

29. ALTERATION ZONES NEAR VEINS IN BASALTS FROM DEEP SEA DRILLING PROJECT SITES 501/504 AND 505, COSTA RICA RIFT¹

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ABSTRACT

Cores from Deep Sea Drilling Project Holes 501, 504B and 505B have an unusual near-vein zonation in basalts. Megascopically, zonation occurs as differently colored strips and zones whose typical thickness does not exceed 6 to 7 cm. Microscopically, the color of zones depends on variably colored clay minerals which are the products of low-temperature hydrothermal alteration in basalt. These differently colored zones form the so called "oxidative" type of alteration of basalts. Another "background," or, less precisely termed, "non-oxidative," type of alteration in basalts is characterized by large-scale, homogeneous replacement of olivine, and filling of vesicles and cracks by an olive-brown or olive-green clay mineral. The compositions of clay minerals of the "background" type of alteration, as well as the composition of co-existing titanomagnetites, were determined with an electron microprobe. There are sharp maxima in potassium and iron content, and minima in alumina, silica, and magnesia in clay minerals in the colored zones near veins. Coloring of clay and rock-forming minerals by iron hydroxides and a decrease of the amount of titanomagnetite, which apparently was the source of redeposited iron, occur frequently in colored zones. We assume that the large-scale "background" alteration in the basalts occurred under the effect of pore waters slowly penetrating through bottom sediments. Faulting can facilitate access of fresh sea water to basalts; thus above the general homogeneous background arise zones of "oxidative" alteration along fractures in basalts. The main factors controlling these processes are time (age of basalt), grain size, temperature, thickness of sedimentary cover, and heat flow.

INTRODUCTION

During DSDP Legs 68 and 69, basalts were recovered which have some intervals with distinctly colored zones associated with fracture fillings. These zones are seen particularly well on wet surfaces of samples, and they attracted attention by their bright red, orange, yellow, and dark-green coloring. Similar, though not so strongly displayed oxidized zones near veins occur at many DSDP sites (e.g., Leg 34, Bass, 1976; Leg 46, Honnorez et al., 1979). Near-vein zonation in calcite and the distribution of smectite adjacent to quartz-bearing veins was discovered during the study of the core from holes of the Bermuda Rise "megaleg" (Legs 51-53; Pertsev and Rusinov, 1980). Because of the unusually bright coloring of zonation in basalts drilled during Leg 69, we decided to study its mineralogical and chemical peculiarities mainly by microprobe and optical methods.

CHARACTERISTICS OF NEAR-VEIN ZONATION OCCURRENCES

Figure 1 shows intervals in the cores where basalts occur having the type of zonation just described. These are schematically marked along the columns of the holes. The figure also depicts larger intervals characterized by formation of unzoned oxidized products of alteration. These basalts are mostly brown (mainly along cracks) with veins having red-brown clay minerals. The schematic column of the deepest Hole (504B) on Figure 1 shows that oxidized alteration products are restricted to the top of basement. This is confirmed by the extensive development of pyrite in lower units of the basement,

observed during shipboard study of the core (see site report, this volume). Near-vein zonation with red and yellow products of alteration occurs only within intervals of oxidized alterations (Fig. 1).

Dark-green (or bright-green in a thin-section) clay minerals accompany oxidative zonation; the origin of this clay is likely to be connected with "oxidative processes," as noted for similar clays during the Bermuda Rise "megaleg" (Pertsev and Rusinov, 1980). According to X-ray structural analysis, the clay is hydromica of the celadonite-glaucanite type (Table 1). The diffractogram was made on mineral powder selected from a polished thin-section and glued into a globule with rubber cement. The association of celadonite with zones of oxidative alteration can be seen distinctly on a diagram of the distribution of various products of alteration in Hole 501 (Fig. 2).

Within near-vertical veinlets along which near-vein zonation occurs, one can see vertical zonality which can be traced for comparatively large distances. This is schematically shown in Figure 3. Downward in the core, the veinlet first is filled by dark-green smectite. This gives way to a calcite filling with red and yellow zones next to the veinlet, thinning downward. The thicknesses of these red and yellow zones, which occur on either side of the veinlet, do not exceed 6 to 7 cm, and the central veinlet is only 1 to 3 mm wide. Preliminary visual examination revealed two types of near-vein zonation. The first type typically has veins filled by a dark-green clay mineral. The vein is successively adjoined by dark-green, yellow, and red zones, as shown in Figure 3. The second type has an almost inverse zonation. The central veinlet is filled by a red-brown clay mineral. This is surrounded by a red or orange zone, then a dark-green zone, and finally host basalt.

¹ Cann, J. R., Langseth, M. G., Honnorez, J., Von Herzen, R. P., White, S. M., et al., *Init. Repts. DSDP, 69*: Washington (U.S. Govt. Printing Office).

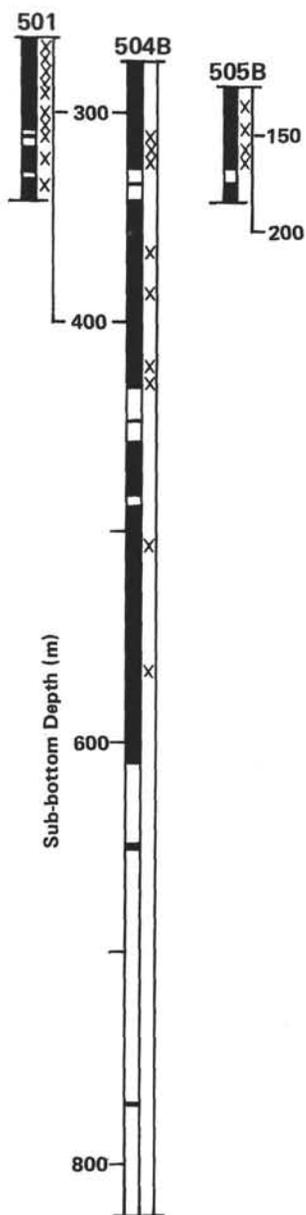


Figure 1. Schematic columns of Holes 501, 504B, and 505B. Intervals of development of colored near-vein zones are marked by cross. Intervals with development of oxide changes (black) predominate in the upper part of the basalt section. Depths are shown in meters sub-bottom.

Microscopic study shows that the color of the zones is determined by the color of the respective clay minerals which fill small vesicles and cracks and form pseudomorphs after olivine phenocrysts and groundmass olivine. In intensity of basalt alteration, these zones differ little from host basalt. Vesicles, small cracks, and pseudomorphs after olivine in this host basalt are simply made up of a lighter-olive-green or olive-brown, homogeneous smectite.

Boundaries between zones are distinct (Plate 1), typical of metasomatic zonation.

STUDY OF MINERAL COMPOSITION

Analysis of minerals was made with an MS-46 Camca electron microprobe using an accelerating voltage of

Table 1. X-ray powder data on celadonite-glaucanite from 504B-16-2, 34-36 cm, Piece 976.

<i>l</i>	<i>d/n</i>
6	9.99
1	5.04
7	4.57
0.05	—
4	3.68
5	3.34
1	3.11
1	2.84
10	2.596
4	2.40
0.5	—
0.5	—
0.5	—
1	1.664
8	1.519
1	1.311

Fe emission; 2*R* = 86.0; *d* = 0.3; analysis performed at the X-ray structural laboratory of IGEM by M. T. Dmitriyeva.

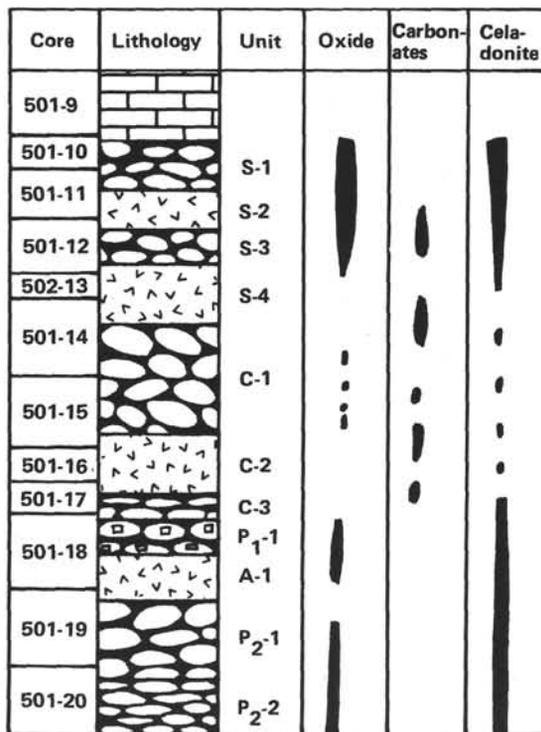


Figure 2. Relationships between development of oxide changes, appearance of carbonates, and bright-green celadonite in basalt basement of Hole 501.

20 kV and probe current of 30 mA. The diameter of the probe beam used for the analysis of clay minerals was 10 to 15 μm, and for other minerals about 1 μm. The calculation of correction coefficients for difference, between samples and standards was performed by the ZAF method according to original program devised by Boronikhin and Tsepín (1980). Additional corrections



Figure 3. The scheme of depth-dependent changes in the composition of oxidative products in systems of veins, Hole 501: 1, "background" basalt; 2, vein filling of crack by dark-green clay mineral; 3, yellow, orange, and red zones, the density of the red color increasing toward the external boundary of near-vein alterations; 4, dark-green zone of near-vein alteration; 5, vein carbonate filling.

were made for dead time, mean atomic mass, absorption, and characteristic fluorescence. It should be noted that most of the investigated clay minerals are relatively stable under the probe beam; however, the loss of water by some minerals during analysis is not excluded.

Secondary-mineral zonation was studied in five samples from various intervals of the holes, chosen in such a way that the greatest variety of differently colored zones was included.

Sample 504B-13-4, 10–12 cm, Piece 802

This sample is microphyric holocrystalline basalt with small, rare phenocrysts of plagioclase and olivine, the latter completely replaced by smectite. The thin-section included basalt and two alteration zones (red and yellow) near a vein (Fig. 4D). The boundary between the red zone and the "non-oxidative" basalt is very distinct (Plate 1, Fig. 1), whereas the transition from the red zone to the yellow one is gradual and is manifested in a decrease of the intensity of coloring of clay minerals. The "background" alteration of basalt consists of the development of light-olive-brown smectite (Fig. 4D, point 3) after olivine of microphenocrysts and groundmass. In the red (Fig. 4D, point 2) and yellow (Fig. 4D, point 1) zones, this smectite is replaced by a red-brown mineral. Also, these zones exhibit a fine-scale network of film-like red veinlets filled with a mixture of clay minerals and iron hydroxides. Such film-like veinlets form the network not only at the interstices of grains, but also within plagioclase and pyroxene crystals. Microprobe analyses of these minerals are given in Table 2.

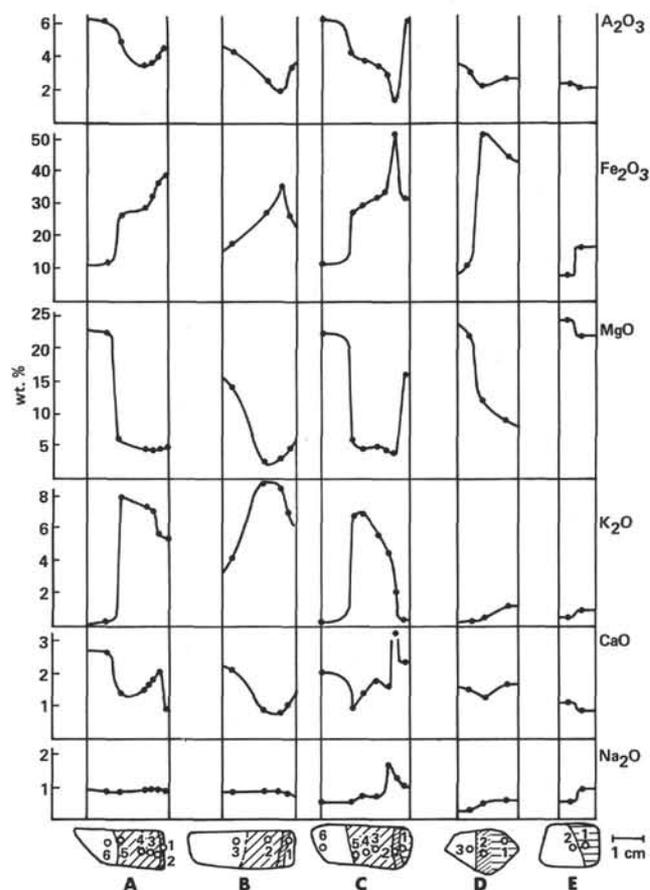


Figure 4. Change of oxide concentrations in clay minerals according to color zones. A. 504B-27-1, 118–120 cm, Piece 1475. B. 504B-28-1, 110–113 cm, Piece 1498. C. 504B-16-2, 34–36 cm, Piece 976. D. 504B-13-4, 10–12 cm, Piece 802. E. 504B-3-2, 99–101 cm, Piece 188.

Structural formulas were calculated on the basis of the crystallochemical classification of smectites (Drits and Kossovskaya, 1980), and by a method used in computing structural formulas of smectites and celadonites (Deer et al., 1962). Because the structural formulas indicate that ferric iron dominates over ferrous iron, the total iron is plotted as Fe_2O_3 in the composition graphs. Titanomagnetite (apparently, titanomaghemite) was preserved as in the basalt proper, and in the yellow zone as well (Table 3).

Undoubtedly, clay minerals of red and yellow zones contain disseminated iron hydroxides which cause a sharp peak of Fe_2O_3 in the composition of the red zone (Fig. 4D).

504B-16-2, 34–36 cm, Piece 976

This sample is microphyric holocrystalline basalt with rare small plagioclase and olivine phenocrysts. Olivine is entirely replaced by brown smectite. The thin-section (Fig. 4C) includes "background" basalt with brown smectite after olivine, a dark-green zone in which smectite is replaced by bright-green celadonite (Fig. 4C), a red zone with development of red shades in celadonite and a network of red film-like veinlets in crystals and

Table 2. Microprobe analyses and structural formulas of clay minerals, 504B-13-4, 10-12 cm, Piece 802.

Component	Analysis ^a		
	1	2	3
SiO ₂	39.25	30.99	55.05
TiO ₂	0.11	0.11	0.16
Al ₂ O ₃	2.91	2.42	3.39
Fe ₂ O ₃	44.24	51.00	10.54
MnO	0.17	0.17	0.08
MgO	8.28	12.22	22.94
CaO	1.62	1.26	1.53
K ₂ O	1.27	0.25	0.16
Na ₂ O	0.44	0.40	0.20
Total	98.29	98.82	93.00
Si	5.32	4.11	8.00
Al	0.47	0.38	—
Fe	2.21	3.51	—
Fe	2.30	1.57	1.15
Al	—	—	0.58
Ti	0.02	0.01	0.02
Mn	0.01	0.02	0.01
Mg	1.67	2.41	2.24
Mg	—	—	2.73
Ca	0.24	0.18	0.24
K	0.22	0.10	0.03
Na	0.11	0.04	0.06

^a 1, Light-olive-brown clay mineral; 2, red-brown clay mineral; 3, yellow-brown clay mineral.

Table 3. Microprobe analyses of titanomagnetites, 504B-13-4, 10-12 cm, Piece 802.

Component	Analysis	
	1	3
SiO ₂	5.10	4.74
TiO ₂	19.78	14.11
Al ₂ O ₃	4.51	4.38
FeO	63.03	69.04
MnO	0.81	0.51
MgO	1.34	4.13
Total	94.60	96.50

interstices of grains, and a yellow zone with a red-brown clay mineral but without a network of the red veinlets. Contacts between all zones are sharp. Results of the microprobe study of the composition of clay-mineral zones are given in Table 4. Titanomagnetite (probably titanomaghemite) occurs in all zones (Table 5), though its abundance is lower in dark-green and red zones.

Point 1 of Figure 4C corresponds to the yellow zone which contains a dark-red-brown clay mineral. Point 2, which corresponds to the red zone, has clay represented by a dark, almost opaque mineral obviously containing finely dispersed iron hydroxides. At this point also a gray-brown clay mineral is prominent, which in composition is similar to clay minerals of the dark-green zone. Red, film-like veinlets in pyroxene and plagioclase crystals give a typical brown shade to this point.

Table 4. Microprobe analyses and structural formulas of clay minerals, 504B-16-2, 34-36 cm, Piece 976.

Component	Analysis ^a									
	1	2-1	2-2	3	4-1	4-2	4-3	5-1	5-2	6
SiO ₂	37.17	26.45	42.67	51.51	50.27	51.43	51.80	53.98	49.97	47.82
TiO ₂	0.48	0.10	0.90	0.19	0.10	0.15	0.19	0.21	1.21	0.08
Al ₂ O ₃	6.23	2.26	1.70	3.91	2.20	5.00	3.69	3.91	3.79	6.22
Fe ₂ O ₃	31.51	60.49	33.00	31.08	33.72	29.08	29.37	27.18	21.94	12.07
MnO	0.18	0.20	0.74	0.11	0.09	0.08	0.07	0.07	0.46	0.04
MgO	16.13	3.04	5.75	5.26	4.55	4.65	4.63	6.27	9.58	22.85
CaO	2.38	1.59	14.03	1.89	1.17	1.38	1.63	1.01	17.49	1.95
K ₂ O	0.16	2.12	0.06	5.58	6.44	6.75	6.55	6.75	0.05	0.07
Na ₂ O	0.89	1.46	1.06	0.54	0.66	0.71	0.79	0.48	0.94	0.44
Total	95.15	97.71	99.89	100.08	99.20	99.22	98.73	99.85	105.49	91.54
Si	4.81	—	6.45	7.07	7.08	7.15	7.28	4.31	—	8.00
Al	0.95	—	0.30	0.63	0.36	0.82	0.61	0.62	—	—
Fe	2.24	—	1.25	0.30	0.56	0.03	0.11	0.07	—	—
Fe	0.83	—	2.51	2.90	2.99	3.01	3.00	2.70	—	1.52
Al	—	—	—	—	—	—	—	—	—	1.23
Ti	0.05	—	0.10	0.02	0.01	0.02	0.02	0.02	—	0.01
Mn	0.02	—	0.09	0.01	0.01	0.01	0.01	0.01	—	0.01
Mg	3.11	—	1.30	1.07	0.96	0.96	0.97	1.27	—	1.23
Mg	—	—	—	—	—	—	—	—	—	4.97
Ca	0.33	—	2.27	0.28	0.18	0.21	0.24	0.15	—	0.35
K	0.03	—	0.01	0.95	1.16	1.20	1.17	1.44	—	0.02
Na	0.22	—	0.31	0.14	0.18	0.19	0.22	0.13	—	0.14

^a 1, dark red-brown clay mineral; 2-1, dark-gray clay mineral; 2-2, opaque clay mineral; 3, greenish-brown clay mineral; 4-1, dark core of the green clay mineral; 4-2, external part of the green clay mineral; 4-3, green clay mineral; 5-1, green clay mineral; 5-2, light-brown clay mineral; 6, light-brown clay mineral.

Table 5. Microprobe analyses of titanomagnetites, 504B-16-2, 34-36 cm, Piece 976.

Component	Analysis					
	1	2	3	4	5	6
SiO ₂	5.81	5.91	5.38	6.21	5.64	7.35
TiO ₂	19.10	18.16	19.22	19.17	18.62	15.39
Al ₂ O ₃	4.82	4.32	4.49	4.89	4.99	4.34
FeO	65.35	64.58	63.79	63.00	64.20	61.04
MnO	0.84	0.87	2.01	1.69	1.19	0.76
MgO	2.06	1.95	1.37	1.42	1.51	2.02
Total	97.96	95.79	96.23	96.37	96.15	96.70

Dark to bright-green celadonite, is common near points 3, 4, and 5 which are in the dark-green zone. Figure 4C clearly shows higher aluminium and potassium and lower iron content in dark-green zones which are near the contact with "background" basalt. The transition from the dark-green zone to "background" basalt is expressed in the replacement of bright-green smectite by a brown clay mineral, seen near point 6. On Figure 4C, this is expressed by a sharp decrease in the content of iron and potassium, and higher values of aluminium and magnesium.

504B-27-1, 118-120 cm, Piece 1475

This sample is medium-grained, holocrystalline basalt with rare, fine plagioclase phenocrysts. The thin-section includes "background" basalt, a dark green zone, a red-brown zone, and a dark-brown clay mineral which fills the central crack (veinlet) (Fig. 4A). Contacts between all the zones are sharp. Table 6 lists results of the microprobe study of clay-mineral composition of the zones in this sample. Titanomagnetite is present in all near-vein zones, but has not been specifically studied.

Near point 1 (Fig. 4A), which is a filled vein, the clay mineral is dark red or brown-green and has the highest content of iron. The adjacent red-brown zone is 1 to 2

Table 6. Microprobe analyses and structural formulas of clay minerals, 504B-27-1, 118–120 cm, Piece 1475.

Component	Analysis ^a							
	1-1	1-2	2	3	4-1	4-2	5	6
SiO ₂	42.12	36.32	44.31	50.22	48.19	40.77	50.81	49.32
TiO ₂	0.06	0.07	0.57	0.29	0.15	0.11	0.19	0.58
Al ₂ O ₃	4.53	2.88	4.44	3.62	3.51	2.24	3.99	6.14
Fe ₂ O ₃	39.56	44.62	36.18	29.88	28.63	60.21	26.97	12.72
MnO	0.10	0.14	0.11	0.08	0.07	0.15	0.05	0.04
MgO	5.45	3.78	4.48	4.68	4.53	2.76	5.60	22.79
CaO	0.87	1.04	2.09	1.72	1.41	0.94	1.32	2.69
K ₂ O	5.61	5.40	5.60	7.33	7.41	3.20	7.97	0.12
Na ₂ O	0.87	0.88	0.99	0.87	0.66	0.79	0.60	0.88
Total	99.17	95.12	98.77	98.69	94.56	111.17	98.50	95.28
Si	5.91	5.51	6.33	7.15	7.15	—	7.23	8.00
Al	0.75	0.51	0.75	0.61	0.61	—	0.67	—
Fe	1.34	1.98	0.92	0.24	0.24	—	0.10	—
Fe	2.84	3.12	2.97	2.97	2.97	—	2.79	1.55
Al	—	—	—	—	—	—	—	1.17
Ti	0.01	0.01	0.06	0.03	0.02	—	0.02	0.07
Mn	0.01	0.01	0.01	0.01	0.01	—	0.01	0.01
Mg	1.14	0.85	0.96	0.99	1.00	—	1.18	1.20
Mg	—	—	—	—	—	—	—	4.31
Ca	0.13	0.17	0.32	0.26	0.22	—	0.20	0.46
K	1.00	1.04	1.02	1.33	1.40	—	1.45	0.03
Na	0.24	0.24	0.27	0.24	0.19	—	0.17	0.28

^a 1-1, brown-green clay mineral; 1-2, dark-red clay mineral; 2, brown-green clay mineral; 3, opaque clay mineral; 4-1, green clay mineral with black cores, green part; 4-2, green clay mineral with black cores, dark core; 5, green clay mineral; 6, light-brown clay mineral.

mm wide and consists of film-like red veinlets in the rock. Points 2, 3, 4, and 5 are in the dark-green zone next to the red zone. From point 2 to point 5, the clay mineral changes color from green-brown to bright green. Toward point 5 the sizes of clay minerals increase, and dark cores with ferric iron content over 50% appear in large flakes (Plate 1, Fig. 2). Near point 6, one can see the brown clay minerals of the “background” basalt.

504B-28-1, 110–113 cm, Piece 1498

The sample is coarse-grained, sparsely-plagioclase-phyric basalt. The thin-section includes “background” basalt, a dark-green zone, a red-brown zone, and a gray zone with a light-green clay mineral (Fig. 4B). Contacts between zones are distinct. A narrow (2–3 mm) red-brown zone in the section has a red-brown clay mineral and a network of red, film-like veinlets which represent a mixture of the clay mineral with finely dispersed iron hydroxides. The location of the red zone here is of particular interest; it is included within the green zone in which the green shade intensifies in the direction of the background basalt. Bright-green clay minerals of the gray zone and dark-brown clay minerals of the brown zone occur near point 1. In the green zone, the largest inclusions of green celadonite contain “relict” spots and aggregates of a brown clay mineral (Plate 1, Fig. 3; Fig. 4B, point 2). Microprobe analyses of the clay minerals are listed in Table 7. Titanomagnetite occurs in all zones (Table 8). Near point 3 is a greenish-brown clay mineral of the “background” basalt, which differs from clay minerals of the “background” basalt in pieces 802, 976, and 1475 by its greenish shade. This probably reflects differences in magnesium and potassium content.

Table 7. Microprobe analyses and structural formulas of clay minerals, 504B-28-1, 110–113 cm, Piece 1498.

Component	Analysis ^a					
	1-1	1-2	1-3	2-1	2-2	3
SiO ₂	52.77	49.47	46.00	50.58	47.62	50.75
TiO ₂	0.19	0.19	0.08	0.16	0.06	0.27
Al ₂ O ₃	3.57	3.46	2.05	3.26	6.29	5.35
Fe ₂ O ₃	27.14	27.37	36.08	27.23	14.48	18.06
MnO	0.07	0.05	0.05	0.05	0.09	0.04
MgO	6.28	6.63	4.32	5.40	20.90	13.56
CaO	1.37	1.15	0.08	0.75	2.07	2.24
K ₂ O	7.09	6.44	7.50	9.26	0.84	4.24
Na ₂ O	0.81	1.17	0.78	0.78	0.95	0.87
Total	99.29	95.93	97.66	97.47	93.30	95.38
Si	7.28	7.05	6.72	7.30	8.00	6.69
Al	0.58	0.58	0.35	0.55	—	0.83
Fe	0.14	0.37	0.93	0.15	—	0.48
Fe	2.68	2.56	3.04	2.81	1.83	1.30
Al	—	—	—	—	1.25	—
Ti	0.02	0.02	0.01	0.02	0.01	0.03
Mn	0.01	0.01	0.01	0.01	0.01	0.01
Mg	1.29	1.41	0.94	1.16	0.90	2.66
Mg	—	—	—	—	4.33	—
Ca	0.20	0.18	0.13	0.12	0.37	0.32
K	1.25	1.17	1.40	1.70	0.18	0.71
Na	0.22	0.31	0.22	0.22	0.31	0.22

^a 1-1, bright-green clay mineral; 1-2, bright-green clay mineral; 1-3, dark-brown clay mineral; 2-1, bright-green clay mineral; 2-2, relic of brown clay mineral; 3, greenish-brown clay mineral.

Table 8. Microprobe analyses of titanomagnetites, 504B-28-1, 110–113 cm, Piece 1498.

Component	Analysis		
	1-1	1-2	3
SiO ₂	5.63	5.07	5.99
TiO ₂	17.13	12.48	15.84
Al ₂ O ₃	4.96	3.63	4.13
FeO	66.84	70.08	67.22
MnO	0.65	0.66	1.04
MgO	1.93	2.82	2.73
Total	97.15	94.75	96.95

505B-3-2, 99–101 cm, Piece 188

This is a pillow lava having a hyalopilitic groundmass with a moderate amount of plagioclase and olivine phenocrysts. Olivine is entirely replaced by a smectite mineral. The thin-section has two zones: (1) a “background” basalt whose clay minerals (olivine pseudomorphs and vesicles) are light-olive-brown smectite, and (2) a yellow-brown zone filled with bright-yellow-brown smectite. The boundary between the zones is very sharp, sometimes even crossing a single smectite crystal. There is no doubt that the brown zone developed after the “background” alteration occurred. Close to the boundary between the zones, distinct relics of light-olive-brown smectite occur in brown smectite (Plate 1, Fig.

4). Microprobe analyses of both smectites made near the point depicted in Plate 1, Figure 4 are given in Figure 4E and Tables 9 and 10. Titanomagnetite occurs in both zones, but was not specifically studied. On Figure 4E, point 1 represents a bright-yellow-brown clay mineral from the yellow-brown zone. Point 2 represents a light-olive-brown smectite of the "background" basalt.

DISCUSSION OF RESULTS

Microprobe study of the composition of clay minerals in alteration zones near veins shows that all the zones change composition in similar ways. Two types of zonation, distinguished visually, are in fact similar compositionally. The main difference in the coloring of zones (red, orange, and yellow shades) is caused by the admixture of finely dispersed iron hydroxides. Our data also confirm the nature of coloring described. Dark-brown to opaque clay minerals owe their color to association of the dark-green mineral with abundant red hydroxides, whereas red-orange and yellow shades reflect light-colored clay minerals. The color of the rock depends as much on the color and density of matrix as on the density of dispersed iron hydroxides. The location of zones containing iron hydroxides varies and probably depends on specific conditions of alteration, especially on the pH. In some cases the red zones are in the central part of the veinlet proper, or close to it. One then can see red-brown zones next to green zones located near veinlets. In other cases, green zones are central (next to veinlets), and red-brown zones rich in iron hydroxides are located at the margins. In those zones where there

Table 9. Microprobe analyses and structural formulas of clay minerals, 504B-3-2,99-101 cm, Piece 188.

Component	Analysis ^a	
	1	2
SiO ₂	47.74	51.74
TiO ₂	0.10	0.12
Al ₂ O ₃	2.24	2.55
Fe ₂ O ₃	17.47	9.22
MnO	0.08	0.05
MgO	22.22	24.67
CaO	0.87	1.03
K ₂ O	0.42	0.31
Na ₂ O	0.62	0.29
Total	91.76	89.98
Si	8.00	8.00
Al	—	—
Fe	—	—
Fe	2.20	1.07
Al	0.44	0.46
Ti	0.01	0.01
Mn	0.01	0.01
Mg	1.34	2.45
Mg	4.20	3.23
Ca	0.16	0.17
K	0.09	0.06
Na	0.20	0.09

^a 1, bright-yellow-brown clay mineral; 2, light-olive-brown clay mineral.

Table 10. Microprobe analyses of clay minerals of the "background" basalt.

Component	Analysis ^a					
	1	2	3	4	5	6
SiO ₂	55.05	47.82	49.32	50.79	51.74	49.37
TiO ₂	0.16	0.08	0.58	0.27	0.12	0.23
Al ₂ O ₃	3.39	6.22	6.14	5.35	2.55	6.28
Fe ₂ O ₃	10.54	12.07	12.72	18.06	9.22	19.57
MnO	0.08	0.04	0.04	0.04	0.05	0.09
MgO	22.94	22.85	22.79	13.56	24.67	18.48
CaO	1.53	1.95	2.69	2.24	1.03	2.30
K ₂ O	0.16	0.08	0.12	4.24	0.31	0.14
Na ₂ O	0.20	0.44	0.88	0.87	0.29	0.63
Total	93.00	91.55	95.28	95.38	89.98	97.10

^a 1, 504B-13-4, 10-12 cm, Piece 802; 2, 504B-16-2, 34-36 cm, Piece 976; 3, 504B-27-1, 118-120 cm, Piece 1475; 4, 504B-28-1, 110-113 cm, Piece 1498; 5, 504B-3-2, 99-101 cm, Piece 188; 6, 504B-27-1, 3-5 cm, Piece 1459.

are abundant iron hydroxides, there are also increases of iron and potassium content and decreases in magnesium and silica in clay minerals as compared to "background" clay minerals in host basalts and the central crack fillings. This process is far more complicated than mere oxidation of iron, because it involves loss or gain of cations other than iron in the clay minerals. Despite the fact that titanomagnetite (or titanomaghemite) occurs in all alteration zones near veins, its concentration is always significantly decreased. It is likely that the smaller grains of titanomagnetite, which are now gone, supplied iron for the increase in the iron content of clay minerals and the formation of free iron hydroxides. Two total analyses (XRF) made during Leg 69 for revealing chemical differences in background basalt and basalt of red zones (data in Etoubleau et al., this volume) showed no increase in iron in red zones.

In addition, Bass (1976) correctly stated that this type of oxidative diagenesis was induced by oxygen-rich bottom sea water which oxidized previously formed pyrite. This was followed evidently by a decrease in pH at the expense of the formation of sulfuric acid. In the thin-section of 504B-13-4, 7-10 cm, Piece 802, one can see clearly that the veins of smectite and pyrite in "background" basalt reach the red-brown zone of "oxidation," but do not occur *in* it. At the contact of the veinlet with the red zone, pyrite is replaced by iron hydroxides. On the whole, our data confirm this hypothesis. It is likely that non-oxidative, iron-rich solutions could deposit a clay mineral with high iron and low alkali concentrations in small cracks. Parallel to the diffusion of the solution into host basalt normal to the walls of the crack, solutions leached magnesium from earlier-formed smectites, replacing them partly by ferrous and mostly by ferric smectites. At a certain point, excess iron began to deposit as hydroxides, and smectite was replaced by celadonite. Depletion of the diffusing solution in oxygen, iron, and alkalis as the minerals precipitated reduced the reactivity of the solutions and allowed earlier formed smectite to remain unaltered. In order to form sharp boundaries between alteration zones near veins and host rock, sharp changes in the degree of oxidation

must have taken place. Microprobe analyses reveal, however, that the iron content in smectites of host basalts varies only slightly at the contact with zones (Fig. 4) for distances of several millimeters. This situation cannot be described with the help of Korzhinskii's equations of diffusion metasomatic zonality (Korzhinskii, 1970). Changes in the composition of alteration zones near veins (Fig. 3) may be accounted for by changes through time in the composition of the solution flowing along cracks as it moves through basalt basement and reacts with it. Because of exchange of components between basalt and solution as the solution moves deeper, the solution becomes enriched in magnesium and calcium, and depleted in iron and oxygen. Its acidity becomes lower as well. These factors contribute to the formation of carbonate, which begins to fill cracks instead of smectite, and to the disappearance of alteration zones along the cracks with free iron hydroxides.

As stated above, we distinguish two patterns of basalt alteration: (1) a more or less uniform "background" alteration, and (2) a local alteration occurring along cracks and other permeable zones.

Bass (1976), upon study of these essentially different types of alteration, came to the conclusion that early alteration of the inner parts of lava flows and pillows is non-oxidative ("non-oxidative diagenesis"); it takes place in chilled basalts as a consequence of penetration of sea water into sediments and basalts. Bass suggests that in quenched margins, which are rich in cracks, and near them, alteration should be oxidative even at early stages (on account of easy access of oxygenated sea water to these parts of basalts just after their quenching). The second, oxidative stage of basalt alteration takes place upon influx of sub-bottom sea waters into basalts along cracks formed by tectonic movements which accompany sea-floor spreading. We accept, in general, this scheme of the relationship between "oxidative" and "non-oxidative" alterations, yet we somewhat disagree with the early oxidative alteration in quenched margins. If it were so, development of oxidative alterations in them would be quite regular.

Observations made on holes of the Bermuda Rise "megaleg" and in DSDP Legs 68 and 69 prove that many quenched margins do not show oxidative alteration. As a rule, oxidatively altered quenched margins occur in those places where oxidative alteration is noticeable in the inner parts of pillows and flows. There is a general tendency for oxidative alteration to decrease with depth, contradicting the idea that there was early oxidative alteration in quenched margins.

Early-formed, "non-oxidative" alteration is more universal and is widespread in chilled margins. Smectites formed during this alteration are uniform in composition. Table 10 lists their compositions from different parts of the holes under consideration. Variations in the composition are insignificant. Study of the three holes at Site 505 revealed that, although there have been considerably better conditions of penetration of cold sea water into basalts than at Sites 501/504 (see site reports, this volume), they are considerably less altered, either under "oxidative" or "non-oxidative" conditions. Even groundmass olivine is locally preserved, evidently be-

cause of decreased heat flow and decreased basalt temperature at Site 505. Obviously, all the three kinetic factors of alteration—time (basalt age), grain size, and temperature (especially the last two)—play an important part in the processes of "non-oxidative" and "oxidative" alteration in basalt. Intensity of tectonic movements facilitating access of near-bottom sea waters to basalts and increased temperature of basalts should favor oxidative alteration. The thickness of sedimentary cover is critical: if thick enough, it aids basalt heating, but hinders penetration of fresh sea waters. The case of the holes at Site 505, where the basalt age is less than 4 m.y., indicates that both types of basalt alteration—"non-oxidative" and "oxidative"—can proceed simultaneously during the early stages of alteration. Faulting allows access of sea water to basalts and facilitates oxidative alteration on a background of a longer-term "non-oxidative" alteration which is still going on under the effect of very slowly penetrating pore waters. This may account for the variety of age relationships inferred for the paragenesis of typical minerals in fillings of veins and vesicles (Pertsev and Rusinov, 1980).

CONCLUSIONS

Our studies permit us to state that the alteration zones in basalts near veins are similar in chemical composition at several places in the holes, induced by kinetic factors and exchange between basalt and sea water moving along the system of cracks in the rocks. The alteration was primarily oxidative. Nearest the veins, clay minerals show maxima of iron and potassium content and minima of magnesia, silica, and alumina. Also near most veins are more abundant iron hydroxides, formed at the expense of titanomagnetite and earlier-formed secondary pyrite.

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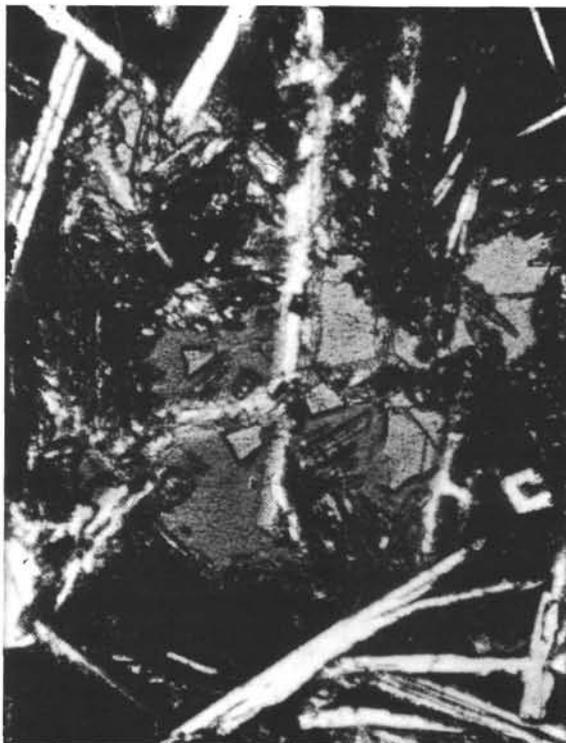
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2



3



4

Plate 1. Alteration Zones. 1. Boundary between "background" basalt (bottom, lighter part of the photograph) and "red" near-vein zone (upper, darker half of the photograph). X40, plane light. 504B-13-4, 10-12 cm, Piece 802. 2. Dark-green clay mineral with black cores. X40, plane light. 504B-27-1, 118-120 cm, Piece 1475. 3. Green clay mineral with "relict" spots of brown clay mineral. X40, plane light. 504B-28-1, 110-113 cm, Piece 1498. 4. The boundary between light-olive-brown clay mineral and brown clay mineral is seen even within one grain. Metasomatic, later development of brown smectite after light generation is apparent. X40, plane light. 505B-3-2, 99-101 cm, Piece 188.