

Fe³⁺-RICH MONTMORILLONITE-BEIDELLITE SERIES IN AYVACIK BENTONITE DEPOSIT, BIGA PENINSULA, NORTHWEST TURKEY

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Abstract—The Ayvacık bentonites, products of Miocene calc-alkaline volcanic rocks, are composed of smectite of the montmorillonite-beidellite series. Fault-related hydrothermal solutions have altered andesitic rocks to dioctahedral smectites. Differences in the micro-morphology of the two end-members are distinguished by scanning electron microscopy (SEM) studies. The beidellite particles are of delicate ribbons and rosette habits, whereas montmorillonite particles are very thin, curled sheets and flakes. Clay size (<2 μm) fractions contain (in wt. %) 54.90–56.80 SiO₂, 19.65–28.54 Al₂O₃, 0.45–6.28 Fe₂O₃, 0.10–1.72 CaO, 0.80–4.15 MgO, 0.55–1.88 K₂O, and 0.08–1.15 Na₂O, which confirm that the beidellites are Fe-rich (5.06–6.28 wt. %), except for one sample (0.45 wt. % Fe₂O₃). The Greene-Kelly test (Li-saturation and heating) gave very good results for the measurement of the *d*(001) of the two end-members. Nickel, Ti, and Cr enrichment in smectite is related to the chemical composition of hydrothermal solutions that passed through the ophiolite complex.

Key Words—Biga Peninsula, Fe-rich Beidellite, Montmorillonite, Turkey.

INTRODUCTION

Beidellite represents the Al → Si tetrahedrally substituted end-member of the dioctahedral smectite series, whereas montmorillonite represents the Mg → Al octahedrally substituted end-member (Brindley, 1980). Lim and Jackson (1986) reported the presence of montmorillonite-rich smectite with randomly interstratified beidellite. These intermediate compositions between montmorillonite and beidellite are difficult to interpret because detailed experimental studies have not been performed to determine the phase relations between the end-members.

Yamada *et al.* (1991) completed a detailed investigation on the experimental synthesis of smectites in the montmorillonite-beidellite series utilizing X-ray diffraction (XRD) and the Li test of Greene-Kelly (1953a). According to Yamada *et al.* (1991) montmorillonite decomposed into an assemblage of beidel-

lite, saponite, and silica above 375°C. Because Mg ions are divalent and essential for the crystallization of trioctahedral smectite, Mg-free or Mg-containing systems behave differently at higher temperatures. In the Mg-free system, M₀B₁₀₀ occurs and trioctahedral smectites such as saponite and trioctahedral smectite with octahedral charges are absent. Whereas in the Mg-containing system, M₁₀₀B₀-M₂₅B₇₅, both dioctahedral and trioctahedral smectites were observed. Yamada *et al.* (1991) concluded that phase relations in the montmorillonite-beidellite pseudo-binary system indicate that no complete solid-solution series exist.

Larsen and Wherry (1925) named beidellite for a clay specimen from the type locality in Beidell, Colorado. Ross and Hendricks (1945) redefined beidellite as the aluminium-rich end-member of an isomorphous series of dioctahedral montmorillonites. Weir and Greene-Kelly (1962) reported that the clay specimen

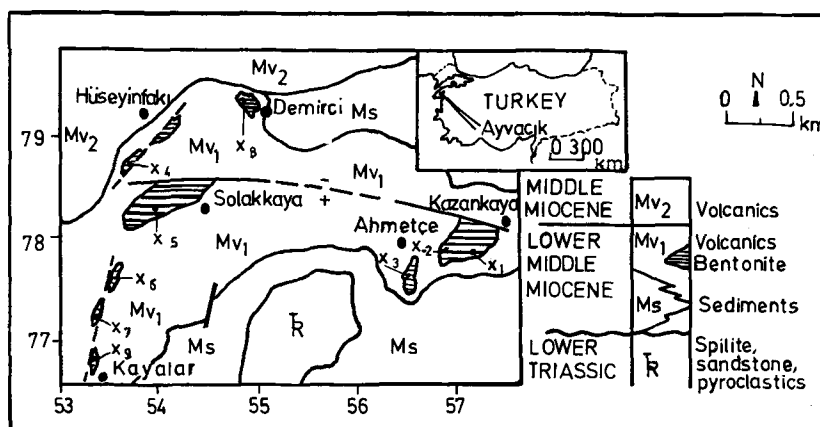


Figure 1. Index geological map of the study area. (X₁₋₉: Samples in the study).

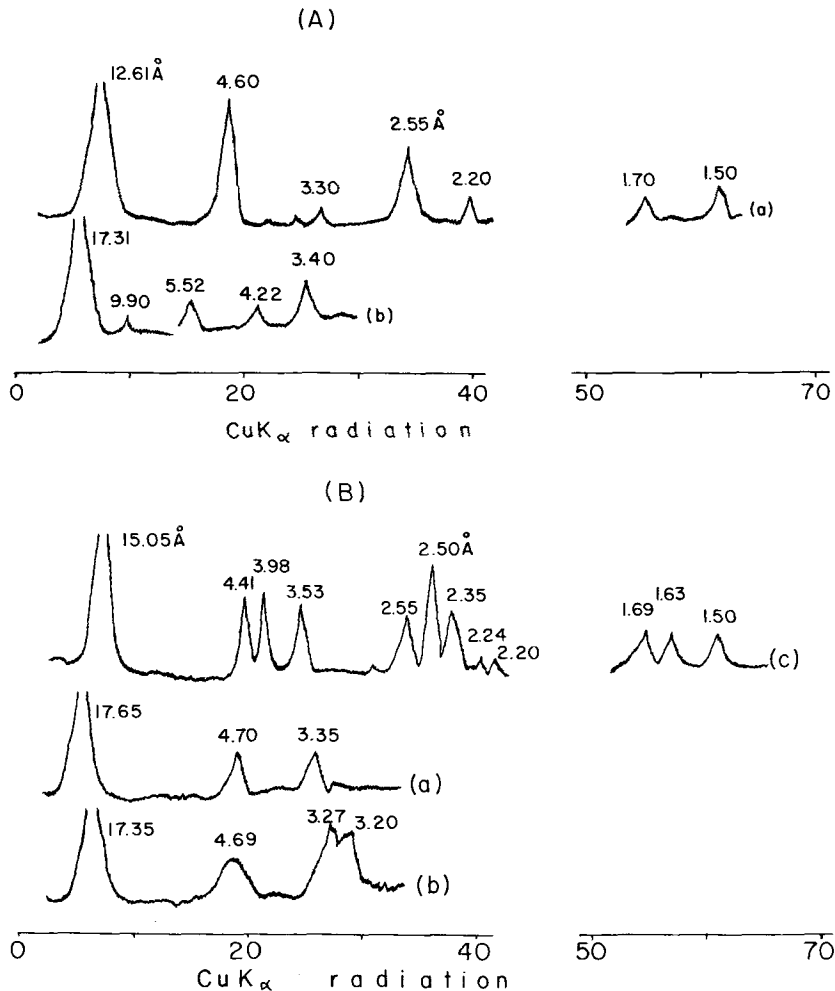


Figure 2. XRD data to distinguish montmorillonite from beidellite. (A) Montmorillonite [(a) air-dried, (b) ethylene-glycol saturated] in sample 1. (B) Beidellite [(a) ethylene-glycol saturated, (b) Greene-Kelly test + glycerol treated, (c) air-dried] in sample 9.

from the Black Jack Mine, Idaho, was a beidellite, and it is a dioctahedral montmorillonite mineral containing very little Mg or Fe. Nagelschmidt (1938) calculated the structural formula for the Beidell, Colorado sample from the analysis given by Larsen and Wherry, as shown: $(\text{Si}_{3.58}\text{Al}_{0.42})(\text{Al}_{1.39}\text{Fe}_{0.50}\text{Mg}_{0.09}\text{Ca}_{0.03})(\text{Ca}_{0.19}\text{Na}_{0.14})\text{O}_{10}(\text{OH})_2$, with excess charge (valency units) deviating from the ideal of -0.42 (tetrahedral), -0.11 (octahedral sites in 2:1 layer), and $+0.52$ (interlayer) and an exchange capacity equal to 0.46 M^+ per half unit cell. From Ross and Shannon (1925), a clay sample from the Black Jack Mine, Carson District, Owyhee County, Idaho, has a structural formula of: $(\text{Si}_{3.46}\text{Al}_{0.54})(\text{Al}_{1.96}\text{Fe}_{0.04}\text{Ca}_{0.23}\text{Na}_{0.02}\text{Mg}_{0.02}\text{K}_{0.01})\text{O}_{10}(\text{OH})_2$, with excess charge deviating from the ideal of -0.54 (tetrahedral), and $+0.53$ (interlayer) valency units and an exchange capacity equal to 0.54 M^+ per half unit cell. Shapiro and Brannock (1956) proposed the following structural formula for Na-saturated samples: $(\text{Si}_{3.48}\text{Al}_{0.52})(\text{Al}_{1.98}\text{Fe}^{3+}_{0.02})$

$\text{Mg}_{0.01})(\text{Na}_{0.45}\text{K}_{0.01})\text{O}_{9.98}(\text{OH})_2$ with charges deviating from the ideal of -0.52 (tetrahedral), $+0.02$ (octahedral), and $+0.46$ (interlayer) valency units.

Ross and Hendricks (1945) defined beidellite as a mineral with Al in tetrahedral coordination. They gave the structural formula $(\text{Si}_{7.88}\text{Al}_{0.12})(\text{Al}_{3.26}\text{Mg}_{0.84})\text{O}_{20}(\text{OH})_4\text{X}_{1.04}$ where X is a monovalent cation. Dioctahedral smectite minerals are found as weathering products of volcanic ash, tuff, and other rocks, as the result of hydrothermal processes. These rocks are generally always associated with a fault zone that creates favorable conditions for transporting ascending geothermal waters. Montmorillonite is a common dioctahedral mineral, but beidellite is more rare (Güven, 1988).

Hydrothermal alteration of andesitic tuffs commonly produced Fe-rich montmorillonite in Turkey (Çoban and Ece, 1990; Ece, 1992; Çoban, 1993), but Fe-rich beidellite occurrences from the same parent rocks are rare. Most iron-rich, high-charge beidellites in verti-

Table 1. Comparison of XRD data of Ayvacık bentonites and Ca-BJM beidellite of Idaho (Weir and Greene-Kelly, 1962) and DeLamar Mine, Idaho (Post *et al.*, 1997).

(hkl)	Black Jack Mine (d Å)	DeLamar Mine (d Å)	Ayvacık (d Å)
110	4.42	4.471	4.41
022	3.95	4.055	3.98
023	3.54	3.524	3.53
200	2.57	2.565	2.56
202	2.52	2.508	2.50 ¹
203	2.36	2.348	2.35 ¹
040	2.24	2.234	2.24
041	2.19	—	2.20
240	1.693	1.696	1.69
243	1.623	1.652	1.635
060	1.498	1.491	1.500
001	15.1	15.10	15.05 ²
001	16.8	17.00	17.35 ³
001	17.6	17.58	17.65 ⁴

¹ broad

² air dried

³ ethylene glycolated

⁴ Green-Kelly test + glycerol treated.

sols and mollisols have been reported as a product of mica weathering (Badraoui *et al.*, 1987; Badraoui and Bloom, 1990). They also reported that during weathering, soil mica is transformed first to vermiculite and then to beidellite, preserving the tetrahedral character of the charge. The type locality of beidellite is in Idaho, USA, and the locality has a Cretaceous granodiorite basement intruded and overlain by basalts, rhyolites, and latites. Most of the host rock has been altered by weathering and hydrothermal alteration (Cupp, 1989). Beidellite was found along a primary vein, which dips steeply along a northerly trend and consists of a thin, highly altered basalt dike containing discontinuous clay seams on the east side and deposits of silver and gold on the west side (Post *et al.*, 1997).

The objective of this work is to document parent-rock alteration and to identify and characterize the Fe³⁺-rich montmorillonite-beidellite series. The compositional variation described above suggests a com-

Table 2. DTA results of Ayvacık bentonite samples; Ca-BJM is beidellite from Black Jack Mine, Idaho (Greene-Kelly, 1957).

Sample no:	Endothermic dehydration	Reactions (OH) loss	Exothermic reactions
1	135°C	670°C	920°C
4	195°C	880°C	918°C
	145°C	600°C	
8	135°C	555°C	975°C
	210°C	800°C	
9	140°C	560°C	975°C
	205°C		
Ca-BJM	140°C	560°C	970°C
	210°C		

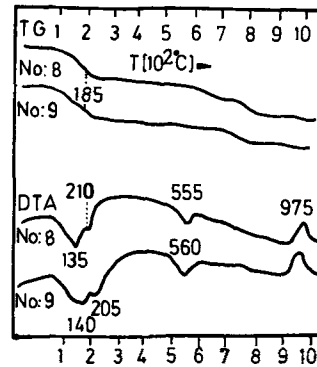


Figure 3. DTA data.

plex volcanogenetic history for the bentonite deposits. Hydrothermal alteration of volcanic rocks commonly produces a wide variety of clay minerals and other non-clay mineral products as a consequence of their complex thermal and chemical histories and morphological features.

GEOLOGIC SETTING

Widespread calc-alkaline magmatism occurred in Early-Middle Miocene in the Biga Peninsula. Wide areas covered by andesites, dacites, rhyolites, acidic tuffs, and several large granodiorite plutons were emplaced during this period (Borsi *et al.*, 1972).

The study area is SE of the town of Ayvacık. The lithology of the oldest rocks consists of carbonate blocks, spilitic rocks, sandstones, mudstone, and pyroclastics. The montmorillonite-beidellite series was found in the Ayvacık bentonites. These bentonites were formed along a fault zone within Miocene andesitic and trachyandesitic tuffs, as a result of volcanism and young tectonic events of the Aegean Region (Çoban, 1993). The stratigraphic succession in the region where bentonite occurs starts with gray, yellow, reddish brown highly fractured, hard, partially altered andesite and trachyandesite at the base, and passes upward to yellow-brown, highly altered tuffs and agglomerates. This is followed by black and hard basalt, basaltic andesite, and partially trachyandesite lavas. The lower part of the volcanic succession is both similar to "Ezine Volcanics" (Siyako *et al.*, 1989) and

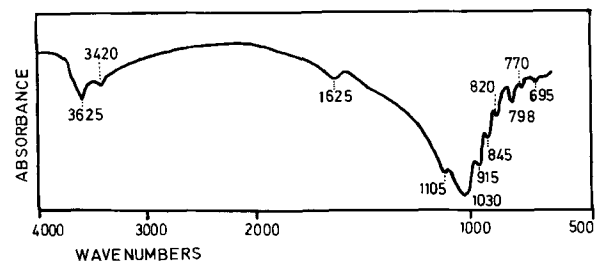


Figure 4. IR data.

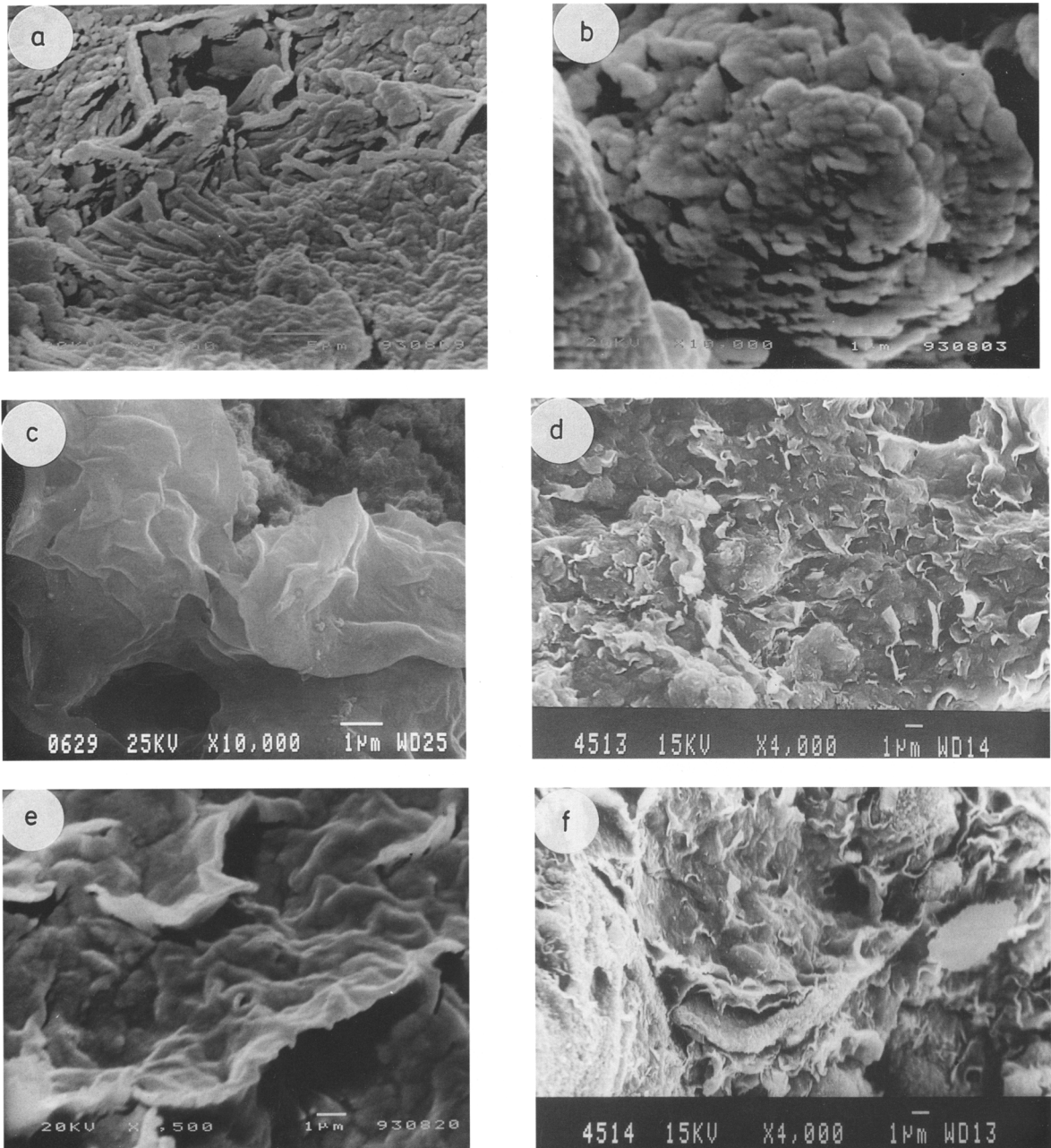


Figure 5. SEM photomicrographs of Ayvacık bentonites. (a) Beidellite exhibits ribbon textures which are 2–3 μm in length and $<0.2 \mu\text{m}$ wide in sample 9. (b) Rosette morphology of beidellite in sample 5. (c) Mossy aggregate with felt-like texture of montmorillonite-beidellite series. (d) Montmorillonite-beidellite series exhibit short and small flakes on the matrix in sample 7. (e) Wavy flakes of montmorillonite-beidellite series in sample 7. (f) Vitrification process of volcanic glass like an opening of onion skins and forming of montmorillonite flakes in sample 4.

Lower-Middle Miocene “Behram Volcanics”; the upper part of this succession is the time-equivalent of Middle Miocene “Hüseyinfaki Volcanics” (Erçan *et al.*, 1995). Fine-grained, lacustrine sedimentary rocks of carbonate cemented fine-grained sandstone, siltstone, claystone, and clayey rocks show a lateral tran-

sition to a volcanic series. Andesites with glassy texture were altered to smectite and cryptocrystalline cristobalite. They are concentrated in the areas where bentonites are present (Figure 1).

Stratigraphically, bentonite is present in the middle horizon of the volcanic succession. Major deposits are

Table 3. The results of whole rock bentonite analyses (wt. %). Samples 1, 2, and 3 from Ahmetçe; 4 and 5 from Hüseyinfaki; 6, 7, and 9 from Kayalar; 8 from Demirci villages. LOI = loss on ignition.

Sample no:	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	K ₂ O	Na ₂ O	LOI	Total
1	62.01	19.15	5.71	4.07	2.06	1.26	1.08	3.90	99.30
2	64.76	18.62	5.57	3.62	1.91	1.25	1.10	3.07	99.30
3	64.33	16.42	7.73	2.89	1.94	1.96	0.86	3.45	99.58
4	67.60	19.03	3.82	2.39	1.48	1.73	1.45	2.45	99.95
5	64.33	16.42	7.83	2.89	1.94	1.96	1.20	3.09	99.66
6	63.28	19.81	5.84	3.33	1.48	1.65	1.23	3.15	99.97
7	56.21	22.32	9.34	2.28	1.53	0.55	1.95	5.54	99.72
8	63.80	19.45	5.10	1.89	1.91	1.68	1.80	4.09	99.72
9	63.43	19.60	5.85	2.05	1.72	1.98	1.05	3.85	99.53

exposed especially in the Solakkaya area, south of Hüseyinfaki (Fe-rich), the Kazankaya area east of Ahmetçe (quartz and cristobalite-rich bentonite) and Kayalar (mostly white bentonite) village. A total of nine deposits, which originated from andesitic tuffs, are distributed as irregular lenses and vary in thickness (5–20 m) in the region. Petrographic studies revealed that the bentonization process is associated with andesite, andesitic tuffs, and minor trachyte. Widely distributed and extremely altered andesites and minor trachyte exhibit mostly microlitic porphyritic texture containing little glass. Andesitic rocks are made of (phenocrysts) plagioclase (oligoclase-andesine; 65–70%), hornblende (10–15%), biotite (10%), and pyroxene (augite; 5%). Generally, the matrix consists of fine-grained plagioclase microlite and some samples are composed completely of volcanic glasses. In the vicinity of the bentonite deposits, vitric tuffs are widely altered to the smectite group and chalcedony (authigenic silica) crystals were formed under the influence of warm hydrothermal solutions as a secondary mineral.

METHOD OF STUDY

During field studies, samples were collected for mineralogical, thermal, and chemical analyses. The samples were washed with deionized water three to four times and filtered under vacuum to remove excess cations that cause flocculation. Excess water was removed by centrifuge. Then, the size fraction <2 µm was separated by sedimentation according to Stoke's law (Gibbs, 1965 and 1968).

For XRD analyses, a RIKAGU DMAX-2200 X-ray diffractometer with CuKα radiation was used. The XRD analyses involved random powder specimens, and oriented clay mineral aggregates of air-dried, ethylene glycol treated and heated (600°C for 1 h) specimens. The Hofmann and Klemen (1950) and Greene-Kelly (1952, 1953a, 1953b) tests were used to distinguish montmorillonite from beidellite. The Hofmann and Klemen (1950) and Greene-Kelly (1952, 1953a, 1953b) tests consist of heating a Li-saturated (LiCl and 80% ethanol) sample of a mineral known to belong to the montmorillonite-beidellite series to 250–300°C overnight and treating in a glycerol bath at 90°C for

12 h. If the Li-saturated sample treated with glycerol displays a *d*(001)-value at 9.5 Å, it indicates a montmorillonite and a *d*(001)-value of 17.7 Å indicates a beidellite.

For differential thermal analyses (DTA), a Netzsch STA model apparatus was used to test 30 mg clay samples <2 µm, equilibrated at 58% RH, and heated at the rate of 10°C/min. Fourier Transform Infrared Spectroscopy (FTIR) used the KBr pellet technique (200 mg KBr + 0.2 mg sample). A JEOL-SCM-330 SEM was used for morphological studies. Small broken hand specimens of the original undisturbed clay samples, without any other pretreatments, were dried at room temperature and coated with Au under vacuum conditions in an argon atmosphere for the SEM studies.

Chemical analyses were determined by decomposition using the Na₂CO₃ fusion method (Hutchison, 1974) in a platinum crucible, silica was determined by gravimetric method, and other elements were analyzed by Perkin-Elmer 3030 model atomic absorption spectrophotometer after dissolution of subsamples by an HF-HClO₄ digestion method. The results of chemical analyses between whole rock and <2 µm size fractions are compared and the structural formula of the Fe³⁺-rich montmorillonite-beidellite series was calculated based on 11 oxygens.

Cation exchange capacity (CEC) was measured by displacing K⁺ for air-dried K-saturated clays using 1 mol ammonium acetate at pH 7. The respective CECs, referred to as K-CEC and K⁺, were analyzed using flame emission photometry.

RESULTS AND DISCUSSION

XRD studies

Fe³⁺-rich montmorillonite-beidellite series with intermediate compositions are found in the bentonites. X-ray powder data indicated the presence of an unusually well-ordered layer-stacking arrangement of dioctahedral smectite, and minor amounts of cristobalite (6%), illite, kaolinite, quartz, and biotite (rare) are also present. The *d*(001)-values of the smectites were between 12.61–15.49 Å which expanded to 17.31

Table 4. Chemical analyses and estimated elemental composition of <2 µm-size fractions (wt. %). LOI = loss on ignition.

Sample no:	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	K ₂ O	Na ₂ O	LOI	Total
1	54.90	20.10	5.55	1.58	4.15	1.30	0.85	9.28	88.43
2	55.15	19.85	5.06	0.96	3.35	1.20	1.02	9.95	86.59
3	54.58	20.05	5.95	1.72	3.20	1.75	0.85	9.10	88.10
4	55.02	19.56	5.15	0.98	4.14	1.25	0.78	11.15	86.88
5	54.64	20.08	5.84	1.18	3.87	1.85	1.10	11.04	88.56
6	55.26	19.75	5.80	0.95	4.10	1.60	0.98	10.28	88.44
7	54.88	20.45	6.28	1.02	3.96	1.48	1.15	10.75	89.22
8	56.10	19.65	5.20	1.12	4.05	1.88	0.92	11.50	88.92
9	56.80	28.54	0.45	0.10	0.80	0.55	0.08	12.10	87.32

Å after ethylene glycol treatment. In eight samples, $d(060)$ -values of 1.50 Å were obtained from random powder from XRD samples. These peaks were symmetric and narrow, which indicated good crystallinity. In areas where alteration is not complete, feldspar is the major mineral, and minor halloysite and kaolinite occurrences in the bentonite increase close to the fault zone.

As shown in Figure 2, the Ayvacik sample displays a $d(001)$ -value of 17.35 Å after ethylene glycol treatment and 17.65 Å after the Greene-Kelly Li-test. The similarities in XRD data between Ayvacik, the Black Jack Mine, Idaho and DeLamar Mine, Idaho (Post *et al.*, 1997) beidellites are shown in Table 1.

DTA studies

The results of DTA are summarized in Table 2. A major DTA peak occurs at 135–145°C and a minor peak occurs at 205°C (Figure 3). Thermal gravimetric (TG) curves revealed that interlayer water molecules were lost at 185°C and a second weight loss occurred between 600–800°C.

DTA data of Black Jack Mine, Idaho beidellite exhibits two endothermic peaks (140 and 210°C). These two peaks are due to loss of hydration water. The low-temperature peak is quite sharp, in contrast the higher-temperature endothermic peak is relatively small. A third endothermic peak, around 560°C, represents loss of hydroxyl, and the high-temperature exothermic peak is related to phase changes (Weir and Greene-Kelly, 1962). The Ayvacik beidellite samples (8 and 9 in Table 2) exhibit endothermic peaks at 135, 140, 205, and 210°C. Other endothermic reactions between 555–560°C in samples 8 and 9 indicate a release of crystal water and an exothermic peak appears at 975°C. These results show similarities in the thermal

behavior of the Ayvacik and Idaho beidellites. In addition, endothermic reactions between 670–880°C indicate the presence of a chlorite-like interlayer in <2 µm-size fractions.

IR studies

An intense Si-O stretching band was found at 1030 cm⁻¹ (Figure 4). This observation indicates that the position of this band can be attributed to beidellites with Al³⁺ in tetrahedral sites. This band also suggests only minor substitution by Fe³⁺ in the tetrahedral sheet. The absorption band at ~780–800 cm⁻¹ indicates minor amounts of octahedral Mg²⁺. The strong absorption at 3625 cm⁻¹ and at 820–845 cm⁻¹ are associated with vibrations of the Al-OH band in beidellite.

The major OH-bond absorption for H-O-H bonds of bending vibration exhibits bands at 3695 and 1625 cm⁻¹. These observations are similar to the IR results of Van der Marel and Beutelspacher (1976). The shoulders at 3420 cm⁻¹ are interpreted as relating to Fe-OH-Mg and Al-OH-Mg associations. The band at 3420 cm⁻¹ implies that H-bonding in H₂O of the montmorillonite system increases with increasing water content and that H-bonding is reduced in the interlayer H₂O of dehydrated montmorillonite.

The H-O-H stretching (3625 cm⁻¹) vibration of H₂O is readily lost upon heating. The 3695 cm⁻¹ band is related to the H-O-H stretching vibration of firmly bound H₂O, and the 1636 cm⁻¹ band is related to the H-O-H bending vibration. The IR absorptions caused by structural OH in montmorillonite include the O-H stretching vibration at 3625 cm⁻¹ and in-plane vibrations at 1030, 915, 845, and 820 cm⁻¹ relating to AlAl(OH), Fe³⁺AlOH, and MgAlOH interactions (Farmer, 1974; Madejova *et al.*, 1992). If the distri-

Table 5. Trace element contents (ppm) of samples.

Ni	Ti	Cr	Zn	Co	Ba	Sc	Rb	Ag	Mo	Se	W	Nd	Ta	La	Br
3500	1000	3100	127	120	100	9.7	<30	<5	<5	<5	<4	<5	<1	1	<1

Table 4. Extended.

Sample no.	Tetrahedral cations		Octahedral cations			Exchangeable cations			CEC mol/kg	Tetrahedral charge (per half unit cell)	Octahedral charge (per half unit cell)	Total interlayer charge (per half unit cell)
	Si	Al	Al	Fe ³⁺	Mg	Ca	Na	K				
1	3.75	0.25	1.37	0.29	0.42	0.93	0.11	0.11	69.8	0.25	0.18	0.43
2	3.83	0.17	1.46	0.26	0.35	0.03	0.14	0.11	73.9	0.17	0.14	0.31
3	3.76	0.24	1.39	0.31	0.33	0.13	0.11	0.15	68.8	0.24	0.24	0.48
4	3.80	0.20	1.39	0.26	0.43	0.07	0.05	0.06	74.3	0.20	0.19	0.39
5	3.74	0.26	1.36	0.30	0.39	0.09	0.07	0.08	67.2	0.26	0.24	0.50
6	3.76	0.24	1.36	0.30	0.42	0.07	0.06	0.07	72.8	0.24	0.18	0.42
7	3.72	0.28	1.35	0.32	0.40	0.07	0.05	0.06	68.2	0.28	0.19	0.47
8	3.80	0.20	1.37	0.26	0.40	0.08	0.12	0.18	73.2	0.20	0.31	0.51
9	3.76	0.24	1.98	0.02	0.07	0.007	0.01	0.04	54.7	0.24	0.14	0.10

bution of Mg and Fe in the octahedral sheet is random, the Mg-O-Al absorption should be very weak. Thus, some clustering of Mg ions must be present in the octahedral sheets.

However, absorption bands at 820 and 770 cm⁻¹ are attributed to beidellite, representing a typical Si-O-Al vibration band, and these bands help distinguish between montmorillonite and beidellite (Farmer and Russel, 1967). In the Ayvacık sample, a similar 845 cm⁻¹ band indicates a montmorillonite structure, but 820 and 770 cm⁻¹ bands are typical absorption bands of beidellite (Farmer and Russel, 1967). All these, together with XRD data, support the view that Ayvacık bentonites contain the montmorillonite-beidellite series.

SEM studies

SEM studies show that dioctahedral smectites exhibit a wavy leaf appearance. Except for the (001) plane, crystal faces are not well-developed. Thin ribbons, lath-shaped, dispersed thin flakes (Weir and Greene-Kelly, 1962), and xenomorphic planes (Henning and Störr, 1986) are the characteristic morphological structures of beidellite (Figure 5a). Also, rosette-type features with an amorphous Fe-oxide coating occur (Figure 5b), and these features show a sequence of curved thin flakes, which are common features of beidellite as described by Nadeau *et al.* (1985).

Beidellite occurs in a relatively thinner aggregate and shorter leaves (Figure 5a and b) than montmorillonite. Based on SEM studies, the major morphological difference between the two minerals is that curved thin flakes and leaves are shorter and smaller in beidellite (Figure 5c and d) than montmorillonite (Figure 5e and f), and beidellite is found as relatively thinner

aggregates (Figure 5e). Montmorillonite occurrence is seen as a result of the devitrification process of volcanic glass and glassy andesitic tuffs. Figure 5e and f shows the forming of clay flakes similar to the opening of onion skins. Cristobalite forms because of the presence of excess silica in the parent rock, which is mostly glassy andesitic tuffs and basic obsidian. Montmorillonite has longer flakes compared to beidellite (Figure 5e), whereas beidellite exhibits a wavy rosette structure with short and small flakes (Figure 5d).

Chemical analyses

High SiO₂ content in whole-rock analyses is from quartz, feldspar, and cristobalite in bentonite (Table 3). However, SiO₂ content decreases to more typical values in the <2 μm-size fractions (Table 4). The Al₂O₃ and Fe₂O₃ contents in bulk bentonite samples (Table 3) exhibit a wide range of distribution, but they are within an acceptable narrow range for clay-size fractions. The Fe₂O₃ content in whole rock analyses is relatively higher, especially in samples 3, 5, 6, and 7. High K₂O content in the clay-size fractions (samples 3, 5, and 8) is due to the presence of illite or mica. The quality of MgO is low in whole rocks, but high in the clay-size fractions. High MgO content in clays is related to ascending geothermal waters passing through amphibolites and serpentinites as basement rocks. These data indicate that Mg-containing montmorillonite is the main mineral, although sample 9 (Table 4) is closer in composition to beidellite. In XRD studies, chlorite is not clearly identified in all samples due to a very low concentration. However, a high MgO concentration in <2 μm-size fractions (Table 4), high loss on ignition (LOI), and low exchangeable cations probably indicate chlorite contamination.

Table 5. Extended.

Hf	Hg	Sb	Th	U	Sm	Eu	Tb	Yb	La	As	Cs	Sr	Sn	Ce
<1	<1	<0.9	<0.5	<0.5	0.1	<0.2	<0.5	<0.2	0.05	<2	<2	<0.05	<0.01	<5

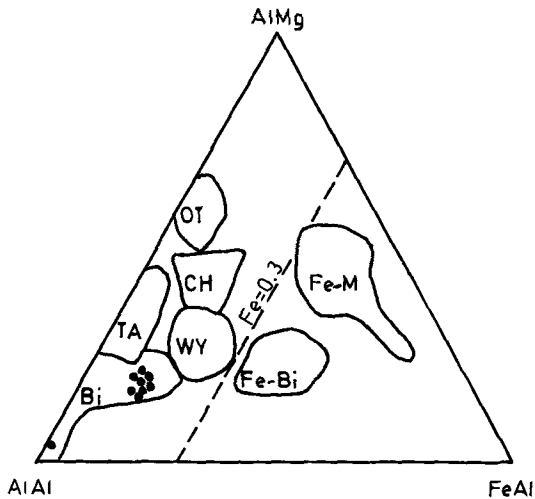


Figure 6. Projection of smectites on the diagram of Güven (1988). Key to the symbols: Bi: Beidellite, TA: Tatatilla montmorillonite, CH: Cheto montmorillonite, OT: Otay montmorillonite, WY: Wyoming montmorillonite, Fe-Bi: Fe-rich montmorillonite. The dashed line at 0.3 Fe atoms separates the Fe-rich smectites. ●: Studied samples.

Tetrahedral sites generally are Si enriched and Al varies between 0.17–0.28. Total interlayer charge (except 9) shows slightly high values (0.31–0.51) in Al content depending on the substitution in the tetrahedra. Al is the dominant cation in the octahedra, which is followed by Mg (0.33–0.43) and Fe (0.26–0.32).

The <2 μm -size fraction of sample 9 was analyzed to obtain trace element compositions of bentonite (Table 5). High concentrations of Ni, Cr, and Ti are related to hydrothermal solutions passing through the Paleozoic amphibolites and Lower Triassic ophiolite rocks in the vicinity of the bentonite deposits. Similar observations on trace element enrichment were made for the Haçılı bentonite deposits that occurred along the thrust fault between the Upper Cretaceous ophiolite complex and the Miocene pyroclastic rocks from the Çankiri Basin, Turkey (Türkmenoğlu *et al.*, 1987). Co, Ba, and Zn values are also high because of partial recrystallization near the Miocene Behramkale and Hüseyinfaki volcanic and Kestanbol granite complexes.

Montmorillonite is distinguished from beidellite on the basis of the site of negative charge on the layer. The ideal structural formula of montmorillonite is $(\text{Si}_{8.00})(\text{Al}_{3.15}\text{Mg}_{0.85})\text{O}_{20}(\text{OH})_4\text{X}_{0.85}\text{nH}_2\text{O}$. The charge arises from divalent cations, usually Mg, in octahedral sites. In beidellite, $(\text{Si}_{7.15}\text{Al}_{0.85})(\text{Al}_{4.00})\text{O}_{20}(\text{OH})_4\text{X}_{0.85}\text{nH}_2\text{O}$, the charge arises from Al^{3+} in tetrahedral sites; X is a monovalent interlayer cation. The structural formula of the montmorillonite-beidellite series as given by Heystek (1963) is: (a) $(\text{Si}_{7.27}\text{Al}_{0.73})(\text{Al}_{3.66}\text{Ti}_{0.3}\text{Fe}^{3+}_{0.04}\text{Mg}_{0.39})\text{Ca}_{0.31}\text{Na}_{0.02}\text{K}_{0.08}\text{O}_{20}(\text{OH})_4$, based on samples from the Castle Mountains, California, (b) $(\text{Si}_{6.97}\text{Al}_{1.03})(\text{Al}_{3.98}\text{Fe}^{3+}_{0.04}\text{Mg}_{0.02})\text{Na}_{0.91}\text{K}_{0.02}\text{O}_{20}(\text{OH})_4$, Black Jack Mine,

Idaho (Weir, 1965), (c) $(\text{Si}_{7.49}\text{Al}_{0.51})(\text{Al}_{3.49}\text{Fe}^{3+}_{0.02}\text{Mg}_{0.53})\text{Na}_{0.90}\text{K}_{0.01}\text{O}_{20}(\text{OH})_4$, Unterrupsroth, Germany (Weir, 1965). The structural formulae based on the Ayvacik samples are: (9) $(\text{Si}_{7.52}\text{Al}_{0.48})(\text{Al}_{3.96}\text{Fe}^{3+}_{0.02}\text{Mg}_{0.07})\text{Ca}_{0.007}\text{Na}_{0.01}\text{K}_{0.04}\text{O}_{20}(\text{OH})_4$, (7) $(\text{Si}_{7.44}\text{Al}_{0.56})(\text{Al}_{2.70}\text{Fe}^{3+}_{0.64}\text{Mg}_{0.80})\text{Ca}_{0.07}\text{Na}_{0.15}\text{K}_{0.12}\text{O}_{20}(\text{OH})_4$, (5) $(\text{Si}_{7.48}\text{Al}_{0.52})(\text{Al}_{2.72}\text{Fe}^{3+}_{0.60}\text{Mg}_{0.78})\text{Ca}_{0.09}\text{Na}_{0.14}\text{K}_{0.16}\text{O}_{20}(\text{OH})_4$. The above structural formulae of Ayvacik low-charge beidellites indicate the presence of chlorite or a chloritic interlayer. According to Weir (1965) and Heystek (1963), the total interlayer charge of ideal beidellites is >0.85 per unit cell, and >50% of the layer charge is from tetrahedral substitutions. The Ayvacik montmorillonite-beidellite series has a layer charge of <0.52 per half unit cell and <50% of the interlayer charge arising from tetrahedral substitution, except sample 9 (Table 4). Newman and Brown (1987) reported that in all beidellite analyses, Al_2O_3 ranges from 24.76 to 36.11 wt. % and Na, K, and Fe concentrations are very low.

An Al-Mg-Fe ternary diagram in Figure 6 of the main octahedral cations (Güven, 1988) shows that the Ayvacik samples belong to the beidellite section. Nadeau *et al.*, (1985) reported that the Fe_2O_3 concentration ranges from 0.03 to 0.05 wt. % and K_2O is <0.01 wt. %. Also, Ayvacik sample 9 exhibits close similarities with beidellite from Unterrupsroth, Germany.

CONCLUSIONS

Based on XRD, SEM, IR, and chemical composition, we conclude that beidellite is present in Ayvacik bentonites. These beidellites are not pure and are a mixture of two smectite end-members, formed as a result of hydrothermal alteration of calc-alkaline volcanic rocks. Petrographic and XRD studies revealed that beidellite, which is formed as a result of bentonitization, is especially common in altered plagioclase-rich (labradorite) samples.

Beidellite coexists with montmorillonite and secondary minerals, such as opal-CT, quartz, cristobalite, chlorite, and kaolinite in the clay-size fractions. Neither mica nor vermiculite were identified in these soils. These beidellite-rich samples were examined in detail by DTA, SEM, IR, and chemical analysis, and they exhibit typical beidellite features. Chemical analysis of sample 9 shows that tetrahedral substitution is not high (0.24), octahedral total charge is 2.08 and so there is no excess charge, total interlayer charge is 0.76, and exchangeable cations are K, Na, and Ca. Mg also may be in the exchange sites. Exchangeable cations of the original material show this. In addition, beidellite contains Ni (3500 ppm), Cr (3100 ppm), and Ti (1000 ppm) indicating the important influence of hydrothermal solutions during bentonitization. The trace-element enrichment of geothermal waters is a result of the deep-leaching process from the ophiolite complex.

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REFERENCES

- Badraoui, M. and Bloom, P.R. (1990) Iron-Rich High Charge Beidellite in Vertisols and Mollisols of the High Chaouia Region of Morocco. *Soil Science Society of America Journal*, **54**, 267–274.
- Badraoui, M., Bloom, P.R., and Rust, R.H. (1987) Occurrence of High-Charge Beidellite in a Vertic Haplaquoll of Northwestern Minnesota. *Soil Science Society of America Journal*, **51**, 813–818.
- Borsi, S., Ferrara, G., Innocenti, F., and Mazzuoli, R. (1972) Geochronology and petrology of recent volcanics in the Eastern Aegean Sea (West Anatolia and Lesbos Island). *Bulletin Volcanologique*, **36**, 473–496.
- Brindley, G.W. (1980) Order-disorder in clay mineral structures. In *Crystal Structures of Clay Minerals and Their X-ray Identification*, G.W. Brindley and G. Brown, eds., Mineralogical Society, London, 125–195.
- Cupp, B.L. (1989) The age relations and geochemical characteristics of the mineralization at the DeLamar Mine, Owyhee County, Idaho, M.S. thesis, Miami University, Oxford, Ohio, 55 pp.
- Çoban, F. (1993) Geology and mineralogy of some Turkish bentonites. *Mineralogica et Petrographica Acta*, **36**, 103–110.
- Çoban, F. and Ece, Ö.I. (1990) Geological features and mineralogical studies of the bentonite occurrences in the Başören region, Kütahya. *Istanbul Technical University Bulletin*, **48**, 56–63.
- Ece, Ö.I. (1992) Hydrothermal alteration of Miocene pyroclastic rocks and occurrence of bentonite deposits along fault zones in the Çankırı region, Turkey. Mediterranean Clay Meeting, Sept. 27–30, 1992, Lipari-Italy, 60–61.
- Ercan, T., Satir, M., Steinitz, G., Dora, A., Sarfakioğlu, C., Adis, C., Walter, J.H., and Yıldırım, T. (1995) Biga Yarımadası ile Gökçeada, Bozcaada ve Tavşan Adalarındaki (KB Anadolu) Tersiyer volkanizmasının özellikleri (in Turkish). *Maden Tetkik ve Arama Enstitüsü Dergisi*, **117**, 5–86.
- Farmer, V.C. and Russel, J.D. (1967) Infrared absorption spectrometry in clay studies. *Clays and Clay Minerals*, **15**, 121–142.
- Farmer, V.C. (1974) Layer silicates. In *Infrared Spectra of Minerals*, V.C. Farmer, ed., Mineralogical Society, London, 331–363.
- Gibbs, R.J. (1965) Error due to segregation in quantitative clay mineral x-ray diffraction mounting techniques. *American Mineralogist*, **50**, 741–751.
- Gibbs, R.L. (1968) Clay mineral mounting techniques for x-ray diffraction analysis: A discussion. *Journal of Sedimentary Petrology*, **38**, 242–244.
- Greene-Kelly, R. (1952) Irreversible dehydration in montmorillonite. *Clay Minerals Bulletin*, **1**, 221–227.
- Greene-Kelly, R. (1953a) The identification of montmorillonoids in clays. *Journal of Soil Science*, **4**, 233–237.
- Greene-Kelly, R. (1953b) Irreversible dehydration in montmorillonite. *Clay Minerals Bulletin*, **2**, 52–56.
- Greene-Kelly, R. (1957) The montmorillonite minerals (smectites). In *The Differential Thermal Investigation of Clays*, R.C. MacKenzie, ed., Mineralogical Society, London, 140–164.
- Güven, N. (1988) Smectites. In *Hydrous Phyllosilicates (Exclusive of Micas) Volume 19*, S.W. Bailey, ed., Mineralogical Society of America, Washington, DC, 497–559.
- Henning, K.H. and Störr, H. (1986) *Electron Micrographs (TEM, SEM) of Clays and Clay Minerals*. Akademia-Verlag Press, Berlin, 350 pp.
- Heystek, H. (1963) Hydrothermal rhyolitic alteration in the Castle Mountains, California. *Clays and Clay Minerals*, **11**, 158–168.
- Hofmann, U. and Klemen, E. (1950) Loss of exchangeability of lithium ions in bentonite on heating. *Zeitschrift für Anorganische und Allgemeine Chemie*, **262**, 95–99.
- Hutchison, C.S. (1974) *Laboratory Handbook of Petrographic Techniques*. John Wiley and Sons, New York, 527 pp.
- Larsen, E.S. and Wherry, E.T. (1925) Beidellite, A new mineral name. *Journal of the Washington Academy of Science*, **15**, 465.
- Lim, C.H. and Jackson, M.L. (1986) Expandable phyllosilicate reactions with lithium on heating. *Clays and Clay Minerals*, **34**, 346–352.
- Madejova, P., Komadel, P., and Cicel, B. (1992) Infrared spectra of some Czeck and Slovak smectites and their correlation with structural formulas. *Geologica Carpathica Clays*, **1**, 9–12.
- Nadeau, P.H., Farmer, V.C., McHardy, W.J., and Bain, D.C. (1985) Compositional variations of the Unterruproth beidellite. *American Mineralogist*, **70**, 1004–1010.
- Nagelschmidt, G. (1938) On the atomic arrangement and variability of the members of the montmorillonite group. *Mineralogical Magazine*, **25**, 140.
- Newman, A.C.D. and Brown, G. (1987) The chemical composition of clays. In *Chemistry of Clays and Clay Minerals, Mineralogical Society Monograph 6*, A.C.D. Newman, ed., Mineral Society, London 1–129.
- Post, L.J., Cupp, L.B., and Madsen, F.T. (1997) Beidellite and associated clays from the DeLamar Mine and Florida Mountain area, Idaho. *Clays and Clay Minerals*, **45**, 240–250.
- Ross, C.S. and Shannon, E.V. (1925) Chemical composition and optical properties of beidellite. *Journal of the Washington Academy of Science*, **15**, 467.
- Ross, C.S. and Hendricks, S.B. (1945) Minerals of the montmorillonite group. *US Geological Survey Professional Paper*, 205-B, 23–79.
- Shapiro, L. and Brannock, W.W. (1956) Rapid analysis of silicate rocks. *US Geological Survey Bulletin*, 1036-C, 19–56.
- Siyako, M., Bürkan, K.A., and Okay, A.I. (1989) Biga ve Gelibolu Yarımadalarının Tersiyer jeolojisi ve hidrokarbon olanakları (Tertiary geology and hydrocarbon potential of the Biga and Gelibolu Peninsulas). *Bulletin of Turkish Petroleum Geologists*, **1**, 183–199.
- Türkmenoğlu, A., Aker, S., Göğüs, G., and Turan, C. (1987) Mineralogy, petrography and origin of bentonites from Ankara-Çankırı region. *3rd National Clay Symposium Proceedings*, Ankara, Turkey, 101–112.
- Weir, A.H. and Greene-Kelly, R. (1962) Beidellite. *American Mineralogist*, **47**, 137–146.
- Weir, A.H. (1965) Potassium retention in montmorillonite. *Clay Minerals*, **6**, 17–22.
- Van der Marel, H.W. and Beutelspacher, H. (1976) *Atlas of IR Spectroscopy of Clay Minerals and Their Admixtures*. Elsevier, Amsterdam, 396 pp.
- Yamada, H., Nakazawa, H., Yoshioka, K., and Fujita, T. (1991) Smectites in the montmorillonite-beidellite series. *Clay Minerals*, **26**, 359–369.

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