

Palagonitization of basaltic glass from DSDP Site 335, Leg 37: Textures, chemical composition, and mechanism of formation

Z. ZHOU,* W. S. FYFE

Department of Geology, University of Western Ontario, London, Ontario N6A 5B7, Canada

ABSTRACT

Palagonitization of basaltic glass of DSDP Site 335 is initiated on glass surfaces, along fractures, and around vesicles in glass. The alteration front is populated with empty etch pits. A typical cross section from glass to palagonite contains a fresh glass core, an alteration front, gel palagonite, and fibrous palagonite. Fracture-filling authigenic minerals include smectite clays, phillipsite, calcite, and iron and manganese oxides. Gel palagonite is dark brown, translucent, and isotropic and may contain spherical protocrystallites. Fibrous palagonite is orange or yellow, transparent, birefringent, and fibrous and may be composed of stevensitic smectite. The latter shows well-organized crystallinity along the *a* and *b* axes, but poor crystallinity along the *c* axis. Fe and Ti contents increase from glass to gel palagonite and decrease from gel palagonite to fibrous palagonite. K content increases during the course of palagonitization.

Palagonitization is divided into a Ti-constant step and a volume-constant step. In the first step, glass is dissolved and gel palagonite of protocrystalline nature is formed. This step is accompanied by volume reduction and loss of over 60% of the SiO₂, Al₂O₃, MgO, CaO, and Na₂O. Ti and Fe are immobile and accumulate in the process. In the second step, gel palagonite is replaced in situ by fibrous palagonite. CaO and Na₂O continue to be lost, and K₂O continues to increase during this process. However, SiO₂, Al₂O₃, and MgO are taken back from solution. Ti and Fe are locally mobilized to nearby fractures and incorporated into clay and oxide minerals. K enrichment is proposed as a maturity index for palagonite.

INTRODUCTION

The alteration of sea-floor basalt has an important impact on sea-water chemistry and on the geochemical budget of the upper oceanic crust. The most important reactions in such alteration are the decomposition of basaltic glass, plagioclase, and olivine (Staudigel and Hart, 1983). The alteration of basaltic glass can also provide a natural analogue to the long-term behavior of nuclear waste glass (Lutze et al., 1985; Byers et al., 1987; Zhou et al., 1987).

Low-temperature alteration of basaltic glass produces palagonite. The word "palagonite" was first used by von Waltershausen in 1846 to describe the altered basaltic glass of the hyaloclastites from Palagonia in the Hyblean Mounts, Sicily (Honnorez, 1981). Peacock (1926) was the first to present a comprehensive petrographic study of palagonite. He distinguished two main varieties that he termed "gel palagonite" and "fibrous palagonite" in the Breccia Formation of Iceland. More recent studies have focused on chemical and mineralogical changes during palagonitization (Ailin-Pyzik and Sommer, 1981; Andrews, 1977, 1978; Bonatti, 1965; Eggleton and Keller, 1982; Furnes, 1978, 1980; Furnes and El-Anbaawy, 1980;

Hay and Iijima, 1968a, 1968b; Honnorez, 1978; Jakobsson, 1978; Jakobsson and Moore, 1986; Melson and Thompson, 1973; Shido et al., 1974; Singer, 1974; Staudigel and Hart, 1983) and recently, these observations were reviewed by Honnorez (1981), Thompson (1983), and Fisher and Schmincke (1984). The mechanism and kinetics of palagonitization have been discussed by Byers et al. (1987). In this study, we combine conventional petrographic methods with modern electron microscopy to quantify the chemical composition and textures of the palagonite from the Mid-Atlantic Ridge. The mechanism of palagonitization will also be discussed.

SAMPLES AND EXPERIMENTAL METHODS

The samples studied are from the FAMOUS area of the Mid-Atlantic Ridge at lat 36°N and were recovered during Leg 37 of the Deep Sea Drilling Project (DSDP) at Site 335. The acoustic basement at the site consists of a very uniform sequence of pillow basalt with numerous glass rinds and intercalations of nannofossil chalk, which underlies a 454-m-thick sequence of foraminifera-bearing nannofossil ooze (Aumento, Melson et al., 1977). A best estimate of basement age for this site is approximately 13 m.y. (Miles and Howe, 1977). Ten samples were collected from the glass rinds of pillow basalt, distributed

* Present address: Civil Research Department, Ontario Hydro, 800 Kipling Avenue, Toronto, Ontario, M8Z 5S4, Canada.

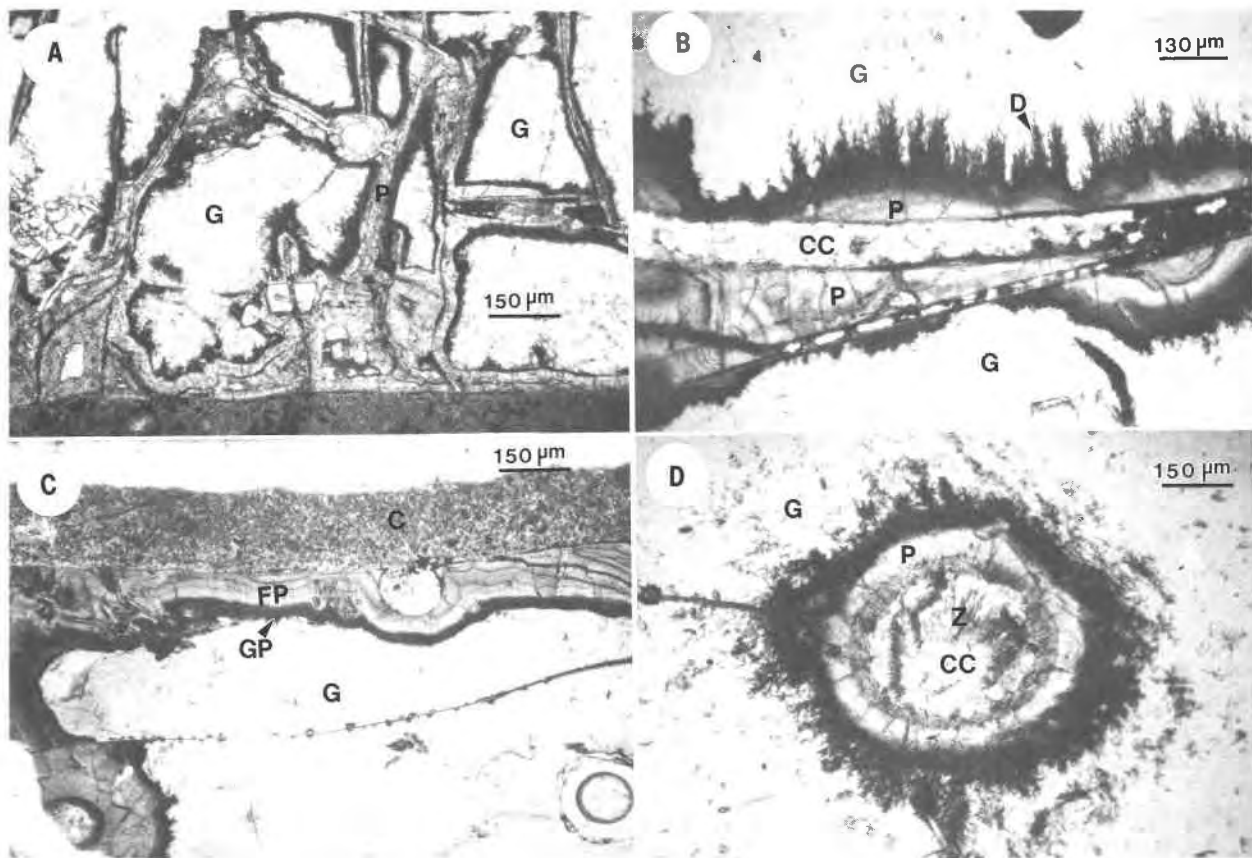


Fig. 1. Micrographs of palagonite. Palagonitization (A) along fractures in glass, (B) alteration front of dendrite form, (C) on the glass surface, and (D) around vesicles in glass. C, clay vein; CC, calcite; D, dendritic alteration front; G, glass; GP, gel palagonite; FP, fibrous palagonite; P, palagonite; Z, zeolite.

from Cores 335-6-2 to 335-14-4 (450–540 m below sea floor, Table 1). The glass is primarily dark brown to black sideromelane, with yellowish-orange palagonite rinds on surfaces and along fractures.

Bulk samples were used to prepare thin sections for optical-microscope and electron-microprobe (EMP) analysis. Slightly crushed bulk samples were mounted onto Al stubs for scanning electron microscopy (SEM) study. In order to characterize the nature of palagonite, the glass and associated palagonite were mechanically separated. The palagonite separates were then ultrasonically cleaned

in an acetone bath and ground into powder. Suspensions of the powders were made and deposited onto glass slides for X-ray diffraction (XRD) or deposited onto 3-mm holey C grids for transmission electron microscopy (TEM) analysis.

XRD analyses were carried out with a Rigaku X-ray diffractometer system. SEM study was done with an ISI DS-130 research instrument equipped with an EDX detector, operated at an accelerating voltage of 20–25 kV. Structural characteristics of palagonite were observed using a JEOL JEM 100C TEM, with an accelerating voltage of 100 kV. Chemical compositions of glass and palagonite were analyzed with a JEOL 8600 Superprobe (15 kV of accelerating voltage), and the size of the electron beam was defocused to 15–20 μm to reduce Na loss.

PETROGRAPHY

Palagonitization of Site 335 glass was initiated on glass surfaces, along fractures, and around vesicles in glass (Figs. 1A–1D). An ideal and complete cross section of the glass-palagonite interface contains, from the center outward, a glass core, a dark zone of dendritic form, a dark brown palagonite zone, and a laminated orange or yellow palagonite zone. Authigenic minerals, including smectite clays,

TABLE 1. The sampling positions at Site 335

No.	Core	Section (cm)
335-1	6-2	134–136
335-2	6-6	22–24
335-3	7-2	70–72
335-4	7-2	141–143
335-5	7-3	29–31
335-6	9-3	14–17
335-7	9-5	46–48
335-8	10-2	37–39
335-9	12-1	36–38
335-10	14-4	63–65

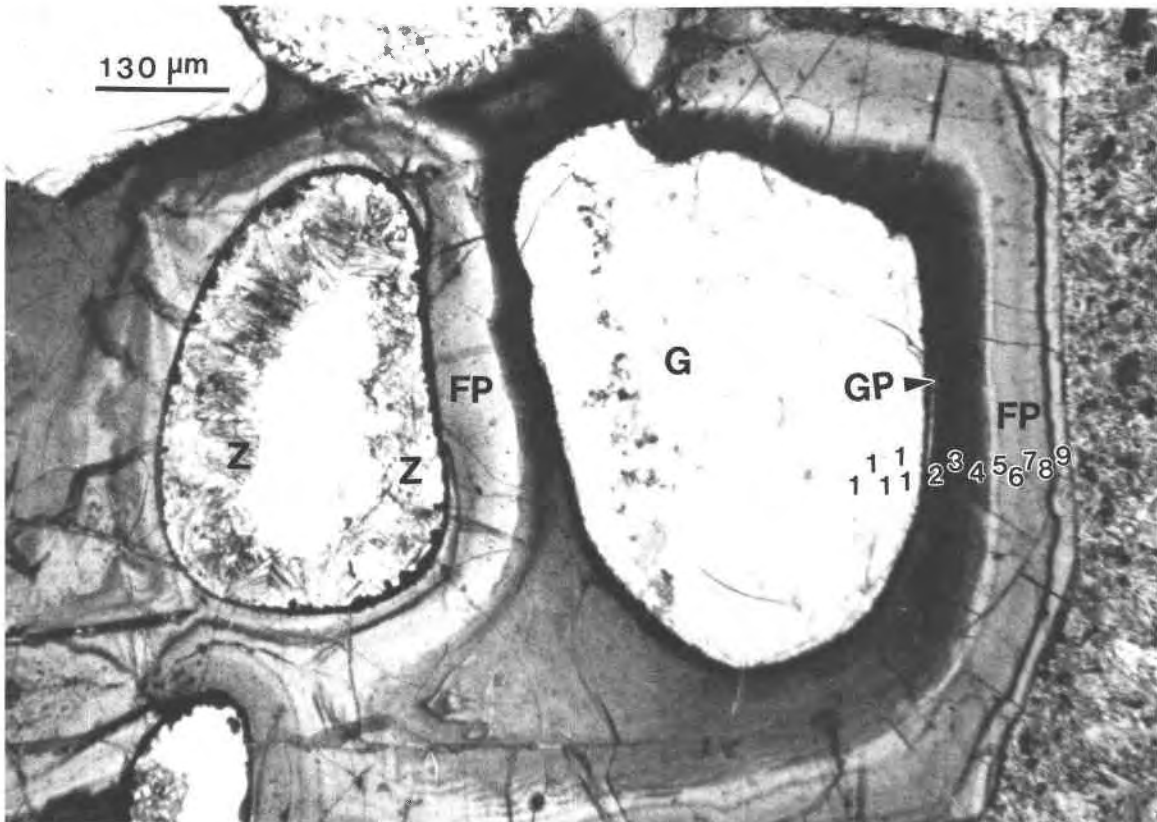


Fig. 2. Typical cross section from glass core to palagonite. Symbols as in Fig. 1. The numbers represent approximate positions of EMP analyses of Table 3.

phillipsite, calcite, and iron and manganese oxide minerals, fill nearby fractures (Fig. 2).

In most cases, a zone of dendritic form develops first along interfaces between glass and solution. This zone represents the alteration front and is located between glass and palagonite. Under polarized light, it is completely dark. The dendritic branches are perpendicular to the alteration front and extend into the fresh glass (Fig. 1b). Probably because it occupies only a very small space (usually less than 50 μm in thickness), this zone has not been adequately addressed in the literature. It was termed "mist zone" by Morgenstein and Riley (1974) and was included in "immobile product layer" by Staudigel and Hart (1983). These authors suggested that the dendritic zone is riddled with microchannels or microcracks that permit water to move into glass. Our SEM analysis indicates that it is a zone populated with etch pits, and the latter are empty (Fig. 3). Under the SEM, no alteration can be detected on glass in the areas between etch pits. The composition of the glass is not significantly different from glass in the cores. These observations have important bearings on the mechanism of glass alteration (see Discussion). Although this alteration front has distinct optical and physical properties, it does not constitute a separate mineralogic unit and is considered to be a physical mixture of glass and etch pits. This zone will not be dis-

cussed further except in connection with the mechanism of glass alteration.

Palagonite next to the alteration front is dark brown and translucent and has no lamination. This zone is usually less than 0.5 mm thick. Farther away from the fresh glass is orange or yellow, finely laminated, transparent, birefringent, fibrous structured palagonite. Both dark brown and orange palagonites may contain unaltered phenocrysts of plagioclase, pyroxene, and olivine. These observations are consistent with those of Andrews (1978). The dark brown palagonite may correspond to gel palagonite, and orange palagonite to the fibrous palagonite of Peacock (1926). In the following discussion, we will use "gel palagonite" and "fibrous palagonite" instead of the terms "dark brown palagonite" and "orange palagonite." Fibrous palagonite can be replaced in situ by a greenish clay phase, which is extremely Mg rich (Table 2). The small amount of this phase may prevent it from being detected by the XRD method, but this clay is important for the geochemical budget for elements like Mg.

Beyond the palagonite are zeolite and clay veins. The zeolite is mainly composed of K-rich phillipsite, in radiating or prismatic crystals. Clays in the veins contain moderate amounts of Fe and Ti (Table 2). The presence of manganese and iron oxides are indicated by fine red dots between clay minerals and by those clay minerals

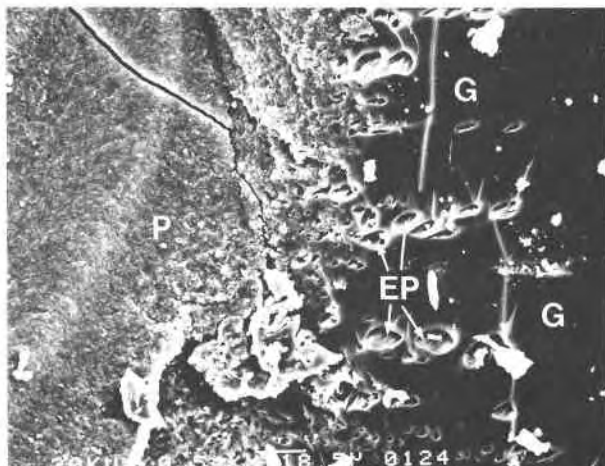


Fig. 3. Electron micrograph of palagonitization front. G, glass; P, palagonite; EP, etch pits.

stained with red color. Electron-microprobe analysis indicates that they have unusually high contents of Mn and Fe (Table 2). The Fe- and Ti-bearing authigenic minerals in fractures indicate that it is not appropriate to assume Ti or Fe is immobile during palagonitization.

The nature of palagonite is not well defined. Palagonite has been shown to be a material of variable composition. Honnorez (1981) considered palagonite to be a mixture, in variable proportions, of altered, hydrated, and oxidized glass with authigenic minerals such as clay, zeolites, and chlorites. However, X-ray diffraction of palagonite shows only a poorly resolved layered silicate (Andrews, 1978; Bonatti, 1965; Hay and Iijima, 1968a, 1968b; Singer, 1974; Stokes, 1971). Eggleton and Keller (1982) noted the similarity of average palagonite to smectite when recalculated to a cation charge of +22, and they concluded that palagonite is composed of a dioctahedral smectite with significant Mg in the octahedral sheet. Direct evidence regarding the mineralogic composition of palagonite is generally lacking.

XRD study of Site 335 palagonite shows two strong peaks at 4.5 and 2.6 Å and a moderate 060 peak at 1.52 Å. The 001 peak of smectite is weak and variable from 12 to 15 Å and disappears after treatment with ethylene glycol. TEM study indicates that most of the palagonite is composed of fibrous to lathy or folded-layer particles similar to smectite minerals (Fig. 4). These particles usually have well-organized crystallinity along the *a* and *b* axes (Z. Zhou, W. S. Fyfe, K. Tazaki, and S. J. van der Gaast, manuscript in preparation), which is consistent with observations by Singer (1974). Lattice images of the palagonite particles show a *d* spacing of 10–13 Å. These structural characteristics are very similar to those of stevensite, and such particles will be called stevensitic smectite in the following discussion. The precursors of stevensitic smectite are clusters of small, spheroidal particles, a few hundred angstroms in diameter (Fig. 5). They are very

TABLE 2. Composition of selected authigenic minerals from Site 335

	Clay (335-2)	Clay (335-5)	Zeolite (335-3)	Red clay (335-3)	Red clay (335-7)	Mg clay (335-3)
SiO ₂	45.20	43.09	49.51	36.55	28.18	39.39
TiO ₂	0.55	0.21	0.07	3.24	2.52	0.61
Al ₂ O ₃	20.12	16.93	20.92	11.93	16.18	19.47
Cr ₂ O ₃	0.00	0.36	0.08	0.08	0.33	0.03
FeO(T)	2.48	4.85	0.00	24.97	11.99	4.14
MnO	0.48	0.01	0.04	0.20	8.65	0.02
MgO	1.19	2.34	0.00	1.79	2.28	21.11
CaO	1.03	0.88	0.10	1.94	2.79	0.81
Na ₂ O	3.52	2.83	6.12	1.86	0.82	1.33
K ₂ O	4.92	5.46	6.31	2.04	1.15	0.72
P ₂ O ₅	0.11	0.00	0.13	0.44	0.58	0.05
Total	79.60	76.96	83.27	85.04	75.47	87.69

poor in crystallinity and similar to the “protocrystallite” described by Banfield and Eggleton (1990). Protocrystallite is less abundant than stevensitic smectite. The former is considered to be a major component in gel palagonite and the latter may represent those in fibrous palagonite. Because physical separation of gel palagonite from fibrous palagonite is not feasible, and the samples used for TEM analysis were mixtures of gel and fibrous palagonites, the above suggestion cannot be proved with the analytical methods used in this study. A full account of the microstructures of the palagonite will be discussed elsewhere (Z. Zhou, W. S. Fyfe, K. Tazaki, and S. J. van der Gaast, manuscript in preparation).

CHEMICAL CHANGES DURING PALAGONITIZATION

The chemical changes resulting from palagonitization have been the subject of many studies in the past (e.g., Hay and Iijima 1968a, 1968b; Furnes, 1978, 1980; Honnorez, 1978; Furnes and El-Anbaawy, 1980; Andrews, 1978; Ailin-Pyzik and Sommer, 1981; Staudigel and Hart, 1983; Eggleton and Keller, 1982). However, controversy still remains over the directions and magnitude of chemical changes. One of the issues is whether such chemical changes are isovolumetric or Ti or Fe constant.

To make the best possible estimate of chemical changes involved in any metasomatic processes, volume changes associated with alteration or the absolute variation of one chemical constituent must be known (Gresens, 1967). The usual practice is to compare the chemical analysis of unaltered and altered material assuming that either volume or one of the less mobile components does not change during the course of alteration. On the basis of petrographic observations, Hay and Iijima (1968a, 1968b) and Furnes (1978, 1980) concluded that palagonitization is an isovolumetric process and calculated the chemical changes on an isovolumetric basis. However, Andrews (1978) and Eggleton and Keller (1982) pointed out the problems associated with this method and made their calculation based on a Ti-constant method. The later assumption requires that authigenic minerals associated with palagonite are Ti (or Fe) free or, at least, Ti (or Fe) poor and that no or little Ti (or Fe) is dissolved and carried

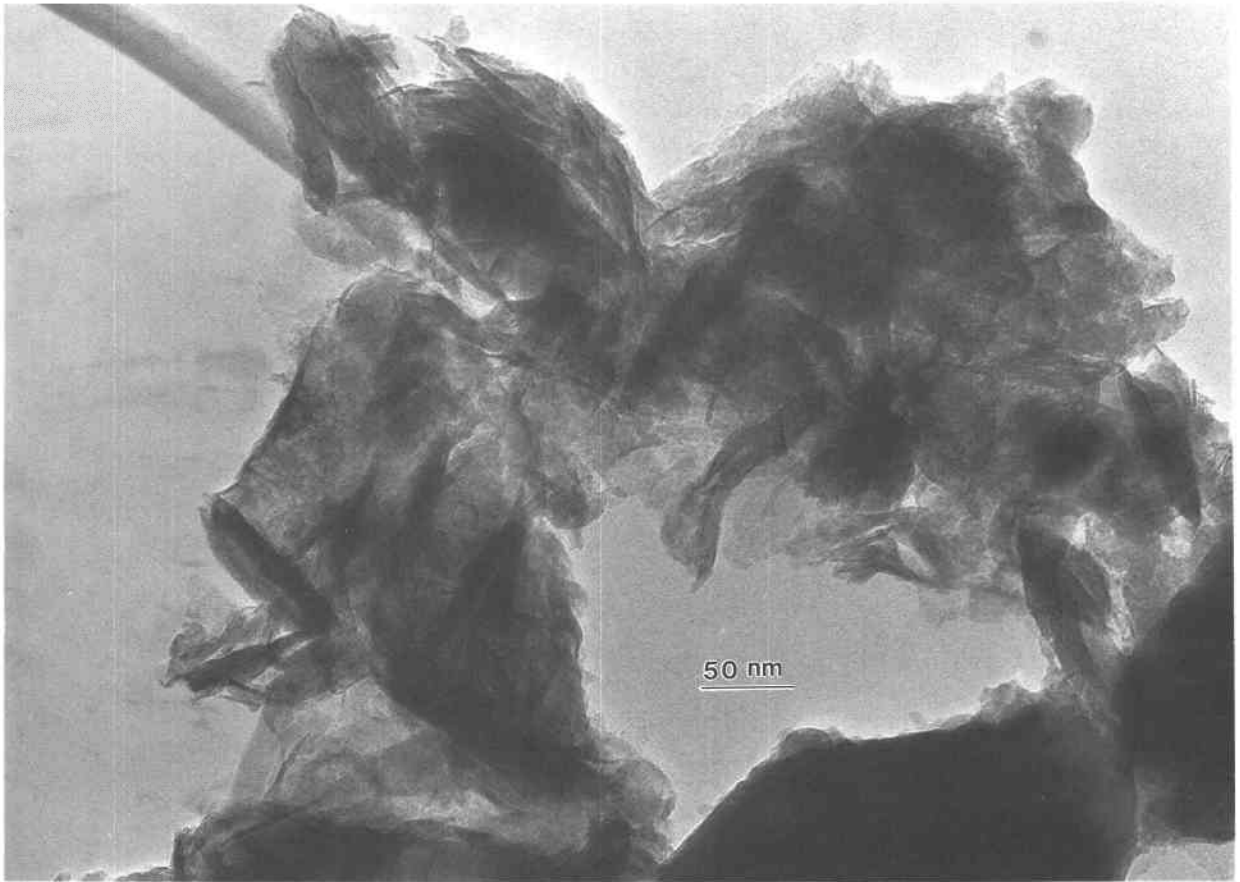


Fig. 4. TEM micrograph of palagonite. The palagonite is composed of fibrous to lathy or folded particles similar to smectite minerals.

away in solution during the alteration. Such conditions can usually be met only in the early stage of palagonitization (see following discussion).

Relative losses and gains of eight major elements during submarine palagonitization have been compared at different degrees of Ti accumulation (Staudigel and Hart, 1983). This unique treatment reveals the interrelationship between major elements during submarine alteration of glass. It was suggested by those authors that Ti accumulation may be used as a maturity indicator for palagonites. However, this generalization must be treated with caution. As discussed previously, a representative cross section as in Figure 2 includes zones of fresh glass, dark dendrites, gel palagonite, and fibrous palagonite. Several microprobe traverses were made through such palagonite to glass cross sections. Table 3 presents the results of the traverse through the cross section shown in Figure 2. Changes in Ti and Fe content through the section are plotted in Figure 6. Textural relationships indicate that dark brown gel palagonite, being closer to glass, is certainly later or less mature than the orange fibrous palagonite (palagonitization develops inward). Ti and Fe contents, on the other hand, increase from glass to gel

palagonite and then decrease from gel palagonite to fibrous palagonite. Such variations in Fe and Ti content are common for the palagonite from Site 335. Therefore, Ti or Fe accumulation is not a good indicator for "maturity" of palagonite.

To explain the compositional variations shown in Figure 6, a multistep process of palagonite formation is required. In the early step, basaltic glass is dissolved and gel palagonite is formed. The authigenic mineral formed during this stage is mainly phillipsite, which is Ti and Fe poor. Therefore Ti and Fe may not be mobile during this stage but tend to accumulate as a result of removing other elements. The physicochemical condition required for this is an alkaline solution, in which Si and Al may be mobile while Ti and Fe are not. It is possible to produce a localized alkaline solution during glass alteration from ion exchange between H^+ and alkalis in basaltic glass. In the later step, gel palagonite is converted in situ to fibrous palagonite. Small amounts of Ti and Fe are locally remobilized. Ti and Fe lost from palagonite probably moved to fractures adjacent to it and were incorporated into clay minerals or oxides. Local mobility of Ti during low-temperature alteration was also noticed by Robinson et al.

TABLE 3. Microprobe traverse along the cross section shown in Fig. 2

	1	2	3	4	5	6	7	8	9
SiO ₂	49.86	39.24	35.97	41.10	44.91	43.65	43.75	43.58	44.25
TiO ₂	1.24	2.40	2.87	2.41	1.47	1.88	1.97	1.88	2.03
Al ₂ O ₃	14.98	12.22	11.10	11.74	12.27	13.26	12.65	12.39	12.67
Cr ₂ O ₃	0.26	0.18	0.18	0.11	0.14	0.11	0.20	0.36	0.00
FeO	9.11	20.08	19.81	18.76	14.57	15.85	16.23	15.14	16.17
MnO	0.20	0.00	0.10	0.00	0.06	0.00	0.00	0.00	0.12
MgO	7.96	2.10	1.55	3.03	4.32	4.31	4.83	4.86	4.69
CaO	11.81	2.23	1.78	1.93	1.51	1.15	1.19	1.21	1.18
Na ₂ O	2.70	2.18	1.84	1.64	1.19	0.73	0.74	0.72	0.53
K ₂ O	0.16	2.32	2.02	2.75	3.54	4.03	4.37	4.10	4.33
P ₂ O ₅	0.36	0.11	0.00	0.08	0.21	0.03	0.27	0.03	0.45
Cl	0.01	0.09	0.09	0.04	0.07	0.08	0.09	0.08	0.03
Total	98.65	83.15	77.31	83.60	84.25	85.09	86.25	84.35	86.44

Note: (1) glass (mean value of five analyses); (2–4) gel palagonite; (5–9) fibrous palagonite. See Fig. 2 for reference.

(1977) in Site 332, where leucoxene was found in vesicles of a few basalts. However, it is not clear as to why Fe and Ti appear to be mobile in this stage.

It seems that the first step in palagonitization, glass to gel palagonite, is Ti and Fe constant but not volume constant because a large accumulation of Ti and Fe must result from loss of other elements. Such loss must result in a volume reduction. Should volume remain constant, density change during palagonitization (assuming 2.75 g/cm³ for glass and 2.10 g/cm³ for palagonite) could only result in a 30% increase in Ti and Fe content. An accumulation factor greater than 1.3 may indicate the volume reduction involved. The second step, gel palagonite to fibrous palagonite, may be isovolumetric because of in situ replacement. However, as pointed out earlier, Ti and Fe may be mobile during this process.

The two steps of palagonitization discussed here should be considered part of a continuum during which palagonite changes structure and chemical composition as alteration proceeds. It is also important to note that the generalization made here may only apply to submarine (or even more site-specific) conditions. In addition, some features of secondary order in Figure 2 may not be readily explained by the model of two-step palagonitization. For

example, the light-colored band (at point 5) is poor in Fe and Ti compared with the rest of fibrous palagonite, whereas a small dark band between points 8 and 9 is rich in Fe and Ti. These small variations may reflect localized changes in physicochemical conditions at the time of formation of these fine palagonite bands.

Mean compositions of glass, gel palagonite, and fibrous palagonite were used to calculate elemental mobility during palagonitization (Table 4). Elemental mobility during the first step of palagonitization, assuming constant Ti, is shown as L1. SiO₂, Al₂O₃, MgO, CaO, and Na₂O all suffered more than 60% weight loss. K₂O was enriched over 600%, and FeO appears to be constant. This process is accompanied by about 60% total weight loss.

Elemental mobility during the second step of palagonitization is shown as L2 in Table 4, based on an assumption of constant volume. CaO and Na₂O continue to be lost and K₂O continues to increase during isovolumetric conversion of gel palagonite to fibrous palagonite. However, SiO₂, Al₂O₃, and MgO are taken back from solution; in contrast, total FeO and TiO₂ are lost in this process. The overall elemental gain or loss is the resultant effect of steps 1 and 2 and is shown as L and X% in Table 4.

TABLE 4. Elemental mobility during palagonitization

	G	GP	FP	L1	X1%	L2	X2%	L	X%
SiO ₂	49.86	38.77	44.03	-31.08	-62.34	5.26	13.57	-28.53	-57.23
Al ₂ O ₃	14.98	11.69	12.65	-9.32	-62.20	0.96	8.21	-8.85	-59.10
TiO ₂	1.24	2.56	1.85	0.00	0.00	-0.71	-27.73	-0.34	-27.73
Cr ₂ O ₃	0.26	0.16	0.16	-0.18	-70.19	0.00	0.00	-0.18	-70.19
FeO	9.11	19.55	15.59	0.36	3.95	-3.96	-20.26	-1.56	-17.11
MnO	0.20	0.03	0.04	-0.19	-92.73	0.01	33.33	-0.18	-90.31
MgO	7.96	2.23	4.60	-6.88	-86.43	2.37	106.28	-5.73	-72.01
CaO	11.81	1.98	1.25	-10.85	-91.88	-0.73	-36.87	-11.20	-94.87
Na ₂ O	2.70	1.89	0.78	-1.78	-66.09	-1.11	-58.73	-2.32	-86.01
K ₂ O	0.16	2.36	4.07	0.98	614.45	1.71	72.46	1.81	1132.13
P ₂ O ₅	0.36	0.06	0.20	-0.33	-91.93	0.14	233.33	-0.26	-73.09
Cl	0.01	0.07	0.07	0.02	239.06	0.00	0.00	0.02	239.06
Total	98.56	81.35	85.28	-59.16		3.93		-17.69	

Note: (G) glass; (GP) gel palagonite (mean value of 2–4 of Table 3); (FP) fibrous palagonite (mean value of 5–9 of Table 3); (L1 and X1%) elemental mobility and percent of changes in the first step of palagonitization; (L2 and X2%) those of the second step of palagonitization; (L and X%) those of the whole process.

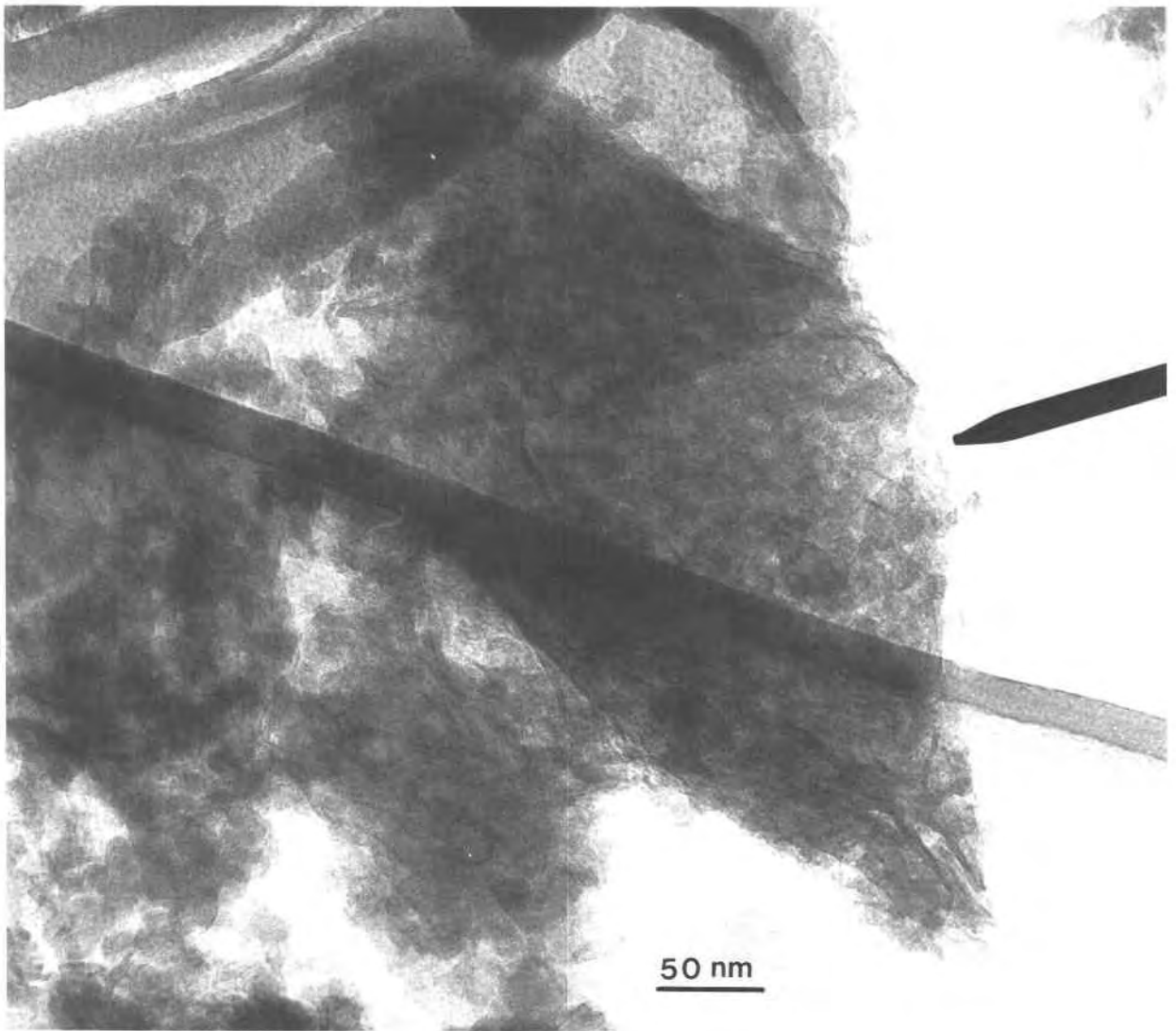


Fig. 5. TEM micrograph of spheroidal "protocrystallite." These particles are interpreted as precursors of the smectite minerals shown in Fig. 4.

There is a significant difference between these data and previous calculations (Andrews 1978; Eggleton and Keller 1982; Furnes 1978, 1980). In previous calculations, Fe and Ti were either assumed to be constant or to have increased. This is not compatible with the fact that clay veins next to palagonite contain significant amounts of Fe and Ti. Our calculations indicate that about 27% of Ti and 17% of Fe in glass can be mobilized during the process of palagonite formation. The magnitude of Ti and Fe mobilization may vary depending on local physico-chemical conditions, but our calculations explain the source of Fe and Ti in clay minerals.

A distinction should be made between the two steps of palagonitization discussed here and the three stages of palagonitization suggested by Honnorez (1978, 1981). The discussion in this paper refers mainly to the "initial" stage

of palagonitization according to Honnorez's classification.

For submarine alteration of basaltic glass, the enrichment of K may be used as a maturity index of palagonite. It has been well documented that K is enriched in palagonites relative to their parent glasses during submarine alteration. Figure 7 shows that K concentration increases from glass core, to gel, to fibrous palagonites. This indicates that K is taken up from sea water not only during the formation of gel palagonite but also during the in situ conversion of gel palagonite to fibrous palagonite. K enrichment as a maturity index of palagonite can be justified by the mineralogical changes during palagonitization. Smectite minerals formed during the course of palagonitization are K rich. Palagonite may eventually be replaced by K-rich phillipsite and smectite (Honnorez, 1978, 1981).

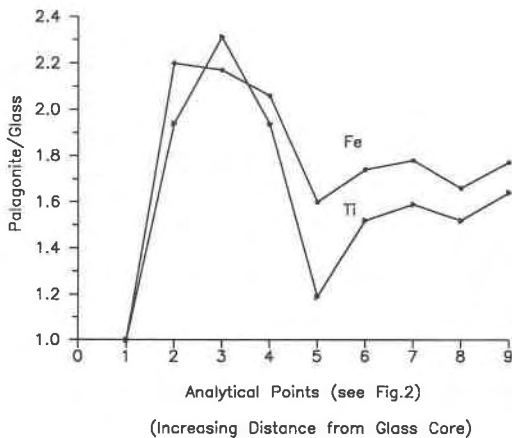


Fig. 6. Fe and Ti contents from glass core to palagonite corresponding to the cross section of Fig. 2. Both Fe and Ti contents show maxima in gel palagonite and decrease from gel palagonite to fibrous palagonite.

MECHANISM OF ALTERATION OF THE BASALTIC GLASS

The mechanism by which palagonite forms has been proposed as a hydration process (Peacock, 1926), solid-state diffusion and hydration (Moore, 1966), or solution-precipitation (Hay and Iijima, 1968b). The solution-precipitation mechanism is based on the physical characteristics of altered samples (sharp contact between glass and palagonite and an etched glass surface) as well as the chemical changes which result from palagonitization (Byers et al., 1987). Figure 3 provides new evidence for this mechanism. Presence of empty etch pits along the boundary between glass and palagonite indicates that fresh glass is dissolved, and the material moved and deposited over very short distances. It is interesting to note, however, that palagonite itself is not thermodynamically stable and changes its chemistry and structure over the course of alteration (see previous sections and Staudigel and Hart, 1983). Palagonite appears to be in disequilibrium with the solution from which it precipitates. This situation is explained if the removal of material from the glass is not by dissolution but by mechanical removal of 100- to 8000-Å-sized globules (Trichet, 1969, 1972). Such globules deposited from solution are not necessary in equilibrium with the solution. This mechanism was suggested by Honnorez (1972) and demonstrated by Trichet (1969, 1972). Staudigel and Hart (1983), however, questioned this idea and pointed out that Trichet's experimental observations can be equally well explained by dissolution.

Eggleton and Keller (1982), by using high-resolution transmission electron microscopy, noted that palagonite forming from basaltic glass by hydration consists of spherical structures with diameters ranging from 200 to 600 Å. Exfoliation of 10-Å 2:1 clay layers allows the development of thin (30–60 Å) crystals of dioctahedral smectite with significant Mg in the octahedral site, which ultimately forms a tangled network of submicrometer-

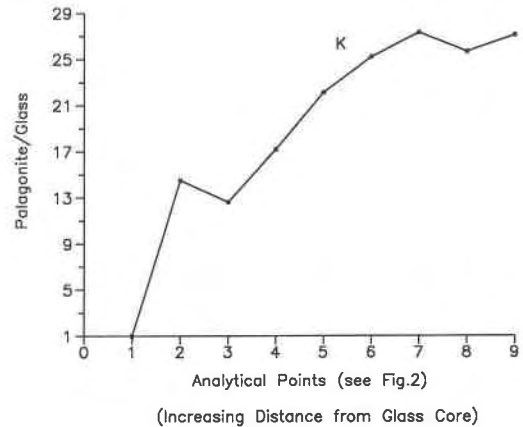


Fig. 7. K contents from glass core to palagonite corresponding to the cross section of Fig. 2. K shows continuous enrichment across the section.

sized bent flakes. Both Trichet (1969, 1972) and Eggleton and Keller (1982) showed that a spherical phase is formed first during glass alteration, and this spherical phase is not stable and tends to transform to smectite. Eggleton and Keller considered the spherical particles as a hydration product of basaltic glass, whereas Trichet had suggested that they were formed by deposition of physically removed globules from the glass.

As shown in Figure 5, palagonitization of DSDP Site 335 glass is initiated by the formation of clusters of small spheroidal particles. Morphologically, they are different from those described by Trichet (1969, 1972). These spheroidal particles were not found in the parent glass. It is unlikely that they were formed by deposition of physically removed globules from the glass. Hydration of glass can be considered as a preceding step of glass dissolution (Bunker, 1987) but may not result in spherical morphology. We suggest that protocryallites in palagonite are formed by precipitation from solution at the very beginning of palagonitization. The protocryallites are metastable and change their structure and chemistry and are replaced in situ by stevensitic smectites with changes in physicochemical conditions.

SUMMARY

Palagonitization of basaltic glass of DSDP Site 335 is initiated on glass surfaces, along fractures, and around vesicles in glass. The alteration front is populated with empty etch pits. A typical cross section from glass to palagonite contains a fresh glass core, an alteration front, gel palagonite, and fibrous palagonite. Fracture-filling authigenic minerals include clays, phillipsite, calcite, and iron and manganese oxides. Phillipsite, which is formed in the early stage of alteration, contains little Fe or Ti. The authigenic clays, however, contain moderate amounts of Fe and Ti. Gel palagonite is dark brown, translucent, and isotropic and may contain spherical protocryallites. Fibrous palagonite is orange or yellow, transparent, birefringent, and fibrous, and may be composed of steven-

sitic smectite. The latter shows well-organized crystallinity along the *a* and *b* axes, but poor crystallinity along the *c* axis. Fe and Ti contents increase from glass to gel palagonite and decrease from gel palagonite to fibrous palagonite. K content increases during the course of palagonitization.

Palagonitization is divided into an early Ti-constant step and a volume-constant step. In the first step, glass is dissolved and gel palagonite of protocrystalline nature formed. This step is accompanied by volume reduction and loss of over 60% of SiO₂, Al₂O₃, MgO, and CaO, and Na₂O. Ti and Fe are immobile and accumulate in the process. In the second step, gel palagonite was replaced in situ by fibrous palagonite. CaO and Na₂O continue to be lost and K₂O continues to increase during this process. However, SiO₂, Al₂O₃, and MgO are taken back from solution in the second step. Ti and Fe are locally mobilized to nearby fractures and incorporated into clay and oxide minerals. K enrichment is proposed as a maturity index for palagonite.

ACKNOWLEDGMENTS

We are grateful to Department of Geology, Dalhousie University, for providing DSDP samples. We are also grateful to Dr. Paul T. Robinson for his comments on the early version of this paper. The critical review and constructive comments by Drs. W. S. Wise and R. M. Haymon are very much appreciated. The financial support of this study was from a grant to W.S.F. from the Natural Sciences and Engineering Research Council of Canada.

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