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COLOUR AND RHEOLOGICAL PROPERTIES OF SOME WHITE BENTONITES FROM MILOS AND KIMOLOS ISLANDS

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ABSTRACT

The colour and the rheological properties of some white bentonites from the islands of Milos and Kimolos were examined in order to evaluate these materials and to establish the factors which affect their properties. The data obtained show that the Miloan white bentonites have inferior colour properties compared with their Kimolian counterparts. This is because in Milos the major Fe-bearing phase is Fe-oxides causing red colourations and thus deteriorating the colour properties of the white bentonites, while in Kimolos iron is bound mainly by smectite. The inferior rheological properties of the Miloan white bentonites has been attributed to the presence of abundant opal C-T which prevents smectite crystallites of forming a rigid gel, thus developing a relatively low yield stress.

INTRODUCTION

The term white bentonite is applied to smectite-rich clays which combine the well known physical properties of bentonites (gelling properties, high cation exchange capacity, swelling power) with properties like whiteness and brightness (Clarke, 1985, Russell, 1991). These materials are used in a variety of industrial applications, including electrical ceramics, pharmaceuticals, cosmetics, toiletries, and household products like detergents.

Despite the increasing importance of these special clay materials they seem to have been neglected as far as scientific contributions are concerned. This is especially true for the Greek white bentonites although they have been exploited for many years. The only existing references are those of Clarke (1985) and Russell (1991). The latter stressed the importance of white bentonites of Kimolos and characterized them as "special grade white bentonites", without further information. Also, Marcopoulos and Christidis (1988) provided data about the mineralogical assmblages of some white bentonites among the smectite-rich clays of Kimolos they studied.

The purpose of this contribution is to provide data about the useful properties of some of the Greek white bentonites and to make comparisons among the different deposits.

LOCATION AND GEOLOGY OF THE DEPOSITS

Two deposits of white bentonites were studied. The first is located in the area of Ano Komia in the eastern part of Milos (Fig. 1a), while the second is in NE Kimolos, in the Prassa area (Fig. 1b). The deposit in Ano Komia, Milos is composed of two bentonite horizons (Fig. 2a). The lower horizon is a grey

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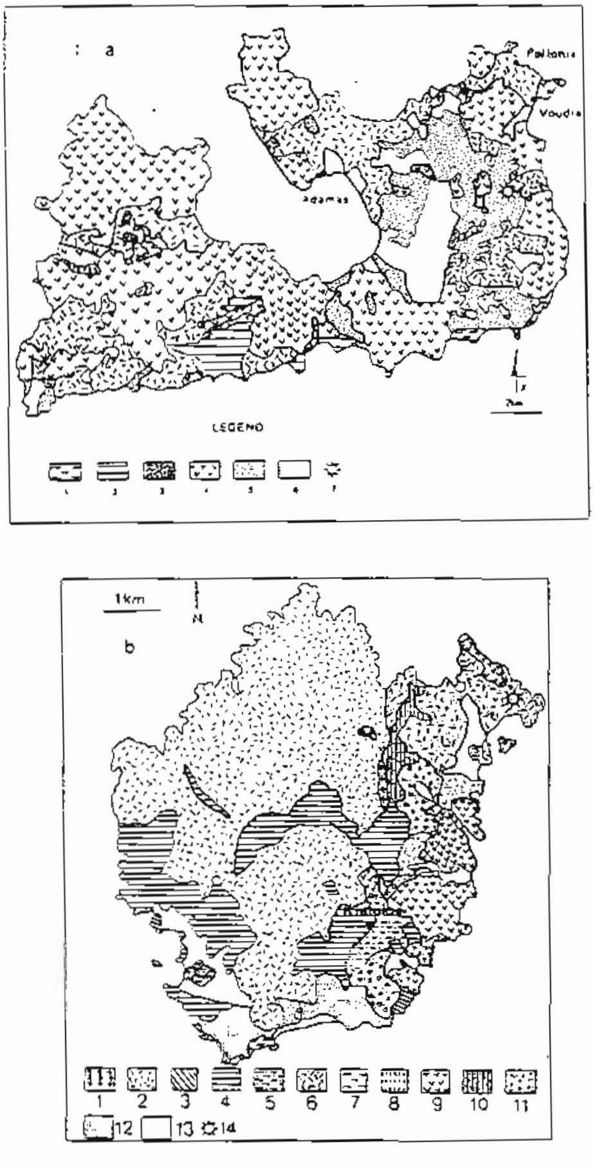

Figure 1. Geological maps of the study areas: a) Milos Island (modified after Fyticas et al., 1986), b) Kimolos Island (modified after Fyticas & Vougioukalakis, 1992). Key to the numbers: a) 1=metamorphic basement, 2=Neogene sediments, 3=pyroclastic rocks undifferentiated, 4=lavas undifferentiated, 5='green lahar, 6=Alluvial deposits, 7=Ano Komia deposit. b) 1=granitic body, 2=Kastro ignimbrite, 3=hydrothermally altered volcanic rocks, 4=andesitic and dacitic dykes, lava flows and domes, 5=Kimolos village breccia, 6=ignimbrite of Prassa area, 7=pumice flows, 8=Maar-type pyroclastics, 9=lava flows of the Geronicola area and domes and flows of the Psachi area, 10=nuee' ardente pyroclastic breccia of the Korakies area, 11=reworked pyroclastic breccia of the Korakies area, 12=Alluvial deposits, 13=scree and beach deposits, 14=location of the Prassa bentonite.

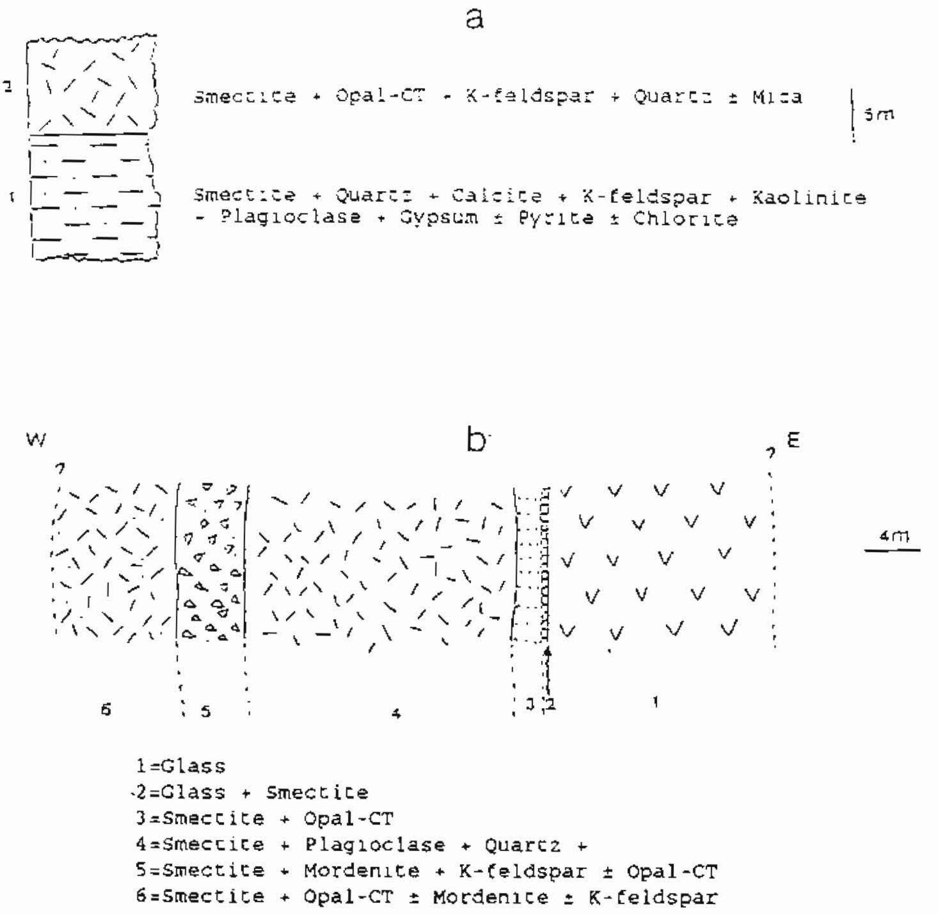

Figure 2. Sections of the white bentonite deposits a) stratigraphic section of the Ano Komia deposit, Milos. b) vertical section through the Prassa deposit, Kimolos.

lapilli-tuff which has been altered to bentonite. It has an exposed thickness varying from 10 to 20m. It has been affected by intense hydrothermal alteration caused by the circulation of S-rich fluids. The higher stratigraphic horizon is a white bentonite, formed from alteration of a volcaniclastic rock, possibly a pyroclastic flow. In places stainings of Fe-oxides are common.

The deposit of Prassa, Kimolos has been formed at the expense of an unwelded pumice flow (ignimbrite). Several white bentonite bodies have been recognized. The main body is dominated by the development of six different alteration zones. The white bentonite constitutes a 5m thick zone situated between a plastic grey bentonite, and a light grey-white opal-bearing bentonite (Fig. 2b).

EXPERIMENTAL METHODS

All analyses were carried out in the Geology Department, University of Leicester, unless stated. Mineralogical investigation was carried out with XRD methods, using a computer controlled Philips PW1729 X-Ray Diffractometer. Rock powders, randomly orientated were used for mineralogical investigation of bulk samples. Characterization of the silica polymorphs was made according to the terminology of Jones & Segnit (1971). The -2μm clay fractions were separated by means of sedimentation methods, dropped on glass microscopic slides, treated with ethylene-glycol at 70^{o}C for 16h and X-rayed immediately. Chemical analyses were made by means of XRF method, using an ARL 8420^{+} Spectrometer.

Colour measurements were carried out using an Evans Electroselenium Limited (EEL) single beam reflectance spectrophotometer equipped with a DS29 Unigalvo Recording Unit of Diffusion Systems. Measurements followed the CIE system. The light source used was *illuminant C*, the observer was the *1931 2o standard observer*, and the geometry of the illumination and observation had a $45^{o}/90^{o}$ arrangement. For each sample, the reflectivity corresponding to the red, green and blue primary colours was determined. The values obtained were mathematically transformed to the X, Y, and Z tristimulus values respectively. The reflectivity value obtained from the green filter is unchanged during transformation; therefore it is equal to the the Y tristimulus value. The Y tristimulus value corresponds to the lightness or brightness of the colour. The standard used was a ceramic tile calibrated by the British Ceramic Research Ltd against the perfect white diffuser. For selected samples the whole spectrophotometric curve was constructed using $MgCO_3$ as a standard. All samples were ground in a Tema Mill for 10 minutes and passed through a 125μm sieve (BS 410). Since sample preparation is very important in colour properties (Scott, 1990) care was taken to make the preparation method consistent for all samples.

Viscosity measurements were conducted with a Fann Viscometer type 35S Fann V-G meter at the British Geological Survey, according to the O.C.M.A. specifications (OCMA, 1973). The viscometer has been described by Savins and Roper (1954). The properties measured are apparent viscosity, plastic viscosity and yield.

RESULTS AND DISCUSSION

a) Colour measurement.

The colour measurement values obtained (Table 3) clearly demonstrate that the white bentonite from Prassa deposit exhibits very high brightness (values well in excess of 90% in many samples *i.e* higher than those of St. Austell kaolin). The corresponding values for Milos white bentonites are lower. In other words Kimolos bentonites are whiter materials than those of Milos. This can also be observed from the relevant spectrophotometric curves (Figure 4). Nevertheless, Milos bentonites are still characterized by high reflectance values which in some cases are as high as those from Kimolos.

The factors which affect colour in white pigments include both physical and chemical parameters_(Scott 1992). Important physical parameters are the mean particle size and shape and particle size distribution. The chemical parameters

Table 3

Colour measurent results for the white bentonites of Milos and Kimolos Islands. The values quoted correspond to reflectance. X, Y, and Z are the tristimulus values for the primary colours (red, green and blue respectively)

REFLECTANCE

Sample	**X**	**Y**	**Z**
	Ano Komia deposit, Milos		
SM146	71.9	77.8	82.6
SM149	80.9	82.4	92.5
SM150	73.5	75.8	79.5
SM153	77.2	80.5	82.2
SM155	74.3	75.0	85.2
SM156	84.4	86.0	98.6
	Prassa deposit, Kimolos		
SM258	88.0	90.0	101.0
SM261	86.8	88.9	98.5
SM266	90.1	91.4	104.5
SM268	89.9	91.7	102.6
SM271	88.9	90.6	102.2
SM277	85.6	88.0	96.1
SM280	72.0	73.6	82.8
SM282	90.1	92.0	103.7

Table 4

Viscosity measurements for the white bentonites from Milos and Kimolos. SM156 comes from the Ano Komia deposit, Milos, the others from the Prassa deposit, Kimolos.

Sample	**Apparent Viscosity (Centipoise)**	**Plastic Viscosity (centipoise)**	**Yield ($lb/100ft^2$)**	**pH**
SM156	10.3	5.0	10.5	7.5
SM261	15.5	7.0	17.0	7.7
SM268	6.3	4.0	4.5	6.9
SM277	36.0	14.0	21.5	7.5

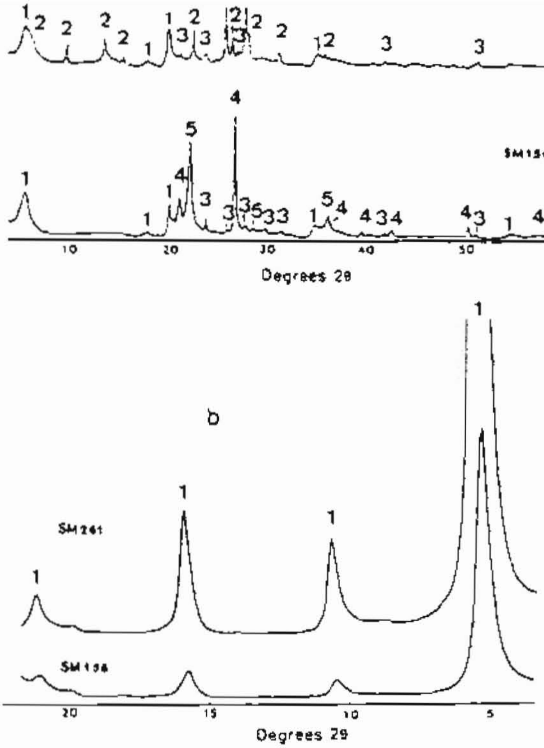

Figure 3. Representative XRD traces of the bulk samples (a) and of the clay fraction (b) of the white bentonites (Ni-filtered CuKa radiation). Key to the numbers: 1=smectite, 2=mordenite, 3=K-feldspar, 4=quartz, 5=cristobalite.

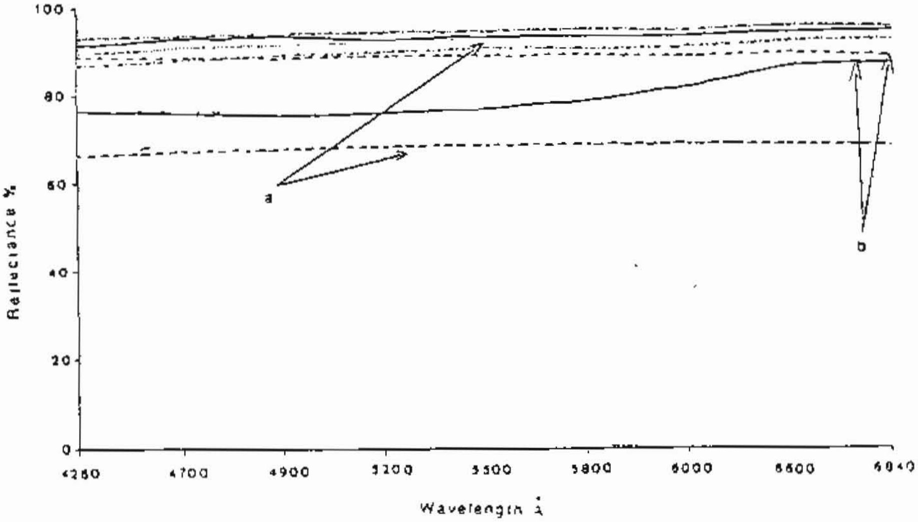

Figure 4 Spectrophotometric curves for some Greek white bentonites. The reflectance values are related to $MgCO_3$ standard. a=Kimolos bentonites, b=Milos bentonites

include the absolute concentration of various chemical elements in the rock, as well as the distribution of each element, *i.e* the mineral phases present. The oxidation state of certain elements like iron should also be taken into account. Since the sample preparation method followed was the same for the different samples and since all samples passed through the same sieve size the mean grain size should not be expected to vary substantially. Nevertheless, the existence of abundant silica phases in Milos (Table 1) implies that the size distibution might be different and that the mean grain size might be higher compared to the opal and/or quartz-free white bentonites of Kimolos due to the greater resistance of silica phases to comminution. However, opal-CT-bearing samples collected from smaller white bentonite bodies in Kimolos (for example SM268, SM266, SM282) have very high brightness values (see Table 3). This means that the presence of silica polymorphs does not affect colour properties as far as physical properties like particle size, shape, and size distribution are concerned.

Iron is one of the most characteristic undesired elements in applications where "white" is important, especially in its ferric state. However, the iron content of samples from the different deposits are not much different. In Tables 2 and 3 it can be seen that sample SM277, which contains more iron than SM146, has a higher brightness. Furthermore, there is not much difference in brightness between samples SM261 and SM277 both from the Prassa deposit, although their iron contents vary substantially.

In the Prassa deposit the smectite present is Cheto-type montmorillonite with crystal-chemical characteristics between those of Chambers and of Tatatilla type without chemical variations. These smectites contain about 0.15-0.2 Fe^{3+} atoms per unit cell corresponding to an average 1.75% Fe_2O_3 (Christidis, 1992). This value is almost identical to the total Fe_2O_3 content of SM280 which contains more than 95% smectite, if the differences in LOI between smectite and the bulk sample are taken into account. This fact indicates that in Prassa deposit the Fe-bearing phase is smectite. SM277 and SM261 contain less iron than SM280 because they carry abundant Fe-free mordenite. On the other hand, smectites in the Ano Komia deposit display important crystal-chemical variation between beidellite and Tatatilla (Cheto) montmorillonite *i.e* Al-rich smectites, with less than 0.1 Fe^{3+} atoms per unit cell (Christidis, 1992). Many are iron free. This significant difference implies that the Fe-bearing phase in Ano Komia deposit is not smectite. The red stainings observed in several sites in Ano Komia deposit indicate the existence of Fe-oxides. The aforementioned comparison indicates that the most important reason for the better colour properties of the Kimolian white bentonites might be the existence of smectite as the principal Fe-bearing phase, instead of Fe-oxides.

The white bentonites of Milos have different mineralogy and chemistry from their counterparts of the main horizon in Kimolos. They are characterized by a higher SiO_2 content which corresponds to the presence of a free silica phase. However, white bentonites from small bodies in the Prassa deposit have SiO_2 content and mineralogy similar to that of Milos bentonites (see Tables 1 and 2). It should be noted that the comparison of the colour properties between the opal-CT-bearing and the opal-CT-free white bentonites from Kimolos indicates that the presence of the silica phases itself is not the reason for the inferior colour properties of Milos bentonites.

The SiO_2 content of the samples SM261 and SM277 is significantly higher (especially in the former) than the average SiO_2 of the montmorillonite present. Nevertheless no silica phase has been determined by XRD methods (Fig. 3a). This means that there must be a silica-rich phase which binds the remaining Si. This phase is mordenite (Figure 3, Table 1). The mordenite-bearing white bentonite is sold in the British market at a high price, while the opal-CT bearing one is not sold although it has better colour characteristics. Therefore, different paragenetic assemblages in a white bentonite might cause variation in properties other than those concerning colour, like hardness, due to the presence of silica phases.

Table 1

Mineralogical composition of the Greek white bentonites

Sample	**Mineralogical assemblage**
	A. Ano Komia deposit, Milos
SM146	Smectite(A) + Quartz(A) + Opal-CT(A) + K-feldspar(B)
SM149	Smectite(A) + Quartz(A) + Opal-CT(A) + K-feldspar(B) + Mica(C)
SM150	Smectite(A) + Quartz(A) + Opal-CT(A) + K-feldspar(B)
SM153	Smectite(A) + Quartz(A) + Opal-CT(A) + K-feldspar(B)
SM155	Smectite(A) + Opal-CT(A) + K-feldspar(C)
SM156	Smecrite(A) + Quartz(A) + Cristobalite(A) + K-feldspar(C)
	B. Prassa deposit, Kimolos
SM258	Smectite(A) + Mordenite(A) + Opal-CT(A) + K-feldspar(B)
SM261	Smectite(A) + Mordenite(A) + K-feldspar(B)
SM266	Smectite(A) + Opal-CT(A)
SM268	Smectite(A) + Opal-CT(A) + Plagioclase(C)
SM271	Smectite(A) + Opal-CT(A) + Mordenite(B)
SM277	Smectite(A) + Mordenite(A) + K-feldspar(C)
SM280	Smectite(A) + Plagioclase(C)
SM282	Smectite(A) + Opal-CT(A) + K-feldspar(C)

A=Major moneral phase, B=Minor mineral phase, C=trace mineral phase

Table 2

Representative chemical analyses of the white bentonites from Milos and Kimolos Islands

Sample	**SM146**	**SM261**	**SM268**	**SM277**	**SM280**	**SM285**
SiO_2	75.03	67.74	74.32	69.63	61.80	72.52
TiO_2	0.18	0.13	0.11	0.17	0.16	0.09
Al_2O_3	14.52	16.79	13.03	19.06	20.60	12.06
Fe_2O_3	1.50	1.19	1.05	1.63	1.92	0.56
MnO	0.03	0.02	0.01	0.01	- -	0.01
MgO	1.93	1.99	3.06	3.41	5.12	0.27
CaO	0.59	1.43	0.85	1.08	1.11	0.51
Na_2O	0.30	1.94	0.70	1.17	0.76	3.51
K_2O	2.45	2.30	0.32	1.69	0.20	4.19
P_2O_5	0.01	- -	- -	- -	0.02	- -
LOI	4.98	7.29	7.30	7.43	7.85	6.46
Total	100.45	100.82	100.74	100.10	99.54	100.18

b) Rheological properties.

Viscosity measurements (both apparent and plastic viscosity) show that the rheological properties of the various white bentonites vary between broad limits (Table 4). Milos bentonite does not develop high viscosities. The value obtained is well below the OCMA specifications. In contrast, Kimolos white bentonites exhibit a variety of qualities. There are samples which develop high viscosity, while others are well below OCMA specifications.

The factors which control rheological properties are not well understood, although systematic research has been carried out for a long time. Factors affecting viscosity are pH (Brandenburg & Lagaly, 1988, Lagaly, 1989), the exhangeable Ca:Na ratio (Alther, 1986, Lagaly, 1989) the particle size and shape (Brandenburg & Lagaly, 1989) and the presence of organic matter (van Olphen, 1963). It is generally accepted that the development of high viscosity is associated with the ability of the clay suspension to form rigid gels through the so-called "card-house" structure (van Olphen, 1963, 1977, Brandenburg & Lagaly, 1988). It is well known that gellation is a particular type of flocculation (van Olphen, 1963, 1977). This means that the card-house structure is formed from edge-to-face floccculation of the clay particles.

In the case of Greek white bentonites pH does not seem to be the primary reason for the inferior rheological properties of the Miloan bentonites (compare the pH values of the samples SM156 and SM277). The pH values obtained are on the neutral-alkaline side. Consequently, low viscosity values should be expected due to destabilization of the "card-house" structure (Brandenburg & Lagaly, 1988). Similar observations were made by Elzea & Murray (1990) for even higher pH values.

The particle shape and size does not seem to be an important reason since there is no indication that the smectites present in Milos bentonite have different particle characteristics. This is indicated from the fact that in both deposits Cheto montmorillonites are present, while the Ano Komia bentonite contains also beidellites. Smectites form aggregates even in very dilute suspensions (Mering & Oberlin, 1971, Güven & Pease, 1975, Güven, 1988, Christidis, 1992). Therefore the possible role of the particle size and shape is closely related with disaggregation. Also the Greek bentonites do not contain organic matter.

The possible difference in Na:Ca ratios between the different bentonites might be important. However, the OCMA specifications require addition of Na_2CO_3 during sample preparation. This means that complete Na for Ca exchange should take place, if disaggegation of smectite particles were complete, which however is not certain. Hence, different degrees of disaggregation might contribute to the lower viscosity values measured, since Ca-smectites tend to form tactoids several tens of Å thick (Kleijn & Oster, 1982) which are disaggregated only by vigorous stiring.

Finally, it is likely that the different mineralogical assemblages present in bentonites result in variations in rheological properties. The presence of opal-CT in the Miloan white bentonites is believed to be of primary importance. Opal-CT crystals are present in the clay fraction. It is possible that due to their small size they are closely associated with smectite particles impeding the formation of a rigid gel-structure and thus the development of gel strength. This is also true for the sample SM268 which has abundant opal-CT and inferior rheological properties compared with the rest Kimolian white bentonites from Prassa deposit (Table 4). This is also true for the sample SM268 which has abundant opal C-T and inferior rheological properties compared with the rest white bentonites from Prassa deposit (Table 4).

CONCLUSIONS

The three main conclusions derived from the comparative study of the Greek white bentonites from Milos and Kimolos Islands are:

a) The inferior colour properties of the Miloan white bentonites compared to their Kimolian counterparts which were derived from similar [illegible] rocks are mainly due to the source of Fe in these deposits. More specificaly in Milos the

Fe-bearing minerals are Fe-oxides while in Kimolos smectite. The existence of Fe-oxides results in colourations which adversely affect the colour properties.

b) The presence of abundant silica phases in Miloan and some Kimolian white bentonites renders them inferior materials for certain applications (cosmetics, pharmaceuticals), although their colour properties might not be affected.

c) The development of good rheological properties of the Kimolian bentonites indicates that they can also be used successfully in traditional applications of bentonites, like the drilling industry.

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