

30. B, Li, AND ASSOCIATED TRACE ELEMENT CHEMISTRY OF ALTERATION MINERALS, HOLES 597B AND 597C¹

Michael Berndt and William E. Seyfried, Jr.
Department of Geology and Geophysics, University of Minnesota²

ABSTRACT

B, Li, and other trace elements were analyzed in samples from 12 celadonite and smectite-rich veins from oxidative and non-oxidative alteration zones in basalts from Holes 597B and 597C. The oxidative alteration zones are characterized by celadonite and Fe-oxyhydroxide and conspicuously high K, Rb, and B concentrations. In contrast, the non-oxidative alteration zones are characterized by Mg-rich smectite (saponite), talc, and calcite and high Li concentrations. Neither B nor Li reaches high concentrations in high-Al high-Ti veins that appear to have formed by replacement of basalt. B, Li, and Rb enrichments in vein assemblages of low-temperature origin reflect an important removal mechanism from seawater for these species.

The alteration zones characterized by Mg-smectite and talc are strikingly enriched in Ni. There is a correlation between the Ni-enriched smectite and the presence of olivine in the host basalt; the correlation indicates that olivine alteration may be the source of the Ni. Other transition elements, including Cr, Mn, Co, Cu, and Zn, are often found in significant concentrations in the celadonite and high-Mg smectite veins, but their enrichments are neither as large nor as consistent as the enrichment of Ni in the Mg-smectite veins.

Two high-Al, high-Ti vein assemblages of smectite and noncrystalline phases have transition element abundances similar to those of the host basalts but are relatively depleted in Cu and Cr. The material in these veins may have formed by replacement with concomitant release of Cu and Cr to circulating aqueous fluids.

INTRODUCTION

Low-temperature basalt-seawater interaction significantly affects the chemistry and mineralogy of the upper portions of oceanic crust. In basalt exposed to oxygenated seawater, zeolites (e.g., phillipsite), celadonite, Fe-oxides and oxyhydroxides, and Mn-oxides fill fractures and vesicles; in deeper basalts, which are exposed to a relatively oxygen-depleted, chemically evolved fluid of seawater derivation, such phases as saponite, talc, and calcite characterize alteration (Bass, 1976; Donnelly, Thompson, et al., 1980; Honnorez, 1981; Thompson, 1983). These ubiquitous alteration products greatly influence the geochemical cycles of numerous elements (e.g., oxygen isotopes, Muehlenbachs and Clayton, 1976; K, Rb, Cs, and U, Hart and Staudigel, 1982; and other elemental components dissolved in seawater, Thompson, 1983, and references therein).

The geochemical cycles of B and Li appear to be strongly influenced by both low-temperature diagenesis and the hydrothermal alteration of basalt (Edmond et al., 1979; Thompson, 1983; Seyfried et al., 1984; Stoffyn-Egli and Mackenzie, 1984). B and Li are conspicuously enriched in basalt altered by seawater at relatively low temperatures (Thompson, 1983; Donnelly, Pritchard, et al., 1980) but are leached from basalt during high-temperature hydrothermal alteration (Edmond et al., 1979; Edmond et al., 1982). Seyfried et al. (1984) have experimentally demonstrated that B and Li are removed

from solution and enriched in various alteration phases at temperatures below 150°C during basalt-seawater interaction, whereas at temperatures greater than 150°C these species partition effectively into the fluid phase. B, however, is more effectively leached than Li (Seyfried et al., 1984).

Recent estimates of the magnitude of B and Li removal from seawater during low-temperature basalt-seawater interaction range up to 40% and 78% of the river flux of these species, respectively (Seyfried et al., 1984; Stoffyn-Egli and Mackenzie, 1984). However, the accuracy of these estimates is critically dependent on the actual abundances of B and Li concentrations in discrete alteration phases of basalt and vein minerals. In this study the distribution of B and Li in vein alteration assemblages is studied in detail. We are particularly concerned about the following:

1. How are B and Li distributions influenced by redox reactions as reflected by the concentrations of these species in oxidative and non-oxidative portions of altered oceanic crust?
2. What is the extent of chemical and mineralogic control on the distribution of B and Li in low-temperature alteration phases?
3. What are the chemical and mineralogic controls on the distribution of other selected trace elements (e.g., Rb, Sr, Ba, Sc, V, Cr, Co, Ni, Cu, Zn, Y, Ga)?

METHODS AND PROCEDURES

Samples were carefully separated from 12 different veins and ground lightly in an agate mortar until each sample was homogeneous. Aliquots of 5 to 10 mg were used for X-ray diffraction analysis; an additional aliquot of 10 mg was used for B analysis. The remaining material was used for major, minor, and trace element analysis. If sufficient material was available, a < 1 μ m fraction was size separated for clay mineral X-ray diffraction purposes.

¹ Leinen, M., Rea, D. K., et al., *Init. Repts. DSDP*, 92: Washington (U.S. Govt. Printing Office).

² Address: Department of Geology and Geophysics, University of Minnesota, Minneapolis, MN 55455.

X-ray diffraction analysis was carried out on bulk and $<1\ \mu\text{m}$ fractions by using a Norelco X-ray diffractometer with curved crystal monochromator and $\text{CuK}\alpha$ radiation. Diffractograms were run from 2 to $30^\circ\ 2\theta/\text{min}$ on oriented mounts to enhance clay mineral basal reflections. Both untreated and glycerated samples were analyzed to distinguish smectite from other phyllosilicate phases.

A spectrophotometric technique modified after that of Bhargava and Hines (1970) was employed for B analysis. This technique involved the dissolution of the sample in a mixture of HF , H_3PO_4 , H_2O_2 , $\text{NH}_4\text{F} \cdot \text{HF}$, and Fe metal, which was followed by the addition of methylene blue and hexamethylene tetramine solution. Fe metal was dissolved along with the sample to catalyze formation of the BF_4^- complex. Spectrophotometric measurements were made on the fluoroborate-methylene blue complex after it was separated from the matrix by a double extraction process with dichloroethane. Appropriate rock standards spiked with B were used to evaluate the accuracy of the technique, and the accuracy of the B values reported for these samples was $\pm 5\%$.

The major and minor element chemistry of all samples was analyzed; each analysis used 10 to 60 mg of material. Sample material was digested at room temperature in a mixture of HF and HCl . Following dissolution, sufficient boric acid was introduced to complex excess F^- . Major element chemistry was determined on highly diluted solutions by DC-plasma atomic emission spectrometry. Solutions chemically equivalent to the major element chemistry of samples were then prepared from ultra-pure chemicals. These solutions were spiked with appropriate additions of Li, Rb, Ba, Sr, Sc, V, Cr, Co, Ni, Cu, Zn, Y, and Ga and used as standards for trace element determinations. The blank solution for these determinations contained the major element chemistry of the sample but lacked addition of the trace element components. Error analysis revealed that the accuracy of the reported concentrations of trace elements ranged from ± 2 to $\pm 10\%$.

RESULTS

X-Ray Diffraction Analysis

X-ray diffraction analysis of vein separates revealed celadonite, smectite, talc, and calcite (Table 1). In some veins the celadonite was very poorly crystallized (it is called proto-celadonite in Table 1), as indicated by the relative sparsity and typical asymmetry of X-ray diffrac-

tion reflections. In addition, the celadonite was often discolored red or yellow, indicating the presence of a discrete Fe-oxyhydroxide phase. This phase was amorphous, as indicated by its failure to generate any X-ray diffraction reflections, but, as will be discussed later, chemical analysis reveals it to be a significant phase in at least three of the veins.

Smectite, talc, and calcite, in contrast, were well crystallized, as indicated by sharp and relatively intense X-ray reflections. These phases often occur together (Table 1), and their well crystallized nature and the absence of discrete Fe-oxide phases suggest formation under relatively reducing conditions.

Vein material contamination by nonvein minerals was indicated by the presence of plagioclase feldspar reflections in many of the X-ray diffraction patterns. Such contamination was unavoidable, because many of the veins were extremely thin and irregular, and large amounts of material were required for trace element analysis. However, the contamination complicates the handling of the chemical data.

Major Element Chemistry

Major element chemistry of vein alteration reflects, as one would expect, mineralogic variability. For example, celadonite-rich samples are characterized by relatively high K_2O and $\text{Fe}_2\text{O}_{3\text{T}}$ and low Al_2O_3 (Table 2). The extremely high concentration of $\text{Fe}_2\text{O}_{3\text{T}}$ in several of the celadonite-rich veins (for example 597C-7-1, 7-9 cm) is well above that found in pure celadonite at other localities (where it was generally $<25\%$; Weaver and Pollard, 1973). Thus, we infer the presence of Fe-oxyhydroxides, which act to dilute celadonite components and enhance $\text{Fe}_2\text{O}_{3\text{T}}$. The high Ca and Ti contents of some of the celadonites indicate that the samples are not pure mineral separates. An attempt was made to estimate the total amount of impurities in collected samples from the amount of Ti they contain.

Ti is considered to be essentially immobile during low-temperature basalt-seawater interaction (Honnorez, 1981). Two explanations are possible for the occurrence of appreciable amounts of Ti in some of the samples: (1) it can be considered a sampling artifact, because small but significant amounts of basaltic material were included with vein materials; or (2) it can be considered a residual phase; that is, Ti may have been left behind during the alteration and replacement of host rock components. Microprobe analysis of high-Mg smectites (saponites) and celadonites from other DSDP drill cores generally reveals average TiO_2 concentrations below 0.07 wt. % (Donnelly, Pritchard, et al., 1980), but many individual analyses reveal much higher Ti contents. All samples in the present study have TiO_2 contents of 0.14 wt. % or more. Samples with the highest TiO_2 contents in this study were usually obtained from the thinnest veins and revealed plagioclase reflections in their X-ray diffraction patterns. Therefore, it is assumed that most of the Ti in the samples came from the sampling of altered wallrock immediately adjacent to the vein. An exception to this generalization is Sample 597C-9-3, 6-8 cm, which not only had the highest TiO_2 concentrations but also came from a thick,

Table 1. Description and mineralogy of veins from Hole 597B and 597C basalts.

Sample (interval in cm)	Description	Mineralogy
597B-2-3, 89-93	0.4-mm-wide vein filled with light green to yellow mineral	Proto-celadonite ^a
597C-4-4, 16-23	Very thin coating of dark green clay minerals on both surfaces of open fracture	Smectite
597C-7-1, 7-9	0.6-mm-wide vein filled with light green mineral, stained yellow to red in places	Proto-celadonite, Fe-oxyhydroxide
597C-7-1, 129-132	0.5-mm coating of brown to yellow brown stained mineral on fracture surface	Proto-celadonite, Fe-oxyhydroxide
597C-8-3, 110-112	0.4-mm-wide vein filled with green mineral	Celadonite, minor smectite
597C-9-3, 6-8	~1-mm-thick coat of flaky green gray material on a fracture surface	Smectite
597C-9-4, 122-128	Extremely thin coat of green gray mineral on a fracture surface	Smectite
597C-10-1, 7-12	Fracture surface coated with dark green mineral, stained red brown in places	Celadonite, Fe-oxyhydroxide, minor smectite
597C-10-6, 57-62	Fracture surface coated with dark green to brown clay mineral and minor calcite	Smectite, calcite
597C-10-6, 90-94	Fracture surface with thick coat of green to brown clay minerals	Smectite, talc
597C-11-2, 21-27	Fracture surface with thick coat of dark green mineral and calcite	Smectite, calcite, talc
597C-11-2, 77-84	Fracture surface with somewhat thick coat of dark green clay, stained red in places	Smectite, calcite

^a Very poorly crystallized celadonite; see Results (this chapter).

Table 2. Chemical analyses of celadonite-rich veins, interlaboratory basalts, and smectite-talc-calcite veins from Holes 597B and 597C.

Sample Interval (cm)	Celadonite-rich veins					Interlab basalts		High-Mg smectite-rich veins					High-Al, high-Ti, smectite-rich veins	
	597B-2-3 89-93	597C-7-1 7-9	597C-7-1 129-132	597C-8-3 110-112	597C-10-1 7-12	597C-4-5 120-130	597C-8-2 85-96	597C-4-4 16-23	597C-10-6 57-62	597C-10-6 90-94	597C-11-2 21-27	597C-11-2 77-84	597C-9-3 6-8	597C-9-4 122-128
Oxides (wt. %)														
SiO ₂	48.1	41.8	36.4	48.2	43.3	50.8	50.8	46.8	41.2	47.0	36.9	42.6	45.6	49.9
TiO ₂	0.40	0.20	0.29	0.37	0.18	1.35	1.50	0.67	0.29	0.16	0.15	0.14	1.94	0.86
Al ₂ O ₃	3.85	2.85	4.30	5.94	2.67	14.8	13.8	7.25	9.0	5.48	8.1	9.1	13.5	10.7
Fe ₂ O _{3T} ^a	26.5	37.0	41.2	23.4	33.8	11.8	13.2	16.2	16.5	13.6	12.3	18.7	15.2	15.4
MnO	0.038	0.14	0.14	0.14	0.11	0.164	0.196	0.10	0.21	0.14	0.19	0.14	0.14	0.12
MgO	4.3	3.2	4.7	4.6	3.9	7.34	7.25	10.6	14.8	21.0	13.2	14.3	10.5	10.5
CaO	2.38	2.01	2.85	6.11	1.85	11.8	11.1	4.69	6.73	2.34	15.0	2.57	4.79	6.35
Na ₂ O	0.05	0.35	0.67	1.65	0.53	2.44	2.50	1.83	0.65	1.17	1.57	2.55	2.94	2.62
K ₂ O	5.55	4.36	2.07	2.59	4.59	0.052	0.116	0.17	0.56	0.40	0.36	0.34	0.13	0.14
P ₂ O ₅	NA	NA	NA	NA	0.04	0.104	0.121	NA	0.06	0.99	0.05	NA	0.19	0.08
Total	91.2	91.9	92.6	93.0	90.9	100.7	100.6	88.3	90.0	92.3	87.8	90.4	94.9	96.7
Element (ppm)														
B	670	660	335	NA	477	NA	NA	NA	108	63	50	NA	11	39
Li	18	8	8	<2	11	NA	NA	41	71	77	72	43	14	<4
Rb	220	151	71	82	258	<1	2	<10	169	12	9	<3	4	6
Sc	36	10	7	26	11	44	46	25	12	6	15	5	35	42
V	106	67	75	121	130	345	390	192	91	120	53	95	399	256
Cr	85	72	51	47	27	197	97	373	63	5	192	18	22	39
Co	<4	20	<4	19	17	42	46	16	88	47	56	79	40	43
Ni	47	61	29	28	25	63	55	159	287	175	206	231	37	41
Cu	166	41	21	8	10	136	149	22	531	77	177	95	2	9
Zn	180	22	32	60	33	97	105	62	71	31	44	54	83	98
Sr	29	32	39	44	25	88	82	51	200	30	66	32	78	54
Ba	9	33	10	10	19	12.2	10.3	10	52	110	7	12	10	10
Y	NA	NA	NA	NA	38	33	35	NA	20	23	14	NA	52	21
Ga	NA	NA	NA	NA	10	17	15	NA	<20	10	14	NA	10	12

Note: NA = not analyzed.

^a Total Fe expressed in wt. % Fe₂O₃.

easy-to-sample vein and revealed no contaminants in X-ray diffraction patterns. Thus, (2) above best explains the relatively high Ti content of this sample.

The amount of Ti that a sample contains can be used to estimate the upper limit of the sampling-induced contamination of vein samples by basalt. The Ti contents of the interlaboratory basalts collected from Hole 597C, if these basalts are assumed to be representative of the host basalts (Table 2), suggest that the upper limit of the amount of basalt included with vein mineralization as a result of sampling ranges from 10 to 60%. This estimate seems high, and the X-ray diffraction results suggest that some Ti occurs in the vein minerals themselves.

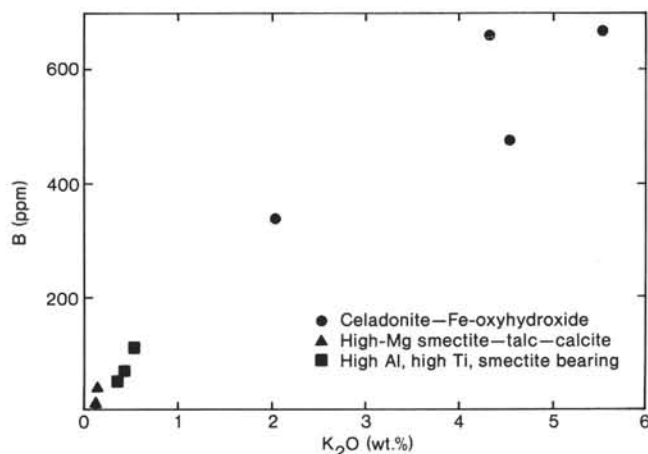
Smectite-rich assemblages contain relatively high Fe₂O_{3T} and MgO contents, are low in alkalis (especially K₂O), and contain variable amounts of Al₂O₃ (Table 2). The high Al₂O₃ and TiO₂ contents of smectite-rich samples from the veins at 597C-9-3, 6-8 cm and 597C-9-4, 122-128 cm, combined with the samples' high total oxides, indicate that these veins probably contain large components of extensively altered basalt in addition to the smectite clay minerals that were revealed in the X-ray patterns. These smectites may be dioctahedral Al-rich varieties, although this possibility has not been verified by X-ray diffraction. Material chemically analogous to dioctahedral Al-rich smectite has been identified at numerous DSDP sites (see Honnorez, 1981, and references therein), as has the high-Mg variety of smectite, which is presumably a trioctahedral phase, possibly iron-rich saponite (Seyfried et al., 1978).

The surprisingly large amount of P₂O₅ in Sample 597C-10-6, 90-94 cm (0.99%, Table 2) can only be interpreted as being due to the presence of a mineral such as apatite or a compositional equivalent.

Trace Elements

Boron

Trace element data for the vein alteration assemblages (Table 2) indicate that relative to the mid-ocean-ridge basalt B is greatly enriched in highly oxidized celadonite-dominated alteration zones but only slightly enriched in Mg-rich smectite zones; that is, the B concentration in celadonite greatly exceeds that in the Mg-rich smectite phases. The abundance of B in these low-temperature alteration products of basalt is directly related to the abundance of K (Fig. 1), a relation that indicates that celadonite is the dominant repository for the B. The K/B ratio of 65 is less than that of seawater (88), a comparison that suggests that B is extracted from seawater slight-

Figure 1. B versus K₂O for Hole 597B and 597C vein samples.

ly more efficiently than K; we are assuming, of course, that a fluid of seawater chemistry was involved in the alteration processes that resulted in celadonite formation. Donnelly, Pritchard, et al. (1980) noted a K/B ratio of 470 in altered basalts, 310 in hyaloclastites, and 100 in fresh basalts from DSDP Hole 417D. Thus, for whole rock alteration, it would appear that K is more efficiently extracted from seawater than B.

Typical celadonites have a K_2O content of about 7% (Donnelly, Pritchard, et al., 1980). Thus, a K/B ratio of 65 would suggest that pure celadonite contains roughly 900 ppm B, less than half the 2000 ppm predicted by Harder (1970) for micas precipitated from seawater.

Lithium

The distribution of Li in the vein assemblages is more difficult to interpret than the distribution of B. In general, Li concentrations are low in the celadonite-rich alteration zones and in high- Al_2O_3 smectite-rich veins, but they are high in the high-Mg smectite-rich, talc-bearing veins (Table 2). Thus, the concentration of lithium covaries with the concentration of Mg (Fig. 2) and is inversely related to the concentration of K. The fairly low Li concentrations in the celadonite and Fe-oxyhydroxide-rich veins may be related to the relatively low MgO contents of these phases. The low concentrations of Li in the veins at 597C-9-3, 6-8 cm and 597C-9-4, 122-128 cm are anomalous and may be related to the particular mode of formation of the smectites in these veins.

Selected Transition Elements (Sc, Ti, V, Cr, Mn, Co, Ni, Cu, Zn)

Transition element concentrations (except for Fe) for the three groups of alteration phases are presented in Table 2 and Figures 3A to C. In Figures 3A to C the maximum amount of trace element addition due to contamination by host basalt can be inferred by noting the level at which Ti plots on the diagram and drawing a straight horizontal line through it. In effect, this type of diagram illustrates the relative mobility of each of the elements. An element that plots significantly above the Ti

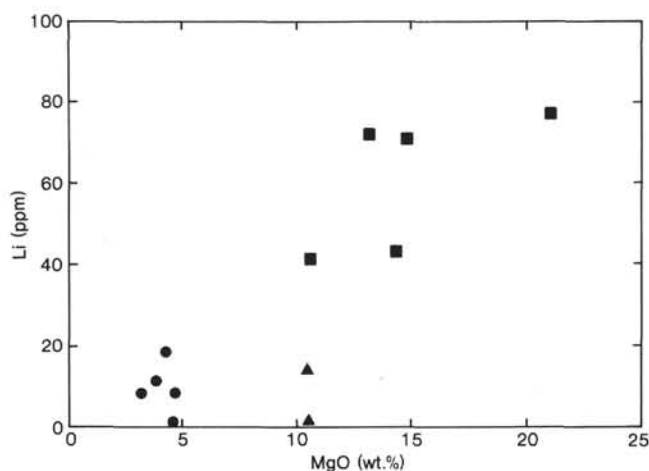


Figure 2. Li versus Mg for Hole 597B and 597C vein samples. Legend as in Figure 1.

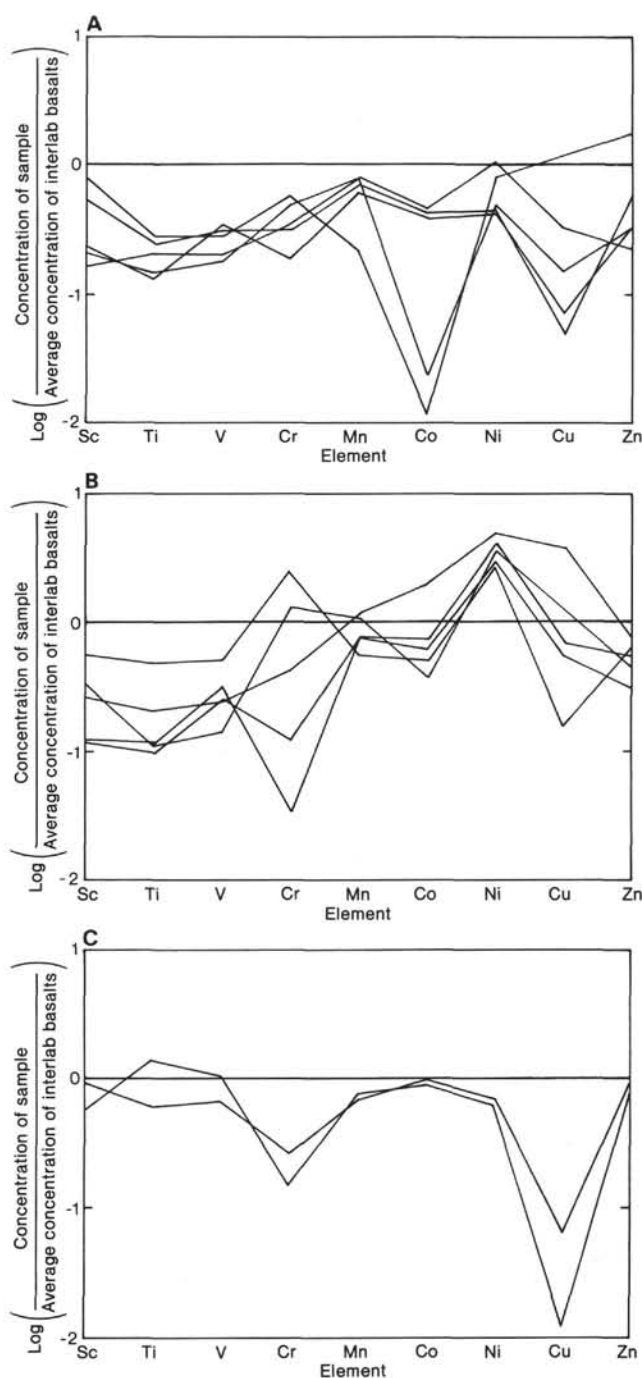


Figure 3. Normalized transition element (except Fe) concentrations of Hole 597B and 597C vein materials. The normalizing values are the average concentrations of interlab basalts (listed in Table 2) from Hole 597C. A. Celadonite-Fe-oxyhydroxide assemblages. B. High-Mg smectite-talc-calcite assemblages. C. High-Al, high-Ti, smectite-bearing assemblages.

ratio for a given sample indicates transport to the vein in fluids during alteration of the rock. Conversely, an element that plots significantly below this ratio indicates removal of that element from basalt during the alteration of the host rock.

Definite trends are apparent within each group. For example, celadonite-rich samples show only slight and

variable enrichment of the Cr–Zn transition elements in comparison with the so-called immobile elements (Sc, Ti, V; Fig. 3A). High-Mg smectite, talc-rich veins (Fig. 3B) are generally enriched in Cr–Zn transition elements (especially Ni) compared with Sc, Ti, and V, whereas in the high- Al_2O_3 , high- TiO_2 smectite assemblage (Fig. 3C), the transition element ratios are similar to unaltered host basalt, with the exception of Cr and Cu.

Rb

The concentrations of Rb in vein assemblages are closely related to the concentrations of K (Fig. 4). Sample 597C-10-6, 57–62 cm does not obey this relationship, however, and may have a source of Rb other than celadonite, the dominant K-rich mineral. The relationship between K and Rb in altered oceanic basalt has been previously reported (e.g., see Humphris et al., 1980; Hart and Staudigel, 1982). Typically, whole rock alteration results in higher K/Rb ratios than the alteration of vein-rich assemblages. For example, Humphris et al. (1980) report a K/Rb ratio of 800 for whole rock alteration at DSDP Holes 417A and 418A, and Hart and Staudigel (1982) report K/Rb values of approximately 533 and 348 for whole rock and smectite-palagonite-rich alteration, respectively, at DSDP Hole 418A. The K/Rb ratio of approximately 240 (excluding Sample 597C-10-6, 57–62 cm) in vein assemblages from Holes 597B and 597C is distinctly lower than any previously reported ratio.

Y, Ga, Ba, Sr

Our data show that Y and Ga concentrations in vein alteration from Holes 597C and 597B are not greatly different from an inferred unaltered host basalt (i.e., interlab basalts 597-4-5, 120–130 cm; Table 2). Two low- Al_2O_3 , smectite-rich samples (597C-10-6, 57–62 cm and 597C-10-6, 90–94 cm) have conspicuously high Ba values; all other samples have Ba concentrations similar to unaltered basalt. The Ba-rich samples may contain small but significant amounts of calcareous sediment. Calcite was identified in one of these samples (597C-10-6, 57–62 cm); the other (597C-10-6, 90–94 cm) contained anom-

alous P_2O_5 but no detectable carbonate- or phosphate-bearing phase.

Sr was less concentrated in the vein samples than in the interlab basalts in all except one sample (597C-10-6, 57–62 cm). As noted previously, this sample was also anomalous in Rb. The high Sr in this sample may be related to the presence of calcite, although Sample 597C-11-2, 21–27 cm, which contained considerably more calcite, had distinctly less Sr. It is more likely that the anomalous behavior of Rb, Sr, and Ba in Sample 597C-10-6, 57–62 cm is related to a single as yet unknown cause.

DISCUSSION

Seyfried et al. (1984) have experimentally documented the temperature dependence of B and Li exchange during basalt–seawater interaction. In addition to temperature, however, alteration chemistry and mineralogy greatly constrain the exchange reactions of these two species. For example, the results of the present investigation leave little doubt that celadonite or proto-celadonite is the primary repository for B in oceanic crust altered by seawater at relatively low temperatures.

Shaskina (1961) described the formation of celadonite veins in altered basalt as the process of “joint coagulation of Fe_2O_3 , Al_2O_3 , and SiO_2 from colloidal solutions saturated with alkalis.” This seems like a reasonable explanation for celadonite formation in DSDP basalt, where, as noted previously, celadonite is typically associated with ferric oxide and characterizes alteration under relatively oxidizing conditions. As is typical of micas and mica-like minerals, celadonite has a relatively high layer charge (0.88 per half unit cell), and the greater portion of this octahedral substitution is specifically Fe^{2+} or Mg^{2+} replacing Al^{3+} or Fe^{3+} . Tetrahedral charge (0.1 to 0.2 per half unit cell) invariably results from Al^{3+} for Si^{4+} substitution (Weaver and Pollard, 1973). Indeed, the composition of some natural celadonites can approach the pure tetrasilic end member (Foster, 1969).

The mechanism by which B is taken up by celadonite and other mica minerals (e.g., illite) has been discussed in detail by Harder (1970). In general, the charge of the B atom and its size (0.23 Å) make it probable that the B atom replaces aluminum in the highly accessible outer tetrahedral positions. Leaching studies have shown that most of the B is not mobilized by acid treatments unless acids that dissolve the mineral (HF) are used (Harder, 1970). In addition, infrared studies of B-rich clays (Stubican and Roy, 1962) reveal the presence of B in tetrahedral positions. Thus, B enrichment in appropriate clay minerals appears to be a two-step process: first, adsorption of B on the surface of the clay, a step that can be described by a Freundlich adsorption equation (Lerman, 1966); then, slow incorporation of B into tetrahedral layers.

On the other hand, Harder (1970) suggests that B uptake during the formation of authigenic mica minerals in sediments may not be related to a simple adsorption process. In such cases, the B content may be quite high as the result of the direct incorporation of B into the lattice of the newly formed minerals. For example, B

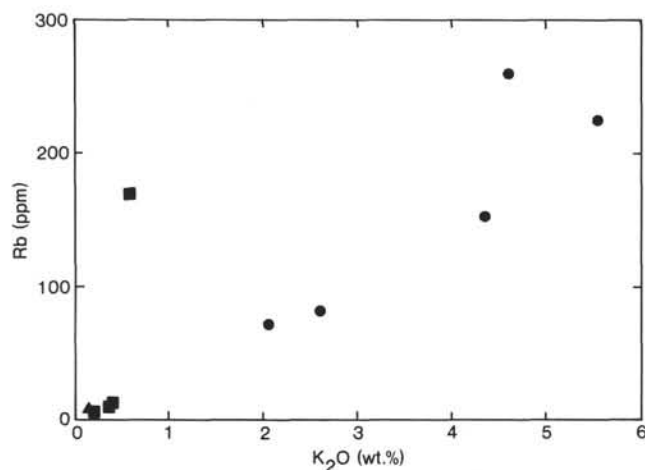


Figure 4. Rb versus K_2O for Hole 597B and 597C vein minerals. Legend as in Figure 1.

concentrations of 2000 ppm are common for authigenic glauconites that formed under marine conditions. It would not be surprising to find comparable B concentrations in celadonites, since celadonites are chemically and structurally similar to glauconites, differing mostly in the location of layer charge (e.g., much of the layer charge in glauconites is derived from substitution of Al^{3+} for Si^{4+} in the tetrahedral layer). However, this study has shown that although celadonites from Site 597 are highly enriched in B, pure celadonite separates probably contain only about 900 ppm B.

The conspicuously high B concentrations in micas (celadonite, illite, etc.) relative to other phyllosilicates suggest that the mica structure is inherently favorable for B substitution. Stubican and Roy (1962) suggest that K ions have some influence on the stabilization of BO_4 groups in the tetrahedral layers. Thus, B uptake by celadonite-rich portions of altered oceanic crust results as much from the structural control as it does from the availability of B in seawater.

The behavior of Li in vein alteration, like that of B, reflects a considerable degree of structural control. For example, Li and Mg have similar ionic radii (0.76 Å and 0.72 Å, respectively), so it is not surprising that alteration phases rich in Mg (smectites) are rich in Li as well (see Table 2). This assessment is consistent with experimental results (Seyfried et al., 1984) that have shown that during relatively low-temperature (<150°C) basalt-seawater interaction, Mg removal from solution precedes Li removal. These results indicate that the presence of a Mg-rich substrate may be necessary before Li can be removed from solution.

In addition to concentrating elements from seawater (e.g., B, Li), the vein assemblage and whole rock alteration phases can act as a repository for transition elements liberated from primary igneous minerals and glass rendered unstable by the action of aqueous fluids at low temperatures. For example, the Mg-rich smectites are conspicuously enriched in Ni compared with the other alteration phases and the inferred unaltered host basalt. At least one study (Donnelly, Thompson et al., 1980) has noted a slight correlation between high Ni concentrations and saponite abundance. Seawater, which typically contains less than 2 ppb Ni, is an unlikely source for the Ni unless disturbingly great amounts of seawater are involved in the alteration process.

Olivine, which can have high Ni contents because of its high partition coefficient for Ni in magmatic systems, is a good candidate as the source of this Ni. Olivine appears to be a minor phase in the basalts at Site 597; however, its distribution seems to be related to the distribution of Ni-rich smectite. That is, in the core interval between 121.3 and 143.5 m, where olivine is absent, smectites are not Ni enriched (e.g., 597C-9-3, 6–8 cm and 597C-9-4, 122–128 cm), whereas smectite samples from above or below this interval contain abundant Ni. Such a correlation suggests not only that olivine alteration is the source of the Ni but also that Ni derived from olivine alteration is transported only locally. Ni mobilization suggests that sulfide ion, which severely restricts

the solubility of Ni^{2+} (Garrels and Christ, 1965), is probably absent during the formation of these Ni-bearing smectites.

It is not surprising that high-Mg smectites and possibly talc are compatible hosts for Ni. Ni^{2+} ion (0.69 Å) is similar to Mg^{2+} ion in both size and charge, so these ions are easily interchangeable. These characteristics and the high crystal field octahedral site preference energy of Ni^{2+} may explain why Ni appears to be so much more enriched in the high-Mg smectite assemblages than in the other transition elements.

The high-Mg smectites and (to a lesser degree) the celadonites are also enriched in some of the other transition elements. The source of these elements is unknown, although the alteration of olivine may have supplied some of them. Another possible source is the alteration of glass. Previous studies have shown that mobilization of transition elements (Sc, Co, Cr, Ni, Cu, Zn) occurs during palagonitization of basaltic glass (Ailin-Pyzik and Sommer, 1981; Staudigel and Hart, 1982).

An element that may be relatively mobile during basalt alteration but not retained by secondary phases is Cu. Evidence for this is provided by the conspicuous depletion of Cu from basalt altered to high-Ti, high-Al, smectite-bearing assemblages.

The slight to moderate enrichment of nearly all of the transition elements compared with Ti in the celadonites and high-Mg smectites (Figs. 3A, B) lends support to the hypothesis that Ti is the most immobile of the transition elements in the low-temperature system studied here. These slight differences, however, are probably not large enough to be within the limits of resolution of bulk rock studies. More detailed work on larger vein samples will be necessary to further our understanding of transition element mobility in the low-temperature basalt-seawater system.

SUMMARY

This study has demonstrated the importance of mineralogic control on the distribution of B, Li, and Rb during low-temperature alteration of the oceanic crust; celadonite is preferentially enriched in B and Rb, whereas high-Mg smectite and talc are enriched in Li. B probably substitutes for Al in tetrahedral sites in celadonite, whereas Rb substitutes for K in interlayer sites. Maximum concentrations of B in pure celadonite are probably about 900 ppm, which is less than the 2000 ppm B concentrations reported for authigenic glauconites.

Li, which has an ionic radius similar to that of Mg, substitutes for Mg in octahedral sites in Mg-rich smectite and talc. Its lower abundance in the celadonite-rich zones is probably due to the absence of a suitable host mineral.

Cr-Cu transition elements, especially Ni, show enrichment compared with Sc, Ti, and V in high-Mg smectite-rich assemblages. Olivine alteration is a likely source for the Ni and possibly for the other transition elements. High Ni concentrations in high-Mg, low-Al smectite and talc demonstrates the similarity between Ni^{2+} and Mg^{2+}

in size and charge and the high affinity of Ni^{2+} for crystalline octahedral sites.

In contrast to the high-Mg smectite samples, celadonites show slight, if any, enrichment of Cr-Cu transition elements. In addition, two high-Al, high-Ti vein assemblages that contain smectite and amorphous materials have transition element patterns similar to those of the host basalt, except for Cu and Cr, which are depleted.

ACKNOWLEDGMENTS

This work was supported by grants OCE-8315116, OCE-8400676, and OCE-8542276 from the National Science Foundation. We owe gratitude to H. Staudigel for helpful criticisms on the first draft of this paper, and we are grateful to R. L. Knoche for his assistance in the lab. This work was also aided by discussions with D. R. Janecky.

REFERENCES

- Ailin-Pyzik, I. B., and Sommer, S. E., 1981. Microscale chemical effects of low temperature alteration of DSDP basaltic glasses. *J. Geophys. Res.*, 86:9503-9510.
- Bass, M. N., 1976. Secondary minerals in oceanic basalts, with special reference to Leg 34, Deep Sea Drilling Project. In Yeats, R. S., Hart, S. R., et al., *Init. Repts. DSDP*, 34: Washington (U.S. Govt. Printing Office), 393-432.
- Bhargava, O. M., and Hines, W. G., 1970. Rapid spectrophotometric determination of boron in steel. *Talanta*, 17:61-66.
- Donnelly, T. W., Pritchard, R. A., Emmermann, R., and Puchelt, H., 1980. The aging of oceanic crust: synthesis of the mineralogical and chemical results of Deep Sea Drilling Project, Legs 51 through 53. In Donnelly, T., Francheteau, J., Bryan, W., Robinson, P., Flower, M., Salisbury, M., et al., *Init. Repts. DSDP*, 51, 52, 53, Pt. 2: Washington (U.S. Govt. Printing Office), 1563-1577.
- Donnelly, T. W., Thompson, G., and Salisbury, M. H., 1980. The chemistry of altered basalts at Site 417, Deep Sea Drilling Project Leg 51. In Donnelly, T., Francheteau, J., Bryan, W., Robinson, P., Flower, M., Salisbury, M., et al., *Init. Repts. DSDP*, 51, 52, 53, Pt. 2: Washington (U.S. Govt. Printing Office), 1319-1330.
- Edmond, J. M., Measures, C., 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.*, 46:1-19.
- Edmond, J. M., Von Damm, K. L., McDuff, R. E., and Measures, C. I., 1982. Chemistry of hot springs on the East Pacific Rise and their effluent dispersal. *Nature*, 297:187-191.
- Foster, M. D., 1969. Studies of celadonites and glauconite. *Geol. Surv. Prof. Pap. U.S.* 614F.
- Garrels, R. M., and Christ, C. L., 1975. *Solutions, Minerals, and Equilibria*: San Francisco (Freeman, Cooper and Co.).
- Harder, H., 1970. Boron contents of sediments as a tool in facies analysis. *Sediment. Geol.*, 4:153-172.
- Hart, S. R., and Staudigel, H., 1982. The controls of alkalies and uranium in seawater by ocean crust alteration. *Earth Planet. Sci. Lett.*, 58:202-213.
- Honnorez, J. J., 1981. The aging of the oceanic crust at low temperature. In Emiliani, C. (Ed.), *The Sea* (Vol. 7): New York (Wiley), pp. 525-587.
- Humphris, S. E., Thompson, R. N., and Marriner, G. F., 1980. The mineralogy and geochemistry of basalt weathering, Holes 417A and 418A. In Donnelly, T., Francheteau, J., Bryan, W., Robinson, P., Flower, M., Salisbury, M., et al., *Init. Repts. DSDP*, 51, 52, 53, Pt. 2: Washington (U.S. Govt. Printing Office), 1201-1217.
- Lerman, A., 1966. Boron in clays, an estimation of paleosalinities. *Sedimentology*, 6:267-286.
- Muehlenbachs, K., and Clayton, R. N., 1976. Oxygen isotopes composition of the oceanic crust and its bearing on seawater. *J. Geophys. Res.*, 81:4365-4369.
- Seyfried, W. E., Jr., Janecky, D. R., and Mottl, M. J., 1984. Alteration of the oceanic crust: implications for geochemical cycles of lithium and boron. *Geochim. Cosmochim. Acta*, 48:557-569.
- Seyfried, W. E., Jr., Shanks, W. C., and Dibble, W. E., Jr., 1978. Clay mineral formation in DSDP Leg 34 basalt. *Earth Planet. Sci. Lett.*, 41:265-276.
- Shaskina, V. P., 1961. Mineralogy of weathered basalt in Volynia. *Int. Geol. Rev.*, 3:393-407.
- Staudigel, H., and Hart, S. R., 1982. Alteration of basaltic glasses: mechanisms and significance for the oceanic crust-seawater budget. *Geochim. Cosmochim. Acta*, 47:337-350.
- Stoffyn-Egli, P., and Mackenzie, F. T., 1984. Mass balance of dissolved lithium in the oceans. *Geochim. Cosmochim. Acta*, 48:859-872.
- Stubican, V., and Roy, R., 1962. Boron substitution in synthetic micas and clays. *Am. Mineral.*, 47:1166-1173.
- Thompson, G., 1983. Hydrothermal fluxes in the ocean. In Riley, J. P., and Chester, R. (Eds.), *Chemical Oceanography* (Vol. 8): New York (Academic Press), 272-338.
- Weaver, C. E., and Pollard, L. D., 1973. *The Chemistry of Clay Minerals*: New York (Elsevier).

Date of Initial Receipt: 2 July 1984

Date of Acceptance: 26 December 1984