Eldholm, O., Thiede, J., Taylor, E., et al., 1989
Proceedings of the Ocean Drilling Program, Scientific Results, Vol. 104

24. Rb-Sr SYSTEMATICS OF SITE 642 VOLCANIC ROCKS AND ALTERATION MINERALS[1,4]

A. P. LeHuray[2] and E. S. Johnson[3]

ABSTRACT

Subaerially erupted tholeiites at Hole 642E were never exposed to the high-temperature seawater circulation and alteration conditions that are found at subaqueous ridges. Alteration of Site 642 rocks is therefore the product of the interaction of rocks and fluids at low temperatures. The alteration mineralogy can thus be used to provide information on the geochemical effects of low temperature circulation of seawater.

Rubidium-strontium systematics of leached and unleached tholeiites and underlying, continentally-derived dacites reflect interactions with seawater in fractures and vesicular flow tops. The secondary mineral assemblage in the tholeiites consists mainly of smectite, accompanied in a few flows by the assemblage celadonite + calcite (± native Cu). Textural relationships suggest that smectites formed early and that celadonite + calcite, which are at least in part cogenetic, formed later than and partially at the expense of smectite.

Smectite precipitation occurred under variable, but generally low, water/rock conditions. The smectites contain much lower concentrations of alkali elements than has been reported in seafloor basalts, and sequentially leached fractions of smectite contain Sr that has not achieved isotopic equilibrium. $^{87}Sr/^{86}Sr$ results of the leaching experiments suggest that Sr was mostly derived from seawater during early periods of smectite precipitation. The basalt-like $^{87}Sr/^{86}Sr$ of the most readily exchangeable fraction seems to suggest a late period of exposure to very low water/rock. Smectite formation may have primarily occurred in the interval between the nearly 58-Ma age given by the lower series dacites and the 54.5 ± 0.2 Ma model age given by a celadonite from the top of the tholeiitic section. The 54.5 ± 0.2 Ma Rb-Sr model age may be recording the timing of foundering of the Vøring Plateau. Celadonites precipitated in flows below the top of the tholeiitic section define a Rb-Sr isochron with a slope corresponding to an age of 24.3 ± 0.4 Ma. This isochron may be reflecting mixing effects due to long-term chemical interaction between seawater and basalts, in which case the age provides only a minimum for the timing of late alteration. Alternatively, inferrential arguments can be made that the 24.3 ± 0.4 isochron age reflects the timing of the late Oligocene–early Miocene erosional event that affected the Norwegian–Greenland Sea.

Correlation of $^{87}Sr/^{86}Sr$ and 1/Sr in calcites results in a two-component mixing model for late alteration products. One end-member of the mixing trend is Eocene or younger seawater. Strontium from the nonradiogenic endmember can not, however, have been derived directly from the basalts. Rather, the data suggest that Sr in the calcites is a mixture of Sr derived from seawater and from pre-existing smectites. For Site 642, the reaction involved can be generalized as smectite + seawater ↔ celadonite + calcite. The geochemical effects of this reaction include net gains of K and CO_2 by the secondary mineral assemblage. The gross similarity of the reactions involved in late, low-temperature alteration at Site 642 to those observed in other sea floor basalts suggests that the transfer of K and CO_2 to the crust during low-temperature seawater-ocean crust interactions may be significant in calculations of global fluxes.

INTRODUCTION

The formation and subsequent cooling of ocean crust results in the overprinting of alteration effects of near-ridge, high-temperature seawater–basalt interactions by long-lived, low-temperature alteration. Determining the relative importance of high temperature and ongoing, lower temperature effects is necessary if we are to achieve an understanding of the fluxes between ocean crust and seawater, but multiple generations of alteration have made the complexities of varying hydrothermal conditions difficult to unravel.

The early Tertiary tholeiites recovered at Ocean Drilling Program (ODP) Site 642 (Fig. 1) were erupted subaerially (Eldholm, Thiede, Taylor et al., 1987) and had almost certainly cooled to ambient temperatures before foundering. The virtually pristine major and trace element characteristics of most flows (Parson et al., Viereck et al., this volume) suggests that the basalts were little affected by high-temperature seawater–rock interactions. In the tholeiitic section (upper volcanic series Fig. 2), vesicles that have remained unfilled by secondary minerals predominate (Shipboard Scientific Party, 1987), suggesting that seawater–rock reactions have been of limited extent during postfoundering history, as might be expected under low-temperature conditions.

The virtual isolation of low-temperature alteration in Hole 642E tholeiites can provide a basis for evaluating the importance of low-temperature seawater–ocean crust interactions. In this paper we report the results of an Sr isotope and alkali element study of host rocks and secondary minerals from the volcanic section of Hole 642E, and reflect on their implications for the timing of events in the Norwegian–Greenland Sea as well as for the extent of low-temperature seawater/basalt interactions.

BACKGROUND

As Layer 2 ocean crust is formed and cooled, it is subjected to a variety of alteration events. Workers who have studied alteration assemblages in basalts have proposed highly similar parageneses of secondary minerals (e.g., Bass, 1976; Stakes and Scheidegger, 1981; Staudigel et al., 1981b). Textural evidence that smectites are the earliest clay minerals to form agrees with experimental results (e.g., Hajash, 1975; Bischoff and Dickson, 1975; Seyfried and Bischoff, 1977; Seyfried and Janecky, 1985). At least some smectite formation is associated with the circulation of seawater at elevated temperature, and the fluids involved in the reactions are at relatively low pH and are oxygen-poor.

---

[1] Eldholm, O., Thiede, J., Taylor, E., et al., 1989. *Proc. ODP, Sci. Results*, 104: College Station, TX (Ocean Drilling Program).

[2] Lamont-Doherty Geological Observatory, Columbia University, Palisades, NY 10964.

[3] Department of Geology, Colorado College, Colorado Springs, CO 80903.

[4] L-DGO Contribution No. 4355.

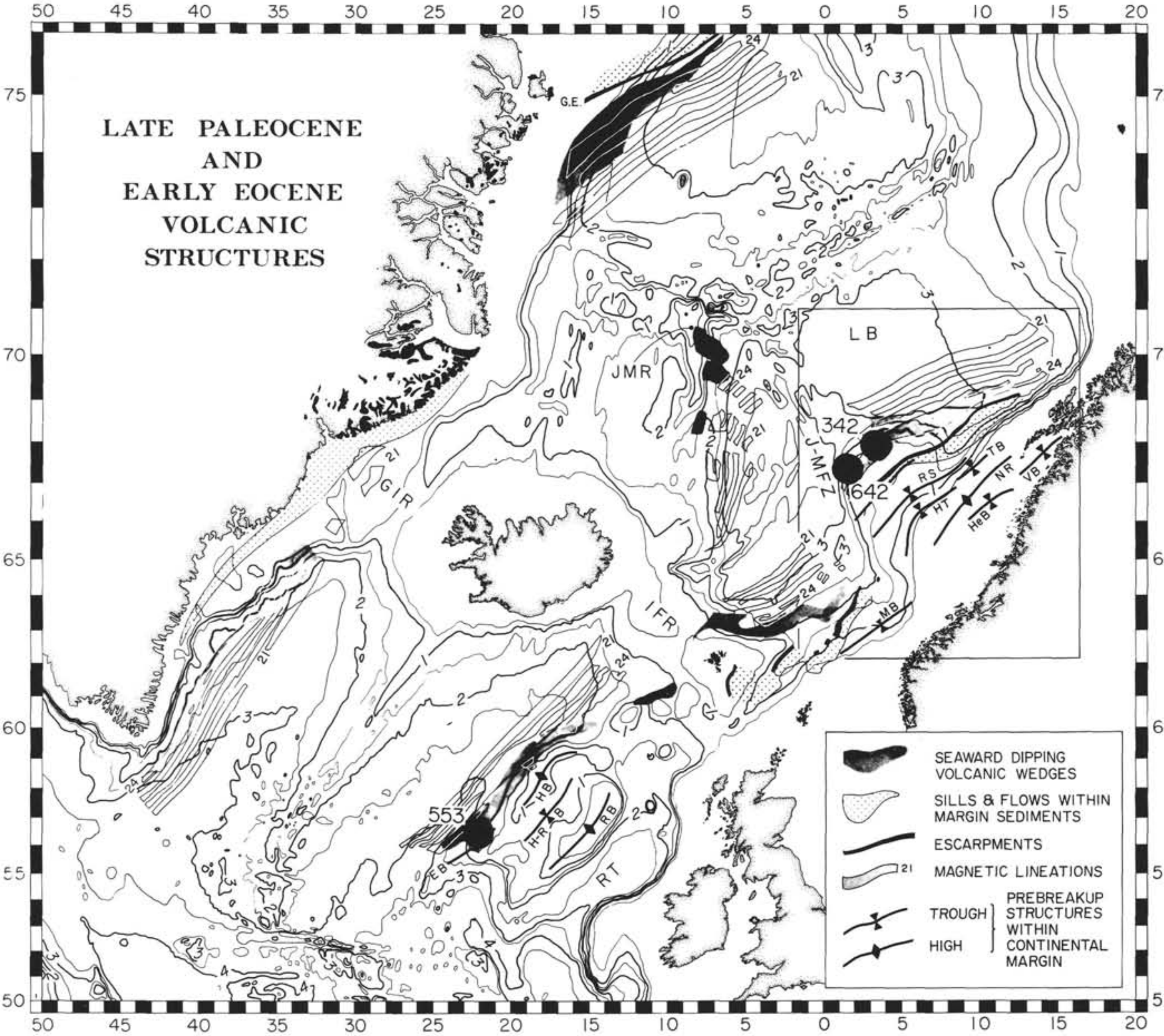

Figure 1. Index map of the North Atlantic showing the locations of DSDP Sites 342 (Vøring Plateau) and 553 (Rockall Plateau) and of ODP Site 642. The map is from Mutter et al. (1988), to which the reader is referred for full discussion of the features shown.

The smectites are major sinks for Fe, Mg, K, Na, and other alkali elements and transition metals.

Calcite is generally observed to be a late-forming mineral and has been associated with the incursion of low-temperature, oxidated seawater into basalts. (e.g., Bass, 1976; Lawrence, 1979; Lawrence and Drever, 1981). Celadonites are also associated with late, low-temperature alteration (e.g., Scheidegger and Stakes, 1980; Stakes and Scheidegger, 1981).

In Site 642 tholeiites, early formed smectites replace basaltic mesostases and fill vesicles and fractures. Celadonite and calcite are associated, and appear to form at least in part at the expense of smectite. Native copper is often associated with the celadonite + calcite assemblage (LeHuray, this volume). The observed paragenesis supports the Scheidegger and Stakes (1980) and Stakes and Scheidegger (1981) suggestion that celadonite is a reaction product of cold seawater and preexisting smectite, and is similar to that described by Desprairies et al. (1984) in subaerially erupted tholeiites from Deep Sea Drilling Project (DSDP) Hole 553A on the Rockall Plateau (Fig. 1). The smectite–celadonite reaction is similar to the diagenetic illitization of smectites observed in sedimentary sequences (Perry and Hower, 1970; Srodon and Eberl, 1984).

Studies of Rb-Sr systematics of alteration minerals in DSDP basalts have indicated that chemical interaction between seawater and basalt ceases 10–15 Ma after crust formation (Hart and Staudigel, 1978, 1979; Richardson et al., 1980; Staudigel and Hart, 1985). Similarly, Staudigel et al. (1986) found that Rb-Sr and K-Ar ages of celadonites from the Troodos complex formed 7–15 Ma after the cessation of Troodos volcanism. These estimates are in line with the results of thermal modeling, which suggests that thermally driven circulation of seawater in basalts may continue for as long as 15 Ma (e.g., Sleep, 1975). The age information in the cited studies is contained in Rb-Sr and, to a lesser extent, K-Ar systematics of celadonites which, as discussed above, are generally late, low-temperature alteration products. These ages are thought to be closure ages, reflecting either the time at which the hydrothermal system cooled below some blocking temperature or the timing of inhibition of fluid flow due to filling of pore space (Staudigel et al., 1981a; Hart and Staudigel, 1986).

The primary textures and mineralogy of Site 642 upper series basalts are similar to those recovered at DSDP Sites 342 (Vøring Plateau) and 553 (Rockall Plateau; Fig. 1), and so are the secondary mineral assembalges. Desprairies et al. (1984) described the alteration mineralogy of basalts from Hole 553A. They found Fe-rich, K-poor beidellites, Fe oxyhydroxides, and hematite in reddened flow tops, features that they associate with subaerial alteration processes. Outside of reddened flow tops (and superimposed on subaerial alteration in the reddened flow tops), alteration is dominated by a smectite + celadonite (± calcite ± native Cu) association, similar to that observed in Hole 642E basalts, which is thought to have formed at temperatures of $<100°C$.

The lower approximately 50 m of the upper series tholeiites in Hole 642E have been subjected to a late alteration event that resulted in partial bleaching and orange staining due to ankerite precipitation around vesicular zones and fractures (Fig. 2). The ankerite event seems to postdate the main alteration events that affected both upper and lower volcanic series rocks. Pre-ankerite alteration in lower volcanic series dacites (Parson et al., this volume) is dominated by SiO_2 coatings in amygdules and veins. Portions of some lower series flows have been bleached white, and volcaniclastic units contain high-temperature zeolites (Eldholm, Thiede, Taylor, et al., 1987). There is petrographic evidence that an earlier clay mineral alteration assemblage was altered during the silicification event that affected the lower series. Minor amounts of ankeritic carbonates are found coating secondary SiO_2 and primary feldspar phenocrysts.

METHODS

Smectites, celadonites, and calcites were sampled from occurrences in vesicular flow tops and veins using a stainless steel dental tool. The samples were then washed in ultraclean water in an ultrasonic bath, to disaggregate the clays and remove surface contamination.

Hart and Staudigel (1986) report a procedure in which unleached smectites and celadonites are analyzed along with celadonites leached for various times in ammonium acetate (AmAc), which insures a range in Rb/Sr. However, scanning electron microscope (SEM) studies of alteration in Hole 642E tholeiites showed that celadonite is invariably finely intermixed with calcite (Fig. 3), and that some occurrences of smectite also contain submicroscopic calcite. As the calcite may impart an artificially low Rb/Sr to the analysis, and may introduce a bias in $^{87}Sr/^{86}Sr$ if the calcite was formed later than the clays, we subjected all celadonites to a short (about 1/2 hr), room temperature, 1N acetic acid (HOAc) leach. When enough material remained after the HOAc leach, the sample was split after drying, with one half (10–20 mg) subjected to no further leaching and the other subjected to leaching for 4 hr at room temperature in ultraclean 1N AmAc before further processing.

Previous workers have not generally subjected smectites to sequential leaching experiments. However, most evidence from DSDP as well as Site 642 basalts indicates that celadonite (± calcite) is a late assemblage that may result in part from the interaction of smectites formed at higher temperatures and cool seawater. If such is the case, surviving smectites might be expected to show some effects of progressive reaction, effects which might be detectable in changes in characteristic $^{87}Sr/^{86}Sr$ residing in different cation sites. In addition, calcite was occassionally observed to be intimately mixed with smectite under the SEM. To test for the effects of progressive reaction in smectites and to ensure that the effects of intermixed calcite could be constrained, we analyzed unleached smectites as well as smectites that were subjected to HOAc and AmAc leach steps, as described for celadonite above.

Calcite separates were hand-picked for purity, washed in ultraclean water in an ultrasonic bath, dried, spiked, and dissolved in sub-boiling point distilled 2.5 N HCl, and loaded directly onto ion exchange columns.

Leached whole-rocks were subjected to catastrophic leaching, consisting of ultrasonic removal of fines, and multiple cold and hot 6N HCl immersions during which the leachate was decanted and acid changed often to prevent oversaturation and precipitation of chlorides.

Blanks for the smectite, celadonite, and whole-rock procedures were typically 0.15 ng Sr, 0.05 ng Rb, and 1.5 ng K. Blanks were lower for the calcite procedure. None of the blanks are significant for these data.

Isochron ages were calculated according to the method of York (1969). Errors are reported as 2 σ.

References to individual flow (F) and dike (D) units within the Hole 642E volcanic series follow the terminology described in the core logs and in Table 6 and Figure 14 of Shipboard Scientific Party (1987).

RESULTS

Upper Volcanic Series Whole Rocks

Vigorously leached whole rocks from two upper volcanic series flows and a dike near the top of the section have $^{87}Sr/^{86}Sr$ that range from 0.7033 to 0.7038 (Table 1; Fig. 4). These values are high relative to present-day N-type MORB, which generally have $^{87}Sr/^{86}Sr < 0.703$, but are within the range of modern values found in other chemical classifications of MORB. Measured and age-corrected $^{87}Sr/^{86}Sr$ in all but one of the unleached samples have values similar to those in leached fractions. The unleached sample with high $^{87}Sr/^{86}Sr$ (104-642E-25R-3, 137–139 cm) was taken from the vesicular and reddened top of a flow, and the high Rb and K concentrations of the sample indicate a relatively high degree of alteration. The absence of a significant component of seawater Sr in massive flow centers is consistent with the low water/rock ratios expected in zones of low effective permeability. Significant alteration effects were apparently confined to zones of higher effective permeability, such as the upper and lower vesicular zones of flows.

The two texturally distinct upper series flow types (fine- and medium-grained) each has a consistent morphology-depth-in-flow profile (described in Shipboard Scientific Party, 1987), that allows the qualitative use of a parameter that indicates the relative position of an analyzed sample in a flow. Comparison of such a parameter, called β in Table 1 with $^{87}Sr/^{86}Sr$ (Fig. 4c) of samples indicates that the only two samples for which age corrections are significant are also the samples which came from the top or bottom—the most vesicular sections—of a flow. These two samples also have elevated Rb and K concentrations. These results are consistent with the flow position-dependent effects of alteration on major and trace elements reported by Viereck et al. (this volume).

Lower Volcanic Series Whole Rocks

The lower series consists of volcaniclastic layers and dacitic flows intruded by dikes (D4–D7) with upper, lower, and mixed upper and lower series geochemical affinities (Parson et al., Taylor and Morton, both this volume). Three samples analyzed from the lower series (Table 1) define a line with a slope corresponding to an isochron age of 57.8 ± 1.0 Ma and an initial $^{87}Sr/^{86}Sr$ of 0.71107 ± 0.00003 (Fig. 5).

Effects of alteration are difficult to assess in lower volcanic series rocks because of the crustal signatures of lower series rocks and the mixed upper and lower series signatures of some of the units (see Parson et al., Taylor and Morton, both this volume). The effects of mixing are evident, for example, in the $^{87}Sr/^{86}Sr$ of the two analyses of dikes reported here (Table 1, Fig. 5). Both D7 and D5 contain a mixed upper and lower series Sr isotope signature. Comparison of analyses of hand-picked glass and bulk material from Unit F107, however, does provide an indication of seawater/rock interaction and consequent alteration. Unlike the usual case for sea floor tholeiites, addition of Sr from seawater to F107 lowered the $^{87}Sr/^{86}Sr$ of the altered rock (Fig. 5), because the pristine rock had $^{87}Sr/^{86}Sr$ substantially higher than the value in seawater.

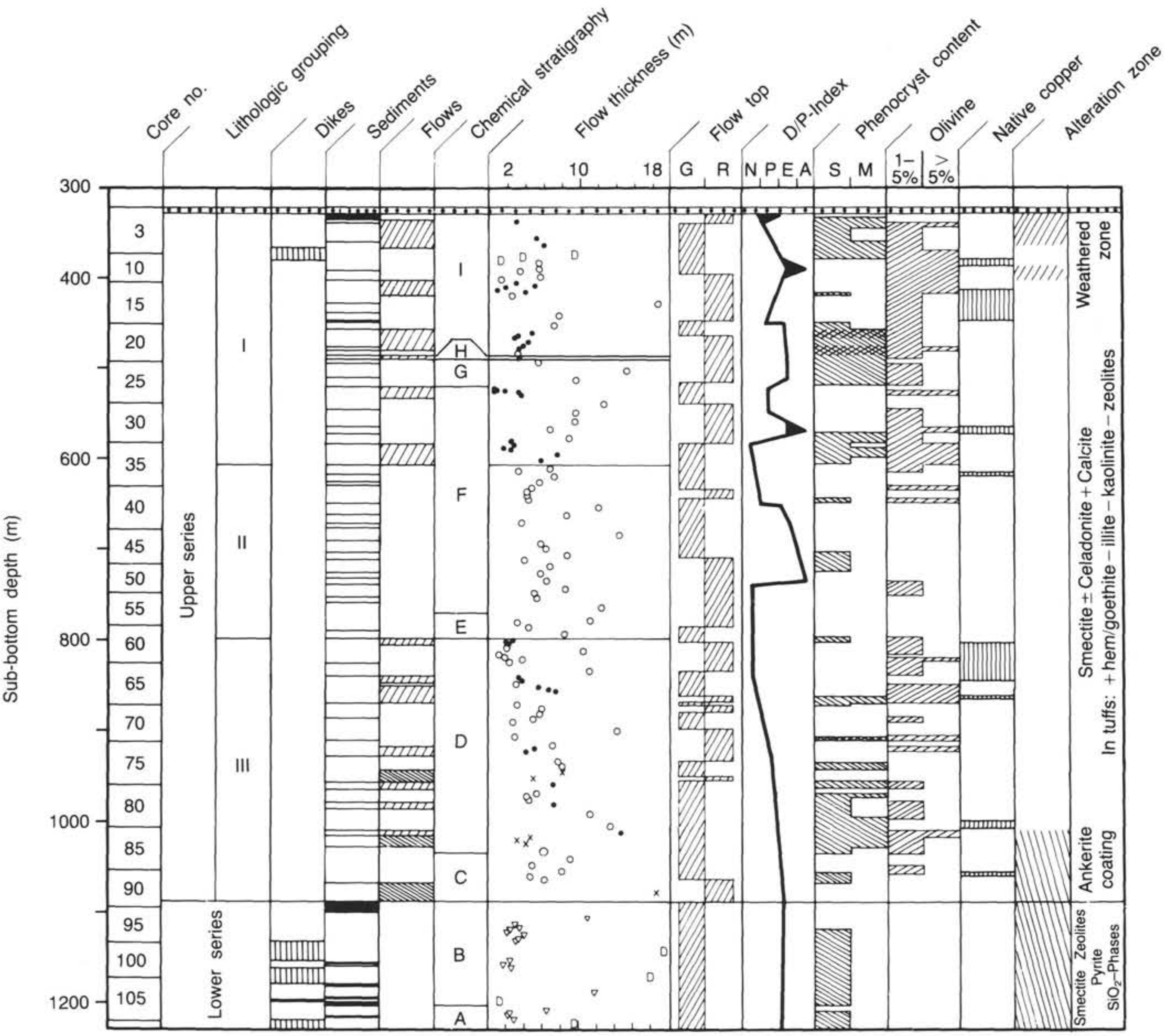

Figure 2. Lithostratigraphy, chemical stratigraphy, petrography, and alteration synthesis of the volcanic sequence, Site 642. Flows: no ornament = fine-grained flows, right-slant hatching = medium-grained flows, left-slant hatching = mixed flows. Flow thickness: open circles = fine-grained flows, filled circles = medium-grained flows, crosses = mixed flows, triangles = lower series flows, D = dykes. Flow top: G = gray, R = reddened. Dinoflagellate/palynomorph index: N = neritic, P = paralic, E = esturine, A = subaerial. Phenocryst content: S = sparsely phyric, M = moderately phyric, cross-hatching = phyric. Alteration zones: no ornament = low-temperature mineral replacement, right-slant hatching = weathered zone, left-slant hatching = zeolitic and mineralized zone. This figure is from Shipboard Scientific Party (1987).

Carbonates

Seawater during the early Eocene and Paleocene had relatively uniform $^{87}Sr/^{86}Sr$ values of 0.7076–0.7077 (Burke et al., 1982). Calcites deposited in upper series amygdules have $^{87}Sr/^{86}Sr$ that range from 0.70680 to 0.70776 (Table 2; Fig. 6). The higher values are indistinguishable from Eocene–Paleocene seawater. The lower values indicate that some component of Sr was ultimately derived from the enclosing basalts. However, as discussed below, we believe that the immediate source of the basaltic component of Sr in the calcites may have been the preexisting smectites.

The high $^{87}Sr/^{86}Sr$ of ankerite from the lower volcanic series is subject to several interpretations. It could reflect Sr derived only from lower series lithologies, or a mixture of lower series and seawater Sr. It seems unlikely, however, that the ankerite contains much of a component of Sr derived from overlying or (hypothetical) underlying tholeiitic rocks.

Smectites

Strontium concentrations in unleached and HOAc-leached smectites from Hole 642E tholeiites fall within a restricted range (30 to 57 ppm; Table 3) and are similar to concentrations reported in unleached smectites from DSDP Hole 418A (42 to 59 ppm) by Staudigel et al. (1981a). Smectites in basalts from other drill holes generally seem to have Sr <30 ppm (e.g., 417A, Staudigel et al., 1981a; 462A, Hart and Staudigel, 1986). Comparison of unleached-HOAc-leached pairs (Fig. 7) indicates that the mild leaching procedure generally removed 8 to 18% of the

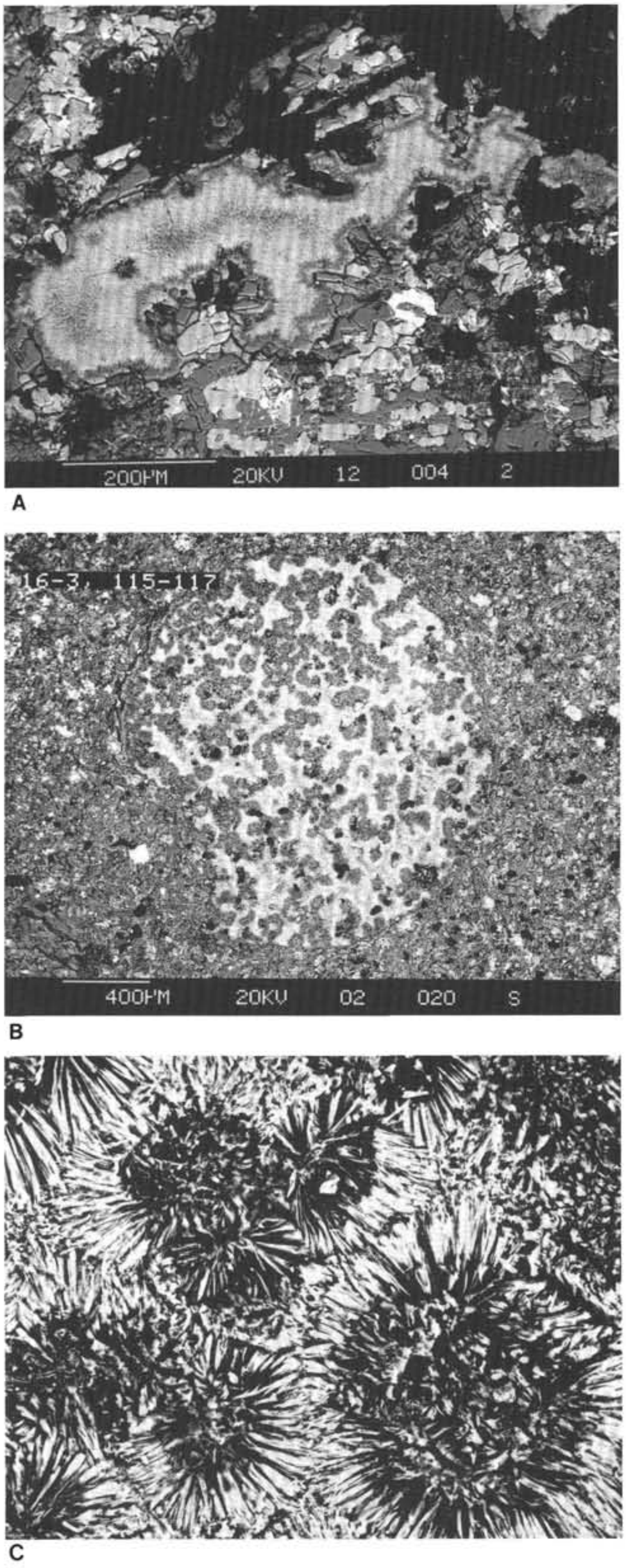

Figure 3. Photographs of SEM backscatter images of alteration minerals from Hole 642E upper series basalts. A. Smectite partially filling a void. The zonation reflects the more Fe-rich composition of the interior of the smectite. Sample 104-642E-33R-3, 142–144 cm. B. Intimately mixed celadonite (white) + calcite filling a vesicle. Sample 104-642E-16R-3, 115–117 cm. C. Closeup view of celadonite + calcite mixture of B. at maximum contrast. The bright material is celadonite and the dark calcite. Field of view is approximately 100 μm across.

Sr. In one case (Sample 104-642E-50R-1, 10–12 cm) the HOAc-leached fraction has a higher Sr content than the unleached fraction, indicating a low concentration of Sr in the leached sites.

Rubidium concentrations in all but one unleached and in all HOAc-leached smectites are generally lower (range: 0.14–0.47 ppm) than any reported in previous studies. Site 418 smectites, for instance, have Rb concentrations that range from 0.5 to 109 ppm (Staudigel et al., 1981a) and Hole 462A smectites contain from 0.7 to 5.4 ppm Rb (Hart and Staudigel, 1986). Potassium and Cs concentrations are also substantially lower in Site 642 smectites than in smectites from other localities. Hart and Staudigel (1982) reported average K concentrations of basalt-hosted smectites/palagonites to be 7955 ppm. The highest K concentration found in an unleached Site 642 smectite is 2650 ppm, and the average is 1000 ppm. Similarly, Hart and Staudigel found an average Cs concentration in smectites from the upper 600 m of ocean crust to be 0.387 ppm; at Site 642 the highest Cs concentration in smectite is 0.09 ppm and the average is 0.03 ppm. In fact, Site 642 smectites average K, Rb, and Cs concentrations are lower than the values used by Hart and Staudigel (1982) to represent average alkali element concentration in unaltered basalts.

In three of the four unleached-HOAc-leached smectite pairs, Rb and Sr concentrations (Fig. 7) and Rb/Sr ratios were decreased by the mild leaching step. Rubidium, however, was affected to a greater extent than Sr, as indicated by decreases of up to 60% in ^{87}Rb/^{86}Sr (Table 3). This result indicates that the sites or phases attacked by the HOAc leach was rich in Rb relative to Sr, and thus, presumably, in K relative to Ca. The leached material could not, therefore, have been predominantly intermixed calcite, which is consistent with the absence of significant *fizzing* during the HOAc leach of smectites.

^{87}Rb/^{86}Sr in all analyzed fractions of smectite was low (0.008 to 0.05); within the range, in fact, of unaltered MORB. ^{87}Sr/^{86}Sr ratios have therefore been little affected by radiogenic growth, and may be discussed without age correction.

The HOAc-leached fractions have higher ^{87}Sr/^{86}Sr than the unleached fractions. As all of the smectite fractions have low ^{87}Rb/^{86}Sr, the differences cannot be accounted for by radiogenic growth of ^{87}Sr/^{86}Sr. Instead, the data indicate that Sr in the various sites within the smectites has not achieved isotopic equilibrium. The variation in ^{87}Sr/^{86}Sr suggests that smectite formation at Site 642 occurred over an interval of time during which water/rock varied greatly. Based on the consistently low Rb concentrations, however, water/rock in Site 642 tholeiites probably never achieved values as high as those that have been reported during early alteration of MORB at subaqueous ridges.

The lower ^{87}Sr/^{86}Sr in the most readily leachable sites cannot be recording interaction with later, unexchanged seawater because ^{87}Sr/^{86}Sr in seawater has generally increased throughout the Tertiary (Burke et al., 1982; DePaolo, 1986). Instead, the lower ^{87}Sr/^{86}Sr in unleached smectites suggests that the most readily leachable sites in the smectites record exchange with fluids that had extensive contact with basalt in a rock-dominated environment.

Mass balance calculations for samples from 104-642E-50R-1, 76–78 cm and 104-642E-77R-2, 107–109 cm indicate that ^{87}Sr/^{86}Sr in the sites leached by HOAc must have been 0.703–0.704, within the range of Hole 642E tholeiite values (Table 1; Taylor and Morton, this volume). Calculations for Sample 104-642E-60R-2, 21–23 cm give an unrealistically low value of 0.699 for ^{87}Sr/^{86}Sr in the leached sites, which suggests an analytical (e.g., unhomogeneous splits) problem.

The successive AmAc procedure was attempted on two samples of smectite, following the same procedure as that used for celadonite. The AmAc leaches removed about 70 to 80% of the

Table 1. Sr isotope ratios of leached and unleached upper and lower series volcanic rocks recovered at Site 642, and Rb, Sr, and K concentrations of unleached samples. Dashes indicate not determined.

Core-section,[a] interval (cm)	Depth[b] (mbsf)	Unit[c]	Type[d]	$^{87}Sr/^{86}Sr$	$^{87}Rb/^{86}Sr$	Sr (ppm)	Rb (ppm)	K (ppm)	Ba (ppm)	$^{87}Sr/^{86}Sr$[e] (55 Ma)	β[f]
Upper Series - Leached											
9-1, 135-137	367.1	D1	WR(L)	0.70326±5	0.0233*	39.1	0.315	621	–	0.70324	
15-5, 20-22	413	F12	WR(L)	0.70330±3	0.0538*	102	1.9	1589	–	0.70326	.89
86-2, 12-14	1015.7	F98	WR(L)	0.70376±4	0.0126*	69.1	0.302	525	–	0.70375	.85
Upper Series - Unleached											
15-2, 110-112	408	F11	WR(U)	0.70370±6	0.0138	164	0.783	948	–	0.70369	.33
15-5, 20-22	413	F12	WR(U)	0.70357±2	0.0381	160	2.11	–	29.1	0.70354	.89
21-4, 15-17	467.4	F21	WR(U)	0.70356±3	0.0112	203	0.787	1003	15.4	0.70355	.44
25-3, 137-139	496.4	F28	WR(U)	0.70468±3	0.396	127	17.4	4724	–	0.70437	.04
28-5, 3-5	526.5	F33	WR(U)	0.70366±4	0.0108	214	0.747	1352	–	0.70365	.79
86-4, 41-43	1024.4	F99A	WR(U)	0.70386±3	0.101	158	5.53	1520	49.0	0.70378	.97
Lower Series -Unleached, Leached, & Glass											
97-2, 7-10	1113.7	F107	Glass†	0.71315±2	2.48	154	132	13,239	–	0.71121	
100-2, 19-21	1132.7	D4	WR(U)†	0.71121±3	0.174	221	13.3	4348		0.71107	
102-2,107-108	1159.4	F116	WR(U)†	0.71306±3	2.539	163	141	6380	388	0.71108	
97-1, 121-123	1111.1	F107	WR(U)	0.71015±5	1.54	76.9	41	4976	109	0.70894	
105-3,130-132	1178.7	D5	WR(L)	0.70563±6	0.456*	25.1	3.96	1201	–	0.70527	
110-1, 12-14	1219.1	D7	WR(U)	0.70961±2	0.135	160	7.48	–	197	0.70951	

[a] All sample numbers have the prefix "104-642E" and all cores are of type "R". A complete sample number will therefore read, for example "104-642E-9R-1, 135-137 cm".

[b] mbsf = meters below sea floor.

[c] Units are individual flows (F) and dikes (D), as defined in Eldholm, Thiede, Taylor, *et al.* (1987).

[d] WR = whole-rock; L = leached; U = unleached; Glass = hand-picked glass.

[e] Corrected to 55 Ma using measured $^{87}Rb/^{86}Sr$ and $\lambda = 1.42 \times 10^{-11}$.

[f] β is a measure of the position of the analyzed sample in the flow, calculated as depth below flow top divided by total flow thickness.

* Leaching of whole-rocks produces incongruent dissolution of Rb- and Sr-bearing phases. Thus, although the residue consists mostly of plagioclase, $^{87}Rb/^{86}Sr$ values may in part reflect the incongruent behavior. They are used only to provide a rough estimate for age correction.

† Lower Series samples that define an isochron age of 57.8 ± 1.0 Ma.

Sr present in unleached and HOAc-leached splits. Rubidium concentrations were not as significantly affected. In one instance (Sample 104-642E-77-2, 107–109 cm) the additional leaching resulted in $^{87}Sr/^{86}Sr$ indistinguishable from $^{87}Sr/^{86}Sr$ in the portion of the smectite subjected only to HOAc leaching. In the other case (Sample 104-642E-60R-2, 21–23 cm), however, the AmAc leach removed a component of more seawaterlike Sr, resulting in a lower $^{87}Sr/^{86}Sr$, approximately 0.7055. This is not as low a value as those calculated to have been present in the most readily leachable sites, but is lower than most values that have been reported from basalt-hosted smectites.

Celadonites

Celadonites in vesicles and veins in upper series basalts formed after smectite mineralization, and may have in part formed at the expense of smectite. The celadonites range in color from vivid turquoise to a dull greenish blue. All celadonites viewed under the SEM were intimately mixed with calcite at the submicroscopic level, making hand-picking an ineffective purification method. Acid leaching experiments on glauconite, which is structurally and chemically similar to celadonite, have met with mixed success, although mild acid leaching has generally been found to lower common Sr concentrations (through removal of intergrown carbonate or phosphate) and to increase age precision (e.g., Morton and Long, 1980). Treatment of glauconites (e.g., Morton and Long, 1980) and celadonites (e.g., Hart and Staudigel, 1986) with AmAc has also been found to lower concentrations of common Sr, presumably through removal of Sr in the most readily exchangeable sites.

Three samples of celadonite from upper series vesicle fillings were analyzed. All three were subjected to HOAc leaching to re-

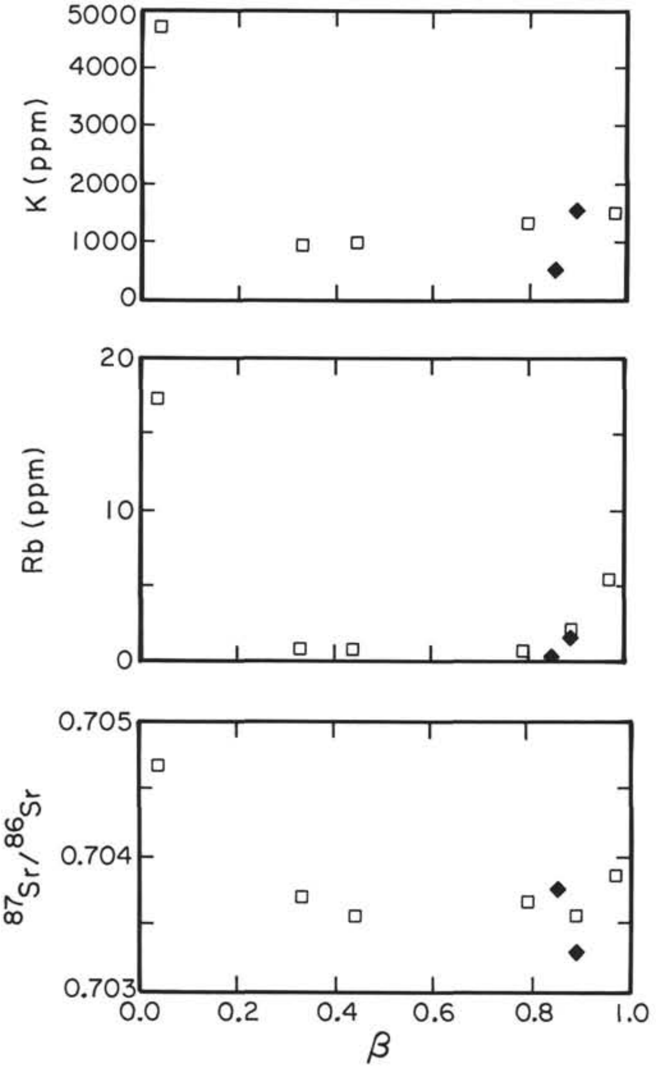

Figure 4. $^{87}Sr/^{86}Sr$, Rb, and K concentrations plotted against β, a factor indicating the position of a sample in a flow, defined as depth of sample below flow top/total thickness of flow. β is useful for Hole 642E upper series flows because of the general similarity of flow morphology consisting of an upper vesicular zone, central massive zone, and lower vesicular zone. Thus, although samples are from different flows, β allows a comparison of alteration effects in a generalized flow profile. Note the increased $^{87}Sr/^{86}Sr$, Rb, and K concentrations in the upper and lower vesicular zones, in which high water/rock is allowed due to increased effective permeability. Filled diamonds = leached whole-rocks. Open squares = unleached whole rocks.

move calcite. A split of one larger sample (104-642E-19R-2, 4-8 cm) was then treated with AmAc (Table 3).

The low Sr concentrations and high $^{87}Rb/^{86}Sr$ of the analyzed fractions indicate that calcite was effectively removed by the mild HOAc leach. As has been observed in other glauconites and celadonites, the AmAc leach step had the effect of increasing $^{87}Rb/^{86}Sr$ and $^{87}Sr/^{86}Sr$ of the residue.

AGE RELATIONS

The volcanic rocks drilled at Site 642 were formed during the time of magnetic anomaly 24, which has been estimated to have occurred between 53 and 56 Ma (e.g., Talwani and Eldholm, 1977; Talwani et al., 1981) and is the oldest seafloor-spreading magnetic anomaly identified in the Norwegian-Greenland Sea (e.g., Hinz et al., 1987). Vøring Plateau basalts recovered from within anomaly 24 at Sites 338 and 342 (DSDP Leg 38) were found to have K-Ar ages of 44 to 46 Ma (Kharin et al., 1976). The young K-Ar ages may be due to argon loss, a common problem in seafloor tholeiites (Seidemann, 1977). Macintyre and Hamilton (1984) reported K-Ar whole-rock ages for least-altered basalts from Site 553 (Rockall Plateau), two of which closely match the estimated age of North Atlantic volcanism: 54.5 ± 2.0 and 52.3 ± 1.7 Ma. The remaining five *ages* reported by Macintyre and Hamilton (1984) are older (66 to 397 Ma), suggesting the presence of excess Ar. If, as seems likely, the Rockall Plateau is structurally similar to the Vøring Plateau, the *excess* Ar may have been derived from underlying continental material.

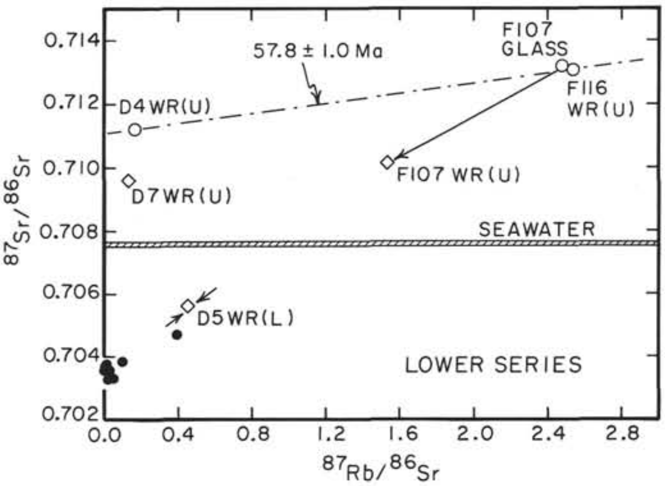

Figure 5. $^{87}Sr/^{86}Sr$ vs. $^{87}Rb/^{86}Sr$ plot illustrating Rb-Sr systematics of lower series flows (F) and dikes (D). Samples from three units (open circles) define an isochron indicating an age of 57.8 ± 1.0 (2 σ) Ma and an initial $^{87}Sr/^{86}Sr$ of 0.71107 ± 0.00003. One of the samples was hand-picked glass from F107. Analysis of an unleached whole-rock fraction of F107 (glass + alteration products) suggests that posteruptive interaction with seawater may have occurred (tie-line connects glass and whole-rock data). The relatively low $^{87}Sr/^{86}Sr$ in D5 and D7, however, is consistent with assimilation of lower series Sr in a tholeiitic upper series magma. Closed circles are data from upper series basalts shown for comparison.

Timing of Volcanism at Site 642

Two whole-rock and one hand-picked glass samples from Hole 642E lower series dacites define a line with a slope that corresponds to an isochron age of 57.8 ± 1.0 Ma and an initial $^{87}Sr/^{86}Sr = 0.71107 \pm 0.00003$ (Fig. 4). This is essentially a two-point isochron age because F107 (glass) and F116 (WR) are isotopically similar. Two-point isochrons are always of questionable significance, but the approximately 58-Ma age indicated here is in reasonable agreement with the timing of events related to the opening of the Norwegian-Greenland Sea, and the high initial $^{87}Sr/^{86}Sr$ is consistent with other isotopic results from the lower volcanic series (Table 1). Taylor and Morton (this volume) report a Rb-Sr isochron age of 63 ± 19 Ma (initial $^{87}Sr/^{86}Sr = 0.7116 \pm 0.0004$) for lower series volcanic rocks.

Celadonite from Unit F4, near the top of the tholeiitic upper volcanic series, gives a model Rb-Sr age of 54.5 ± 0.2 Ma (Fig. 8). $^{87}Sr/^{86}Sr$ of Paleocene-Eocene seawater (0.7077 ± 0.0001) was used in the model age calculation. Because the $^{87}Rb/^{86}Sr$ of this celadonite is so high (Table 3), the assumed initial ratio could vary significantly without significant effect on the model age. The 54.5 ± 0.2-Ma age is associated with a late alteration product, and therefore may provide a lower age limit on the formation of the upper volcanic series. This model age is some-

Table 2. Sr concentration and isotopic composition of calcites precipitated in vesicles of Hole 642E volcanic rocks.

Core-section,[a] interval (cm)	Depth (mbsf)	Unit	Type	$^{87}Sr/^{86}Sr$	Sr (ppm)
Upper Series					
9-1, 135-137	367.2	D1	calcite	0.70747±3	98.9
17-1, 139-141	430.6	F17	calcite	0.70776±9	5823
18-5, 22-24	439.4	F18	calcite	0.70762±3	122
94-3, 114-116	1086.8	F105	calcite	0.70680±4	35.9
Lower Series					
102-2, 32-33	1158.2	F115	ankerite	0.70928±7	1036

[a] All sample numbers have the prefix "104-642E" and all cores are of type "R". A complete sample number will therefore read, for example, "104-642E-9R, 135-137 cm".

what lower than the Rb-Sr age indicated for the lower series (57.8 ± 1.0) and is indistinguishable from the generally accepted approximately 55-Ma timing of North Atlantic volcanism.

Timing of Alteration

Celadonites in basalts are generally thought to be the product of seawater-rock interaction at relatively low temperatures (less than or equal 25°C), oxidative conditions, and high K availability (Stakes and Scheidegger, 1981; Stakes and O'Neil, 1982). Like some of the celadonites in Nazca plate basalts studied by these authors, Site 642 celadonites appear to have formed after, and partially at the expense of, the main stage of smectite mineralization. The intergrown texture of celadonite and calcite (Fig. 3) indicates that these minerals are, at least in part, cogenetic. We may thus describe seawater-basalt interactions as having occurred in two broad stages:

1. smectite formation under conditions of variable, but generally low, water/rock; and
2. celadonite + calcite formation.

The 54.5 ± 0.2 Ma model age of celadonite from Unit F4 may provide an upper limit on the beginning of Stage 2 alteration. If so, then smectite mineralization must have been substantially completed shortly after the eruption and cooling of the basalts, within 1 Ma or less. The preservation of such an early age in F4 celadonite suggests that the effects of ongoing, low temperature circulation of seawater were limited near the top of the tholeiitic lava pile and that alteration effectively ceased shortly after the Vøring Plateau foundered. A possible explanation for this anomalously early cessation of alteration may be that the soils that had formed in the flows immediately above F4 became saturated with seawater, expanded, and formed a water-tight seal at the top of the section. Formation of such an impermeable barrier could then have effectively prevented further circulation of seawater in directly underlying units.

The three analyzed fractions of celadonite from F17 and F18 define a line on a $^{87}Sr/^{86}Sr$ vs. $^{87}Rb/^{86}Sr$ plot (Fig. 8) that has a slope corresponding to an isochron age of 24.3 ± 0.4 Ma and indicates an initial $^{87}Sr/^{86}Sr = 0.7087 \pm 0.0008$. This young age, about 30 m.y. younger than the model age of celadonite from the top of the section, is subject to several interpretations. It could be the result of ongoing exchange reactions, and thus be a mixing line with the apparent 24.3 ± 0.4 Ma age, in fact having no age significance beyond suggesting a minimum age for the cessation of celadonite formation. This interpretation is consistent with what is known about the ongoing nature of seawater circulation in oceanic basalts.

Alternatively, the 24.3 ± 0.4-Ma isochron could be dating some real event that promoted seawater circulation through Site 642 basalts about 30 m.y. after foundering. We can envisage a scenario that would allow this interpretation to be correct.

1. The impermeable barrier that may have formed from the water-saturated soils at the top of the volcanic sequence was laterally continuous and inhibited seawater circulation through most of the volcanic pile from about 54 to about 24 Ma, thus preventing early celadonite mineralization.
2. During the early Miocene to late Oligocene erosional event that affected the Norwegian-Greenland Sea (see Eldholm, Thiede, Taylor, et al., 1987), the barrier was breached and seawater gained entry to the (underpressured?) basaltic sequence.
3. Because no source of heat was available to drive prolonged circulation, reactions were of limited extent.

In this scenario, the 24.3 ± 0.4-Ma Rb-Sr isochron age would reflect the timing of the erosional event, which may have been contemporaneous with the late Oligocene sea-level low proposed by Vail and coworkers (Vail et al., 1977; Vail and Hardenbol, 1979).

Although we cannot discriminate between the mixing line and isochron interpretations with the currently available data, the scenario outlining the case for the isochron alternative has several features that are consistent with alteration at Site 642.

1. Celadonite mineralization is of limited extent, occurring in fewer than 10% of the flows. If low-temperature circulation of seawater occurred for a great length of time, late-alteration reactions might be expected to have been more ubiquitous.
2. The great majority of vesicles within the tholeiitic section are only lined or partially filled with alteration products of any sort. If circulation of seawater had occurred continuously for long periods of time, precipitation of secondary minerals might have been more extensive.

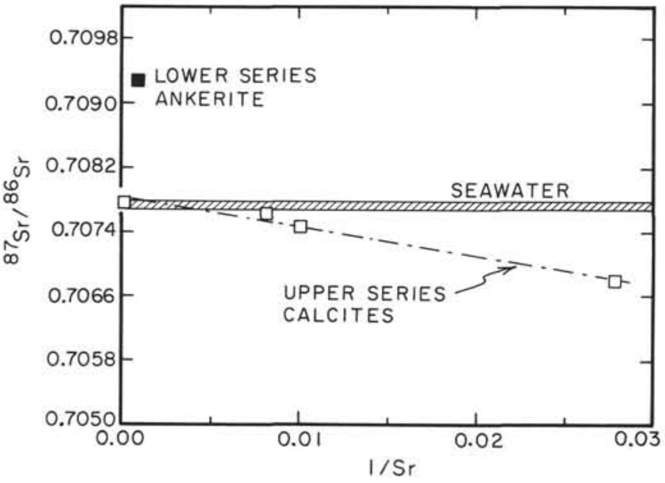

Figure 6. $^{87}Sr/^{86}Sr$ vs. 1/Sr concentration showing data from calcites precipitated in voids in upper series basalts (open squares) and ankerite from the lower series (filled square). The hachured area represents $^{87}Sr/^{86}Sr$ in Paleocene-Eocene seawater (0.7076–0.7077; Burke et al., 1982). The apparent mixing trend in calcites must be related to water/rock. Calcites formed at lower water/rock have lower Sr and a larger fraction that was ultimately derived from basalt. Tholeiitic basalts cannot be fit to the simple two- component mixing trend directly, but smectite containing about 30 ppm Sr and $^{87}Sr/^{86}Sr = 0.7066$ are consistent with the calcite mixing trend. Thus we believe that the calcite data support the conclusion that most of the late alteration involved reactions between seawater and preexisting smectites.

3. Finally, the scenario outlined above for producing a 24.3 ± 0.4-Ma age in the three celadonite fractions is consistent with geologic events that have affected the Norwegian–Greenland Sea.

GEOCHEMISTRY OF LOW-TEMPERATURE ALTERATION

Hydrothermal fluids venting at ridge crests allow direct investigation of fluid endproducts of high-temperature seawater–ocean crust interaction (e.g., Edmond et al., 1979; Von Damm et al., 1985a, b). Pore-water studies allow direct investigation of fluids involved in low-temperature processes (e.g., Lawrence et al., 1975; Lawrence and Gieskes, 1981). Direct studies of the rock side of the equation have been numerous, but the results are not as straightforward as those of studies of fluids because alteration products in the rocks generally reflect the continuum of high-to-low temperature effects present in most oceanic basalts.

The alteration history of tholeiites at Site 642 must have been quite different from that of typical MORB. During subaerial eruption and (closed system) sub-solidus cooling, alteration would primarily be manifest in mineralogic changes, oxidation states, and loss of volatile constituents, which would have little effect on the alkali element concentrations and $^{87}Sr/^{86}Sr$ discussed here.

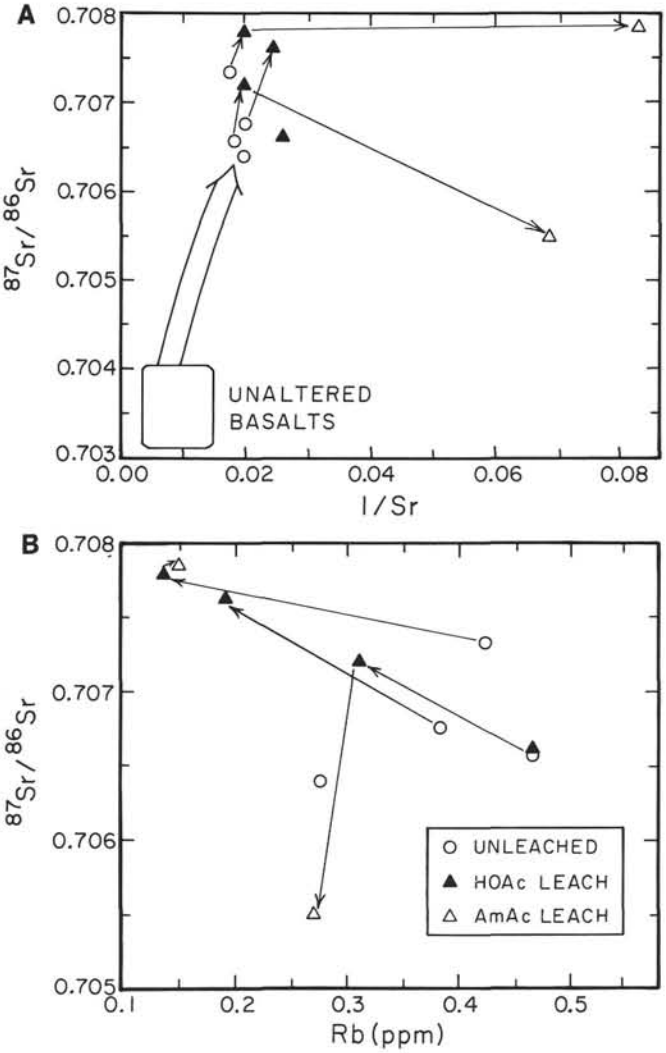

Figure 7. $^{87}Sr/^{86}Sr$ plotted against 1/Sr (A) and Rb concentration (B), showing the results of leaching experiments on smectites. A. Bulk (unleached) smectites appear to roughly define a trend indicating the mixing of Sr from seawater and from basalts. Acetic acid (HOAc) leaching, in every case, resulted in an increase in $^{87}Sr/^{86}Sr$ relative to bulk smectites. The $^{87}Sr/^{86}Sr$ of the Sr removed by HOAc leaching is calculated to have been in the range 0.703–0.704, identical to values in unaltered basalts. Further leaching with ammonium acetate (AmAc) resulted in substantial decreases in Sr concentrations and had variable effects on $^{87}Sr/^{86}Sr$. The diversity in $^{87}Sr/^{86}Sr$ within the smectites suggests exposure to Sr-bearing fluids at highly variable water/rock. The preservation of isotopic disequilibrium, which can not be due to radioactive decay, indicates that ongoing exchange reactions were of limited extent. B. Rubidium concentrations were significantiy lowered by the HOAc leach step. The AmAc leaching had much less of an effect on Rb.

Weathering in an intertidal environment (Shipboard Scientific Party, 1987) would produce subaerial alteration products and expose the recently erupted tholeiites to seawater in some limited fashion, but would not be expected to result in the sustained high water/rock and high-temperature fluid circulation typical of subaqueous ridge crest volcanism. The effects of low seawater/rock is evident at Site 642 in (a) the K, Rb, and Cs concentrations of the smectite population relative to concentrations observed in smectites in subaqueously erupted and altered basalts, and (b) the small effects of alteration on the alkali element concentrations and $^{87}Sr/^{86}Sr$ of the basalts themselves.

Early low seawater/rock conditions could also be the reason for the low $^{87}Sr/^{86}Sr$ in the AmAc-leached fraction of smectite from Sample 104-642E-60R-2, 21–23 cm. If the Sr removed by the HOAc leach resides in sites in smectites that most readily exchange with seawater, then the low $^{87}Sr/^{86}Sr$ (0.703–0.704) calculated to have been removed by mild acid leaching cannot be recording the earliest period of low seawater/rock, but must be reflecting a later episode of low water/rock that postdated the seawater-dominated system recorded in Sr isotope compositions of HOAc-leached fractions.

Table 3. Rb and Sr concentrations and Sr isotopic compositions of smectites and celadonites precipitated in vesicles in Hole 642E tholeiites.

Core-section,[a] interval (cm)	Depth (mbsf)	Unit	Type[b]	$^{87}Sr/^{86}Sr$	$^{87}Rb/^{86}Sr$	Sr (ppm)	Rb (ppm)	K (ppm)	Cs (ppm)
Smectites									
21-3, 128-131	467.0	F21	Unlchd	0.70640±2	0.0158	50.6	0.276	446	0.0070
33-5, 26-28	571.5	F38	Unlchd			50.4	8.51	2650	0.091
50-1, 10-12	711.2	F56	Unlchd			31.1	0.383	1156	0.023
			HOAc	0.70662±6	0.0352	38.2	0.465		
50-1, 76-78	711.8	F56	Unlchd	0.70676±6	0.0223	49.9	0.384	712	0.0090
			HOAc	0.70763±9	0.0136	40.8	0.192		
60-2, 21-23	784.3	F63	Unlchd	0.70657±5	0.0248	54.3	0.466	827	0.0084
			HOAc	0.70721±6	0.0179	50.3	0.311		
			AmAc	0.70551±3	0.0533	14.6	0.270		
77-2, 107-109	934	F89	Unlchd	0.70734±5	0.0217	56.6	0.424	261	0.022
			HOAc	0.70781±6	0.00784	50.4	0.137		
			AmAc	0.70786±3	0.0358	12.1	0.150		
Celadonites									
10-3, 57-60	381.7	F4	HOAc	0.80288±6	123	4.46	143		
16-3, 115-130	420.9	F17	HOAc	0.72362±5	42.6	10.2	150		
19-2, 4-8	443.7	F18	HOAc	0.71867±4	28.6	9.82	97.1		
			AmAc	0.72173±6	38.4	7.72	102		

[a] All sample numbers have the prefix "104-642E" and all cores are of type "R". A complete sample number witll therefore read, for example, "104-642E-21R-3, 128-131 cm".

[b] "Unlchd" refers to unleached mineral separates. "HOAc" and "AmAc" refer to acetic acid and ammonium acetate leaching, respectively, as described in text.

After the foundering of the Vøring Plateau, more sustained high seawater/rock would have been possible. The laterally continuous structure of flood basalt cooling units, along with the absence of deformation of the basalts, would, however, tend to restrict fluid flow to vesicular zones and fractures. If fluid flow was restricted in this manner, reactions involving cold seawater would have mainly occurred in vesicles and fractures that were partially to completely filled with preexisting smectite. The reactions that occurred during low temperature alteration, therefore, may have been due primarily to seawater-smectite interactions, without significant participation of the basalts.

From this point of view, the calcite data are most revealing. The correlation between $^{87}Sr/^{86}Sr$ and 1/Sr (Fig. 6) in the calcites indicates mixing of Sr between two endmembers: a radiogenic (approx. 0.708) endmember with high Sr concentration and a low Sr, nonradiogenic (<0.7068) endmember. Regression of the mixing line results in the equation

$$^{87}Sr/^{86}Sr = 0.70783—0.03622(1/Sr).$$

The intercept value of the regression suggests that the radiogenic endmember was Eocene or younger seawater. There is no way to fit a basaltic end-member containing 150–200 ppm Sr and with $^{87}Sr/^{86}Sr$ values of 0.703- 0.704 to the simple two-component mixing line. A smectite containing 30 ppm Sr and $^{87}Sr/^{86}Sr = 0.7066$, however, would be consistent with the mixing trend observed in calcites. These values are in line with Sr concentrations and isotope ratios observed in Hole 642E smectites.

The derivation of the unradiogenic Sr in calcites from preexisting smectites supports the suggestion that cold seawater and smectite react to form the late assemblage celadonite + calcite. The reactions involved may be generalized as

$$(1) \quad 2[(0.5\ Ca)(Fe, Al, Mg)_4(Si, Al)_8O_{20}(OH)_4 \,.\, nH_20 + 2K^+] \leftrightarrow$$
(smectite)

$$2[K_2(Fe, Al, Mg)_4(Si, Al)_8O_{20}(OH)_4 + nH_20 + 0.5\ Ca^{++}]$$
(celadonite)

$$(2) \quad 2(0.5\ Ca^{++}) + CO_2 + H_2O = CaCO_3 + 2H^+$$

The CO_2 of reaction (2) could be in the form of the carbonate or the bicarbonate ion, in the general case. The reaction as written, however, would result in an excess of H^+, which would facilitate a third reaction, something similar to which must have occurred in the subaerially oxidized basalts at Site 642 to account for the native Cu associated with the celadonite + calcite assemblage (LeHuray, this volume):

$$(3a) \quad 2(0.5\ CuO) + 2H^+ = Cu^\circ + H_20$$

and/or

$$(3b) \quad Cu_2O + 2H^+ = 2Cu^\circ + H_20.$$

If the scenario that late low-temperature alteration primarily involved preexisting secondary minerals and seawater is correct, then reactions must have proceeded under conditions ranging from very low to high water/rock. Low water/rock is indicated

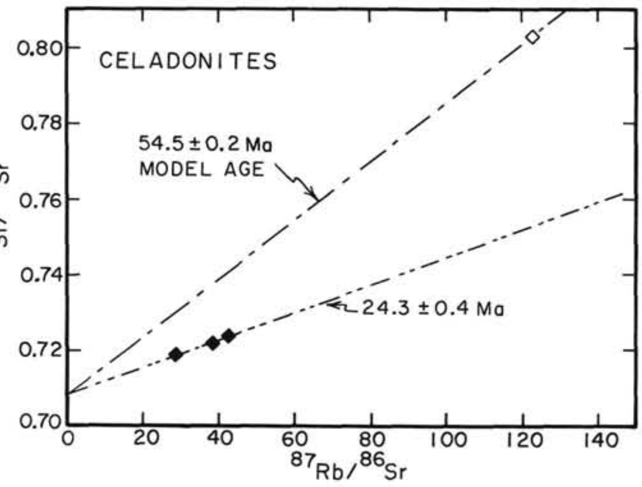

Figure 8. $^{87}Sr/^{86}Sr$ vs. $^{87}Rb/^{86}Sr$ plot of celadonite data. The single dashed line represents the slope required by the model age (54.5 ± 0.2 Ma; 0.7077 ± 0.0001 used as initial $^{87}Sr/^{86}Sr$) of celadonite from F4 (open diamond). Celadonites from F17 and F18 (filled diamonds) define an isochron with an age of 24.3 ± 0.4 Ma (initial $^{87}Sr/^{86}Sr$ = 0.7087 ± 0.0008). The older age is thought to reflect the timing of foundering of the Vøring Plateau. The younger age may represent a mixing line generated during prolonged low- temperature alteration or reflect a real event. One explanation that allows the latter interpretation of the young celadonite age could be that the soils at the top of the basaltic section formed an impermeable seal, preventing seawater from circulating through the basalts. The seal may have been breached during the late Oligocene, allowing seawater circulation and low-temperature formation of celadonites.

by the smectitelike Sr concentrations and $^{87}Sr/^{86}Sr$ of calcite from F105. High water/rock must have obtained in F17 to produce $^{87}Sr/^{86}Sr$ in calcite that is indistinguishable from that of seawater, and to produce calcite containing over 5000 ppm Sr (Table 2).

Without more complete information on the compositions of the smecites and celadonites involved and better thermodynamic data for clay minerals, evaluation of the reactions can only be qualitative. We can say, however, that the reaction is not isochemical, as has been suggested for smectite - celadonite transformations in other basalts (e.g., Stakes and Scheidegger, 1981), but involves net gains of K and CO_2 in the basalts. As celadonite is generally highly enriched in Fe relative to most smectites in seafloor basalts, another result may be a shift of smectites to more Mg-rich compositions. We cannot determine from the data presented here the extent of Fe-Mg exchange reactions, nor the degree to which they may be isochemical.

The smectites at Site 642 are not typical of smectites found in most altered seafloor basalts, particularly in their lower alkali element concentrations and probably in their higher Fe/Mg. The differences in K concentrations, however, are not as great as those between smectites in general and celadonite. We believe that it is reasonable to infer from the data presented here and from the gross similarity of Site 642 alteration events to those reported in subaqueously erupted basalts that the reaction smectite + seawater ↔ celadonite + calcite reflects net addition of K and CO_2 to ocean crust during late, low-temperature circulation of seawater.

ACKNOWLEDGMENTS

Conversations with H. Staudigel about technique were an invaluable help, as were ongoing discussions about the meaning of leaching results with H. Brueckner, D. Seidemann, and H. Staudigel. J. Mutter and C. Zehnder helped us understand the geology of the Norwegian margin and provided the map used for Figure 1. Patty Catanzaro drafted all other figures.

This work was supported by NSF-USSAC grant TAMRF76252. ESJ also acknowledges a Columbia University Dept. of Geological Sciences (L-DGO) Summer Internship.

REFERENCES

Bass, M. N., 1976. Secondary minerals in oceanic basalt, with special reference to Leg 34, Deep Sea Drilling Project. *In* Yeats, R. S., Hart, S. R., *Init. Repts. DSDP*, 34: Washington (U.S. Govt. Printing Office), 393-432.

Bischoff, J. L., and Dickson, F. W., 1975. Seawater-basalt interaction at 200°C and 500 bars: Implications for origin of seafloor heavy-metal deposits and regulation of seawater chemistry. *Earth Planet. Sci. Lett.*, 25: 385-397.

Burke, W. H., Denison, R. E., Hetherington, E. A., Koepnick, R. B., Nelson, H. F., and Otto, J. B., 1982. Variation of seawater $^{87}Sr/^{86}Sr$ throughout Phanerozoic time. *Geology*, 10: 516-519.

DePaolo, D. J., 1986. Detailed record of the Neogene Sr isotopic evolution of seawater from DSDP site 590B. *Geology*, 14: 103-106.

Desprairies, A., Bonnot-Courtois, C., Jehanno, C., Vernhet, S., and Joron, J. L., 1984. Mineralogy and geochemistry of alteration products in Leg 81 basalts. *In* Roberts, D. G., Schnitker, D., et al., *Init. Repts. DSDP*, 81: Washington (U.S. Govt. Printing Office), 733-742.

Edmond, J. M., Measures, C. I., McDuff, R. E., Chan, L. H., Collier, R., Grant, B., Gordon, L. I., and Corliss, J. B., 1979. Ridge crest hydrothermal activity and the balances of the major and minor elements in the ocean: The Galapagos data. *Earth Planet. Sci. Lett.*, 46: 1-18.

Eldholm, O., Thiede, J., Taylor, E., et al., 1987. *Proc. ODP, Init. Repts.*, 104: College Station, TX (Ocean Drilling Program).

Hajash, A., 1975. Hydrothermal processes along mid-ocean ridges: An experimental investigation. *Contrib. Mineral. Petrol.*, 53: 205-226.

Hart, S. R., and Staudigel, H., 1978. Oceanic crust: Age of hydrothermal alteration: *Geophys. Res. Lett.*, 5: 1009-1012.

Hart, S. R., and Staudigel, H., 1979. Ocean crust-sea water interaction: Sites 417 and 418. *In* Donnelly, T., Francheteau, J., et al. (Eds)., *Init. Repts. DSDP*, 51, Pt. 2, 52, 53: Washington (U.S. Govt. Printing Office), 1169-1176.

Hart, S. R., and Staudigel, H., 1979. Ocean crust-sea water interaction: Sites 417 and 418. *In* Donnelly, T., Francheteau, J., et al. (Eds)., *Init. Repts. DSDP*, 51, Pt. 2, 52, 53: Washington (U.S. Govt. Printing Office), 1169-1176.

Hart, S. R., and Staudigel, H., 1982. The control of alkalies and uranium in seawater by ocean crust alteration. *Earth Planet. Sci. Lett.*, 58:202-212.

Hinz, K., Mutter, J. C., Zehnder, C. M., and the NGT Study Group, 1987. Symmetric conjugation of continent-ocean boundary structures along the Norwegian and East Greenland margins. *Mar. Pet. Geol.*, 5: 166-187.

Kharin, G., Udintsev, G. B., Bogatikov, 0.·A., Dmitriev, J. I., Raschka, H., Kreuzer, J., Mohr, M., Harre, W., and Eckhart, F. J.,, 1976. K/Ar ages of the basalts of the Norwegian-Greenland Sea, DSDP Leg 38. *In* Talwani, M., Udintsev, G., *Init. Repts. DSDP*, 38: Washington (U.S. Govt. Printing Office), 755-759.

Lawrence, J. R., 1979. Temperatures of formation of calcite veins in the basalts from DSDP holes 417A and 417D. *In* Donnely, M., Francheteau, J., et al., *Init. Repts. DSDP*, 51, 52, 53, Pt. 2: Washington (U.S. Govt. Printing Office), 1183-1184.

Lawrence, J. R., and Drever, J. I., 1981. Evidence for cold water circulation at DSDP site 395: Isotopes and chemistry of alteration products: *J. Geophys. Res.*, 86: 5125-5133.

Lawrence, J. R., and Gieskes, J. M., 1981: Constraints on water transport and alteration in the oceanic crust from the isotopic composition of pore water. *J. Geophys. Res.*, 86: 7924-7934.

Lawrence, J. R., Gieskes, J. M, and Broecker, W. S., 1975. Oxygen isotope and cation compositions of DSDP pore waters and the alteration of layer II basalts. *Earth Planet. Sci. Lett.*, 27: 1- .

Macintyre, R. M., and Hamilton, P. J., 1984. Isotopic geochemistry of lavas from Sites 553 and 555. *In* Roberts, D. G., Schnitker, D., et al., *Init. Repts. DSDP*, 81: Washington (U.S. Govt. Printing Office), 775-781.

Morton, J. P., and Long, L. E., 1980. Rb-Sr dating of Paleozoic glauconite from the Llano region, central Texas. *Geochim. Cosmochim. Acta*, 44: 663- 672.

Mutter, J. C., Buck, W. R., and Zehnder, C. M., 1988. Convective partial melting 1. A model for the formation of thick basaltic sequences during the initiation of spreading. *J. Geophys. Res.*, 93: 1031-1048.

Mutter, J. C., 1984. Cenozoic and late Mesozoic stratigraphy and subsidence history of the Norwegian margin. *Geol. Soc. Am. Bull.*, 95: 1135-1149.

Perry, E., and Hower, J., 1970. Burial diagenesis in Gulf Coast pelitic sediments. *Clays and Clay Miner.*, 18: 165-177.

Richardson, S. H., Hart, S. R., and Staudigel, H., 1980. Vein mineral ages of old ocean crust. *J. Geophys. Res.*, 85: 7195-7200.

Scheidegger, K. F., and Stakes, D. S., 1980, X-ray diffraction and chemical study of secondary minerals from Deep Sea Drilling Project Leg 51, holes 417A and 417D. *In* Donnelly, T., Francheteau, J., et al., *Init. Repts. DSDP*, 51, 52, 53, Pt. 2: Washington (U.S. Govt. Printing Office, 1253-1263.

Seidemann, D. E., 1977. The effects of alteration on K-Ar dates of deep-sea basalts. *Geol. Soc. Am. Bull.*, 88:1660-1666.

Seyfried, W. E., and Janecky, D. R., 1985. Heavy metal and sulfur transport during subcritical and supercritical hydrothermal alteration of basalt: influence of fluid pressure and basalt composition and crystallinity. *Geochim. Cosmochim. Acta*, 49:2545-2560.

Shipboard Scientific Party, 1987. Site 642: Norwegian Sea. *In* Eldholm, O., Thiede, J., Taylor, E., et al., 1987. *Proc. ODP, Init. Repts.*, 104: College Station, TX (Ocean Drilling Program), 53-453.

Sleep, N. H., 1975. Formation of ocean crust: some thermal considerations. *J. Geophys. Res.*, 80: 4037-4042.

Srodon, J., and Eberl, D. D., 1984. Illite. *In* Bailey, S. W., (Ed.), Micas: *Rev. Mineral.*, 13: 495-544.

Stakes, D. S., and O'Neil, J. R., 1982. Mineralogy and stable isotope geochemistry of hydrothermally altered oceanic rocks. *Earth Planet. Sci. Lett.*, 57: 285-304.

Stakes, D. S., and Scheidegger, K. F., 1981. Temporal variations in secondary minerals from Nazca Plate basalts: *Geol. Soc. Am. Mem.* 154, 109-130.

Staudigel, H., and Hart, S. R., 1985. Dating of ocean crust hydrothermal alteration: strontium isotope ratios from Hole 504B and a reinterpretation of Sr isotope data from Deep Sea Drilling Project Sites 105, 332, 417, and 418. *In* Anderson, R. N., Honnorez, J., et al., *Init. Repts. DSDP*, 83: Washington (U.S. Govt. Printing Office), 297-303.

Staudigel, H., Gillis, K., and Duncan, R., 1986. K/Ar and Rb/Sr ages of celadonites from the Troodos ophiolite, Cyprus. *Geology*, 14: 72-75.

Staudigel, H., Hart, S. R., and Richardson, S. H., 1981a. Alteration of the oceanic crust: processes and timing. *Earth Planet. Sci. Lett.*, 52: 311-327.

Staudigel, H., Muehlenbachs, K., Richardson, S. H., and Hart, S. R., 1981b. Agents of low temperature ocean crust alteration. *Contrib. Mineral. Petrol.*, 77: 150-157.

Talwani, M., and Eldholm, O., 1977. Evolution of the Norwegian-Greenland Sea. *Geol. Soc. Am. Bull.*, 88: 969-999.

Talwani, M., Mutter, J., and Eldholm, O., 1981. Initiation of the opening of the Norwegian Sea. *Ocean. Acta*, no.SP, 23-30.

Vail, P. R., and Hardenbol, J., 1979. Sea-level changes during the Tertiary. *Oceanus*, 22: 71-79.

Vail, P. R., Mitchum, R. M., Todd, R. G., Widmier, J. M., Thompson, S., Sangree, J. B., Bubb, J. N., and Hatlelid, W. G., 1977. Seismic stratigraphy and global changes of sea level. *Am. Assoc. Pet. Geol., Mem.*, 26: 49-212.

Von Damm, K. L., Edmond, J. M., Grant, B., Measures, C. I., Walden, B., and Weiss, R. F., 1985a. Chemistry of submarine hydrothermal solutions at 21°N, East Pacific Rise. *Geochim. Cosmochim. Acta*, 49: 2197-2220.

Von Damm, K. L., Edmond, J. M., Measures, C. I., and Grant, B., 1985b. Chemistry of submarine hydrothermal solutions at Guaymas Basin, Gulf of California. *Geochim. Cosmochim. Acta*, 49: 2221-2237.

York, D., 1969. Least squares fitting of a straight line with correlated errors. *Earth Planet. Sci. Lett.*, 5: 320-324.

Date of initial receipt: 28 April 1987
Date of acceptance: 27 June 1988
Ms 104B-138