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THE STRUCTURAL CHARACTERISTICS OF PALAGONITE FROM DSDP SITE 335

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ABSTRACT

The palagonite from the FAMOUS area of the Mid-Atlantic Ridge at 36°N, DSDP Site 335, is mainly composed of smectite-like particles and their spheroidal precursors. The crystallinity of the smectite-like particles is good along the ***a*** and ***b*** axes, but poor along the ***c*** axis. Although they show structural similarities to stevensite and nontronite, the smectite-like minerals are compositionally different from the two minerals. Their spheroidal precursors have very poor crystallinity, and are rich in Al and Fe. Neither oxide phases of Fe, Mn, and Ti, nor zeolites were found in the palagonite. The palagonite is considered a composite material that contains di- and trioctahedral smectite of variable composition and crystallinity, and their precursors.

Keywords: palagonite, smectite, mineral structure, alteration, X-ray diffraction, transmission electron microscopy, Mid-Atlantic Ridge.

SOMMAIRE

La palagonite du site DSDP 335 de la région FAMOUS, le long de la ride médio-atlantique (36°N), contient surtout des particules ressemblant à la smectite, et ses précurseurs sphéroïdes. Le degré de cristallinité des particules à aspect smectitique est élevé le long des axes ***a*** et ***b***, mais faible le long de ***c***. Tout en ayant des caractéristiques structurales semblables à la stevensite et la nontronite, la composition des particules à aspect smectitique diffère de celle de ces deux minéraux. Les précurseurs sphéroïdes ont un degré de cristallinité très faible, et sont enrichis en Al et Fe. Nous n'avons trouvé ni oxyde de Fe, Mn et Ti, ni de zéolite dans la palagonite. La palagonite serait un matériau composite contenant smectites di- et tri-octaédrique de composition et degré de cristallinité variables, ainsi que leurs précurseurs.

(Traduit par la Rédaction)

Mots-clés: palagonite, smectite, structure cristalline, altération, diffraction X, microscopie électronique par transmission, ride médio-atlantique.

INTRODUCTION

The palagonitization of sideromelane has been the subject of many studies since 1846, when von Waltershausen introduced the term *palagonite* to describe altered basaltic glass of hyaloclastites from Palagonia in the Hyblean Mounts, Sicily. Despite an impressive number of publications on the subject (*e.g.*, Byers *et al.* 1987, Crovisier *et al.* 1987, Furnes 1978, 1980, Honnorez 1978, 1981, Jakobsson (1978), Jakobsson & Moore 1986, Jercinovic *et al.* 1990, Staudigel & Hart 1983), the nature of palagonite is still not well defined. Honnorez (1981) suggested that palagonite is a mixture, in variable proportions, of altered, hydrated, and oxidized glass with authigenic minerals such as clays and zeolites, and proposed to abandon the term. However, studies by X-ray diffraction of carefully separated palagonite show only a poorly resolved layer silicate (Andrews 1978, Bonatti 1965, Hay & Iijima 1968a, b, Singer 1974, Stokes 1971). Eggleton & Keller (1982) noted the similarity of average palagonite to smectite when recalculated to a cation charge of +22, and concluded that palagonite is composed of a dioctahedral smectite with significant Mg in the sheet of octahedra. In a previous paper (Zhou & Fyfe 1989), we discussed the chemical composition and mechanism of formation of the palagonite from the Mid-Atlantic Ridge. The present com-

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munication focuses on the structural characteristics of the palagonite.

SAMPLES AND EXPERIMENTAL METHODS

The samples studied are from the FAMOUS area, at 36°N of the Mid-Atlantic Ridge, and were recovered during Leg 37 of the Deep Sea Drilling Project (DSDP) at Site 335. The sampled portion of acoustic basement at Site 335 underlies a 454-m thick sequence of foram-bearing nannofossil ooze and consists of a very uniform sequence of pillow basalts with numerous glass rinds and intercalations of nannofossil chalk (Aumento *et al.* 1977). A best estimate of the basement age for this site is approximately 13 Ma (Miles & Howe 1977). The samples were collected from the glass rinds of pillow basalts (see Zhou & Fyfe 1989). The glass is primarily dark brown to black sideromelane, with a yellowish orange palagonite rind on surfaces and along fractures.

In order to characterize the nature of the palagonite, glass and associated palagonite were mechanically separated and then hand-picked under a binocular microscope. Both the glass and palagonite separates were 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 carbon grids for analysis by transmission electron microscopy (TEM). Thin sections with a thickness of about 600 A also were prepared for TEM analysis. The ultramicrotomy followed procedures described by Lee *et al.* (1975).

XRD analyses were first carried out with a Rigaku X-ray diffractometer system (Cu*Kα* radiation). A low-angle X-ray powder-diffraction study (Co*Kα* radiation) was further performed on selected samples according to the method described by van der Gaast *et al.* (1986). The glass samples for low-angle XRD were milled in dried cyclohexane because dry-milling causes destruction of structures and milling in water results in clay formation (Kühnel & Van der Gaast 1989). The palagonite samples were Ca-exchanged in water. Structural characteristics of palagonite were observed using a JEOL JEM 100C TEM, with an accelerating voltage of 100 kV. High-resolution TEM studies were carried out with a Philips 400 STEM system equipped with EDX detector, operated at 100 kV. Electron-diffraction patterns were recorded wherever possible, but the crystalline structure was generally destroyed by the high-energy electron beam. From the electron-diffraction patterns, *d* values were calculated through calibration with a pulverized gold standard.

RESULTS

An XRD pattern of the parent glass from Site 335 shows a hump from 4.95 to 2.43 Å, with peak position at 3.26 Å (Fig. 1A), The hump is typical of glass and other amorphous materials, although its peak position shifts depending on the composition of the glass. The glass also shows a broad hump at about 12 Å with low-angle XRD (Fig. 1B). A change in relative humidity shows no shift or increase in intensity at low angles. The glass shows a smooth surface under TEM, and its electron-diffraction pattern shows no diffraction rings or spots. This further confirms its amorphous nature. Therefore, clay minerals or clay mineral precursors are not present in the parent glass.

An XRD study of palagonite from Site 335 shows two strong peaks at 4.53 Å and 2.60 Å and a moderate-intensity peak at 1.52 Å (Fig. 2A). An "amorphous" hump similar to that of the glass can still be seen. The basal reflection of palagonite is weak and variable from 12 to 15 Å, and becomes more diffuse after treatment with ethylene glycol. With the low-angle XRD method, one can see a peak that shifts with changing humidity (Fig. 2B). The peak is located at 16.2 Å at 100% RH, 15.8

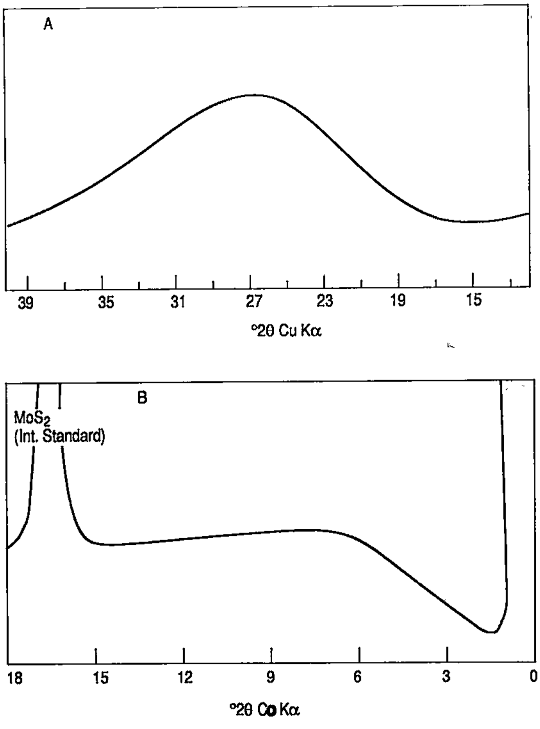

FIG. 1. X-ray-diffraction (XRD) patterns of the glass. A. Normal XRD. B. Low-angle XRD.

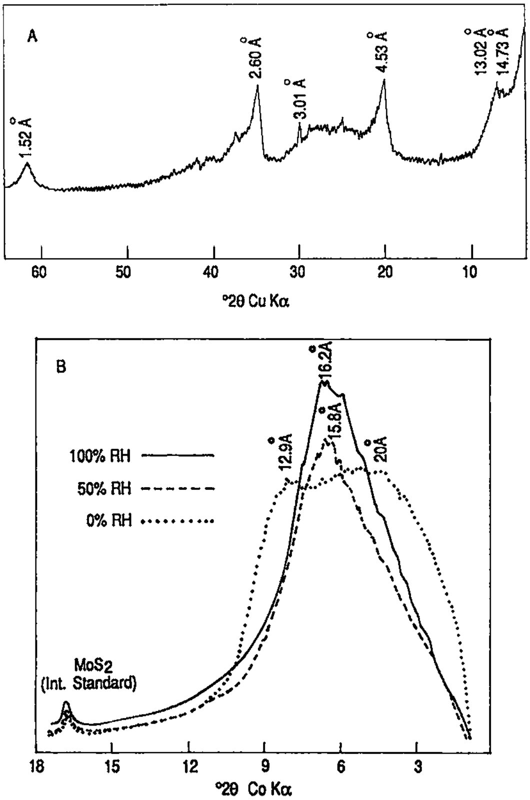

FIG. 2. X-ray-diffraction patterns of palagonite. A. Normal XRD. B. Low-angle XRD.

Å at 50% RH, and 12.9 Å at 0% RH. This kind of peak shift with changing RH is normal for smectite minerals (Van der Gaast *et al.* 1986). However, the scale of peak shift for the palagonite is smaller than most of the smectite minerals reported by van der Gaast *et al.* (1986). In addition to the shifting peak, there is a low-angle hump at 20 Å that can best be seen at 0% RH (Fig. 2B); this feature points to the presence of curved or folded layers (see also Van der Gaast *et al.* 1986).

The TEM study indicates that most of the palagonite is composed of fibrous to lath-like or strongly folded layered particles similar to smectite minerals (Fig. 3A). Lattice images of the palagonite particles show a *d* value of 10 Å (Fig. 3B), which corresponds to the low-angle X-ray diffraction maximum at 12.9 Å at 0% RH. This difference in *d* value reflects the change in the degree of dehydration of the material in the two techniques. In low-angle XRD at 0% RH, Ca-exchanged smectite still keeps one layer of absorbed water (Kühnel & Van der Gaast 1989), whereas at vacuum conditions applied in TEM, all interlayer water is lost. Electron-diffraction patterns of the palagonite show diffraction rings or diffuse spots at 4.55, 2.61, and 1.52 Å (Fig. 4A), which agrees with the XRD results very well. This indicates that degree of dehydration has little or no effect on these *d* values, and thus these diffraction maxima must belong to the [001] zone. In fact, the electron-diffraction pattern is consistent with [001] diffraction pattern

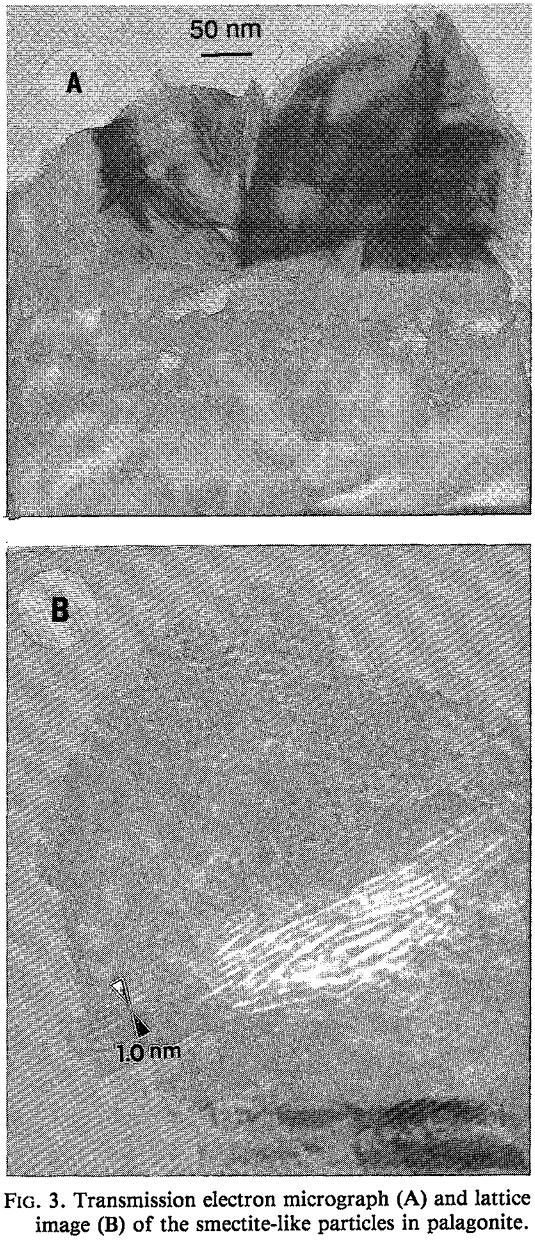

FIG. 3. Transmission electron micrograph (A) and lattice image (B) of the smectite-like particles in palagonite.

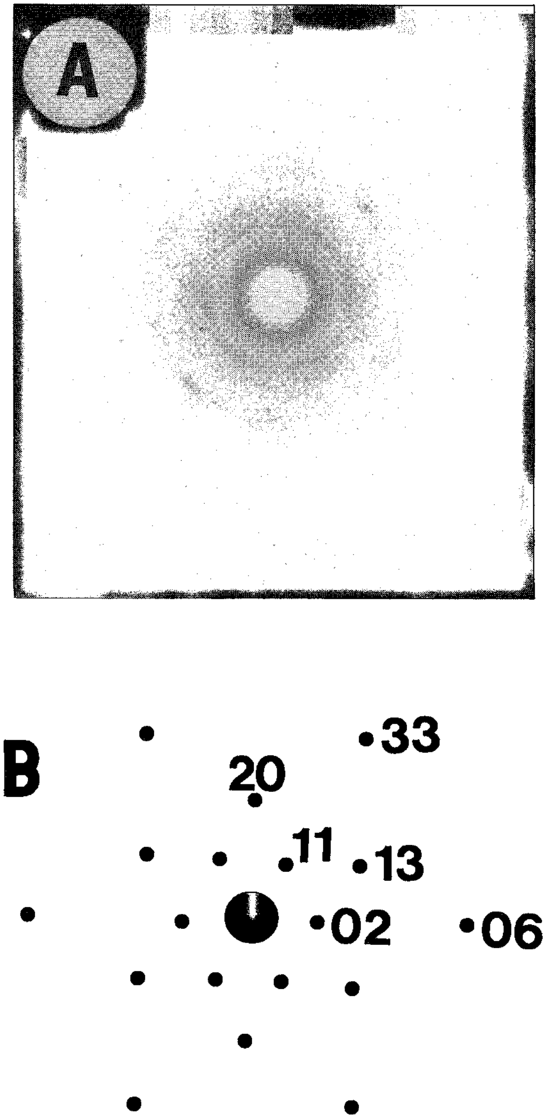

FIG. 4. Electron-diffraction patterns of the smectite-like particles in palagonite. A. Diffuse diffraction-spots. B. Indexed diffraction pattern A.

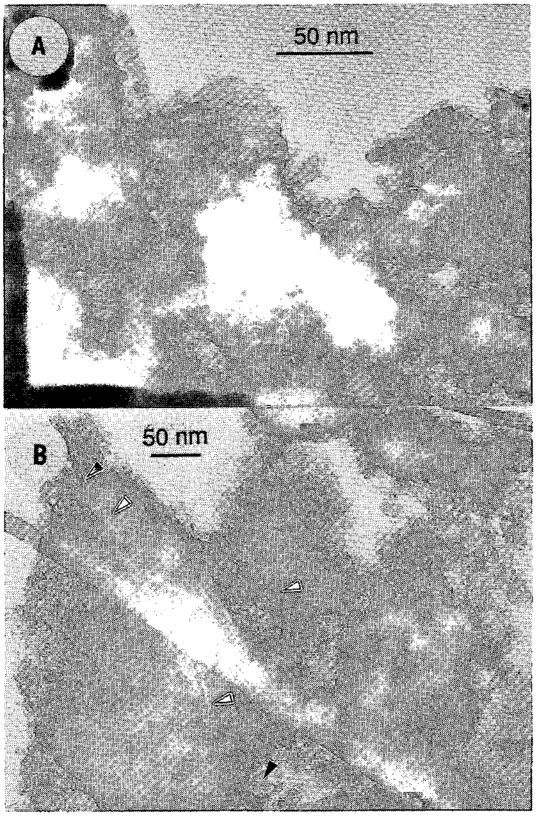

FIG. 5. Spheroidal particles in palagonite (A) and their replacement by randomly oriented short line-structures (arrows) (B).

of smectite minerals and can be indexed as (02) and (11), (13) and (20), and (06) and (33) (Fig. 4B).

We also noted that the particles of smectite-like palagonite usually have well-organized crystallinity along the *a* and *b* axes. Along the *c* axis, the number of stacked layers is usually less than 7. The crystallinity along *c* axis of the smectite-like particles may be poor in general, as their (00*l*) peaks on XRD are weak. A high degree of crystallinity of palagonite along *a* and *b* axes also was observed by Singer (1974).

Associated with the smectite-like particles are clusters of small, spheroidal particles, a few hundred angströms in diameter (Fig. 5A). They are very poorly crystalline and similar to the "cell-like structures" described by Banfield & Eggleton (1990). These spheroidal particles may represent the precursors of smectite-like clays. Figure 5B shows the progressive replacement of these spheroidal particles by small, randomly oriented line-structures, which lead to formation of smectite-like clays.

The chemical composition of palagonite is known to be variable (Honnorez 1981). The compositional changes during palagonitization at Site 335 has been discussed by Zhou & Fyfe (1989). Using a scanning transmission electron microscope equipped with an EDX detector, we were able to analyze palagonite particles having different morphology. Compositional variations are quite large,

TABLE 1. CHEMICAL COMPOSITION OF SELECTED PARTICLES IN THE PALAGONITE FROM DSDP SITE 335[1]

	Smectite-like Particles				Spheroidal	
	1	2	3	4	5	6
SiO_2	52.2	53.0	52.3	53.2	47.4	49.9
Al_2O_3	18.7	17.1	5.9	—	24.8	19.0
Fe_2O_3[2]	15.2	14.0	7.5	9.8	15.3	19.5
TiO_2	1.6	1.4	1.8	—	0.9	3.2
MgO	10.3	11.7	31.7	35.3	2.1	7.1
CaO	—	—	—	1.8	1.7	0.2
K_2O	2.1	2.9	0.9	—	7.6	1.1
Total	100.1	100.1	100.1	100.1	99.8	100.0

[1] Determined by transmission electron microscopy with energy–dispersion X–ray spectra; reported as wt% of oxides on anhydrous basis. [2] Total iron as Fe_2O_3.

even within each individual sample (Table 1). The major oxides present are SiO_2, Al_2O_3, Fe_2O_3, MgO, TiO_2 and K_2O. The spherical particles (Table 1, analyses 5 and 6) are rich in Al and Fe, whereas the smectite-like particles (Table 1, analyses 1–4) are Mg- and Fe-rich silicates.

DISCUSSION

The structural characteristics of smectite-like minerals described above are similar to those of stevensite and nontronite. Table 2 compares the XRD data of palagonite and those of stevensite, saponite, and nontronite. The match between the palagonite and stevensite data is very good. Not only the positions of the diffraction peaks of the palagonite but also their relative intensities are similar to those of stevensite. Stevensite was established as a member of smectite group by Faust & Murata (1953). This was confirmed in subsequent studies (Brindley 1955, Faust *et al.* 1959), although the detailed structural characteristics of the mineral remain to be defined (Brindley & Brown 1980). The smaller shift of the 001 peak position of palagonite with changing RH (as compared with most smectite minerals) also is consistent with the low cation-exchange capacity and small swelling ability of stevensite (Brindley 1955).

TABLE 2. X–RAY–DIFFRACTION DATA FOR STEVENSITE, SAPONITE, NONTRONITE, AND PALAGONITE FROM DSDP SITE 335

Stevensite[a]		Saponite[b]		Nontronite[c]		Palagonite			
Å	I	Å	I	Å	I	Å	I	Å	I
24	20?	-	-	-	-	20	w	-	-
						14.6	w	-	-
12.4	100	14.2	100	14.6	100	13.0	12.80	w	
		7.4	10	7.56	10	-	-	-	-
5.0	20	4.96	40	4.98	10	-	-	-	-
4.54	100	4.57	50	4.53	100	4.53	vs	4.53	vs
3.50	50	3.67	80	3.67	20	3.60	w	3.49	s
3.0	-	2.99	10	3.01	30	3.01	w	-	-
2.62	90	2.58	20	2.60	50	2.60	vs	2.60	vs
2.28	20	2.30	20	2.27	10	-	-	2.28	w
1.73	40	1.73	20	1.72	20	-	-	1.75	s
1.52	90	1.53	90	1.52	80	1.52	s	1.52	s

[a]ASTM # 7-357; [b]ASTM #13-86; [c]ASTM #34-842

However, the chemical composition of the palagonite from Site 335 is variable and can be significantly different from that of stevensite (Table 1). The structural formula of stevensite was suggested by Faust & Murata (1953) to be: $[Mg_{2.88}Mn_{0.02}Fe_{0.02}^{3+}]Si_4O_{10}[OH]_2$, which differs from saponite in lacking essential aluminum. Stevensite found in experimental alteration of basaltic glass (Trichet 1969) is a nearly pure Mg-silicate hydrate. The Mg-rich smectite-like particles in the palagonite invariably contain significant amount of Fe or Al (or both). Thus, they are compositionally incompatible with stevensite. In chemical composition, the smectite-like palagonite particles are similar to saponite, but the 060 peak of the palagonite has a *d* of 1.52 Å compared to 1.53 Å for saponite (Table 2).

The XRD data could also be accounted by nontronite, although the fit is not as good as with stevensite. However, those nontronite peaks that are absent in the palagonite are of the 00*l* type. As discussed above, the crystallinity of palagonite is poor along the *c* axis, and the discrepancy could result from this poor crystallinity.

However, nontronite alone cannot account for the observed chemical composition of the palagonite either. Its structural formula (Brindley & Brown 1980) is $[M^+_x \bullet nH_2O][Fe^{3+}_2][Si_{4-x}Al_xO_{10}][OH]_2$, *i.e.*, it should contain little or no Mg. In contrast, the smectite-like particles in the palagonite usually contain more than 10 wt.% MgO (Table 1, analyses 1–4).

We suggest here that the discrepancy is due to the composite nature of the palagonite. Both dioctahedral nontronite and trioctahedral stevensite (or saponite) may be present. The close association of the smectite minerals of variable composition at a submicrometer scale leads to a variable chemical composition that cannot be accounted for by either mineral alone. The chemical analysis of the palagonite also is complicated by the spherical particles that are closely associated with the smectite-like particles. In this respect, it should be noted that the area covered by electron beam during EDX analysis was about 0.05 μm in diameter. This size is much greater than that of the smectite-like particles in the palagonite. Therefore the chemical composition determined as such may be that of a composite material. In fact, diffuse diffraction spots and diffraction rings observed for the palagonite (Fig. 4) provide direct evidence that the material is both polycrystalline and poorly crystalline. It is also interesting to note that the basal reflection of the palagonite varies between 12 and 15 Å, and may be split (Fig. 2A). This again suggests that the palagonite is composite in nature.

Thus the observed structural and compositional characteristics of the palagonite from DSDP Site 335 can explained by the microscale association of dioctahedral nontronite and trioctahedral stevensite (or saponite). This finding contrasts with the observation of Eggleton & Keller (1982) that their palagonite is composed of a dioctahedral smectite with significant Mg in the octahedral sites. Dioctahedral (nontronite) and trioctahedral (saponite) clays also were suggested to occur in the palagonite of Contrada Acqua Amara, near Palagonia (Crovisier *et al.* 1987).

The spherical particles are probably the precursors of the smectite-like minerals. Eggleton & Keller (1982) noted the formation of smectite from spherical particles during palagonitization. Our observation indicates that spherical particles are first replaced by short-range crystalline domains that eventually develop into smectite-like minerals. The presence of spherical particles may account for the "amorphous" hump seen in XRD pattern of the palagonite (Fig. 2A).

It should be noted that oxide phases of Fe, Mn and Ti and zeolites were not found in the palagonite itself, although they are closely associated with it (Zhou & Fyfe 1989). Therefore, it may be inappropriate to consider this palagonite as a mixture of altered glass with clays, oxides and zeolite. Rather, the palagonite from DSDP Site 335 can be considered as a composite material that contains smectite minerals (of variable composition and crystallinity) and their precursors.

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