

## TEXTURAL VARIATION AND COMPOSITION OF BENTONITE DERIVED FROM BASALTIC ASH

JIRI KONTA

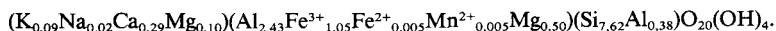
Department of Petrology, Charles University, Albertov 6  
12843 Prague 2, Czechoslovakia

**Abstract**—The Rokle bentonite deposit is part of an accumulation of argillized volcanoclastic rocks in the Tertiary stratovolcanic complex of the Doupovské Mountains east of Karlovy Vary (Carlsbad), about 100 km westnorthwest of Prague, Czechoslovakia. The arenite basalt ash was originally composed of hyaloclasts and subordinate biotite. The following types of montmorillonite aggregates were produced during the alteration of the ash in a stagnant, lacustrine environment: (1) extremely fine-grained microcrystalline aggregates that have honeycomb textures and that replace the original hyaloclasts, and (2) coarse crystalline aggregates that have more open honeycomb textures and that fill pores and cracks in altered hyaloclasts and in pumice vesicles. Both types of aggregates have the same chemical composition according to energy dispersive X-ray analysis.

Montmorillonite, separated as the <1- $\mu\text{m}$  size fraction from olive gray bentonite, has the following crystallochemical formula:  $(\text{K}_{0.09}\text{Na}_{0.02}\text{Ca}_{0.29}\text{Mg}_{0.10})(\text{Al}_{2.43}\text{Fe}^{3+}_{1.05}\text{Fe}^{2+}_{0.005}\text{Mn}^{2+}_{0.005}\text{Mg}_{0.50})(\text{Si}_{7.62}\text{Al}_{0.38})\text{O}_{20}(\text{OH})_4$ . Biotite was apparently stable during the alteration of the hyaloclasts. Anatase and possible accessory heulandite-clinoptilolite were also formed in small amounts, but were not observed by scanning electron microscopy. Goethite is the youngest oxidation product in some parts of the bentonite. Minute fragments of sodium-rich plagioclase, potassium feldspar, quartz, and muscovite are ubiquitous accessories of the original hyaloclasts. Together with kaolinite, they formed from the underlying fresh or kaolinized orthogneiss.

**Abstrakt**—Ložisko bentonitu Rokle je součástí série argilizovaných vulkanoklastických akumulací v terciárním stratovulkanickém komplexu Doupovských hor východně od Karlových Varů, asi 100 km západoseverozápadně od Prahy, Československo. Psamitový bazaltový popel byl složen z hyaloklastů a biotitu jako podřadné součástky. Během přeměny popela ve stagnujícím jezerním prostředí se vytvořily následující typy agregátů montmorillonitu: (1) extrémně jemnozrnné mikrokrytalické agregáty s plástečnou mikrotexturou, které nahradily původní hyaloklasty; (2) hruběji krystalické agregáty s plástečnými mikrotexturami více otevřenými, které vyplňují pory a trhliny v přeměněných hyaloklastech a také vesikuly v pemze. Oba typy agregátů s různou mikrotexturou mají stejné chemické složení, zjištěné energiovou dispersní analýzou paprsků X.

Montmorillonit, separovaný jako velikostní frakce pod 1  $\mu\text{m}$  z olivově šedého bentonitu, má následující krystallochemický vzorec:



Biotit zůstal stabilní během přeměny hyaloklastů. Anatas a pravděpodobný akcesorický heulandit-klinoptilolit (podle jediné velmi slabé rentgenové reflexe 8,85 Å) vznikly jako malá příměs, avšak nebyly pozorovány pod SEM. Goethit je nejmladší oxidační produkt v některých partiích bentonitu. Drobné úlomky plagioklasu bohatého sodíkem, draselného živce, křemene a muskovitu jsou všudypřítomnými akcesoriemi, které se vyskytují vně tvarů původních hyaloklastů. Spolu s kaolinitem pocházejí z podložní čerstvé nebo kaolinizované ortoruly.

**Key Words**—Basaltic ash, Bentonite, Chemical composition, Hyaloclast, Petrography, Scanning electron microscopy, Texture.

### INTRODUCTION

Many of the world's bentonites were formed by the *in situ* alteration of volcanoclastic accumulation in aqueous environments (Grim, 1953). Two newly described microenvironments that prevailed during the formation of montmorillonite, i.e., the space left by the dissolution of preexisting hyaloclasts and the free pores among solid hyaloclasts, and the cracks and vesicles in the pumice glass, provide additional information about the different microtextures found in bentonites. The concept of different microenvironments in profiles of the clay-rich residual rocks is valuable

for experts interpreting scanning electron micrographs of newly formed clay mineral aggregates (Konta, 1981). The best developed and largest crystals of clay minerals generally occur in what was originally the most open or drained microspace. Although they are the most photogenic, they do not necessarily characterize the bulk of the profile.

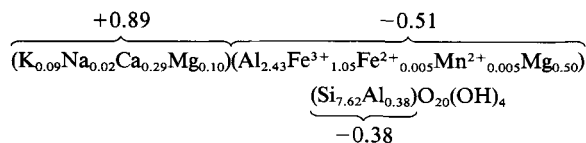
The present study was conducted to show whether some geochemical microenvironments existed during the montmorillonitization of a basaltic ash composed mostly of hyaloclasts and to compare these microenvironments with those existing during the argillization of dense granitoid rocks. The identification of well-

Table 1. Chemical analyses of (1) raw, olive gray bentonite, and (2) separated <1- $\mu\text{m}$  size fraction of montmorillonite, Rokle deposit, southeast of Kadaň, Czechoslovakia.<sup>1</sup>

	(1) Raw bentonite (wt. %)	(2) <1- $\mu\text{m}$ size fraction:	
		Room temperature (wt. %)	Water-free (calculated) (wt. %)
SiO <sub>2</sub>	48.11	49.94	54.32
TiO <sub>2</sub>	4.16	5.65	6.68
Al <sub>2</sub> O <sub>3</sub>	14.56	14.42	17.05
Fe <sub>2</sub> O <sub>3</sub>	7.48	8.48	10.03
FeO	0.19	0.03	0.03
MnO	0.05	0.02	0.02
MgO	2.73	2.44	2.88
CaO	1.93	1.69	2.00
Na <sub>2</sub> O	0.12	0.06	0.07
K <sub>2</sub> O	0.92	0.42	0.50
Li <sub>2</sub> O	—	0.002	0.00
P <sub>2</sub> O <sub>5</sub>	0.07	0.05	0.06
H <sub>2</sub> O+	4.59	5.38	6.36
H <sub>2</sub> O-	14.75	15.12	—
Total	99.66	99.70	100.00

Trace elements in the raw bentonite (ppm): Zn, 138; Cu, 150; Ni, 60; Co, 56; Cr, 44.

Crystallochemical formula of montmorillonite formed by the alteration of basaltic glass, calculated from water-free data:



<sup>1</sup> Analyst: Dr. L. Mráz.

preserved crystalline minerals in the bentonite (biotite, quartz, muscovite, sodium-rich plagioclase, and potassium feldspar) allow a comparison to be made of their chemical stabilities and that of the basaltic glass completely replaced by iron-rich montmorillonite in the same aqueous environment.

### GEOLOGIC SETTING

The Rokle deposit contains more than 40 million tons of bentonite and occurs about 3 km southeast of the town of Kadaň in western Bohemia, about 100 km westnorthwest of Prague. The bentonite forms an asymmetric, lens-like body, several hundred meters long. In its central part it is 32 to 52 m thick. The bentonite is partly eroded in the western part of the deposit. The thickest and richest bentonite is in the eastern and southern parts of the deposit where it was covered by a basalt lava flow that acted as a protective shield against denudation.

The bentonite deposit is part of a series of argillized volcanoclastic accumulations in the Tertiary strato-volcano complex in the Doupovské Mountains, east of Karlovy Vary (Carlsbad), Czechoslovakia. As in other economically important bentonite deposits in northern and western Bohemia, which were formed by the

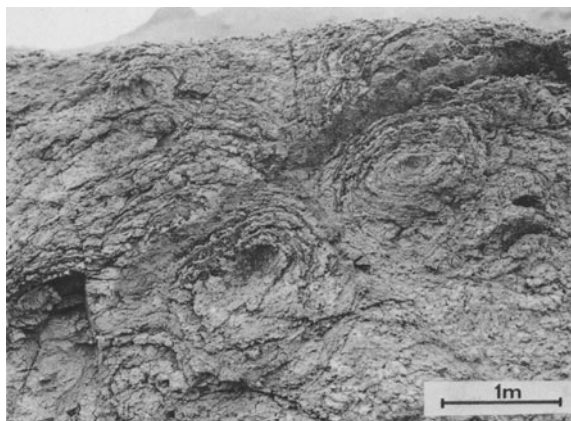


Figure 1. Typical volcanoclastic slump structure preserved in the bentonite from Rokle, southeast of Kadaň, Czechoslovakia. Height of wall is about 3.5 m.

alteration of the basaltic products of Tertiary volcanic activity (mainly ash or tuffs, volcanic breccias, and basalt rocks), the bentonite southeast of Kadaň is genetically related to an arenite basalt ash. The bentonite deposits of this region were formed in shallow, lacustrine environments, either in the pre-Tertiary relief in newly formed tectonic through syngenetic faults, or in valleys dammed by lava flows.

### EXPERIMENTAL

#### Optical and electron microscopy

Fragments of representative samples of bentonite, about 15 × 20 × 10 mm in size and dried at room temperature, were immersed in Canada balsam in small glass vessels. The removal of superfluous water and

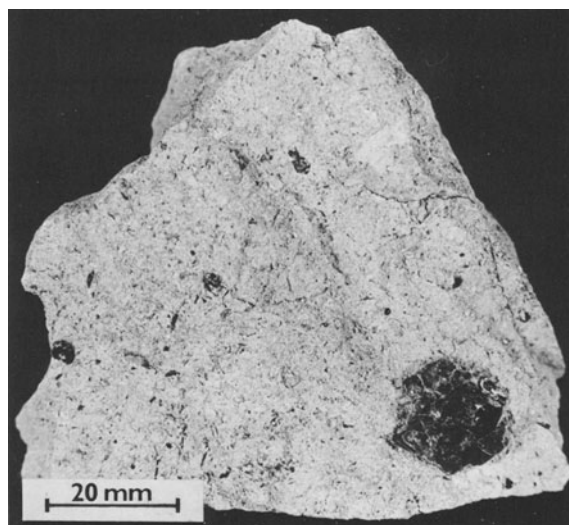


Figure 2. Hand specimen of olive gray bentonite containing fresh biotite (black), mostly <5 mm but locally as large as 20 mm. Diameter of biotite crystal at bottom right is 18 mm.

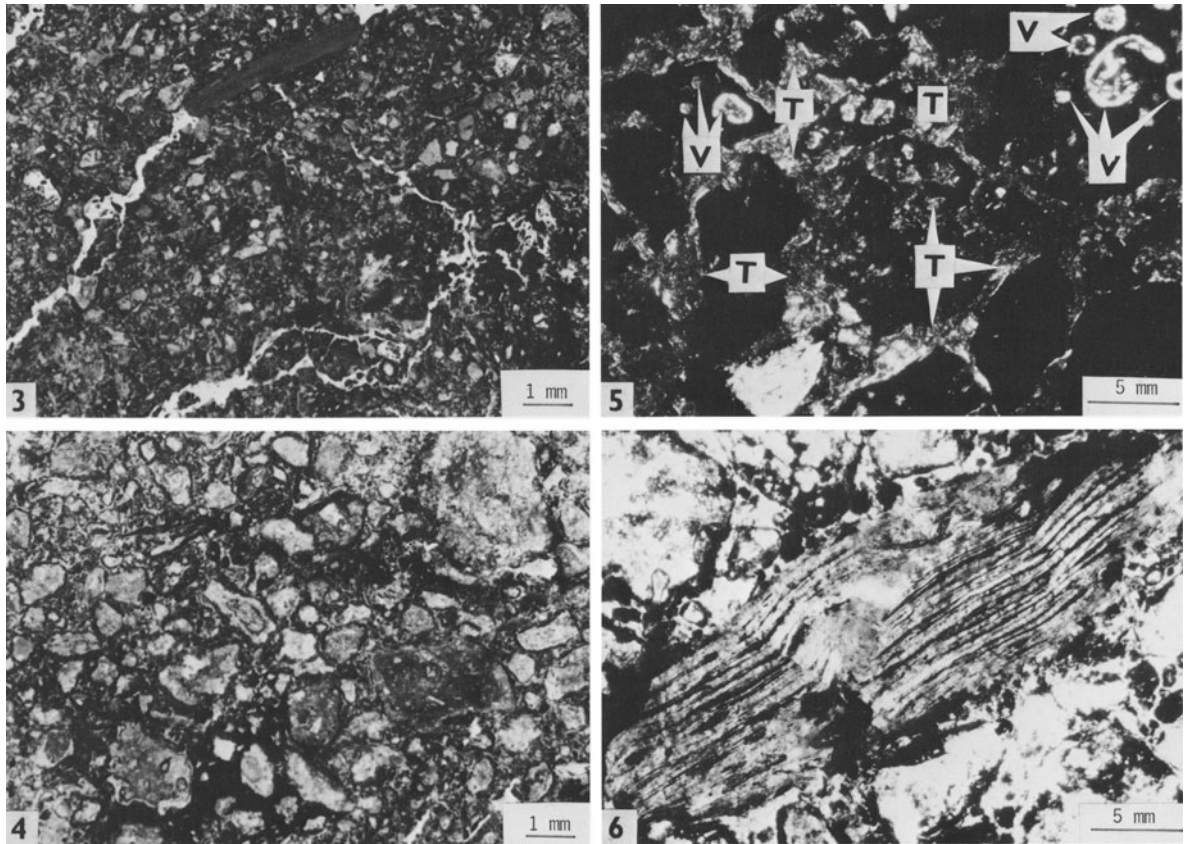


Figure 3. Photomicrograph of thin section of original shapes of fine-grained arenite hyaloclasts transformed into montmorillonite, Rokle bentonite deposit, Czechoslovakia; uncrossed nicols, 12 $\times$ . Note one black-gray biotite in top center.

Figure 4. Photomicrograph of thin section of original shapes of medium- to coarse-grained arenite to fine rudite hyaloclasts transformed into montmorillonite, Rokle bentonite deposit; uncrossed nicols, 12 $\times$ .

Figure 5. Photomicrograph of thin section showing small vesicles filled with coarser montmorillonite (V) locally with goethite, occurring in some arenite pumice hyaloclasts, completely bentonitized. Crossed nicols, 32 $\times$ . Note coarser, "fibrous" montmorillonite in intergranular space (T). Rokle bentonite deposit, Czechoslovakia.

Figure 6. Photomicrograph of thin section of deformed, fresh biotite crystal surrounded by arenite hyaloclasts completely altered to montmorillonite. Uncrossed nicols, 32 $\times$ . Rokle deposit, Czechoslovakia.

the soaking in Canada balsam took 10 days in a vacuum drying oven. The process began at 25°C and continued slowly with temperatures increasing in steps of 5°–10°C to 90°C. The thin sections were studied by polarized light.

Small representative chips were then broken from the corresponding bentonite samples and mounted in noncrystalline graphite paste. Fresh surfaces were examined without further processing. Energy dispersive X-ray analysis (EDX) was made of ultramicrocrystalline montmorillonite aggregates in the space of original hyaloclasts and the honeycombed montmorillonite that fills pores. The fragments were coated with a thin layer of gold to aid in taking micrographs. Each specimen was first studied at a low magnification to distinguish the original shapes of the altered hyaloclasts from pores, cracks, and vesicles.

#### Chemical analyses

About 200 g of dry, untreated olive-gray bentonite was coarsely ground in an agate dish. The <1- $\mu$ m size fraction was separated from about 20 g of the homogenized sample in distilled water at pH 9.5 after the addition of several drops of dilute NH<sub>4</sub>OH. A 15-min treatment in an ultrasonic vessel yielded the dispersion. The separated aqueous suspension of the <1- $\mu$ m size fraction was centrifuged to concentrate solid particles.

The chemical components present were determined by the following methods: SiO<sub>2</sub>, gravimetrically with the obtained value being complemented colorimetrically as silicomolybdic acid from SiO<sub>2</sub> passing into solution; Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, total Fe<sub>2</sub>O<sub>3</sub>, MnO, and MgO, and later Zn, Cu, Ni, Co, and Cr, by atomic absorption spectrometry; CaO, by complexometric titration from an aliquot portion of the solution; FeO, from a separate

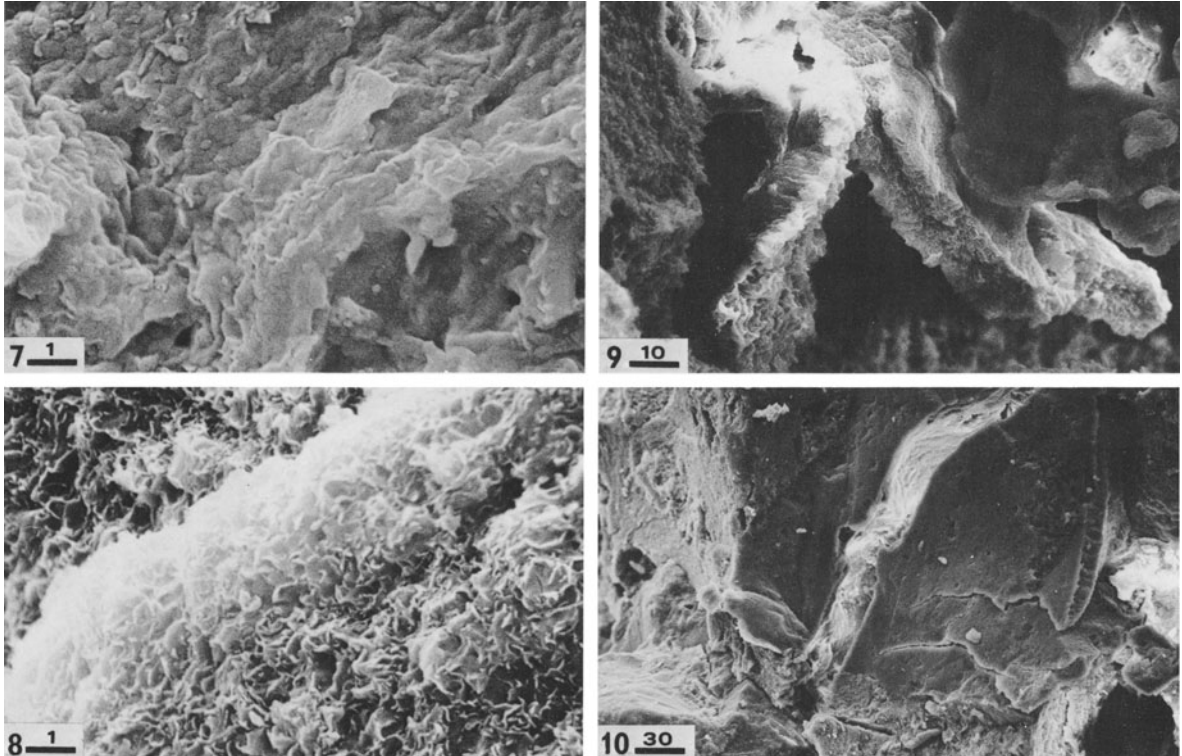


Figure 7. Scanning electron micrograph of ultrafine, dense aggregate of montmorillonite filling space of original hyaloclasts. Rokle bentonite, Czechoslovakia. Bar = 1  $\mu\text{m}$ .

Figure 8. Scanning electron micrograph of open, but very fine honeycomb texture of montmorillonite aggregate on surface of arenite hyaloclast altered to montmorillonite. Rokle bentonite, Czechoslovakia. Bar = 1  $\mu\text{m}$ .

Figure 9. The light colored coarse montmorillonite fillings contrast to the dense and ultrafine montmorillonite aggregates in space of original hyaloclasts. Rokle bentonite, Czechoslovakia. Bar = 10  $\mu\text{m}$ .

Figure 10. Scanning electron micrograph of crack filled with coarse montmorillonite (light-colored area in center) in former hyaloclast transformed to dense, ultrafine montmorillonite aggregate. Rokle bentonite, Czechoslovakia. Bar = 30  $\mu\text{m}$ .

portion of the sample by potentiometric titration with potassium dichromate solution; alkali oxides, by emission flame photometry;  $\text{P}_2\text{O}_5$ , colorimetrically as phosphovanadatomolybdic acid;  $\text{H}_2\text{O}-$ , as the loss on drying to constant weight at 110°C; and  $\text{H}_2\text{O}+$ , as the loss on ignition to constant weight at about 1000°C; (no traces of  $\text{CO}_2$  or S were found in the analyzed samples).

#### *X-ray powder diffraction*

The following X-ray powder diffraction (XRD) technique was used for the identification and semiquantitative determination of the crystalline minerals. One-half gram of the homogenized sample dried at room temperature was finely ground in an agate dish for 3 min and then mounted in an aluminum cylindrical holder. The surface of the preparation was made even by light pressure using a microscopic slide. Dry aggregates of microcrystalline montmorillonite, when finely ground, produced strongly cohesive fragments without preferential orientation. The same was valid for minute fragments of nonclay minerals embedded in the mont-

morillonite. Only biotite, the largest non-equidimensional crystal in the bentonite, was partly oriented in the preparations. Five individual preparations of the raw bentonite yielded well-reproducible XRD patterns with deviations of their integrated intensities of no more than 5% from the average values (Figure 15, no. 1). A semiquantitative evaluation of the intensities of selected XRD reflections was possible only after considering artificial mixtures of the corresponding nonclay minerals, kaolinite, and the separated <1- $\mu\text{m}$  size fraction of bentonite, and after a consideration of the chemical data (see Table 1). The following operating conditions were used on the diffractograph Dron 3: Ni-filtered  $\text{CuK}\alpha$  radiation, 40 kV, 30 mA; sensitivity =  $2 \times 10^3$  or  $4 \times 10^3$  impulse/s; time constant = 2.5 s; the speed of recording paper = 600 mm/hr; goniometer speed =  $1^\circ/\text{min}$ . The determined  $\text{K}_2\text{O}$  content minus the equivalent percentage of  $\text{K}_2\text{O}$  from the potassium feldspar and from 80% of montmorillonite was equated to biotite which, in basaltic rocks, usually contains about 7%  $\text{K}_2\text{O}$ . Clastic

muscovite was not found in thin sections of the olive-gray variety of bentonite studied.

The well-dispersed, <1- $\mu$ m size fraction was transferred onto microscopic slides as a dilute aqueous suspension. XRD patterns were obtained using these oriented preparations dried at room temperature, saturated by ethylene glycol, and heated at 550°C for 2 hr (Figure 15).

### MEGASCOPIC DESCRIPTION

Twenty-two samples of bentonite of various colors and structures were collected from the walls of a freshly dug pit of a height of 2.3 to 6.5 m on a hillside about 390 m above sea level. Figure 1 shows a common volcanoclastic slump structure in the uppermost level of the bentonite profile. The remaining 31 samples were taken from two bore holes in the central part of the deposit. The bentonite samples were highly variable in color. The basic color was olive gray, but admixed secondary iron and manganese oxides has produced a wide range of colors, from olive gray or green through violet, bluish, rust, yellow, and red, to brown. The colors alternated not only along the stratification, but commonly in any direction through the rock. In some samples, dendritic coatings of iron-manganese oxide material were abundant and locally attained a thickness of more than 1 mm. The most intense iron oxide pigmentation occurred in the uppermost parts of the bentonite deposit. The admixture of sand was small but variable. Bentonite cracked or disintegrated into small fragments on the surfaces due to atmospheric drying and shrinking.

The original fragments of the volcanoclastic material, in which volcanic glass was completely altered to montmorillonite, represented the dominant textural component of all samples of bentonite studied. The size of these altered hyaloclasts ranged from a coarse lutite through arenite to a fine rudite with lapilli several millimeters in size. An arenite volcanoclastic fraction of 0.063 to 2 mm prevailed.

Biotite crystallized from the basalt magma was brownish black to nearly black, and had on fresh surfaces a glassy luster (Figure 2). It was irregularly distributed, locally only as an accessory admixture, but commonly amounted to more than 10% of the sample. The size of the biotite flakes was generally about 1 mm, but it may have been as much as 5 to 8 mm in many samples, and locally it may have been as much as 10–20 mm.

Muscovite, quartz, and feldspar occurred as tiny angular fragments in very small admixtures and were observable only with a hand lens.

### EXAMINATION UNDER THE POLARIZING MICROSCOPE

Microscopic studies of bentonites in thin sections are rare in the geological literature in contrast to papers containing scanning electron micrographs or those re-

porting chemical and physicochemical properties, or X-ray or other radiation results. Still rarer are photographs of the textures of bentonites visible under the polarizing microscope.

The 53 samples of bentonite studied can be divided into two groups according to the grain size of the original dominant hyaloclasts, now completely altered to montmorillonite: (1) bentonites formed by the alteration of lutite to fine-grained arenite hyaloclasts (Figure 3); and (2) bentonites formed by the alteration of medium- to coarse-grained arenite to rudite hyaloclasts (Figure 4). The hyaloclasts were irregularly shaped but massive, with a high degree of sphericity. The original vesicular texture of the foamy volcanic glass was still visible in some altered hyaloclasts (Figure 5, vesicles = V). Euhedral to subhedral flakes of biotite, commonly deformed by pressure (Figure 6), occurred in all samples of bentonite as a subordinate to accessory primary constituent. The biotite was still fresh and therefore was apparently more chemically stable than the basaltic glass.

In all color varieties of bentonite, the original hyaloclasts were altered into ultramicrocrystalline montmorillonite (Figure 5, black), whereas the original, mostly spheroidal or slightly deformed, vesicles in the glass (Figure 5, V) were filled with coarser, fibrous, translucent montmorillonite. Similarly, the originally open intergranular space among the altered hyaloclasts was also filled with coarsely crystallized, translucent aggregates of montmorillonite (Figure 5, T). From this observation only, it is apparent that in the saturated-sialic stage of alteration that prevailed during the decomposition of the volcanic hyaloclasts in a stagnant lacustrine environment, montmorillonite formed two different types of aggregates: (1) extremely fine microcrystalline aggregates filling the space of the original hyaloclasts (Figure 5, most of the black areas); and (2) much coarser microcrystalline aggregates filling the space of vesicles and free pores among the original hyaloclasts covering their surface (Figure 5, light colored sites, T). Dainyak *et al.* (1984) observed under the polarizing microscope similar, coarse scale-like aggregates of trioctahedral montmorillonite, rich in Mg and Fe, that formed in the interstitial pores or gas vesicles of amygdaloidal dolerite of the Tunguska syncline.

The angular equidimensional fragments of sodium-rich plagioclase, potassium feldspar, and quartz and flakes of muscovite in the sand and silt-size fractions were always detected outside the original hyaloclasts. Their shapes and microscopic features corresponded to those of the same minerals occurring in the underlying fresh or kaolinized orthogneiss. The rare clastic grains of quartz derived from the underlying orthogneiss were full of cracks, probably caused by thermal effects. These observations strongly suggest that these minerals were derived from the underlying orthogneiss.

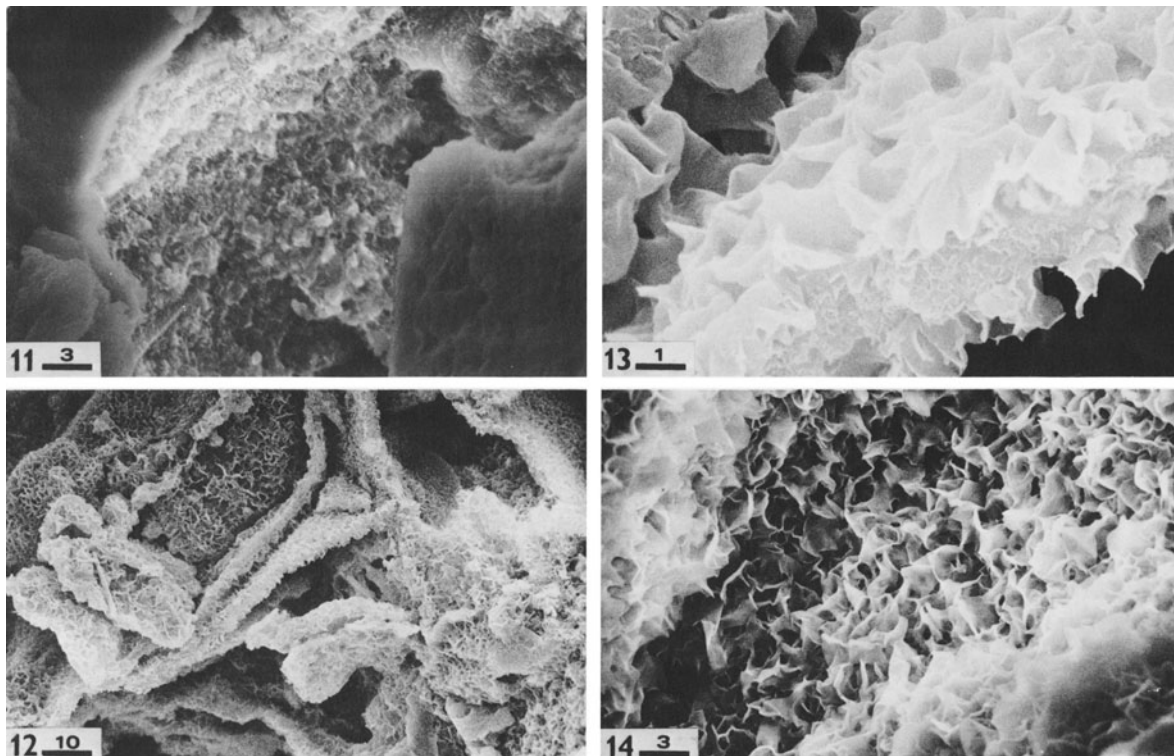


Figure 11. Imperfect but coarse honeycomb texture of montmorillonite aggregate filling crack. Rokle bentonite, Czechoslovakia. Bar = 3  $\mu\text{m}$ .

Figure 12. Scanning electron micrograph of pore space between altered hyaloclasts, filled with a more open and coarse honeycomb of montmorillonite. Rokle bentonite, Czechoslovakia. Bar = 10  $\mu\text{m}$ .

Figure 13. Higher magnification of central part of Figure 12 showing coarse honeycomb of montmorillonite. Bar = 1  $\mu\text{m}$ .

Figure 14. Scanning electron micrograph of honeycomb of montmorillonite filling space of pores in original arenite basaltic ash transformed to bentonite. Rokle bentonite, Czechoslovakia. Bar = 3  $\mu\text{m}$ .

The iron oxide pigment, locally quite dense and displaying a slight metallic luster in incident light, was determined by XRD to be goethite. The accessory kaolinite detected by XRD was not observed in thin sections nor under the scanning electron microscope.

#### SCANNING ELECTRON MICROSCOPY

The scanning electron microscopic data for most samples of the bentonite can be summarized as follows: (1) Montmorillonite occurred either as ultrafine, thin, leaf-like crystals forming a dense aggregate, or in a more open honeycomb texture. (2) The original space of the hyaloclasts was always filled with the denser aggregates of ultrafine montmorillonite crystals (Figure 7) or with the finer honeycomb montmorillonite (Figure 8). (3) The pores among the original hyaloclasts (Figure 9) which have been completely altered to the fine aggregates of montmorillonite, or vesicles or cracks (Figure 10), were always filled with montmorillonite which has a coarse and more open honeycomb texture (Figures 11–13). Thus, the coarse and open honeycomb texture of the montmorillonite aggregates appears to

have developed in more open microspace than the denser and much finer aggregates of montmorillonite which filled the space occupied by hyaloclasts. Shrubná and Vaněk (1981) observed similar microtextures in the Braňany bentonite, about 30 km northeast from the Rokle deposit.

EDX data show that all types of montmorillonite aggregates in the bentonite studied, i.e., from the coarsest and most open honeycomb textures to the densest ultramicrocrystalline aggregates, possessed the same chemical composition. The intensities of the corresponding emission lines of the major metallic elements were:  $\text{Si} > \text{Al} > \text{Fe} > \text{Ti} > \text{Mg} > \text{Ca} > \text{K}$ . Their ratios are constant in montmorillonite aggregates free of goethite. In sites rich in goethite, the intensities of the emission lines of iron increased and the emission lines of manganese were present.

#### CHEMICAL COMPOSITION

The chemical data in Table 1 relate to the olive-gray bentonite free of secondary iron oxide and the  $< 1\text{-}\mu\text{m}$  size fraction of montmorillonite from it. This variety

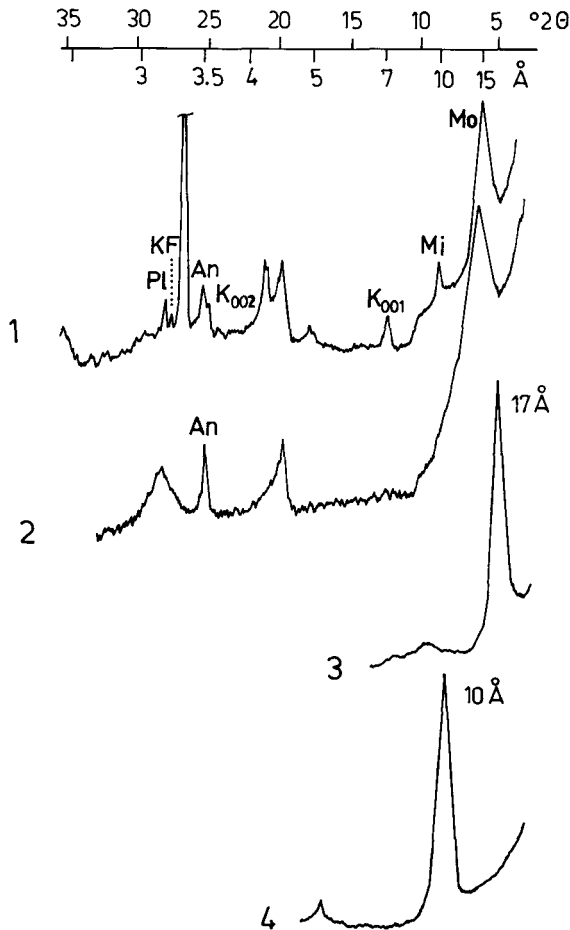


Figure 15. X-ray powder diffractograms of (1) the olive gray, raw bentonite, unoriented preparation, and of its  $<1\text{-}\mu\text{m}$  size fraction as oriented preparation, in (2) natural, (3) glycolated state, and (4) heated at  $550^\circ\text{C}$  for 2 hr.

of bentonite was formed from the fine-grained arenite volcanic ash. The differences between the chemical composition of the raw bentonite and the montmorillonite separated from it can be explained as follows: The higher percentage of  $\text{SiO}_2$  in the bentonite is due mainly to a slight admixture of quartz, sodic plagioclase, potassium feldspar, and mica (here, only biotite) and possibly accessory heulandite-clinoptilolite. The increase of  $\text{TiO}_2$  from 4.16% in the raw bentonite to 5.65% in the  $<1\text{-}\mu\text{m}$  separated size fraction and the simultaneous rise of the XRD intensity of anatase strongly suggests that anatase followed montmorillonite into the finest size fraction. The lower content of  $\text{Fe}_2\text{O}_3$  in the raw bentonite is due to dilution by the nonclay minerals, because montmorillonite is the main bearer of  $\text{Fe}_2\text{O}_3$ . The strong decrease of  $\text{FeO}$  in the  $<1\text{-}\mu\text{m}$  size fraction is due to the complete elimination of biotite, the chief  $\text{Fe}^{2+}$  mineral in the bentonite. Mn and Mg were noted in both the biotite and the newly formed montmorillonite. Therefore, the decrease of

Table 2. Integrated intensities of selected X-ray powder diffraction reflections of the minerals present (A) and their calculated mass percentage (B), olive gray bentonite, Rokle deposit, Czechoslovakia.

	Reflection d (Å)	A Integrated intensities (unitless)	B Calculated wt. %
Montmorillonite	15.	1056	76.6
Mica (biotite)	10.	115	12.5
Quartz	4.26	36	2.6
Heulandite-clinoptilolite (?)	8.8	11	0.8
Kaolinite	7.15	27	2.0
Goethite	4.18	—	—
Anatase	3.51	184	4.4
K-feldspar	3.24	8	0.2
Na-plagioclase	3.18	35	0.9
		1472	100.0

MnO and MgO contents in the separated montmorillonite is not profound. The decrease of CaO in the  $<1\text{-}\mu\text{m}$  size fraction is due mainly to the separation of sodic plagioclase, the very small amount of apatite, and possibly, heulandite-clinoptilolite. Similarly, the decrease of  $\text{Na}_2\text{O}$  in the  $<1\text{-}\mu\text{m}$  size fraction is influenced by the separation of a slight admixture of sodic plagioclase and possibly, heulandite-clinoptilolite. The remaining portion of CaO and  $\text{Na}_2\text{O}$  is assumed to be bonded in the interlayer space of montmorillonite. The strong decrease in  $\text{K}_2\text{O}$  from 0.92% in the raw bentonite to 0.42% in the  $<1\text{-}\mu\text{m}$  size fraction is due chiefly to the absence of biotite and accessory potassium feldspar. The increase of  $\text{H}_2\text{O}^+$  and  $\text{H}_2\text{O}^-$  in the  $<1\text{-}\mu\text{m}$  size fraction under the same conditions of humidity is due to the high content of montmorillonite in this fraction. After subtracting 5.65%  $\text{TiO}_2$  for anatase and 0.12% ( $\text{CaO} + \text{P}_2\text{O}_5$ ) for apatite from the second column in Table 1, the percentage of  $\text{H}_2\text{O}^+$  in laboratory-dry "pure" montmorillonite increased from 5.38% to 5.73%. Then, if 5.73%  $\text{H}_2\text{O}^+$  was bonded in montmorillonite alone, the 4.59%  $\text{H}_2\text{O}^+$  found in the raw bentonite corresponds (after  $4.59:5.73 = x:100$ ) to about 80% montmorillonite in the original bentonite.

The crystallochemical formula of montmorillonite was calculated from the data of the third column in Table 1 on the basis of the 44 anion charges of  $\text{O}_{20}(\text{OH})_4$ . The  $\text{TiO}_2$  content was subtracted as anatase determined by the XRD method; the stoichiometric portion of CaO was subtracted together with the necessary  $\text{P}_2\text{O}_5$  required for apatite. The  $\text{Fe}^{3+}$  content in the octahedral sheet of the montmorillonite appears to be unusually high. According to Grim and Güven (1978), montmorillonites in common bentonite belong to the montmorillonite-beidellite series and contain only small amounts of iron (about 3%  $\text{Fe}_2\text{O}_3$ ) in their crystal structures. They reported that only 1 of 30 montmorillonites examined contained as much as 9.66%  $\text{Fe}_2\text{O}_3$ , calculated to the sample free of iron oxide pigment, whereas

a second iron-rich sample contained only 5.84%  $\text{Fe}_2\text{O}_3$ , calculated as material without molecular water.

The negative charge of the 2:1 layer of the montmorillonite studied was  $-0.89$ , i.e., near the arithmetic mean of the 30 montmorillonites studied by Grim and Güven (1978) which had negative charges ranging from  $-0.50$  to  $-1.20$ . The unusually high strength of the bonding of the interlayer cations is therefore likely due to the relatively high negative charge ( $-0.38$ ) of the tetrahedral sheets closer to and thus having more influence on the interlayer space compared with the octahedral sheets with a negative charge of  $-0.51$ . The marked substitution of  $(\text{Al} + \text{Fe}^{3+})$  by  $(\text{Mg} + \text{Fe}^{2+} + \text{Mn}^{2+})$  in the octahedral sheet in the ratio  $(2.43 + 1.05)$ : $(0.50 + 0.1)$ , i.e., about 7:1, classifies the montmorillonite studied as a Cheto type. Nontronites may contain  $(\text{Al}_{1.6}\text{Fe}^{3+}_{2.4})$  as the highest possible Al concentration in the octahedral sheet and extremely low Mg portions (Vitovskaya, 1985).

#### X-RAY POWDER DIFFRACTION IDENTIFICATION

Figure 15 shows an XRD pattern of the olive-gray bentonite and three patterns of  $<1\text{-}\mu\text{m}$  size fractions from it. The XRD peaks of minerals identified in both samples are indicated by letters. Anatase was the sole admixture detected in the highly concentrated montmorillonite in the  $<1\text{-}\mu\text{m}$  size fraction. The accessory presence of apatite was deduced from the chemical data.

Table 2 contains a semi-quantitative estimation of the amounts of the minerals detected by XRD in the olive-gray variety of the raw bentonite using the method after Biscaye (1965) and Konta (1983).

#### CONCLUSIONS

The bentonite from the Rogle deposit reflects not only the chemical properties but also the textural features of its basaltic volcanoclastic parent. The observation of different microtextures of iron-rich montmorillonite, i.e., (1) dense and ultramicrocrystalline aggregates of montmorillonite in the space of the original hyaloclasts, and (2) more open and coarser honeycomb montmorillonite developed in the free space of intergranular pores separating the original hyaloclasts or in cracks and vesicles in the hyaloclasts, suggests that physically diverse microenvironments in a weathering profile can influence the resulting microtexture of newly formed clay aggregates.

In the bentonite studied, the hyaloclasts in the basaltic ash were apparently the sole source of the newly formed iron-rich montmorillonite. Neither biotite as a subordinate product of the basaltic magma nor contaminating clastic quartz, sodic plagioclase, potassium feldspar, kaolinite, and locally muscovite, originating in the underlying kaolinized or fresh orthogneiss, di-

rectly influenced the formation of the principal alteration product, iron-rich montmorillonite.

The chemical composition of the ultramicrocrystalline montmorillonite aggregates in the space of the original hyaloclasts was identical to that of the more open and coarse honeycomb montmorillonite in pore spaces. Both of the two types of montmorillonite also contained the same admixture of anatase. Thus, the participating chemical components in the aqueous solutions attained the same ratios in the bentonite body regardless of the original microenvironment. These data represent a fundamental difference from the variously crystalline kaolinite aggregates in primary kaolins that arose from granites or similar rocks. Here, better developed and coarse kaolinite crystals formed in microenvironments free of K, whereas poorly crystallized and poorly developed kaolinite crystals formed in microenvironments containing some K and commonly a detectable admixture of illite or related interstratification (Konta, 1981).

The decisive cations passing into solution from the basaltic glass, especially Ca and Mg, are characteristically more mobile because of their stronger hydration force compared to the less hydrated, and, therefore, less mobile K, typical of the weathering crusts of granitic or similar rocks. This high mobility of Ca and Mg in the aqueous environment contributed to a rapid attainment of chemical homogeneity between the space of the hyaloclasts and that of the free pores. The ratios of chemical components transported from the space of hyaloclasts into any free microspace in the vicinity were the same during the montmorillonitization of the unstable basaltic glass. The development of different microtextures of montmorillonite in the bentonite studied was controlled only by the diverse microenvironments. It is logical to assume that within the solid hyaloclasts of the basic silicate composition, the saturation of aqueous solution by less mobile chemical elements was higher than in any free space in their vicinity.

#### REFERENCES

- Biscaye, P. E. (1965) Mineralogy and sedimentation of Recent deep-sea clay in the Atlantic Ocean and adjacent seas and oceans: *Bull. Geol. Soc. Amer.* **76**, 803–832.
- Dainyak, L. G., Drits, V. A., Kudryavcev, D. I., and Slonimskaya, M. V. (1984) O mekhanisme vtorichnykh preobrazovaniy  $\text{Fe}^{3+}$ -soderzhashchikh smektitov iz kontinentalnykh bazaltov: *Litolog. Polez. Isk.* No. **2**, 110–117.
- Grim, R. E. (1953) *Clay Mineralogy*: McGraw-Hill, New York, 384 pp.
- Grim, R. E. and Güven, N. (1978) *Bentonites: Geology, Mineralogy, Properties and Uses*: Elsevier, Amsterdam, 256 pp.
- Konta, J. (1981) The products arisen from acid plagioclase and potassium feldspar during the kaolinization of Karlovy Vary granite: in *8th Conf. Clay Mineralogy and Petrology, Teplice, 1979*, J. Konta, ed., Univ. Karlova, Praha, 173–180.



- Konta, J. (1983) Crystalline suspended particles in the Niger, Paraná, Mackenzie and Waikato Rivers: *Mitt. Geol.-Paläont. Inst. Univ. Hamburg*, SCOPE/UNEP Sonderband, Heft 55, 505–523.
- Shrbená, B. and Vaněk, J. (1981) Scanning electron microscope investigation of the Braňany bentonite: in *8th Conf. Clay Mineralogy and Petrology, Teplice, 1979*, J. Konta, ed., Univ. Karlova, Praha, 119–128.
- Vitovskaya, I. V. (1985) Nontronite—its structure and genesis: in *Proc. 5th Meeting of the European Clay Groups, Prague, 1983*, J. Konta, ed., Univ. Karlova, Praha, 157–162.

(Received 27 April 1985; accepted 23 September 1985; Ms. 1482)