53. MINERALOGY AND CHEMISTRY OF SECONDARY PHASES IN LOW TEMPERATURE ALTERED BASALTS FROM DEEP SEA DRILLING PROJECT LEGS 51, 52, AND 53

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INTRODUCTION

During DSDP Legs 51, 52, and 53, three deep holes were drilled in the Cretaceous crust of the Atlantic Ocean. Despite their proximity, the intensity of alteration in the first hole (417A) appeared to be very different from that of two others (417D and 418A). Rocks from Hole 417A were strongly altered and oxidized, whereas rocks from Holes 417D and 418A looked relatively fresh. A detailed study of the occurrence and the chemistry of secondary phases has been undertaken to specify the characteristics of alteration and the differences between the holes. The objective of this work was the understanding of the alteration process, in other words, the reaction of the oceanic Layer 2 with sea water in the case of this old crust.

METHODS

The samples obtained for this study were all examined in their section, except the clay veins. About 15 were selected for more detailed investigation.

Secondary minerals analyses were made on a CAMECA microprobe, using natural minerals as standards. Data reduction was made with the EMPADR VII program (Rucklidge and Gasparrini, 1969). A defocused beam was used to analyze clay minerals and zeolites which decomposed quickly under the beam. Despite the frequent fine-grained texture of most of the clays, compositions are homogeneous, except for the palagonites. X-ray diffraction powder patterns were used to specify the nature of the minerals.

Seven samples were selected for bulk analysis by M. Lenoble in the Laboratoire de Pétrographie using the XRF method.

HOLES 417D AND 418A

General Features

These two holes show about the same type of alteration. The most striking characteristic is the relative freshness of the rocks, compared to their age, as evidenced by the common presence of fresh glass in pillow margins.

The rocks of the two sequences show no evidence of oxidation. They are typically gray, with no altered halo around the numerous cracks. The intensity of alteration is rather low (almost all the magmatic minerals are preserved) and it shows no striking correlation with depth. However, it obviously is related to the thickness of individual cooling units (thick flows are usually fresher than pillows), and to the density of the cracks.

The samples studied are mostly plagioclase-olivine ± clinopyroxene phyric basalts, including flow interiors, pillow interiors and margins, and a few breccias (Tables 1 and 2).

The more common secondary minerals are clays and carbonates. Minor quantities of zeolites, quartz, pyrite, iron hydroxides, and exceptional K-feldspar and analcite are also present. Excepting a chlorite found in Hole 418A, they are all consistent with a low-temperature alteration.

The rock's reaction to alteration is the same in the two holes and the occurrences of secondary minerals are identical (Table 3). Secondary minerals are mainly found in vesicles and vein fillings and in breccia matrix, but they also occur replacing magmatic phases.

Clinopyroxene phenocrysts are always fresh. Except in a few samples, e.g., when the crystals are cut by calcite veinlets, plagioclase phenocrysts are also fresh. Olivine phenocrysts are always altered, except in the center of a

TABLE 1
Petrography of the Secondary Phases in the Samples Studied, Hole 417D

Sample (Interval in cm)	Rock Type	Fresh Glass	Palagonite	Fibropalagonite	Green Clay	Brown Clay	Carbonates	Zeolites	Analcite	Quartz/Chalcedony	Pyrite	Iron Hydroxide
22-3, 99-101	Pillow margin	+		+	+	+	+	+				
28-6, 9-12	Pillow margin	+	+	+	+	+	+	+			+	
28-6, 14-17	Pillow interior					+	+					+
28-6, 40-43	Pillow interior				+	+	+				+	+
28-6, 51-54	Pillow interior					+	+					
28-6, 66-69	Pillow interior				+	+	+					
28-6, 81-84	Pillow margin			+	+	+	+				+	+
28-6, 90-93	Pillow margin			+	+	+	+		+		+	
29-2, 16-19	Breccia					+	+					
29-3, 141-146	Pillow interior				+	+	+					
29-4, 73-78	Pillow margin			+	+	+	+					+
31-4, 137-141	Pillow interior					+	+					+
31-5, 58-63	Pillow margin			+	+	+	+					
34-5, 66-68	Pillow interior				+	+						
34-5, 115-117	Pillow margin	+	+		+	+		+	+		+	
34-6, 136-138	Pillow margin			+	+	+					+	
35-6, 25-30	Pillow margin	+		+	+	+						
37-3, 33-37	Vein					+	+					
38-1, 3-9	Breccia					+	+	+				
39-1, 28-31	Breccia					+	+	+				
39-4, 2-8	Pillow margin	+	+		+	+	+					
59-3, 141-145	Pillow margin				+		+					
59-4, 3-5	Pillow interior				+	+	+					
59-4, 27-29	Pillow interior				+	+	+					+
62-3, 14-17	Pillow margin	+	+		+		+	+				
62-3, 33-35	Pillow interior				+	+	+				+	
62-3, 53-55	Pillow interior				+	+	+			+		+
62-3, 166-168	Pillow interior					+	+					
63-2, 56-58	Flow					+	+					

TABLE 2
Petrography of Secondary Phases in the Samples Studied, Hole 418A

Sample (Interval in cm)	Rock Type	Fresh Glass	Palagonite	Fibropalagonite	Green Clay	Brown Clay	Carbonates	Zeolites	Quartz/Chalcedony	K-feldspar	Pyrite	Iron Hydroxide	Chlorite
20-1, 66-70	Flow					+							
33-1, 29-31	Pillow interior				+	+	+				+	+	
33-1, 51-53	Pillow interior				+	+	+				+	+	
38-3, 4-6	Pillow margin			+	+	+	+	+				+	
38-3, 16-18	Pillow interior				+	+							
38-3, 46-48	Pillow interior				+	+	+						
38-3, 50-52	Pillow margin			+	+	+	+	+					
40-2, 32-37	Breccia				+	+	+						
42-2, 138-143	Pillow margin			+	+	+	+	+			+		
50-4, 31-36	Pillow margin			+	+	+							
50-4, 102-106	Vein					+							
51-1, 34-35	Vein					+							
55-2, 33-37	Vein					+							
56-6, 56-60	Pillow margin			+	+	+		+			+		
58-1, 96-98	Hyaloclastite				+	+	+				+	+	
59-4, 134-140	Breccia				+	+	+		+	+			
60-2, 101-104	Pillow margin			+	+	+	+				+	+	
60-4, 136-140	Flow					+							
60-5, 65-69	Flow					+							
63-3, 52-55	Quartz geode								+				
65-1, 130-132	Pillow margin			+	+	+		+	+				
65-5, 58-62	Breccia					+	+						
67-2, 115-120						+							
71-2, 69-71	Pillow margin	+	+		+	+	+						
71-4, 102-106	Pillow margin			+	+	+	+	+			+	+	
73-6, 103-106	Vein					+							
75-5, 10-14	Pillow margin		+	+	+	+	+						
77-1, 69-73	Breccia					+	+					+	
84-1, 17-19	Flow					+							
84-3, 45-48	Flow					+							
85-1, 136-138	Flow					+							+
85-7, 3-7	Flow					+							
86-1, 68-71	Hyaloclastite				+	+							
86-1, 132-135	Breccia					+	+						
86-2, 91-94	Pillow margin			+	+	+	+				+	+	

thick cooling unit (lithologic Unit 14 in Hole 418A) or in fresh glassy margins. Olivine is replaced either by clay minerals (brown or green smectite) or calcite associated with opaque grains, probably iron hydroxides, and/or clay minerals (Plate 1, Figure 1). Most of the groundmass minerals (clinopyroxene, plagioclase, opaques) are usually fresh. But again, olivine grains, when present, are altered usually to brown smectite. The interstitial glass is always altered, even in the thickest flows, and usually it is replaced by brown or green smectite, sometimes with patches of calcite. However in one sample, it is replaced by a pale green chlorite.

From one sample to the other, pillow glassy margins show different stages of alteration. But it is interesting to notice that in fresh glass, fresh olivine is usually preserved. This probably means that the fluids cannot circulate in glass when there is no crack.

Clay Minerals

Two main types of clay minerals occur in the two holes, easily distinguished by their color in thin section: a green type and a brown type. They fill veins and vesicles and replace olivine phenocrysts, interstitial glass, and glassy fragments in brecciated pillow margins. A few XRD diagrams were made on clays filling thick veins or from

TABLE 3
Occurrence of Secondary Minerals in Holes 417D and 418A

	Palagonite	Protoceladonite	Saponite	Zeolites	Analcite	K-feldspar	Quartz	Chlorite	Calcite	Pyrite	Iron Hydroxide
Plagioclase phenocrysts						(+)			+		
Olivine		++	++						++		++
Glassy margins	++	++	++	+					++	+	
Interstitial glass		++	++					(+)	+		
Breccia matrix			++				+		++		
Vesicles		++	++				+		++	+	+
Veins		++	++	+	(+)				++	++	++

Note: ++ = abundant, + = rare, (+) = exceptional.

altered pillow margins. They all show smectite patterns, swelling with glycol, but further investigation is still necessary to specify their structure.

In veins and vesicles, the relationships between the green and the brown clays are always the same, i.e., the green lines the walls and the brown is in the center and was obviously the last to crystallize (Figure 2). Olivine phenocrysts are replaced usually by brown or green smectite but in one sample (417D-39-4, 2-8 cm), brown and green clay occur together in each individual pseudomorph and seem in equilibrium. In brecciated pillow margins, the two types replace formerly glassy fragments, but it is impossible to say if one crystallized before the other. However, the matrix between the fragments is always a light brown smectite.

The two types of clay are clearly distinct optically and chemically.

Green clay is always very fine grained and has a low birefringence. Its composition (Table 4) is FeO total, K_2O and SiO_2 rich, and MgO relatively poor. The water content (the difference between the microprobe analysis total and 100) is also relatively low (8 to 10%). The brightness of the green reflects the K_2O contents. The very bright green minerals contain up to 7 per cent K_2O and 27 per cent FeO*. The name "protoceladonite" has been suggested for them (Legs 51-53 post-cruise meeting). The lighter green clays (Table 4, Samples 3, 5, and 14) are consistently poorer in K_2O and FeO* and are correspondingly enriched in aluminum. They are not very common in these holes, but have been found commonly in Hole 417A, where the aluminum supply is plentiful.

Brown clay is better crystallized and its birefringence is notably higher. It occurs sometimes in spherulitic fibrous aggregates (Plate 1, Figure 3), mostly in veins and breccia matrix. Compared to the green clay, it is richer in magne-

TABLE 4
Representative Analysis of Green Clays, Holes 417D and 418A

	1[a]	2	3	4	5	6	7	8	9[b]	10	11	12	13	14	15
SiO_2	48.32	52.95	52.46	50.21	50.05	49.44	51.09	46.12	48.09	50.07	49.61	49.86	51.26	45.35	49.69
TiO_2	0.15	0.20	0.33	-	-	0.24	0.10	0.32	0.05					0.79	
Al_2O_3	5.54	6.60	15.14	3.67	14.10	4.23	2.53	6.83	7.55	4.66	6.39	9.08	7.99	11.06	7.21
FeO	27.75	20.18	12.57	26.81	12.16	25.83	25.71	24.34	24.37	24.13	21.49	20.74	19.53	22.75	20.68
MnO	0.06	0.03	0.04	0.31	0.07	0.07	0.04	0.09	0.12	0.06	0.04	0.14	0.09	0.08	0.06
MgO	3.27	6.89	5.97	5.11	6.03	3.98	4.89	6.32	4.77	4.51	7.25	6.61	5.69	5.87	5.90
CaO	1.04	1.32	1.95	0.74	1.35	0.48	0.64	1.21	0.44	0.70	1.35	0.68	0.12	1.14	0.68
Na_2O	-	-	-	-	-	-	-	-	-	-	-	-	0.20	-	-
K_2O	6.62	5.73	3.48	6.81	2.73	6.78	7.85	5.10	5.33	6.97	5.78	5.25	5.73	5.17	6.03
Total	92.75	93.89	91.94	93.66	86.48	91.05	92.85	90.32	90.77	91.10	92.01	92.36	90.40	92.42	90.26
On 22 oxygens															
Si	7.586	7.761	7.401	7.760	7.469	7.816	7.953	7.289	7.498	7.839	7.550	7.454	7.761	6.929	7.652
Al	0.414	0.239	0.599	0.240	0.531	0.184	0.047	0.711	0.502	0.161	0.450	0.546	0.239	1.071	0.348
Al	0.611	0.900	1.918	0.428	1.949	0.605	0.417	0.561	0.886	0.699	0.696	1.054	1.187	0.920	0.961
Ti	0.017	0.023	0.036	-	-	0.028	0.012	0.038	0.005	-	-	-	-	0.090	-
Fe	3.644	2.473	1.483	3.466	1.518	3.416	3.347	3.217	3.177	3.160	2.735	2.593	2.473	1.906	2.664
Mn	0.008	0.004	0.005	0.041	0.008	0.009	0.005	0.013	0.015	0.008	0.005	0.017	0.012	0.011	0.008
Mg	0.766	1.504	1.256	1.177	1.341	0.938	1.135	1.489	1.108	1.051	1.644	1.472	1.284	1.337	1.354
	5.046	4.904	4.698	5.112	4.816	4.996	4.916	5.318	5.191	4.918	5.080	5.136	4.956	5.264	4.987
Ca	0.176	0.207	0.295	0.122	0.215	0.082	0.106	0.205	0.073	0.117	0.221	0.109	0.019	0.187	0.112
Na	-	-	-	-	-	-	-	-	0.017	-	0.030	-	-	0.060	-
K	1.325	1.071	0.627	1.343	0.519	1.368	1.559	1.028	1.060	1.391	1.123	1.002	1.106	1.008	1.185
	1.501	1.278	0.922	1.465	0.734	1.450	1.665	1.333	1.158	1.508	1.374	1.111	1.125	1.255	1.297

[a] 1 to 8: Hole 417D (1 = Sample 22-3, 99-101 cm, bright green, vein filling; 2 = same sample as 1, bright green, vesicle filling; 3 = same sample as 1, light green, vesicle filling; 4 = Sample 28-6, 9-12 cm, bright green, vein filling; 5= Sample 34-5, 115-117 cm, light green, vein filling; 6 = Sample 39-4, 2-8 cm, bright green, vein filling; 7 = same sample as 6, bright green, olivine pseudomorph; 8 = Sample 62-3, 14-17 cm, bright green, vein filling).

[b] 9 to 15: Hole 418A (9 = sample 38-3, 4-6 cm, bright green, vein filling; 10 = Sample 38-3, 31-33 cm, bright green, vein filling; 11 = Sample 38-3, 50-52 cm, bright green, vein filling; 12 = Sample 42-2, 138-143 cm, bright green, in brecciated pillow crust; 13 = Sample 59-4, 134-140 cm, bright green, in brecciated pillow crust; 14 = Sample 74-2, 69-71 cm, bright green, vein filling; 15 = Sample 86-2, 91-94 cm, bright green, in brecciated pillow crust).

sium (~18%) and poorer in potassium, iron, and silica (Table 5). Its water content also seems higher (~11 to 14%). Its composition is not far from that of a saponite. This type is more abundant, mostly in Hole 418A. It fills the thick veins cutting the pillows and often occurs as breccia matrix, whereas the "protoceladonite" was never seen in thick volumes.

Alteration of Pillow Glassy Margins

Altered pillow margins are typically dark green. Their alteration gives three main types of products.

1) When some fresh glass is still present, it is commonly rimmed on the outer side of the pillow or replaced in narrow zones adjacent to the cracks by a yellow to brown, apparently poorly crystallized, nearly isotropic product (Plate 1, Figure 4), which may be called palagonite.

2) On the inner side of the glassy margin, replacing the glass between the varioles, occurs a yellow, birefringent, fibrous product which may be called fibropalagonite (Plate 1, Figure 5). It is frequently separated from the palagonite rim by a zone of fresh glass. When there is no fresh glass left, this fibropalagonite, commonly associated with sparse zeolite crystals, occurs alone. It probably represents a more evolved stage of the glass alteration. This is consistent with the observations in the upper part of Hole 417A, where only the fibropalagonite was observed.

3) The pillows often show an outer crust brecciated to hyaloclastite. I did not observe any fresh glass in these crusts. The once-glassy fragments are altered to either brown or green, or both clay minerals (see above) and cemented by a light brown smectite (saponite) or calcite matrix.

Palagonite and fibropalagonite both have been analyzed and compared with the parental fresh glass when possible.

In the four samples of Hole 417D (Table 6), the palagonite compositions are rather inhomogeneous, mostly for their silica, aluminum and iron contents. Compared to the parental glass, they always show (Figure 1) a decrease in Na_2O and CaO and an increase in H_2O and K_2O. The behavior of the other elements is less constant. Magnesium decreases in all the samples except Sample 417D-62-3, 14-7 cm. Titanium shows a tendency to increase but is sometimes variable (417D-34-3, 115-117 cm) and eventually decreases (417D-62-3, 14-17 cm). Palagonites are always depleted in manganese compared to fresh glass but all the values are very low. Silica and iron are highly variable, even in a single sample. In Hole 417D, except in Sample 417D-34-3, 115-117 cm, where silica is variable but iron rather constant, there seems to be an inverse correlation between these two elements, the iron-rich palagonite being silica poor (Figure 2). The fluids inducing the leaching of silica could favor the iron concentration and vice-versa.

TABLE 5
Brown Clay Analysis in Holes 417D and 418A

	1	2	3	4	5	6	7	8
SiO_2	46.70	47.51	42.37	45.98	43.02	43.85	44.56	44.23
TiO_2	0.07	0.15	-	-	-	0.23	-	-
Al_2O_3	5.22	6.57	8.02	8.52	8.00	7.19	5.98	7.85
FeO	16.89	15.80	16.01	13.04	9.31	16.94	12.01	13.06
MnO	0.04	0.09	0.04	0.07	0.05	0.05	0.08	0.05
MgO	17.63	17.02	18.01	20.25	20.88	18.45	19.61	20.81
CaO	1.00	1.82	1.72	0.52	0.34	0.88	0.37	0.35
Na_2O	-	-	0.03	-	0.03	-	-	0.06
K_2O	0.33	0.42	0.16	0.02	0.02	0.02	0.02	0.01
	87.87	89.32	86.37	88.40	81.85	87.59	82.62	86.43
On 22 oxygens								
Si	7.112	7.075	6.603	6.800	6.802	6.725	7.031	6.722
Al	0.888	0.925	1.397	1.200	1.198	1.275	0.969	1.278
Al	0.050	0.229	0.077	0.285	0.294	0.025	0.143	0.128
Ti	0.008	0.017	-	-	-	0.027	-	-
Fe	2.151	1.968	2.087	1.613	1.231	2.173	1.585	1.660
Mn	0.005	0.011	0.005	0.009	0.007	0.007	0.010	0.007
Mg	4.002	3.777	4.183	4.465	4.921	4.220	4.611	4.713
	6.216	6.002	6.352	6.372	6.453	6.452	6.349	6.508
Ca	0.164	0.290	0.287	0.083	0.060	0.144	0.062	0.057
Na	-	-	0.010	-	0.010	-	-	0.017
K	0.065	0.080	0.032	0.004	0.005	0.004	0.004	0.003
	0.229	0.370	0.329	0.087	0.075	0.148	0.066	0.077

Note: 1 = Sample 417D-22-3, 99-101 cm (vesicle filling); 2 = Sample 417D-39-4, 2-8 cm (olivine pseudomorph); 3 = Sample 418A-38-3, 50-52 cm (vein filling); 4 = Sample 418A-42-2, 138-143 cm (vesicle filling); 5 = Sample 418A-42-2, 138-143 cm (vein filling); 6 = Sample 418A-56-6, 56-60 cm (vein filling); 7 = Sample 418A-59-4, 134-140 cm (breccia matrix); 8 = Sample 418A-86-2, 91-94 cm (vein filling).

In Hole 418A, palagonite and parental fresh glass have been analyzed in only one sample (Figure 3). The behavior of water, sodium, potassium, and calcium is the same as in Hole 417D. For the other elements, it is close to Sample 417D-39-4, 2-8 cm (Table 7).

In both Holes 417D and 418A, fibropalagonites are also rather inhomogeneous and vary widely from one sample to the other (Tables 6 and 7), mostly in their iron, magnesium, and titanium contents. However, they are always poorer in SiO_2, CaO, and Na_2O, and richer in K_2O than the fresh glass analyzed in the same rock (when present) or in the same lithologic unit (Byerly and Sinton, this volume). In only one sample (417D-28-6, 9-12 cm), both palagonite and fibropalagonite were analyzed; the fibropalagonite is more hydrated and K_2O-enriched than the palagonite and shows a marked decrease in silica, magnesium, and calcium.

Alteration of glassy margins appears as a fairly complex phenomenon, as emphasized by the compositional variability of the secondary products. These are probably poorly crystallized clays, and the necessity of using a defocused beam for microprobe analysis does not help to understand their composition. Palagonite and fibropalagonite are commonly cut by veins filled with green and brown clay, identical to the clays replacing glassy fragments in the brecciated pillow crusts (Plate 1, Figure 6). Thus, the alteration occurs probably in three steps : (1) formation of an outer rim of palagonite; (2) penetration of the fluids in the pillow along cracks and formation of the fibropalagonite which can even replace the palagonite; and (3) the glassy fragments of the brecciated crust continue to evolve with the ongoing circulation of fluids between the pillows and are finally replaced by brown and/or green clay minerals.

Chlorite

The microprobe analysis of the pale green mineral replacing the interstitial glass in Sub-unit 14C flow (Sample 418A-85-1, 136-138 cm) gives a typical chlorite composition (Table 8). However, this could not be confirmed by XRD because of the small size and the scarcity of the crystals. In the same sample, the olivine is partly fresh but shows an incipient alteration to a brown mineral. It has a clay composition similar to the brown clay already described (Table 8). The occurrence of chlorite in this 30-meter-thick flow could be related to an early-stage transformation of the glass, when the flow was not completely cold. Thus, this chlorite can be regarded as a deuteric mineral. This idea is supported by the fact that chlorite was only observed in this thick cooling unit, and never in pillows. The occurrence of deuteric minerals in submarine basalts has already been reported (Bass, 1976). The olivine alteration may have occurred later and have been related to the sea-water circulation, when the rock was completely cooled.

Zeolites and Analcite

The scarcity of zeolites is a striking characteristic of these two holes. In Holes 417D and 418A, they occur in altered

TABLE 6
Representative Microprobe Analysis of Glass and Palagonite, Hole 417D

	1		2			3		4		5	
	G	FP	G	P	FP	G	P	G	P	G	P
SiO_2	49.76	46.03	49.94	52.94	48.72	50.28	50.98	50.74	53.05	50.61	47.18
TiO_2	1.48	1.03	1.75	2.18	1.98	1.98	2.50	1.72	2.90	1.82	0.76
Al_2O_3	14.91	13.47	15.13	13.56	15.26	14.01	16.87	14.86	16.81	14.65	12.86
FeO+	11.52	18.32	11.38	12.18	12.89	12.23	11.31	11.62	9.44	12.33	18.29
MnO	0.27	0.13	0.28	0.02	0.04	0.25	0.13	0.24	0.07	0.25	0.12
MgO	7.66	4.33	8.00	7.49	3.60	7.02	6.71	7.35	5.93	7.72	11.86
CaO	11.98	1.42	11.16	4.06	1.71	11.74	3.06	11.38	3.37	10.88	4.22
Na_2O	2.30	0.07	2.30	0.38	0.21	2.26	0.18	2.35	0.44	2.22	0.04
K_2O	0.09	4.19	0.07	0.85	2.94	0.06	0.60	0.10	0.60	0.10	0.17
	99.97	88.97	100.02	93.67	87.29	99.82	92.27	100.36	92.62	100.59	95.50

Note: G = fresh glass, P = palagonite, FP = fibropalagonite. 1 = Sample 22-3, 99-101 cm; 2 = Sample 28-6, 9-12 cm; 3 = Sample 34-5, 115-117 cm; 4 = Sample 39-4, 2-8 cm; 5 = Sample 62-3, 14-17 cm.

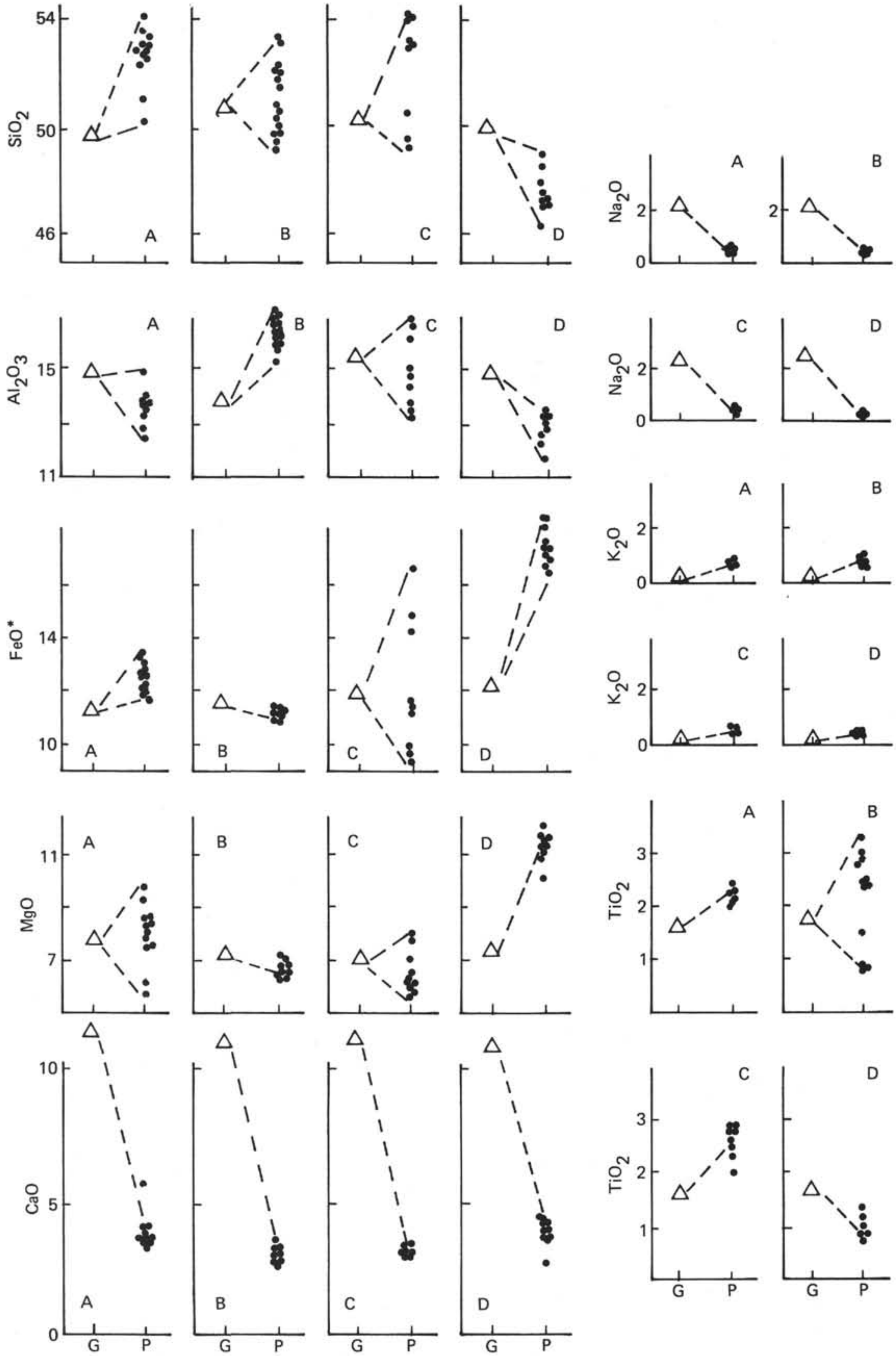


Figure 1. *Hole 417D: chemical comparison between palagonites (P) and parental fresh glass (G). A = Sample 28-6, 9-12 cm; B = Sample 34-5, 115-117 cm; C = Sample 39-4, 2-8 cm; D = Sample 62-3, 14-17 cm.*

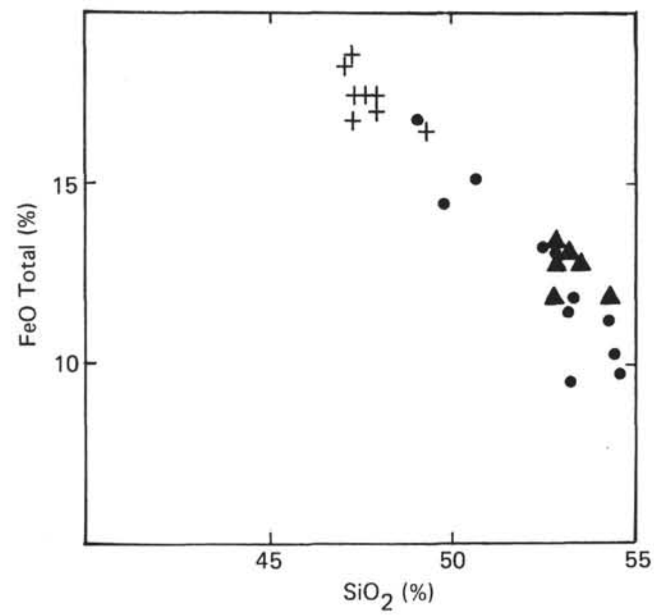


Figure 2. *Hole 417D: FeO total versus SiO_2 in some palagonites.* ▲ = *Sample 28-6, 9-12 cm;* ● = *Sample 39-4, 2-8 cm;* + = *Sample 62-3, 14-17 cm.*

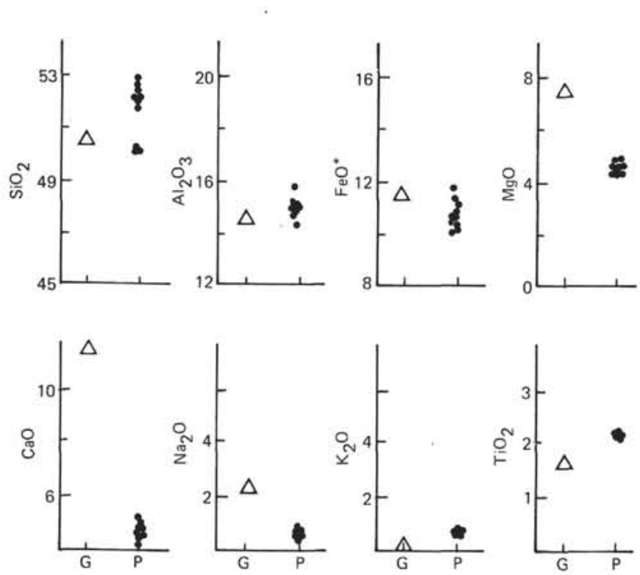


Figure 3. *Sample 418A-71-2, 69-71 cm: chemical comparison between palagonite (P) and parental fresh glass (G).*

TABLE 7
Representative Analysis of Fibropalagonites, Fresh Glass, and Palagonite in Hole 418A

	1	2	3	4	5
SiO_2	43.89	47.28	48.59	50.71	52.10
TiO_2	1.22	1.30	4.06	1.70	2.12
Al_2O_3	17.14	14.99	15.34	14.45	14.95
FeO	15.26	10.19	13.75	11.46	10.64
MnO	0.08	0.04	0.05	0.29	0.04
MgO	13.06	14.64	8.15	7.57	4.51
CaO	0.70	1.73	1.81	11.62	4.69
Na_2O	0.10	-	-	2.34	0.42
K_2O	1.12	0.27	0.65	0.07	0.62
Total	92.56	90.45	92.40	100.21	90.08

Note: 1 to 3 = fibropalagonites (1 = Sample 38-3, 4-6 cm; 2 = Sample 42-2, 138-142 cm; 3 = Sample 56-6, 56-60 cm); 4 and 5 = fresh glass and palagonite (Sample 71-2, 69-71 cm).

TABLE 8
Representative Analysis of Chlorite and Smectite in a Thick Flow, Hole 418A

	1	2
SiO_2	36.75	47.90
Al_2O_3	9.64	2.97
FeO	15.22	9.68
MnO	0.23	0.12
MgO	24.27	22.88
CaO	0.29	1.19
K_2O	0.13	0.21
	86.52	84.95
Si	7.347	7.280
Al	0.652	0.530
	On 28	**22 Oxygens**
Al	1.621	–
Fe	2.545	1.230
Mn	0.039	0.015
Mg	7.232	5.183
Ca	0.061	0.194
K	0.031	0.042
	11.529	6.664

Note: Sample 418A-85-1, 136-138 cm. 1 = chlorite replacing glass. 2 = smectite replacing olivine.

glassy margins as pinkish crystals associated with fibropalagonite (Plate 1, Figure 5). They are commonly cut by veins filled with clay mineral or calcite. Microprobe analyses of these zeolites are very homogeneous and do not vary much from one sample to the other. They are calcium and potassium rich and sodium poor (Table 9). The X-ray diffraction results show a phillipsite pattern. Considering the composition, it is a silica-rich variety of phillipsite.

In Hole 417D only, zeolite occurs as small individual crystals scattered in calcite veins. They are distinct in composition (Table 9), silica rich and calcium poor. No X-ray diffraction diagram could be obtained because of the scarcity and the small size of the crystals.

Analcite was observed in only two samples in Hole 417D, in late-stage calcite veins.

Calcite

Calcite is widespread in the whole sequence of the two holes. It occurs mainly in vesicles, thick vein fillings, and breccia matrix. It sometimes replaces olivine phenocrysts, in association with iron hydroxides and brown clay, and occasionally plagioclase phenocrysts when they are cut by a vein. It is also present in the groundmass, mostly in zones adjacent to thick veins.

In vein filling and breccia matrix, calcite forms large crystals and (in the specimen studied) never looks like

TABLE 9
Representative Analysis of Zeolites in Holes 417D and 418A

	1	2	3	4	5	6	7
SiO_2	54.91	53.65	53.48	54.27	60.75	58.54	59.56
Al_2O_3	17.69	19.92	20.71	18.61	18.44	19.40	18.67
CaO	4.69	5.56	5.72	6.35	0.	0.41	0.36
Na_2O	1.55	0.78	2.10	0.68	2.59	3.14	3.26
K_2O	3.51	2.54	3.61	2.88	6.90	7.38	7.00
	82.36	82.45	85.63	82.78	88.67	88.88	88.86

Note: 1 to 4 = zeolites associated to fibropalagonite (1 = Sample 417D-62-3, 14-17 cm; 2 = Sample 418A-38-3, 50-52 cm; 3 = Sample 418A-42-2, 138-143 cm; 4 = Sample 418A-56-6, 56-60 cm). 5 to 7 = zeolites in calcite veins (5 = Sample 417D-22-3, 99-101 cm; 6 = Sample 417D-28-6, 9-12 cm; 7 = Sample 417D-34-5, 115-117 cm).

sediments trapped between the pillows, e.g., as described in Leg 37 rocks (Robinson et al., 1977). In the vesicles, it often forms radial aggregates.

Everywhere calcite appears as the later stage product of alteration. Calcite is always in the center of veins and vesicles when they contain clays also (Plate 2, Figure 1). In breccia matrix, it is sometimes associated to saponite (Plate 1, Figure 3). Calcite veins cut most of the secondary minerals, except rare zeolites and analcite in Hole 417D and quartz and iron hydroxides in both holes.

The iron, magnesium, and manganese contents of the calcite have been tested with the microprobe. Results (only semi-quantitative because calcite is quickly burnt by the beam even when defocused) show that the calcite is always very pure, with usually only traces of these elements. However, in one sample (417A-38-3, 50-52 cm), calcite contains about 0.30 per cent MnO.

Other Minerals

Quartz and chalcedony have been found in a few samples as a late-stage product, mainly in breccia matrix. In Hole 418A, a well-crystallized geode of quartz fills a vug in Section 63-3, attesting the circulation of silica-rich fluids.

Potassium feldspar has been observed in only one sample, replacing a few plagioclase phenocrysts in basalt fragments of breccia (microprobe determination).

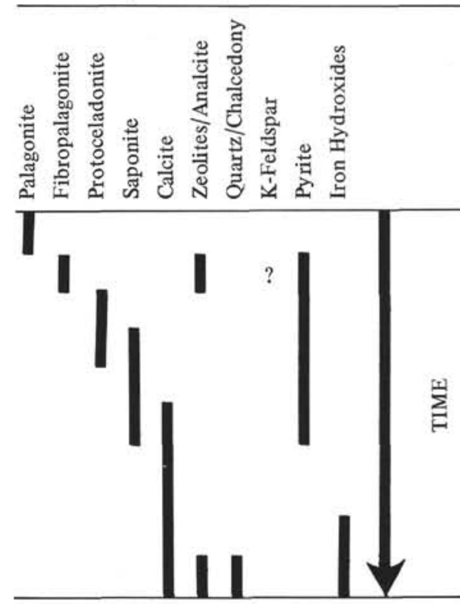
Secondary pyrite is widespread though not abundant in the two holes. It occurs often in altered pillow margins, in euhedral crystals scattered in fibropalagonite or brecciated crust. In veins and vesicles, it is usually associated with green or brown clay or lines the calcite center, but was never seen in the calcite itself.

Iron hydroxides are not very abundant in these two holes and occur mainly in calcite veins.

Alteration Sequence

The occurrence and the textural relationship between the different secondary minerals suggest a crystallization sequence with time, as summarized in Table 10. It is, however, impossible to evaluate the period of time between the rocks' crystallization, the formation on the early-stage secondary products, and the end of the alteration process. The persistence of fresh glass through the whole sequences suggests that the fluid circulation stops rather quickly as soon as the filling of the veins seals the rocks.

TABLE 10
Tentative Crystallization Sequence
Secondary Minerals, Holes 417D and 418A



HOLE 417A

General Features

In hand specimen, alteration looks quite different in rocks from Hole 417A. The major differences are the high intensity of alteration in the top of the hole and the marked decrease with increasing depth.

At the top of the hole, the samples are typically brown, showing an evidence of strong oxidation. No fresh glass was observed in pillow margins. Oxidation decreases with depth and the rocks become gray as in Holes 417D and 418A. At the bottom of the hole, fresh glass was observed in one pillow margin.

The samples studied are pillow margins and interiors and some breccias (Table 11).

The nature of the secondary minerals is not very different from the two other holes, but the abundance of some of the minerals varies. Clay minerals and calcite are still the more common but potassium feldspar, zeolites, and analcite are more widespread than previously. They are still consistent with a low temperature alteration.

As in Holes 417D and 418A, secondary minerals occur in vesicles and veins or they replace the glass. But they also commonly replace magmatic minerals (Table 12). Clinopyroxene phenocrysts are the only phases to be fresh through the whole sequence.

In the more-altered rocks, plagioclase phenocrysts are replaced by pinkish clay, potassium feldspar, or zeolites. The altered/fresh plagioclases ratio decreases with depth. Olivine phenocrysts are always altered. In the top of the hole, the groundmass is usually altered to a dark brown, almost isotropic material, responsible for the color of the rocks. In the bottom of the hole, it looks much fresher.

Clay Minerals

Clay minerals are also very common in Hole 417A. Preliminary X-ray diffraction results all gave smectite patterns

TABLE 11
Petrography of Secondary Phases in the Samples Studied, Hole 417A

Sample (Interval in cm)	Rock Type	Fresh Glass	Palagonite	Fibropalagonite	Green Clay	Grayish Clay	Pinkish Clay	K-feldspar	Carbonates	Zeolites	Analcite	Iron Hydroxides
24-3, 21-23	Pillow interior					+	+	+	+			+
24-3, 27-29	Pillow interior					+	+	+	+			+
24-3, 34-36	Pillow interior					+	+	+	+			+
24-3, 55-59	Pillow margin			+	+	+	+	+	+			+
26-5, 77-80	Pillow margin			+	+	+	+	+	+	+	+	+
26-5, 87-89	Pillow interior				+	+	+	+	+			
26-5, 90-92	Pillow interior				+	+	+	+	+			
26-5, 99-101	Pillow interior				+	+	+	+	+			+
26-5, 112-114	Pillow interior				+	+	+	+	+			+
28-2, 69-74	Pillow margin			+	+	+	+	+	+		+	+
29-5, 25-30	Pillow margin			+	+	+	+	+	+		+	+
29-5, 117-121	Pillow margin			+	+	+	+	+	+	+		+
30-1, 95-99	Breccia					+			+	+		+
35-5, 2-6	Breccia					+			+	+	+	+
36-1, 115-119	Pillow margin			+		+			+	+	+	+
38-3, 3-7	Pillow margin			+	+	+	+	+	+	+	+	+
38-3, 105-107	Pillow interior				+	+	+		+	+		+
38-3, 110-113	Pillow interior				+	+	+		+	+		+
38-3, 122-125	Pillow interior				+	+	+		+	+		+
38-3, 130-133	Pillow interior				+	+	+		+			
38-3, 140-143	Pillow interior								+	+		+
40-3, 48-52	Pillow margin			+	+	+			+			+
46-1, 41-46	Pillow margin	+	+	+	+	+			+	+		+
46-2, 92-96	Breccia				+	+			+	+		+

TABLE 12
Occurrence of Secondary Minerals in Hole 417A

	Palagonite	Pinkish Clay	Grayish Clay	Protoceladonite	K-feldspar	Zeolites	Analcite	Calcite	Iron Hydroiydes
Plagioclase phenocrysts		++			++	++	+	+	
Olivine phenocrysts			++	++				++	++
Glassy margins	++		++	+				+	
Interstitial glass		+	++	++				+	
Breccias			++	++			++	++	++
Vesicles			++	++				++	+
Veins		+	++	++			+	++	++

Note: ++ = abundant; + = rare.

swelling with glycol. But as in Holes 417D and 418A, further investigations are still necessary.

Clays replace magmatic minerals and glass or fill veins and vesicles. Three main types can be distinguished by their chemical compositions which are again reflected by their color in thin section: a pinkish type, a grayish to yellowish type, and a green type. The late-stage brown saponite, common in Holes 417D and 418A, was not observed in this hole.

The pinkish clay is mainly found in the plagioclase pseudomorphs usually associated with potassium feldspar. Often, only the plagioclase center, more calcic, is altered, while the more sodic rim is preserved (Plate 2, Figure 2). Occasionally, the clay replaces the interstitial glass or occurs in vein filling. It is usually well crystallized and moderately birefringent. Its composition is well defined (Table 13). It is distinctly Al_2O_3 rich (~ 30%) and FeO total poor (1 to 4%). MgO is rather variable. It contains about 1 per cent K_2O and almost no Na_2O.

The grayish to yellowish clay is the more abundant in the samples studied. In pillow interiors, it commonly replaces olivine or interstitial glass. In pillow margins or hyaloclastites, it usually replaces glassy fragments. It also fills some veins and vesicles, usually lining the edge, while the center is occupied by a green clay. In hand specimen, this clay is light green and typically waxy and the pillow margins and hyaloclastites look quite different from those in Holes 417D and 418A where they are dark green. In thin section, its color actually varies from grayish to light green or yellowish.

Its composition seems intermediary between pinkish clay and green clay (Table 14). It contains only 15 to 20 per cent Al_2O_3 and is correspondingly enriched in total FeO (10 to 15%) and K_2O (3%). The grayish clays are richer in

TABLE 13
Representative Analysis of Pinkish, Aluminum-Rich Clays, Hole 417A

	1	2	3	4	5
SiO_2	46.52	44.55	45.45	48.27	48.60
Al_2O_3	31.12	30.32	28.97	29.97	26.92
FeO	1.05	1.07	2.20	1.87	4.09
MnO	0.16	0.26	0.36	0.05	0.23
MgO	6.48	10.14	10.92	5.74	3.73
CaO	1.77	1.47	1.41	0.83	2.47
Na_2O	-	-	-	0.30	-
K_2O	0.95	0.68	0.68	0.58	1.66
	88.04	88.48	89.99	90.31	87.69
On 22 Oxygens					
Si	6.348	6.090	6.154	6.587	6.781
Al	1.652	1.910	1.846	1.413	1.219
Al	3.354	2.975	2.777	3.407	3.209
Fe	0.119	0.122	0.249	0.214	0.477
Mn	0.018	0.030	0.041	0.006	0.027
Mg	1.318	2.067	2.205	1.167	0.775
	4.809	5.707	5.272	4.704	4.488
Ca	0.258	0.215	0.205	0.121	0.369
Na				0.079	
K	0.166	0.118	0.117	0.101	0.147
	0.424	0.333	0.322	0.301	0.516

Note: 1 = Sample 24-3, 27-29 cm (replacing plagioclase); 2 = Sample 26-5, 87-89 cm (replacing plagioclase); 3 = Sample 26-5, 87-89 cm (filling a vein); 4 = Sample 38-3, 122-125 cm (replacing plagioclase); 5 = Sample 38-3, 122-125 cm (replacing glass).

TABLE 14
Grayish to Yellowish Clay, Hole 417A

	1	2	3	4	5	6	7	8
SiO_2	45.56	47.42	47.30	44.25	43.16	49.61	50.23	46.60
TiO_2	-	0.40	0.04	0.34	0.23	0.49	0.65	-
Al_2O_3	13.60	13.36	18.77	16.01	14.09	20.94	19.35	26.92
FeO	16.57	15.47	13.82	15.96	17.18	9.93	9.77	4.09
MnO	0.21	0.21	0.12	0.29	0.18	0.04	0.06	0.23
MgO	7.30	6.59	5.00	7.71	8.55	4.49	4.84	3.73
CaO	1.46	1.05	2.30	0.73	0.58	1.57	1.64	2.47
Na_2O	-	-	0.27	-	-	0.20	0.72	-
K_2O	3.15	2.62	3.57	2.63	3.23	3.16	2.46	1.66
	87.85	87.14	91.22	87.92	87.20	90.41	89.23	87.69
On 22 Oxygens								
Si	6.977	7.204	6.852	6.720	6.709	7.002	7.117	6.781
Al	1.023	0.796	1.148	1.280	1.291	0.998	0.883	1.219
Al	1.432	1.595	2.053	1.586	1.291	2.485	2.349	3.208
Ti	-	0.046	0.005	0.039	0.027	0.052	0.070	-
Fe	2.123	1.966	1.672	2.027	2.233	1.171	1.158	0.477
Mn	0.027	0.028	0.015	0.037	0.024	0.004	0.008	0.027
Mg	1.667	1.492	1.078	1.746	1.981	0.944	1.044	0.776
	5.249	5.128	4.823	5.435	5.557	4.656	4.629	4.488
Ca	0.240	0.172	0.356	0.118	0.097	0.237	0.249	0.369
Na	-	-	0.077	-	-	0.054	0.198	-
K	0.615	0.509	0.650	0.509	0.641	0.568	0.444	0.295
	0.845	0.681	1.083	0.627	0.738	0.859	0.891	0.664

Note: 1 = Sample 24-3, 27-29 cm (olivine pseudomorph); 2 = Sample 24-3, 27-29 cm (vesicle filling); 3 = Sample 26-5, 77-80 cm (replacing glassy fragments in brecciated pillow margin); 4 = Sample 26-5, 87-89 cm (olivine pseudomorph); 5 = Sample 26-5, 87-89 cm (vesicle filling); 6 = Sample 28-3, 69-74 cm (replacing glassy fragments in brecciated pillow margin); 7 = Sample 29-5, 117-121 cm (id); 8 = Sample 38-3, 140-143 cm (replacing interstitial glass).

TABLE 15
Representative Analysis of Green Clays (protoceladonites), Hole 417A

	1	2	3	4	5
SiO_2	47.68	50.91	49.81	45.72	50.33
Al_2O_3	7.00	6.11	4.24	5.65	3.08
FeO	24.37	22.58	24.88	26.49	24.65
MnO	0.22	0.13	0.18	0.24	0.15
MgO	4.92	4.55	5.07	4.62	5.29
CaO	0.72	0.91	0.49	1.15	0.65
Na_2O	-	0.18	-	-	0.04
K_2O	4.79	6.22	7.02	6.02	6.17
	89.85	91.60	91.70	89.89	90.37
On 22 Oxygens					
Si	7.509	7.802	7.790	7.410	7.938
Al	0.491	0.198	0.210	0.590	0.062
Al	0.808	0.905	0.572	0.489	0.510
Fe	3.210	2.894	3.255	3.591	3.252
Mn	0.030	0.017	0.024	0.033	0.020
Mg	1.154	1.040	1.181	1.116	1.244
	5.202	4.856	5.032	5.229	5.026
Ca	0.121	0.149	0.083	0.199	0.111
Na	-	0.055	-	-	0.012
K	0.963	1.216	1.401	1.245	1.242
	1.084	1.420	1.484	1.444	1.265

Note: 1 = Sample 24-3, 21-23 cm (vesicle filling); 2 = Sample 26-5, 77-80 cm (vein filling); 3 = Sample 26-5, 87-89 cm (vesicle filling); 4 = Sample 38-3, 122-125 cm (replacing interstitial glass); 5 = Sample 46-1, 41-46 cm (vein filling).

aluminum, the yellowish poorer. Again, magnesium varies widely and sodium is absent. In pillow margins and hyaloclastites, the clay analyses show a certain amount of titanium, absent in clays crystallized in veins or vesicles. Chemically, it is quite similar to clay minerals replacing glassy fragments described by Melson and Thompson (1973). It is also close to the light green clay in Holes 417D and 418A.

The green clay is similar to the protoceladonite described for Holes 417D and 418A. It occasionally replaces interstitial glass, but more commonly fills veins and vesicles. Typically bright green in thin section, it is always very fine grained and low birefringent. As in the two other holes, it is rich in FeO total (25%) and K_2O (6%), and poor in Al_2O_3 and MgO (Table 15). This clay seems to be the last to crystallize. I observed two examples of veins filled with protoceladonite in the center and grayish clay on the edges (Plate 2, Figure 3). Green clay also cuts plagioclases altered to pinkish clay (Plate 2, Figure 4).

The clay minerals found in Hole 417A show some differences from those found in the two other holes. The occurrence of aluminum-rich clays undoubtedly is related to the breakdown of plagioclase, as suggested by Scheiddeger and Stakes (1977) for the Peru Trench basalts. The relationships between the three types of clays suggest the following crystallization sequence: (1) pinkish clay in plagioclase pseudomorphs; (2) grayish to yellowish clay replacing glassy fragments, lining veins and vesicles; and (3) protoceladonite in veins and vesicles. Correspondingly, the smectites become aluminum poor and rich in iron and potassium. This is consistent with a low mobility of aluminum compared to iron and potassium, which are easily transported in solution. The magnesium evolution is more complex. The most striking characteristic of the samples studied in this hole is the absence of a magnesium-rich clay while magnesium is obviously leached from olivine and glass by the circulating fluids.

Clay mineral compositions of the three holes have been plotted in two diagrams (Figure 4): Al:Fe total:K and Al:Fe total:Mg. Both diagrams show that the clays can be distributed into two groups. The first group corresponds to the brown clay (saponite) and is distinctly MgO rich and K_2O poor. It is a trioctahedral smectite. The second group comprises all the others, from the aluminum-rich (pinkish) clays to protoceladonite rich in iron and potassium. As the oxidation state of the iron is not known (microprobe analysis), it is difficult to know what kind of substitution occurs.

Alteration of Glassy Margins

In the top of the sequence, pillow glassy margins are strongly altered. One striking difference with Holes 417D and 418A is the obvious oxidative characteristics of this alteration. Under the light green brecciated crust, the pillows show a dark brown rim; the varioles and the whole spherulitic zone are altered to a dark brown material, impossible to identify optically (Plate 2, Figure 5). Semiquantitative probe analyses of this material gave highly variable results, but always with a consistently low total suggesting the presence of abundant water. One constant

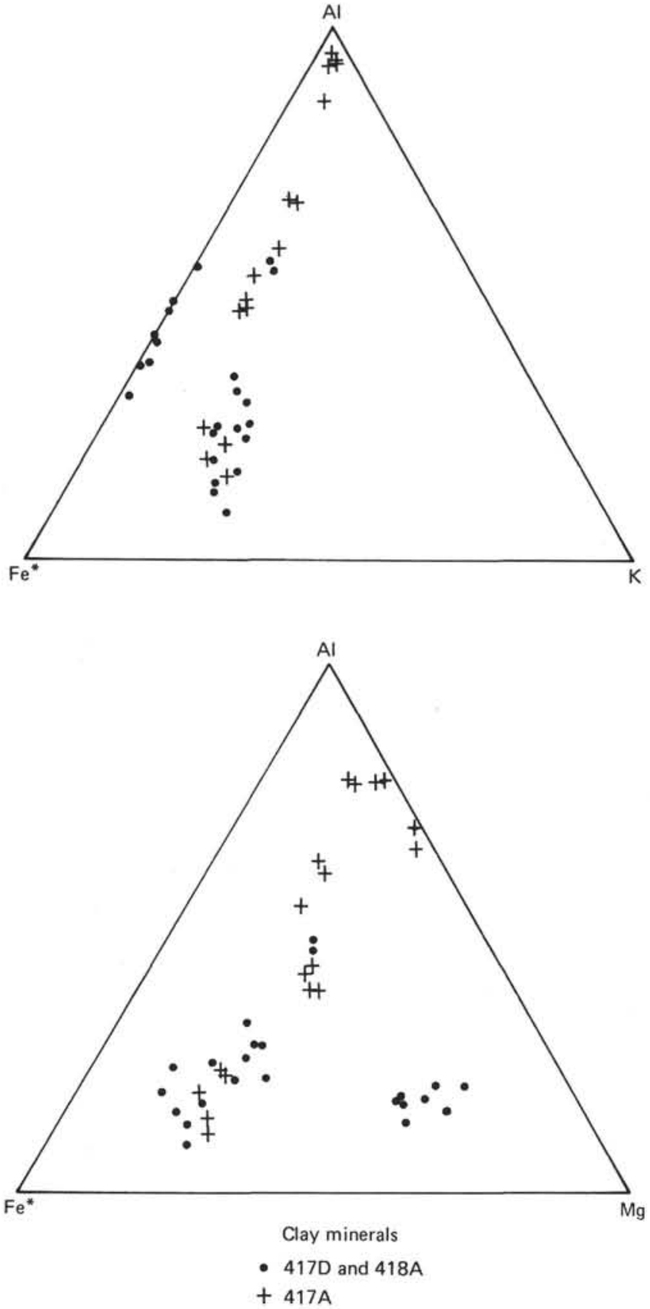


Figure 4. *Clay minerals. + = Hole 417A; • = Holes 417D and 418A.*

feature, however, is the high iron content (between 30 and 50%); this means that iron hydroxides are probably one of its main phases. No palagonite *per se* was observed, but the glass between the varioles is altered to a bright yellow or orange fibropalagonite, probably strongly oxidized. Chemically (Table 16), it is not very different from the grayish clay replacing glassy fragments in the pillow crust.

Alteration decreases with depth, and in the bottom of the sequence I found a pillow margin with fresh glass remaining (Sample 417A-46-1, 41-46 cm). The fresh glass zone is enclosed in palagonite (Plate 2, Figure 6). In this case, the varioles appear fresh. The palagonite, almost isotropic and very fine grained, is either brown or greenish brown, with

TABLE 16
Alteration of Pillow Glassy Margins, Hole 417A

	1	2	3	4	5	6
SiO_2	47.09	46.64	50.10	44.92	40.51	45.87
TiO_2	1.41	1.58	1.83	2.92	3.47	2.47
Al_2O_3	19.68	20.43	14.84	17.95	15.42	18.71
FeO	13.64	15.08	11.47	10.20	15.90	13.54
MnO	0.05	0.10	0.33	0.05	0.08	0.06
MgO	4.18	4.43	8.01	1.69	2.93	2.76
CaO	1.46	1.66	11.43	7.05	5.58	3.70
Na_2O	0.31	0.30	2.48	1.12	0.72	0.49
K_2O	3.48	2.95	0.08	0.42	0.18	1.90
	91.30	93.17	100.57	86.32	84.79	89.50

Note: 1 = fibropalagonite (Sample 28-3, 69-74 cm); 2 = fibropalagonite (Sample 29-5, 117-121 cm); 3 = fresh glass (Sample 46-1, 41-46 cm); 4 = green palagonite (Sample 46-1, 41-46 cm); 5 = brown palagonite (Sample 46-1, 41-46 cm); 6 = fibropalagonite (Sample 46-1, 41-46 cm).

sharp contacts between the different color zones and no evidence of particular distribution of the two types. The two colors reflect marked differences in composition (Table 16). Figure 5 shows that the green type is considerably richer in SiO_2 and Al_2O_3 and somewhat richer in CaO and K_2O than the brown type, while poorer in FeO total and MgO. Compared to fresh glass, they both show a leaching of SiO_2, MgO, CaO, and Na_2O, and a concentration in TiO_2 and K_2O. The reason for the coexistence of these two distinct palagonites is not clear. The textural relationships do not reveal if they are in equilibrium, or if one crystallized after the other one. In any case, it is clear from their composition that they are distinct from the green protoceladonite and the brown saponite found in brecciated pillow margins of Hole 418A. Here, the color is certainly related to the iron oxidation state. Fibropalagonite is also present between the

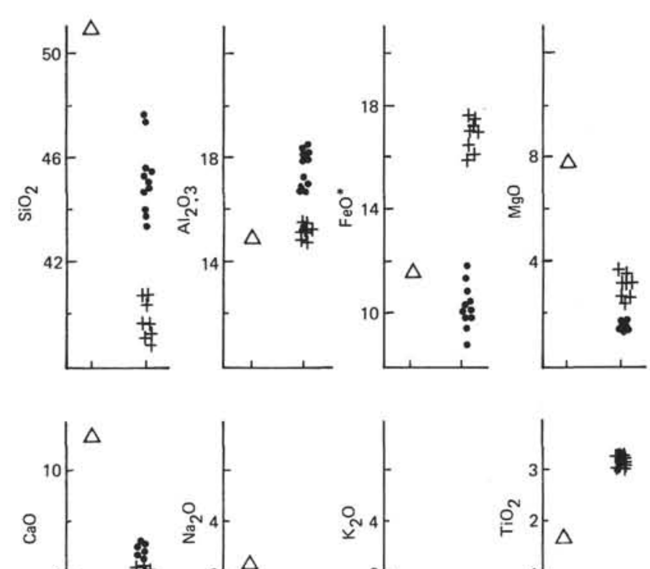


Figure 5. *Sample 417A-46-1, 41-46 cm: chemical comparison between fresh glass (G) and palagonite (P; • = green palagonite; + = brown palagonite).*

varioles, in the inner side of the pillow. Its composition is similar to those of the fibropalagonites analyzed in more altered samples (Table 16).

One striking difference between the palagonite in Holes 417A and 417D is their water content. In Hole 418A, it is about 15 per cent, while in Hole 417D it is less than 10 per cent. The former could be a more evolved type of palagonite, having undergone a severe leaching of SiO_2 and MgO, similar to those described in other altered pillow basalts (Melson, 1973; Scarfe and Smith, 1977).

Potassium Feldspar

Potassium feldspar is widespread in the whole sequence (microprobe identification). It always occurs in plagioclase pseudomorphs, associated with pinkish clay (Plate 2, Figure 2) or alone. It is, however, more abundant in the top of the sequence, while in the bottom plagioclases are more often replaced either by zeolites or analcite.

Potassium feldspar seems to be a rather early-stage secondary mineral.

Zeolites

While zeolites are more abundant in Hole 417A than in Holes 417D and 418A, they do not have the same occurrence. They completely replace plagioclase phenocrysts. In the same rock, plagioclase can be replaced either by zeolite or analcite or clay and K-feldspar.

Microprobe analyses (Table 17) gave variable compositions from one sample to the other, but homogeneous in a single rock. In Sample 417A-38-3, 122-125 cm, the zeolite is a Ca-rich variety whose formula is close to a chabazite (also found by XRD in this hole by Juteau et al., personal communication). In the other samples, the zeolites have rather similar Si and Al contents, but their Ca/Na/K ratios vary. Further determination would require XRD patterns.

Because they are commonly cut by clay and calcite veins, zeolites seem to be an early-stage alteration product.

Analcite

Analcite was not common in the set of samples studied (mostly pillows), but it seems more abundant in breccias (Juteau et al., personal communication). Typically isotropic, it replaces plagioclase phenocrysts, but also occurs in veins or forms the matrix between altered glassy fragments in brecciated pillow margins.

It was analyzed in one sample and has a very pure composition (Table 18).

TABLE 17
Zeolite Compositions in Hole 417A Samples

	1	2	3	4
SiO_2	49.83	51.02	47.73	53.45
Al_2O_3	22.59	22.53	26.89	22.60
CaO	4.40	4.95	12.31	5.67
Na_2O	6.45	3.45	1.12	3.30
K_2O	0.31	3.19	0.12	0.20
	83.58	85.14	88.15	85.22

Note: 1 = Sample 26-5, 77-80 cm; 2 = Sample 35-5, 2-6 cm; 3 = Sample 38-3, 140-143 cm (chabazite ?); 4 = Sample 46-2, 92-96 cm.

TABLE 18
Analcite Composition in Hole 417A

SiO_2	54.47
Al_2O_3	22.82
Na_2O	13.97
K_2O	0.03
	91.28
On 6 Oxygens	
Si	2.007
Al	0.991
Na	0.998
K	0.001
	0.999

Note: Sample 28-2, 69-74 cm (vein).

Textural relationships show that analcite began to crystallize, like zeolites, in the early stage of alteration and continued to form much later. But is has not been observed in calcite veins as in Hole 417D.

Calcite

Calcite is very common in Hole 417A, as in Holes 417D and 418A, and occupies the same position in the rocks. It mostly occurs in vein and vesicle fillings and breccias. Occasionally, it replaces olivine phenocrysts, in association with opaque grains or clay. It has also been observed replacing the groundmass or plagioclase phenocrysts when they are cut by a veinlet.

The FeO, MgO, and MnO contents of the calcite have been tested. The calcite is always very pure, with traces of iron and magnesium, and up to 0.50 per cent manganese.

Calcite always appears as late-stage product. In veins and vesicles, it forms large crystals filling the center, the edge being sometimes lined by clays. In breccias, it forms the matrix.

Iron Hydroxides

I did not see any pyrite in Hole 417A rocks, but this could be a matter of sampling. However, the oxidative conditions of the alteration in the top of the hole could have precluded the formation of pyrite.

Iron hydroxides are abundant, usually associated with calcite in veins or olivine pseudomorphs. The common occurrence of these minerals in late-stage calcite veins means that ferric iron is mobile until the very end of the alteration process.

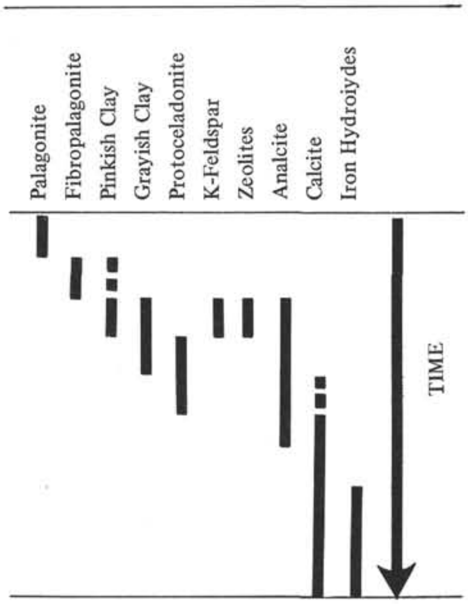
Alteration Sequence

A tentative crystallization sequence for the secondary minerals is given in Table 19. There are no striking differences with Holes 417D and 418A. The absence of the late-stage brown saponite should be noted.

DISCUSSION

Despite some differences between the three holes, alteration shows some constant characteristics.

TABLE 19
Tentative Crystallization Sequence of Secondary Minerals, Hole 417A



All the secondary phases have been already described in altered oceanic basalts and (except for the probably deuteric chlorite) are consistent with a low-temperature alteration.

Most of the secondary phases are hydrated and their formation implies a fluid circulation. The oxygen isotopes results (Fouillac and Javoy, this volume) show that this fluid was sea water.

The major secondary phases are clays and calcite. The scarcity of zeolites (which are abundant in Leg 45 and 46 samples, e.g., Juteau and Noack, personal communication) is undoubtedly related to a high CO_2 pressure which favored calcite precipitation (Thompson, 1971). Further work on this problem is necessary.

The distribution of secondary minerals in the rocks is very irregular and depends on the fluid circulation. This emphasizes the importance of the sampling.

Even when there are no cracks, the fluids can circulate through the whole rocks, as evidenced by the fact that olivine phenocrysts are altered to secondary products similar to those found in veins. The example of pillow glassy margins shows that first the outer glassy rim reacts with sea water to form palagonite and then the fluids penetrate the pillow interior through the numerous cracks. In the crystalline interior, they circulate along crystal boundaries inducing the alteration of olivine and possibly plagioclase phenocrysts. The mechanism explains why fresh olivine persists only in fresh glassy zones, and has been invoked already (Scott and Hajash, 1976).

The alteration processes stop when the cracks are filled by secondary products which prevent fluids from circulating.

To evaluate the chemical balance of alteration, it is important to keep in mind that secondary products either replace pre-existing phases (magmatic minerals or glass) or crystallize in vugs, cracks, or veins. Main secondary phases are silicates containing potassium (K-feldspar, protoceladonite, zeolites), iron and magnesium (clay minerals), and/or aluminum (K-feldspar, zeolites, clay minerals) and calcite.

Because no primary phase transformation gives potassium, it is obvious that the rocks have been enriched in potassium, the source of which is probably sea water. This is typical for low-temperature alteration (Hart, 1970, 1973; Matthews, 1971; Thompson, 1973; Aumento et al., 1976) and contrasts with hydrothermal alteration.

The leaching of primary phases induces the mobilization by fluids of Na_2O, CaO, SiO_2 (glass and plagioclase alteration), MgO and total FeO (olivine and sometimes glass alteration), and Al_2O_3 (plagioclase and sometimes glass alteration). In the prevailing conditions, aluminum is undoubtedly the less mobile element. Most of it stays *in situ*, entering clay minerals, zeolites, or potassium feldspar in plagioclase pseudomorphs. Silica, iron, and magnesium circulate in fluids and form clay minerals in vein and vesicle fillings. Sodium, strongly leached from glassy margins, enters zeolites and analcite. However, in Holes 417D and 418A, these minerals are very rare compared to the volume of altered glass and a leaching of sodium by sea water may have occurred. This is a main difference with the hydrothermal alteration which induces a Na_2O enrichment of the basalts (Wolery and Sleep, 1976; Hart, 1970, 1973; Hajash, 1975). Calcite is a late-stage product. In the prevailing conditions, calcium is the more mobile element and the last to precipitate. Obviously, the fact that calcite occupies the center of vein fillings is not related in this case to a late-stage alteration of plagioclases as described by Scheiddeger and Stakes (1977) in the Peru Trench basalts.

The varying composition of the fluid phase when it percolates through the rocks governs the irregular distribution of the secondary minerals, a characteristic feature of this low-temperature alteration. It also explains the heterogeneity of the palagonites, the fluid composition changing as it reacts with glass when it penetrates the pillow.

Hole 417A differs from Holes 417D and 418A mainly in the following: (1) intensity of alteration (plagioclase phenocrysts and the groundmass are commonly altered in the former); (2) strong decrease of alteration with depth; and (3) high oxidation of rocks in the upper part of the hole and its decrease with depth (the absence of pyrite has been emphasized).

To compare the effects of alteration on the bulk rock compositions, seven rocks from the three holes were analyzed (Table 20). To permit comparison, the samples selected were all pillow interiors (when samples are described as glassy margins, only the crystalline part was ground), and thick veins of secondary minerals were avoided. Despite the very small number of analyses, a few observations can be made.

Considering the K_2O content and the Fe_2O_3/FeO ratio of the rocks which are regarded as good indicators of alteration (Hart, 1970; Matthews, 1971; Thompson, 1973), we see a marked decrease in both values with increasing depth for Hole 417A rocks, while Hole 417D and 418A rocks do not vary much and have always low values (Figure 6). Further, the apparent correlation between K_2O and Fe_2O_3/FeO suggests that oxidative conditions favor the K_2O fixation, though more analyses would be desirable.

TABLE 20
Bulk Rock Analysis of Selected Samples From Holes 417A, 417D, and 418A

	1	2	3	4	5	6	7
SiO_2	46.30	45.42	47.06	45.98	46.38	46.37	47.44
TiO_2	1.56	1.42	1.48	1.24	1.41	1.13	1.20
Al_2O_3	18.72	17.00	15.70	15.67	17.25	16.81	16.64
Fe_2O_3	9.62	7.26	5.89	7.19	4.48	4.99	4.31
FeO	1.18	3.22	4.74	4.16	5.21	4.60	4.81
MgO	3.58	3.88	5.23	4.43	6.16	6.07	5.86
CaO	5.46	12.74	13.04	13.97	12.71	13.27	12.02
Na_2O	2.48	2.50	2.70	2.36	2.58	2.52	2.47
K_2O	3.62	0.96	0.57	0.80	0.04	0.31	0.16
H_2O+	4.90	2.97	2.02	2.41	2.14	1.80	1.97
H_2O-	2.11	1.93	0.89	1.40	1.33	1.70	2.00
Total	99.53	99.30	99.32	99.61	99.69	99.57	98.93
Fe_2O_3/FeO	8.15	2.25	1.24	1.73	0.86	1.08	0.89

Note: 1 = Sample 417A-24-3, 34-36 cm; 2 = Sample 417A-38-3, 140-143 cm; 3 = Sample 417A-46-1, 41-46 cm; 4 = Sample 417D-28-6, 14-17 cm; 5 = Sample 417D-62-3, 33-35 cm; 6 = Sample 418A-38-3, 46-48 cm; 7 = Sample 418A-71-4, 102-106 cm.

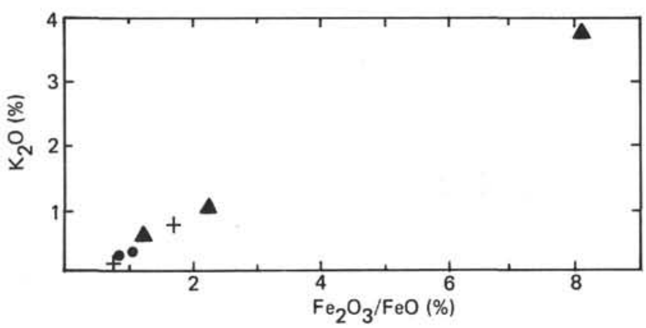


Figure 6. *K_2O versus Fe_2O_3/FeO in bulk-rock analysis.* *▲ = Hole 417A; + = Hole 417D; ● = Hole 418A.*

The absence of magnesium-rich clays (saponite) in Hole 417A is certainly a problem. In this hole, magnesium is obviously leached from glasses and olivine, as in the two others, but is not fixed in a clay. This fact is difficult to explain with a limited number of samples; perhaps this saponite was present in other parts of the hole. However, a leaching of magnesium by sea water has been observed in altered basalts by several authors (Hart, 1970; Thompson, 1973). The stronger conditions of alteration could have induced the leaching of MgO in this hole and not in the two others.

The differences between the holes are probably related to their topographic position. Hole 417A is located on a topographic prominence above the two other holes and stayed without a sediment blanket until the Late Cretaceous. This long direct contact of the basalts with sea water is probably responsible for the more intense alteration of the hole. This is consistent with the decreasing alteration with depth to an intensity similar to the two other holes at the bottom of the sequence. But the problem of the stronger oxidation is still to solve.

The vicinity of holes exhibiting marked differences in the intensity of alteration shows that time is not the main factor. Apparently, the possibility for sea water to circulate in the rocks is essential and can depend on local conditions.

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PLATE 1

Figure 1	Sample 418A-86-2, 91-94 cm. Brown smectite (saponite) replacing olivine phenocrysts in a pillow interior.
Figure 2	Sample 417D-22-3, 99-101 cm. Vesicle filled with green smectite (protoceladonite) on the edge and brown smectite (saponite) in the center.
Figure 3	Sample 418A-59-4, 134-140 cm. Radial aggregates of brown smectite (saponite) in calcite, in a breccia matrix.
Figure 4	Sample 417D-39-4, 2-8 cm. Altered pillow glassy margin. A zone of fresh glass (light gray) is rimmed by palagonite (dark gray). Palagonite penetrates the fresh glass along a vein filled with protoceladonite.
Figure 5	Sample 418A-42-2, 138-143 cm. Altered pillow margin. Between the varioles, glass is replaced by fibropalagonite (light gray) and zeolites (white).
Figure 6	Sample 417D-39-4, 2-8 cm. Altered pillow margin. The fresh glass is partly altered to palagonite (on the right), cut by a protoceladonite vein.

PLATE 1

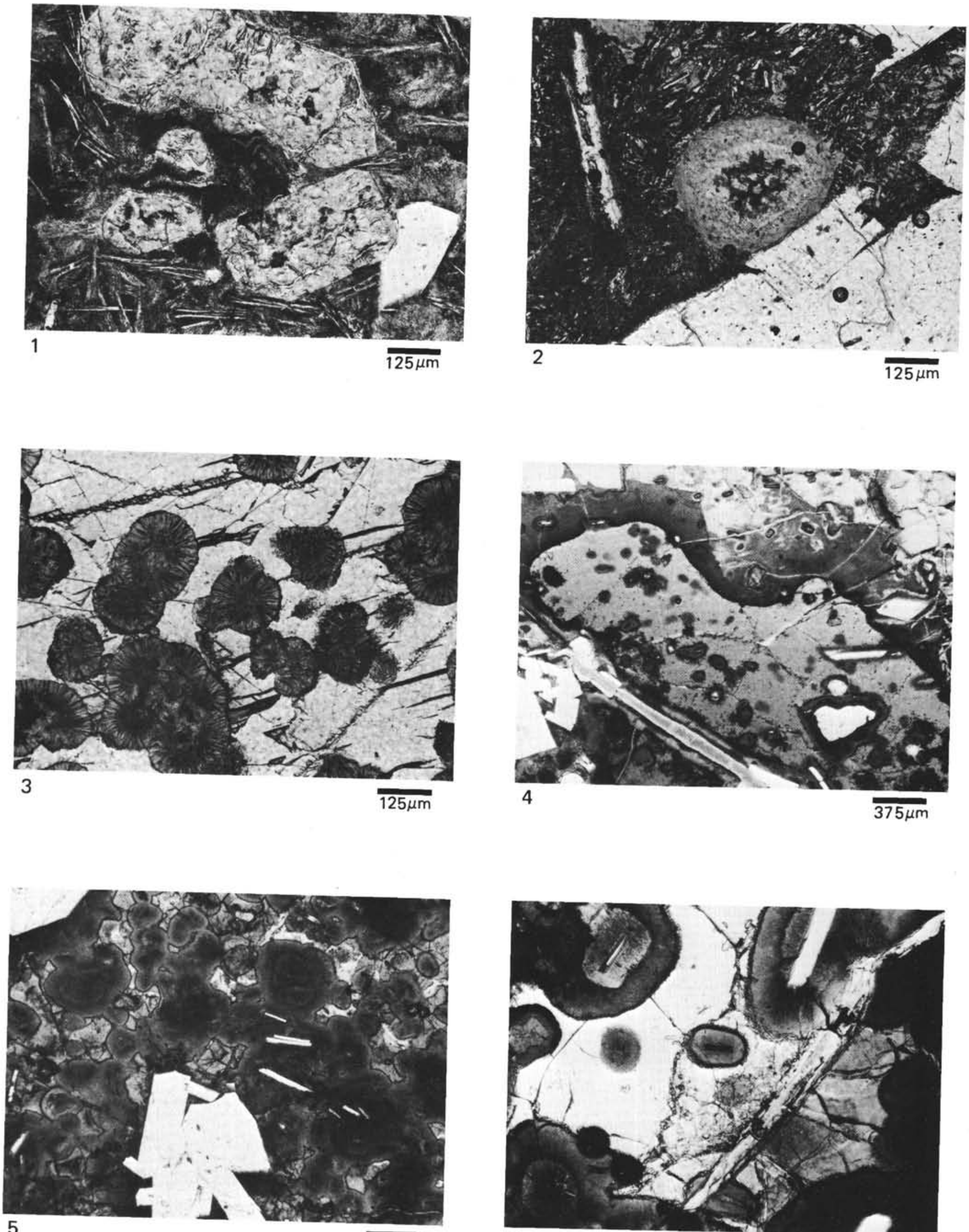

PLATE 2

Figure 1	Sample 417D-22-3, 91-94 cm. Amygdule filled with protoceladonite on the edge, brown smectite and calcite (white) in the center.
Figure 2	Sample 417A-26-5, 77-80 cm. Plagioclase phenocryst altered to aluminum-rich clay (gray) and potassium feldspar (white). The more sodic rim of the plagioclase is preserved.
Figure 3	Sample 417A-28-2, 69-74 cm. Vein filled with grayish clay on the edges and protoceladonite in the center. The vein cuts the groundmass, completely altered to a dark brown material.
Figure 4	Sample 417A-24-3, 21-23 cm. Plagioclase phenocryst altered to clay and potassium feldspar and cut by a protoceladonite vein.
Figure 5	Sample 417A-28-2, 69-74 cm. Altered pillow margin. The varioles and the spherulitic zone of the pillow are completely altered to a dark brown material. The glass between the varioles is replaced by fibropalagonite.
Figure 6	Sample 417A-46-1, 41-46 cm. Altered pillow margin in the bottom of Hole 417A. A zone of fresh glass (light gray) is enclosed in palagonite (dark gray). The varioles still look fresh.

PLATE 2