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Palagonite – a review

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Abstract Palagonite is the first stable product of volcanic glass alteration. It is a heterogeneous material, usually with highly variable optical and structural properties, ranging from a clear, transparent, isotropic, smooth and commonly concentrically banded material, commonly called “gel-palagonite”, to a translucent, anisotropic, slightly to strongly birefringent material of fibrous, lath-like or granular structure, commonly called “fibropalagonite”. The color of palagonite ranges from shades of yellow to shades of brown. Palagonite forms rinds of variable thickness on every mafic glass surface exposed for some time to aquatic fluids. It is formed by either incongruent dissolution or by congruent dissolution of glass with contemporaneous precipitation of insoluble material at the glass–fluid interface. The process of palagonitization is accompanied by extensive mobilization of all elements involved in the alteration process, resulting in the depletion or enrichment of certain elements. The extent and direction of element mobility and the palagonitization process itself (including the rate of palagonitization) depend on a number of different, complex interacting properties: e.g. (1) temperature, (2) the structure of the primary material, (3) the reactive surface area of the primary material, (4) the structure of the precipitating secondary phases, (5) the growth rates of the secondary phases, (6) time, and (7) fluid properties such as fluid flow rates, pH, Eh, ionic strength, and oxygen fugacity. The fluid properties themselves are affected by different hydrogeological properties such as porosity, permeability, and pressure gradients.

Keywords Palagonite · Glass alteration · Element fluxes · Reaction mechanism · Kinetics · Palagonitization rates

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Introduction

During the last three decades the alteration of volcanic glass, including the formation of secondary products, has become a topic of major interest for several reasons:

- alteration processes in general, and the alteration of volcanic glass in particular, have a significant impact on the chemistry of natural waters (Maynard 1976; Stumm and Morgan 1996);
- bentonite deposits formed by alteration of glassy pyroclastics have become of economic importance (Grim and Güven 1978); and
- glass-alteration processes have been used as a natural analog for modeling the long-term behavior of nuclear waste glasses (Lutze et al. 1985).

Volcanic glasses are not only a component of the upper oceanic crust, they also form large hyaloclastite bodies in marine and meteoric environments. Also, because of their thermodynamic instability, volcanic glasses are more reactive than associated primary mineral assemblages. The initial element flux during alteration of glass-bearing volcanic deposits is thus the consequence of the interaction of glass with aqueous solutions.

At more advanced stages of alteration, element fluxes are also influenced by the formation of secondary phases (e.g. palagonite, clay minerals, zeolites, or carbonates). It is generally accepted that palagonite is the first stable product of aquatic mafic glass alteration (Peacock 1926; Hay and Iijima 1968; Staudigel and Hart 1983; Furnes 1984; Thorseth et al. 1991). The composition, structure and evolution of palagonite have, therefore, a major influence on element fluxes, formation of authigenic mineral assemblages and the alteration process itself.

In this context, the physical properties, texture, mineralogical and chemical composition, evolution (including chemical and structural changes) and the growth rate of palagonite, and the kinetic constraints involved in the overall alteration process, will be discussed in detail.

Early work

Palagonite and the process of palagonitization have been subjects of intense studies since the “discovery” of palagonite by von Waltershausen in 1845. Von Waltershausen (1845) used the term “palagonite” to describe a transparent, yellow to brown, resin-like substance he found in altered basaltic glasses of hyaloclastite deposits in the area of Palagonia, Iblean Mountains, Sicily. He defined palagonite as a new, single mineral phase with a specific weight of 2.64 g cm^{-3} formed by submarine alteration of volcanic glass at ambient temperature. Bunsen (1847), working on Icelandic hyaloclastites, noticed the chemical similarity of palagonite and associated basaltic glass, except for the addition of large amounts of H_2O and the loss of Ca and Na. He interpreted palagonite as having been formed by submarine hydration after magma emplacement of a special, alkali-rich magma. The first microscopic investigation of palagonite (Fischer 1869) revealed that palagonite is a mixture of different phases. Subsequently palagonite was postulated as representing a hyaline, amorphous material (Rosenbusch 1872) directly formed during extrusion and cooling of magma under high-temperature conditions (Rosenbusch 1872; Anger 1875). Penck (1879), on the basis of his detailed review on palagonite, concluded that palagonite does not actually exist as a distinct mineral phase. He interpreted the material hitherto described as palagonite as a mixture of glass and matrix produced by basaltic eruptions. Penck (1879) was proved wrong by the first comprehensive microscopic and chemical study of altered glasses from Iceland (Peacock 1926).

Peacock (1926) distinguished two main palagonite varieties – gel-palagonite and fibro-palagonite – a distinction still accepted today. He also recognized zeolites as crystalline constituents of palagonite and, like other early and later workers, e.g. Bunsen (1847) and Correns (1930), noted that the alteration of sideromelane to palagonite results in a significant loss of some elements. Peacock (1926) postulated that palagonite formation is accompanied by oxidation of Fe, uptake of H_2O , and loss of CaO and Na_2O , whereas Correns (1930) argued that palagonitization is accompanied by loss of SiO_2 and Al_2O_3 . The extensive uptake of H_2O is one of the most distinct changes occurring during the transformation of sideromelane to palagonite. It has been one of the major reasons why most workers, until the pioneering work of Moore (1966) and Hay and Iijima (1968), believed that palagonite was basically hydrated glass.

Until now, the term “palagonite” has been used for any hydrous reaction product of mafic glass alteration. In general the different theories about the mechanism of palagonite formation and evolution, and its chemical, mineralogical and structural nature, remain highly controversial. Previous reviews include those of Honnorez (1972), Fisher and Schmincke (1984), and Singer and Banin (1990).

From macro- to micro-cosmos – physical properties, texture, and nanoscale structure

Macroscopically palagonite is an earthy or clay-like substance building discrete colored rinds on every mafic volcanic glass surface exposed to aquatic fluids (e.g. pillow rims, hyaloclastite particles, fractures, vesicle walls), often leaving islands of fresh glass embedded in palagonite rinds of variable thickness (Fig. 1b). The color of palagonite is highly variable, ranging from shades of yellow to shades of orange or brown, and is probably temperature-dependent. The much more common, lighter-colored palagonite is formed at lower, ambient temperatures, whereas the rare, dark-brown to red-brown palagonite is formed at elevated temperatures in the vicinity of fumarolic activity or in tropical climates (Furnes 1975; Jakobsson 1978). Palagonite, because of its distinct color, can be recognized easily in outcrops, hand specimens, and thin section. Palagonitized outcrops of, e.g., hyaloclastites, pillows, or pillow-breccias usually have a yellow or yellow-brown color, in contrast with the dark-gray to black appearance of fresh basalt (Fig. 1a). The macroscopic appearance of volcanic glass-bearing deposits usually depends on the intensity of alteration, which includes palagonitization and the formation of other secondary phases (cement) such as clays, zeolites, and carbonates. The most striking macroscopic feature of palagonitized rocks is this change in color. The formation of other secondary phases in pore spaces (cementation) not only results in increasing massiveness of the rock body but also in increasing bulk rock density. For example, the formation of secondary phases during alteration of sideromelane tuff to palagonite tuff caused a porosity-decrease in the Koko Crater deposits, Oahu, Hawaii from 36% to 9% and a density-increase from 1.67 g cm^{-3} to 2.05 g cm^{-3} (Hay and Iijima 1968). The density of palagonite itself, however, is significantly lower than that of fresh sideromelane, ranging from 1.90 to 2.10 g cm^{-3} (Hay and Iijima 1968; Staudigel and Hart 1983), whereas fresh sideromelane has a density of approximately 2.75 g cm^{-3} . The density of palagonite characteristically increases with age, because of its transformation into fully crystalline material.

Primary structural and textural volcanic features are usually well preserved in outcrops of palagonitized basaltic rocks (Fig. 1a) despite the intense changes; a phenomenon which can be observed down to the microscopic scale (Fig. 1c) (Hay and Iijima 1968; Jercinovic et al. 1990; Stroncik and Schmincke 2001), as is apparent in thin section (Fig. 1c). Features such as primary glass shard morphology, particle size, particle size distribution, vesicularity, and porosity can still be detected even in substantially altered rocks. Nonetheless, the structural differences between fresh glass and palagonite are striking (Fig. 1c). Basaltic glass (sideromelane) in thin section is usually homogeneous, clear, transparent, and isotropic with a smooth surface structure. Palagonite, on the other hand, is quite heterogeneous in its optical and structural properties. Gel-palagonite, which forms next

Fig. 1a–h Macroscopic and microscopic images of palagonite and fresh glass. **a** Outcrop of fresh and palagonitized mafic glass (source R. Werner). **b** Hand specimen of submarine palagonitized glass. **c** Thin section micrograph of gel-palagonite. **d** Thin section micrograph of fibro-palagonite. **e** HR-TEM micrograph of gel-palagonite. **f** HR-TEM micrograph of fibro-palagonite (Zhou and Fyfe 1992). **g** AFM image of gel-palagonite. **h** AFM-image of evolved-palagonite

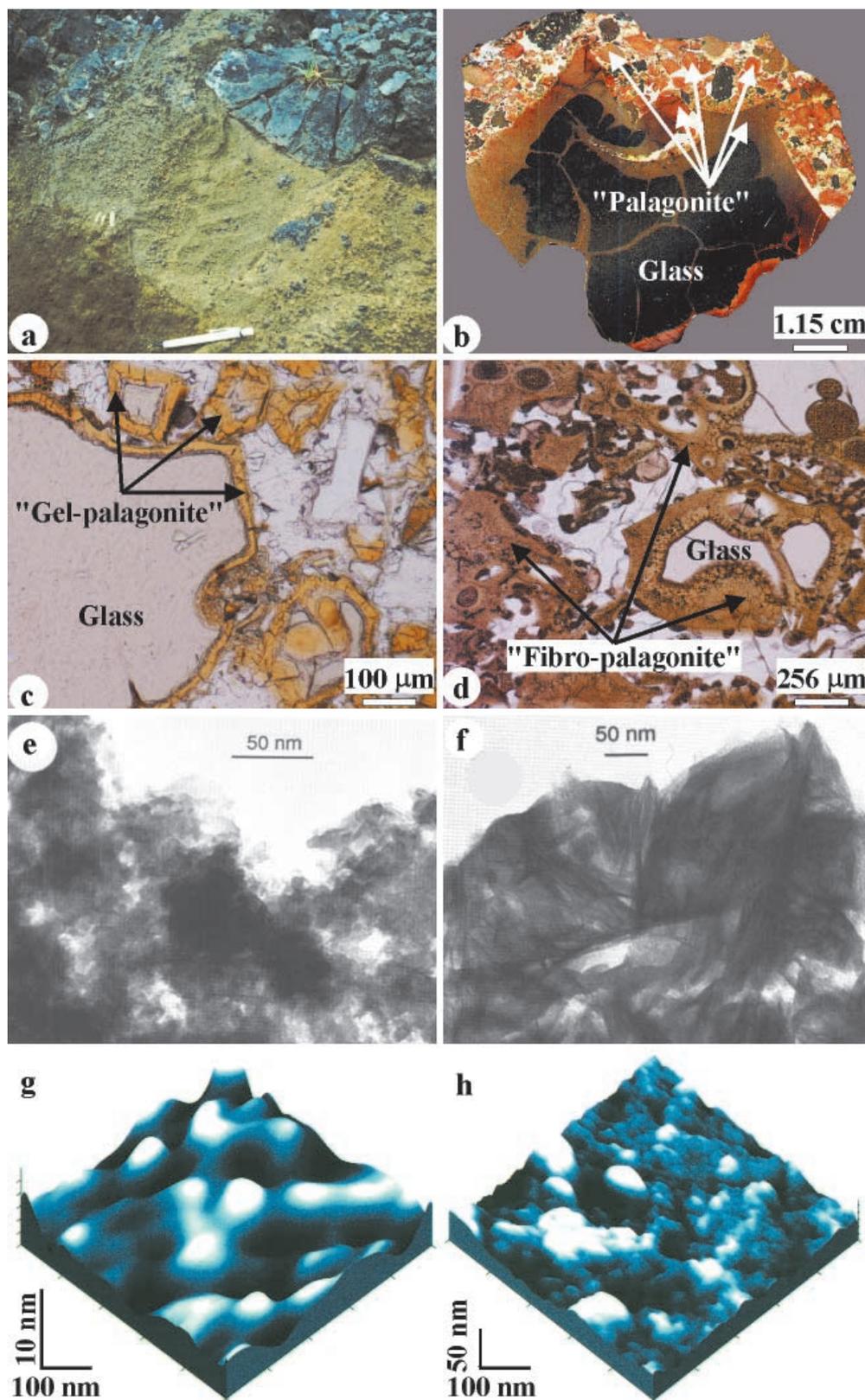
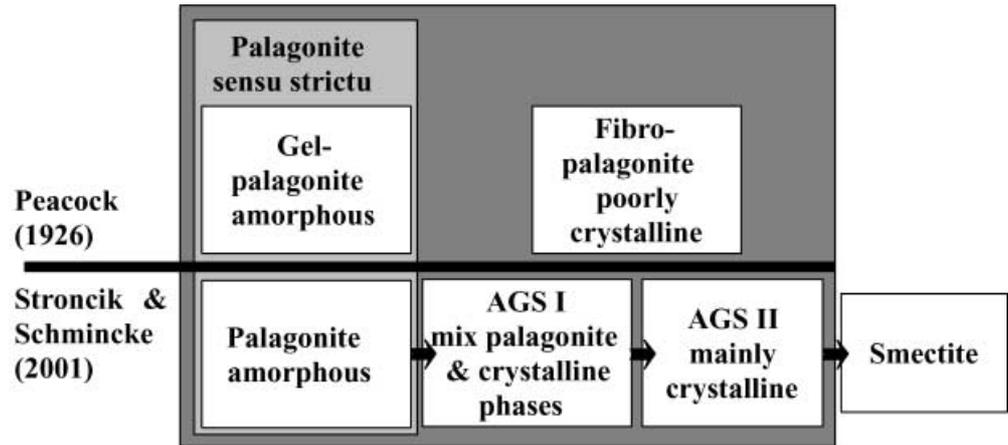


Fig. 2 Usage of the term “palagonite” (after Stroncik and Schmincke 2001)



to the unaltered glass surface, is clear, transparent, isotropic, smooth, and commonly concentrically banded (Fig. 1c). Layers enriched with opaque minerals (Staudigel and Hart 1983; Schmincke and Sunkel 1987), such as Fe or Ti oxides, and layers of palagonite with different degrees of aging (Stroncik and Schmincke 2001) often enhance this concentric banding. The more intensely-colored fibro-palagonite develops during later stages of palagonitization on the outer surface of the gel-palagonite (Fig. 1d) (Peacock 1926; Zhou and Fyfe 1989). It is translucent, anisotropic, slightly to strongly birefringent, and of fibrous, lath-like or granular structure. According to Stroncik and Schmincke (2001), fibro-palagonite is a mixture of gel-palagonite and crystallizing smectite, developing during the aging of gel-palagonite. Stroncik and Schmincke (2001) suggest the use of the term “palagonite” for the amorphous, gel-like phase only, and avoidance of the terms gel- and fibro-palagonite (Fig. 2). Gel- and fibro-palagonite are not, however, different varieties of the “species” palagonite – instead they represent different evolutionary stages, ranging from purely amorphous (palagonite) to fully crystalline (smectite). The interface between fresh sideromelane and palagonite is often occupied by a ~100- μm thick zone covered with microchannels entering the fresh glass from the palagonite–glass interface (Fig. 1d) (Melson and Thompson 1973; Staudigel and Hart 1983). Morgenstein and Riley (1975) called this zone the “immobile product layer”.

High resolution transmission electron microscopy (HRTEM) and atomic-force microscopy (AFM) have been used to study the structure of palagonite in detail. Eggleton and Keller (1982) noted, on the basis of HRTEM studies, the occurrence of spherical structures (200–600 Å) even in gel-palagonite (Fig. 1e). Apparently, “exfoliation of 10 Å (2:1) clay layers” from these spheroids results in the development of small, dioctahedral smectite crystals (30–60 Å) “which ultimately form a tangled network of sub-micron-sized bent flakes” (Fig. 1f). By use of a combination of HRTEM and X-ray diffraction studies, spherical particles have been detected in palagonite from DSDP Site 335 (Zhou et al. 1992). They become progressively replaced by small, randomly oriented linear-structures, seemingly leading to the for-

mation of smectites. These spheroids have been interpreted as microcrystallite precursors of smectites (Zhou et al. 1992). A combination of AFM, XRD, and EM studies on gel- and fibro-palagonites (Fig. 1g, h) from Iceland and the Cocos Ridge has shown that the isotropic “gel-palagonite” (Fig. 1g) is crystallite-free, whereas the anisotropic “fibro-palagonite” (Fig. 1h) contains crystallites growing mainly perpendicularly to the glass surface in the “gel-palagonite” (Stroncik and Schmincke 2001). “Fibro-palagonite” thus seems to be a mixture of crystallites and “gel-palagonite”. Palagonite usually has a sponge-like structure (Fig. 1g, h) with large amounts of heterogeneously distributed pores.

Mineralogy

Since its definition as a new mineral species (Von Waltershausen 1845), most workers have accepted that palagonite is a heterogeneous substance composed of different clays, zeolites, and oxides, or mixtures of these (Peacock and Fuller 1928; Eggleton and Keller 1982; Furnes 1984; Jercinovic et al. 1990; Zhou et al. 1992). X-ray diffraction studies on separated palagonite from Koko Craters, Oahu, Hawaii revealed weak reflections of montmorillonite and mixed-layer mica-montmorillonite (Hay and Iijima 1968). Singer (1974) concluded, on the basis of X-ray and electron diffraction studies of separated palagonite, that palagonite contained “a dioctahedral micaceous clay mineral with well organized crystallinity along the a- and b-axes”, and random interstratification of expanding and non-expanding 14-Å layers. On the basis of scanning electron microscopy and X-ray diffraction studies of palagonites from Santa Maria, Azores, and Gran Canaria, kaolinite, illite and mixed-layer illite-montmorillonite, zeolites, hematite, ilmenite, gibbsite, gypsum, and apatite have been added as possible constituents of palagonite (Furnes and El Anbaawy 1980; Furnes 1984). Eggleton and Keller (1982) noticed the similarity of average palagonite to smectite when recalculated on a water-free basis, to a cation charge of +22. By combining the results from detailed HRTEM and XRD studies of palagonite with the

results from electron microprobe analysis of palagonite, Zhou and Fyfe (1992) argued that palagonite from DSDP Site 335 consists of an intimate mixture of the clay minerals stevensite and nontronite and their precursors. Stroncik and Schmincke (2001), working on palagonites from the Columbia River Plateau, USA, Mt Iblei, Sicily, Iceland, and the Cocos Plate, obtained similar results. They postulated that a mixture of nontronite and saponite crystallizes from the thermodynamically unstable, amorphous palagonite during its evolution. In summary, most workers today agree (Eggleton and Keller 1982; Staudigel and Hart 1983; Jercinovic et al. 1990; Daux et al. 1994; Stroncik and Schmincke 2001) that palagonite is actually composed of a variety of smectites and very minor amounts, if any, of zeolites and oxides.

At more advanced stages of alteration, palagonitization of sideromelane is accompanied by the formation of other secondary phases, such as different types of clays, zeolites, hydroxides, and oxides, and calcite, aragonite, opal, and gypsum.

Element mobilities, mass balancing, and major element chemistry

The chemical composition of alteration products basically reflects the prevailing element mobility of the water-rock system during the alteration process (Bonatti 1965; Staudigel and Hart 1983; Viereck et al. 1985; Lasaga et al. 1994; Stumm and Morgan 1996). The quantification of this element mobility and its direction must be accomplished by mass-balance calculations, because consistent kinetic models for glass alteration processes are not available. These mass-balance calculations cannot be based on mere comparison of analytical data, because of the physical changes, e.g. volume or density shifts, accompanying alteration processes. They must, therefore, be based on assumptions such as the immobility of elements or the volume constancy of the alteration process. The extent and direction of element mobility can be variable depending on the approach used. On use of the mass-balance algorithm developed by Gresens (1967), which implements a volume factor to account for volumetric changes occurring during alteration, it becomes obvious that results from calculations based on isovolumetry can be remarkably different from those based on immobility of a particular element (Fig. 3).

Because elements such as Ti, Al, and Fe_{tot} are usually quite insoluble in natural waters, it has been assumed that they remain unchanged during rock alteration. Thus, mass gains or losses of other elements have been calculated in relation to the glass/palagonite Ti, Al or Fe_{tot} ratios, using bulk analytical and microprobe data (Hoppe 1941; Brey and Schmincke 1980; Crovisier et al. 1992). Hoppe (1941) based his mass-balance calculations for experimentally altered glass on the assumption of Fe_{tot} -immobility. Eggleton and Keller (1982) performed similar calculations on meteorically palagonitized limburgite glasses from Limburg, Kaiserstuhl, Germany, assuming

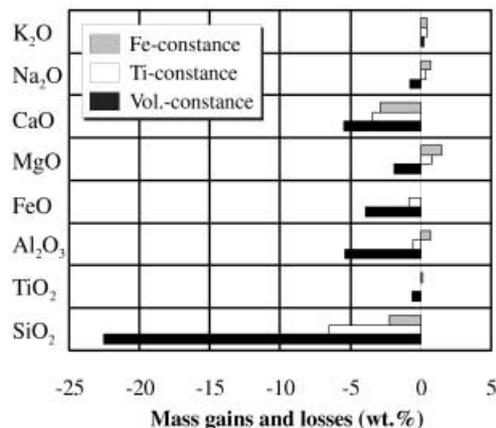


Fig. 3 Comparison of the results from mass balance calculations based on volume-constancy, Ti constancy, and Fe constancy

that Fe_{tot} and Ti have remained immobile. Staudigel and Hart (1983), in a more general study of submarine glass alteration, also based their mass balance calculations on Fe_{tot} - and Ti-immobility, as did Crovisier et al. (1992). These assumptions of element immobility might not be strictly valid, however, and, as indicated by the formation of other Ti-, Al-, and Fe-bearing secondary phases, these elements do not remain entirely immobile during palagonitization (Figs. 4a-c) (Hay and Iijima 1968; Furnes 1984; Jakobsson and Moore 1986; Jercinovic et al. 1990; Stroncik and Schmincke 2001).

Because of petrographic constraints, palagonitization might be an isovolumetric process and thus element mobilities have been calculated on a weight per unit volume basis from the chemical analysis and specific gravities of sideromelane and palagonite (Hay and Iijima 1968; Furnes 1984; Jakobsson and Moore 1986; Jercinovic et al. 1990; Stroncik and Schmincke 2001). Hay and Iijima (1968) saw the excellent preservation of the primary texture of hyaloclastite samples from Koko Crater, Hawaii, as evidence of the isovolumetry of the palagonitization process. The same conclusion has been reached for palagonitized hyaloclastites from Gran Canaria and Iceland (Furnes and El Anbaawy 1980; Jakobsson and Moore 1986). Jercinovic et al. (1990) argued, on the basis of studies by Crovisier et al. (1987), that non-isovolumetric alteration should result in the formation of open fractures. The absence of open fractures in palagonitized hyaloclastites has, therefore, usually been taken as proof of isovolumetric alteration (Fig. 5).

Irrespective of the numerical approach used for mass-balance calculations, the extent of element mobility can be variable, as reflected in the often heterogeneous chemical composition of palagonites derived from a single sample (Table 1). This indicates that the water-rock system undergoes chemical evolution with progressive alteration. Because consistent overall alteration rates are not available, chemical analysis of alteration products and subsequent mass-balance calculations only supply a snapshot of an evolutionary stage which cannot be related to a definite time factor. Thus, modeling of

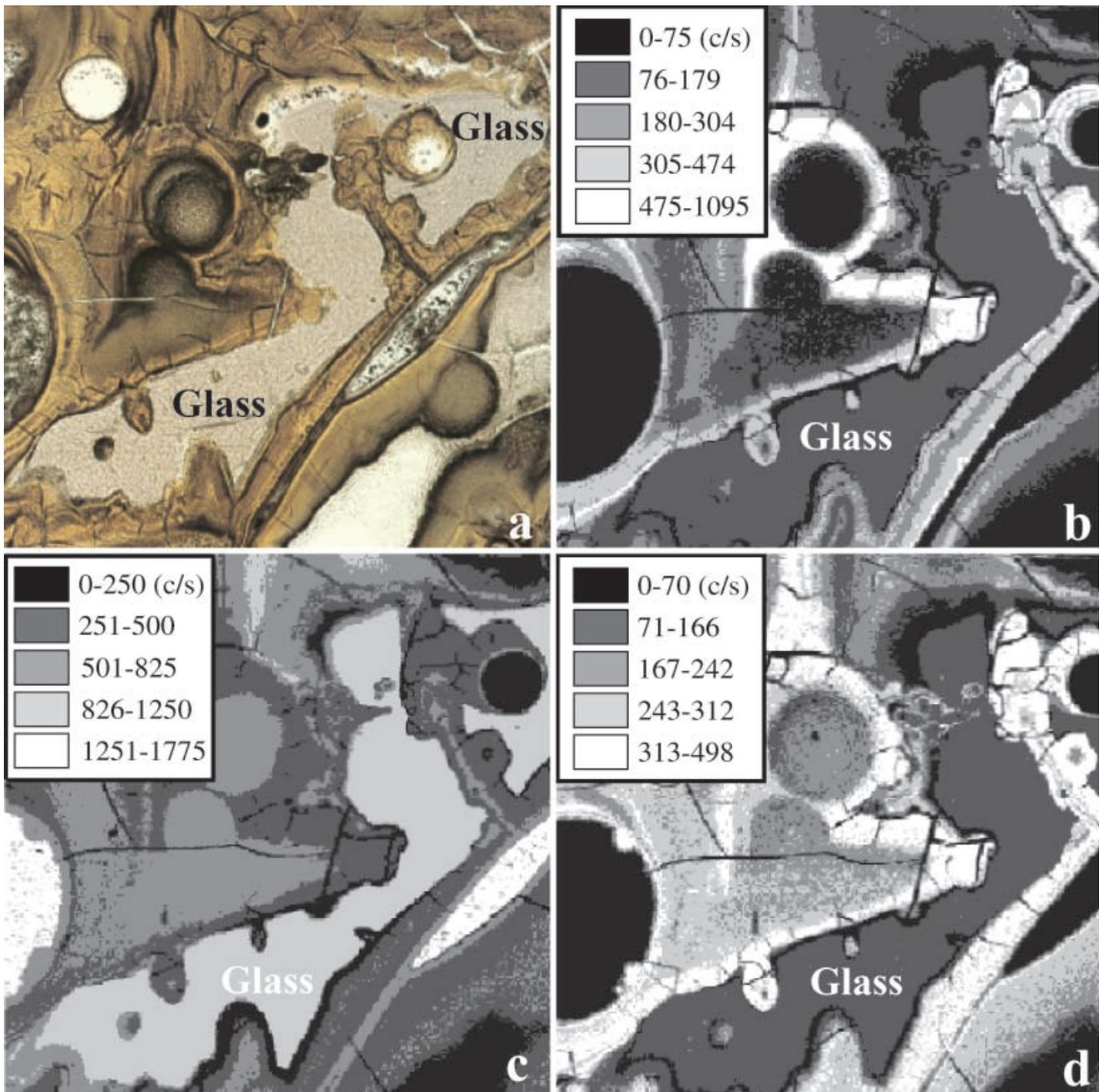


Fig. 4a-d Thin section micrographs and electron microprobe element mappings, in counts per second, of palagonitized mafic glass. **a** Thin section micrograph (2,048x2,048 μm). **b** Electron microprobe element mapping of Ti (2,048x2,048 μm). **c** Electron microprobe element mapping of Al (2,048x2,048 μm). **d** Electron microprobe element mapping of Fe (2,048x2,048 μm). (after Stroncik and Schmincke 2001)

chemical evolution during palagonitization must be accomplished on the basis of a measure of alteration advancement – denoted the “reaction progress”. There are, however, several definitions of “reaction progress”, for example:

1. it can be defined as mass of dissolved primary material compared with the mass of alteration phases pro-

duced, which leaves out the element exchange caused by further evolution of secondary phases;

2. it can be defined as decrease in the water/rock ratio during alteration; and
3. it can be defined on the basis of the behavior of a particular element, e.g. percentage Ti accumulation defined by the ratio $[\text{Ti}_{\text{palagonite}} - \text{Ti}_{\text{glass}}]/\text{Ti}_{\text{glass}}$ has been used as a maturity index denoting reaction progress (Staudigel and Hart 1983).

Staudigel and Hart (1983) studied the relationship between this index and the results obtained by mass-balance calculations based on palagonite in relation to the parent glass, using electron microprobe data normalized to 100% on a volatile-free basis. They concluded that Si

Table 1 Average composition of palagonites and the corresponding parent glasses (between 100 and 200 single EMP measurements per sample) from different volcanic regions and alteration environments. Variances are calculated according to the algorithm $\frac{\sum x^2 - (\sum x)^2}{n^2}$, where n is the number of measuring points and x is the analytical value, and express the chemical heterogeneity of the different palagonite samples (Stroncik and Schmincke 2001)

Region	Cocos Plate									Iceland		
Sample	396CO			4296CO			5196CO			12791H		
Material	Glass	“Palagonite”	Variance	Glass	“Palagonite”	Variance	Glass	“Palagonite”	Variance	Glass	“Palagonite”	Variance
SiO ₂	48.65	17.80	1.75	50.29	25.76	4.39	49.43	25.09	5.83	48.40	22.82	2.78
TiO ₂	3.84	5.08	0.52	3.42	5.90	2.39	3.08	3.83	0.42	2.64	5.35	0.54
Al ₂ O ₃	16.59	5.05	0.21	15.47	5.23	0.16	15.52	5.82	0.83	14.17	13.35	3.05
FeO	9.13	18.12	2.76	10.04	20.08	3.97	8.99	15.28	2.64	12.52	21.25	6.15
MnO	0.18	0.01	0.00	0.21	0.02	0.00	0.13	0.02	0.00	0.22	0.03	0.00
MgO	5.01	0.70	0.01	4.90	1.08	0.13	6.04	0.90	0.04	6.90	0.18	0.04
CaO	9.86	0.61	0.02	9.85	0.67	0.03	10.73	0.57	0.02	11.74	1.92	0.31
Na ₂ O	3.86	1.60	0.05	3.03	2.02	0.42	3.05	2.20	0.49	2.64	0.21	0.00
K ₂ O	2.22	0.76	0.01	1.95	1.28	0.07	2.17	1.22	0.08	0.36	0.05	0.00
P ₂ O ₅	0.58	0.44	0.03	0.65	0.18	0.01	0.72	0.14	0.01	0.39	0.34	0.00
Total	100.00	50.30	13.62	100.00	62.37	24.08	100.00	55.19	8.16	100.00	65.53	7.37
Region	Iceland			Mt. Iblei / Sicily								
Sample	194Ht			2196Pala			2196Pald			1396VcS		
Material	Glass	“Palagonite”	Variance	Glass	“Palagonite”	Variance	Glass	“Palagonite”	Variance	Glass	“Palagonite”	Variance
SiO ₂	48.41	32.96	2.71	53.72	44.02	3.91	53.33	45.66	1.53	52.96	51.57	8.83
TiO ₂	1.55	2.53	0.03	1.82	3.38	0.15	1.78	3.48	0.21	1.74	1.27	0.27
Al ₂ O ₃	14.92	6.72	0.17	14.91	10.41	1.95	14.65	11.61	0.65	14.77	16.13	11.75
FeO	11.47	12.85	1.46	9.92	15.60	8.34	9.83	17.86	1.07	10.53	10.46	4.99
MnO	0.22	0.14	0.00	0.15	0.10	0.00	0.17	0.06	0.00	0.18	0.03	0.00
MgO	8.00	2.01	0.76	6.61	1.60	0.52	7.10	4.41	1.23	6.93	2.98	1.77
CaO	12.85	6.09	0.36	10.03	10.05	1.49	9.42	4.97	0.18	9.11	2.60	0.28
Na ₂ O	2.11	0.21	0.00	2.61	0.74	0.07	3.00	0.44	0.00	3.04	0.36	0.00
K ₂ O	0.15	0.02	0.00	0.23	0.29	0.00	0.21	0.34	0.01	0.23	0.36	0.01
P ₂ O ₅	0.28	0.22	0.00				0.35	0.13	0.01	0.29	0.06	0.00
Total	100.00	63.79	4.95	100.00	86.20	5.22	100.00	89.12	3.99	100.00	85.95	28.12

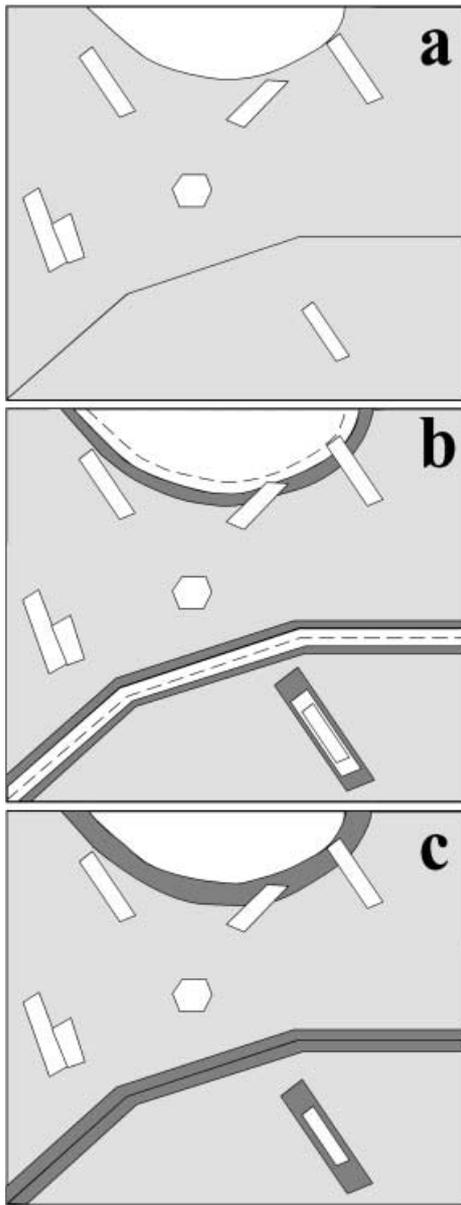


Fig. 5a-c Volume relationships between palagonite and glass. **a** Unaltered glass shard with vesicles, fractures, and scattered plagioclase and olivine crystals. **b** Sketched results of palagonitization with volume loss. *Dotted lines* represent the initial glass surface. **c** Sketched results of constant volume palagonitization (after Jercinovic et al. 1990)

and Al are lost in proportion to Ti accumulation, whereas the relationship between Ti accumulation and the amounts of other cations is not quite that strong (Fig. 6).

Crovisier et al. (1992) defined the reaction progress T.R.Z. (Taux de Réaction jusqu'à la formation de Zéolites) for each element of the system as the mass ratio between dissolved primary material and the precipitating material expressed as the ratio $R = (\text{SiO}_2/\text{MgO})_{\text{glass}} / (\text{SiO}_2/\text{MgO})_{\text{alteration products}}$. From relationships between T.R.Z. and mass-balance calculations based on Fe_{tot} immobility they deduced that the amount of Si, Ti, Al, and Mg lost during bulk meteoric alteration of Icelandic hya-

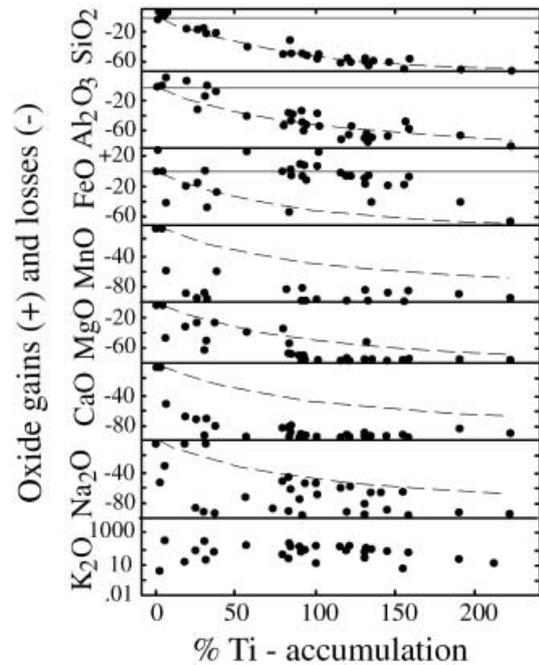


Fig. 6 Mobility behavior of major oxides from a variety of submarine palagonites as a function of % Ti accumulation. Increasing Ti accumulation reflects increasing reaction progress (after Staudigel and Hart 1983)

loclastites decreased with increasing reaction progress, whereas amounts of Ca and K remain constant and Na is lost continually. They also argued that the incipient stage of alteration, corresponding to the lowest reaction progress, is accompanied by a volume loss of approximately 15–20%, whereas the increase in reaction progress is accompanied by a volume increase of approximately 45%. Daux et al. (1994) calculated the reaction progress as the mass of dissolved glass per kilogram of solution, on the basis of the knowledge that fluid–rock interaction is accompanied by Sr exchange (Staudigel and Hart 1983; Crovisier et al. 1992), resulting in significant changes in the Sr-isotopic composition of both altering fluid and rock, by use of the equation:

$$\xi = M_G/M_W = [Sr_w \times (I_w - I_{SP}) \times (I_G + 9.375)] / [Sr_G \times (I_{SP} - I_G) \times (I_w + 9.375)],$$

where M_G and M_W are the masses of glass and water involved in the reaction, I_w , I_G , and I_{SP} are the isotopic Sr ratios of initial water, of pristine glass, and of secondary products respectively and Sr_w and Sr_G are the Sr contents of initial water and glass. By relating ξ to results obtained from mass-balance calculations based on Fe immobility, Daux et al. (1994) concluded that losses of Si, Mg, and Ca decrease with increasing reaction progress, whereas losses of Ti and Al are only minor and losses of Na are consistent, irrespective of reaction progress. By plotting the results of their mass balance calculations against the T.R.Z. proposed by Crovisier et al. (1992), they concluded that the amount of element loss, on a bulk rock basis, generally decreases with increasing

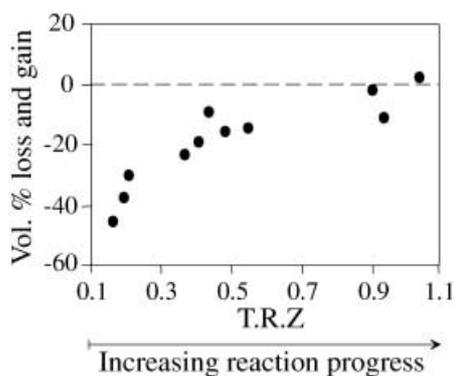


Fig. 7 Dependence of the variation of total element amount (%) on T.R.Z., the index of reaction progress proposed by Crovisier et al. (1992). The losses of elements undergone by the rock during alteration decrease with increasing reaction progress (after Daux et al. 1994)

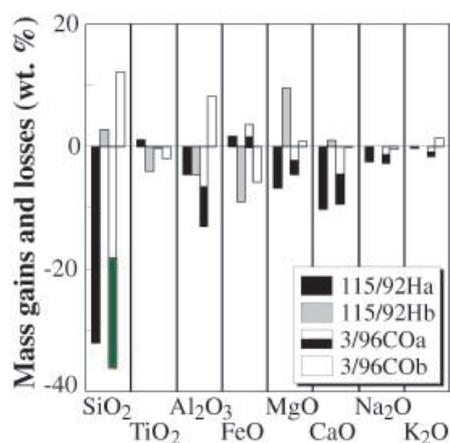


Fig. 8 Mass gains and losses of major oxides as function of palagonite aging. The signatures *a* and *b* after the sample name indicate the stage of aging of the sample, sample *a* being less aged than sample *b* (after Stroncik and Schmincke, 2001)

reaction progress (Fig. 7). Stroncik and Schmincke (2001) used the increase in the crystallinity of palagonite, expressed as increasing Mg-content as a maturity index, and related this maturity index to the results of mass-balance calculations obtained based solely on palagonite and based on a bulk-rock scale. They argued that the formation of the purely amorphous “gel-palagonite” is related to Si, Al, Mg, Ca, Na and K loss, H₂O gain, and immobile Ti and Fe behavior (Fig. 8), whereas the maturity increase of palagonite is related to increases in Si, Al, Mg and K, to continuing but decreasing losses of Ca and Na, and to losses of H₂O, Ti, and Fe (Fig. 8). On a bulk rock scale, element loss as a result of loss of all major oxides decreases with increasing maturity.

The transition of volcanic glass to palagonite accounts for only part of the element fluxes occurring in a water–rock-system. Calculated element fluxes based solely on glass palagonitization can be extrapolated to a bulk-rock scale only if palagonite appears as the only alteration product, whereas several partly counterbalancing

processes usually alter the composition of a water–rock system. For example, the chemical behavior of Mg and Ca are affected by two opposing reactions – both elements are released into solution during glass palagonitization whereas Mg is restored from solution during further evolution of palagonite (Stroncik and Schmincke 2001) and additional subsequent precipitation of smectites, and Ca is restored from solution because of calcite or zeolite precipitation.

Trace elements

Studies focussing on the trace-element composition of palagonite and the trace element flux accompanying palagonite formation are rare and the results published are often contradictory (Pearce and R. 1973; Thompson 1973; Staudigel and Hart 1983; Furnes 1984; Jercinovic et al. 1990; Daux et al. 1994). For example, Pearce and Cann (1973) and Thompson (1973) postulated that the elements B, Li, Rb, Cs, Pb, Cu, and LREE are usually enriched during submarine alteration of basalt glass, whereas changes in the amounts of V, Cr, Co, Ni, Zn, Sr, Y, Zr, Nb, Ba, HREE, and Hf are less consistent, being either enriched or depleted. Furnes (1978) argued, on the basis of studies of palagonitized subglacial hyaloclastites from Iceland, that Sr, Ba, Zr, Nb, and LREE undergo depletion during glass palagonitization, Y is enriched, and trends for V and Ni vary. From his studies of alkali olivine basaltic glass from Santa Maria, Azores, however, Furnes (1980) concluded that Zr, Nb, La, Ce, and Nd had been enriched relative to the parent sideromelane. He interpreted this enrichment as indicating progressive clay mineral and zeolite formation. Staudigel and Hart (1983) calculated that Zn, Cu, Ni, Cr, Hf, Sc, Co, and REE are lost during palagonitization, whereas Rb and Cs are gained. As reflected in the ⁸⁷Sr/⁸⁶Sr ratios of palagonite, which are intermediate between those of seawater and parental glass, Sr has been exchanged during the course of alteration. During their study of “fresh water” palagonites from Tuya Butte, British Columbia, Canada, Jercinovic et al. (1990) calculated that Rb, Cs, Sr, Ba, and REE are easily enriched during alteration, whereas Co, Ni and Cr parallel the behavior of Al, becoming either enriched or depleted. They concluded that the colloidal nature of palagonite, in conjunction with the effects of low fluid flow rates, enables enhanced adsorption of trace alkali and alkaline earth metals and REE.

Daux et al. (1994) studied, in detail, the mobility of REE (La, Nd, Sm, Eu, Gd, Dy, Er, Yb, and Y) and Th of meteorically palagonitized hyaloclastites from Iceland. According to their mass-balance calculations, the mobility behavior of these elements can be highly variable, with either enrichment or depletion. The mobility of these elements is independent of the progress of the reaction, as shown by the relationship between the results obtained by mass-balance calculations and the progress of the reaction. Thus these elements do not seem to participate in the structure of the precipitating alteration

phases but are absorbed on their surfaces (Daux et al. 1994). Consequently, the mobility of REE and Th is controlled by the absorption capacity of the secondary phases precipitating during glass alteration. The absorption capacity of clay minerals, e.g., is a function of particle size, crystallinity, and the absolute amount of secondary phases (Byrne and Kim 1990). Daux et al. (1994) supported these conclusions by comparing the REE- and Th-content of slightly crystallized palagonite and authigenic phases with those of highly crystalline palagonite and authigenic phases – the more crystallized material having the higher REE and Th content.

The process of palagonitization

Some general statements

Although palagonite has been interpreted as an alteration product of basaltic glass (sideromelane) since its “discovery” by von Waltershausen in 1845, theories about the onset of palagonite formation were contradictory until the 1970s and those concerning the reaction mechanism and its controls remain controversial. For example, Rosenbusch (1872), Anger (1875), Correns (1930), Bonatti (1965), and Pierce (1970) concluded that palagonite is formed directly during extrusion and cooling of magma under high-temperature conditions, whereas von Waltershausen (1845), Bunsen (1851), Peacock (1926), Moore (1966), Hay and Iijima (1968), and later authors postulated that palagonite is formed mostly during ambient-temperature sea- or meteoric water alteration of sideromelane, starting any time after magma emplacement. Basically, palagonite is formed after magma emplacement, mostly during low-temperature alteration. This is indicated by:

1. the discovery (Moore 1966) that palagonite rinds on the glassy rim of submarine pillows have grown systematically in thickness with time;
2. palagonite rinds do occur on subaerially emplaced lava flows (Eggleton and Keller 1982); and
3. the chemical composition of palagonite changes systematically with time, indicating an evolving system (Hay and Iijima 1968; Staudigel and Hart 1983; Zhou and Fyfe 1989; Daux et al. 1994; Stroncik and Schmincke 2001).

Because of the very high H₂O content (~10–40% w/w) of palagonite, workers proposed, before routine microprobe analysis and the work of Hay and Iijima (1968), that palagonite was simply formed by hydration of basaltic glass accompanied by oxidation of Fe and, possibly, minor losses of elements as oxides such as SiO₂, Al₂O₃, CaO, and Na₂O (Peacock 1926; Correns 1930). Moore (1966) envisaged the process of palagonitization as a hydration and element-exchange process controlled by diffusion. Hay and Iijima (1968) interpreted the rather distinct contact between palagonite and fresh glass as indicating a microsolution–precipitation mechanism of pal-

agonite formation. This process, in their opinion, can be viewed either as a process of hydrogen-ion metasomatism of glass or as a process of replacement of metal oxides in glass by water molecules.

It is generally accepted today that some type of dissolution (either incongruent or congruent)–precipitation mechanism is responsible for the alteration of sideromelane to palagonite (Berger et al. 1987; Crovisier et al. 1987; Jercinovic et al. 1990; Daux et al. 1994; Thorseth et al. 1995). This is indicated by the physical characteristics of alteration products, reaction rates, and element mobilities. Besides this general agreement on a dissolution–precipitation process being responsible for the formation of palagonite from glass, the mechanisms controlling these processes, especially the precipitation of palagonite, are still not fully understood.

Temperature dependence of the palagonitization process

Temperature has a major influence – especially on the rate of palagonitization and on alteration processes in general (Hoppe 1941; Furnes 1975; Jakobsson 1978; Jakobsson and Moore 1986; Crovisier et al. 1987; Berger et al. 1994; Stumm and Morgan 1996). Temperature not only dramatically enhances the rate of dissolution of the primary material and the rate of precipitation of secondary phases, but might also change the mechanism of the alteration process in general, as shown by experimental studies (Berger et al. 1987; Crovisier et al. 1987; Gislason et al. 1993) and by studies of natural environments (Jakobsson 1978; Jakobsson and Moore 1986). For example, Berger et al. (1987) postulated, on the basis of experimental studies, that at temperatures between 200 and 300 °C, the alteration of basaltic glass is controlled by diffusion of dissolved species through an altered layer and not, as at low temperatures, by surface chemical reactions (Dibble and Tiller 1981; Lasaga 1984; Steefel and Van Cappellen 1990). Jakobsson and Moore (1986) showed that at temperatures above 120 °C, for example, glass alteration results directly in the formation of crystalline clay minerals by passing formation of palagonite.

The mechanism of palagonitization – influence of fluid properties

In view of the controlling mechanisms of alteration processes it must be emphasized that water–rock systems in general are characterized by complex feedback mechanisms between the primary components of the parental rocks and the properties of the surrounding fluids (Gieskes and Lawrence 1981; Berner 1983; Gislason and Eugster 1987; Gislason et al. 1993; Steefel and Lasaga 1994; Stumm and Morgan 1996). Incipiently, the primary phase assemblage changes with time, in response to the influx of reactive fluids, as a result of either congruent or incongruent dissolution and precipitation of sec-

ondary phases which have reached their solubility limit. These changes, in return, exert control on fluid composition, as a result of water–rock reactions which occur as the fluid moves along the flow-path. These reactions might even partly or completely buffer the composition of the solution. Considering, for example, fluid pH, several workers have noticed a change in the pH during the course of alteration. The increasing amounts of zeolites formed after the initial stages of alteration to palagonite, for example, suggest removal of Al from the glass, Al solubility and zeolite formation being favored at pH>9 (Hay and Iijima 1968; Dibble and Tiller 1981). Furnes (1984) noted a change from depletion to enrichment of trace elements during palagonitization, explaining this in terms of a change of solution pH from acidic to neutral or basic.

Experimental studies on the interaction of basalt and seawater have demonstrated the influence of the water/rock ratio on solution pH (Seyfried and Bischoff 1979; Seyfried and Mottl 1982). High water/rock ratios resulted in the precipitation of Mg(OH)₂ and acidic pH, whereas when water/rock ratios are low dissolution of the glass more effectively buffers the pH, resulting in the precipitation of montmorillonite and basic pH. In principle, dissolution of silicates results in an increase in solution pH because of consumption of H⁺ ions during the dissolution process. Although solution pH usually has a major effect on glass alteration processes, according to Gislason and Eugster (1987) dissolution rates are pH-independent between pH 7 and 9.5. As a consequence the incipient stages of seawater alteration, at least, are pH-independent, because the pH of average seawater is ~8. Basically, fluid pH not only has a major influence on dissolution processes, incongruent dissolution usually being favored at low fluid-pH and congruent dissolution at higher fluid-pH (Bunker et al. 1983; Scholze 1988), but also on the stable phase assemblage precipitating during the alteration process (Helgeson et al. 1984; Crovisier et al. 1992; Gislason et al. 1993; Stumm and Morgan 1996).

Thus, when considering the entire process of glass palagonitization one must not only be aware of the two-stage process of glass palagonitization, glass dissolution and palagonite precipitation and their different controlling mechanisms, but also keep in mind these complex feedback mechanisms. Numerous experimental studies have been performed on the glass-dissolution process (White 1983; Crovisier et al. 1987; Bourcier et al. 1989; Anbeek 1990; Rowe and Brantley 1993; Berger et al. 1994; Eick et al. 1996; Yanagisawa et al. 1997; Techner et al. 1998) but experimental studies on the process of palagonite precipitation and its controlling mechanism, including the evaluation of the thermodynamic properties of its formation, are rare. Most statements about the formation of palagonite and its evolution are based on analytical studies of naturally palagonitized glasses. The different experiments on glass and on mineral dissolution can be summarized in four general theories concerning the reaction kinetics of the dissolution process:

1. “Precipitate–layer hypotheses” (Correns 1938; Wollast 1967; Hay and Jones 1972; Crovisier et al. 1992), according to which the primary phase is protected by a precipitate layer. Alteration is thus controlled by diffusion through this precipitate layer.
2. “Surface-reaction hypotheses” (Berner 1978; Dibble and Tiller 1981; Steefel and Van Cappellen 1990; Stumm 1992; Steefel and Lasaga 1994), according to which the alteration rate is controlled by reactions occurring at the primary phase–fluid interface.
3. “Leached-layer hypotheses” (Doremus 1983; Lasaga 1984; Berger et al. 1987; Eick et al. 1996), in which diffusion through a cation-depleted layer controls the release of other cations deeper in the primary material. At more advanced stages, a steady state is developed between dissolution and development of the leached layer.
4. “Hydrated-layer hypotheses” (Peacock and Fuller 1928; Moore 1966; Hodder et al. 1993), according to which a hydrated layer develops before dissolution of the primary phase. Alteration is thus controlled by diffusion of fluids into the primary phase.

One of the first three theories is usually proposed as the mechanism controlling the process of glass dissolution during palagonite formation. Referring to, for example, Thorseth et al. (1991, 1992), palagonitization proceeds according to the “leached-layer-hypotheses” as a combination of incongruent dissolution of the network-modifying elements at a fluid pH<3 with later congruent network dissolution at a fluid pH>9, yielding a chemically zoned palagonite with changing porosity. The chemical heterogeneity of palagonite is a result of changes in the solubility of the single elements constituting the glass in response to the changing fluid pH.

According to other workers, palagonite forms as a result of congruent dissolution of the glass with contemporaneous re-precipitation of insoluble materials at the glass–fluid interface (Crovisier et al. 1987; Jercinovic et al. 1990; Daux et al. 1994; Stroncik and Schmincke 2001). This conclusion is based on:

1. an Si- and Al-rich residue layer that could not be detected in the samples studied; and
2. palagonitization rates that are higher than water-diffusion rates in glass, as shown by glass dissolution experiments (Burn and Roberts 1970; Doremus 1983; Nogami and Tomozawa 1984; Tomozawa 1985; Zhang et al. 1991; Yanagisawa et al. 1997) in conjunction with palagonite rind thickness measurements and sample ages.

In detail, Crovisier et al. (1987, 1992) proposed that palagonitization proceeds through congruent dissolution of the glass, and is controlled by surface reactions, with re-precipitation of dissolved species which have reached their solubility limits in thermodynamic equilibrium with the corresponding fluid. Hence, palagonite precipitation and thus palagonite chemistry is controlled by fluid composition – the chemical evolution of palagonite is thus a

mirror of the constant re-equilibration of this material to the changing fluid properties. Crovisier et al. (1992) also emphasized the influence of the water/rock ratio on the formation and composition of alteration products. From their studies on the alteration of subglacial volcanic glasses on Iceland, they stated that high water/rock ratios result in an almost complete loss of Na₂O, MgO, K₂O, and CaO, >50% loss of SiO₂, and 20 to 30% loss of Al₂O₃ and TiO₂, without palagonite formation. At low water/rock ratios SiO₂, MgO, Al₂O₃, and TiO₂ are trapped in secondary products whereas >50% of the K₂O and CaO and almost all of the Na₂O are lost to solution. Zhou and Fyfe (1989) also interpreted the results of their analytical studies on altered basaltic glasses from DSDP site-335 as indicative of a congruent dissolution-precipitation mechanism of palagonite formation. They argued that palagonitization is a two-step process. The first step consisted in glass dissolution and precipitation of gel-palagonite with a protocrystalline smectite structure, accompanied by loss of >60% SiO₂, Al₂O₃, MgO, CaO, and Na₂O, gain of K₂O, and passive Ti- and Fe-enrichment; the second step consisted in the in-situ-replacement of gel-palagonite by fibro-palagonite as a result of changes in the physicochemical conditions of the alteration environment, and was accompanied by minor mobilizations of Ti and Fe, continuing losses of CaO and Na₂O, and gains of SiO₂, Al₂O₃, MgO, and K₂O. Jercinovic et al. (1990), on the basis of their analytical data from palagonites from north-central British Columbia, Canada, explained the replacement of glass by amorphous, gel-like palagonite in terms of the precipitation of insoluble materials as critical nuclei of smectite structure under conditions of supersaturation in the near-glass environment. They interpreted Al-, Ca-, Fe-, and Mg-zonation observed in their rock samples as a manifestation of changing fluid composition and pH with time under closed-system conditions, thus emphasizing the control of fluid properties on the process of palagonitization and palagonite evolution. Daux et al. (1994) also proposed a congruent dissolution precipitation mechanism for the formation of palagonite from glass. They concluded that the nature, composition, and evolution of secondary phases formed during glass alteration are governed by the progress of the reaction (mass of dissolved primary phase per kilogram of solution) of the system – which actually determines fluid composition – which is, in turn, controlled by the permeability of the rock body.

It should be mentioned that in most studies of palagonitization it is emphasized that fluid properties, especially fluid composition, have a major effect on palagonite formation, composition, and compositional evolution. Single chemical characteristics of palagonites, e.g. the contrasting major element signatures of palagonites (Table 1) derived from meteoric and submarine alteration, zonation, and microscale chemical fluctuations are essentially interpreted as clear evidence of this control (Hay and Iijima 1968; Furnes 1975; Fisher and Schmincke 1984; Jercinovic et al. 1989; Thorseth et al. 1991). For example, differences between the K content

of meteoric and submarine palagonites (submarine palagonites being enriched in K) noticed in a variety of studies are taken as evidence for the compositional control of the fluid on the palagonitization process, and are explained in terms of the higher concentration of K in seawater than in average meteoric water (Staudigel and Hart 1983; Zhou and Fyfe 1989; Jercinovic et al. 1990; Thorseth et al. 1991). In reality, however, things seem more complicated:

1. K is initially adsorbed by surface layers in both environments (Staudigel and Hart 1983; Fisher and Schmincke 1984), and
2. Stroncik and Schmincke (2001) have shown that seawater palagonite is not necessarily enriched in K during the incipient stages of alteration.

Stroncik and Schmincke (2001) performed a systematic, comprehensive study on palagonites from different alteration environments, different volcanic settings, and different alteration stages in conjunction with continuous flow-through experiments, using natural basaltic glasses from Hawaii. On the basis of several observations:

1. precipitation of a thermodynamically unstable amorphous gel-phase;
2. variations in the crystallinity of palagonite detected by XRD and AFM analysis;
3. microscale intra- and intergrain chemical fluctuations of palagonites derived from one homogeneous parent;
4. gradual changes in element content and optical behavior observed within one palagonite rind; and
5. the general decrease of element loss with increasing reaction progress determined by mass-balance calculations of palagonite samples with different degrees of crystallinity

and detailed petrographic and analytical data they concluded that glass palagonitization proceeds through a congruent microsolution and contemporaneous precipitation process. Subsequent observations led to their proposal that precipitation of the insoluble material at the glass–fluid interface, and evolution of this material, follows the Ostwald step rule (or law of stages).

In principle, the Ostwald step rule (or law of stages) states that development of a thermodynamically unstable phase is favored and that this phase undergoes a sequence of irreversible reactions over time to form progressively more stable phases. The step rule operates, especially at low temperatures and high supersaturation, in a large variety of mineralogical systems – for example, carbonates, silica polymorphs, iron oxides, clays, and zeolites (Morse and Casey 1988; Steefel and Van Cappellen 1990; Nordeng and Sibley 1994). Explanations of this rule are based either on irreversible thermodynamics or on chemical kinetics. Dibble and Tiller (1981) postulated that the formation of metastable phases can reduce the total free energy of the system faster than the precipitation of a stable phase assemblage. Steefel and Van Cappellen (1990) concluded that the formation of a more soluble, less stable phase is kinetically fa-

vored, because the more soluble phase has a lower mineral–solution interfacial energy than the more stable, less soluble phase. Thus Stroncik and Schmincke (2001) emphasize kinetic controls exerted by high supersaturation developed at the glass–fluid interface through the congruent dissolution of the thermodynamically unstable, easily soluble volcanic glass as being responsible for the formation and composition of palagonite and that later the aging of this metastable phase mainly determines the fluid evolution.

The role of microorganisms in the process of palagonitization

Other experimental studies emphasize the influence of microorganisms with a strong affinity for the surface of glasses on the process of glass alteration (Thorseth et al. 1992, 1995a, 1995b; Staudigel et al. 1995, 1998; Furnes et al. 1996). Basically, bacteria and microorganisms create a local microenvironment as a result of the fluids of their metabolic products. These fluids have either acidic or basic pH, depending on the type of bacteria. An acidic pH basically results in incongruent glass dissolution, whereas a basic pH results in congruent glass dissolution, leaving large pits on the glass surface (Fig. 9). Overall, microbial activity enhances the rate of dissolution of volcanic glass. Microbial alteration also results in the formation of authigenic phases and is accompanied by redistribution of elements (Thorseth et al. 1992; Staudigel et al. 1995, 1998; Furnes et al. 1996; Drewello and Weissmann 1997). The chemical composition of biotic alteration products, and their structures, can be highly variable, indicating that different types of bacteria might accumulate different elements. Thorseth et al. (1995), for example, detected the formation of a leached layer enriched in Si and occasionally Cl, and depleted in Ti, Fe, Al, Ca, K, and Na in some experiments, whereas in others biotic alteration resulted in the accumulation of all elements except Mg and Ti. No experiment on the biotic alteration of glass has yet resulted in the formation of palagonite. The authigenic phases developed during experiments are mainly composed of aragonite and siliceous materials (Staudigel et al. 1998). Element mobility during biotic alteration also seems to differ significantly from that during abiotic alteration. For example, abiotic seawater alteration is usually accompanied by Ca depletion and Mg enrichment, whereas biotic seawater alteration seems to be accompanied by Ca enrichment and Mg depletion (Staudigel et al. 1998).

The occurrence of microorganisms in natural alteration systems has also been documented (Thorseth et al. 1992, 1995a, 1995b; Furnes et al. 1996; Fisk et al. 1998; Torsvik et al. 1998):

1. micropits and microchannels have been interpreted as indicative of microbial activity (Fig. 9); and
2. epifluorescence microscopy of natural samples stained with DAPI (4,6-diaminophenylindole, a fluo-

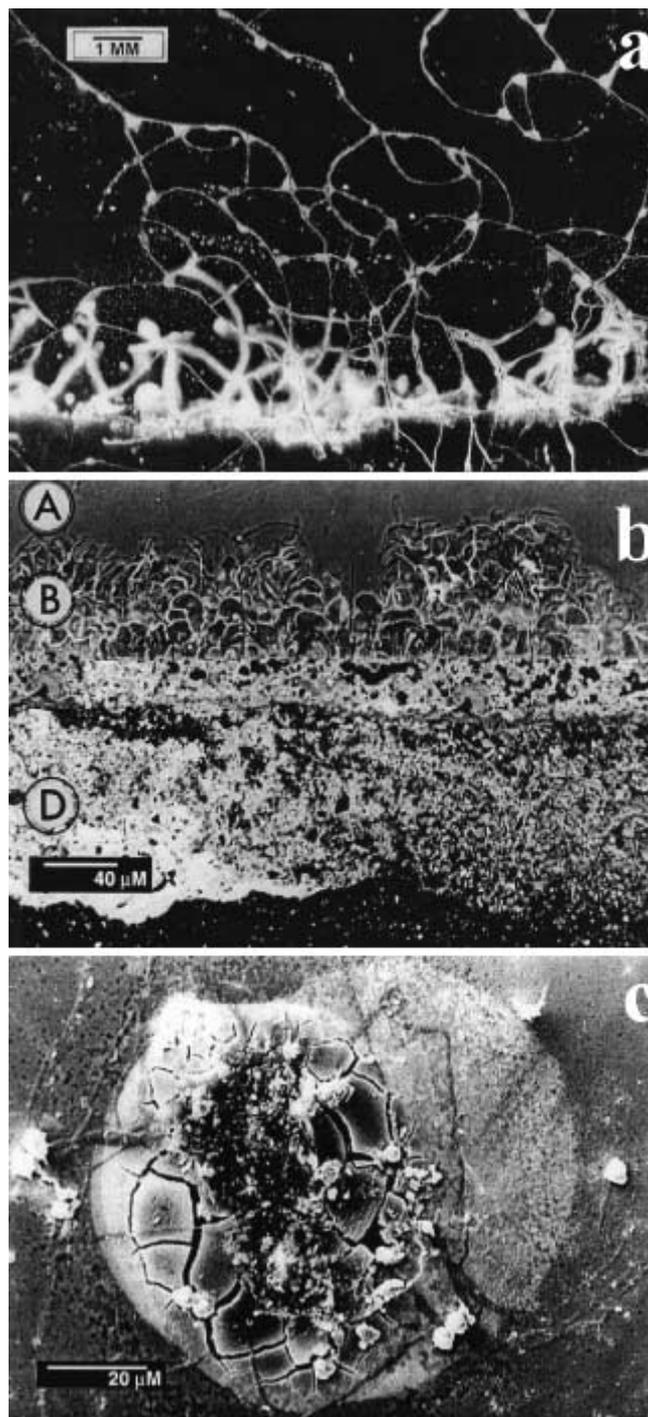


Fig. 9a–c Images of altered glasses showing textures developed by microbial activity. **a** Light microscopy image of fungal growth on the surface of an optical glass (BK7), starting from the lens edge. **b** Scanning electron micrograph (SEM) of biotically altered potash–lime–silicate glass: *A* uncorroded bulk glass; *B* hydrated silicate layer; *D* biomat of fungi. **c** SEM of pit corrosion and re-deposition of leached metals on an optical lens (LLF2) (Drewello and Weissmann 1997)

rescent dye that specifically stains DNA) have revealed the presence of DNA.

Relative rates of abiotic versus biotic alteration are, however, still lacking.

Rate of palagonitization

A better understanding of the relationship between rock age and thickness of palagonite crust would be very useful for assessing the mechanisms and rates of long-term glass corrosion. Estimation of palagonitization rates and of alteration rates in general, including dissolution of primary material and precipitation of secondary phases, is, however, an exceedingly difficult task. These rates depend on several different, complex interacting factors, e.g.:

1. temperature,
2. the structure of the primary material,
3. the reactive surface area of the primary material,
4. the structures of the precipitating secondary phases,
5. the growth rates of the secondary phases,
6. time, and
7. different fluid properties, e.g. pH, Eh, ionic strength and oxygen fugacity.

The fluid properties are, in turn, affected by other properties, e.g. porosity and permeability.

Palagonitization rates are usually calculated according to Fick's laws, assuming diffusion as the controlling mechanism of glass palagonitization. Moore (1966) following Friedman and Smith (1960), postulated that the rate of palagonitization at low temperatures is proportional to the square root of time. He suggested the following algorithm for the calculation of the thickness of palagonite rinds: $S = \sqrt{CT}$, where S is the thickness of the produced palagonite layer, C is a constant, and T is the duration of the process. The constant C ranges from 480 to 2,000 $\mu\text{m}/10^3$ years. C depends on glass composition and whether alteration proceeds in sea or fresh water; much lower values of C result from meteoric alteration. Palagonitization rates for sea and fresh water alteration are no different (Furnes 1975). The constant C is evaluated by measuring the thickness of naturally formed palagonite rinds in conjunction with the duration of the alteration process, estimated by dating of the sample (Fig. 10) (Moore 1966; Hekinian and Hoffert 1975; Jakobsson 1978; Moore et al. 1985; Abrajano et al. 1990). Hekinian and Hoffert (1975) calculated a palagonitization rate of 3 $\mu\text{m}/10^3$ years for basaltic rocks from the Mid-Atlantic Rift Valley near 36°50' N.

More recently, Jakobsson and Moore (1986) calculated palagonitization rates as a function of temperature based on the same mathematical approach as described above (Fig. 11). They showed that palagonitization around a hydrothermal anomaly caused by near surface intrusions proceeded much faster than in much cooler areas (<50 °C) and calculated that the rate of pal-

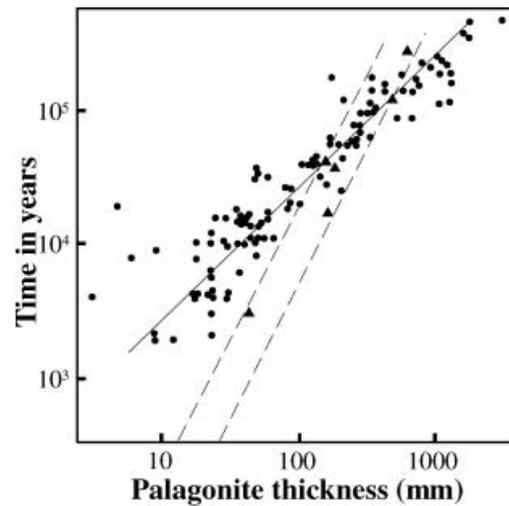


Fig. 10 Relationship between the thickness of palagonitic layers and time. *Circles* represent the measurements made by Hekinian and Hoffert (1975) on palagonites from the Rift Valley (Mid-Atlantic Ridge). The *solid line* corresponds to the relationship thickness= $k \cdot t$. *Triangles* represent the measurements made by Moore (1966) on palagonites from Mauna Kea and Mauna Loa volcanoes (Hawaii). The *dashed lines* represent the palagonitization rates proposed by Moore (1966) (after Crovisier et al. 1987)

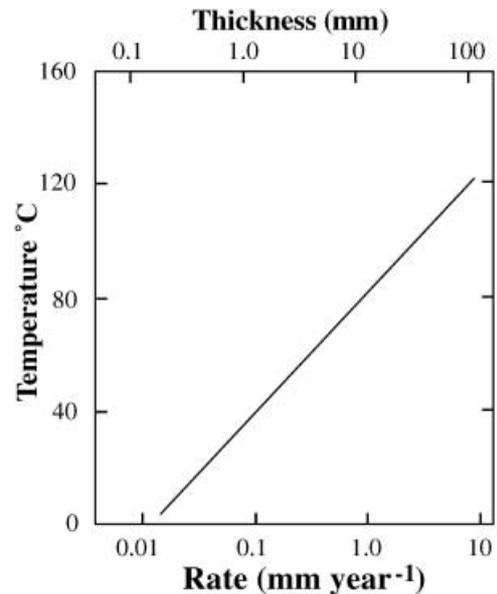


Fig. 11 Relationship between measured temperature in drill hole (Surtsey Volcano, Iceland), palagonite rind thickness (*top*) and palagonitization rate (*bottom*) assuming a 12-year age for the hydrothermal system (after Jakobsson and Moore 1986)

agonitization increases linearly with temperature, doubling for every 12-degree increase in temperature and attaining 2.8 $\mu\text{m}/\text{year}$ at 100 °C (Jakobsson and Moore 1986). Numerous authors have argued, on the basis of experimental data, however, that the palagonitization of volcanic glass is not a diffusion-controlled process but is controlled by reactions at the glass surface and thus

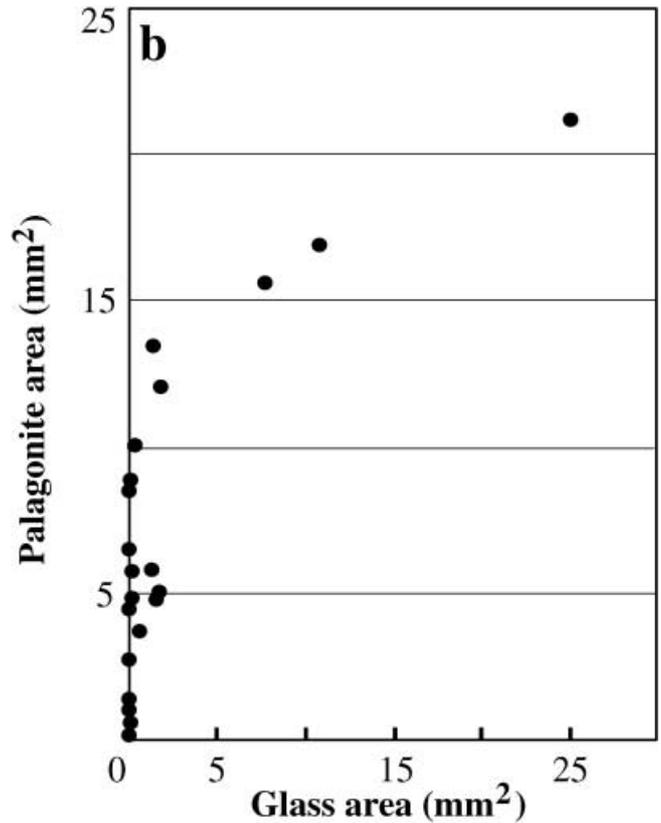
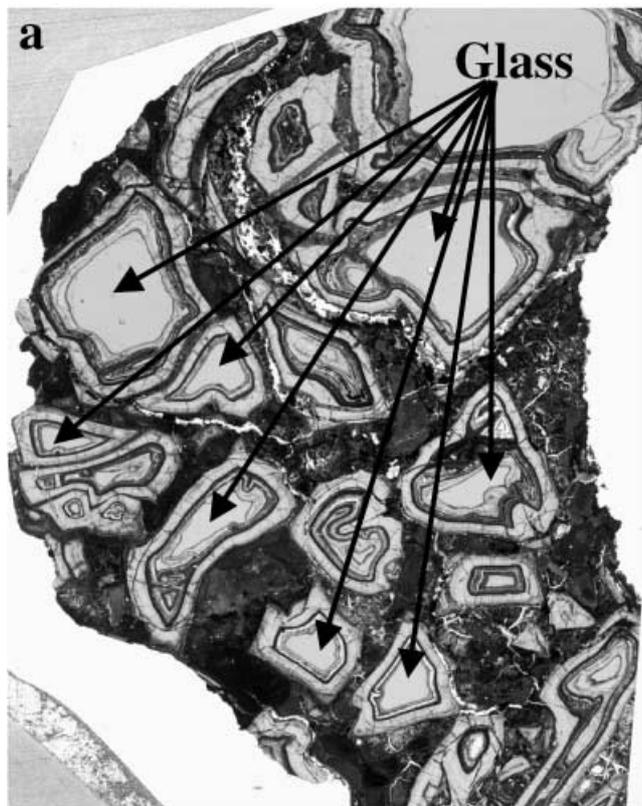


Fig. 12a, b Variability of palagonite rind thickness within one sample. **a** Thin section micrograph of submarine palagonitized glass (1.95×2.44 cm). **b** Palagonite area as function of fresh glass area. Each *dot* represents one single glass shard of the thin section sample (after Stroncik and Schmincke 2001)

palagonitization rates could not be calculated on the basis of Fick's laws (Tomozawa 1985; Wakabayashi and Tomozawa 1989; Crovisier et al. 1992; Yanagisawa et al. 1997). Calculations of palagonitization rates based on thickness measurements of palagonite rinds are, moreover, based on assumptions that might not be realized in nature, e.g.:

1. palagonitization starts directly after glass formation and continues until the date of sampling;
2. the alteration system does not change during the entire course of alteration;
3. the rate of palagonitization does not change during the duration of alteration; and
4. palagonitization depends mainly on time.

Although palagonite rind thicknesses are easily measured, the relationship between age and thickness seems to be purely empirical (Crovisier et al. 1987; Jercinovic et al. 1990; Daux et al. 1994; Stroncik and Schmincke 2001), as indicated by:

1. although entirely palagonitized hyaloclastite deposits of Pleistocene age do exist (Schmincke et al. 1997; Stroncik and Schmincke 2001), fresh sideromelane cores have been found in strongly cemented palagonite deposits of Oligocene (Stroncik and Schmincke

2001), Cretaceous (Staudigel et al. 1981), and Carboniferous age (Schmincke and Sunkel 1987);

2. samples derived from the same alteration environment can have palagonite rind of different thickness;
3. the thickness of palagonite rinds, even in a single thin-section sample, can be highly variable (Figs. 12a, b) (Jercinovic et al. 1990; Stroncik and Schmincke 2001).

Thus, as many formulas expressing palagonite rind growth can be generated as there are geochemical environments or experimental setups (Malow et al. 1984).

Conclusions

1. Palagonite is a well-defined product of mafic glass alteration in terms of its appearance and its optical and physical properties.
2. The structure of palagonite has been studied by many workers. In summary, they detected 200 to 600 Å spherical structures and interpreted them as microcrystallite precursors of smectite. Nonetheless, the atomic structure of palagonite and, especially, its structural evolution cannot be regarded as fully evaluated, but both are important to glass-alteration rates and to the evolution of the whole water-rock system.
3. Most workers today agree that palagonite is composed of a variety of smectite.
4. The chemical composition of palagonite can be heterogeneous, generally reflecting the prevailing element mobility of the water-rock system during altera-

- tion. The properties of the altering fluid (mainly fluid composition and pH) have been regarded as most important in determining the chemistry of palagonite.
5. Most workers agree that a microsolution–precipitation process is responsible for glass palagonitization. The controlling mechanisms of this process are still uncertain. Most workers emphasize fluid properties as possible determining factors, but it should be kept in mind that any water–rock system is usually characterized by complex feedback mechanisms between the primary phases and, later, the secondary phases of the rock and the properties of the surrounding fluids. Thus, one should rather think of a set of different controlling mechanisms operating at different times.
 6. The rate of palagonitization can be highly variable even within one sample, indicating that this rate does not depend solely on time. The character of age–thickness relationships seems to be empirical.
 7. The term “palagonite” is commonly used both as a general term for any hydrous alteration product of volcanic glass and also for the crystalline material evolving from the palagonite itself. Kinetic and thermodynamic modeling, however, and mass-balance calculations, necessitate exact differentiation of all the secondary products developing during alteration in a water–rock system. Consequently, the term palagonite should be used for the amorphous alteration product only (Stroncik and Schmincke 2001).
 8. Most studies on palagonitization have focused on explanation of single features of the alteration process, e.g. element mobility, chemical heterogeneity, glass dissolution, etc. Systematic, comprehensive studies on palagonite from different alteration environments, different volcanic settings, and at different stages of the alteration process are necessary to explain the palagonitization process as a whole, including identification of the different controlling mechanisms operating at different times. Such studies are rare.

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