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ABSTRACT: Major and trace chemical elements from eleven Lower Pleistocene bentonite deposits from Eastern Milos Island, Aegean, Greece, were used for geochemical fingerprinting of the bentonites, by means of scatter binary and ternary plots and canonical discriminant analysis. The trace elements were selected according to their immobility during bentonite formation and subsequent hydrothermal alteration. The bentonites can be separated into at least four geographically distinct groups, each consisting of materials with similar geochemical affinities. The deposits of each group were derived from protoliths erupted from different volcanic centres, suggesting the existence of at least two distinct volcanic provinces, having rhyolitic and andesitic affinities respectively. Several deposits consist of more than one bentonite horizon, indicating that in some volcanic centres the character of volcanism changed with time. Geochemical fingerprinting, supplemented with geological, mineralogical, and textural evidence, may be useful for correlation and exploration of bentonites, in terrains with complex geological histories.

KEYWORDS: bentonite, geochemical fingerprinting, Milos Island, Greece.

Bentonites are clays derived from the alteration of volcanic ash and consist essentially of smectite, the physical and chemical properties of which dictate the characteristics of the clay (Grim & Güven, 1978; Fischer & Schmincke, 1984). In some cases bentonites form extremely widespread deposits and are thus useful for stratigraphic correlation purposes. Ordovician K-bentonite beds, for example, are distributed over 1.3×10^6 km^2 in eastern North America (Huff & Kolata, 1989), while K-bentonite beds of similar age extend from the Southern Uplands of Scotland across the Irish Sea into Ireland (Huff *et al.,* 1991). Moreover, the well known Clay Spur Bed of Cretaceous age extends from South Dakota to Wyoming through Montana (Patterson & Murray, 1983).

Exploration for bentonite deposits mainly involves the application of geological-stratigraphic criteria and is based on knowledge of the nature and age of volcanic activity and the lateral extent of the volcanic ash beds. Usually prospecting is focused around known occurrences and frequently employs shallow drilling. Such exploration may not be successful in tectonically active terrains with a complex geological history, especially when deposits are composite, consisting of multiple horizons. Geochemical fingerprinting, which has been successfully applied to the stratigraphic correlation of bentonites (e.g. Huff *et al.,* 1991), might be a helpful additional tool in exploration for bentonite deposits.

The Upper Pleistocene bentonite deposits of Milos Island, Aegean, Greece, formed at the expense of pyroclastic rocks, mainly pyroclastic flows, in a submarine environment (Christidis *et al.,* 1995). The deposits are quite thick, exceeding 50 m in places, and are not laterally extensive. The bentonites were affected by at least two hydro-thermal events, which, in places, caused extensive illitization (Christidis, 1995). Most deposits can be

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placed in one of three groups corresponding to different geographic regions, with a limited number of exposures located between them. The deposits in the various areas formed at the expense of different precursors, which erupted from volcanic centres with different affinities (Christidis et al., 1995). In this contribution, geochemical fingerprinting, using conventional geochemical plots and canonical discriminant analysis, is attempted in order to: (a) test the *a priori* assumption about the existence of different bentonite precursors and to confirm the extension of some bentonite horizons beyond certain bentonite quarries in the three areas; and (b) assess the possibility of using chemostratigraphic correlation as an alternative tool in exploration for bentonites in areas with complex geological histories.

MATERIALS AND METHODS

Sampling and analytical methods

The study area for the bentonites is located in Eastern Milos (Fig. 1). The geology, stratigraphy and mineralogy of the deposits were described by

Christidis et al. (1995). The deposits of Angeria, Aspro Horio, Zoulias and Ano Komia are composite, while the remaining deposits consist of a single bentonite horizon. Stratigraphic sections of the composite deposits are given in Christidis et al. (1995). The term horizon describes materials with specific macroscopic characteristics (grainsize, sedimentary structures, texture, colour, etc.). Most deposits are characterized by the presence of brecciated texture ("brocken tuff" according to Wetzenstein, 1969). Different horizons often have comparable mineralogical compositions. Representative samples were collected from stratigraphic horizons of ten bentonite deposits from the three groups, where there was an indication that they had formed from common precursors (Christidis et al., 1995), as well as from the Agrilies deposit located between groups 2 and 3 (Fig. 1). Also, samples from the various horizons of the composite Zoulias deposit were obtained in order to trace the degree of heterogeneity in this deposit.

The materials were dried at 105°C, ground in a Tema mill and passed through a 75 µm sieve. Analytical data were obtained by XRF analysis (ARL8420$^+$ WD/XRF and Philips PW1400

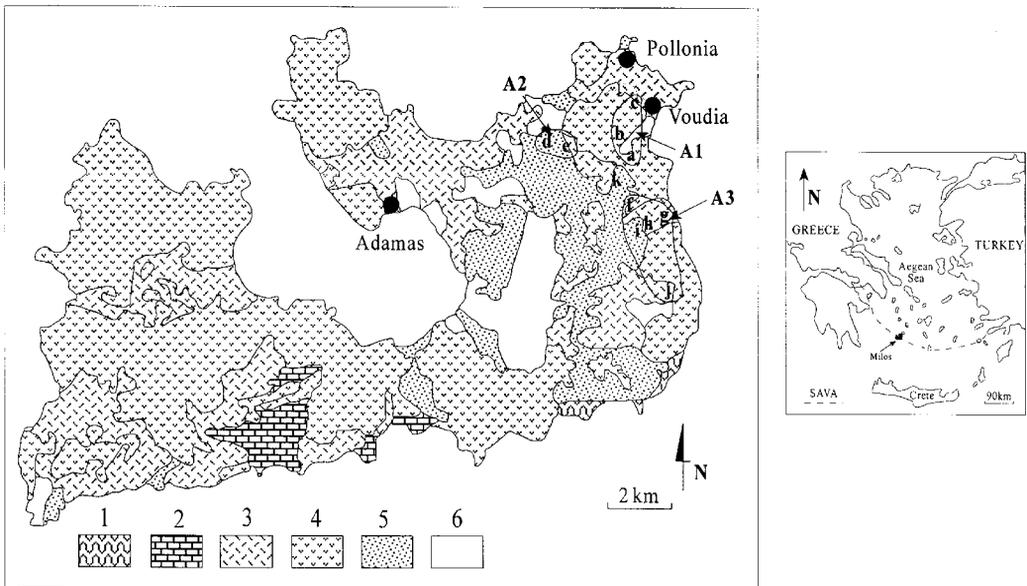FIG. 1. Simplified geological map of Milos Island (after Fyticas et al., 1986). 1 = Metamorphic basement; 2 = Neogene sedimentary sequence; 3 = pyroclastic rocks; 4 = lavas; 5 = chaotic formation; 6 = alluvial deposits. a = Tsantilis; b = Aspro Horio; c = Zoulias; d = Ankeria; e = Koufi; f = Ano Komia; g = Kato Komia; h = Garyfalakena; i = Mavrogiannis; j = Rema; k = Agrilies. A1 = Area 1 (Group 1); A2 = Area 2 (Group 2); A3 = Area 3 (Group 3). SAVA = South Aegean Volcanic Arc.

WD/XRF spectrometers). Major elements (Si, Al, Ti, Fe, Mn, Mg, Ca, Na, K, P and S) were determined from fusion beads (Bennett & Oliver, 1976, modified by N. Marsh, University of Leicester, UK), and trace elements from powder pellets. Sample preparation methods, analytical precision and accuracy for the instruments, and the methods used are given in Christidis (1998).

Statistical analysis of the data

Correlation of the bentonite deposits and determination of the geochemical affinity of the various groups was made with conventional geochemical plots and multivariate statistics (canonical discriminant analysis). Conventional plots involved three types of diagrams: (1) binary plots using trace elements; (2) ternary plots using trace elements; and (3) ternary plots using Si, Al, Mg and Fe. The major element ternary diagrams give an indication of the smectite chemistry and the ratio of smectite:Si-phases. This is because Al, Fe and Mg essentially reflect the crystal chemistry of the smectites (since feldspars are not abundant), only minor amounts of Fe-oxides are present, and Si exists in both smectite and Si-polymorphs. Inasmuch as calcite and other carbonates, which might not be related to bentonite formation, are abundant in most deposits, CaO was not included in these diagrams. The ternary diagrams using trace elements always have V and Cr and a light rare earth element (*LREE*) (namely La, Ce and Nd) or a High Field Strength (HFS) element (Zr, Th or Nb) in the third. Finally, in the discriminant analysis, the samples from the Zoulias deposit came only from the uppermost bentonite horizon.

Criteria for selection of chemical elements

Selection of elements was based on: (1) the number of elements necessary for reliable correlation and discrimination between the various groups, because it might affect the importance of the information obtained (Huff & Kolata, 1989); and (2) their geochemical behaviour during bentonite formation, since immobile elements are usually employed for discrimination purposes in conventional diagrams (Winchester & Floyd, 1977; Pearce *et al.,* 1984). Recently, it was found that the heavy rare earth elements (*HREE*) and Y, which are usually considered immobile, are mobile during bentonite formation (Christidis, 1998).

Authigenic minerals like zeolites, and/or K-feldspar in some Miloan bentonite deposits, are expected to affect the distribution of major chemical elements, which might reflect the nature of the parent material, thus masking the original elemental distribution. Also, post-formation hydrothermal alteration, associated with illitization, kaolinization and alunitization can increase the complexity during correlation of the bentonites. Therefore, care was taken to avoid: (1) elements which are mobile during bentonite formation and/or are bound by authigenic or/and hydrothermal minerals other than smectite, which are not present in all deposits, such as zeolites, K-feldspar, mixed-layer illite-smectite or carbonates; and (2) elements which were leached or added during subsequent hydrothermal alteration which post-dated the formation of the Miloan bentonites. Using this reasoning, the trace elements selected were Nb, Zr, Th, Cr, Ni, V, La, Ce and Nd. The influence of mobile elements in discriminant analysis was tested by the use of Y and comparison with an additional analysis without this element. This is considered a rough assessment of the influence of possible different behaviour (i.e. mobilization) of any of the selected elements, in the various deposits.

RESULTS

Correlation using conventional plots

The binary plots and the ternary plots using major elements confirm the existence of materials with different geochemical characteristics. Two different groups can be observed: one with intermediate and one with acidic affinities, with a small number of bentonite deposits in between (Figs 2, 3). The two groups are separated according to their V content (Fig. 2). Deposits from Areas 1 and 2 are inseparable and have a higher Al:Si ratio compared to the bentonites from Area 3, which belong to the second group (Fig. 3), in accordance with the mineralogical composition. The bentonites of Area 3 contain abundant Si phases while those from Areas 1 and 2 are in general quartz- and/or opal-CT-free (Christidis *et al.,* 1995). Opal-CT-bearing samples from the Angeria deposit (Area 2) and some horizons from the Zoulias deposit (Area 1) do not plot with the remaining samples of this group (Figs 2, 3). Also, those samples from the Tsantili deposit, which
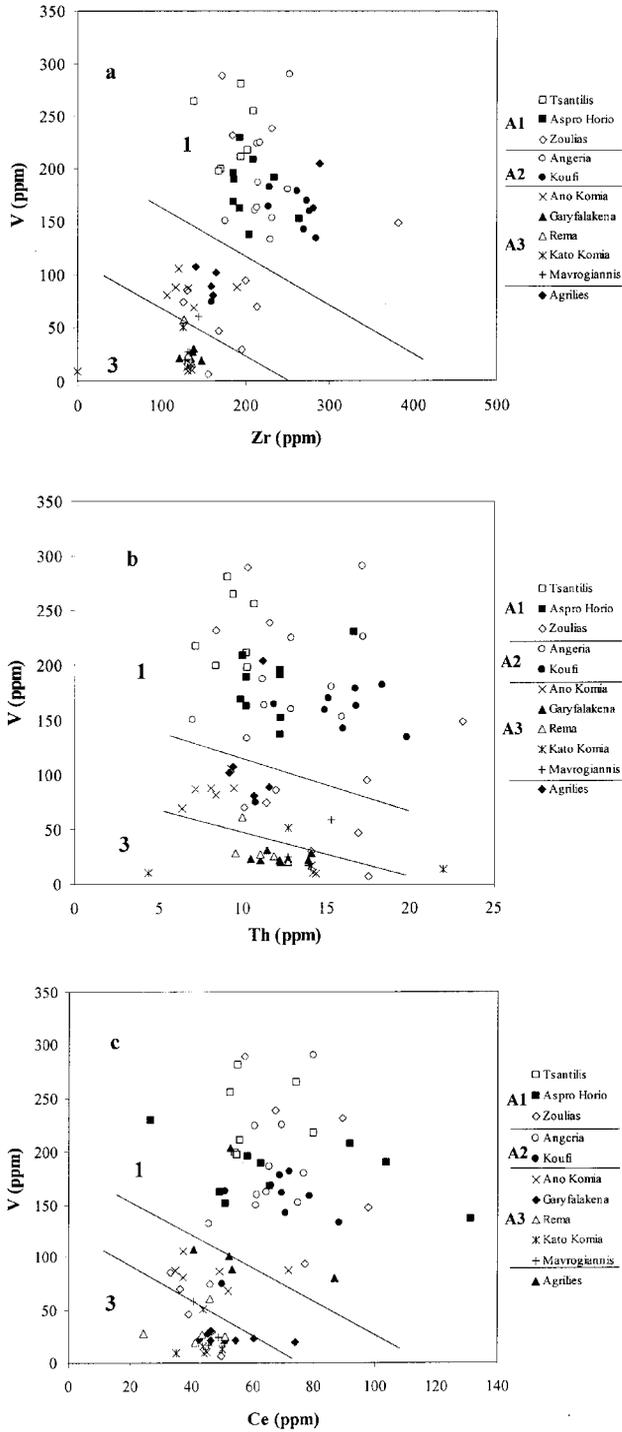
FIG. 2. Binary plots using trace elements. Number 1 denotes the field occupied by the deposits from Areas 1 and 2, while number 3 denotes the field occupied by the deposits from Area 3. A1, A2 and A3 denote Areas 1, 2 and 3 respectively.
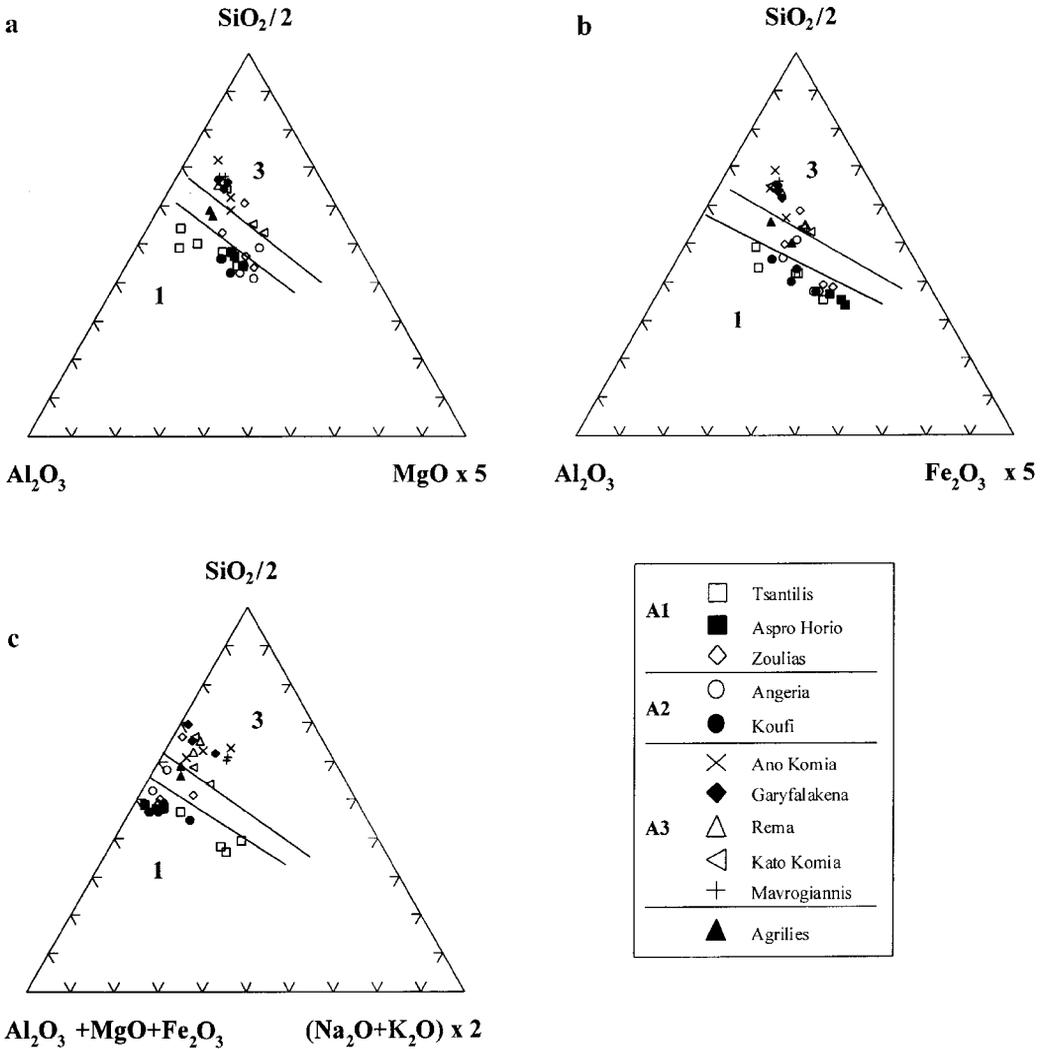
FIG. 3. Ternary plots using major elements. Number 1 denotes the field occupied by the deposits from Areas 1 and 2, while number 3 denotes the field occupied by the deposits from Area 3. A1, A2 and A3 denote Areas 1, 2 and 3 respectively.

contain mixed-layer I-S instead of smectite (Christidis, 1995), plot separately from the remaining samples of the group, due to the considerably larger amount of K (Fig. 3c).

The ternary diagrams using trace elements are more effective in separating the deposits (Fig. 4). The distribution of bentonites in the V-Cr-Zr diagram (Fig. 4b) suggests the existence of three groups belonging to two provinces, related to

materials with different affinities, acidic (V-poor, Zr-rich), and intermediate (V-rich, Zr-poor), respectively. The Angeria deposit (Area 2) seems to consist of two bentonite horizons; the lower (encircled points) is more basic and includes the three lower bentonite horizons of the deposit (Christidis *et al.,* 1995), while the upper is more acidic and plots with the samples from the Koufi deposit. The lowermost horizon of the Koufi
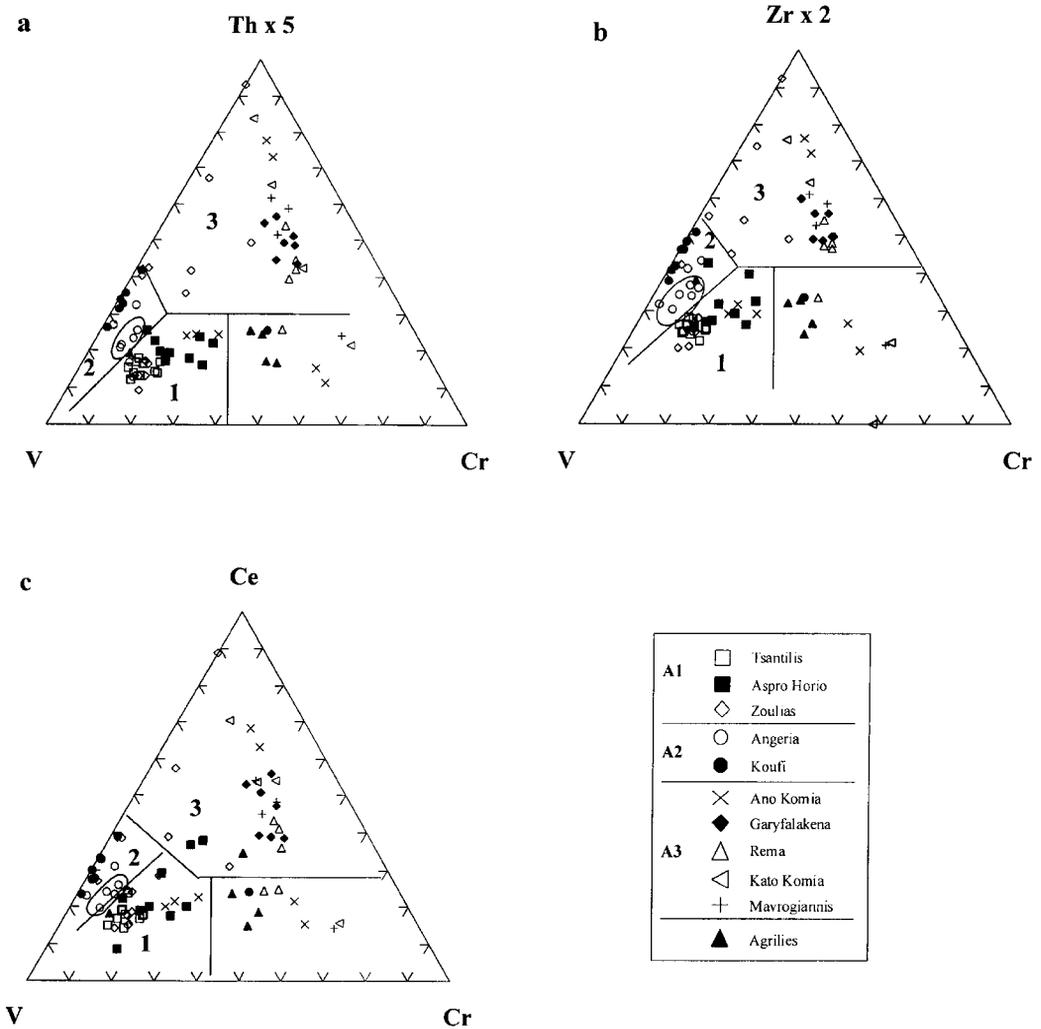
FIG. 4. Ternary plots using trace elements. Numbers 1, 2 and 3 denote the fields occupied by the deposits from Areas 1, 2 and 3 respectively. The encircled points correspond to materials from the three lower horizons of the Angeria deposit. A1, A2 and A3 denote Areas 1, 2 and 3 respectively.

deposit plots with materials from the Agrilies deposit. The samples from the Tsantilis deposit, the lower horizon of Aspro Horio and the highest horizon of Zoulias deposit (Christidis *et al.,* 1995), which have a similar brecciated texture ("brocken-tuff" according to Wetzenstein, 1972), plot in the same area. In contrast, samples from lower horizons of the Zoulias deposit are scattered towards the field occupied by more acidic materials. Finally, the bentonites from the Ano Komia deposit plot as three separate groups. The lower bentonite horizon is associated with the upper horizon of the Aspro Horio deposit, while the upper horizon plots with the deposits of Area 3. The third group includes samples from the lower stratigraphic horizon which have been affected by hydrothermal alteration. It seems, therefore, that alteration adversely affected the discriminant power of these diagrams. Two samples from the Kato Komia deposit plot close to the Cr corner, probably because of the presence of ophiolitic material derived from the metamorphic basement.

TABLE 1. F statistics for the trace elements used for discrimination of the Miloan bentonites.

Element	F ratios	F probability
V	45.7454	0.0001
Zr	20.5912	0.0001
Nd	6.2517	0.0001
Th	5.5796	0.0001
Nb	3.7229	0.0005
Cr	3.6965	0.0005
Ce	3.3634	0.0013
Ni	3.1853	0.0020
La	1.7017	0.0975
Y	1.4348	0.1834

Replacement of Zr by Th in the graphical display enhanced the separation of the deposits (Fig. 4a), whereas the use of Ce increased the degree of scattering (Fig. 4c). Nevertheless, the bentonites from the different volcanic centres are clearly separated. The similarity in distribution of the different deposits in the various ternary diagrams suggests that the separation of the various bentonites is not an artifact, but results from the different geochemical characteristics of these materials.

Fingerprinting using discriminant functions

The F ratio and F probability results for the trace elements are listed in Table 1. The F ratio (between-group mean square/within-group mean square) expresses the extent to which between-group variations are due to non-random variation. The probability that the between-group differences of Zr, V, Nd, Th, Nb and Cr (F probability) are not real, but accidental or due to random variations is almost zero. In the case of Ce and Ni this probability is slightly greater and only for La and especially for Y, when the latter was included for testing purposes, is it significant. Thus the suggestion of limited importance of Y in geochemical fingerprinting was confirmed. The F ratio can also be used to determine the relative contribution of each element to the discrimination (Rock, 1988). In this context, V contributes most, followed by Zr, Nd, Th, Nb, Cr, Ce, Ni, La and finally Y (Table 1).

The discriminant analysis results (Table 2) show that the first discriminant function accounts for 66.4% and the first two for 86.39% of the discriminating power of the variables used. The third function adds <5%, being much weaker, while almost 99% of the information can be obtained by using five functions. According to the canonical correlation results, the first two discriminant functions are well correlated with the groups (r = 0.95 and 0.86 respectively), while the remaining functions are less correlated. The importance of the first two discriminant functions for discriminant purposes is confirmed by the Wilks' lambda test, the multivariate F ratio and the F probability (Table 2). Therefore, these functions were used to make a 'territorial map'.

Projection of the discriminant scores in the territorial map (Fig. 5) separates the acidic and the intermediate provinces of Eastern Milos along function 1. Moreover, there are distinct subgroups

TABLE 2. Results from canonical discriminant analysis of the bentonites from Milos.

| Canonical function	Eigenvalue	Proportion	Cumulative % of variance	Canonical correlation	Wilk's Lambda	Approx. F	F proba- bility
1	9.3833	0.6640	0.6640	0.950627	0.005195	4.8665	0.0001
2	2.8250	0.1999	0.8639	0.859398	0.053939	2.8886	0.0001
3	0.6578	0.0465	0.9104	0.629901	0.206320	1.8190	0.0004
4	0.5484	0.0388	0.9492	0.595115	0.342029	1.5816	0.0111
5	0.3999	0.0283	0.9775	0.534464	0.529589	1.2469	0.1658
6	0.1687	0.0119	0.9895	0.379957	0.741360	0.8278	0.7045
7	0.1035	0.0073	0.9968	0.306208	0.866447	0.6165	0.8687
8	0.0336	0.0024	0.9992	0.180379	0.956093	0.3427	0.9593
9	0.0118	0.0008	1.0000	0.108111	0.988247	0.2045	0.9355
10	0.0001	0	1.0000	0.008107	0.999934	0.0046	0.9461
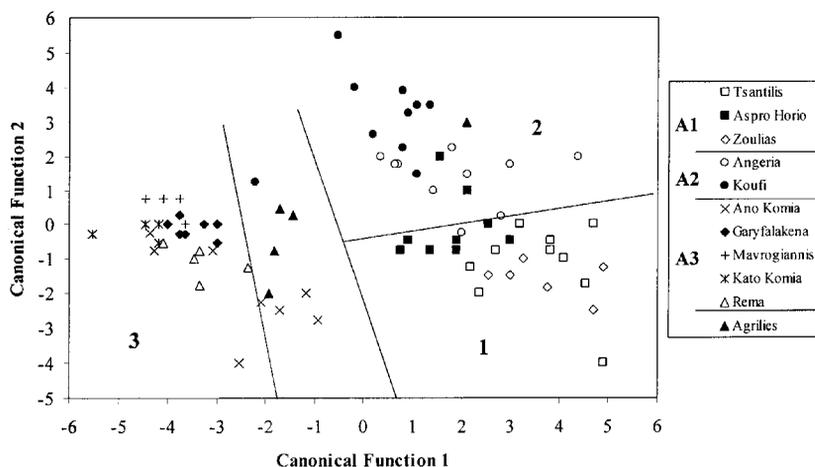
F<small>IG</small>. 5. Territorial map constructed using the data obtained from the canonical discriminant analysis. Numbers 1, 2 and 3 correspond to Areas 1, 2 and 3 respectively. Samples from the Zoulias deposit come from the uppermost bentonite horizon. The lines separate materials from the different areas. A1, A2 and A3 denote Areas 1, 2 and 3 respectively.

within the two major provinces, which cannot be considered parts of the same horizon. Although the variation in the Y content might be accidental (Table 1), its influence in the discriminating power of the total number of elements is restricted to a greater scattering of points belonging to a particular group (data not shown).

Comparison of Figs 4 and 5 shows several similarities between ternary diagrams with trace elements and the territorial map. The deposits from Area 1 plot in the same area and are separated from those of other areas. Although two samples from the Aspro Horio deposit plot in the space occupied by the Angeria deposit, it is obvious that this deposit has a closer affinity to the deposits of Area 1 than to their counterparts of Area 2. Also, all samples from the Angeria deposit plot in the same area and do not seem to be related to the Koufi deposit. The bentonites from Area 3, including the upper horizon of the Ano Komia deposit, plot in the same area. Moreover, all but one altered sample from the lower horizon of this deposit plot as a separate group in the same area. This, although expected, was not observed in the ternary diagrams (Fig. 4). Finally, all but one sample from the Agrilies deposit plot in the space among the bentonites from the three other areas, with the samples from the lower horizon of the Koufi deposit.

DISCUSSION

Geological implications of geochemical fingerprinting

The various methods of geochemical finger-printing confirm the *a priori* hypothesis that the bentonite deposits of eastern Milos are not parts of a single horizon. Therefore any attempt to assign them to a single volcanic event will lead to misleading interpretations. Also, several deposits are composite and consist of more than one bentonite horizon. Some horizons might be present in more than one bentonite deposit. These aspects are discussed below.

Except for the lower horizon of the Ano Komia deposit, the deposits of Area 3 have similar geochemical and geological characteristics, indicating that they might have been derived from a similar parent material, with acidic affinities. The vicinity of their occurrence suggests formation from the same parent magma. In contrast, the lower horizon of the Ano Komia deposit formed during a different volcanic episode. Similarly, the bentonites of Tsantili, Aspro Horio and the upper horizon of the Zoulias deposit might be parts of a common horizon and therefore may have been derived from andesitic parent magma. The remaining horizons of the Zoulias deposit were derived from precursors

with variable chemistry, suggesting that the character of volcanism changed with time in this deposit. In both cases the possibility of a common precursor is supported by the fact that the chemical composition of the smectites is comparable and is controlled by similar parameters (Christidis & Dunham, 1993, 1997).

The Angeria deposit consists of four bentonite horizons with different colours (Christidis *et al.,* 1995). However, only two distinct horizons can be separated by ternary diagrams using trace elements; the three lower horizons plot separately from the upper one (Fig. 4). This separation is not observed in the discriminant analysis (Fig. 5). It has been suggested (by Komadel *et al.*, 1990) that the different colorations might reflect different degrees of oxidation of Fe, and/or that the parent rocks had comparable geochemical characteristics. The similarity in smectite chemistry (Christidis & Dunham, 1993) and the texture of these bentonites indicate that the first hypothesis is possible.

The lowermost horizon of the Koufi deposit plots within the 'field' of the Agriles deposit (Figs 4, 5), but the limited number of samples from this horizon does not allow definite assignment to a common precursor. The smectites in these deposits show different chemical trends (Christidis & Dunham, 1993). It is suggested that similar geochemical trends might not necessarily indicate a common origin of bentonites. Additional criteria which must be taken into consideration include:

(1) *Geological criteria.* Similar textural characteristics support a common origin, but should always be examined cautiously, because even different colours might reflect different physico-chemical conditions during and/or after bentonite formation. Moreover, similar macroscopic characteristics might have resulted from similar geological processes, which involved different parent rocks. The bentonites from Areas 1 and 3 have similar textural characteristics although the parent rocks were different.

(2) *Geographical criteria.* Geochemical similarity between two deposits located close together increases the possibility of a common origin, especially in bentonites, which do not extend over long distances.

(3) *Smectite chemistry.* The major chemical elements of smectites, the principle constituents of bentonites, with the possible exception of Mg, originate from parent rocks. Different compositional trends in smectites derived from different precursors

might reflect different parent-rock chemistry. However, substantial mass transfer affects the microenvironmental chemistry (Christidis, 1998).

Differences between the ternary diagrams using trace elements and the territorial map were also observed. In the territorial map (Fig. 5), the correlation between the Angeria and the Koufi deposits is not unambiguous. Some samples from the upper horizon of the Aspro Horio deposit plot with the samples of Area 2. This might be due to the influence of the subsequent hydrothermal alteration on the relative mobility of the elements, or to the number of elements used (Huff, 1983). It is suggested that both types of diagrams combined with the existing geological information, might provide valuable information about the different features of the bentonite deposits and might be used for correlation purposes, even in terrains with complex geological history like Milos. However the geochemical model must be further tested and even extended with additional sampling from the Miloan deposits.

The existence of bentonite horizons spread over a considerable distance does not preclude compositional variability within these horizons. This variability contributes to the observed scattering in the various geochemical diagrams, and its extent can be traced by study of the chemistry of certain primary (igneous) phases such as plagioclase. The plagioclase in the Zoulias bentonite (Area 1), for example, is more calcic and more homogeneous than that of the Tsantilis deposit (Table 3), although the two deposits have similar trace element geochemistry. The observed differences may be attributed to the variability in the composition of the parent magma, the mechanism of eruption (*cf.* Cas & Wright, 1988) and on hydrothermal events, which post-dated bentonite formation. The latter mechanism is considered important because the Tsantilis deposit has been affected by intense illitization (Christidis, 1995) and because pure

TABLE 3. Composition of plagioclases present in bentonites.

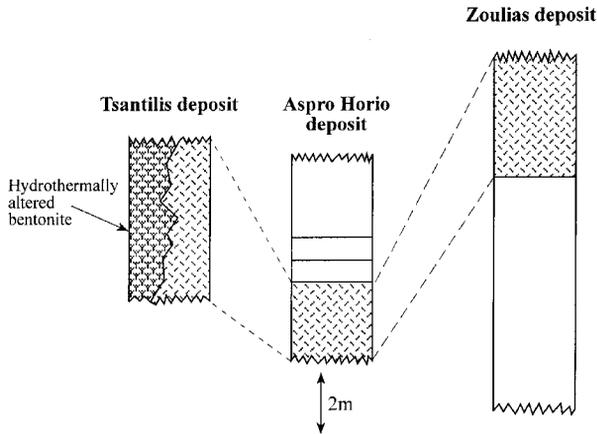|	Tsantilis	Zoulias	Angeria	Koufi
% An	22−35*	38−53	36−47	20−37
Mean value	28	45	40	29

* = presence of discrete albite

FIG. 6. Schematic sections of the bentonite deposits in Area 1, which show the correlation of certain bentonite beds. Correlation was based on geochemical fingerprinting and was supported by geological and mineralogical evidence.

albite crystals are present (Table 3). In Area 2 the plagioclase of the Ankeria deposit is more calcic compared to the Koufi deposit (Table 3).

Exploration of bentonite deposits

Application of various methods of geochemical fingerprinting indicates that the bentonites of Eastern Milos can be separated into at least four different groups, which are not related genetically. Each group consists of deposits with similar geochemical characteristics, which might be used for correlation purposes. In several cases the bentonite deposits constitute parts of a common horizon. The geochemical correlation of the different bentonite horizons can be used to explore for new bentonite reserves. This can be shown in a series of examples.

The possibility that the Tsantilis deposit, the lower horizon of the Aspro Horio deposit and the upper horizon of the Zoulias deposit (Area 1) formed from a common precursor, suggests that the same bentonite horizon might extend between them (Fig. 6). This assumption was confirmed recently by the discovery of an 'additional' deposit between the Tsantili and the Aspro Horio deposits at a greater depth (Silver & Baryte Ore Mining Co., pers. comm., 1994). Since the area between the Tsantili and the Aspro Horio deposits was influenced by intense fault tectonism, such fluctuations in the level of the bentonite horizon are expected. Similarly, the possibility of a common precursor in Area 3 suggests that the same bentonite horizon extends in the area between the deposits of Ano Komia and Garyfalakena (Fig. 7). Since the potential area of this horizon is within a faulted zone, it might be located under the thin alluvial cover.

Finally, the upper horizon in the Angeria deposit plots with the samples from the Koufi deposit in the ternary diagrams. In Fig. 4 they also plot in the same area and seem to be more acidic than the three lower horizons of the Angeria deposit. This suggests that they might have been derived from a common precursor. Again, if this is the case, then the bentonite bed is expected to occur between the two deposits. This was confirmed recently with exploration drilling by the mining company, which operates in the area.

The results obtained in this study show that geochemical fingerprinting is potentially a helpful tool in the exploration for bentonite deposits, even in terrains with complex geological history. However, limitations which stem from the specific geological features of each type of deposit should be taken into account prior to application. Since most bentonites are alteration products of pyroclastic rocks (Grim & Güven, 1978), compositional variability within the deposits due to inhomogeneity of the parent magma or due to the eruption mechanism might give misleading genetic interpretations. In contrast, the influence of hydro-
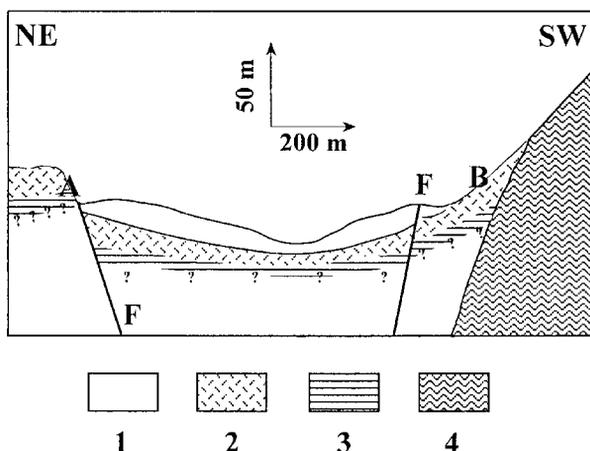
Fig. 7. Schematic cross-section, showing the location of the Ano Komia and the Garyfalakena deposits (A and B, respectively), Area 3, based on the data from geochemical fingerprinting. 1 = alluvial deposits; 2 = main bentonite horizon in Area 3; 3 = lower horizon in Ano Komia deposit; 4 = rhyolitic dome.

thermal alteration, which might mask the original geochemical trends, can be anticipated by the use of suitable, immobile trace elements.

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