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Do bentonites have contradictory characteristics? An attempt to answer unanswered questions

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ABSTRACT: The formation of bentonites *via* alteration of volcanic glassy rocks is associated with apparently contradictory mineralogical, geological and geochemical characteristics, which remain poorly understood. This contribution attempts to answer some of the questions based on the work carried out in our laboratory over the past 15 y. The first question concerns the formation of opal-CT-free bentonites from acidic precursors. It is suggested that the formation of opal-CT-free bentonites is closely related to the mechanism of eruption and emplacement of parent volcanic rocks if the temperature of the parent glass after emplacement is high and/or the establishment of hydraulic gradients coupled with high permeability after deposition of volcanic glass (i.e. diagenetic alteration) if the temperature of the parent glass is low. The second question pertains to the behaviour of Fe during bentonite formation. Based on mineralogical and geological characteristics of different bentonite deposits, it is suggested that Fe is present mainly as Fe²⁺ and hence may be mobilized during alteration. Oxidation of Fe may take place when bentonites are exposed to more oxidizing conditions close to the surface. Assignment of Fe as Fe²⁺ increases the layer charge of smectites and decreases significantly the range of layer charge. Thus the smectites may have considerably different properties when formed compared with their counterparts on the surface. The third question considers the possible influence of parent-rock chemistry on the crystal chemistry of smectites. It is proposed that the parent rock may affect the chemistry of the neoformed smectites to some degree; therefore the smectite chemistry may provide indications about the geochemical affinities of the parent rock.

KEYWORDS: bentonite, smectite, volcanic glass alteration, temperature gradient, Fe oxidation state, parent-glass chemistry.

Bentonites are clays derived from the alteration of volcanic ash and consist essentially of smectite: the physical and chemical properties are dictated by this mineral (Grim & Güven, 1978; Fisher & Schmincke, 1984). Large bentonite deposits are found in many countries around the world (Elzea & Murray, 1994), suggesting that bentonite formation via alteration of volcanic glass is a rather common

geological process. However, although the role of water is essential for bentonite formation, alteration of volcanic glass is not always observed in water-dominated environments such as seawater (Hein & Scholl, 1978; Weaver, 1989). Therefore fresh or slightly altered glass shards are frequently observed in recent marine sediments.

It has been proposed that leaching of alkalis and a high Mg-activity are necessary for the formation of smectite instead of zeolites during alteration of volcanic glass (Hay, 1977; Senkayi *et al.*, 1984, among others). This was confirmed by Christidis (1998) who studied the mobilization of chemical

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elements in different alteration profiles, dominated either by smectite (bentonites) or by zeolites. More recently Christidis (2001), using mass-balance calculations, confirmed that high water:rock ratios (~13:1) are necessary for the formation of smectites on a large scale, i.e. for bentonite formation. Moreover, in open systems with continuous fluid flow, the water:rock ratios necessary for smectite formation may be even larger. Such high water:rock ratios are facilitated by high permeability of the parent rocks. In contrast, zeolites form under lower water:rock ratios, dictated by lower permeability.

Notwithstanding the large number of studies on bentonites and their formation, there are several matters which remain to be clarified, including: (1) the possibility of systematic changes in smectite composition during alteration (Christidis & Dunham, 1997; Calarge *et al.*, 2003; Caballero *et al.*, 2005); (2) the long-standing question about the existence of solid solution among the different types of smectites, especially those with similar composition such as Tatatilla-type montmorillonite and beidellite (Christidis & Dunham, 1993, 1997); (3) the reason for the formation of smectites instead of SiO₂ polymorphs and alkali-rich zeolites (mordenite and HEU-type zeolites) from rocks of unfavourable composition, such as acidic rocks; (4) the importance of the chemistry of the parent rocks in controlling the chemistry of neofomed smectites in bentonites; and (5) the role of Fe in the formation of smectite during alteration of glass. The purpose of this contribution is to resolve, at least partly, points 3–5 above.

THREE UNANSWERED QUESTIONS ABOUT BENTONITES

Why do high-quality (i.e. opal-CT free) bentonites form from rocks of unfavourable compositions?

Grim & Güven (1978) suggested that although dioctahedral smectites form from the alteration of nearly all types of volcanic rocks, trachyandesites are the most suitable precursor materials for high-quality bentonites. In contrast, acidic rocks are not suitable precursors, because they have high SiO₂:Al₂O₃ ratios, which favour alkaline zeolites such as HEU-type zeolites and mordenite. Also, bentonites forming from acidic precursors usually contain abundant SiO₂ polymorphs, such as opal-CT (Christidis & Dunham, 1997; Christidis & Scott,

1997; Cravero *et al.*, 2000). Nevertheless high-quality opal-CT-free bentonites formed from acidic precursors are also common (Elzea & Murray, 1990; Christidis, 1998; Berry, 1999; Ddani *et al.*, 2005). On the other hand, trachyandesitic or even basaltic–andesitic rocks may also yield bentonites with abundant opal-CT (Christidis *et al.*, 1999; Christidis, 2006). In the latter cases, the excess SiO₂ is at least partly biogenic. So, why do high-quality opal-CT-free bentonites form from acidic rocks and under what circumstances is excess SiO₂ removed (leached) during alteration?

The low alkali-content of bentonites (e.g. Grim & Güven, 1978; Senkayi *et al.*, 1984; Christidis, 1998, among many others) indicates that they form in open hydrological systems in which alkalis are leached. This is because pore waters with high (Na⁺+K⁺+Ca²⁺)/H⁺ activity ratios favour zeolites instead of smectites (Hay & Sheppard, 2001). In contrast, the moderately high MgO contents (2–4 wt.%) of most bentonites do not necessarily indicate Mg uptake, at least in bentonites derived from intermediate rocks. On the other hand, alteration of most acidic rocks to bentonites is associated with Mg uptake from the pore fluids, usually seawater, especially in bentonites with high smectite contents (cf. Zielinski, 1982; Christidis, 1998; Berry, 1999; Ddani *et al.*, 2005). Hence a question is raised about the conditions favouring release of alkalis and Si and simultaneous uptake of Mg during alteration of acidic volcanic rocks.

The mobility of major elements from various types of volcanic rocks at various temperatures (25–300°C) has been studied thoroughly in experiments which simulate closed and quasi-open systems. Experiments in closed systems have been carried out in basalts (Mottl & Seyfried, 1980; Seyfried & Mottl, 1982; Crovisier *et al.*, 1983, 1987; Berger *et al.*, 1987; Gislason & Eugster, 1987; Petit *et al.*, 1990, among others), rhyolites (White & Claasen, 1980; White, 1983; Shiraki *et al.*, 1987; Shiraki & Iiyama, 1990; Kawano *et al.*, 1993; Petit *et al.*, 1990; Fiore *et al.*, 2001, among others) and andesites (Shiraki *et al.*, 1987). Similarly, experiments simulating open systems have been carried out on basalts (Berger *et al.*, 1994; Daux *et al.*, 1997), rhyolites (Fiore *et al.*, 1999) and andesites (Caballero *et al.*, 1991). An outline of the experimental conditions used in the various experiments is shown in Table 1. In summary, these experiments indicate that alkalis, Ca and Mg (network modifiers) and Si are mobile

TABLE 1. Summary of experimental conditions used in volcanic glass dissolution experiments.

Parent rock	Type of aqueous solution	Temperature	System	Reference
Rhyolite	(Na,K)Cl aqueous solution	200–300°C	closed	Shiraki & Iiyama (1990)
Rhyolite-andesite	Seawater	300°C	closed	Shiraki <i>et al.</i> (1987)
Rhyolite-trachyte	De-ionized water	25°C	closed	White (1983)
Rhyolite	De-ionized water	25°C	closed	White & Claasen (1980)
Rhyolite	De-ionized water	150–225°C	closed	Kawano <i>et al.</i> (1993)
Rhyolite	MgCl ₂ aqueous solution	100–200°C	closed	Fiore <i>et al.</i> (2001)
Rhyolite	De-ionized water	82±5°C	open	Fiore <i>et al.</i> (1999)
Andesite	De-ionized water	82±5°C	open	Caballero <i>et al.</i> (1991)
Basalt	Seawater	50°C	closed	Crovisier <i>et al.</i> (1983)
Basalt	Seawater	60°C	closed	Crovisier <i>et al.</i> (1987)
Basalt	Meteoric water	25–65°C	closed	Gislason & Eugster (1987)
Basalt	Seawater	200–320°C	closed	Berger <i>et al.</i> (1987)
Basalt, rhyolite	De-ionized water/(Na,K)Cl aqueous solution	60–200°C	closed	Petit <i>et al.</i> (1990)
Basalt	De-ionized water/dilute HCl solutions	150, 300°C	open	Berger <i>et al.</i> (1994)
Basalt	De-ionized water/Si-enriched water	90°C	open	Daux <i>et al.</i> (1997)

elements during alteration of glass. The high mobility of alkalis usually yields a leached layer at the surface of the glass (Berger *et al.*, 1987, 1994; Petit *et al.*, 1990; Yanagisawa *et al.*, 1997), although this is not always the case (Fiore *et al.*, 1999). Fe and Al are essentially immobile, whereas the release rate of Si depends on the fluid-flow rate and decreases with increasing flow rate (Daux *et al.*, 1997) (Fig. 1).

The behaviour of Mg seems to depend more on the type of aqueous phase used and the experimental setup rather than the type of rock in experimental alteration of glass. Hence, during alteration of andesitic, dacitic and rhyolitic glass

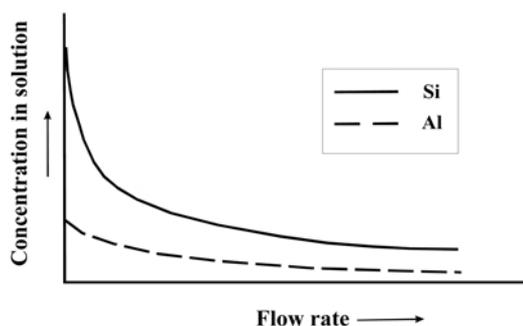


FIG. 1. Concentration of Si and Al in output solutions derived from experiments on alteration of basaltic glass (modified from Daux *et al.*, 1997).

with distilled water using a Soxhlet extractor, which simulates quasi open-system conditions, Mg is slightly mobilized (Caballero *et al.*, 1991) or remains essentially immobile (Kawano *et al.*, 1993; Fiore *et al.*, 1999). Experiments under continuous flow using Mg-doped distilled water yielded a significant Mg-uptake (Makri, unpublished data). Similarly, alteration experiments using seawater resulted in significant Mg uptake regardless of rock type (Seyfried & Mottl, 1982; Berger *et al.*, 1987; Shiraki *et al.*, 1987). In natural systems the Mg content of opal-CT-free bentonites depends on the type of precursor rock. Thus, in open systems dominated by seawater, alteration of acidic rocks is associated with Mg uptake, whereas alteration of basic rocks is associated with Mg release (Christidis, 1998, 2006). Therefore in open systems with high permeability, dominated by seawater as the fluid phase, the chemistry of the parent rock affects the behaviour of Mg during bentonite formation. Note that the behaviour of Mg in natural systems seems to be different compared to its behaviour under experimental conditions.

Leaching of chemical elements during dissolution of glass is followed by partial precipitation in the leached layer of silicates (mainly smectite or zeolites), free oxides and oxyhydroxides, which also bind Mg taken up from the fluid phase (Berger *et al.*, 1987, 1994; Petit *et al.*, 1990; Yanagisawa *et al.*, 1997). The ratio of precipitation rate vs. release

rate ($R_{\text{Prec}}/R_{\text{Rel}}$ ratio) for each chemical element determines those neoformed phases which form during alteration (Fig. 2). In open oxidized systems, with the exception of Fe, which is not affected by flow rate, an increase of flow rate decreases both the concentration of the accumulated elements in solution and the $R_{\text{Prec}}/R_{\text{Rel}}$ ratio for most elements in basaltic and acidic glasses (Daux *et al.*, 1997; Makri, unpublished data). Therefore, in open systems, both the accumulation of Si in the fluid phase and the precipitation rate of free SiO_2 seem to depend on the flow rate of the fluid phase (Figs 1, 2). This raises another question about the parameters which control fluid-flow rate during bentonite formation.

The circulation tendency of the fluids is proportional to the gradient of the fluid temperature, the isobaric coefficient of thermal expansion and the mean density of the fluid (Norton, 1984). For temperatures of $<250^\circ\text{C}$, as is the case during the formation of bentonites, the density and viscosity of water depend mainly on temperature (Forster & Smith, 1990). Several bentonites, such as the Greek deposits, form from alteration of volcanoclastic rocks, mainly pyroclastic flows, many of which are hot when emplaced in water. In the case of pyroclastic flows, the emplacement temperature may range from 300 to 800°C (Cas & Wright, 1988). Such permeable hot rocks sustain water circulation and thus convective flow. In these environments it is the altered rock itself and not a magmatic body at depth, which provides the necessary energy for circulation of the fluid phase, thereby sustaining a hydrothermal *s.l.* system and causing alteration of the parent glassy rock. As long as the temperature gradient within the volcanic body and between the volcanic body and

the bulk fluid can sustain convective flow, the system is active. The decay of such temperature gradients will control: (1) the paragenetic sequence of the neoformed minerals (smectite, opal-CT, alkali-zeolites and authigenic feldspars); and (2) the distribution of fundamental properties of smectites, such as layer charge and charge heterogeneity within a bentonite deposit.

At the onset of alteration, high-temperature gradients due to maximum difference between the volcanic rock and the fluid phase will maximize fluid flow and facilitate leaching. Low-temperature SiO_2 polymorphs and zeolites are not favoured because Si and alkalis leached from the volcanic glass are removed. Hence, formation of high-quality bentonites from acidic rocks is likely when temperature gradients are maintained for an adequate time so as to keep a high $(\text{Mg}^{2+})/(\text{H}^+)$ activity ratio and a low H_4SiO_4 activity. In the case of pyroclastic flows, such conditions are expected when the parent rocks are emplaced at a high temperature in water-saturated environments and this in turn is related to the mechanism of the eruption (Sparks *et al.*, 1978; Cas & Wright, 1988). Alternatively, a high $(\text{Mg}^{2+})/(\text{H}^+)$ activity ratio and a low H_4SiO_4 activity in the fluid phase may be observed in hydrothermal *s.s.* systems characterized by high fluid-flow rate around the main structural features (fracture zones, faults). The energy which sustains circulation of aqueous solutions in such high fluid-flow rate hydrothermal systems is provided by underlying, hot igneous rocks. The different mechanisms of formation control the geometric characteristics of the deposits; when structural control is absent, alteration of pyroclastic flows yields stratiform bentonites (Christidis *et al.*, 1995) whereas, in the case of structural control, the bentonite bodies are elongated or elliptical and often display zonation parallel to the axis of the structural feature (e.g. Ddani *et al.*, 2005; Yildiz & Kuşcu, 2007).

Pyroclastic flows emplaced at lower temperatures will not sustain high flow rates for extended times, thus favouring precipitation of amorphous SiO_2 , which converts to opal-CT. Formation of smectite is incompatible with aqueous solutions that are in equilibrium with quartz at temperatures $<200^\circ\text{C}$ (Aagaard & Helgeson, 1983). Similar results are expected in hydrothermal systems around fractures with moderate fluid-flow rates. In all these systems the crystallization rates of smectite *vs.* amorphous SiO_2 will determine the final mineralogical

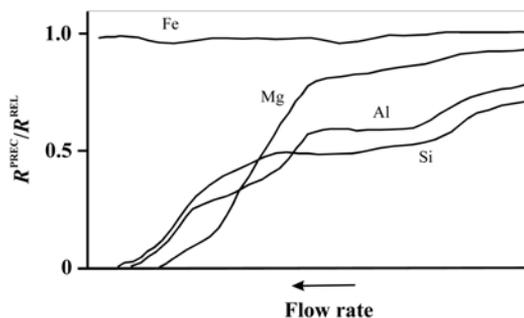


FIG. 2. Precipitation rate to release rate ratios of Si, Al, Mg and Fe as a function of flow rate (log scale) (modified from Daux *et al.*, 1997).

composition. Finally, in low-temperature systems which acquire temperature equilibrium at or shortly after deposition, fluid flow may be sustained by hydraulic gradients and will be controlled by permeability. In such systems, temperature gradients are not considered important to support fluid flow. This type of alteration may be characterized as diagenetic rather than hydrothermal. Such environments are typical of bentonites formed from alteration of ash-fall deposits far from the volcanic centre. The temperature of volcanic ash at the time of deposition is low and decreases with increasing distance from the volcanic vent. Bentonites, which form at the expense of such ash-fall deposits, often constitute extremely widespread deposits and thus are useful for stratigraphic correlation purposes. For instance, Ordovician K-bentonite beds are distributed over 1.3×10^6 km² in eastern North America (Huff & Kolata, 1989), and K-bentonite beds of similar age extend from the Southern Uplands of Scotland across the Irish Sea into Ireland (Huff *et al.*, 1991). Moreover, the Cretaceous Clay Spur Bed extends from South Dakota to Wyoming and Montana (Elzea & Murray, 1994). In the latter case, bentonite was formed during burial via alteration of volcanic glass by evolved diagenetic pore fluids (Elzea & Murray, 1994).

What is the role of Fe in the smectite structure?

Iron is an important element of Al-rich dioctahedral smectites, replacing Al in octahedral sites. It is well known that in dioctahedral smectites, including the Fe-rich ones, Fe is present mainly as Fe³⁺ (Goodman *et al.*, 1988; Murad *et al.*, 1990, among many others). Nevertheless, there are reports of smectites with very low Fe³⁺/Fe²⁺ ratios, i.e. in which iron is present mainly as Fe²⁺ (Foster, 1953; Elzea & Murray, 1990). Most importantly, when exposed to air, Fe²⁺ readily oxidizes to Fe³⁺ without special treatments (Foster, 1953; Williams *et al.*, 1953). The oxidation state of Fe affects the swelling properties of smectites (Foster, 1953; Knechtel & Patterson, 1962). Oxidation of Fe²⁺ in reduced Fe-rich smectites is rapid and causes structural reorganization (Manceau *et al.*, 2000; Komadel, 2003).

Smectites in bentonites display considerable compositional heterogeneity (Christidis & Dunham, 1993, 1997; Christidis, 2006). The

source of this heterogeneity is located in the variable substitutions in octahedral positions, the proportion of tetrahedral charge relative to octahedral charge, the variation of the total layer charge and the relative abundances of the various exchangeable cations. The oxidation state of Fe affects the first three sources of compositional heterogeneity of smectite. Moreover, it has been found that the abundance of Fe can vary considerably within a few millimetres in smectites and that this variation may be representative of the whole deposit (Christidis & Dunham, 1993, 1997; Christidis, 2006). Since the parent volcanic glass is not expected to be heterogeneous, at least to an extent which may explain the compositional heterogeneity of smectites, it follows that Fe is mobilized during alteration and that Fe release is accompanied by a concomitant migration of Mg and Si, so as to keep the appropriate cation ratios. In other words, the micro-environmental variability during formation of smectites, due to differential mobility of major chemical elements, seems to control their compositional variations.

Iron can be mobilized by two possible mechanisms, either by leaching during alteration of the glass, and/or by migration from an external source with the pore fluid. In both mechanisms, in inorganic systems Fe can be mobilized if it is present as Fe²⁺, because Fe³⁺ is mobile only at very acidic pH and very high Eh (Garrels & Christ, 1965), which are incompatible with smectite formation. The possibility for migration in the form of the Fe³⁺ ligand in organic chelate complexes is not considered a major mechanism for mobilization of Fe in bentonites, due to the limited abundance of organic matter. Nevertheless, results from hydrothermal experiments of alteration of various types of volcanic glass show that Fe resides as Fe³⁺ mainly in Fe oxides and to a lesser degree in silicate minerals (mainly saponite), which form on altered glass surfaces (Berger *et al.*, 1987; Petit *et al.*, 1990; Daux *et al.*, 1997). In these experiments, although Eh was not recorded, it seems that the Eh and pH of the fluid phase favour hematite. Note that seawater is in equilibrium with hematite in Eh-pH diagrams (Garrels & Christ, 1965). However, in marine environments, diagenetic zonation with respect to Eh is usually observed beneath the sea floor. Eh decreases with depth and the depositional environment gradually changes from aerobic at the sea floor to suboxic and finally anaerobic at shallow depths close to the sea

floor, even within the area affected by storm reworking (Taylor & Curtis, 1995).

It is interesting that bentonite deposits throughout the world (Wyoming–Montana, USA; Pembina Canada; Surrey, England; Hungary and Greece) contain various accessory Fe^{2+} -rich phases such as pyrite and/or siderite (Knechtel & Patterson, 1962; Grim & Güven, 1978; Morgan *et al.*, 1979; Christidis *et al.*, 1995). Pyrite and siderite are typical authigenic minerals forming during early diagenesis in suboxic or anaerobic environments from pore fluids with high HS^- or HCO_3^- activity, respectively (Taylor & Curtis, 1995). According to the latter authors, in marine sedimentary environments favouring the formation of Fe-rich carbonates and sulphides, pH varies much less widely than anion activities, with the latter controlling the Fe phases forming. Formation of siderite or/and pyrite in suboxic or anaerobic environments requires that Fe is present as Fe^{2+} . Both Fe^{3+} and Fe^{2+} may be present in the composition of the parent volcanic glass (e.g. Best, 1982) according to the f_{O_2} in the volcanic vent. However, in the suboxic–anaerobic environment during bentonite formation, as suggested by the presence of pyrite and/or siderite, any Fe^{3+} released during alteration of glass will be reduced to Fe^{2+} .

Additional evidence for mobilization of Fe during alteration of volcanic glass to bentonites can be observed in the field, an example being the Ankeria bentonite deposit of Milos Island, Greece (Fig. 3). In this deposit, a pyroclastic flow of dacitic–andesitic composition has been converted to a high quality green–yellow bentonite. The bentonite

is overlain by reddish impure chalky limestone containing ~90% calcite, ~10% smectite, and minor hematite known as ‘red marl’ (Fig. 3). This carbonate horizon is restricted only over the bentonite and does not occur in other sites in the island, suggesting that it is associated with the formation of the bentonite deposit. The formation of hematite is attributed to the formation of the underlying bentonite. Since alteration occurred in a marine environment, the red marl suggests that Fe was mobilized during alteration of the underlying parent dacitic–andesitic pyroclastic flow as Fe^{2+} and precipitated on the sea floor, probably as $\text{Fe}(\text{OH})_3$ via oxidation in sea water. Hence, the upper boundary of the bentonite, which in fact was the palaeo-sea-floor, acted as a reduction–oxidation front. Similarly, the calcite in this impure limestone resulted from precipitation of Ca, which was released during alteration of the bentonite and transported by the same fluid.

The aforementioned discussion suggests that smectites, which form during alteration of glass, would contain predominantly Fe^{2+} in octahedral sites. This in turn suggests that they may have a greater layer charge and greater cation exchange capacity when they form at depth than when they are exposed to surface conditions, because Fe^{2+} oxidizes to Fe^{3+} as has been well documented in the early work of Foster (1953). Hence, the smectites present in surface outcrops are expected to be different minerals and thus have different properties from those which formed at various depths. Most importantly, oxidation of Fe^{2+} to Fe^{3+} is associated with reduction of layer charge. Layer charge affects

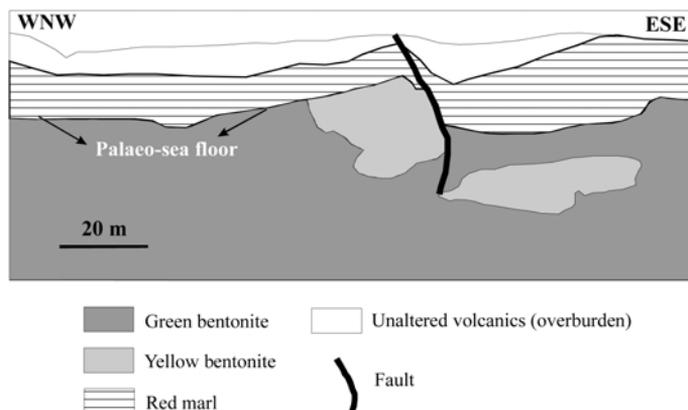


FIG. 3. Schematic cross section of the Ankeria bentonite quarry, Milos, Greece, showing the distribution of the various bentonite horizons and the ‘red marl’. See text for discussion.

important physical properties of smectites such as cation exchange capacity, ion exchange selectivity, swelling and rheological properties (Maes & Cremers, 1977; Laird, 2006; Christidis *et al.*, 2006). It is well known that oxidation of octahedral Fe improves the physical properties of bentonites substantially (Elzea & Murray, 1994). Fe^{2+} in smectites can be oxidized readily by contact with water, by exposure to salt solutions, or upon heating (Rozenson & Heller-Kallai, 1978).

To date, the mechanism of oxidation of Fe^{2+} is not known, although the reverse process, i.e. the reduction of octahedral Fe^{3+} in Fe-rich smectites, has been studied extensively. The most common agents used for reduction of Fe^{3+} are dithionite and bacteria (Stucki & Roth, 1977; Stucki *et al.*, 1987; Kostka *et al.*, 1996; see also Stucki, 2006, for a review). Hence the reduction of Fe^{3+} does not merely involve electron transfer; it affects the surface properties of smectites also (Stucki *et al.*, 2002; Stucki, 2006). Different alternative mechanisms have been proposed for reduction of Fe^{3+} in Fe-rich smectites, which suggest partial dehydroxylation of the smectite (Stucki & Roth, 1977; Lear & Stucki, 1985, 1989; Komadel *et al.*, 1990; Drits & Manceau, 2000; see also Stucki, 2006, for a thorough review). Partial dehydroxylation has been proposed to take place either (1) *via* electron transfer to Fe^{3+} and de-protonation of structural hydroxyls, followed by partial protonation of oxygens and subsequent formation of hydroxyls (Lear & Stucki, 1985; Stucki, 2006), or (2) *via* electron transfer followed by protonation of structural hydroxyls, causing migration of Fe atoms in *trans*-vacant sites (Drits & Manceau, 2000), i.e. similar to dehydration of nontronite (Manceau *et al.*, 2000). It is interesting that dehydroxylation according to the latter mechanism is not energetically favoured in montmorillonites and that the excess layer charge formed by reduction of Fe^{3+} is balanced by excess exchangeable cations (Drits & Manceau, 2000). Also, in the former mechanism, a proportion of the structural hydroxyls which are destroyed during the de-protonation stage is replaced by partial protonation of oxygen atoms (Stucki, 2006). It is not known if oxidation of Fe^{2+} in dioctahedral smectites takes place *via* any of the aforementioned mechanisms. None of these mechanisms can be inferred as being more plausible, because some of the structural modifications caused during the inverse process (i.e. reduction of Fe^{3+}) are irreversible (Stucki *et al.*,

2002). Moreover, except for smectites, other Fe-phases such as pyrite and/or siderite oxidize to Fe-oxyhydroxides when exposed to aerobic conditions. Oxidation of pyrite and/or siderite may provide one possible mechanism for formation of goethite, which is usually present in bentonites (Komadel *et al.*, 2008).

Considering that Fe is present as Fe^{2+} , we used the data of Schultz (1969) and recalculated the layer charge of those Al-rich smectites with balanced chemical formulae. During recalculation it was considered that the increase in layer charge is compensated only by sorption of additional exchangeable cations and is not associated with significant dehydroxylation, due to the relatively small amount of Fe (Drits & Manceau, 2000). Those samples, which contained impurities with a complex structural formula, such as feldspars and/or micas (biotite or muscovite), were excluded. The Fe-rich smectites, both montmorillonites and beidellites, were also excluded. Forty four different smectites were eventually used. The results, which are listed in Table 2, display some interesting trends. Firstly, after recalculation of structural formulae, the layer charge of smectites increased as expected. Secondly, the layer-charge variability of smectites has decreased significantly. In fact, the smectites can be separated in two groups, one group with lower layer charge (~0.50 charge equivalents per half unit cell – p.h.u.c.), which includes the Wyoming-type and the Tatatilla-type montmorillonites (Al-rich montmorillonites) and beidellites, and a second group with greater layer charge (~0.60 charge equivalents p.h.u.c.), which includes Chambers-type montmorillonites and Otay-type montmorillonites (Table 2). Hence, if Fe is present as Fe^{2+} , the smectites display lower layer-charge

TABLE 2. Layer charge of various types of smectite after allocation of octahedral Fe as Fe^{2+} . Values in parentheses indicate number of analyses in each type of smectite. Data are from Schultz (1969).

Smectite type	Mean layer charge (equivalents p.h.u.c.)	Standard deviation
Wyoming (14)	0.51	0.04
Tatatilla (5)	0.51	0.02
Chambers (9)	0.61	0.06
Otay (11)	0.62	0.05
Beidellite (5)	0.53	0.03

variability regardless of their crystal-chemical characteristics. Thirdly, with the exception of the Fe-poor smectites (Tatatilla-type montmorillonites and beidellites), the smectites with reduced Fe display lower tetrahedral charge (and thus a greater Si content) than their oxidized counterparts (Fig. 4). This is because the structural formula is calculated on the basis of 22 fixed anionic charges p.h.u.c. Hence, the presence of Fe^{2+} instead of Fe^{3+} causes an additional charge deficiency in the octahedral sheet, which is balanced by the introduction of a greater number of Al^{3+} cations in the octahedral sheet according to Pauling's rules (Pauling, 1960). This, in turn, decreases the number of tetrahedral Al cations because total Al remains essentially unchanged when Fe is present as Fe^{2+} . In contrast, the abundance of Mg is hardly affected by reduction of Fe, because its contribution to the balance of the anionic charge does not change. Note that Foster (1953) obtained similar results for two natural Wyoming smectites with initial Fe^{2+} , which was oxidized gradually when the smectites were exposed to air. The Fe-poor smectites display different behaviour probably due to the small amount of Fe.

An additional important finding regarding the role of Fe during the formation of smectites is the well defined negative relationship between octahedral Al ($^{\text{VI}}\text{Al}$) and Fe^{3+} regardless of the type of the parent rock (Christidis & Dunham, 1993, 1997; Christidis, 2006). These data were obtained from a large number of microanalyses of smectites. In contrast, analyses of the whole clay fractions have

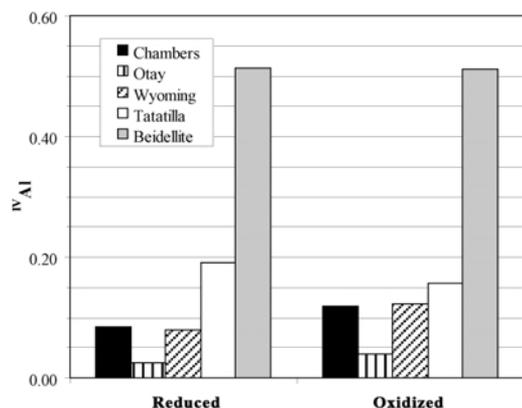


FIG. 4. Variation of $^{\text{IV}}\text{Al}$ of smectites (mean values) by considering Fe as Fe^{2+} (reduced form) and as Fe^{3+} (oxidized form). Data are from Schultz (1969).

not revealed an important relationship between $^{\text{VI}}\text{Al}$ and Fe^{3+} (Schultz, 1969; Weaver & Pollard, 1973; Grim & Güven, 1978; Güven, 1988). Mg^{2+} and $^{\text{VI}}\text{Al}$ also display an inverse relationship, which in general is weaker than the relationship between $^{\text{VI}}\text{Al}$ and Fe^{3+} (Christidis & Dunham, 1993, 1997; Christidis, 2006). This is at odds with the definition of montmorillonite, in which layer charge is attributed predominantly to substitution of $^{\text{VI}}\text{Al}$ by Mg^{2+} and may be explained by considering that Fe^{2+} is present. Mg displays a weak negative relationship with Fe^{3+} and with Fe^{2+} after recalculation of the structural formulae.

The aforementioned observations suggest that it may be useful to reconsider the nature of Al-rich smectites in bentonites formed from volcanic rocks. A possible different approach should take into account mainly the small variation of layer charge in smectites with Fe^{2+} in octahedral sites, because smectites when formed seem to have layer charge varying between 0.50 and 0.60 equivalents p.h.u.c. Subsequent oxidation of Fe decreases layer charge. Nevertheless, more data from unexposed smectites present at depth are necessary to substantiate this possibility. Finally, one topic which might influence the physical properties of smectites, and thus industrial application of bentonites, is the oxidation mechanism itself. Since oxidation may be caused by several processes (Rozenon & Heller-Kallai, 1978), an interesting point for further research should be the investigation of the influence of the mechanism of oxidation on physical properties such as swelling or rheology.

Does the chemistry of the parent rocks of bentonites affect smectite crystal chemistry?

Micro-environmental chemistry is an important parameter controlling smectite chemistry. In this sense it may be expected that the chemistry of the parent volcanic rock may not affect the crystal chemistry of smectites. However, previous reports have shown that this may not always be the case and that the parent rock may influence the type of smectite formed (cf. Christidis, 2001). Moreover, research on the relative mobility of chemical elements during alteration of volcanic glass has shown that certain elements such as Al and Fe may not be leached but may be residually enriched in bentonite (Christidis, 1998). Finally, several bentonites, such as those from Wyoming, which have been derived from acidic precursors, have relatively

high Fe content compared to the original material, suggesting that Fe has been transported from an external source. Hence the answer to the question about the possible influence of the chemistry of the precursor volcanic material on the crystal chemical characteristics of smectites remains unclear.

Previous studies on the nature of parent rocks of bentonites are based mainly on the geochemical characteristics (geochemical fingerprinting) of bentonites. Hence, geochemical fingerprinting has been used widely in the past either for estimation of the geochemical affinities of parent volcanic rocks of bentonites and of the geotectonic environment into which they erupted (e.g. Merriman & Roberts, 1990; Maccioni *et al.*, 1995; Huff *et al.*, 1997; Christidis, 1998; Wray, 1999; Pellenard *et al.*, 2003; Calarge *et al.*, 2006) by means of various types of discriminating diagrams (e.g. Winchester & Floyd, 1977; Pearce *et al.*, 1984) and/or for correlation purposes, usually employing multivariate statistical methods (e.g. Huff, 1983; Huff & Kolata, 1989; Huff *et al.*, 1991, 1993, 1997; Kolata *et al.*, 1996; Wray, 1999; Christidis, 2001). These approaches utilize mainly trace chemical elements which in general are considered immobile, both during bentonite formation and during subsequent burial diagenesis and/or anchimetamorphism. Although their validity has been questioned in as much as elements like Y, which are generally considered as immobile, can be mobilized substantially during bentonite formation (Christidis, 1998), these approaches are straightforward and therefore easy to follow. However, with limited exceptions (Christidis, 2001), the possible influence of volcanoclastic/volcanic parent rock chemistry on the crystal chemistry of the smectites formed has

not been taken into consideration in the aforementioned studies.

Recently, the possibility of such an influence was examined using the database of Grim & Güven (1978), and data from Eberl *et al.* (1986), Čičel *et al.* (1992), Christidis & Dunham (1993, 1997), Ddani *et al.* (2005) and Christidis (2006). The selected database included structural formulae obtained from microanalyses and chemical analyses of clay fractions from which structural formulae of dioctahedral smectites were calculated. Structural formulae of 75 dioctahedral smectites were eventually obtained, for which the nature of the precursor volcanics was more or less known and which were free of contamination or contained known amounts of kaolinite or SiO₂ polymorphs. Structural formulae obtained from microanalyses were essentially free from impurities and were used as provided in the relative references. This was not always the case for structural formulae calculated from chemical analyses of the clay fraction (database of Grim & Güven, 1978). Those analyses, which contained impurities with complex structural formula (plagioclase feldspar, illite and chlorite), were discarded.

The parent rocks were classified as acidic, intermediate and basic according to their geochemical affinities described by previous authors (Grim & Güven, 1978; Eberl *et al.*, 1986; Čičel *et al.*, 1992; Christidis & Dunham, 1993, 1997; Ddani *et al.*, 2005; Christidis, 2006). Both regression analysis and multivariate statistics (canonical discriminant analysis) were used (Kokidis, 2006). It was shown that smectites derived from precursors with different geochemical affinities can be differentiated by their average Fe and, to a lesser

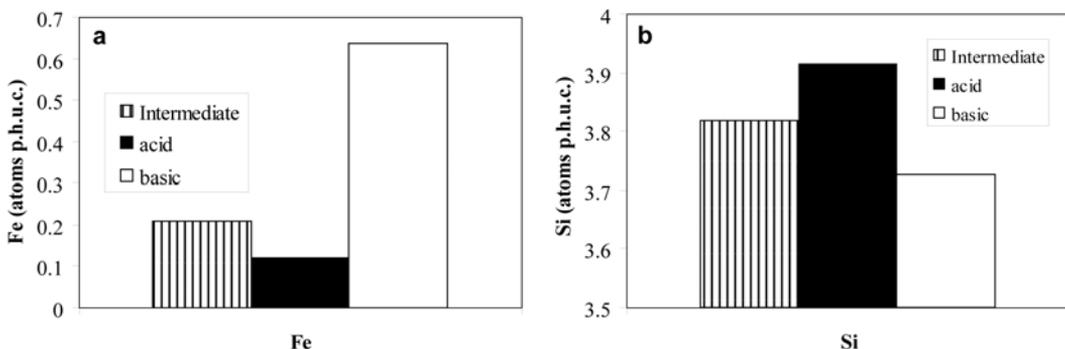


FIG. 5. Average cation occupancy of Fe³⁺ and Si in smectites derived from acidic, basic and intermediate rocks (Kokidis, 2006). See text for discussion.

degree, by their average Si content (Fig. 5). Smectites derived from alteration of basic rocks have on average 0.63 Fe³⁺ atoms p.h.u.c., whereas smectites derived from intermediate and acidic rocks have, on average, 0.21 and 0.12 Fe³⁺ atoms p.h.u.c. respectively (Fig. 5). Also, smectites derived from alteration of acidic rocks have on average 3.92 Si atoms p.h.u.c., whereas smectites derived from intermediate and basic rocks have on average 3.82 and 3.73 Si atoms p.h.u.c., respectively (Fig. 5). Hence, it seems that smectites derived from basic precursors tend to have a greater tetrahedral charge. In contrast, smectites cannot be differentiated on the basis of their Mg, total Al, ^{VI}Al or ^{IV}Al contents.

Iron has discriminating power in regression analysis when plotted against Si, Al and Mg, since smectites derived from basic rocks have a greater Fe³⁺ content (Fig. 6). However, smectites derived from acidic and intermediate rocks cannot be differentiated because of their comparable Fe contents. Moreover, smectites from basic rocks seem to have lower Al contents than those of smectites derived from acidic and intermediate rocks. Finally, smectites cannot be differentiated with respect to their Mg content (Fig. 6). The same is true for Si although smectites derived from different precursors have different average Si occupancy. These results show that binary diagrams, which use the main structural cations, are not useful for discriminating precursor rocks from the smectite crystal chemistry, due to significant overlapping of the various structural cations. In contrast, canonical discriminant analysis which used all structural cations showed that all structural cations contribute to the differentiation of smectites (Fig. 7). The canonical discriminant functions with greater discriminant power were the following (Kokidis, 2006):

$$F1: 5.15Si + 1.86^{IV}Al + 10.39^{VI}Al + 1.626Fe^{3+} + 0.90Mg - 38.39$$

and

$$F2: 19.18Si + 15.14^{IV}Al - 3.39^{VI}Al - 3Fe^{3+} - 6.83Mg - 67.89.$$

Application of canonical discriminant analysis assigned a score (value) to each smectite and allocated correctly, on average, 91% of the smectites studied (Fig. 7). The main reason for incorrect allocation of the remaining smectites is

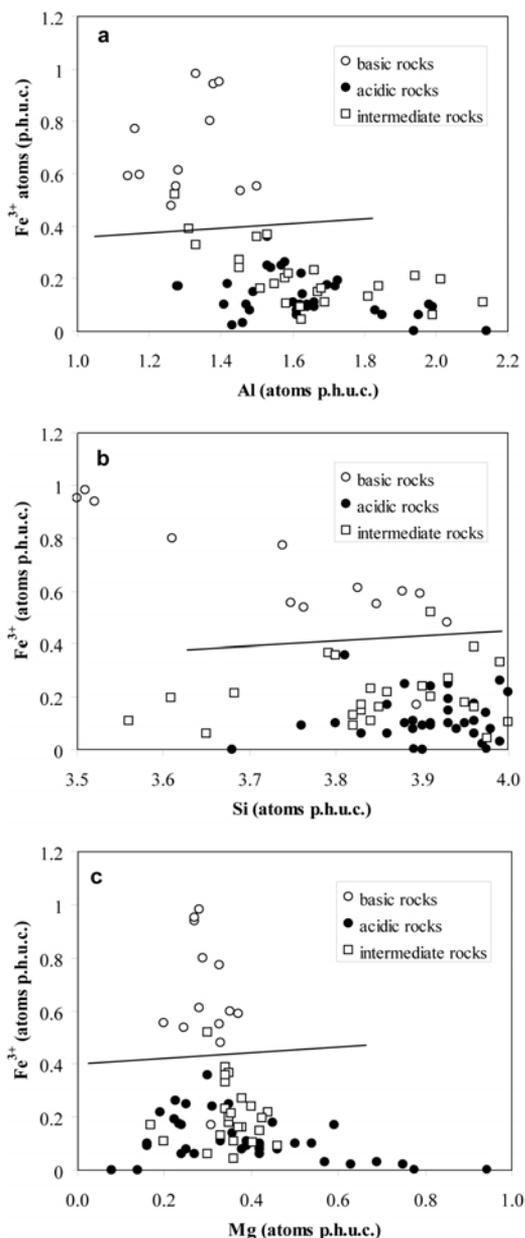


Fig. 6. Binary plots showing the discrimination of smectites derived from basic volcanic rocks from those derived from acidic and intermediate volcanics based (separated by straight lines) mainly on the Fe³⁺ content.

attributed to the uncertainty about the geochemical affinities of the precursor volcanic rocks. Nevertheless, these results suggest that the chemistry of the parent rock may exert influence on

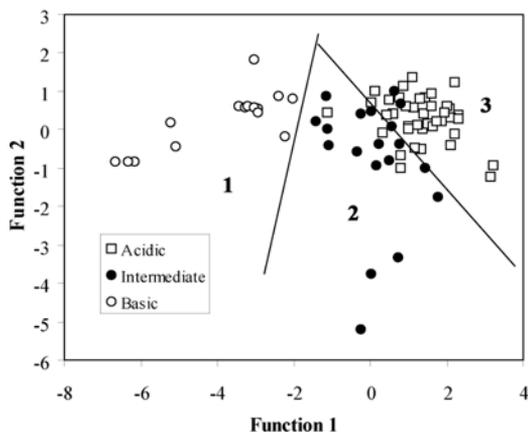


FIG. 7. Distribution of smectites formed from basic (1), intermediate (2) and acidic (3) volcanic rocks using canonical discriminant analysis (Kokidis, 2006). Data from Grim & Güven (1978), Eberl *et al.* (1986), Čičel *et al.* (1992), Christidis & Dunham (1993, 1997), Ddani *et al.* (2005) and Christidis (2006). Discrimination was obtained by means of the structural cations. See text for discussion.

smectite crystal chemistry at least to some extent. The canonical discriminant analysis can be used in an opposite manner. Hence, using equations F1 and F2 a score (value) can be obtained for any smectite derived from volcanic rocks of unknown composition according to its crystal chemistry. From this score the nature of the parent rock may be inferred. However, a larger data set from other smectites derived from known precursors is needed to further verify this model and substantiate the validity of equations F1 and F2. Also, an additional independent test of this approach would include the use of immobile trace elements of the smectitic clay fractions in the canonical discriminant analysis. The main problem of this independent testing approach is that the trace elemental composition of most of the bentonite samples and the clay fractions used in this study have not been provided in the literature, i.e. the database used included only major elements.

The approach used showed that, in general, dioctahedral Fe-rich smectites (montmorillonites and beidellites) form from basic precursors, whereas alteration of acidic volcanics yields Fe-poor smectites. Nevertheless there are exceptions to this trend; hence *s.s.* Wyoming-type smectites may contain abundant Fe ($>0.25 \text{ Fe}^{3+}$ atoms p.h.u.c.) although they have formed from acidic precursors.

In this case it is considered that Fe has been transported from an external source during diagenetic alteration of the precursor volcanic glass. Also, it is interesting that, in several bentonites derived from acidic rocks, smectites have high Mg contents. This is certainly the case for the SAz-1, Kinney and Otay smectites (Eberl *et al.*, 1986; Berry, 1999), as well as several smectites in Greek and US deposits (Zielinski, 1982; Christidis *et al.*, 1999; Christidis, 2001). In all these cases, pore-water chemistry affected significantly the chemical composition of the neoformed smectites.

CONCLUSIONS

The questions about the contradictory characteristics of bentonites now have answers, i.e.:

(1) The formation of high-quality bentonites from acidic precursors is related to fluid flow, and this in turn to the mechanism of eruption. High-quality bentonites may be derived from acidic volcanoclastic rocks emplaced at high temperature, which may sustain fluid flow for a greater amount of time and facilitate leaching of Si and alkalis. With decreasing emplacement temperature (and hence alteration temperature), the possibility for crystallization of SiO_2 polymorphs increases.

(2) Several of the mineralogical and geological characteristics of bentonites can be explained if it is considered that Fe^{2+} is present when smectites are formed. Iron may be easily oxidized at a later stage when the deposits are brought close to the surface, probably by contact with surface pore waters. The role of microbial activity may also be important for oxidation of Fe^{2+} but it has not been considered in the present study. The properties of smectites in bentonites formed at depth may change when brought close to, or exposed at the surface.

(3) The nature of the parent rock exerts influence on the composition of smectites at least to some degree. In general, basic precursors yield Fe-richer and Al-poorer smectites (both Fe-montmorillonites and Fe-beidellites). The influence of parent-rock chemistry on the crystal chemistry of smectites is certainly modified by pore-water chemistry.

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REFERENCES

- Aagaard P. & Helgeson H.C. (1982) Activity/composition relations among silicates and aqueous solutions; II, Chemical and thermodynamic consequences of ideal mixing of atoms on homological sites in montmorillonites, illites, and mixed-layer clays. *Clays and Clay Minerals*, **31**, 207–217.
- Berger G., Shott J. & Loubet M. (1987) Fundamental processes controlling the first stage of alteration of basaltic glass by seawater: an experimental study between 200°C and 320°C. *Earth and Planetary Science Letters*, **84**, 431–445.
- Berger G., Claparols C., Guy C. & Daux V. (1994) Dissolution rate of a basalt glass in silica-rich solutions: implications for long-term alteration. *Geochimica et Cosmochimica Acta*, **58**, 4875–4886.
- Berry R.W. (1999) Eocene and Oligocene Otay-Type Waxy Bentonites of San Diego County and Baja California: Chemistry, mineralogy, petrology and plate tectonic implications. *Clays and Clay Minerals*, **47**, 70–83.
- Best M.G. (1982) *Igneous and Metamorphic Petrology*. Freeman, New York, 630 pp.
- Caballero E., Reyes E., Huertas F., Linares J. & Pozzuoli A. (1991) Early stage smectites from pyroclastic rocks of Almeria, Spain. *Chemical Geology*, **89**, 353–358.
- Caballero E., Jimenez de Cisneros C., Huertas F.J., Huertas F., Pozzuoli A. & Linares J. (2005) Bentonites from Cabo de Gata, Almeria, Spain: a mineralogical and geochemical overview. *Clay Minerals*, **40**, 463–480.
- Calarge L., Lanson B., Meunier A. & Formoso M.L. (2003) The smectitic minerals in a bentonite deposit from Melo (Uruguay). *Clay Minerals*, **38**, 25–34.
- Calarge L., Meunier A., Lanson B. & Formoso M.L. (2006) Chemical signature of two Permian volcanic ash deposits within a bentonite bed from Melo, Uruguay. *Anais da Academia Brasileira de Ciencias*, **78**, 525–541.
- Cas R.A.F. & Wright J.V. (1988) *Volcanic Successions Modern and Ancient*. Unwin Hyman, London, 93–128.
- Christidis G.E. (1998) Comparative study of the mobility of major and trace elements during alteration of an andesite and a rhyolite to bentonite, in the islands of Milos and Kimolos, Aegean Greece. *Clays and Clay Minerals*, **46**, 379–399.
- Christidis G.E. (2001) Formation and growth of smectites in bentonites: a case study from Kimolos Island, Aegean, Greece. *Clays and Clay Minerals*, **49**, 204–215.
- Christidis G.E. (2006) Genesis and compositional heterogeneity of smectites. Part III: Alteration of basic pyroclastic rocks – a case study from the Troodos Ophiolite Complex, Cyprus. *American Mineralogist*, **91**, 685–701.
- Christidis G. & Dunham, A.C. (1993) Compositional variations in smectites. Part I. Alteration of intermediate rocks. A case study from Milos Island, Greece. *Clay Minerals*, **28**, 255–273.
- Christidis G. & Dunham, A.C. (1997) Compositional variations in smectites. Part II. Alteration of acidic precursors. A case study from Milos Island, Greece. *Clay Minerals*, **32**, 253–270.
- Christidis G.E. & Scott P.W. (1997) The origin and control of colour of white bentonites from the Aegean islands of Milos and Kimolos, Greece. *Mineralium Deposita*, **32**, 271–279.
- Christidis G., Scott P.W. & Marcopoulou Th. (1995) Origin of the bentonite deposits of Eastern Milos, Aegean, Greece: geological, mineralogical and geochemical evidence. *Clays and Clay Minerals*, **43**, 63–77.
- Christidis G.E., Marcopoulou Th. & Foscolos A. (1999) Origin, physical and chemical properties of a bentonite deposit of Chios Island, eastern Aegean, Greece. *Proceedings of the 11th International Clay Conference*, Ottawa, Canada, 75–82.
- Christidis G.E., Blum A.E. & Eberl D.D. (2006) Influence of layer charge and charge distribution of smectites on the flow behaviour and swelling of bentonites. *Applied Clay Science*, **34**, 125–138.
- Čičel B., Komadel P., Bednarikova E. & Madejová J. (1992) Mineralogical composition and distribution of Si, Al, Fe, Mg and Ca in the fine fractions of some Czech and Slovak bentonites. *Geologica Carpathica-Series Clays*, **1**, 3–7.
- Cravero F., Keith K.S., Murray H.H. & Toth T. (2000) A white bentonite from San Juan Province, Argentina – geology and potential industrial applications. *Applied Clay Science*, **16**, 31–43.
- Crovisier J.L., Thomassin J.H., Juteau T., Eberhart J.P., Touray J.C. & Baillif P. (1983) Experimental seawater–basaltic glass interaction at 50°C: study of early developed phases by electron microscopy and X-ray photoelectron spectrometry. *Geochimica et Cosmochimica Acta*, **47**, 377–387.
- Crovisier J.L., Honnorez J. & Eberhart J.P. (1987) Dissolution of basaltic glass in seawater: mechanism and rate. *Geochimica et Cosmochimica Acta*, **51**, 2977–2990.
- Daux V., Guy C., Advocat T., Crovisier J-L. & Stille P. (1997) Kinetic aspects of basaltic glass dissolution at 90°C: Role of aqueous silicon and aluminium. *Chemical Geology*, **142**, 109–126.

- Ddani M., Meunier A., Zahraoui M., Beaufort D., El Wartiti M., Fontaine D., Boukili B. & El Mahi B. (2005) Clay mineralogy and chemical composition of bentonites from the Gourougou volcanic massif (northeast Morocco). *Clays and Clay Minerals*, **53**, 250–267.
- Drits V.A. & Manceau A. (2000) A model for the mechanism of Fe^{3+} to Fe^{2+} reduction in dioctahedral smectites. *Clays and Clay Minerals*, **48**, 185–195.
- Eberl D.D., Srodoń J. & Northrop R. (1986) Potassium fixation in smectite by wetting and drying. Pp. 296–326 in: *Geochemical Processes at Mineral Surfaces* (J.A. Davis & K.F. Hayes, editors). ACS Symposium Series **323**, American Chemical Society, Washington, D.C.
- Elzea J. & Murray H.H. (1990) Variation in the mineralogical, chemical and physical properties of the Cretaceous Clay Spur bentonite in Wyoming and Montana. *Applied Clay Science*, **5**, 229–248.
- Elzea J. & Murray H.H. (1994) Clays: Bentonite. Pp. 233–246 in: *Industrial Minerals & Rocks: 6th edition* (D.D. Carr, editor). Society of Mining Engineers, Littleton, Colorado, USA.
- Fiore S., Huertas F.J., Tazaki K., Huertas F. & Linares J. (1999) A low-temperature experimental alteration of a rhyolitic obsidian. *European Journal of Mineralogy*, **11**, 455–469.
- Fiore S., Huertas F.J., Huertas F. & Linares J. (2001) Smectite formation in rhyolitic obsidian as inferred by microscopic (SEM-TEM-AEM) investigation. *Clay Minerals*, **36**, 489–500.
- Fisher R.V. & Schmincke H.U. (1984) *Pyroclastic Rocks*. Springer Verlag, Berlin, 472 pp.
- Forster G. & Smith L. (1990) Fluid flow in tectonic regimes. Pp. 1–47 in: *Short course on fluids in tectonically active regimes of the continental crust* (B.E. Nesbitt, editor). Mineralogical Association of Canada, Ontario, Canada.
- Foster M.D. (1953) Geochemical studies of clay minerals: II relation between ion substitution and swelling in montmorillonites. *American Mineralogist*, **38**, 994–1006.
- Garrels R.M. & Christ C.L. (1965) *Solutions, Minerals, and Equilibria*. Harper, London, 450 pp.
- Gislason S.R. & Eugster H.P. (1987) Meteoric water-basalt interactions. I: A laboratory study. *Geochimica et Cosmochimica Acta*, **51**, 2827–2840.
- Goodman P.H., Nadeau P.H. & Chadwick J. (1988) Evidence for the multiphase nature of bentonites from Mössbauer and EPR spectroscopy. *Clay Minerals*, **23**, 147–159.
- Grim R.E. & Güven N. (1978) *Bentonites. Geology, Mineralogy, Properties and Uses*. Elsevier, Amsterdam, pp. 143–155.
- Güven N. (1988) Smectite. Pp. 497–559 in: *Hydrous Phyllosilicates* (S.W. Bailey, editor). Reviews in Mineralogy, **19**, Mineralogical Society of America, Washington, D.C.
- Hay R.L. (1977) Geology of zeolites in sedimentary rocks. Pp. 53–64 in: *Mineralogy and Geology of Natural Zeolites* (F.A. Mumpton, editor), Reviews in Mineralogy, **4**, Mineralogical Society of America, Washington, D.C.
- Hay R.L. & Sheppard R.A. (2001) Occurrence of zeolites in sedimentary rocks: an overview. Pp. 217–232 in: *Natural Zeolites: Properties, Applications and Uses* (D.L. Bish & D.W. Ming, editors). Reviews in Mineralogy and Geochemistry, **45**, Mineralogical Society of America and the Geochemical Society, Washington, D.C.
- Hein J.R. & Scholl D.W. (1978) Diagenesis and distribution of late Cenozoic volcanic sediments in the southern Bering Sea. *Bulletin of the Geological Society of America*, **89**, 197–210.
- Huff W.D. (1983) Correlation of Middle Ordovician K-bentonites based on chemical fingerprinting. *Journal of Geology*, **91**, 657–669.
- Huff W.D. & Kolata D.R. (1989) Correlation of K-bentonite beds by chemical fingerprinting using multivariate statistics. Pp. 567–577 in: *Quantitative Dynamic Stratigraphy* (T.A. Cross, editor). Prentice Hall, New Jersey, USA.
- Huff W.D., Anderson T.B., Rundle C.C. & Odin G.S. (1991) Chemostratigraphy, K-Ar ages and illitization of Silurian K0-bentonites from the Central Belt of the Southern Uplands-Down-Longford terrane, British Isles. *Journal of Geological Society of London*, **148**, 861–868.
- Huff W.D., Merriman R.J., Morgan D.J. & Roberts B. (1993) Distribution and tectonic setting of Ordovician K-bentonites in the United Kingdom. *Geological Magazine*, **130**, 93–100.
- Huff W.D., Bergström S.M., Kolata D.R. & Sun H. (1997) The Lower Silurian Osmundsberg K-bentonite. Part II: mineralogy, geochemistry, chemostratigraphy and tectonomagmatic significance. *Geological Magazine*, **135**, 15–26.
- Kawano M., Tomita K. & Kamino Y. (1993) Formation of clay minerals during low temperature experimental alteration of obsidian. *Clays and Clay Minerals*, **41**, 431–441.
- Knechtel M.M. & Patterson S.H. (1962) Bentonite deposits of the Northern Black Hills District, Wyoming, Montana and South Dakota. *Bulletin 1082-M, US Geological Survey*, 893–1030.
- Kokidis N. (2006) *Study of the Influence of Parent Rock Chemistry on the Chemical Composition of Smectites present in Bentonites*. Unpublished Diploma Thesis. Technical University of Crete, Greece, 114 pp.
- Kolata D.R., Huff W.D. & Bergström S.M. (1996) Ordovician K-bentonites of eastern North America. *Geological Society of America Special Paper*, **313**, 84 pp.
- Komadel P. (2003) Chemically modified smectites. *Clay*

- Minerals*, **38**, 127–138.
- Komadel P., Lear P.R. & Stucki J.W. (1990) Reduction and reoxidation of nontronite: extent of reduction and reaction rates. *Clays and Clay Minerals*, **38**, 203–208.
- Komadel P., Anastacio A.S., Andrejkovičova S. & Stucki J.W. (2008) Iron phases identified in bentonite from the Lieskovec deposit (Slovakia) by variable-temperature Mössbauer spectroscopy. *Clay Minerals*, **43**, 107–115.
- Kostka J.E., Stucki J.W., Nealon K.H. & Wu J. (1996) Reduction of structural Fe(III) in smectite, by a pure culture of the Fe-reducing bacterium *Shewanella putrefaciens* I strain MR-1. *Clays and Clay Minerals*, **44**, 522–529.
- Laird D.A. (2006) Influence of layer charge on swelling of smectites. *Applied Clay Science*, **34**, 74–87.
- Lear P.R. & Stucki J.W. (1985) The role of structural hydrogen in the reduction and reoxidation of iron in nontronite. *Clays and Clay Minerals*, **33**, 539–545.
- Lear P.R. & Stucki J.W. (1989) Effects of iron oxidation state on the specific surface area of nontronite. *Clays and Clay Minerals*, **37**, 547–552.
- Maccioni L., Marchi M., Padalino G. Palomba M. & Sistu G. (1995) Bentonite occurrences in Tertiary volcanic rocks of Central Sardinia, Italy. *Exploration and Mining Geology*, **4**, 73–79.
- Maes A. & Cremers A. (1977) Charge density effects in ion exchange. Part 1. Heterovalent exchange equilibria. *Faraday Transactions of the Royal Chemical Society*, **73**, 1807–1814.
- Manceau A., Drits V.A., Lanson B., Chateigner G., Wu J., Huo D., Gates W.P. & Stucki J.W. (2000) Oxidation–reduction mechanisms of iron in dioctahedral smectites. I. Structural chemistry of oxidized reference nontronites. *American Mineralogist*, **85**, 133–152.
- Merriman R.J. & Roberts B. (1990) Metabentonites in the Moffat Shale Group, Southern Uplands of Scotland: Geochemical evidence of ensialic marginal basin volcanism. *Geological Magazine*, **127**, 259–271.
- Morgan D.J., Highley D.E. & Bland D.J. (1979) A montmorillonite, kaolinite association in the Lower Cretaceous of South-East England. Pp. 301–310 in: *International Clay Conference 1978* (M.M. Mortland & V.C. Farmer, editors). Elsevier, Amsterdam.
- Mottl M.J. & Seyfried W.E. (1980) Sub-seafloor hydrothermal systems: rock- vs. seawater-dominated. *Earth and Planetary Science Letters*, **66**, 137–150.
- Murad E., Cashion J.D. & Brown L.J. (1990) Magnetic ordering in Garfield nontronite under applied magnetic fields. *Clay Minerals*, **25**, 261–269.
- Norton D.L. (1984) Theory of hydrothermal systems. *Annual Reviews in Earth and Planetary Science*, **12**, 155–177.
- Pauling L. (1960) *The Nature of the Chemical Bond*. Cornell University Press, Ithaca, New York.
- Pearce J.A., Harris N.B.W. & Tindle A.G. (1984) Trace element discrimination diagrams for the tectonic discrimination of granitic rocks. *Journal of Petrology*, **25**, 956–983.
- Pellenard P., Deconinck J.F., Huff W.D., Thierry J., Marchand D., Fortwengler D. & Trouiller A. (2003) Characterization and correlation of Upper Jurassic (Oxfordian) bentonite deposits in the Paris Basin and the Subalpine Basin, France. *Sedimentology*, **50**, 1035–1060.
- Petit J.C., Della Mea G., Dran J.C., Magonthier M.C., Mando P.A. & Paccagnella A. (1990) Hydrated-layer formation during dissolution of complex silicate glasses and minerals. *Geochimica et Cosmochimica Acta*, **54**, 1941–1955.
- Rozenson I. & Heller-Kallai L. (1978) Reduction and oxidation of Fe³⁺ in dioctahedral smectites. III. Oxidation of octahedral iron in montmorillonite. *Clays and Clay Minerals*, **26**, 88–92.
- Schultz L.G. (1969) Lithium and potassium adsorption, dehydroxylation temperature and structural water content of aluminous smectites. *Clays and Clay Minerals*, **17**, 115–149.
- Senkayi A.L., Dixon J.B., Hossner L.R., Abder-Ruhman M. & Fanning D.S. (1984) Mineralogy and genetic relationships of tonstein, bentonite and lignite strata in the Eocene Yegua Formation of east-central Texas. *Clays and Clay Minerals*, **32**, 259–271.
- Seyfried W.E. Jr. & Mottl M.J. (1982) Hydrothermal alteration of basalt by seawater under seawater-dominated conditions. *Geochimica et Cosmochimica Acta*, **46**, 985–1002.
- Shiraki R. & Iiyama J.T. (1990) Na–K ion exchange reaction between rhyolitic glass and (Na,K)Cl aqueous solutions under hydrothermal conditions. *Geochimica et Cosmochimica Acta*, **54**, 2923–2931.
- Shiraki R., Sakai H., Endoh M. & Kishima N. (1987) Experimental studies on rhyolite– and andesite–seawater interactions at 300°C and 1000 bars. *Geochemical Journal*, **21**, 139–148.
- Sparks R.S.J., Sigurdsson H. & Carey S.N. (1978) Theoretical modeling of the generation, movement and emplacement of pyroclastic flows by column collapse. *Journal of Geophysical Research*, **83**, 1727–1739.
- Stucki J.W. (2006) Properties and behaviour of iron in clay minerals. Pp. 423–475 in: *Handbook of Clay Science* (F. Bergaya, B.K.G. Theng & G. Lagaly, editors). Elsevier, Amsterdam.
- Stucki J.W. & Roth C.B. (1977) Oxidation–reduction mechanism for structural iron in nontronite. *Soil Science Society of America Journal*, **41**, 808–814.
- Stucki J.W., Komadel P. & Wilkinson H.T. (1987) Microbial reduction of structural iron(III) in smectites. *Soil Science Society of America Journal*, **51**, 1663–1665.

- Stucki J.W., Lee K. Zhang L. & Larson R.A. (2002) Effects of iron oxidation states on the surface and structural properties of smectites. *Pure and Applied Chemistry*, **74**, 2145–2158.
- Taylor K.G. & Curtis C.D. (1995) Stability and facies association of early diagenetic mineral assemblages: an example from a Jurassic ironstone-mudstone succession, U.K. *Journal of Sedimentary Research*, **65**, 358–368.
- Weaver C.E. (1989) *Clays, Muds, and Shales*. Developments in Sedimentology, **44**, Elsevier, Amsterdam.
- Weaver C.E. & Pollard L.D. (1973) *The Chemistry of Clay Minerals*. Elsevier, Amsterdam, pp. 55–77.
- White A.F. (1983) Surface chemistry and dissolution kinetics of glassy rocks at 25°C. *Geochimica et Cosmochimica Acta*, **47**, 805–815.
- White A.F. & Claesen H.C. (1980) Kinetic model for the short-term dissolution of a rhyolitic glass. *Chemical Geology*, **28**, 91–109.
- Williams F.J., Elsley B.C. & Weintritt D.J. (1953) The variations of Wyoming bentonite beds as a function of the overburden. *Clays and Clay Minerals*, **2**, 141–151.
- Winchester J.A. & Floyd P.A. (1977) Geochemical discrimination of different magma series and their differentiation products using immobile elements. *Chemical Geology*, **20**, 235–243.
- Wray D.S. (1999) Identification and long-range correlation of bentonites in Turonian–Coniacian (Upper Cretaceous) chalks of northwest Europe. *Geological Magazine*, **136**, 361–371.
- Yanagisawa N., Fujimoto K., Nakashima S., Kurata Y. & Sanada N. (1997) Micro FT-IR study of the hydration-layer during dissolution of silica glass. *Geochimica et Cosmochimica Acta*, **61**, 1165–1170.
- Yildiz A. & Kuşcu M. (2007) Mineralogy, chemistry and physical properties of bentonites from Başören, Kütahya, W. Anatolia, Turkey. *Clay Minerals*, **42**, 399–414.
- Zielinski R.A. (1982) The mobility of uranium and other elements during alteration of rhyolite ash to montmorillonite: a case study in the Troublesome Formation, Colorado, USA, *Chemical Geology*, **35**, 185–204.