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Abstract

Bentonite deposits of Kimolos Island, Aegean, Greece were investigated in order to determine their physical and chemical properties. Testing included measurement of CEC (cation exchange capacity), swelling capacity, pH, rheological properties and some important foundry properties including green and dry compression strength, shatter index, wet tensile strength, compactability and permeability. The rheological and foundry properties are mainly influenced by the bentonite grade (smectite content) and the degree of disaggregation of the smectite quasicrystals due to the nature of the interlayer cation, the presence of mordenite and undevitrified glass shards, the degree of the oxidation of iron and the type of smectite–opal-CT interaction. Na-activation improves green compressive strength and especially wet tensile strength and decreases permeability, while its influence on the remaining foundry properties is unpredictable. Swelling properties are affected by bentonite grade, expressed by CEC, and the presence of characteristic phases (glass shards and opal-CT) decreases swelling, while zeolites increase CEC. The swelling capacity is closely related to the CEC, if smectite chemistry is controlled. It is shown that although the presence of zeolites like mordenite or small amounts of opal-CT may not affect rheological properties, the bonding properties always deteriorate. However, the presence of undevitrified glass reduces viscosity. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: bentonite; smectite; swelling; cation exchange capacity; rheological properties; foundry properties

1. Introduction

Bentonites are clays rich in smectite regardless of their mode of origin (Patterson and Murray, 1983), which are valued for their properties such as

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crystal shape and size, cation exchange capacity (CEC), hydration and swelling, thixotropy, bonding capacity, impermeability, plasticity and tendency to react with organic compounds (Highley, 1972; Odom, 1984). After treatment with acids bentonites acquire decolourizing properties and can be used in the clarification of edible and mineral oils (e.g., Srasra et al., 1989; Christidis et al., 1997). As a result they have many industrial applications including oil drilling, as a foundry sand bonding material, in iron ore and animal and poultry feed pelletization, in civil engineering, and in paints, cosmetics and pharmaceuticals, among many others (Harben, 1995).

Generalized laboratory experiments are often used for evaluation of the quality (indication of the expected performance in various applications) and grade (smectite content) of bentonites (Inglethorpe et al., 1993) and the physico-chemical parameters which control their behaviour, especially the water–clay interaction (Callaghan and Ottewill, 1974; Low, 1980; van Olphen, 1977). These experiments provide indirect information on the industrial performance of bentonites and can be used by industry in conjunction with standard tests, for more complete information. The evaluation of the quality of bentonites for use in various industries require more specific tests which are essential for the determination of particular physical properties. These tests control the suitability of a bentonite in each application by means of controlled laboratory experiments, which follow certain specifications and which simulate the use of the bentonite (e.g., A.P.I., 1969; O.C.M.A., 1973; Odom, 1984).

The Aegean Islands of Milos and Kimolos are the extractive centres for bentonite in Greece, which is the third largest world producer after the USA and the former countries of Soviet Union (ca. 1 million tonnes in 1995). In a recent contribution Christidis and Scott (1996) examined the physical and chemical properties of the Miloan bentonites and the influence of hydrothermal alteration on these properties. In this work, (a) the physical and chemical properties of the most important bentonite deposits from Kimolos island are examined, (b) the possibility for correlation between them is assessed, and (c) the factors which control them are examined.

2. Geology of the Kimolian bentonites

Kimolos is an almost entirely volcanic island (Fig. 1) consisting predominately of pyroclastic rocks ranging in age between 3.5 and 0.9 million years (Fyticas and Vougioukalakis, 1993). The geological and volcanological features of the island have been described by Fyticas and Vougioukalakis (1993). The bentonites studied are the Prassa and Loutra deposits located in the NE area of the island, and the Fanara deposit located in the southern part of the island (Fig. 1). Currently, only the Prassa deposit is exploited. The Prassa bentonite has been
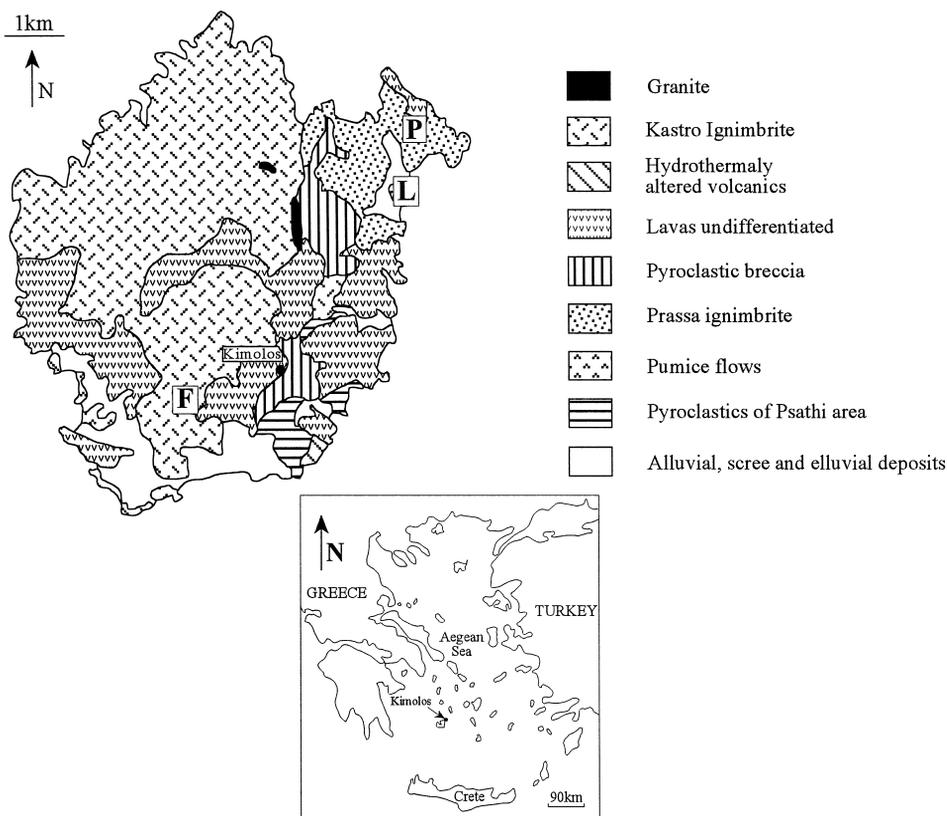
Fig. 1. Simplified geological map of the Kimolos Island modified after Fyticas and Vougioukalakis (1993). P = Prassa, L = Loutra and F = Fanara deposit.

formed at the expense of an unwelded ignimbrite deposited in shallow marine environment. The deposit consists of relatively small pockets of high quality material associated with two fault systems having N–S and NE–SW direction (i.e., it is a structurally controlled deposit). The larger outcrop, which is presented in this contribution, is a 30 m × 35 m × 10 m body which continues in depth and which can be divided into six distinct zones (Christidis and Scott, 1997; Christidis, 1998) (Fig. 2): (a) the fresh glass zone; (b) the zone of incipient alteration (smectite + glass); (c) the smectite + opal-CT zone; (d) the smectite zone (i.e actual bentonite); (e) the smectite + mordenite zone (white bentonite); and (f) the smectite + opal-CT + mordenite zone.

The Loutra bentonite is stratiform, well bedded, having light-grey colour which has been derived from fine grained volcanic ash, altered in a shallow marine environment. The degree of devitrification increases with depth, the higher sectors containing abundant fresh glass shards. The deposit is cut by fault zones, along which deposition of Fe-oxides has taken place. The Fanara
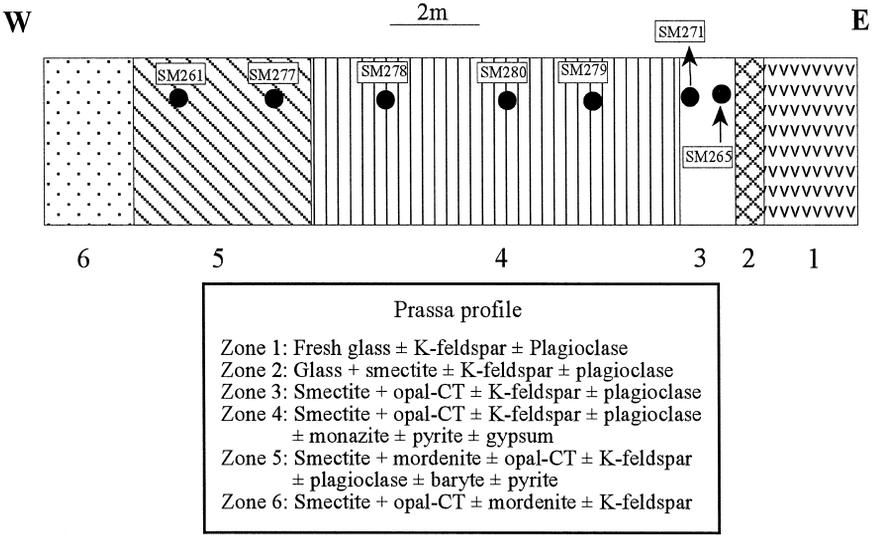
Fig. 2. Schematic cross section of the sampling site and mineralogical composition of the alteration profile in the Prassa deposit.

bentonite formed at the expense of a lapilli tuff with conglomerate texture indicating deposition of the parent material in very shallow seawater depths and epiclastic reworking. The pebble size becomes smaller in the lower topographic levels of the quarry eventually grading to volcanic sand. This indicates an increase of the depth of deposition. The higher stratigraphic horizons of this rock have been silicified. At the lower topographic levels of the quarry, a small outcrop of a high quality white bentonite derived from an unwelded ignimbrite similar to the precursor of the Prassa bentonite is noticeable.

3. Materials and methods

Sixty samples were collected from the three bentonite deposits (Fig. 1), representing both horizontal and vertical profiles. All samples were examined by X-ray diffraction for bulk and clay mineralogy with a Philips diffractometer, equipped with a PW1710 computerized control unit, operating at 40 kV and 30 mA, using Ni-filtered radiation, with the conditions described by Christidis and Dunham (1993). Epoxy impregnated polished blocks of the samples were utilized for electron microprobe analyses (EPMA) (JEOL JXA-8600 Super-probe, with a Link series 1 energy dispersive spectrometer (EDS)), using both defocused (5 μm diameter) and focused (< 1 μm wide) beam. Back scattered electron images eliminated contamination from Ti- and Fe-oxides. The condi-

tions, the assumptions and the cation assignments used for calculation of the structural formulae have been described by Christidis and Dunham (1993). The accuracy, precision and detection limits of the method are given in Dunham and Wilkinson (1978).

The materials were subsequently homogenized to a total of 13 samples according to their geological and mineralogical features corresponding to vertical profiles of the deposits. These samples were used to determine the CEC and the swelling index of the bentonites. The materials were dried at 60°C for 12 h, crushed with pestle and mortar and passed through a 125 µm sieve. The CEC, which is a direct indication of the bentonite grade (Christidis and Scott, 1993; Inglethorpe et al., 1993), was determined with a Kjeldahl microsteam apparatus after saturation with 1 M ammonium acetate. The swelling index was determined using the method of Inglethorpe et al. (1993), modified from Christidis (1992). The samples were activated with 1, 2, 3, 4, 5 and 6% Na_2CO_3. The amount of Na_2CO_3 which caused greater swelling in bentonites was considered the optimum concentration and was used as a guide for the following tests. The swelling volume provides an indirect indication of the bentonite grade (Christidis and Scott, 1993; Inglethorpe et al., 1993).

Representative samples were selected on the basis of the CEC and the swelling tests for determination of their rheological properties. The materials were dried for 12 h at 60°C, ground in a Tema mill for 45 s and passed through a 250 µm sieve, treated with the optimum concentration of Na_2CO_3 and allowed to age overnight. The apparent and the plastic viscosity and yield were determined with a 35S Fann V-G viscometer at the laboratories of the British Geological Survey, according to the OCMA specifications (O.C.M.A., 1973). In samples with apparent viscosity greater than 10 cp, filtrate loss was also determined using a Baroid 1/2-area cell, which filters over a 2.5 in. diameter area at a pressure of 100 lb/in². Complete rheograms, thixotropic loops and gel strength measurements were obtained in bentonites from the Prassa deposit. pH measurements were performed with a WPA CD30 digital pH-meter using a Russell pH-electrode.

Homogenized samples prepared from materials belonging to the same horizon in each deposit and having similar CEC and swelling properties, were used for determination of the green and dry compression strength, shatter index, compactability, permeability and the wet tensile strength in the laboratories of the British Cast Iron Research Association (BCIRA). The materials were dried at 65°C, ground in a Tema Mill and passed through a 150 µm sieve. The greensands were prepared using 92.5% Chelford silica sand, 5% bentonite and 2.5% tempering water. All samples except for the Loutra bentonite were subsequently activated in situ (i.e., during mulling) with Na_2CO_3 and the foundry properties were redetermined. The types of instruments used for sample preparation and determination of foundry properties are given in Christidis and Scott (1996).

4. Results

The mineralogy of the Kimolian bentonites studied is summarized in Table 1. All deposits contain dioctahedral smectite and silica polymorphs (opal-CT and/or quartz) as major phases, associated by plagioclase and K-feldspar. The smectites do not display considerable compositional variation (Table 2), their chemistry varying between Chambers and Tatatilla-type montmorillonite (see Güven, 1988 for a description of the smectite types). The Prassa deposit contains abundant mordenite (smectite + mordenite zone in Fig. 2) while the Loutra bentonite contains clinoptilolite in places as a minor phase. The Fanara deposit contains minor calcite and subordinate kaolinite. The existence of tiny amounts of mica, gypsum and halite was verified by EPMA. Finally, the presence of fresh glass shards in the Loutra bentonite indicates incomplete alteration of the parent rock.

The results from the CEC measurements and the swelling volumes are given in Table 3. The accuracy of CEC measurements is ± 1 meq/100 g and that of swelling volume is $\pm 5\%$ of the reported values. The values obtained reflect the differences in mineralogy of the various bentonites. As expected, in the Prassa deposit the smectite zone displays maximum swelling, while the mordenite bearing zone displays maximum CEC (Fig. 3a). Both properties display minimum values in the smectite + opal-CT zone. Sample SM271 from this zone is an exception to this trend due to the small amount of opal-CT present. In the Loutra deposit both the CEC and swelling properties increase with depth

Table 1
Mineralogical composition of the Kimolian bentonites

Mineral	Prassa	Loutra	Fanara
Smectite	M	M/Min	M
Type	Mont/nite Cheto (TA/CH)	Mont/nite Cheto (TA/CH)	Mont/nite
Fresh glass	–	Min	–
Kaolinite	–	–	Min/T ($\pm$)
Mica	T ($\pm$)	T ($\pm$)	–
Opal-CT	M/Min	M/Min	–
Quartz	–	Min	M/Min ($\pm$)
Mordenite	M/Min ($\pm$)	–	–
Clinoptilolite	–	Min ($\pm$)	–
K-feldspar	T ($\pm$)	T ($\pm$)	Min
Plagioclase	T/Min	M/Min	?
Calcite	–	–	M/Min ($\pm$)
Gypsum	T ($\pm$)	–	–
Halite	T ($\pm$)	–	–

M = major phase, Min = minor phase, T = accessory phase. TA = Tatatilla-type montmorillonite, CH = Chambers-type montmorillonite.

Table 2
Electron microprobe microanalyses of smectites from the Kimolian bentonites

	Prassa deposit $n = 21$				Loutra deposit $n = 16$			
	Mean	sd	max	min	Mean	sd	max	min
SiO_2	51.98	2.17	56.72	48.30	58.56	2.29	62.47	55.15
Al_2O_3	18.26	0.75	20.21	16.93	20.30	0.87	21.36	19.05
Fe_2O_3	1.73	0.17	2.06	1.48	1.62	0.22	1.94	1.26
MgO	3.92	0.34	4.64	3.43	4.51	0.34	4.90	3.91
CaO	1.00	0.34	1.62	0.56	1.04	0.11	1.15	0.88
Na_2O	0.45	0.25	0.80	0.00	0.30	0.37	1.04	0.00
K_2O	0.53	0.30	1.08	0.00	0.00	–	–	–
Total	77.87				86.37			
Structural formulae per 11 atoms of O								
Si	3.92	0.02	3.97	3.88	3.95	0.02	3.98	3.90
Al^{IV}	0.08	0.02	0.12	0.03	0.05	0.02	0.10	0.02
Al^{VI}	1.54	0.02	1.59	1.50	1.57	0.02	1.59	1.54
Mg	0.44	0.03	0.48	0.39	0.45	0.02	0.48	0.40
Fe^{3+}	0.10	0.01	0.11	0.09	0.08	0.01	0.10	0.07
VI cations	2.08	0.02	2.11	2.04	2.10	0.01	2.12	2.09
Ca	0.08	0.03	0.13	0.04	0.08	0.01	0.09	0.06
Na	0.06	0.04	0.12	0.00	0.04	0.05	0.14	0.00
K	0.05	0.03	0.11	0.00	0.00	–	–	–
L. charge	0.28	0.05	0.37	0.19	0.20	0.04	0.27	0.15
I. charge	0.27	0.05	0.37	0.19	0.19	0.04	0.27	0.15

Analyses of the Prassa deposit are from Christidis and Scott (1997).
n = number of analyses, sd = standard deviation, min = minimum value, max = maximum value.
L. charge = layer charge, I. charge = interlayer charge.

(Fig. 3b). Although the material contains clinoptilolite it has a low CEC, due to the limited devitrification (presence of fresh glass shards) and the presence of opal-CT. These factors also dictate the inferior swelling capacity of the material compared to the smectite zone in the Prassa deposit. The volcanic conglomerate (SM306) in the Fanara deposit has also inferior cation exchange and swelling properties reflecting the moderate smectite content (Table 1). On the other hand, the white bentonite which crops out in this deposit (SM307), has a high CEC and good swelling properties, i.e., it has similar properties to SM271 from the Prassa deposit, although it contains small amounts of opal-CT (Fig. 3a).

Swelling volume and CEC display a well expressed linear relationship (solid line in Fig. 4). However, the samples from the mordenite bearing zone, Prassa deposit, deviate from the overall trend. A similar but less well determined linear correlation has been observed in the Miloan bentonites (Christidis and Scott, 1993). The dashed line 1 in Fig. 4 indicates the theoretical trend expected to hold considering that the essentially monomineralogic samples from the smectite zone, Prassa deposit, display maximum swelling and that a smectite-free rock

Table 3
Cation exchange capacity (CEC) and swelling volumes of bentonite samples from the Prassa, the Loutra and the Fanara deposits

Prassa deposit				Loutra deposit				Fanara deposit		
	CEC (meq/100 g)	Swelling index (ml gel/10 g clay)			CEC (meq/100 g)	Swelling index (ml gel/10 g clay)			CEC (meq/100 g)	Swelling index (ml gel/10 g clay)
SM261	124.8	131 (4)		SM295	40.75	33 (3)		SM306	35.25	38 (2)
SM277	126.35	110 (4)		SM296	46	40 (3)		SM307	90.25	230 (5)
SM278	94.9	189 (4)		SM297	56.55	59 (4)				
SM279	99.8	235 (4)		SM298	59.25	80 (3)				
SM280	99.55	206 (4)								
SM271	94.3	205 (5)								
SM265	63.95	121 (3)								

In the Fanara deposit, SM307 comes from the white bentonite body, while SM306, from the volcanic conglomerate (see text for geological description of the deposits).
The values in parentheses are the amounts of Na_2CO_3 (%) added to obtain maximum swelling.
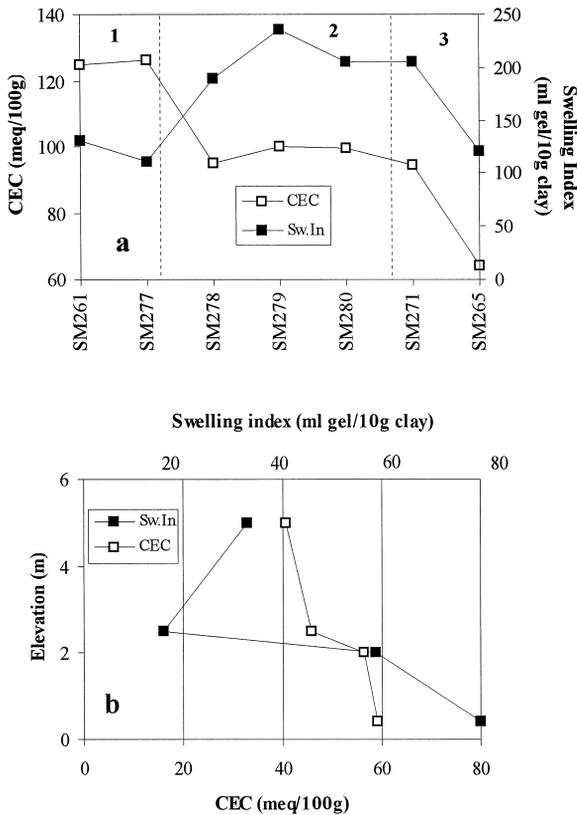
Fig. 3. Variation of the CEC (meq/100 g) and swelling index (ml gel/10 g clay) (a) Prassa deposit. 1 = Mordenite bearing zone, 2 = smectite zone, 3 = smectite + opal-CT zone. The length of zone 2 is 8 m. (b) Loutra deposit.

does not swell. Line 2, which is subparallel to the trend observed in this study, expresses the overall linear relationship which is observed in the Miloan bentonites (Christidis and Scott, 1993). Note that the smectites present in the deposits studied have similar chemical characteristics; they are Chambers–Tatatilla-type montmorillonites (Table 2).

Except for SM265 which has a low CEC, the samples which were collected from the Prassa deposit were activated with 4 and 5% sodium carbonate, while those from the Loutra deposit with 3% carbonate. Also, sample SM307 was activated with 5% and SM306 with 3% carbonate. The amount of sodium carbonate added depends on both the abundance of Na in the exchangeable sites and the smectite content in the bentonite. Although both factors might be responsible for the lower amount of Na_2CO_3 added in the Loutra deposit and samples SM265 and SM306, the low grade of these deposits (abundance in opal-CT and undevitrified glass shards), expressed by the low CEC, is a more plausible explanation. In the Prassa deposit and SM307 (Fanara deposit) the
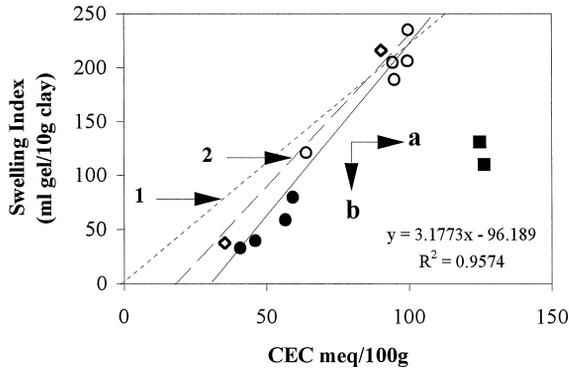
Fig. 4. CEC vs. swelling index in the Kimolian bentonites studied. The dashed line 1 corresponds to the theoretical regression line in considering that the bentonites from the smectite zone in the Prassa deposit display maximum swelling and a smectite-free bentonite does not swell. Line 2 corresponds to the regression line obtained for the Miloan bentonites (after Christidis and Scott, 1993). Arrow (a) corresponds to the deviation from the theoretical trend caused by zeolites, and arrow (b) corresponds to the deviation caused by glass shards and opal-CT (see Section 5). Open circles = smectite zone, Prassa deposit, solid circles = Loutra deposit, diamonds = Fanara deposit. Solid squares = mordenite bearing zone, Prassa deposit.

higher amount of Na_2CO_3 added is attributed to the predominance of Ca as an exchangeable cation (Christidis, 1992).

The results of viscosity measurements are given in Table 4. The accuracy of the measurements is ± 0.5 cp of the reported values. The samples from the

Table 4
Rheological properties of the Kimolian bentonites studied

Deposit	Apparent viscosity (cp)	Plastic viscosity (cp)	Yield (kg/m^2)	Filtrate loss (cm^3)	pH
Prassa					
SM261	15.5	7	0.83	10.0	7.7
SM277	36	14.5	1.05	7.2	7.5
SM278	25	7.5	1.71	7.6	8.3
SM279	9.8	7	0.27	7.0	8.0
SM280	11.3	6.5	0.46	6.8	8.5
SM271	25	11	1.32	8.1	7.7
Loutra					
SM295	1.5	1.5	0	–	8.2
SM296	1.3	1.5	0.07	55	8.3
SM297	2.5	2	0.1	18.5	7.6
SM298	3.7	2.5	0.12	10.0	7.4
Fanara					
SM306	2.5	2	0.05	18	6.8
SM307	114	68	4.49	4.0	7.2

Loutra bentonite and sample SM306 (Fanara deposit) develop very poor rheological properties which do not meet OCMA specifications (O.C.M.A., 1973). The samples from the Prassa deposit develop higher viscosity. However, except for SM278, samples from the smectite zone which contains more than 90% smectite develop low apparent viscosity and do not meet OCMA specifications. On the contrary, SM271 from the smectite + opal-CT zone and samples from the mordenite-bearing zone develop high viscosity, meeting the OCMA specifications. Moreover, SM307 which contains small amounts of opal-CT yields exceptionally viscous suspensions (Table 4). With the exception of SM307 and SM277 the Kimolian bentonites have low plastic viscosity, compared to Wyoming bentonites (Elzea and Murray, 1990), similar to the Miloan bentonites (Christidis and Scott, 1996). Thus, Na-activation increased only the apparent viscosity in these samples; the rheograms of the Na-treated materials have been shifted to higher shear strength values, but the linear part must be parallel to that of the raw materials.

Most of the bentonite samples examined exhibit neutral to slightly alkaline pH (Table 4). The samples from the smectite zone at the Prassa deposit yielded pH values greater than 8, similar to the bentonites from Groups 1 and 2 in Milos (Christidis and Scott, 1996). Also, the pH of bentonites in the Loutra deposit decreases with depth. The lowest pH was recorded in sample SM306 (Fanara deposit), which contains kaolinite, reflecting the influence of hydrothermal alteration. Finally the filtrate loss values obtained (Table 4) vary between broad limits. In general the Prassa bentonite, the lower sectors of the Loutra deposit and the white bentonite body in the Fanara deposit (SM307) yielded low filtrate loss indicating good filter cake characteristics, while the higher sectors of the Loutra deposit and SM306 yielded a high filtrate loss.

The complete rheograms of SM278 and SM280 from the smectite zone, Prassa deposit, are shown in Fig. 5a. From the slope of the linear part of the
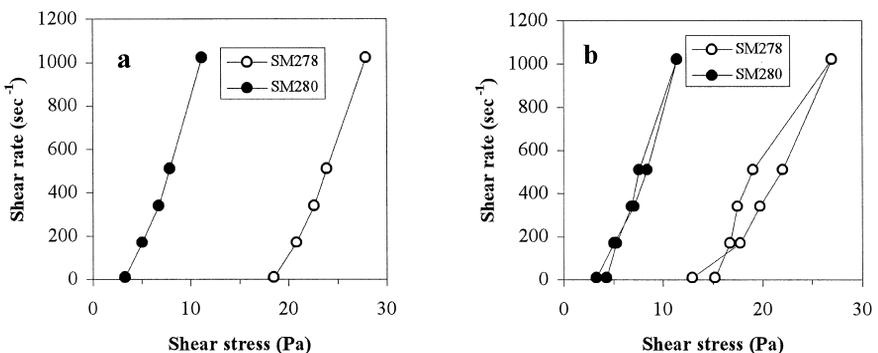
Fig. 5. Complete rheograms (a) and thixotropic loops (b) of materials from the smectite zone in the Prassa deposit.

rheograms it is inferred that SM278 develops higher plastic viscosity than SM280; the results corroborate the plastic viscosity measurements performed according to the OCMA specifications (Table 4). The thixotropic loops (Fig. 5b) indicate that SM278 is more thixotropic than SM280 (the thixotropic loop of the former bentonite sample is wider). Due to the similar treatment of the materials, the influence of gel preparation ('shear history factor' Mewis, 1979) probably has not affected the thixotropic loops. Both materials are thixotropic under high and antithixotropic under low rates of shear. This behaviour is rather common in bentonites with these pH values (Brandenburg and Lagaly, 1988).

The foundry properties in both the untreated and the sodium activated bentonites are listed in Table 5. The accuracy of the shatter index and compactability measurements is $\pm 2\%$ and $\pm 1\%$ of the reported values, respectively, while that of wet tensile strength is ± 1 g/cm^2. It is evident that the Loutra bentonite has very poor foundry properties (Table 5). The untreated materials from the smectite zone in the Prassa deposit display higher green compression strength, shatter index and wet tensile strength and lower permeability than the materials from the mordenite-bearing zone, the smectite + opal-CT zone, the Loutra bentonite and SM307 (Table 5). The wet tensile strength of all untreated materials is low. Positive relationships hold between green compression strength and both the shatter index and the wet tensile strength (Fig. 6a,b) and between compactability and shatter index (Fig. 6c). It is evident that the shatter index increases up to a maximum remaining essentially constant thereafter (Fig. 6a), in accordance with Parkes (1971). The dry compression strength values also vary in a rather systematic way in the various bentonite samples; in the Prassa deposit it decreases from the mordenite bearing zone to the smectite + opal-CT zone (Table 5), and has a maximum value in SM307. The Loutra bentonite displays low dry compression strength. Except for the Loutra deposit, compactability is always greater than the optimum 45–50%

Table 5
Foundry properties of the Kimolian bentonites

Deposit	Green compression strength (kPa)	Shatter index (%)	Compactability (%)	Dry compression strength (kPa)	Wet tensile strength (g/cm^2)
Prassa					
A	52.4	62	56	695.8	10
B	87.6 (96.5)	73 (74)	58 (57)	595.1 (380)	14 (34)
C	70.3 (96.5)	73(68)	58 (50)	595.1 (344.8)	14 (25)
D	55.9 (64.1)	63 (66)	54 (58)	474.4 (695.8)	8 (29)
Fanara	55.9 (64.8)	66 (63)	57 (58)	806.8 (644.1)	11 (24)
Loutra	42.8	43	47	200	3

The values in parentheses correspond to Na-treated bentonites.
A = mordenite bearing zone, B,C = smectite zone, D = smectite + opal-CT zone.
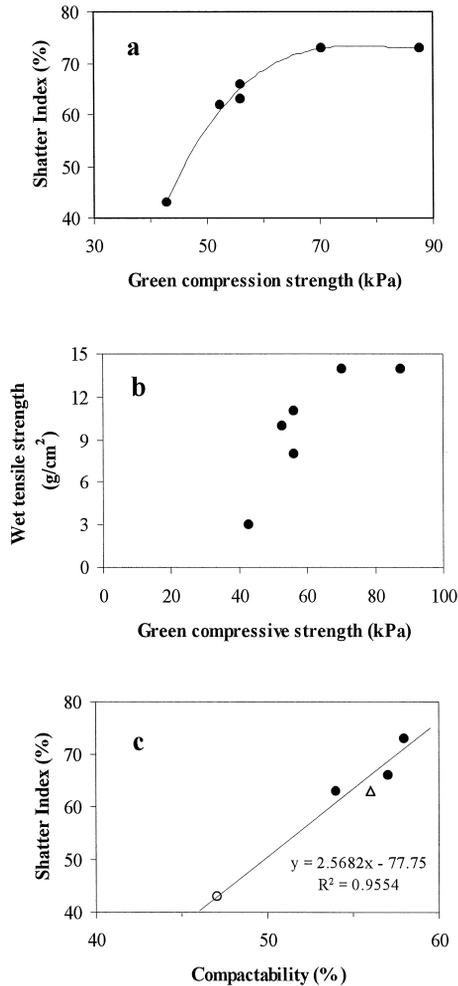
Fig. 6. Correlation of foundry properties in the untreated Kimolian bentonites. Open circle = Loutra deposit, solid circles = Prassa deposit, open triangle = Fanara deposit.

(Table 5); it is higher in the smectite zone, Prassa deposit and SM307 and lower in the smectite + opal-CT zone, Prassa deposit.

Activation with sodium carbonate increased the green compression strength, and the wet tensile strength (up to 350%), and decreased permeability; however, systematic changes are not observed in the remaining properties (Table 5). Except for the green compression strength similar trends were observed for the Miloan bentonites (Christidis and Scott, 1996). Na-activation is known to produce unpredictable changes in physical properties (Boenisch and Patterson, 1967; Stephens and Waterworth, 1968).

5. Discussion

5.1. Correlation between properties of bentonite

The positive correlation between CEC and swelling index (solid line in Fig. 4) underlines the importance of the grade component (Christidis and Scott, 1996) for the swelling of bentonites. The limited scattering observed reflects the rather insignificant influence of the layer charge on both properties, because the smectites present in the bentonites have similar chemical characteristics (Table 2). However, the regression line does not pass through the origin as expected, if it is considered that a smectite-free material does not swell (theoretical line 1). All other samples plot also on regression line 2, obtained for the Miloan bentonites (Christidis and Scott, 1993). Moreover, the smectite rich samples plot on theoretical line 1 as well. Note that the regression line 2 also deviates from the theoretical line 1, although to a lesser degree. Again, deviation from line 1 is maximized for low grade bentonites, which in the case of Milos contain abundant silica polymorphs, especially opal-CT.

The CEC gives a good estimation of the proportion of impurities in bentonites if zeolites are absent. Although it may vary due to the different layer charge of the various types of smectites (cf. Schultz, 1969; Newman and Brown, 1987), in this study smectite chemistry does not vary among the various deposits (Table 2), i.e., the pure swelling factor (Christidis and Scott, 1996) is minimized; therefore, it is believed that deviations from the theoretical regression line 1 provide valuable information about the mineralogical influence on both properties. In Fig. 4 it is observed that the presence of either opal-CT and fresh glass (the solid circles correspond to the Loutra bentonite which contain abundant glass shards) cause a migration of plotting points from theoretical line 1 parallel to the ordinate, i.e., the swelling axis (indicated by arrow b). The influence of glass seems more significant. The type of association of fine grained opal-CT with smectite might be important, because intimate intergrowths of these minerals are expected to retard separation of smectite flakes reducing swelling (Christidis and Scott, 1996). The influence of other coarse grained minerals without swelling or cation exchange properties (e.g., feldspars, carbonates, sulphates) is not known, although it is expected to be less important. This is because, zeolites which possess CEC substantially higher than smectites, cause migration of the plotting points from the theoretical line 1 parallel to the CEC axis (arrow a), without affecting swelling.

The strength of a bentonite gel has been attributed to the repulsive forces of the interactive double layers (secondary electroviscous effect) or/and to the formation of three-dimensional band-like structures and the formation of the effective double layers is a result of swelling (Callaghan and Ottewill, 1974; Rand et al., 1980; Permien and Lagaly, 1994). Therefore, a relationship between plastic viscosity and swelling is expected, which is observed (Fig. 7a). Contrary
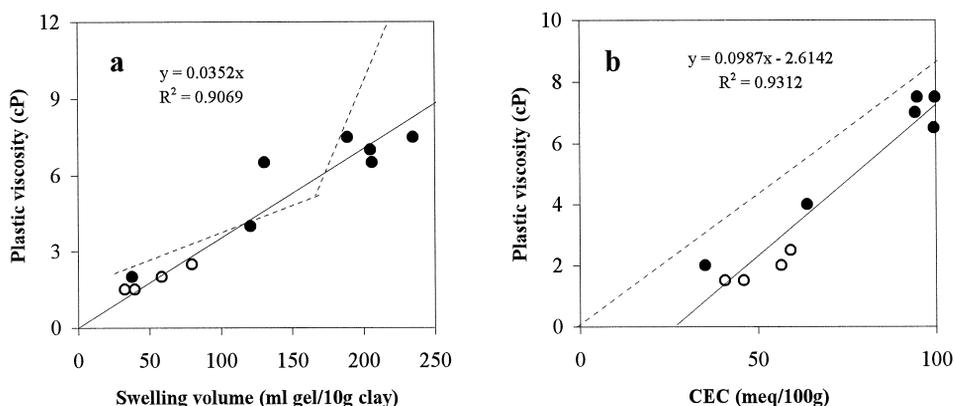
Fig. 7. Correlation between plastic viscosity and (a) swelling and (b) CEC. The dashed lines correspond to the regression lines obtained for the Miloan bentonites (Christidis and Scott, 1996). Solid circles = Prassa deposit, open circles = Loutra deposit.

to the Miloan bentonites in which a dual trend is observed, suggesting that high viscosity develops only after smectite flakes have swollen beyond a certain limit (Christidis and Scott, 1996), in their Kimolian counterparts a single linear relationship is observed. This discrepancy can be explained from the uncertainty in the exact location of the breaking point of the curves in the Miloan bentonites and the variable degree of disaggregation of smectite quasicrystals (Christidis and Scott, 1996) as well as the similar crystal chemistry of smectites in the Kimolian bentonites; smectites in the Miloan bentonites are extremely heterogeneous (Christidis and Scott, 1996).

Similar to the Miloan bentonites a well expressed ($R^2 = 0.93$) positive linear trend holds between CEC and plastic viscosity (Fig. 7b), suggesting that in bentonites with similar smectite chemistry, materials with higher grade yield more viscous suspensions. However, the regression line does not pass through the origin as in Miloan bentonites (dashed line in Fig. 7b). Moreover, it is evident that the Kimolian bentonites develop lower plastic viscosity than their Miloan counterparts. The observed deviation is caused principally by the Loutra bentonites which contain fresh glass shards. If the samples from the Loutra bentonite are excluded the regression line passes close to the origin. Finally, contrary to the Miloan bentonites, no relationship holds either between grade and foundry properties or between rheological and foundry properties in their Kimolian counterparts. Moreover, it is observed that high grade bentonites with good rheological properties have rather inferior foundry properties (e.g., SM307).

5.2. Possible factors affecting rheological and foundry properties

The Kimolian bentonites display considerable variation in their rheological properties. Considering the high CEC of several materials (e.g., the smectite

zone in Prassa deposit) both the apparent and the plastic viscosity are rather low compared to commercial Wyoming bentonites (Elzea and Murray, 1990). Treatment with Na_2CO_3 is expected to homogenize interlayer cation differences, unless activation was incomplete due to incomplete disaggregation of the smectite quasicrystals. The shape and size of the smectite particles should also be considered because the original Ca-rich particles are expected to form long stacks consisting of several layers (Kleijn and Oster, 1982; Brandenburg and Lagaly, 1988). Organic matter, which might affect the rheological properties of the clay suspension by adsorption on the clay surface (van Olphen, 1977), is absent.

In a previous study on the Miloan bentonites, Christidis and Scott (1996) considered the influence of abundant fine-grained opal-CT on viscosity; if opal-CT is intimately associated with smectite then the formation of a rigid gel-structure might be retarded. Moreover, the close association of these minerals might prevent disaggregation of the smectite quasicrystals retarding Na-activation. These observations were confirmed in this study, because only materials with minor amounts of opal-CT (SM271, SM307) yielded high viscosity. In these materials, which were derived from acidic precursors, having Si/Al ratio substantially higher than the neoformed smectites (Christidis, 1998), Si-rich phases are not intimately associated with smectite. This probably indicates high fluid flow and high water/rock ratios during bentonitization (Christidis and Scott, 1996). Christidis (1998) has calculated a 13:1 water:rock ratio during bentonitization in the Prassa deposit. Except for opal-CT, the viscosity of bentonite suspensions seems to be affected by the presence of fresh glass shards (Fig. 7). Although the exact influence of glass shards on viscosity is not well understood, it seems that their presence is detrimental.

Two additional factors which might affect rheological properties are the Na/(Ca + Mg) ratio in the untreated materials and the oxidation state of iron. On the contrary, variability of smectite layer charge is not expected to affect rheological properties due to the similarity of smectite chemistry in the various Kimolian bentonites (Table 2). The oxidation state of iron might affect the rheological properties of bentonites (Alther, 1986), because ferrous iron leads to the formation of thicker smectite stacks than those containing ferric iron (Stucki and Tessier, 1991), especially in the presence of Ca ions. The swelling tests indicate a low Na/(Ca + Mg) ratio in the exchangeable cations. Therefore, thick quasicrystals are expected to form in bentonite suspensions (Schramm and Kwak, 1982) retarding disaggregation and thus Na-activation. Thus, if ferrous iron is present, activation might not be successful, unless the quasicrystals are broken by intensive mechanical action (Kleijn and Oster, 1982). The Na-bentonites have good rheological properties in contrast to their Ca counterparts, because the latter form thick crystallites (van Olphen, 1977; Kleijn and Oster, 1982; Brandenburg and Lagaly, 1988). It has been shown that substantial mobilization of Fe under reducing conditions has taken place during the

formation of the Prassa deposit (Christidis, 1998). Although oxidation of Fe due to exposure of the material in the atmosphere is expected, the colour characteristics of the smectite zone indicate that ferrous iron might also be present (Christidis and Scott, 1997).

Surprisingly, the mordenite-bearing zone in the Prassa deposit is characterized by high apparent viscosity which meets OCMA specifications, although the swelling indices of these materials are rather low (Tables 3 and 4). The reason for this discrepancy might be the presence of abundant mordenite in the bentonite. The treatment of bentonites with sodium carbonate during preparation of viscous suspensions is expected to cause Na for (Ca + Mg) exchange in smectites. Mordenites are predominately Na–Ca rich zeolites (Gottardi and Galli, 1985) although those mordenites from Prassa contain also substantial amounts of K in places (Christidis, 1992). Therefore, during Na-activation most of the offered carbonate is expected to be consumed for ion exchange in smectite. During ageing of the clay suspensions (O.C.M.A., 1973), silt size mordenite crystals are expected to settle yielding a more dilute smectite suspension, compared to bentonites from the smectite zone, facilitating penetration of the sodium ions and subsequently disaggregation of the smectite quasicrystals. The fact that the smectites from the different zones of the Prassa deposit have similar chemical characteristics suggests that samples SM279 and SM280 should yield viscous suspensions if they are activated successfully.

The foundry properties of the Kimolian bentonites are also affected by mineralogy. The presence of mordenite, opal-CT and undevitrified glass shards affected adversely the green compression strength and the shatter index of both the untreated and the Na-activated bentonites (Table 5). Thus, the presence of mordenite (mordenite-bearing zone, Prassa deposit), and especially, minor amounts of opal-CT (SM271 and SM307) are adequate to cause inferior foundry properties relative to zeolites opal-CT-free bentonites. On the contrary, these materials develop high viscosity. Therefore, similar to the Miloan bentonites (Christidis and Scott, 1996), although the presence of impurities might not be important for rheological properties, it is crucial for foundry properties, probably because (a) they obstruct the formation of even coatings and the development surface tension between sand grains and smectite flakes (Christidis and Scott, 1996), and (b) they effectively dilute the smectite content in the sand–bentonite mixture.

All high grade bentonites develop high dry compression strength but low wet tensile strength, indicating the presence of exchangeable Mg (Stephens and Waterworth, 1968). The low wet tensile strength is attributed to the fact that the water which migrates from the dehydrated zones is in a liquid form in Ca–Mg smectites (Odom, 1984). If the interlayer water exceeds the swelling capacity of the Ca–Mg smectites it probably remains in liquid form leading to a weaker mould (Odom, 1984). The significant increase of the wet tensile strength after Na-treatment indicates an increasing capacity of the bentonites to retain the

water released from the dehydrated zones, due to an increasing swelling capacity. Furthermore, it suggests that the original Na/Ca ratio might not be the single factor affecting this property, if activation is consistent. The same might also be the case for the untreated bentonites.

The relationship between the green compression strength and the shatter index (Fig. 6a) is expected because both properties depend on the green bonding properties of the bentonites (B.C.I.R.A., 1985). An increase of the mould hardness, expressed by the shatter index, is followed by an increase of the green compression strength; the shatter index increases first but then it remains constant (Parkes, 1971), as observed in this study. The relationship between the wet tensile strength and the green compression strength (Fig. 6b) suggests that the bonding strength of a greensand and the mould hardness might increase with the ability of the material to withstand collapse in the water condensation zone (Stephens and Waterworth, 1968). Also, the relationship between shatter index and compactability (Fig. 6c) indicates that the hardness of the mould is related to the flowability of the greensand, probably because the bond strength, as expressed by both the adhesive and the cohesive strength, affects compactability (Caine and Toepke, 1967). Therefore, the greensands which provide a denser mould are tougher and can probably withstand handling better than less compactable ones.

6. Conclusions

The study of the physical and chemical properties of some bentonite deposits from Kimolos Island Greece, led to the following conclusions.

(a) The variability of most physical and chemical properties of bentonites is related to the differences in the non clay mineralogy, because smectite chemistry is controlled. The presence of undevitrified glass and opal-CT is harmful for most physical and chemical properties and hence for most technological applications of bentonites. Nevertheless if opal-CT is an accessory phase it might not be detrimental for certain applications.

(b) The swelling capacity of the Kimolian bentonites is closely related to the CEC (i.e., the bentonite grade), if smectite chemistry is strictly controlled. The presence of undevitrified glass and opal-CT reduce swelling, while zeolites increase CEC without affecting swelling.

(c) Plastic viscosity depends both on the swelling capacity and the amount of smectites present in the bentonites. Undevitrified glass shards reduce viscosity, while zeolites seem to enhance the formation of viscous suspensions. Several high grade bentonites do not yield viscous suspensions due to incomplete disaggregation of smectite quasicrystals, which leads to incomplete diffusion of sodium in the exchangeable sites during Na-activation. In the case of the Kimolian bentonites disaggregation of smectite quasicrystals depends on the

presence of opal-CT in close association with smectite crystallites, the oxidation state of iron and the original Ca/Na ratio in the interlayer sites of smectites.

(d) Although the presence of impurities might not be important for rheological properties, it is crucial for foundry properties. Even small amounts of non clay minerals like opal-CT and zeolites, commonly present in bentonites, reduce the bonding strength of bentonites without affecting rheological properties.

(e) Due to their physical properties, the materials from the smectite and the mordenite-bearing zones in the Prassa deposit and the white bentonite from the Fanara deposit can be used in both the foundry and the drilling industry, if they are activated successfully. On the other hand, the Loutra bentonite and the bulk material in the Fanara deposit are not suitable materials for industrial applications.

Acknowledgements

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