The origin and control of colour of white bentonites from the Aegean islands of Milos and Kimolos, Greece

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Abstract Some of the Lower Pleistocene bentonites of Milos and Kimolos islands, Greece, are valued for their white colour and physicochemical properties. They contain opal-CT and, sometimes, zeolite along with smectite, and have been derived from the alteration of rhyolitic volcanic rocks. The Miloan white bentonites contain Tatatilla-type montmorillonite and beidellite. The Kimolian ones have Chambers-type montmorillonite. The alteration process involved removal of alkalis and uptake of Mg, probably from sea water. Si is either redistributed or partially removed. The Kimolian white bentonites have higher brightnesses, L^* and whiteness index values, and lower yellowness index and ΔE^*ab values compared with the Miloan ones. The variations in white colour are inversely related to the abundance of Fe oxides and anatase, the occurrence of Fe in the smectite structure and its oxidation state. The presence of silica minerals is not an important factor affecting colour, but is undesirable since it imparts high abrasiveness in commercial products. The formation of white bentonites of high quality requires the removal of alkalis and silica during alteration of acid volcanics in order to avoid crystallization of zeolites and opal-CT. Fe needs to be incorporated into the smectite structure. Such conditions are rarely attained.

Introduction

White bentonites (Clarke 1985) have several high-value industrial applications, including electrical ceramics,

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pharmaceuticals, cosmetics, toiletries and household products, especially detergents. They have been classified as speciality clays (Russell 1991), and because of their whiteness, their market value is higher than the usual coloured bentonites. The main producing areas of white bentonites are the USA and the Mediterranean countries, Greece, Italy, Spain and Turkey.

Despite their increasing industrial importance only limited information has been published so far about white bentonites. Reviews on bentonites, for example by Grim and Güven (1978) and Patterson and Murray (1983), give no special mention of the character of these clays. Limited mineralogical data on some Greek white bentonites have been given previously in Wetzenstein (1969) and Marcopoulos and Craniotis (1982). Some colour and rheological properties are briefly described in Christidis and Dunham (1994). In this contribution, the geological setting, mineralogy and chemistry of the white bentonites from Milos and Kimolos are presented and discussed along with the detailed colour data. A mode of origin for the bentonites is suggested, which might help in the exploration for new deposits.

Geological setting

Geology of Milos and Kimolos Islands

These islands, with similar geological histories, are situated in the SW part of the South Aegean Volcanic Arc (Fig. 1), which was created by the subduction of the African Plate under the deformed margin of the Eurasian Plate (Fyticas et al. 1986). The geology of Milos (Fig. 1) has been described by Fyticas (1977) and Fyticas et al. (1986). It includes pyroclastics and lavas overlying sediments and a metamorphic basement. On Kimolos (Fig. 1), Fyticas and Vougioukalakis (1992) distinguished two cycles of volcanic activity. The first (3.5–2.0 Ma) produced the ignimbrite of Kastro, which covers more than half the island, and the andesite and dacite lavas of the central and western part. The second cycle (Lower and the Middle Pleistocene, 2.0–0.9 Ma), has mainly acidic affinites and produced the ignimbrite at Prassa in the NE, the andesitic pyroclastics and lava domes at Geronicola and the rhyolitic pyroclastics and lava domes in the south and southeast of the island.
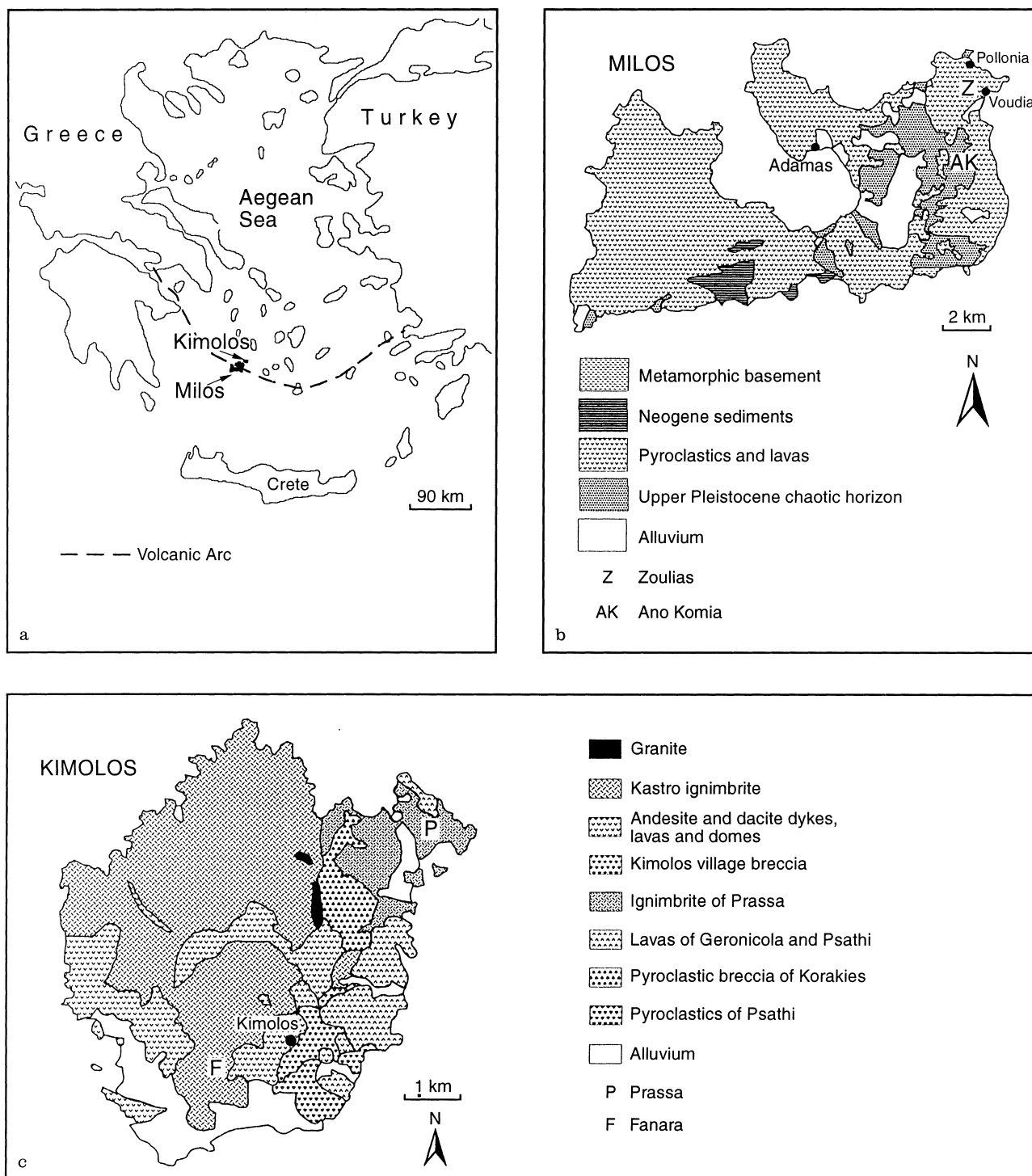
Fig. 1 a Location map of Milos and Kimolos; b simplified geological map of Milos, modified after Fyticas et al. (1986); c simplified map of Kimolos, modified after Fyticas and Vougioukalakis (1992)

Geology of the white bentonite deposits

The locations of four white bentonite deposits (two from each island), are shown in Fig. 1. The Zoulias deposit of Milos is composite. It consists of 11 volcanic horizons, the lower strata having been converted almost totally to bentonite. The white bentonite occurs as elliptical bodies surrounded by thin, hard, green bento-

nite layers, the size increasing in the higher levels. It is derived from pumiceous material, probably welded.

The Ano Komia deposit consists of two bentonite horizons. The lower one (7.2 m thick) is derived from a grey friable lapilli-tuff with high grit content. It has a superimposed hydrothermal alteration which has created yellow 'stockwork' structures crossing the bentonite. The yellow colourations are due to sulphur metaso-

matism. The upper bentonite horizon is white with high silica content. Its thickness is unknown. In places it is stained reddish-pink due to the presence of Fe oxides. The white bentonite formed at the expense of a pyroclastic flow, which probably had rhyolitic affinities (Christidis et al. 1995).

The deposit at Prassa, Kimolos, formed from the unwelded Prassa ignimbrite, the alteration being structurally controlled. It consists of relatively small pockets of high quality white bentonite restricted to areas adjacent to faults. The largest, referred to as P1 bentonite, is 30 m by 35 m across. It continues at depth beyond a visible 10 m. It can be subdivided into six different zones (Christidis and Dunham 1994), the fresh volcanic glass becoming replaced by a thin transition zone, and then successively into yellowish, grey, and white bentonite, the latter two having no noticeable grit content. The white bentonite is followed by a hard, opal-CT rich white bentonite of unknown thickness. The Fanara white bentonite on Kimolos is a small deposit, derived also from an unwelded ignimbrite.

Samples and experimental methods

Samples were taken from each of the white bentonite deposits. At Prassa, both the P1 bentonite, including white and grey varieties, and a smaller P2 body were sampled. The mineralogy was determined by X-ray powder diffraction using a Philips PW1710 powder diffractometer at 40 kV and 30 mA, with Ni-filtered CuKα radiation. Scanning speed was 1°2θ/min. The clay mineralogy was determined using air-dried and glycolated, orientated samples on separated < 2 μm fractions. The major element chemistry was determined by X-ray fluorescence spectrometry using a fusion bead procedure. (Bennett and Oliver 1976, modified by N. Marsh, University of Leicester). Loss on ignition was determined at 1000 °C.

The smectite mineral chemistry was determined by electron microprobe analysis of polished blocks of the white bentonites using a JEOL Superprobe and Link Systems energy dispersive spectrometer with ZAF-4 correction procedure. A 5 μm defocused electron beam at 15 kV, 3 nA sample current and 100 s counting time was used. The areas for analysis were chosen to avoid Ti oxides and Fe oxides and sulphides. The analysis totals are well below 100% and show considerable variation because of differing amounts of water in the smectite structure, the presence of microporosity between the clay particles and possible volatilisation of alkalis, especially Na. This is to be expected in microprobe analysis of smectites (e.g. Ramseyer and Boles 1986; Velde 1984).

The colour of the white bentonites was measured using a Diffusion Systems reflectance spectrophotometer with 45°/90° geometry and illuminant 'C' source. As preparation has a significant effect on colour properties (Scott 1990), samples were dried at 120 °C and ground to pass a 125 μm sieve before measurement. L^*, a^* and b^*, which are calculated from the X, Y and Z tristimulus values, represent lightness on a scale of zero (black) to 100 (white), redness (positive value) – greenness (negative value), and yellowness (positive value) – blueness (negative value) (Billmeyer and Saltzman 1981). The whiteness index (WI), yellowness index (YI), and ΔE^*ab, which is a measure of the difference between the sample and pure white, are useful in comparing the colour difference between samples.

Results

Mineralogy

The mineralogy is summarised in Table 1 and representative X-ray diffraction patterns are shown in Fig. 2. Dioctahedral smectite is the major constituent throughout, but there are distinct differences between the

Table 1 Mineral composition of the white bentonites

Mineral	Zoulias deposit	Ano Komia deposit	Prassa deposit	Fanara deposit
Smectite	M	M	M	M
Quartz	T	M[a]	–	–
Opal-CT	M	M	T	Min
Cristobalite	–	M[a]	–	–
Mordenite	–	–	M	–
K-feldspar	T	Min[b]	T	T
Plagioclase	M	–	T[c]	–
Mica	T[a]	T[a]	–	–

M, Major phase; Min, minor phase; T, accessory mineral
[a] Present only in places
[b] Authigenic K-feldspar
[c] Observed only in the scanning electron microscope

deposits. Opal-CT occurs in variable amounts and is a major mineral in the Ano Komia and Zoulias deposits. Mordenite is a major phase in the Prassa deposit, particularly the P2 bentonite. The Fanara deposit contains only minor amounts of minerals other than smectite. Minor amounts of quartz and plagioclase, presumably relict igneous minerals, often are found in all deposits. Ano Komia has authigenic K-feldspar. Opal-CT is often found in the clay fractions, its presence adversely affecting the use of the bentonite in some applications because of its abrasive nature. Minute pyrite crystals, observable by scanning electron microscopy, occur in very small amounts in all deposits. According to their mineralogical composition, the white bentonites can be subdivided into three different types:

1. White bentonites containing only smectite as a major constituent, referred to as *typical white bentonites* (Fanara bentonite, Kimolos)
2. White bentonites containing mordenite as a major constituent, referred to as *zeolite-bearing white bentonites* (P1 white bentonite, Kimolos)
3. White bentonites containing opal-CT as a major constituent, referred to as *opal-bearing white bentonites* (Ano Komia and Zoulias bentonites, Milos)

Materials with intermediate composition which contain smectite + opal-CT + mordenite as major constituents

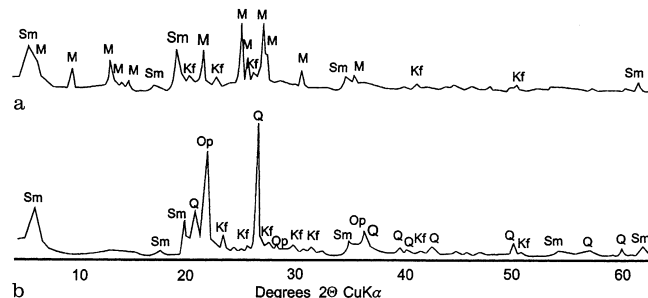Sm = Smectite M = Mordenite Kf = K-feldspar Q = Quartz Op = Opal-CT

Fig. 2a, b Representative X-ray diffraction traces of white bentonites. **a** Prassa P1 white bentonite, Kimolos; **b** Ano Komia deposit, Milos

are also present (P2 bentonite). Typical white bentonites are the least common.

Smectite chemistry

The mineral data for the smectites (Table 2) show differences between the deposits. The Prassa and Zoulias smectites have a higher Mg and lower Al content than the Ano Komia mineral. The latter shows an overall wide variation in composition. The Zoulias smectite contains more Fe than in the other two deposits. In the mineral formulae, there is a greater amount of tetrahedral substitution in the Ano Komia deposit, whereas in the others the layer charge results principally from substitution in the octahedral sites. Using the nomenclature of Schultz (1969) and Güven (1988), the Ano Komia smectite varies from beidellite to Tatatilla-type montmorillonite, the latter being defined as Al-rich smectite having dominantly tetrahedral substitution. The Prassa and Zoulias smectites are typical Chambers-type montmorillonites, displaying significant Fe^{3+}/Mg for Al substitution in octahedral sites. In the interlayer sites the Kimolian smectites have a greater Ca:(Na + K) ratio compared to their Miloan counterparts (0.73 in the Prassa deposit, 0.7 in the Zoulias and 0.46 in the Ano Komia deposit).

Bulk chemistry

The analytical data show some variation (Table 3) between and within deposits, as would be expected from the mineralogical differences. Except for two samples from the Prassa deposit, SiO_2 is $> 66\%$, the threshold for acidic rocks (Carmichael et al. 1974). The grey Prassa material has higher Al_2O_3 and lower SiO_2 than the others. The precursors of both the Miloan and Kimolian white bentonites have rhyolitic affinities and therefore are likely to have similar geochemical characteristics with respect to the major chemical elements. The Si/Al ratio of the Miloan bentonites (analyses 1, 2) is comparable to that of the average rhyolite, (LeMaitre 1976), indicating immobility or redistribution of Si within the rock without loss or addition. On the other hand, the white and grey bentonite horizons of the P1 bentonite, Kimolos, have a Si/Al ratio considerably lower, indicating possible migration of Si. In all deposits where the SiO_2 content is high, there is abundant opal-CT.

The alkali content of the white bentonites is much lower than the average rhyolite (LeMaitre 1976), indicating a major loss of alkalis during alteration, as might be expected (e.g. Senkayi et al. 1984; Shiraki et al. 1987; Altaner and Grim 1990). The relatively high K_2O content of the Ano Komia white bentonite and the 1.85%

Table 2 Electron microprobe analyses of smectites from white bentonites. Analyses of the Ano Komia smectites are from Christidis and Dunham (1997). SD, standard deviation; Min, minimum value; Max, maximum value

%	Prassa deposit $n = 21$				Zoulias deposit $n = 20$				Ano Komia deposit $n = 33$			
	Mean	sd	Max	Min	Mean	sd	Max	Min	Mean	sd	Max	Min
SiO_2	51.98	2.17	56.72	48.30	52.05	0.76	53.09	51.36	49.54	2.24	54.67	44.80
Al_2O_3	18.26	0.75	20.21	16.93	17.20	0.10	17.32	17.19	21.88	1.26	24.47	19.61
Fe_2O_3	1.73	0.17	2.06	1.48	3.57	0.49	4.10	3.12	1.67	0.23	2.10	0.96
MgO	3.92	0.34	4.64	3.43	3.71	0.29	4.11	3.46	1.39	0.32	2.08	0.66
CaO	1.00	0.34	1.62	0.56	0.82	0.15	0.98	0.63	0.78	0.23	1.17	0.18
Na_2O	0.45	0.25	0.80	0.00	0.60	0.17	0.78	0.42	0.53	0.12	0.78	0.00
K_2O	0.53	0.30	1.08	0.00	0.14	0.15	0.29	0.00	1.00	0.35	1.64	0.36
Total	77.87				78.09				76.50			
Structural formulae based on 11 oxygens												
Tetrahedral cations												
Si	3.92	0.02	3.97	3.88	3.93	0.01	3.95	3.92	3.80	0.09	3.97	3.66
Al^{IV}	0.08	0.02	0.12	0.03	0.07	0.01	0.08	0.05	0.20	0.09	0.34	0.03
Octahedral cations												
Al^{VI}	1.54	0.02	1.59	1.50	1.46	0.03	1.49	1.42	1.78	0.03	1.84	1.73
Mg	0.44	0.03	0.48	0.39	0.42	0.03	0.45	0.39	0.16	0.01	0.24	0.08
Fe^{3+}	0.10	0.01	0.11	0.09	0.20	0.03	0.23	0.18	0.10	0.04	0.12	0.06
VICations	2.08	0.02	2.11	2.04	2.08	0.02	2.10	2.06	2.03	0.04	2.13	1.95
Interlayer cations												
Ca	0.08	0.03	0.13	0.04	0.07	0.01	0.08	0.05	0.06	0.02	0.10	0.02
Na	0.06	0.04	0.12	0.00	0.08	0.03	0.12	0.05	0.03	0.04	0.12	0.00
K	0.05	0.03	0.11	0.00	0.02	0.02	0.03	0.00	0.10	0.03	0.17	0.03
Layer charge	0.28	0.05	0.37	0.19	0.25	0.02	0.26	0.20	0.26	0.07	0.39	0.10
Interlayer charge	0.27	0.05	0.37	0.19	0.24	0.02	0.25	0.20	0.25	0.07	0.39	0.10

Table 3 Representative chemical analyses of white bentonites. Key: 1, Ano Komia, Milos; 2, Zoulias, Milos; 3, 4, P1 white bentonite, Prassa, Kimolos; 5, P1 grey bentonite, Prassa, Kimolos; 6–8, P2 white bentonite, Prassa, Kimolos; nd, below detection limit

%	1	2	3	4	5	6	7	8
SiO_2	75.03	73.04	67.74	64.47	61.39	74.32	68.76	76.10
TiO_2	0.17	0.18	0.13	0.15	0.16	0.10	0.12	0.12
Al_2O_3	13.72	12.20	16.79	19.06	20.47	13.03	14.95	11.33
Fe_2O_3	1.51	2.73	1.19	1.63	1.91	1.05	0.97	1.09
MnO	0.03	0.01	0.02	n.d	n.d	0.012	0.02	0.01
MgO	1.82	2.28	1.99	3.41	5.09	3.06	4.33	3.23
CaO	0.56	0.70	1.43	1.08	1.10	0.85	1.24	0.87
Na_2O	0.29	0.40	1.94	1.17	0.75	0.70	1.85	0.83
K_2O	2.33	0.19	2.30	1.69	0.21	0.32	0.41	0.13
P_2O_5	0.01	0.01	0.01	n.d	n.d	0.02	n.d	n.d	0.02
LOI	4.98	7.37	7.43	7.43	7.85	7.30	7.29	6.29
Total	100.45	99.11	100.82	100.10	98.95	100.75	99.94	100.02
Si/Al	5.43	5.99	4.03	3.38	3.00	5.70	4.60	6.72

Na_2O in one sample of the Prassa bentonite reflect the presence of authigenic K-feldspar and mordenite respectively. The MgO content of all white bentonites is considerably higher than the average rhyolite. Thus, although some small-scale local redistribution of Mg may have taken place, there has been uptake of Mg during the alteration of the parent glassy rock. Sea water is the most likely source of Mg, the alteration taking place in a marine environment (Christidis et al. 1995). Mg uptake is a common consequence of alteration of volcanic glass of both basaltic and rhyolitic composition under submarine conditions (Mottl and Holland 1978; Shiraki et al. 1987).

Colour measurement

The colour data (Table 4) show that the white bentonite from the Prassa deposit, Kimolos, has superior properties, with some brightness (Y) values >90%, compared with the material from Milos. Although not exploited, the P2 bentonite appears to have slightly better colour properties compared with the P1 material currently extracted. The brightness, whiteness and yellowness indices generally indicate poorer colour quality in the Miloan white bentonites. As expected the grey bentonite of the P1 deposit has low brightness, L^*, and WI values. Within the grey bentonite horizon, brightness tends to

Table 4 Colour properties of white bentonites from Milos and Kimolos

|	X	Y	Z	L^*	a^*	b^*	WI	YI	ΔE^*ab
Ano Komia, Milos									
SM149	80.90	82.40	92.50	92.80	0.19	3.13	66.00	6.68	2.15
SM155	74.30	75.00	85.20	89.50	1.59	2.35	63.40	6.48	2.39
SM156	86.40	88.30	98.40	95.30	−0.36	3.66	68.30	7.11	2.22
Zoulias deposit, Milos									
SM209	73.30	77.30	77.50	90.60	−4.96	9.68	30.50	15.19	2.63
SM216	81.90	85.20	90.30	94.00	−3.14	6.62	50.40	10.58	2.16
SM226	78.40	80.80	87.60	92.10	−1.53	5.17	54.40	9.29	2.27
P1 white bentonite, Kimolos									
SM258	88.00	90.00	101.00	96.00	−0.35	3.24	72.00	6.28	1.96
SM259	86.40	88.30	98.40	95.30	−0.36	3.66	68.30	7.11	2.22
SM261	86.80	88.90	98.50	95.60	−0.72	4.01	66.90	7.48	2.22
SM277	85.60	88.00	96.00	95.20	−1.26	4.95	61.20	8.84	2.45
P2 white bentonite, Kimolos									
SM267	87.00	89.20	98.60	95.70	−0.89	4.15	66.40	7.60	2.19
SM268	89.90	91.70	102.60	96.70	0.00	3.42	72.50	6.86	2.36
SM269	87.60	89.60	100.60	95.90	−0.36	3.18	72.00	6.17	1.91
SM270	86.60	88.40	99.40	95.40	−0.18	3.06	71.60	6.11	1.94
SM275	83.80	85.90	94.70	94.30	−0.73	4.26	63.10	8.03	2.33
P1 grey bentonite, Kimolos									
SM278	67.80	69.40	77.90	86.80	−0.42	2.91	55.80	6.07	1.12
SM280	72.00	73.60	82.80	88.80	−0.41	2.88	59.60	5.92	1.29
Fanara deposit, Kimolos									
SM307	87.40	89.20	100.00	95.70	−0.18	3.26	71.20	6.48	2.09
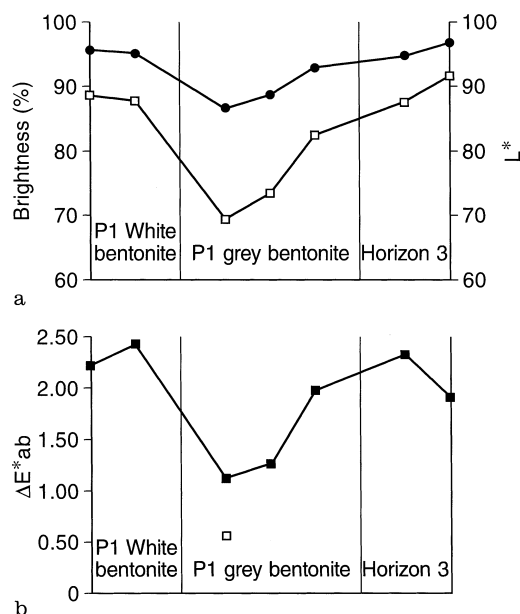
Fig. 3a, b Lateral variation in colour within the P1 Prassa bentonite of Kimolos. **a**, brightness (Y) (lower curve), $L*$ (upper curve); **b**, ΔE^*ab

increase eastwards, away from the white bentonite (Fig. 3). Similar trends are shown by $L*$, and ΔE^*ab but not by any other parameter. No particular trend is observable in any of the colour parameters in the white bentonite horizon of the P1 bentonite.

Excluding the grey Prassa bentonite, there are reasonable correlations between several of the colour properties (Fig. 4). A positive and negative correlation respectively exists between the ΔE^*ab and yellowness index (YI), and ΔE^*ab and whiteness index (WI), as might be expected. Whiteness index and lightness ($L*$) show a positive correlation, and an inverse relationship exists between the yellowness and whiteness indices. The limited scatter of data points can be taken to indicate that there are a restricted number of parameters contributing to the colour variation.

Discussion

Nature of the variation in colour

Differences in both physical properties, such as size and shape of particles, and chemical characteristics can affect the colour of mineral powders (Cornell 1990); and, as colour is a major commercial property of a white bentonite, understanding the factors controlling colour variation is important. The data show that Miloan white bentonites in general have inferior colour compared with the Kimolian samples. Differences in particle size between samples were controlled, as far as possible, with consistent sample preparation. However, opal-CT and quartz are harder and more resistant to comminution relative to smectite and might have led to the coarser
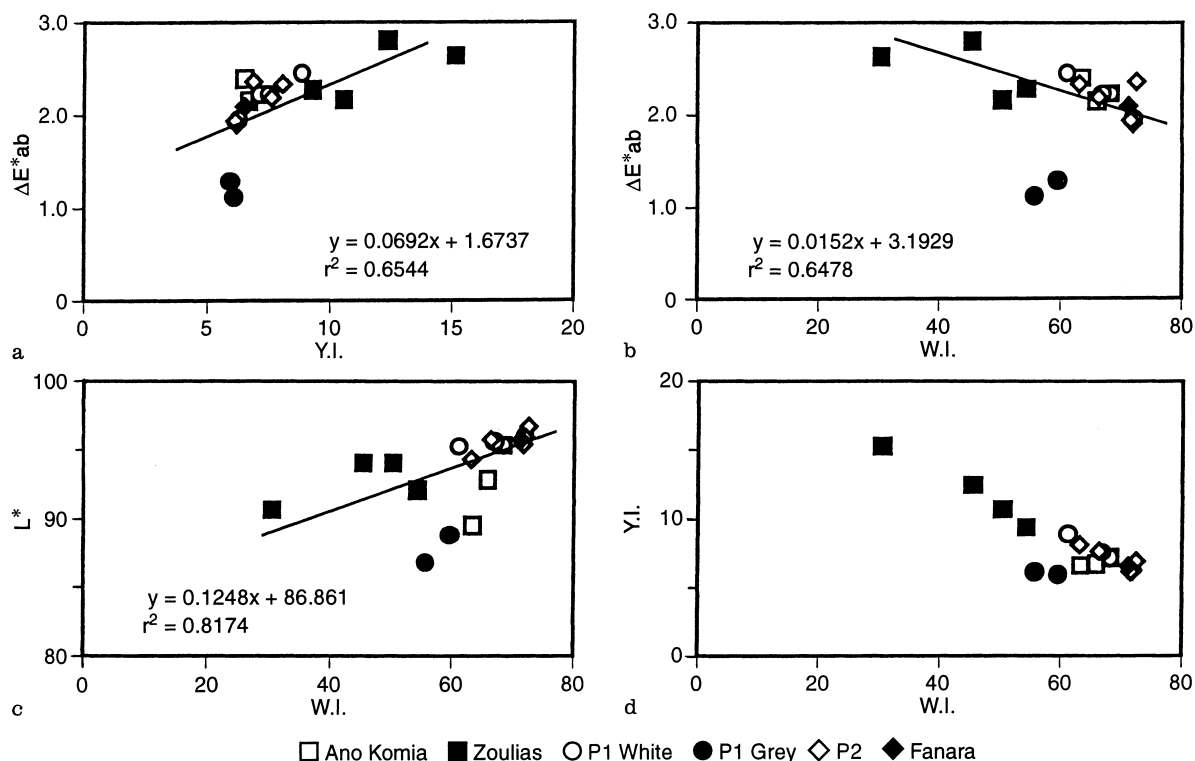

Fig. 4a–d Plots showing the relationship between colour properties of the white bentonites. The plotting points corresponding to the grey Prassa bentonite were not taken into account in the construction of the trendlines

fractions containing more of these minerals in the Miloan bentonites, and consequently inferior colour properties. The different morphology of silica phases might also have an effect. The Miloan white bentonites often contain abundant acicular crystallites of opal-CT (Christidis et al. 1995), while the Kimolian ones contain minute spherical crystallites (Christidis 1992), both of clay size. The colour also could be affected by different degrees of association between the opal-CT and smectite, with the light diffusing differently in aggregates of smectite compared with smectite/opal-CT aggregates, or opal-CT grains coated with smectite. The P2 Kimolian bentonite with the whitest colour properties contains abundant opal-CT. Thus, although the presence of silica phases might affect colour to some degree, they are unlikely to be the main reason for the differences in colour properties.

The role of Fe and Ti is likely to be important in understanding the differences in the colour between the white bentonites. Mn would also be important, but it is present in negligible amounts. The Ti content, possibly present as anatase (Dolcater et al. 1970), is low, but the samples with the highest brightness do have the lowest TiO_2 values (Fig. 5a). Likewise, Fe also appears adversely to affect the brightness (Fig. 5b), at least in part. The form of the Fe, however, is likely to be important, rather than the absolute amount.
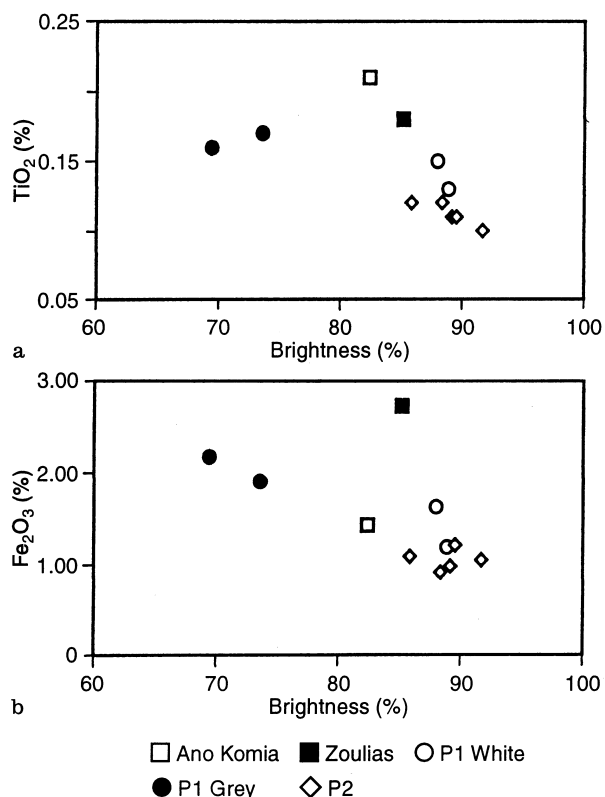

Fig. 5a, b Variation in brightness (Y) of the white bentonites with **a** TiO_2 and **b** Fe_2O_3

The Prassa deposit contains Chambers-type montmorillonite without any major chemical variation (Table 2). There is about 0.1 Fe^{3+} atoms per half unit cell corresponding to 1.75% Fe_2O_3. This is similar to the total Fe_2O_3 content of the grey horizon of the P1 bentonite (taking into account the LOI differences), which contains more than 90% smectite. Thus the main Fe-bearing phase is smectite. In the Zoulias deposit, the smectite is an Fe^{3+} rich Chambers-type montmorillonite with 0.2 Fe^{3+} atoms per half unit cell, corresponding to 3.57% Fe_2O_3. The Fe_2O_3 content of the bentonite is 2.73%. As it contains about 60–70% smectite, it follows that most of the Fe is incorporated in smectite. In the Ano Komia deposit the smectites have a composition ranging between beidellite and Tatatilla-type montmorillonite, with 0.1 Fe^{3+} atoms per half unit cell, corresponding to 1.63% Fe_2O_3. Since the iron content of this rock is about 1.5% and it contains at least 35% opal-CT plus authigenic K-feldspar, it is estimated that around 30% of the total Fe will be present in the form of Fe^{3+} oxides. This will cause a reddish colouration and the positive $a*$ value observed in this material. Fe oxides would be expected in Fe-rich bentonites and nontronites, but have not been reported in bentonites derived from acidic rocks. However, as the main Fe-bearing phase in the Miloan and Kimolian white bentonites is smectite, it leads to a higher brightness than might be expected, and, in most cases gives a greenness (negative $a*$) and yellowness (positive $b*$) rather than redness colouration.

The differences in the colour between the white and grey horizons of the Prassa bentonite might partly be due to changes in the oxidation state of iron in the smectite mineral. This can cause variations in the colour of smectites (Knechtel and Patterson 1962; Anderson and Stucki 1978; Komadel et al. 1990) and the stacking order of the smectite layers (Stucki and Tessier 1991). Complete reduction of Fe produces a grey colouration in nontronites (Komadel et al. 1990). Although there is much less Fe in the Prassa smectites compared with nontronite the grey colouration might be explained to some extent by the dominance of Fe^{2+} atoms in the smectite.

Origin of the white bentonites

All of the white bentonites are derived from rhyolitic precursors. However, the different paragenetic sequences indicates that the alteration proceeds via different paths in different deposits. The presence of abundant opal-CT in the Miloan bentonites implies local redistribution of Si which precipitates in the form of a silica phase after dissolution of volcanic glass. The Kimolian white bentonites have a variable mineralogical composition which is reflected in a variable chemistry. The commercially exploited bentonites, which are devoid of opal-CT, contain mordenite as a major phase.

Acidic rocks are not favourable bentonite precursors (Grim and Güven 1978), since their alteration usually leads to precipitation of silica phases (Henderson et al. 1971). However, such rocks have the low Fe and Ti necessary for high quality white bentonites. Alteration of acidic rocks proceeds via hydration and cation exchange between the fluid phase and the volcanic glass (White and Claasen 1980; White 1983; Shiraki et al. 1987). In the Miloan and Kimolian bentonites, Na, K and Ca have been leached, while Mg has been added. In closed systems the release of alkalis and Ca raises pH and salinity of the fluid phase (Hay and Sheppard 1977), favouring precipitation of alkaline zeolites, unless the outside pore fluid acts as a sink, removing the released elements or it is a supplier of chemical components (Dibble and Tiller 1981). Smectite is favoured only in the early stages of alteration because of the highest supersaturation at that time (Dibble and Tiller 1981) and because the $(Na^+ + K^+)/H^+$ activity ratio might be lowest (Sheppard and Gude 1973).

In open systems the outside pore fluid acts as a sink, creating leaching conditions favouring the formation of smectite (Senkayi et al. 1984). Smectite forms close to the dissolved surface (Dibble and Tiller 1981) leading to pseudomorphic surfaces (Khoury and Eberl 1979; Christidis et al. 1995). Leaching of alkalis associated with immobility of silica probably favours a smectite + opal-CT paragenesis (opal-CT bearing white bentonites) in the Miloan white bentonites which contain beidellite. Partial removal of alkalis and Si might yield the zeolite (mordenite)-bearing white bentonites of Kimolos.

The exact process of formation of smectite and the factors which cause incorporation of Fe in the smectite structure are obscure. Although Banfield et al. (1991) did not observe any precursor phase, other studies report a poorly crystallized precursor of probable allophane composition (Banfield and Eggleton 1990; Kawano and Tomita 1992). If the Al and Si rich precursor has an allophane composition, the uptake of iron might depend on its availability in the pore fluid. This in turn depends on the redox conditions, and the partitioning of Fe and Mg into the octahedral sites. If the precursor material contains abundant iron it is taken up by the forming smectite. The availability of iron in the precursor material depends on the degree of leaching from the parent glass, and this in turn on the redox conditions of the microenvironment. The original Al:Fe ratio of the precursor material might in turn be modified by further Fe-uptake from the fluid phase and the Mg-Fe partition in octahedral sites. Reducing conditions are necessary for the formation of iron rich smectites during the formation of the precursor material (Harder 1976; Decarreau and Bonin 1986; Decarreau et al. 1987).

The reddish colouration in the Ano Komia bentonite is likely to be due to the presence of Fe^{3+} oxides, which are incompatible with reducing conditions. Fe^{3+} oxide minerals may postdate the smectite and might have formed from oxidation of a precursor Fe-bearing phase, possibly pyrite, which occurs in small amounts in some white bentonites. They might also have formed by recrystallization of iron hydroxide gels or from gels which are precursors of smectite, if all of the iron is not taken up by smectite. Also, weathering might have caused oxidation of the structural iron in smectites leading to changes in colour (Knechtel and Patterson 1962; Kozmadel et al. 1990).

In conclusion, it appears that the chemical composition of the parent rhyolitic rock imposes three constraints on the formation of high quality typical white bentonites. Firstly, there has to be an open hydrologic system where alkalis are removed in order to avoid crystallization of zeolites. Secondly, excess silica also has to be removed in order to avoid precipitation of opal-CT, since the Si:Al ratio of smectites is considerably lower than rhyolite; and thirdly, iron has to be incorporated in smectite in order to avoid formation of Fe^{3+} oxides like hematite which adversely affect the white colour.

Exploration and development
of white bentonite deposits

The specific chemical composition of the parent volcanic rocks indicates that exploration should be focused on volcanic provinces with acidic activity. However, white bentonites should be regarded as very rare materials, their formation being constrained by a very specific set of physicochemical conditions. Alteration patterns associated with closed hydrologic systems (e.g. alkaline lakes), leading to formation of zeolite deposits (Surdam 1977; Surdam and Sheppard 1978) are unlikely to yield useful white bentonites.

Most of the Miloan and Kimolian bentonites contain abundant opal-CT or zeolite. Currently only the P1, Prassa bentonite, of Kimolos, which contains abundant mordenite, is exploited. Opal-CT bearing bentonites which are the most commonly occurring white material are not exploited because of their abrasiveness. This renders them unsuitable for certain industrial applications, such as pharmaceuticals and cosmetics. These are high added-value uses. Thus, it might be more appropriate to concentrate on development of mineral separation techniques for these materials rather than to search for new deposits.

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