22. LOW-TEMPERATURE HYDROTHERMAL ALTERATION OF JURASSIC OCEAN CRUST, SITE 801

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ABSTRACT

Low-temperature hydrothermal alteration of basement from Site 801 was studied through analyses of the mineralogy, chemistry, and oxygen isotopic compositions of the rocks. The more than 100-m section of 170-Ma basement consists of 60 m of tholeiitic basalt separated from the overlying 60 m of alkalic basalts by a >3-m-thick Fe-Si hydrothermal deposit. Four alteration types were distinguished in the basalts: (1) saponite-type (Mg-smectite) rocks are generally slightly altered, exhibiting small increases in H2O, 18O, and oxidation; (2) celadonite-type rocks are also slightly altered, but exhibit uptake of alkalies in addition to hydration and oxidation, reflecting somewhat greater seawater/rock ratios than the saponite type; (3) Al-saponite-type alteration resulted in oxidation, hydration, and alkali and 18O uptake and losses of Ca and Na due to the breakdown of plagioclase and clinopyroxene; and (4) blue-green rocks exhibit the greatest chemical changes, including oxidation, hydration, alkali uptake, and loss of Ca, Na, and Mg due to the complete breakdown of plagioclase and olivine to K-feldspar and phyllosilicates.

Saponite- and celadonite-type alteration of the tholeiite section occurred at a normal mid-ocean ridge basalt spreading center at temperatures <20°C. Near- or off-axis intrusion of an alkali basalt magma at depth reinitiated hydrothermal circulation, and the Fe-Si hydrothermal deposit formed from cool (<60°C) distal hydrothermal fluids. Focusing of fluid flow in the rocks immediately underlying the deposit resulted in the extensive alteration of the blue-green rocks at similar temperatures. Al-saponite alteration of the subsequent alkali basalts overlying the deposit occurred at relatively high water/rock ratios as part of the same low-temperature circulation system that formed the hydrothermal deposit. Abundant calcite formed in the rocks during progressive "aging" of the crust during its long history away from the spreading center.

INTRODUCTION

Drilling at Site 801 on Leg 129 of the Ocean Drilling Program (ODP) penetrated more than 100 m into Jurassic oceanic basement in the western Pacific. This is the oldest in-situ oceanic basement ever drilled and presents an excellent opportunity to study processes associated with the formation and evolution of ancient ocean crust. The cores contain a section of tholeiitic basalts separated from overlying alkali basalts by a >3-m-thick siliceous iron-oxyhydroxide hydrothermal deposit.

This paper presents the results of a study of the alteration of basement rocks recovered from Site 801. Data on the secondary mineralogy, whole-rock chemical compositions, and oxygen and carbon isotope ratios are presented in order to constrain the alteration conditions and processes and to evaluate chemical and isotopic exchange between seawater and the crust. One of the questions of interest is whether such old crust has undergone progressive "aging," exhibiting mineralogical and chemical changes related to its long history of seafloor spreading, and whether it is more altered than much younger crust closer to the spreading center.

Site 801

Site 801 is located in the central Pigafetta Basin in the western Pacific, at a water depth of 5673.8 m (Fig. 1). The oldest sediment at the base of the 461.6-m sedimentary section is Callovian-Bathonian in age, giving an age of about 165 Ma for underlying basement (see also Pringle, this volume). Holes 801A and 801B penetrated the sediment section, and Hole 801B extended 48.9 m into basement with 31% recovery. In Hole 801C, located only 20 m from Hole 801B, we penetrated 100.6 m into basement with 60.2% recovery. Basement in both holes consists of pillow basalts, thin flows, and a few thin intrusive units, plus a siliceous hydrothermal deposit in Hole 801C, and is described in detail elsewhere (Lancelot, Larson, et al., 1990). An intrusive unit and its host rock that occurs at approximately the same depth below seafloor in both holes allowed correlation between the closely spaced holes (Lancelot, Larson, et al., 1990). The basement section thus totals 132.7 m, with 16.8 m of overlap between the two cores. On the basis of major and trace element geochemistry, the basement can be divided into two sections separated by the hydrothermal deposit at 525 meters below seafloor (mbsf) in Hole 801C (Fig. 2). The lower section is tholeiitic normal mid-ocean ridge basalt (N-MORB) formed at an active Jurassic spreading center, whereas the upper section consists of alkalic ocean-island-type basalts formed during subsequent near- or off-axis volcanism (Floyd and Castillo, this volume). Both primitive and evolved suites occur within each basement section (Floyd and Castillo, this volume).

METHODS

Secondary minerals were identified by optical examination of polished thin sections and with compositional data from electron microprobe analyses. The latter were performed with an automated Cameca CAMEBAX instrument at the University of Michigan, using 12-kV accelerating voltage, 10-nA current, and rastering the beam over a square area, 6 μm on a side. Analytical techniques and results for whole-rock chemical analyses are given in the "Summary of Geochemical Data" chapter (Castillo et al., this volume). Oxygen and carbon isotopic extractions and analyses were performed at the CRPG in Vandoeuvre, France. Oxygen was extracted from splits of whole-rock powders for oxygen isotopic analysis using the BrF5 method of Clayton and Mayeda (1963). CO2 was extracted from carbonates in whole rocks and from veins for isotopic analysis by dissolution in phosphoric acid at 25°C for 7 days. Yields for whole-rock extractions

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are somewhat lower than total CO$_2$ because of the presence of siderite. One sample was extracted at 150°C in order to dissolve siderite. Results are reported as standard δ notation relative to Pee-Dee belemnite (PDB) and standard mean ocean water (SMOW) (Craig, 1961).

RESULTS
Alteration Types and Distribution

Four different alteration types have been recognized in Site 801 samples on the basis of their secondary mineral assemblages. Three of these types are based on the dominant clay mineral present (saponite, celadonite, or Al-saponite), and the fourth by the blue-green color of the rocks, characteristic mineral assemblage (montmorillonite-beidellite, glauconite, celadonite, and K-feldspar), and restricted distribution in the core. These alteration types are described in the following sections, along with their distribution in the cores.

Saponite-Type Alteration

The most abundant alteration type is characterized by the presence of saponite (triocahedral Mg-smectite) and pyrite (Fig. 3A). The saponite in Site 801 rocks is Fe-bearing, with Fe/Fe + Mg = 0.2–0.6 (Fig. 4 and Table 1). Al contents are low, ≤0.5 atoms per formula O$_{10}$(OH)$_{2}$, and Ca is the dominant interlayer cation.

These rocks are generally dark gray in color, but range to lighter gray and slightly brownish, and occur throughout most of the tholeiitic section below the hydrothermal deposit (from 534 to 591 mbsf, the bottom of the core). The rocks are mostly 10%–20% altered, but
range up to 40% altered. Olivine is totally replaced by saponite, calcite, and small amounts of pyrite. Plagioclase and clinopyroxene are generally unaltered, but both are locally slightly (5%) replaced by saponite. Igneous titanomagnetite is only slightly altered, exhibiting shrinkage cracks due to oxidation (Petersen et al., 1979). Pyrite is commonly disseminated in the rocks, replacing silicates and igneous sulfide globules, and interstitial to silicates. Vesicles and pore space are filled with saponite, calcite, and pyrite, generally with calcite formed as the last phase at the center of the vugs. In more extensively altered samples, fine-grained interstitial material is also apparently replaced by saponite.

The alkali basalts from the upper portion of the hole that were affected by saponite alteration are more extensively altered than the tholeiites (30%-80% vs. about 10%-20%, respectively). Plagioclase and clinopyroxene are generally unaltered in the tholeiites, whereas they are respectively 10%-30% and 20%-90% replaced by saponite and calcite in the alkalic basalts.

Veins in rocks containing the saponite assemblage consist most commonly of saponite ± pyrite ± calcite and range from tens of micrometers to about 1 mm wide. In some samples pyrite partly replaces marcasite in these veins. Several stages of calcite precipitation have occurred in many cases, with the multiple reopening and filling of fractures until originally 1-mm-wide veins are now 1-1.5 cm wide. Fibrous chalcedony fills the center of many of these veins, in some cases with quartz and late-stage calcite.

Celadonite-Type Alteration

In several saponite-assemblage samples, celadonite, and Fe-oxyhydroxide line the walls of veins containing the minerals described previously. Fe-oxyhydroxides also occur with later calcite and chalcedony in some of these veins (Fig. 5A). In some cases celadonite and Fe-oxyhydroxide replace the wallrock of the vein for up to a few hundred micrometers and, along with saponite, generally replace

Figure 2. Lithostratigraphy and chemical compositions of basalts vs. depth for Site 801 basement. E = evolved compositions, P = primitive compositions (after Floyd, this volume).
Al-Saponite-Type Alteration

A third alteration type occurs in the alkali basalts, but only in those from Hole 801C. The rocks are dark brownish gray to light brown in color (Fig. 3B). These rocks are 50%-100% altered, and are characterized by the presence of Al-saponite. Al-saponite is distinguished optically from saponite by its paler color and chemically by its high Al₂O₃ content (11-14 wt% vs. <8 wt%; Fig. 4 and Table 1). The Al-saponites are generally trioctahedral, with octahedral cations totaling about three atoms and with approximately one Al atom in tetrahedral positions per formula O(CH₂OH)₂. Some analyses range to lower octahedral cation totals of 2.3-2.5, however, indicating a partly dioctahedral structure. Calculated formulas have low tetrahedral Al (0.1-0.2 atoms per formula O(CH₂OH)₂), suggesting the presence of saponite mixed with or transitional to montmorillonite.

Olivine is completely replaced by Al-saponite, or by saponite in the less-altered rocks. Plagioclase is generally 20%-30% altered, but is up to 100% altered in some samples, mainly to Al-saponite (Fig. 5B). Natrolite and calcite also replace plagioclase in lesser amounts in some samples. Clinopyroxene ranges from unaltered in the least altered samples to nearly 100% altered. The fine-grained, fibrous pyroxene is cloudy and is replaced by clay minerals and calcite, but the very fine grain size of both pyroxene and secondary phases makes identification difficult. Pore space in the rocks is filled with Al-saponite and calcite. Veins in the rocks consist of Al-saponite ± calcite ± Fe-oxyhydroxide ± pyrite. Clay mineral veins are generally 100 to 500 µm wide, but multiple generations of calcite have resulted in veins up to 2 mm wide.

Blue-Green-Type Alteration

The fourth alteration type is characterized by the light blue-green color of the rocks (Fig. 3C) and is restricted to a single primitive tholeiitic cooling unit from 531 to 535 mbsf, immediately below the siliceous hydrothermal deposit. The rocks are highly altered, ranging from 80% recrystallized for a few samples in the interior of the unit to 100% for the remainder (Busch et al., this volume). The rocks are also highly fractured, forming a net-vein breccia at about 532.5 mbsf. Phyllosilicates include Al-smectite (montmorillonite-beidellite), glauconite, and celadonite. Glauconite is distinguished optically from celadonite in these rocks. Al-smectites are dioctahedral and Al rich, containing 22-35 wt% Al₂O₃ (Fig. 4 and Table 1). The Al-smectites are dioctahedral and Al rich, containing 22-35 wt% Al₂O₃ (Fig. 4 and Table 1). The layer charge is distributed subequally between octahedral and tetrahedral layers, indicating a structure intermediate between montmorillonite and beidellite.

Olivine is 100% replaced by Al-smectite, glauconite, and calcite. Plagioclase is slightly altered to nearly totally replaced by Al-smectite, glauconite, K-feldspar, natrolite, and lesser calcite (Fig. 5C). Fine-grained fibrous groundmass clinopyroxene is slightly to extensively altered, appearing cloudy due to replacement by clays and calcite. Titanomagnetite is completely replaced by granular sphere. Pore space in the rocks is filled with Al-smectite, glauconite, and calcite. The Fe-oxyhydroxides impart a slight brownish color to the rocks. The celadonites are K- and Fe-rich, containing 5.0 to 9.7 wt% K₂O and having Fe/Fe + Mg ratios of 0.5 to 0.8 (Fig. 4 and Table 1). The lower K₂O contents of a few samples suggest that smectite may be present in these cases. Microprobe analyses and structural formulas indicate low Al contents (<0.5 atoms per O(CH₂OH)₂), with no Al in tetrahedral positions. These samples not only differ in containing celadonite and Fe-oxyhydroxides rather than pyrite, but also have characteristic chemical changes distinct from the saponite-bearing rocks, and are thus considered as a second alteration type.
celadonite. Veins comprise 15%–25% of the recovered material, ranging from 0.1 to 7 mm wide. These are filled with clay minerals and calcite, with the general sequence (1) glauconite + Fe-oxyhydroxide, (2) ± Al-smectite, (3) ± calcite, (4) chalcedony ± quartz, and (5) ± late calcite. Celadonite ± Fe-oxyhydroxide veins are also present.

The rocks immediately above and below the hydrothermal deposit in Core 129-801C-4R are oxidized and stained by Fe-oxyhydroxides. The blue-green altered tholeiites just below the deposit range from yellow to red in color, with an abrupt boundary that changes to the blue-green color at 35 cm in Section 129-801C-5R-1. The Al-smectite-bearing alkali basalts above the deposit are stained brown by Fe-oxyhydroxides in the lowermost 10–15 cm of Core 129-801C-3R.

### Hydrothermal Deposit

The hydrothermal deposit comprises essentially all of Core 129-801C-4R. Approximately 3 m of material was recovered from the 9.5-m drilled interval (521.7–531.2 mbsf). At least some recrystallized sediment is present at the top of the deposit (e.g., Sample 129-801C-4R-1, 32–36 cm, consists of layered crystalline calcite with minor amounts of clay mineral [saponite]). The hydrothermal deposit consists of bright yellow-orange ochreous material with irregular banding, much of which is disrupted or broken and cemented by silica (Fig. 6A). In the thin section of Sample 129-801C-4R-1, 100–106 cm, the material is composed of 5- to 200-μm spherules and aggregates of orange to red Fe-oxyhydroxide. This material is silicified and cemented by granular, fine-grained (10–100 μm) quartz. The uniform granular texture of much of the quartz is similar to that formed by recrystallization of opal spherules in other siliceous seafloor hydrothermal deposits (Alt et al., 1987), suggesting a possibly similar origin for some of the quartz in the Hole 801C deposit. Multiple late-stage coarse quartz veins crosscut the deposit, and open vugs are lined with coarse quartz crystals.

Thread-like filaments of orange Fe-oxyhydroxide are locally present in the deposit. These filaments are mostly curved and branching, about 5 μm wide and 50–100 μm long (Fig. 6B, 6C). Double-twisted spiral filaments, up to 200 μm in length, also occur. The morphologies of these filaments are remarkably similar to those of some genera of Fe-oxidizing bacteria. In particular, the double spirals are identical to Gallionella (Buchanan and Gibbons, 1974). The Fe-oxide material in the hydrothermal deposit, including the filaments, is nearly identical to that in Fe-oxide deposits described from seamounts and mid-ocean ridges, and which are actively forming at temperatures of around 10°–15°C (Alt, 1988; Juniper and Fouquet, 1988). By analogy with such Fe deposits, the hydrothermal deposit in Hole 801C is interpreted as a low-temperature Fe-oxyhydroxide precipitate that was later silicified and cut by quartz veins.

### Whole-rock Chemical Changes

The whole-rock chemical analyses discussed in this paper are given in the “Summary of Geochemical Data” chapter (Castillo et al., this volume). Chemical changes in the rocks are discussed here in terms of the four alteration types and alkalic vs. tholeiitic basalt.

Because the main alteration phases in the tholeiites are hydrous (saponite and celadonite), H₂O content of the rocks can be used as an indicator of extent of alteration. Two different trends can be seen on a plot of K₂O vs. H₂O (Fig. 7). H₂O increases without a corresponding change in K₂O at low H₂O contents (<1 wt%), whereas both K₂O and H₂O increase at higher H₂O contents (>1 wt%). These two trends separate the two alteration types present in these rocks: K-poor saponite-bearing rocks are hydrated but not enriched in K, whereas K-rich celadonite-bearing rocks are both hydrated and enriched in K.

Like the K₂O-H₂O plot there is little or no change in MgO, CaO, Na₂O, or Fe₂O₃T at low H₂O contents in the tholeiites (<1 wt%, Fig. 7). At higher H₂O contents, however, slight decreases of these elements occur, most notably CaO but also MgO in the tholeiites. In contrast, there is a direct increase in Fe³⁺/Fe⁺ with H₂O content (Fig. 7). These chemical changes reflect hydration and slight oxidation with little corresponding other chemical changes during saponite-type alteration in the tholeiites. The only other change appears to be increased δ¹⁸O values (see “Oxygen and Carbon Isotopes” section, this chapter).

The increased K₂O and Rb and loss of Mg at higher H₂O contents reflect the formation of K-rich, Mg-poor (compared to saponite) celadonite in the rocks. Slight alteration of plagioclase probably contributes to the scatter in CaO and Na₂O contents at higher H₂O contents (Fig. 7). The samples with the highest CaO contents also have high CO₂ contents, indicating that secondary calcite contributes to the scatter in CaO. Increased K₂O in the tholeiites correlates with increased Fe³⁺/Fe⁺ (Fig. 8), indicating oxidation of Fe during celadonite and Fe-oxyhydroxide formation. Sulfur contents of both saponite and celadonite alteration types decrease with increased Fe³⁺/Fe⁺ due to
oxygenation of igneous sulfides (Fig. 8). Thus, excluding the blue-green altered tholeiites immediately below the hydrothermal deposit (from 531 to 535 mbsf), the tholeiites from the lower half of the hole exhibit clear trends toward increased K$_2$O, Rb, Fe$^{3+}$/Fe$^2+$, H$_2$O, and CO$_2$ due to alteration (Fig. 2). Local slight variations in Fe$_2$O$_3^7$, MnO, MgO, CaO, and Na$_2$O are also attributed to alteration.

The blue-green altered rocks below the hydrothermal deposit are the most extensively altered rocks in the tholeiite section. They exhibit chemical trends similar to those of the underlying rocks, but have gained greater amounts of K$_2$O, Rb, Fe$^{3+}$/Fe$^2+$, H$_2$O, and CO$_2$; many have clearly lost Fe$_2$O$_3^7$, MnO, MgO, CaO, and Na$_2$O (see primitive tholeiites in Table 2). This is especially evident for the high H$_2$O blue-green samples (all primitive tholeiites) in Figure 7. The blue-green rocks are also slightly enriched in Ba relative to unaltered rocks. These chemical trends are due to alteration (Fig. 2). Even though unaltered starting concentrations of K$_2$O, Rb, and H$_2$O at low H$_2$O contents. In particular, the primitive alkali basalt from 488 to 495 mbsf exhibit no K$_2$O or Rb gain, but have high H$_2$O contents, reflecting extensive alteration to K-poor saponite. These rocks are slightly oxidized (Fig. 7), but exhibit little or no other chemical changes due to alteration.

At higher H$_2$O contents, K$_2$O, Rb, and Fe$^{3+}$/Fe$^2+$ increase and CaO and Na$_2$O decrease due to celadonite- and Al-saponite-type alteration. The alkali basalt with the highest H$_2$O and K$_2$O contents are also the most oxidized (Figs. 7 and 8). These rocks have lost significant amounts of CaO and Na$_2$O due to the breakdown of plagioclase clinopyroxene during Al-saponite type alteration. The rocks affected by Al-saponite alteration are the most extensively altered alkali basalt and thus exhibit the greatest chemical changes.

A sample of interstitial material from 587.4 mbsf was also chemically analyzed (Table 2). This sample consists of volcanic glass replaced by saponite, celadonite, and calcite, and cemented by cloths of celadonite and saponite containing spherules of chalcedony, in turn, cemented by calcite and fibrous chalcedony. This material has very high CaO and CO$_2$ contents (23% and 19%, respectively), high MnO, K$_2$O, Rb, and H$_2$O contents, high Fe$^{3+}$/Fe$^2+$, and low Na$_2$O, Fe$_2$O$_3^7$, and MgO compared with the altered rocks (Fig. 2).

One sample of the hydrothermal deposit was chemically analyzed (Table 2). The material consists essentially of silica (86.5%) and iron (9.97% Fe$_2$O$_3$), with all iron ferric. It contains less than 0.2% MgO and Al$_2$O$_3$ and less than 0.1% TiO$_2$. CaO, Na$_2$O, K$_2$O, and P$_2$O$_5$. This sample is enriched in Ba compared with the underlying rocks (74 ppm vs. about 10-20 ppm), and is relatively depleted in transition metals (Cu, Ni, and Zn).

**Oxygen and Carbon Isotopes**

Whole-rock δ$^{18}$O values are given in Table 3. Three alkali basalt range from +11.2% to +18.9%, whereas the four tholeiites analyzed...
Figure 5. Thin-section photomicrographs of secondary minerals in Site 801 basement. A. Vein containing celadonite (gray, Ce) cemented by chalcedony (white, Ch) and calcite (white, Ca). Sample 129-801C-7R-3, 53–59 cm. B. Plagioclase phenocryst partly replaced by Al-saponite (dark gray, S) and natrolite (N). Al-saponite type alteration, Sample 129-801C-1R-6, 65–70 cm. C. Plagioclase phenocryst completely replaced by K-feldspar along fractures (white, Ks) and Al-smectite (sm). Sample 129-801C-5R-1, 93–98 cm.

Figure 6. Hydrothermal deposit from Hole 801C. Sample 129-801C-4R-1, 100–106 cm. A. Hand specimen showing disrupted structure (top is to the right). B. Photomicrograph showing spherules, aggregates, and filaments of Fe-oxyhydroxide (gray) surrounded by quartz (white). C. Close-up of filamentous material showing curved and branching structures.

have lower values of +6.5‰ to +8.0‰ (Fig. 9). All these samples are from the saponite, celadonite, or Al-saponite alteration types. The rocks are enriched in $^{18}$O relative to fresh basalts, which average +5.7‰ for MORB and +6.1‰ for ocean-island alkali basalt (Muehlenbachs and Clayton, 1972; Kyser, 1986). Such $^{18}$O enrichments are characteristic of seafloor basalts that have reacted with seawater at low temperatures (about 0°–50°C, Muehlenbachs and Clayton, 1972; Bohlke et al., 1984). The greater $^{18}$O enrichment of the alkali basalts compared to the tholeiites can be attributed in part to the slightly higher $^{18}$O value for unaltered alkali basalt compared with unaltered MORB, but this can only account for about 0.5‰ of the
difference. The generally greater extent of recrystallization of the alkali basalts compared with the tholeiites (30%-80% vs. 10%-20%, respectively) must account for the correspondingly greater $\delta^{18}$O values of the alkali basalts.

Muehlenbachs and Clayton (1972) suggested that seafloor basalts altered at low temperatures could be modeled as a mixing line between fresh basalt and smectite on a $\delta^{18}$O-$H_2O$ diagram. Bohlke et al. (1984) pointed out that variations in temperature and secondary mineral assemblage can complicate such a model, requiring slightly different mixing lines for different mineral assemblages and alteration temperatures. The analyses from Hole 801 are generally consistent with the smectite-basalt mixing model at temperatures of 0°-50°C.
LOW-TEMPERATURE HYDROTHERMAL ALTERATION

Fe³⁺/FeT

Figure 8. Iron oxidation plots. K₂O in weight percent, S in ppm. Symbols as in Figure 2; arrow indicates sample that plots off scale.

(Fig. 9), with the higher δ¹⁸O-H₂O alkali basalts more extensively altered to smectite, and perhaps altered at somewhat higher temperatures (up to about 50°C) than the tholeiites (0°–20°C). Slightly higher temperatures would have increased reaction rates and extent of alteration in the alkali basalts, resulting in the generally higher δ¹⁸O values of the alkali basalts. The duration of seawater circulation may also have been greater in the upper volcanic section, resulting in greater extent of low-temperature alteration and higher δ¹⁸O values of the alkali basalts (Muchenbachs, 1979). The highest δ¹⁸O alkali basalt occurs at the top of the core in proximity to overlying cold seawater (Fig. 10), and may have been altered at somewhat lower temperatures or for a longer duration than the other alkalic basalts. The sample also likely contains relatively low-H₂O, high-δ¹⁸O secondary phases, such as calcite or zeolites, that would make the sample fall above the smectite trend in Figure 9 (Bohlke et al., 1984).

Carbonates separated from whole rocks and veins have δ¹³C values of +2‰ to -8‰ (Table 3 and Fig. 11). The higher values (-2‰ to +2‰) are consistent with formation from normal seawater. The negative values occur mostly in the alkali basalts, where sediments are intercalated with the basalts, suggesting that a component of organic carbon from intercalated or overlying sediments was present in the carbonate-forming fluids. Closed-system evolution of fluid carbon isotopic compositions or contributions of mantle CO₂ can also contribute to such low δ¹³C values for carbonates in altered basalts (Lawrence, 1991), but given the proximity of the Site 801 veins to sediments, the organic carbon contribution appears most likely.

DISCUSSION

Any discussion of alteration of the crust at Site 801 must include some interpretation for the origin of the crustal section, with the alkali basalts overlying tholeiites. Floyd and Castillo (this volume) and Castillo et al. (this volume) interpreted the tholeiites as N-MORB that represent typical oceanic crust formed at a Jurassic mid-ocean ridge spreading center. The overlying alkali basalts have trace element compositions of ocean-island type basalts, and probably formed during subsequent near- or off-axis volcanism, similar to that occurring on young seamounts near the East Pacific Rise (Batiza and Vanko, 1984; Castillo et al., this volume). Dating of Site 801 rocks by the ⁴⁰Ar/³⁹Ar technique gives ages of about 165 Ma for the tholeiites and 158 Ma for the alkali basalts, suggesting a time span of approximately 7 m.y. between formation of the MORB tholeiite section and extrusion
of the alkali basalts (Pringle, this volume). The errors on these ages, particularly for the tholeiites, are sufficient that this time span may be much smaller, less than 2 m.y. (Pringle, this volume).

The saponite- and celadonite-type alteration in the tholeiite section of Hole 801C is similar to that observed in other altered MORB sections from Deep Sea Drilling Project (DSDP)/ODP cores (Andrews, 1977; Lawrence and Drever, 1981; Alt and Honnorez, 1984; Alt et al., 1986). Saponite-type alteration occurs at low seawater/rock ratios, causing hydration but little other chemical change. The common presence of pyrite indicates generally reducing conditions. The uptake of K and Rb and oxidation of Fe during celadonite-type alteration indicates higher seawater/rock ratios and oxidizing conditions. Temperatures for both alteration types in the tholeiite section were less than 50°C, and probably less than about 20°C as indicated by whole-rock and calcite oxygen isotopic data (Table 3; France-Lanord et al., this volume). Some constraints can be placed on the absolute timing of alteration of the tholeiites by analogy with other DSDP/ODP cores. Very young rocks (<1 Ma) contain only nontronite-celadonite in and around veins, whereas saponite is also present in slightly older rocks (2–3.5 Ma, Andrews, 1977; Laverne and Vivier, 1981). Although analytical errors and uncertainties in the true age of the crust are often significant, Rb/Sr dating of secondary vein minerals in various DSDP/ODP cores indicates that smectite and celadonite alteration are complete within about 10 m.y. (Hart and Staudigel, 1986). These observations suggest that the smectitic (saponite and celadonite) alteration of the MORB tholeiite section at Site 801 may have been complete prior to the extrusion of the overlying alkali basalt section, up to several million years later.

The hydrothermal deposit in Hole 801C probably formed by silicification of an Fe-oxide deposit, similar to those presently forming on seamounts and at mid-ocean ridges (Alt, 1988; Juniper and Fouquet, 1988). Edmond et al. (1979) presented a model for the formation of such Fe-rich deposits. In this model, interaction of seawater with oceanic crust near the top of a magma chamber at a mid-ocean ridge results in high temperature (about 350°C), acid hydrothermal fluids depleted in Mg and enriched in metals, H₂S, Ca, alkalis, and silica. These fluids either exit the crust directly to the ocean, forming black smoker-type sulfide deposits at the spreading axis, or mix with cold seawater in the subsurface, precipitating metal sulfide stockwork deposits within the crust. Depending on the Fe/H₂S ratio of the hydrothermal fluid, the resulting mixed and cooled fluid may be Fe-or H₂S-rich following subsurface mixing and sulfide precipitation. Such resultant Fe-rich fluids would be depleted in sulfide-forming metals (Cu and Zn) and would give rise to Fe- (±Mn)-rich deposits during oxidation or pH increase caused by further mixing at the seafloor. The Fe-oxide deposit at Site 801 probably formed from such fluids as they exited the top of the tholeiite section.

Because of kinetic inhibition of quartz nucleation below about 200°C (Rimstidt and Barnes, 1980), rapid mixing of hydrothermal fluids with cold seawater can result in silica-rich low-temperature fluids (Janecky and Seyfried, 1984). Given sufficient time, quartz would precipitate from these fluids, and cooling would result in precipitation of amorphous silica or chalcedony (Janecky and Seyfried, 1984; Tivey and Delaney, 1986). Silicification of the hydrothermal Fe-oxide deposit in Hole 801C may have occurred through cooling of such silica-rich distal, low-temperature hydrothermal fluids to form opal or chalcedony, which was later recrystallized to quartz at temperatures of 30–60°C. The extensive alteration of the blue-green rocks and their restriction to a 5-m interval immediately beneath the hydrothermal deposit suggest that their alteration is related to the formation of the deposit. The rocks were probably altered through reaction with the distal hydrothermal fluids that formed and silicified the hydrothermal deposit. Slightly elevated temperatures (up to about 50°C) likely increased reaction rates and extent of alteration of the rocks. The Mg-poor, alkali-rich nature of the fluids led to the observed Mg loss.

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Table 2. Chemical analyses of the hydrothermal deposit and interpillow material from Hole 801C.

<table>
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<tr>
<th>Sample (cm)</th>
<th>Type of carbonate</th>
<th>Depth (mbsf)</th>
<th>δ¹³C (‰ PDB)</th>
<th>δ⁸⁷⁹O (‰ SMOW)</th>
</tr>
</thead>
<tbody>
<tr>
<td>129-801B</td>
<td>Whole-rock</td>
<td>477.75</td>
<td>-3.6</td>
<td>28.6</td>
</tr>
<tr>
<td>41R-1, 85–91</td>
<td>Whole-rock</td>
<td>483.26</td>
<td>-5.2</td>
<td>29.9</td>
</tr>
<tr>
<td>41R-1, 88–94</td>
<td>Whole-rock</td>
<td>483.88</td>
<td>-4.5</td>
<td>30.2</td>
</tr>
<tr>
<td>43R-2, 31–37</td>
<td>Whole-rock</td>
<td>493.78</td>
<td>-0.4</td>
<td>29.0</td>
</tr>
<tr>
<td>43R-3, 62–65</td>
<td>Vein</td>
<td>493.60</td>
<td>-1.3</td>
<td>26.3</td>
</tr>
</tbody>
</table>

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Table 3. Oxygen and carbon isotopic data for Site 802 basement.

<table>
<thead>
<tr>
<th>Sample (cm)</th>
<th>Type of carbonate</th>
<th>Depth (mbsf)</th>
<th>δ¹³C (‰ PDB)</th>
<th>δ⁸¹⁸O (‰ SMOW)</th>
</tr>
</thead>
<tbody>
<tr>
<td>129-801C</td>
<td>Vein</td>
<td>506.38</td>
<td>-4.0</td>
<td>25.2</td>
</tr>
<tr>
<td>5R-1, 103–105</td>
<td>Whole-rock</td>
<td>532.23</td>
<td>1.9</td>
<td>27.9</td>
</tr>
<tr>
<td>R-2, 87–89</td>
<td>Whole-rock</td>
<td>533.23</td>
<td>0.3</td>
<td>27.3</td>
</tr>
<tr>
<td>5R-3, 38–43</td>
<td>Whole-rock</td>
<td>534.15</td>
<td>0.7</td>
<td>29.5</td>
</tr>
<tr>
<td>5R-3, 116–121</td>
<td>Whole-rock</td>
<td>534.96</td>
<td>2.0</td>
<td>27.5</td>
</tr>
<tr>
<td>5R-3, 125–131</td>
<td>Whole-rock</td>
<td>535.02</td>
<td>1.3</td>
<td>30.4</td>
</tr>
<tr>
<td>6R-2, 34–38</td>
<td>Whole-rock</td>
<td>542.33</td>
<td>0.3</td>
<td>30.4</td>
</tr>
<tr>
<td>8R-1, 65–67</td>
<td>Whole-rock</td>
<td>560.15</td>
<td>1.1</td>
<td>28.2</td>
</tr>
<tr>
<td>8R-2, 78–80</td>
<td>Whole-rock</td>
<td>561.30</td>
<td>0.3</td>
<td>27.7</td>
</tr>
<tr>
<td>9R-4, 15–20</td>
<td>Vein</td>
<td>567.26</td>
<td>1.1</td>
<td>30.7</td>
</tr>
<tr>
<td>11R-3, 58–62</td>
<td>Vein</td>
<td>581.38</td>
<td>-1.2</td>
<td>26.7</td>
</tr>
<tr>
<td>12R-4, 48–52</td>
<td>Vein</td>
<td>587.78</td>
<td>-8.0</td>
<td>24.1</td>
</tr>
</tbody>
</table>

---

Extracted at 150°C.

Extracted at 25°C.
Figure 10. Whole-rock \( \delta^{18}O \) vs. depth for Site 801 basalts. Depth and \( \delta^{18}O \) of hydrothermal deposit also shown.

from the rocks and the formation of abundant K-feldspar. The extensive fracturing of the rocks focused fluid flow and facilitated the extensive alteration of the rocks. Assuming that the K\(_2\)O gained by the rocks (6 wt\%) was added by uptake of all available K in seawater gives seawater/rock ratios of about 150. The altering fluids were likely enriched in K relative to seawater, but probably not all the K was taken up from circulating fluids.

The chalcedony present in veins locally throughout the tholeiite section is highly unusual for altered seafloor basalts from DSDP/ODP cores. These veins are restricted to cores beneath the hydrothermal deposit and were probably pathways for Fe- and silica-rich fluids similar to those that formed the hydrothermal deposit. The fractures are now elogated with chalcedony that precipitated during cooling of the system. The spherulitic and vermicular celadonite intergrown with or cemented by chalcedony in some of these veins (e.g., Fig. 5A) may also be hydrothermal in origin, analogous to low-temperature (about 30°C) nontronite-celadonite deposits on the seafloor (Honnorez et al., 1981; Alt, 1988).

The initial intrusion of alkali basalt magma may have provided the heat source and fracturing necessary to drive the hydrothermal system responsible for the hydrothermal deposit in Hole 801C. Subsequent alkali basalt flows erupted from this chamber then covered the hydrothermal deposit. Alteration of the alkali basalts to saponite and celadonite assemblages occurred under conditions generally similar to those prior alteration of the underlying tholeiites (lower water/rock ratios for saponite, higher ratios for celadonite alteration). Oxygen isotopic data suggest that temperatures in the alkali section may have been slightly higher than those in the tholeiite section, however. This would have contributed to the breakdown of clinopyroxene and the more extensive alteration of the alkali basalts than the tholeiites. The duration of circulation and alteration may also have been longer in the alkaline section, leading to more extensive alteration of the alkali basalts.

The nearly complete breakdown of plagioclase and clinopyroxene and the extensive alteration of the alkali basalts to Al-saponite assemblages suggests high water/rock ratios. Assuming that the K\(_2\)O increase in these rocks (about 4 wt\%) is due to the uptake of all available K from seawater gives a water/rock ratio of about 100. Such high water/rock ratios and extensive alteration may have resulted from convection during the same low-temperature hydrothermal circulation responsible for the Si-Fe deposit in Hole 801C. An active magma chamber or still-hot crystallized alkali basalt magma chamber could have provided a heat source to drive continued convection, leading to somewhat higher temperatures (up to about 50°C) and higher water/rock ratios during alteration of the alkali basalt section. Convection and further alteration in the tholeiite section would have been restricted if fractures sealed with secondary minerals (e.g., calcite, celadonite, and chalcedony) formed during earlier alteration and prior formation and silicification of the hydrothermal deposit.

Similar Al-rich (beidellite) assemblages in extensively altered rocks from DSDP Hole 417A also formed at high water/rock ratios due to enhanced circulation and relatively "warm" basement temperatures (Alt and Honnorez, 1984). The site is located on a basement hill that remained free of sediment for 10 m.y., and alteration temperatures were somewhat elevated, at about 30°-50°C. These factors led to the interpretation that the basement hill acted as a "conduit" for the exit of warm basement fluids from the crust, focusing fluid flow and causing the extensive alteration in Hole 417A (Donnelly et al., 1979; Alt and Honnorez, 1984; Bohlke et al., 1984). On a plot of \( \delta^{18}O \) vs. the square root of K content, the alkali basalts from Site 801 fall along the line defined by samples from Hole 417A (Muehlenbachs, 1980). The rocks from these two sites fall at much higher K contents than altered rocks from any other DSDP/ODP holes (Muehlenbachs, 1980). The similarity of the data for these two sites on such a diagram may be a coincidence, however. The high K contents of Hole 417A rocks are attributed to the presence of abundant K-feldspar and celadonite (Bohlke et al., 1984), whereas the alkali basalts from Site 801 start out with higher primary H\(_2\)O and K contents than normal MORB and would not necessarily be expected to fall along the same alteration trend as MORB (e.g., Fig. 7).

The mineralogical and chemical changes due to alteration of the tholeiites in Hole 801C are generally similar to those typically seen in much younger MORB sections from DSDP/ODP holes (Andrews, 1977; Bohlke et al., 1984; Alt et al., 1986). The extensive alteration of the blue-green rocks is unusual, but is attributed to localized hydrothermal activity associated with formation of the Si-Fe hydrothermal deposit. The generally greater extent of alteration of the alkali basalt section, particularly the rocks altered to Al-saponite assemblages, is also attributed to slightly higher alteration temperatures and enhanced convection associated with the same circulation system that formed the hydrothermal deposit at Site 801 and postdated alteration of the underlying tholeiites. Besides the general lack of observable aging effects in the rocks, the compositions of pore waters in overlying sediments are not particularly highly reacted (Francé-Lanord et al., this volume). This is also inconsistent with continued aging reactions in the basement that would likely have affected overlying pore waters (France-Lanord et al., this volume; Gieskes and Lawrence, 1981; Lawrence and Gieskes, 1981). The low-porosity radiolarites near the base of the sediment section (318–443 mbsf) may have prevented diffusive exchange between basement and overlying sediment pore waters, however.

Thus, it appears that there is little difference in alteration of the Jurassic section from Site 801 compared to young ocean crust. One significant difference, however, may be in the abundance of calcite at Site 801. The younger crust at Hole 504B (5.9 Ma) in the eastern equatorial Pacific has much fewer calcite veins than at Site 801, where multiple generations of calcite have led to abundant calcite veins up to 1.5 cm wide. The volcanics from Hole 504B also have average CO\(_2\) contents an order of magnitude lower than that at Site 801 (about 0.1–0.2 wt\% vs. 2.3 wt\%, respectively; Alt et al., 1986). Staudigel et al. (1981) noted an increase in CO\(_2\) content between younger (3–10 Ma) and older (118 Ma) basement in the Atlantic, and attributed this CO\(_2\) increase to calcite formation during progressive aging of the crust. The data for Site 801 fit this interpretation. Another possible
Figure 11. Oxygen and carbon isotopic data for carbonates in Site 801 basement.

Aging effect is the high δ\(^{18}\)O values and extensive alteration of the alkali basalts from Site 801. Lawrence and Gieskes (1981) showed that transport of \(^{18}\)O by diffusion through sediments into the upper oceanic crust during continued low-temperature alteration results in significant \(^{18}\)O uptake by altered crust. Such a process seems unlikely for Site 801, however, because of the unreacted compositions of pore waters in the sediments immediately overlying basement. Continued flow of seawater along permeable zones in the basement has also been proposed as a means whereby progressive aging reactions can occur between seawater and the crust (Muehlenbachs, 1980; Lawrence and Drever, 1981; Lawrence and Gieskes, 1981). Such reactions could also occur where the crust is sealed from communication with overlying seawater by burial beneath sediments, such as at Site 801.

SUMMARY

Drilling on Leg 129 penetrated more than 100 m into 170-Ma basement at Site 801 in the western Pacific. The lower 60 m of the section consists of tholeiitic basalts formed at a mid-ocean spreading center. A >3-m-thick Fe-Si hydrothermal deposit separates the tholeiites from the overlying 60 m of ocean-island type alkali basalts, which formed near- or off-axis.

Four alteration types have been recognized in Site 801 basement:

1. Saponite-type (Mg-smectite) alteration occurs throughout the tholeiite and alkalic sections. The rocks are generally slightly altered, with olivine replaced by saponite, pyrite, and calcite. The basalts exhibit small increases in \(H_2O\), δ\(^{18}\)O, and oxidation, reflecting relatively low seawater/rock ratios.

2. Celadonite-type alteration occurs locally in both the tholeiitic and alkalic sections. The rocks are slightly altered with olivine replaced by and vugs filled with celadonite, Fe-oxyhydroxides, saponite, and calcite. Chemical changes include uptake of alkalis and greater oxidation and hydration than saponite-type alteration, reflecting higher seawater/rock ratios for celadonite-type alteration.

3. Al-saponite (Al-Mg smectite) alteration occurs only in the alkali basalts above the hydrothermal deposit. These rocks are moderately to extensively altered to Al-saponite, saponite, calcite, and natrolite. The rocks have gained alkalis and \(H_2O\), exhibit increased oxidation and high δ\(^{18}\)O values, and have lost Ca and Na due to the breakdown of olivine, plagioclase, and clinopyroxene.

4. Blue-green rocks are restricted to a 5-m interval immediately beneath the hydrothermal deposit. These are the most extensively altered rocks, with plagioclase, olivine, and pyroxene variably replaced by K-feldspar, Al-smectite (montmorillonite-beidellite), glauconite, celadonite, and calcite. Chemical changes are also the greatest for these rocks, with large increases in alkalis, oxidation, and hydration, and losses of Ca, Na, Fe, and Mg.

Alteration of basement at Site 801 is interpreted in relation to the igneous formation of the crust. The tholeiite section consists of normal MORB formed at a Jurassic mid-ocean spreading center. The saponite- and celadonite-type alteration of these rocks is similar to that in younger altered MORB crust and formed on the flanks of a spreading center at low temperatures (≤20°C).

The hydrothermal deposit consists of spherules, aggregates, and filaments of Fe-oxyhydroxide cemented by quartz. It is interpreted as a low-temperature Fe-oxide deposit, similar to those actively forming on the seafloor at temperatures <30°C, which was later silicified at temperatures up to 60°C. Originally high-temperature (350°C) metal-rich hydrothermal fluids mixed with seawater deeper in the subsurface to provide the cool, distal Fe- and Si-rich fluids that formed the hydrothermal deposit. Focusing of low-temperature hydrothermal fluids by fracturing immediately beneath the deposit resulted in the
extensive alteration and formation of K-feldspar and aluminous phyllosilicates in the blue-green rocks. Following the formation and alteration of the tholeiitic section at a mid-ocean ridge, near- or off-axis intrusion of an alkali basalt magma at depth provided the heat source for hydrothermal fluid reaction and circulation, as well as a magmatic source for the overlying alkali basalts. The latter were altered to saponite and celadonite assemblages, similar to the underlying tholeiites but to a greater extent, reflecting somewhat higher temperatures (up to 50°C) in the alkalic section. Locally higher water/rock ratios resulted in more extensive alteration of plagioclase and the formation of aluminous phyllosilicates in Al-saponite-type alteration in the alkalic section. The generally greater extent of alteration of the alkalic section relative to the tholeiitic section is attributed to magnesite, void-filling calcite during progressive aging of the crust during its long history away from the spreading center. The higher δ¹⁸O values of the crust are interpreted to be due to higher alteration temperatures related to slightly higher temperature circulation in this section following formation of the hydrothermal deposit, but may have been caused in part by a longer duration of seawater circulation in the alkalic section.

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REFERENCES


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