixing of average oceanic basalt (B) and average continental crust (C) with metalliferous sediment from the East Pacific Rise (EPR). Modified from Boström (1970).

than even Pacific pelagic sediments (Fig. 3). Samples 8 and 9 are enriched in Fe by the presence of pyrite, which causes them to appear to have a composition similar to Fe-rich metalliferous sediments enriched in oxides and hydroxides.

The curves in Figure 4 were constructed by Boström (1970) to illustrate mixing of metalliferous sediments from the East Pacific Rise (EPR) with either average oceanic basalt (B) or average continental crust (C). Boström and Peterson (1969) indicated that a value of less than 0.4 for the ratio Al/(Al + Fe + Mn) is indicative of metal enrichment in sediments. Figure 4 shows further that limestone and ash samples from Hole 465A are Al-rich and Fe-poor in contrast to Al-poor, Fe-rich sediments affected by hydrothermal solutions.

Figure 2 shows that the laminated limestone above trachyte basement at Site 465 is enriched in several elements, particularly Mo, Ni, V, and Zn. However, lack of significant enrichment in Fe, Mn, B, and Ba, and the Al-rich, Fe-poor, characteristics shown in Figures 3 and 4, indicate that introduction of metals by hydrothermal solutions venting at the sea floor is unlikely. A comparison with sediments altered by hydrothermal solutions percolating through the sediment column (Corliss



Figure 2. Plots of element concentrations and ratios of Fe, Mn, Cu, Co, and Ni to Al in samples from Core 40, Hole 465A. Element concentrations are in percent or parts per million (ppm), dry weight. Analyses were by X-ray fluorescence (XRF), optical emission spectroscopy (s or no designation), or atomic-absorption spectroscopy (AAS). Results of analyses for Al, Fe, Mg, Mn, and Cu by atomic absorption spectrophotometry at Texas A&M University are indicated by triangles. The arrow at the top of each concentration plot indicates the average concentration of each element in 24 samples of laminated limestone (Lithologic Unit II) listed in Table 1. The arrow at the top of each ratio plot is the ratio in average Pacific pelagic clay (APPC).

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et al., 1978; Scott et al., 1979; Natland, et al., 1979) also shows that the concentrations of metals in rocks above basement in Hole 465A are not high enough to suggest hydrothermal enrichment.

O'Neil and Vallier (this volume) have examined oxygen and sulfur isotopes in calcite, barite, and pyrite from the mineralized zone above trachyte basement in Core 40, Hole 465A. They concluded that the minerals formed in water at about 35°C. Although 35°C is low compared to vent temperatures of 380°C determined on the East Pacific Rise (Spiess et al., 1980), it is higher than normal sea-floor (2 to 4 °C) or sea-surface temperatures. The formation of pyrite, barite, dolomite, and calcite indicates that there has been some redistribution of materials in the rocks above basement in Hole 465A, but the chemical data discussed in this paper suggest that no typical hydrothermal activity has taken place. However, the evidence for some remobilization of trace metals and a temperature of 35°C (O'Neil and Vallier, this volume) suggest the possibility of localized warming of pore fluids that subsequently resulted in the altered chemistry of the laminated limestone immediately above basement. The system apparently was not related to massive circulation of sea water through the crust that has been found in active spreading centers.

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