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## ORIGIN OF THE BENTONITE DEPOSITS OF EASTERN MILOS, AEGEAN, GREECE: GEOLOGICAL, MINERALOGICAL AND GEOCHEMICAL EVIDENCE

GEORGE E. CHRISTIDIS,<sup>1</sup> PETER W. SCOTT,<sup>2</sup> AND THEODOR MARCOPOULOS<sup>1</sup>

<sup>1</sup> Technical University of Crete, Department of Mineral Resources Engineering  
73133 Chania, Crete, Greece

<sup>2</sup> Camborne School of Mines, Redruth Cornwall, TR15 3SE

**Abstract**—The Lower Pleistocene bentonite deposits of Eastern Milos, Greece have been formed at the expense of volcanoclastic rocks under submarine conditions. Systematic variation of the major chemical elements reveals that the deposits were formed from different precursors which were erupted from different volcanic centers belonging to at least two separate volcanic provinces. The volcanic eruptions were probably subaqueous. The major authigenic phases are smectite, K-feldspar, opal-CT and the zeolites mordenite and clinoptilolite. The deposits have a complex history and have been affected by hydrothermal alteration.

The geological features of bentonites coupled by the presence of abundant authigenic K-feldspar indicate that alteration of the parent volcanoclastic rocks took place under low temperatures and is probably not related to hydrothermal alteration, which is a separate event. Hydrothermal alteration has modified both the mineralogical characteristics and the properties of bentonites. Alteration of the parent rocks to bentonites was favoured by high water: rock ratios and fluid flow and is associated with leaching and subsequent removal of Na, K and Ca. The source of Mg was the parent rocks and only small scale Mg-uptake from the sea water has probably taken place. The formation of authigenic K-feldspar has probably been favoured by a high  $K^+/H^+$  activity ratio and high Si activity of the pore fluid. Such conditions might have been favoured by the pH conditions and the cooling history of the parent rocks.

**Key Words**—Authigenic K-feldspar, Bentonite, Electron microscopy, Hydrothermal alteration, Infrared spectroscopy, Low temperature alteration, Smectite, X-ray diffraction, X-ray fluorescence, Zeolites.

### INTRODUCTION

The term bentonite is used for a clay consisting essentially of smectite regardless of origin and whose physical properties are dictated by this mineral (Grim and Güven 1978). Due to their unique physical and chemical properties, bentonites are used in a wide spectrum of industrial applications (Grim 1962, Hartwell 1965, Grim and Güven 1978, Patterson and Murray 1983, Harben and Bates 1990). Bentonites might form at the expense of volcanic, mainly glassy, rocks by means of three processes (Grim and Güven 1978): a) *in situ* alteration of volcanic glass in aqueous environment b) hydrothermal alteration of igneous rocks and c) deuteric alteration of igneous materials involving reactions of vapours and gases with the igneous mass. The same authors considered also the existence of a great number of deposits with uncertain mode of origin.

Many well documented bentonite formations, like those at the Sucker Creek, Eastern Oregon, and the Clay Spur bed in Wyoming and Montana, USA or the English fuller's earth deposits have formed by means of *in situ* alteration of airborne and water transported volcanic ash, in relatively shallow lacustrine and sea water respectively (Altaner and Grim 1990, Elzea and Murray 1990, Jeans *et al* 1977). Several deposits have

been classified as hydrothermal. Hydrothermal alteration patterns associated with argillization might include either vein-filling concentrations of the clay within and/or around structural features (faults, joints, thrust surfaces) or massive changes of the parent rock like those in Kuroko-type deposits (Chamley 1989). In the latter case, smectite (montmorillonite) rich concentrations with or without zeolites (mordenite, clinoptilolite, analcime) are present in the outer alteration zone, known as zone I (Shirozu 1978).

Greece is second in the world after the USA in bentonite production, with major extraction in the eastern part of the Aegean island of Milos. Despite the great economic and scientific importance of the deposits, their mode of origin is still controversial. Wetzstein (1969) proposed a diagenetic origin in a submarine environment with provision of Mg from submarine hot springs, while Fyticas (1977) and Grim and Güven (1978) assumed a hydrothermal origin under subaerial conditions. Finally, based on oxygen isotope data, Liakopoulos (1991) considered a hydrothermal origin in a submarine environment.

With the possible exception of the work of Wetzstein (1969), the previous studies have not examined the bentonite deposits in detail. This contribution studies the geological, mineralogical and geochemical characteristics of the bentonites of Eastern Milos. Its pur-

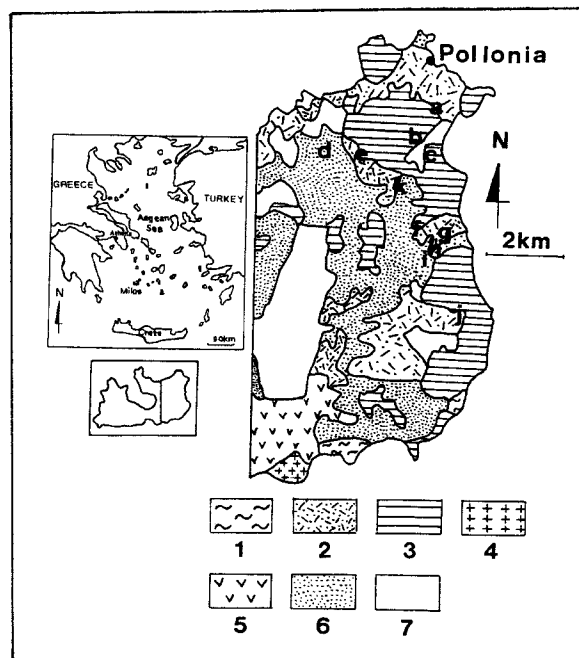


Figure 1. Simplified geological map of the sampling area, modified after Fyticas *et al* (1986). Key to the numbers: 1 = Metamorphic basement, 2 = Lower Pleistocene pyroclastics (protoliths of bentonites), 3 = Lower Pleistocene lava domes, 4 = Lava dome of Halepa (Lower Pleistocene), 5 = Rhyolitic complex of Phryiplaka, 6 = Products of phreatic activity of Quaternary Age, 7 = Quaternary sediments. Key to the letters: a = Zoulias, b = Aspro Horio, c = Tsantili.

pose is: a) to provide new data about the geological, mineralogical and geochemical features of the deposits, b) to propose an alternative possible mode of origin and c) to use the information obtained for exploration of new deposits.

#### LOCATION AND GEOLOGICAL SETTING

Milos is situated in the SW part of the Cyclades group of islands, Aegean Sea, Greece (Figure 1). The geological-volcanological characteristics of Milos (Figure 1) have been studied by Fyticas (1977) and Fyticas *et al* (1986) and have been presented by Christidis and Dunham (1993a).

#### SAMPLING AND METHODS

247 samples were collected from 11 bentonite deposits (Figure 1), along vertical and horizontal profiles from the quarry faces, covering every distinct horizon of each individual deposit. Samples were collected at a depth 35–40 cm from the surface to minimize the effect of weathering (especially in abandoned quarry faces) and contamination, caused by mixing of material during excavation operations on active faces. The mineralogy was determined by X-ray powder diffraction

(Philips diffractometer with a PW1710 computerized control unit operating at 40 KV and 30 mA, using Ni-filtered  $\text{CuK}\alpha$  radiation). Scanning speed for all samples was  $1^\circ 2\theta/\text{min}$ . Bulk mineralogy was studied with randomly oriented air-dried samples. Characterization of clinoptilolite-heulandite-type zeolites was made using the simplified method of Boles and Surdam (1979). The terminology for the silica polymorphs follows Jones and Segnit (1971). Clay mineralogy was determined on less than  $2\ \mu\text{m}$  material prepared by sedimentation, after soaking in distilled water overnight. The clay particles were dispersed using ultrasonic vibration for two minutes, after addition of Na-polymetaphosphate deflocculant. The less than  $2\ \mu\text{m}$  fraction was separated using sedimentation, spread on glass slides and allowed to dry under atmospheric conditions. The dried clay samples were saturated with ethylene-glycol vapour at  $60^\circ\text{C}$  for 16 hours and X-rayed immediately. Semi quantitative analyses of the glycolated clay fractions were obtained using the methods of Reynolds (1989).

Fresh, broken surfaces of representative samples were placed on aluminium stubs, coated with a thin film of gold and examined with a Hitachi S520 SEM, operating at 20 KV accelerating voltage, equipped with a Link AN1000 Energy Dispersive Spectrometer (EDS) for qualitative analyses. Epoxy impregnated polished blocks were used for microanalyses using a JEOL JXA-8600 Superprobe, equipped with three wavelength spectrometers (WDS) and a Link series 1 energy dispersive spectrometer (EDS), with 158 eV resolution at 5, 8 K eV. Microanalyses were carried out with the EDS using the conditions described in Christidis and Dunham (1993a) except for the use of a defocused ( $5\ \mu\text{m}$  diameter) electron beam. The elemental concentrations were automatically corrected for atomic number, adsorption in the sample, fluorescence and dead time (the ZAF correction), using the ZAF-4 computer program provided by Link. The following standards were used: wollastonite for Si and Ca, jadeite (intensity standard) and NaCl (profile standard) for Na, synthetic  $\text{Al}_2\text{O}_3$  for Al, synthetic MgO for Mg, microcline for K, synthetic  $\text{Fe}_3\text{O}_4$  for Fe, rutile for Ti and rhodonite for Mn. The accuracy, precision and detection limits of the method are given in Dunham and Wilkinson (1978).

Infrared (IR) spectra were obtained using a BIORAD FTS40 Fourier Transform Infrared Spectrometer for the clay fraction of representative samples, which were pressed on KBr disks (Russell 1974), in the frequency range  $400\text{--}4000\ \text{cm}^{-1}$ . 3 mg of clay, which had been previously dried at  $150^\circ\text{C}$  overnight to remove the adsorbed water, were mixed with 160 mg of halide.

Representative samples were dried at  $105^\circ\text{C}$ , ground to pass from a  $125\ \mu\text{m}$  sieve and analysed with X-ray Fluorescence (XRF), using an ARL 8420+ XRF spectrometer. Major element concentrations were obtained from fusion beads, using a mixture of 80% Li-tetra-

borate and 20% Li-metaborate as flux (Bennett and Oliver 1976 modified by N. Marsh, University of Leicester). Each sample was analysed for Si, Ti, Al, Fe, Mn, Mg, Ca, Na, K, and P. Total iron was expressed as  $\text{Fe}_2\text{O}_3$ . Pressed powder pellets were used for the determination of the trace elements Nb, Zr, and Y. The accuracy and precision of the analyses for both the main and trace elements was tested by means of international standards given by Govindaraju (1989).

## RESULTS

### *Geological features of the bentonite deposits*

The Lower Pleistocene bentonite deposits of Eastern Milos can be separated into three groups according to their geographical distribution (Figure 1). The first group includes the deposits of Aspro Horio, Tsantili and Zoulia, the second the deposits of Ankeria and Koufi, and the third the deposits of Ano Komia, Kato Komia, Rema, Garyfalakena and Mavrogiannis. Between the deposits of the second and the third group, exists the isolated deposit of Agrilies, which cannot be incorporated in any of the three aforementioned groups.

The deposits are stratiform and most of them are composite, consisting of more than one distinct bentonite horizon (Figure 2), having either different lithological characteristics or different color (the Zoulia deposit consists of ten different bentonite horizons). Their thickness in the exposed quarry faces varies between 10 and 40 m. The bentonites from the Groups 1 and 2 have dark green-blue colors which are converted to bright or/and pale yellow in their higher stratigraphic horizons, probably due to oxidation of Fe (Knechtel and Patterson 1962, Komadel *et al* 1990), after being exposed to atmospheric conditions for prolonged times. The bentonites of Group 3 and the Agrilies deposit have pale grey-off white colors. All deposits are stained in places with reddish or/and yellowish colorations, due to the presence of ferric oxides and sulphates respectively.

The bentonite deposits have well defined upper boundaries, but their basement is not known with certainty. Alteration of the parent rock is almost complete, and only small cores of relatively fresh, undevitrified material have been observed. The intensity of alteration permits only indirect conclusions about the nature of the parent rocks. However, their geological and spatial characteristics indicate that the deposits of the Groups 2 and 3 have been formed *in situ* probably from pyroclastic flows while those of Group 1 formed from a widespread volcanic breccia. Geological, stratigraphic and paleontological evidence indicates that deposition of the parent pyroclastic rocks took place in submarine conditions. However it is not certain whether the parent rocks erupted subaerially or into sea water. Most bentonites are dominated by a characteristic

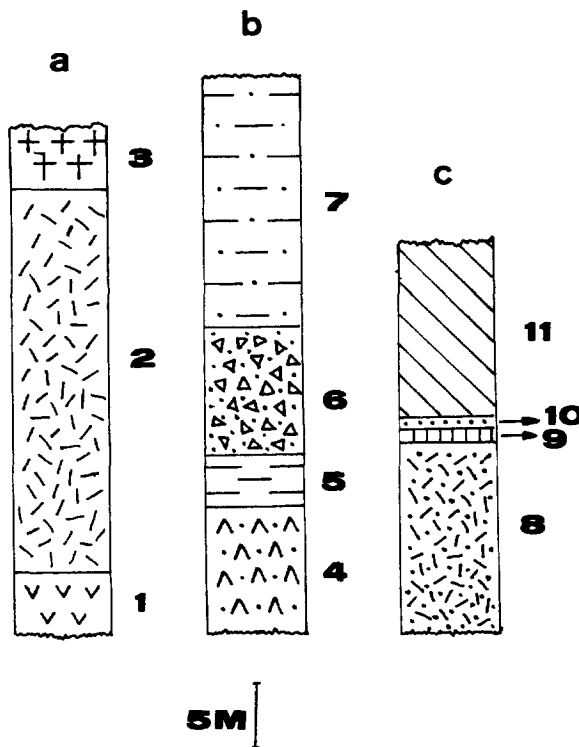


Figure 2. Schematic sections of representative Milos bentonite deposits: a) Koufi deposit: 1 = green basal bentonite derived from a lapilli tuff, 2 = blue-green bentonite with porphyritic texture, 3 = yellow bentonite. b) Ankeria deposit: 4 = blue green plastic bentonite, 5 = bright yellow bentonite, 6 = yellowish bentonite with beds of opal-CT, 7 = grey bentonite. c) Aspro Horio deposit: 8 = blue-green bentonite with "brocken tuff" texture, 9 = pink-reddish bentonite, 10 = grey bentonite, 11 = yellowish bentonite with opalini silica beds in the upper parts.

brecciated texture ("brocken tuff"-texture according to Wetzenstein 1969), resembling hyaloclastite.

Most deposits contain opaline silica, which is either concentrated in separate beds (Groups 1 and 2) or disseminated throughout the entire mass of the bentonites (Group 3 and Agrilies deposit). The bedded opaline silica occurs at various stratigraphic levels but, mainly in the higher units. It does not indicate a general downward movement of free silica. A similar location of opal-CT-rich beds has recently been described by Altaner and Grim (1990) in the Sucker Creek formation, Oregon.

Hydrothermal alteration is ubiquitous throughout the entire island of Milos with examples within and/or in close vicinity of the bentonite deposits. Evidence includes gypsum and barite veins, stockwork textures characterized by sulphur-metasomatism, silicification and solfatara thermal springs, which are still active (Christidis 1992). The type of alteration is controlled by structural criteria. Field observations indicate that

Table 1. Mineralogical composition of the Greek bentonite deposits of Milos Island. The characterization of smectites follows Christidis and Dunham (1993a, 1993b).

Mineral	Group 1			Group 2	
	Tsantili	Asp. Horio	Zoulias	Ankeria	Koufi
Smectite	M (±)	M	M	M	M
Type	Mont/nite (Wyoming)	Mont/nite (Wyoming)	Mont/nite (Cheto/CH)	Mont/nite (Cheto/TA-CH)	Mont/nite (TA) /beidellite
Kaolinite	T/Min (±)	—	T (±)	—	Min (±)
Halloysite	—	T (±)	—	—	—
Mica	—	—	—	—	—
Chlorite	—	—	—	—	—
Opal-CT	—	Min/T	Min/M (±)	Min/M (±)	T/Min (±)
Opal-C	—	—	—	—	—
Quartz	Min (±)	M	M/Min (±)	M	T/Min (±)
Clinoptilolite	—	—	Min (±)	—	—
Mordenite	—	—	—	T (±)	—
K-feldspar <sup>1</sup>	M	—	Min (±)	T (±)	Min (±)
Plagioclase	—	Min	M/Min (±)	Min (±)	Min/M (±)
K-feldspar <sup>2</sup>	—	Min (±)	M/Min (±)	Min/T (±)	Min/T (±)
Calcite	Min (±)	Min/T (±)	—	M/Min (±)	T (±)
Alunite	Min/T (±)	—	—	—	—
Jarosite	Min/T (±)	T/Min (±)	—	Min/T (±)	—
Gypsum	T (±)	T/Min (±)	Min/T (±)	Min/T (±)	T (±)
Baryte	—	—	T (±)	—	T (±)
Pyrite/	T (±)	T (±)	T (±)	T (±)	T (±)
Marcasite	T (±)	T (±)	—	T (±)	T (±)
Hematite	T (±)	—	—	T (±)	—
Halite	T (±)	—	—	—	—

M = major mineral phase, Min = minor mineral phase, T = trace mineral phase, — = not detected, (±) = present in some sectors or horizons of the deposit, ? = not unambiguous identification of the mineral phase, Mont/nite = montmorillonite, CH = Chambers (Cheto) montmorillonite, TA = Tatatilla (Cheto) montmorillonite, K-feldspar<sup>1</sup> = authigenic K-feldspar, K-feldspar<sup>2</sup> = pyrogenetic K-feldspar.

it has been superimposed on the stratiform bentonites (Christidis 1992), implying that the alteration is not associated directly with bentonite formation, but might be a separate event (Christidis and Marcopoulos 1993).

### Mineralogy

The mineralogical composition of the bentonites is shown in Table 1. Dioctahedral smectite (Figure 3) is the main phase present in all deposits. With the exception of the Tsantili deposit, plagioclase feldspars are abundant in the Groups 1 and 2 and subordinate in the remaining deposits, while K-feldspars are abundant in Group 3 and the Tsantili deposit. Kaolinite, calcite and zeolites (clinoptilolite and mordenite) are secondary phases while sulphates (gypsum, alunite-natroalunite/jarosite, barite) and sulphides (pyrite and/or marcasite) are accessory minerals, often concentrated in veins. Clinoptilolite and mordenite are present in the Zoulias, Ankeria and Garyfalakena deposits. Clinoptilolite is characterized as "intermediate" (Boles and Surdam 1979). Groups 1 and 2 are clearly separated from Group 3 and the Agrilies deposit which contain abundant silica phases.

Silica polymorphs occur in the form of opal-CT, opal-C (cristobalite) and quartz. Opal-CT is recognized

from the characteristic large diffraction maximum at d-spacing 4.1 Å followed by a less intense maximum at 4.3 Å (Figure 3), probably corresponding to a disordered a-tricymite structure (Wilson *et al.* 1974). In the bentonite deposits of Group 3, two of the three polymorphs (either opal-CT and quartz or cristobalite and quartz) coexist.

The XRD results for the orientated clay fractions, confirm that smectite is the main clay mineral, with subordinate kaolinite (Figure 4). The ratio smectite/kaolinite varies between 1:0 and 0.6:0.4. High kaolinite contents have been observed in materials which have been affected by hydrothermal alteration. Opal-CT is present in the less than 2 µm fraction of Group 3 deposits.

The XRD characteristics of the K-feldspars present in the deposits of Tsantili, Koufi, Ano Komia, Garyfalakena, Mavrogiannis and Rema resemble those of high sanidines (JCPDS Card 25-618), being different from the characteristics of "normal" igneous sanidines (JCPDS Card 19-1227). They plot in the high sanidine-orthoclase area (Figure 5) in the diagram of K-feldspars (Wright 1968). They are all monoclinic and have been classified as anomalous K-feldspars following Wright (1968). Such characteristics are typical for authigenic K-feldspars (Sheppard and Gude 1973).

Table 1. Extended.

Group 3					
An. Komia	Garyfalakena	Mavrogiannis	K. Komia	Rema	Agrilies
M	M	M	M	M	M (±)
Mont/nite (TA)	Mont/nite (TA)	Mont/nite (TA)	Mont/nite	Mont/nite	Mont/nite (TA)
/beidellite	/beidellite	/beidellite		Cheto (TA)	/beidellite
Min/T (±)	T (±)	T	T	—	Min
—	—	—	—	—	—
Min (±)	—	—	Min	—	Min
Min (±)	T (±)	—	Min	—	—
M (±)	M	M	M	M	—
M (±)	—	—	—	—	—
M	Min	M	M	Min	M
—	Min (±)	—	—	—	—
—	Min (±)	—	—	—	—
Min (±)	Min (±)	T/Min (±)	Min/T	T/Min	?
—	Min (±)	Min	Min	Min	—
Min (±)	T (±)	?	?	?	—
M (±)	T/Min (±)	—	M	—	—
—	—	—	M/Min (±)	—	—
—	—	T (±)	M/Min (±)	T (±)	T (±)
Min/T (±)	T (±)	—	T	—	Min
—	—	—	—	—	T (±)
T (±)	T (±)	T	T	T	T (±)
—	—	—	—	—	T (±)
—	—	—	—	—	—
—	—	—	—	—	—

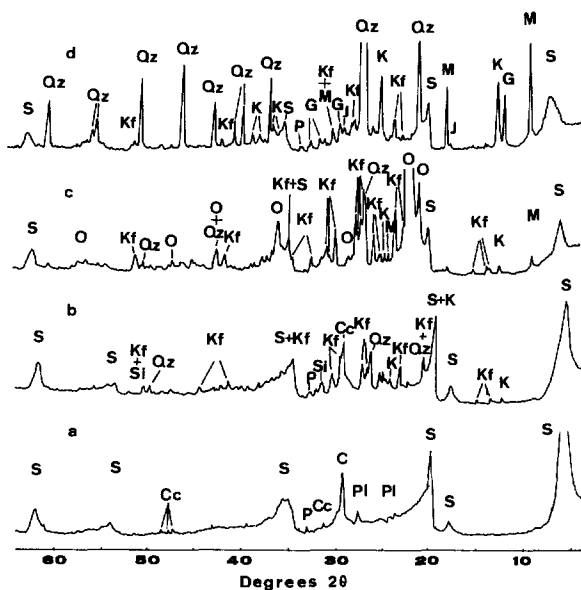


Figure 3. Representative XRD patterns of the Milos bentonites (bulk samples). a = Ankeria deposit, b = Tsantili deposit, c = Garyfalakena deposit, d = Agrilies deposit. Key to the letters: S = smectite, K = kaolinite, M = mica, G = gypsum, Kf = K-feldspar, O = opal-CT, Qz = quartz, J = jarosite, Pl = plagioclase, Cc = calcite, P = pyrite.

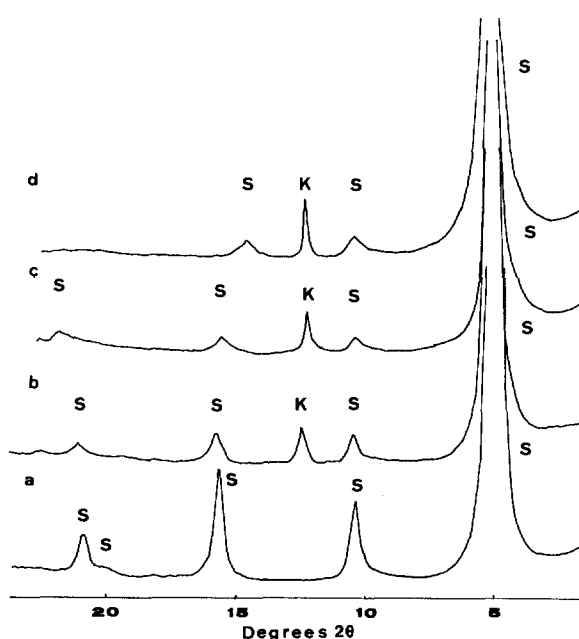


Figure 4. Representative XRD patterns of the less than 2  $\mu$ m clay fractions. a = Ankeria deposit, b = Tsantili deposit, c = Garyfalakena deposit, d = Agrilies deposit. Key to the letters: S = smectite, K = kaolinite.

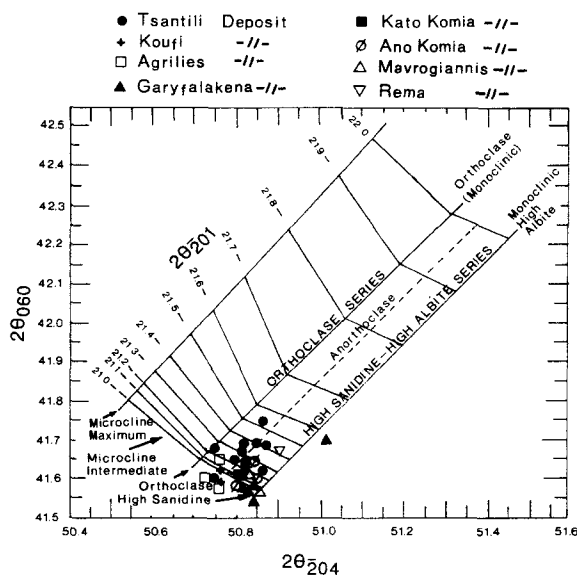


Figure 5. Projection of the K-feldspars from the Miloa bentonites on the diagram of Wright (1968).

### Morphology and mineral chemistry

**Smectite.** Smectite crystals are present in the form of wavy flakes, forming characteristic honeycomb textures, which might be due to dehydration of the specimens in vacuum (Figure 6). No systematic relationship between the smectite morphology and the location of the flakes was observed, contrary to the findings of Konta (1985). The smectite flakes have been formed via two ways: a) at the expense of volcanic glass, which

in places, has led to pseudomorphic replacement textures (Figure 6), (Khouri and Eberl 1979), and b) replacement of igneous feldspars, mainly plagioclases (Figure 6), which also has led to pseudomorphic textures (Figure 7). Other elongated smectite flakes observed along fractures (Figure 6) were determined as nontronite using EDS.

**Feldspars.** Feldspars are present in two distinct morphological types having different crystal-chemical characteristics. The first type includes phenocrysts-microphenocrysts of both plagioclase and K-feldspars of igneous origin, which are usually replaced by smectite (Figures 6, 7). They are frequently compositionally zoned and constitute intermediate members of the feldspars series (Table 2). Their Mg-content is much higher than that of the usual stable feldspars (Smith 1983). The second type includes 5–15  $\mu\text{m}$  long, euhedral, monoclinic crystals placed on smectite flakes (Figure 8). They usually occur filling pore spaces and/or lining pore cavities formed by the dissolution of volcanic glass. They are pure end-member K-feldspars, with perfect stoichiometry (Table 2), without any detectable sodium or calcium. Chemical purity and small crystal size are the most important features for the characterization of a feldspar as authigenic (Kastner and Siever 1979). Their textural relationship with smectites indicates that their formation has probably taken place after the formation of smectite.

**Opal-CT.** Opal-CT occurs in two different crystal forms (Figure 8). One is characterized by spherulitic crystals which are considered diagenetic by-products formed by precipitation during the dissolution of volcanic glass. The second forms axiolitic crystals (Figure 8) which

Table 2. Representative electron microprobe analyses of feldspars present in the Miloa bentonites. Analyses 1–5 correspond to igneous feldspars while analyses 6–10 correspond to authigenic K-feldspars. Note the perfect stoichiometry of authigenic K-feldspars. Analysis No 4 corresponds to an igneous K-feldspar. The difference in the chemistry compared to the authigenic K-feldspar is obvious. Analyses 1, 2 from Ankeria deposit, 3 from Zoulias deposit, 4–7 from Koufi deposit, 8 from Ano Komia deposit and 9–10 from Tsantili deposit.

	1	2	3	4	5	6	7	8	9	10
SiO <sub>2</sub>	58.52	55.78	58.96	653.9	60.06	66.34	65.38	66.26	64.71	64.30
Al <sub>2</sub> O <sub>3</sub>	26.27	27.66	26.01	20.01	24.81	16.78	17.38	16.86	17.71	18.47
Fe <sub>2</sub> O <sub>3</sub>	n.d.	0.50	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
MgO	1.01	0.88	0.81	0.98	0.66	n.d.	n.d.	n.d.	n.d.	n.d.
CaO	6.82	8.72	5.82	0.94	5.44	n.d.	n.d.	n.d.	n.d.	n.d.
Na <sub>2</sub> O	6.57	5.53	6.91	3.57	6.99	n.d.	n.d.	n.d.	n.d.	n.d.
K <sub>2</sub> O	0.34	0.30	0.87	9.80	0.94	16.59	16.66	16.09	16.36	17.03
Total	99.53	99.37	99.38	100.69	98.90	99.71	99.42	99.21	98.78	99.80
Structural formulae based on 32 oxygens										
Si	10.47	10.07	10.56	11.73	10.79	12.28	12.16	12.29	12.10	11.95
Al	5.54	5.89	5.49	4.23	5.25	3.66	3.81	3.68	3.90	4.05
Fe <sup>3+</sup>	—	0.07	—	—	—	—	—	—	—	—
Mg	0.27	0.24	0.22	0.26	0.18	—	—	—	—	—
Ca	1.31	1.69	1.12	0.18	1.05	—	—	—	—	—
Na	2.28	1.94	2.40	1.24	2.43	—	—	—	—	—
K	0.08	0.07	0.20	2.24	0.22	3.92	3.95	3.81	3.90	4.04

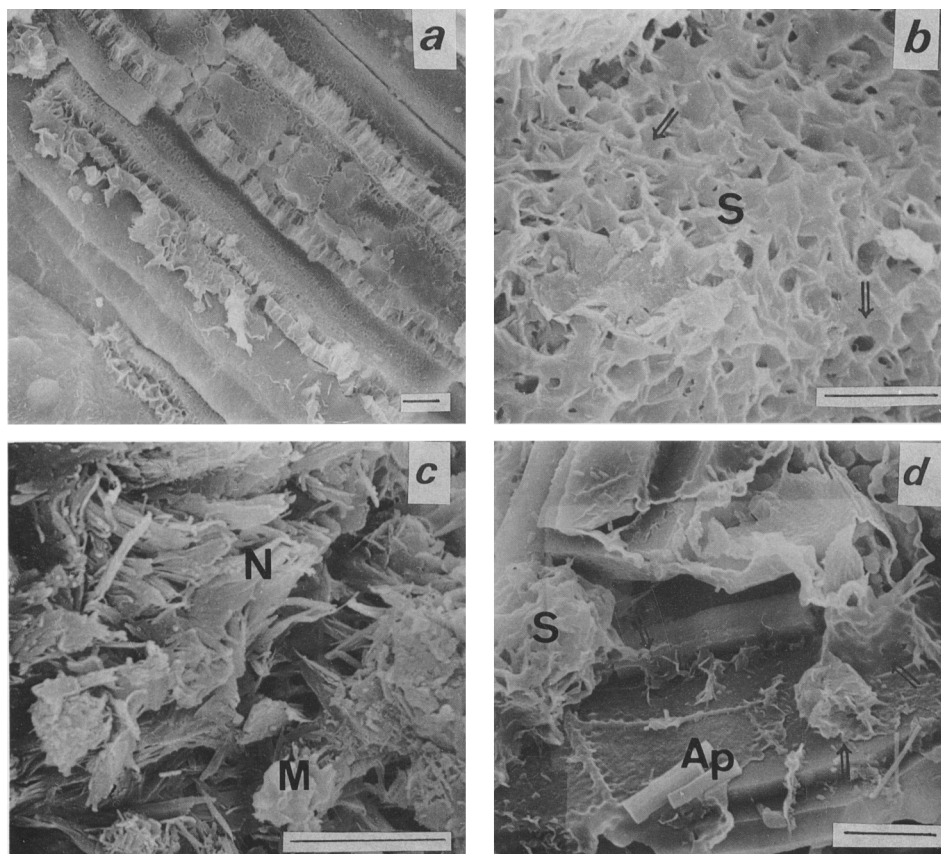


Figure 6. Electron micrographs of smectite textures observed in the Milos bentonites: a) Pseudomorphic textures resulting from complete replacement of volcanic glass by smectite. The glass shards have been completely altered. Aspro Horio deposit. Scale bar 20  $\mu\text{m}$ . b) Typical honeycomb texture shown by the arrow, formed by smectite crystals (S), Ankeria deposit. Scale bar 6  $\mu\text{m}$ . c) Elongated nontronite flakes (N) from the Koufi deposit. M = montmorillonite. Scale bar 9  $\mu\text{m}$ . d) Alteration of igneous plagioclase (Pl) from smectite (S). Smectite forms a thin alteration crust on the surface of plagioclase, shown by the arrow, but with progressive alteration well developed crystals (S) form. The small euhedral crystals draped over the altered plagioclase belong to apatite (Ap). Zoulias deposit. Scale bar 7.5  $\mu\text{m}$ .

might be direct products of devitrification of the volcanic glass (Moncure *et al* 1981). Both types are characterized by clay-size crystals. Also, the size of quartz crystallites coexisting with opal-CT is very small indicating that its origin is not igneous.

**Zeolites.** Mordenite and clinoptilolite/heulandite are present in subordinate amounts (Table 1). Two morphological types of mordenite have been recognized: The first is characterized by well formed long fibres draped over the smectite substrate and the second develops vertical to pore spaces and cavities, linking the two parts of the dissolved cavity. Clinoptilolite/heulandite occurs in the form of small "coffin-type" crystals always found in cavities among the altered shards. Occasionally, they are present as pore linings.

**IR results.** IR spectra of representative clay fractions of the bentonites from the three groups and the deposit of Agrilies are shown in Figure 9. They are typical for

dioctahedral smectites (Farmer and Russell 1964, 1967, Farmer 1974, van der Marel and Beutelspacher 1976). The smectites from Group 2 (Figure 9a) are characterized by a well expressed absorption band at 918  $\text{cm}^{-1}$  and relatively weak absorption bands at 878 ( $\text{AlFe}^{+3}\text{OH}$  bending vibration) and 844  $\text{cm}^{-1}$  ( $\text{Al-MgOH}$  bending vibration). The smectites from Group 1 (Figure 9b) show an intense absorption band at 878  $\text{cm}^{-1}$  and a less well expressed absorption band at 845  $\text{cm}^{-1}$ . The band at 1426  $\text{cm}^{-1}$  belongs to calcite. Smectites from Group 3 (Figure 9c) and the Agrilies deposit (Figure 9d) show a well expressed absorption band at 918  $\text{cm}^{-1}$  and very weak absorption bands at 878 and 844  $\text{cm}^{-1}$ . The latter spectra also display an intense absorption band at about 795  $\text{cm}^{-1}$ , which probably belongs to a poorly crystallized silica phase. The bands at 3693 and 3647  $\text{cm}^{-1}$  observed in the sample from the Agrilies deposit belong to kaolinite, which is abundant in this deposit (Table 1). These results are in



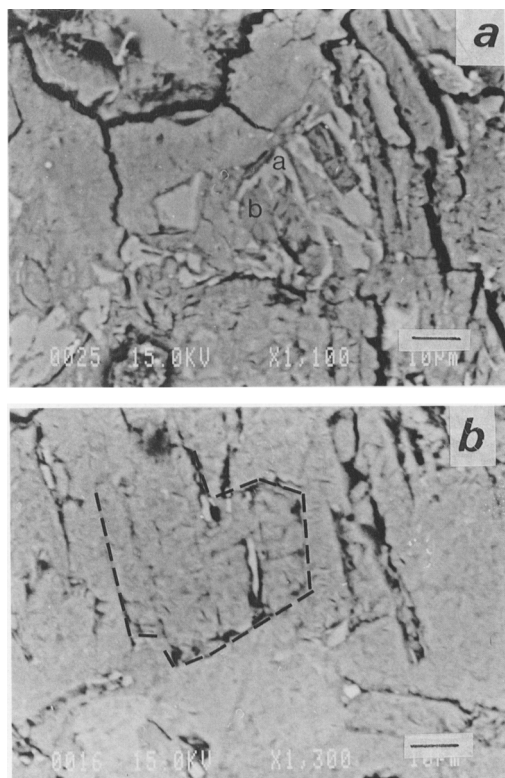


Figure 7. Back scattered electron images depicting progressive replacement of plagioclase by smectite. In photo a the replacement is not complete and remnants of plagioclase (a) are present, although smectite (b) dominates. In photo b the replacement is almost complete. The black dashed line displays the probable rims of the original plagioclase crystal. Koufi deposit. Scale bars 10  $\mu$ m.

accordance with microanalytical results concerning the crystal chemical characteristics of the smectites present in the various bentonite deposits (Table 3).

#### *Chemistry of the bentonites*

Representative chemical analyses are shown in Table 4. For terms of comparison representative analyses of unaltered volcanic rocks from Milos island (Fyticas 1977) are also given. The bentonites from Groups 1 and 2 are characterized by low silica and high MgO and Fe<sub>2</sub>O<sub>3</sub>, while those of Group 3 and the Agrilios deposit are dominated by high silica and low Al<sub>2</sub>O<sub>3</sub>, MgO and Fe<sub>2</sub>O<sub>3</sub>. These differences are reflected in the mineralogy (presence of abundant silica phases, especially opal-CT in the deposits of Group 3 and the deposit of Agrilios) and the crystal chemistry of the smectites (Table 3). With the exception of the Tsantili which contains abundant authigenic K-feldspar, the bentonites from the Groups 1 and 2 also have lower potassium contents. The total alkali-content is very low. Bentonites with higher potassium content contain abundant authigenic K-feldspar. Except for the bentonite from the Ankeria deposit which contains abundant calcite (Table 1), the CaO content is low indicating leaching of Ca during alteration.

Projection of the bentonites on the diagram proposed by Winchester and Floyd (1977) clearly demonstrates that the parent rocks of the bentonites can be separated into three distinct groups (Figure 10). The deposits of Group 1 have probably formed from an andesite-type rock, while those of Group 3 were formed from an acidic rock of rhyodacitic-rhyolitic composition. The

Table 3. Microprobe analyses (average values) and structural formulae of smectites from the bentonite deposits of Milos Island, Greece. Data are from Christidis and Dunham (1993a, 1993b). 1 = Ankeria, 2 = Koufi, 3 = Tsantili, 4 = Aspro Horio, 5, 6 = Ano Komia, 7 = Mavrogiannis, 8 = Rema, L. charge = layer charge, I. charge = interlayer charge.

	1	2	3	4	5	6	7	8
SiO <sub>2</sub>	56.78	57.06	54.10	55.26	51.37	49.54	51.58	51.91
Al <sub>2</sub> O <sub>3</sub>	21.17	20.83	18.09	18.92	20.56	21.88	22.39	21.17
Fe <sub>2</sub> O <sub>3</sub>	3.06	4.55	3.20	3.72	1.45	1.67	1.05	1.04
MgO	3.78	3.39	3.23	3.36	2.18	1.39	2.16	2.48
CaO	1.91	1.49	1.54	1.12	0.58	0.78	0.45	0.86
Na <sub>2</sub> O	0.49	0.68	0.29	0.64	0.69	0.53	0.72	0.81
K <sub>2</sub> O	0.48	0.54	0.40	0.47	0.46	1.00	0.58	0.90
Total	87.14	88.17	80.84	83.50	77.10	76.50	78.48	78.91
Structural formulae based on 11 oxygens								
Si	3.58	3.84	3.95	3.91	3.89	3.80	3.83	3.86
Al <sup>IV</sup>	0.15	0.16	0.05	0.09	0.11	0.20	0.17	0.14
Al <sup>IV</sup>	1.53	1.50	1.50	1.49	1.72	1.78	1.78	1.71
Fe <sup>3+</sup>	0.16	0.23	0.18	0.20	0.08	0.10	0.06	0.06
Mg	0.38	0.34	0.35	0.35	0.25	0.16	0.24	0.27
VI Cations	2.07	2.06	2.03	2.05	2.05	2.03	2.08	2.04
Ca	0.14	0.11	0.12	0.09	0.05	0.06	0.03	0.05
Na	0.03	0.07	0.04	0.09	0.09	0.03	0.06	0.11
K	0.01	0.02	0.04	0.04	0.03	0.10	0.05	0.09
L. charge	0.32	0.31	0.32	0.30	0.22	0.26	0.17	0.30
I. charge	0.32	0.31	0.32	0.30	0.22	0.25	0.17	0.30

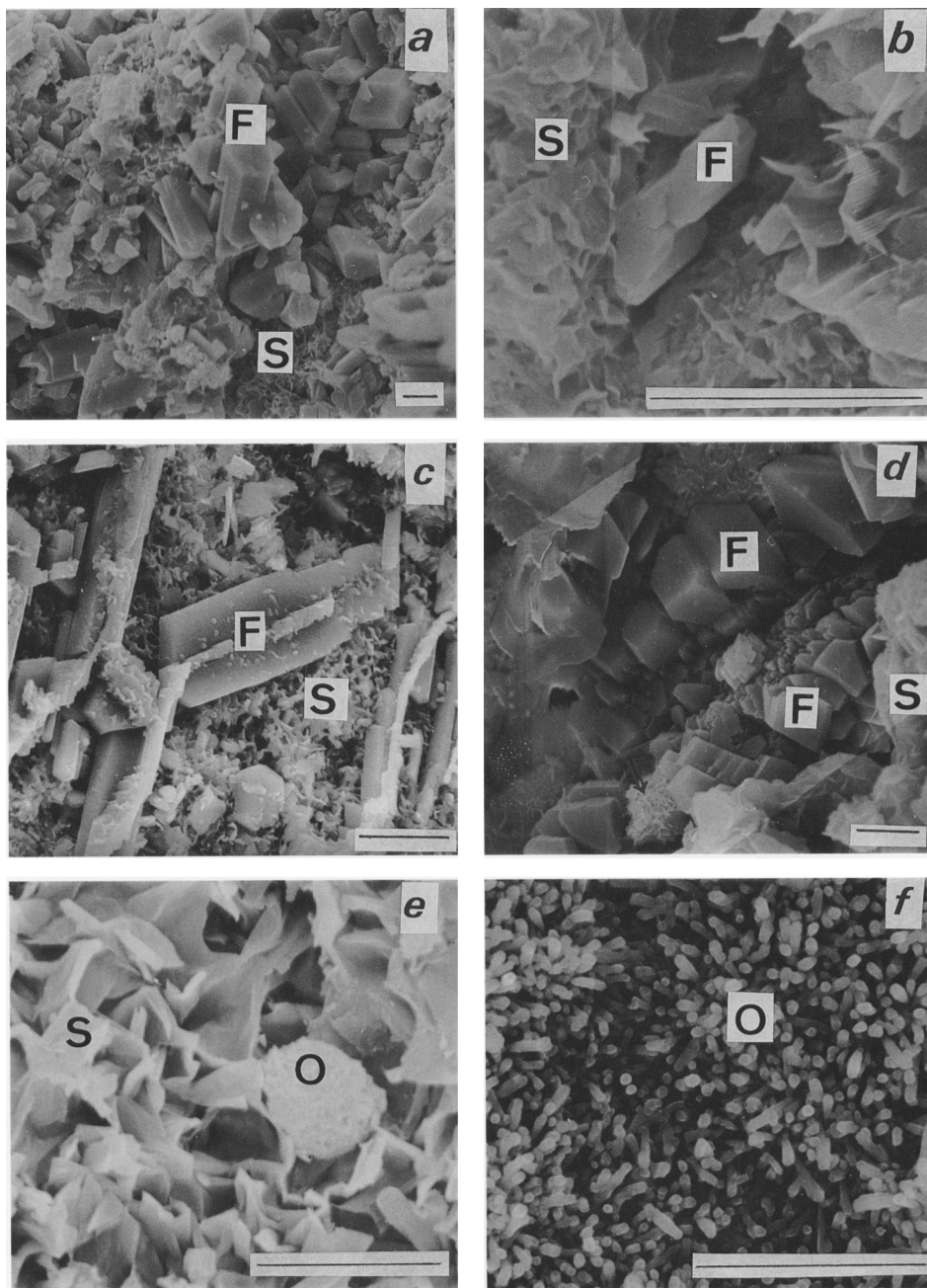


Figure 8. Authigenic K-feldspar (a–d) and opal-CT (e–f) textures observed in the Milos bentonites: In photos a, b and d K-feldspar crystals (F) fill dissolution cavities being associated with smectite (S). In photo c euhedral K-feldspar crystals (F) are draped over smectite (S) groundmass. a = Koufi deposit, b = Ankeria deposit, c = Tsantili deposit, c = Ano Komia deposit. Photo e: spherulitic opal-CT crystal (O) on smectite flakes (S). Ankeria deposit. Photo f: opal-CT crystals (O) with axiolitic texture. According to Moncure *et al* (1981) this texture might be the product of direct devitrification of volcanic glass. Garyfalakena deposit. Scale bars: a, c, d, f: 5  $\mu\text{m}$ , b, e: 2.5  $\mu\text{m}$ .

high silica contents of the bentonites from Group 3 and the textural characteristics and distribution of the silica phases present reject the possibility for large scale mobilization of silica, pointing towards a rhyolitic rather than rhyodacitic precursor. The lower horizon of the

Zoulias deposit (Group 1) has different characteristics from the other horizons of the same deposit.

The two bentonite horizons of the Ano Komia deposit are geochemically separate: the lower has probably dacitic affinities while the higher plots close to the

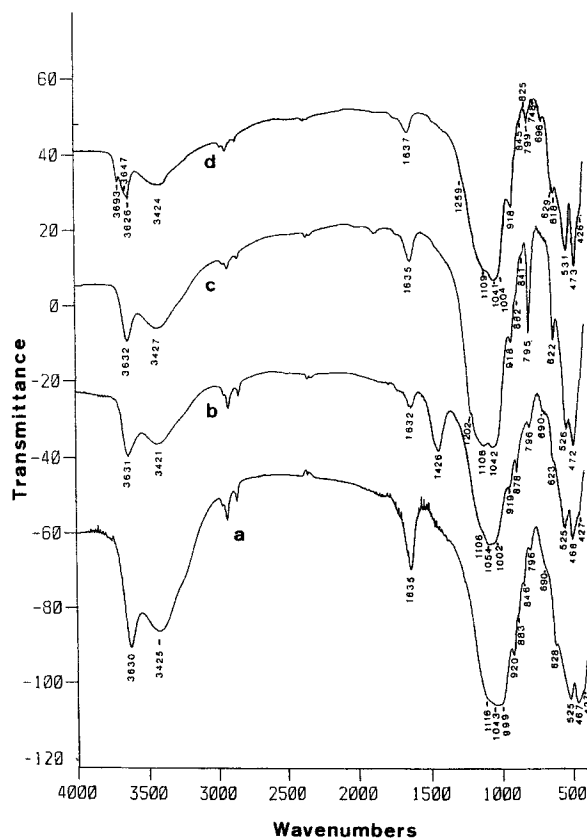


Figure 9. Representative IR spectra of smectites (less than 2  $\mu\text{m}$  fraction) present in the Milos bentonites. a = Ankeria deposit, b = Aspro Horio deposit. c = Ano Komia deposit, d = Agrilios deposit.

bentonites of Group 3. The deposits of Group 2 have probably derived from a precursor with dacitic-basic dacitic composition. In this group, the samples from the higher horizons of the Ankeria deposit plot systematically towards more acidic compositions, close to the samples from the Koufi deposit. Nevertheless, the difference is not obvious. Finally, the bentonites from the Agrilios deposit plot in the same area indicating that they were probably formed from dacitic precursors.

In general, the possible compositions of the bentonite precursors (Figure 10) are in accordance with the bentonite chemical compositions (Table 4). Accordingly, the low silica contents of the bentonites from the Groups 1 and 2 and the high silica contents of the bentonites from Group 3 indicate intermediate and acidic affinities respectively. The relatively high silica content of the bentonite from the Agrilios deposit might indicate migration of Si from an external source or the presence of rhyodacite with low Zr content (i.e., low Zr/Ti ratio) or migration of Zr. However, Zr has been an immobile element, even at extremely leaching conditions in the bentonites of Milos and Kimolos Islands

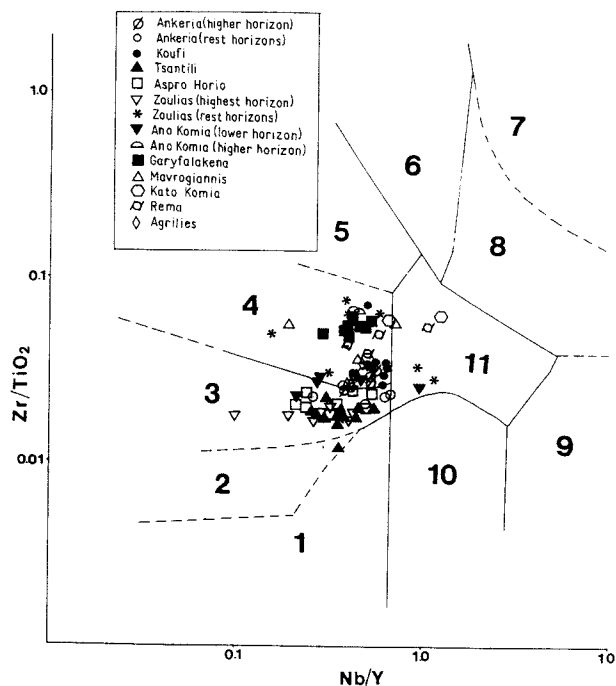


Figure 10. Projection of the Milos bentonites on the diagram proposed by Winchester & Floyd (1977). Key to the numbers: 1 = sub-alkaline basalt, 2 = basalt/andesite, 3 = andesite, 4 = dacite, rhyodacite, 5 = rhyolite, 6 = commendite pantellerite, 7 = phonolite, 8 = trachyte, 9 = basanite, nephelinite, 10 = alkali-basalt, 11 = trachyandesite.

(Christidis 1992). Therefore the possibility of migration of Zr has been rejected.

## DISCUSSION

### *Nature of the bentonite precursors*

The mineralogical and chemical features of the Milos bentonite deposits indicate that they might have not been derived from a common precursor. Also the significantly different affinities of these rocks indicate the existence at least of two volcanic provinces which were active during the Lower Pleistocene, each province including several volcanic centers. The first has andesitic-dacitic affinities and includes the bentonites of the Groups 1 and 2 and the second has acidic affinities and includes the bentonites of Group 3. Moreover, the existence of composite bentonite deposits indicates that the characteristics of volcanism might have changed with time in each volcanic center.

The bentonite precursors of the Groups 1 and 2 might have been intermediate rocks with a moderate Mg-content providing a plausible explanation for the source of MgO, which constitutes a major problem for several deposits (Grim and Güven 1978). A comparison of the Mg-contents of bentonites with that of the fresh rocks (Table 4), taking into account the mass balance effect

from the removal of chemical components, indicates that the main MgO-source was probably the parent rocks, with a possible small scale Mg-uptake from sea water. Significant Mg-uptake from sea water does not seem to have taken place even in the bentonites of Group 3, although they were derived from rhyolitic precursors (Table 4). Small scale mobilization of Mg after dissolution of the volcanic glass has probably also taken place, contributing to the microenvironmental heterogeneity which affects the smectite crystal chemistry (Christidis and Dunham 1993a, 1993b). Thus, the provision of Mg via submarine thermal springs (Wetzelstein 1969) does not seem plausible.

Several deposits have probably been derived from siliceous rocks, which do not seem to favour the formation of bentonites (Grim and Güven, 1978). After the initial hydration and cation exchange between the fluid phase and the volcanic glass (White and Claassen 1980, White 1983, Shiraki and Iijama 1990), alkalies and alkaline earth elements (i.e., network modifiers) are released, raising pH and salinity, if the system is sufficiently closed (Hay and Sheppard 1977). Under such conditions smectite is generally formed in the initial stages of alteration (cf. Sheppard and Gude 1973, Dibble and Tiller 1981, Hay and Guldman 1987), under low salinity and alkalinity of the pore fluid (Sheppard and Gude 1973), because zeolites instead of smectites are favoured by high  $(\text{Na}^+ + \text{K}^+)/\text{H}^+$  ratios (Hess 1966). The very low alkali content of the Milos bentonites and the lack of abundant zeolites indicates that the system was open with respect to alkalies, acting as a sink. Leaching conditions favour the formation of smectites instead of alkali-zeolites (Pevear *et al* 1980, Dibble and Tiller 1981, Senkay *et al* 1984). Subsequent dissolution of the leached glass probably led to the formation of smectite, followed by crystallization of K-feldspars and/or zeolites in the pore spaces formed by the dissolution of volcanic glass. The occurrence of K-feldspar indicates high  $\text{K}^+/\text{H}^+$  activity ratio and high Si activity (Kastner and Siever 1979).

The Si:Al ratio of rhyolitic glasses is higher than that of smectites. Since siliceous alkali-zeolites such as clinoptilolite and/or mordenite with Si:Al ratios similar to those of the siliceous glasses (Breck 1974, Gottardi and Galli 1985) are not present to take up the excess Si, it follows that it will either precipitate in the form of a silica phase or will migrate (Henderson *et al* 1971). In the case studied, the excess silica precipitated in the form of opal-CT, which affects both the properties of bentonites and their performance in various industrial applications (Christidis 1992). On the other hand, intermediate rocks have Si:Al ratios close to those of smectites and do not favour the formation of silica phases. Thus, at least in the case of Milos, the geochemical characteristics of the precursor rocks affect the physical properties of bentonites and their industrial applications; extractive operations have ceased in

Table 4. Representative chemical analyses of the Milos bentonites. Samples 1–2 come from the Ankeria deposit, 3 from Koufi deposit, 4 from Tsantili deposit, 5 from Aspro Horio deposit, 6 from Zoulias deposit, 7 from Ano Komia deposit, 8 from Garyfalakena deposit, 9 from Mavrogiannis deposit, 10 from Agriles deposit, 11 rhyolite, 12 dacite, 13 andesite, 14 andesite poor in  $\text{SiO}_2$ , n.d. = below detection limits. Analyses 11, 12, 13, and 14 are from Fyticas (1977).

	1	2	3	4	5	6	7	8	9	10	11	12	13	14
$\text{SiO}_2$	57.11	53.13	58.71	58.52	60.15	60.38	75.03	75.71	77.27	69.40	73.48	64.85	60.54	54.90
$\text{TiO}_2$	0.86	0.77	0.82	0.90	0.79	1.01	0.17	0.21	0.20	0.45	0.15	0.50	0.56	0.70
$\text{Al}_2\text{O}_3$	18.07	19.16	22.41	19.91	18.40	18.05	13.80	13.72	13.13	17.29	13.27	15.77	16.60	17.90
$\text{Fe}_2\text{O}_3$	2.99	5.02	4.28	4.05	7.26	5.66	1.43	1.98	1.89	2.10	0.80	2.65	3.19	3.75
FeO	—	—	—	—	—	—	—	—	—	—	0.69	1.75	2.11	3.35
MnO	0.09	0.03	0.02	0.11	0.02	0.01	0.03	0.01	0.01	0.01	0.07	0.10	0.14	0.10
MgO	3.45	3.37	3.38	3.34	2.79	4.04	1.82	1.46	1.25	1.42	0.64	2.22	3.23	4.05
CaO	6.13	6.42	1.55	2.21	0.84	1.13	0.56	0.79	0.51	0.76	1.53	5.42	6.85	9.30
$\text{Na}_2\text{O}$	0.53	0.90	0.53	0.48	1.04	1.00	0.29	0.26	0.39	0.26	3.74	3.65	3.46	3.15
$\text{K}_2\text{O}$	0.20	0.32	0.95	1.72	1.28	0.68	2.33	1.23	1.63	1.40	3.78	1.90	2.37	1.70
$\text{P}_2\text{O}_5$	0.12	0.17	0.21	0.13	0.09	0.05	0.01	0.03	0.02	0.05	0.02	0.07	0.14	0.07
LOI	9.71	10.18	7.13	6.69	7.32	7.41	4.98	4.76	4.05	6.39	1.92	1.02	1.04	1.45
$\text{SO}_3$	n.d.	n.d.	n.d.	1.69	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Total	99.26	99.47	99.99	99.75	99.98	99.42	100.45	100.16	100.35	99.53	100.09	99.90	100.23	100.42
Y	17.3	23.6	18.2	30.2	55.4	75.0	18.2	15.3	18.6	19.0	—	—	—	—
Zr	214.5	217.9	228.3	138.6	205.2	184.0	136.3	134.9	126.5	161.1	—	—	—	—
Nb	8.6	9.0	11.1	10.9	13.2	7.4	7.6	8.1	8.4	8.1	—	—	—	—

the bentonites of Group 3 due to their poor physical properties.

Small amounts of smectites have been formed at the expense of plagioclase (Figures 6 and 7). It is possible that this type of alteration proceeds gradually, whereby Mg might be introduced in the leached surface layer of the plagioclase. The source of Mg might be the glass itself (redistribution) or/and (less important) by sea water (metasomatic introduction). Participation of large amounts of Mg might destabilize the plagioclase structure, facilitating dissolution and formation of smectite. However, atomic coordination in the structural units of the volcanic glass might change after leaching of Ca and Na (Casey and Bunker 1990), and this in turn might increase the tolerance for Mg. Further addition of Mg probably cannot be tolerated, plagioclase might dissolve and smectite form. The released Ca probably participates in the formation of calcite. The fact that calcite is preferably present in bentonites derived from intermediate rocks, is not incompatible with this explanation.

The existence of pyrite does not necessarily indicate hydrothermal influx, since during alteration sulphur is taken up from sea water to counterbalance the leaching of alkalis and alkaline-earth elements (Mottl and Holland 1978, Shiraki *et al* 1987). Thus  $f_{O_2}$  might be an important factor determining the oxidation state of sulphur and the mobilization of Fe, contributing further to the compositional heterogeneity of smectites (Christidis and Dunham, 1993a).

#### *Origin of the Miloan bentonites*

The presence of authigenic K-feldspars indicates that the Miloan bentonites have probably formed at a low temperature. The large volume of the deposits, the almost complete alteration of volcanic glass to smectite and the leaching of Na, K and Ca indicate a massive fluid flow and high water: wall-rock ratios, which are expected due to the submarine environment of alteration. Nevertheless, it is not clear why fluid flow prevailed during alteration. Gravity driven flow does not exist because the sea level is the base level for sediments (Hay and Guldman 1987). Compaction of the parent rocks is not a plausible reason because they were never buried under a large overburden. Pressure driven flow derived from influx due to compaction of the surrounding rocks is also rejected because they were never subjected to deep burial. The remaining possibility is to assume that the flow is heat driven.

The precursors to the deposits of Groups 2 and 3 were probably pyroclastic flows, the temperature of which under subaerial conditions varies between 300 and 850°C (Fisher and Schmincke 1984, Cas and Wright 1988), according to the mechanism of eruption (Sparks *et al* 1978). Such temperatures are too high for bentonite formation although in subaqueous environment

the temperatures should be considerably lower. The behaviour of a subaerial pyroclastic flow when entering sea water is not known and only assumptions have been made (Cas and Wright 1988). With the existing geological data it is not certain whether the volcanic eruptions were subaqueous or subaerial, although the degree of alteration points to submarine eruptions. Weaver (1989) attributed the lack of alteration in many volcanic glasses to the source of the glass: submarine eruptions favour alteration, because they permit thorough mixing of sea water with volcanic glass, resulting in high water/rock ratios. The neutral-slightly alkaline conditions of such an environment and the open character of the system lead to pore solution compositions with high  $Na^+/K^+$  ratios compared to the parent rock, because Na is preferentially leached (White and Claassen 1980). This might have led to high  $K^+/Na^+$  ratios in the leached glass promoting the formation of authigenic K-feldspar. Moreover, submarine eruptions facilitate rapid cooling of the volcanic glass, leading to the formation of large interstices in the silicate network and easier accommodation of potassium (Shiraki and Iijama 1990), which might participate in the formation of authigenic K-feldspar. Finally, submarine eruptions might have produced the volcanic breccia which is the parent rock of Group 1 bentonites.

It is possible that alteration was controlled by a vigorous reaction between a *relatively warm* glassy rock and the cold sea water. A temperature gradient was established facilitating fluid flow and migration of the leached chemical elements. The temperature, at least during the precipitation of K-feldspar, was very low indicating a possible temperature decrease during the formation of bentonite. The system was thermodynamically open; therefore it might have not behaved like a geocautoclave (Alexiev and Djourova 1988) and zeolite formation was not favoured.

The presence of minerals like jarosite, alunite/natroalunite replacing pyrite (Christidis 1989) or occurring in veinlets, which are stable in acidic environments with high sulphate activity (Hemley *et al* 1969, Knight 1977), is at odds with the physicochemical conditions which determine the stability fields of smectites and K-feldspar. Also, smectite is usually replaced by isolated crystals or "booklets" of well crystallized kaolinite and/or acicular halloysite in most bentonites (Christidis and Marcopoulos 1993), which are typical hydrothermal minerals formed in relatively acid conditions in similar terrains in Kimolos Island close to eastern Milos (Tsolis-Katagas and Mavronichi 1989). Moreover the geological characteristics of the deposits, and the lack of the systematic alteration zones found in Kuroko-type massive argillic alteration patterns (Shirozu 1978, Utada 1988, Chamley 1989), indicate that hydrothermal alteration might not be the main factor which converted the parent volcanoclastic rocks to bentonites, but might be a separate, later event.

### Exploration for new bentonite deposits

The possibility of formation of the Milos bentonites under diagenetic rather than hydrothermal conditions and the stratiform character of the deposits, indicates that exploration for new deposits should be focused on stratigraphic rather than structural criteria. The use of the diagram proposed by Winchester and Floyd (1977), revealed the existence of different bentonite precursors. Moreover, samples from different deposits are often projected in the same "field", implying a possible common precursor. This in turn leads to the assumption that a bentonite body might extend in the area between two deposits having similar chemical characteristics. This might be the case in the bentonites of Groups 1 and 3 which plot in the same field. Recently (Silver and Barytes Ore Mining Co, oral communication, 1992) it was found that a "new" bentonite deposit is present between the Tsantili and Aspro Horio deposits, indicating the continuity of the bentonite horizon. Use of triangular diagrams using immobile trace elements and multivariate statistics (discriminant functions) corroborate these results and provide more detailed information. It is believed that chemical fingerprinting might be used for exploration of new bentonite deposits in Eastern Milos, notwithstanding the complex nature of the deposits.

### CONCLUSIONS

The Lower Pleistocene bentonite deposits of Eastern Milos were formed from different precursors with distinct geochemical characteristics, belonging to at least two volcanic provinces, through a series of steps which include:

- Emplacement of volcanoclastic rocks, probably pyroclastic flows, via submarine eruptions.
- Through mixing between sea water and volcanic glass leading to:
  - a. Vigorous reaction between cold sea water and warm glass.
  - b. Rapid cooling of the volcanic glass leading to formation of large interstices within the chilled glass.
  - c. Leaching of certain chemical elements mainly alkalis and Ca.
- Alteration of the volcanic glass and formation of smectite, associated with redistribution of Mg and Fe without significant Mg-uptake from the sea water. Redistribution of Si in materials derived from acidic precursors led to deposition of opal-CT.
- Crystallization of authigenic K-feldspars in the pore spaces formed by the dissolution of the volcanic glass. In places where the  $\text{Na}^+/\text{H}^+$  activity ratio was high, the formation of small amounts of mordenite and/or clinoptilolite was probably favoured.

Bentonite formation was followed by hydrothermal alteration which modified both the mineralogical and

chemical composition of deposits and affected their physical and chemical properties.

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