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Studies of Bentonites II*
**The Morphology of Montmorillonite Particles and the Crystal
Form of Free Silica in Some Bentonites**

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In continuation of our investigations determinations have been made of the chemical and mineralogic composition, of the viscosity of suspensions, and of the size and morphology of the particles of bentonites, of which three kinds contained free silica in the form of quartz, one was a pure montmorillonite, whereas four contained montmorillonite with additions of cristobalite and also a small percentage of quartz. The measurements of viscosity have shown that suspensions of bentonites containing free silica, chiefly as cristobalite, have a smaller structural viscosity and thixotropy.

This circumstance may be caused 1. by the dilution and by the negative influence of free silica, 2. by the unfavourable morphologic properties of the montmorillonite present, 3. by the number and kind of isomorphic substitutions in the montmorillonite space lattice. In the present paper special attention is paid to the item 2. and the authors have attempted to prove that those among the bentonites examined, which do not contain any appreciable amounts of cristobalite, have fairly big, well-developed crystals of montmorillonite of highly anisometric qualities.

Considering the conditions of formation of montmorillonite in connection with the physical and chemical factors determining the crystal form of free silica, the authors have concluded that similar conditions which favour the formation of quartz in bentonites are often very likely to favour the growth of well developed and highly anisometric crystals of montmorillonite.

The montmorillonites which belong, with regard to their composition and properties, to the group of clay minerals, show a variable chemical composition, but possess certain common properties, *e. g.* a considerable swelling capacity, a relatively high base exchange, as well as a two-dimensional layer structure. They form the main component of the clays of the bentonite type, with major or minor admixtures of free silica, kaolin, illite, chlorite, hallosite, etc.

Bentonite is used for many purposes. Its utilization for drilling muds, soil amelioration, ceramics, adsorption, etc. is partly due to its colloidal nature; the significance of the plate-like shape of the montmorillonite crystals is fully revealed here, as well as the development of a surface capable of ion exchange.

* Paper I: reference 14

Investigations of the properties of montmorillonite have lead to results of general importance, elucidating the problem of heterogeneous catalysis, interaction of colloidal particles, the mechanism of ion exchange, etc and made possible a rational variation, within certain limits, of properties of the bentonites greatly differing from one another. In spite of the recent progress, however it is often impossible either to explain the behaviour of some particular bentonites or to improve their properties to any considerable extent. In order to show that such a behaviour of certain bentonites may be caused by the presence of various substances besides montmorillonite, and that the knowledge of the genesis of a particular bentonite is often of first importance when its behaviour is to be understood, the authors present in this paper the results of their investigations of a series of bentonites, *viz.* their chemical analysis, base exchange, the results of the X-ray analysis, of the investigations of structural viscosity, particle-size, and of the morphology of particles by means of an electronic microscope.

EXPERIMENTAL

The bentonites investigated were derived from various Yugoslav deposits, often far distant from one another, and which are important either for their quality or their size. The choice was also based on the belief that the genesis of the bentonite is of first importance in determining its quality, and that one of the indications of the genesis is the crystal form of free silica, which it contains besides montmorillonite.

The bentonites were taken from the following deposits: I Vrdnik (Voyvodina), II Ginovci (P. R. Macedonia), III Šmartna ob Paki, Sample G 51 (P. R. Slovenia), IV Studene Bare (P. R. Macedonia), V Rankovci (P. R. Macedonia), VI Klanjec (P. R. Croatia), VII Šmartna ob Paki sample G 31 (P. R. Slovenia), VIII Petrovac na moru (P. R. Crna Gora).*

The chemical analyses of the above bentonites gave the following results:

Bentonite	I.	II.	III.	IV.
Loss of weight 300°—1000°C	6.41	5.20	5.87	6.01
SiO ₂	63.80	61.11	66.99	61.61
Al ₂ O ₃	22.81	21.99	19.11	22.10
Fe ₂ O ₃	2.68	2.98	3.34	4.20
MgO	0.59	6.36	0.53	4.69
CaO	2.66	1.69	3.70	0.41
Na ₂ O	1.20	0.32	0.35	0.39
K ₂ O	0.30	0.12	0.11	0.31
X-ray result	M + Q	M + Q	M + Q	M
Base exchange mequ./100 gr	89	86	86	91

* The Roman numerals given here are used throughout the paper for the different samples of bentonites.

Bentonite	V.	VI.	VII.	VIII.
Loss of weight 300°—1000°C	5.60	4.82	5.01	3.91
SiO ₂	58.08	67.11	74.65	74.59
Al ₂ O ₃	19.31	16.98	12.35	12.78
Fe ₂ O ₃	4.38	2.31	2.65	2.98
MgO	6.77	4.30	0.29	3.12
CaO	4.56	2.91	4.27	2.60
Na ₂ O	0.44	0.62	0.28	0.36
K ₂ O	0.44	0.30	0.12	0.43
X-ray result	M+Cr+Q	M+Cr+Q	M + Cr	M+Cr+Q
Base exchange mequ./100 gr.	83	79	69	71

(M = montmorillonite; Q = quartz; Cr = crystobalite)

The viscosity of the bentonite suspensions was measured with a structure viscosimeter of the Drage type (Epprecht's rotation viscosimeter) with three rotation speeds: $N_1 = 20,48$ rpm; $N_2 = 64$ rpm; $N_3 = 200$ rpm. It is an established fact that the bentonite suspensions have a structural viscosity, and show the phenomenon of thixotropy at a certain concentration of the solid phase. From the rheologic point of view, Newton's liquid is characterized by a constant ratio of the shearing stress and the velocity gradient, whereas this is not the case in a system having a structural viscosity. The apparent viscosity decreases, for instance, with the increase of the shearing stress in a thixotropic system but increases if it is reopex.¹

Speaking generally, Epprecht's viscosimeter belongs to the Couette type² which gives the following formula of viscosity

$$\eta = \frac{M(1 - (R_1/R_2)^2)}{4 \pi R_1^2 \omega L}$$

derived from Margule's equation where

- M = torque
- R_1 = radius of bob
- R_2 = radius of the cup
- ω = angular velocity
- L = length of cylinder

In a given viscosimeter the viscosity is determined by multiplying the constant of the set K by the torque divided by the angular velocity:

$$\eta = K \frac{M}{\omega}$$

The absolute flowing curves with their coordinates, the average velocity gradient D as the ordinate, and the shearing stress τ as the abscissa, are derived from the following equations:

$$D = \frac{2 \omega}{1 - c} \text{ sec}^{-1} \text{ and } \tau = \frac{M}{2 \pi r^2 L'} \text{ dyn/cm}^2,$$

where c is the ratio of the square of the radius of the bob (R_1) and of the square of the radius of the cup R_2 in cm.

L' is the hypthetic length of bob.

The bentonites were prepared for the measurement of viscosity in the following manner: the soluble salts were removed by prolonged washing after which sodium carbonate was gradually added to each particular bentonite in order to determine the quantity of sodium carbonate which effects the maximum viscosity. This quantity was used for the activation of a certain quantity of every bentonite in a water suspension, which was then evaporated. The bentonites thus activated to an optimum degree were dried for 10 hours at 110°C, and then crumbled and sieved through a sieve of 200 mesh. All the above bentonites were prepared in this manner except the bentonite Vrdnik (I) the viscosity of which was measured in its natural state (the viscosity of this bentonite does not make a curve with a clear maximum when sodium carbonate is added gradually; it is slightly sensitive to additions of electrolytes in a wide range of concentrations and its thixotropic properties and structural viscosity are excellent). The suspensions of bentonite in distilled water were prepared with various liquid phase, solid phase ratios (Q). Then the suspensions were subjected for 10 minutes to intensive mixing in a high turbulence mixer (6000 rpm). The measurements of viscosity were carried out 30 minutes after the beginning of the mixing. The results of these measurements are presented in Figs. 1, 2 and 3.

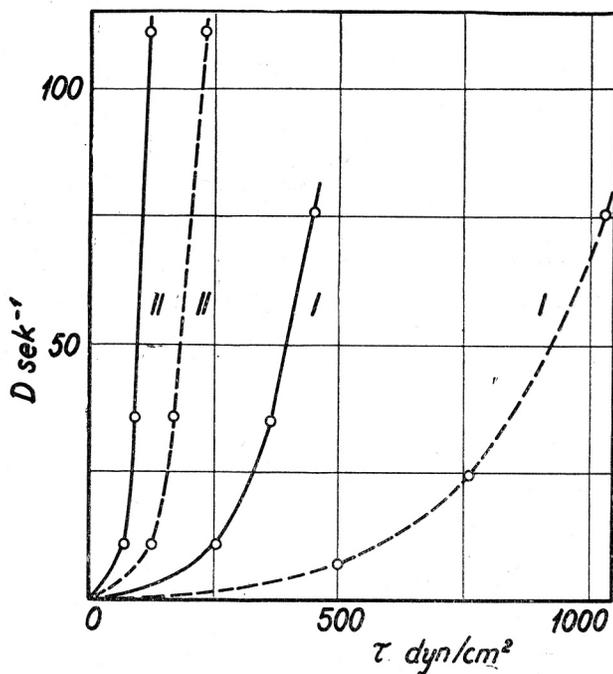


Fig. 1. Relationship between the velocity gradient (D) and the shearing stress (τ) for the suspensions of bentonite I (Vrdnik), bentonite II (Ginovci). Interrupted lines $Q = 8.5$. Full lines $Q = 9.5$.

The curves in Fig. 1 indicate the thixotropic character of the bentonite suspensions in the range of the liquid phase, solid phase ratio (Q) within which measurements were made, whereas the curves of viscosity in Figs. 2 and 3 give the quantitative relationships of the bentonites investigated with various values of Q and two angular velocities ($\omega = 2.14 \text{ sec}^{-1}$ and $\omega = 20.94 \text{ sec}^{-1}$).

The analyses of dispersion of the bentonites investigated were carried out by means of the sedimentation method in a pipette after Schweyer.³ The bentonites were previously dispersed with the optimum amount of sodium pyrophosphate in suspension (3 gr. of bentonite per 600 ml H_2O), subjected to mixing (8000 rpm) and

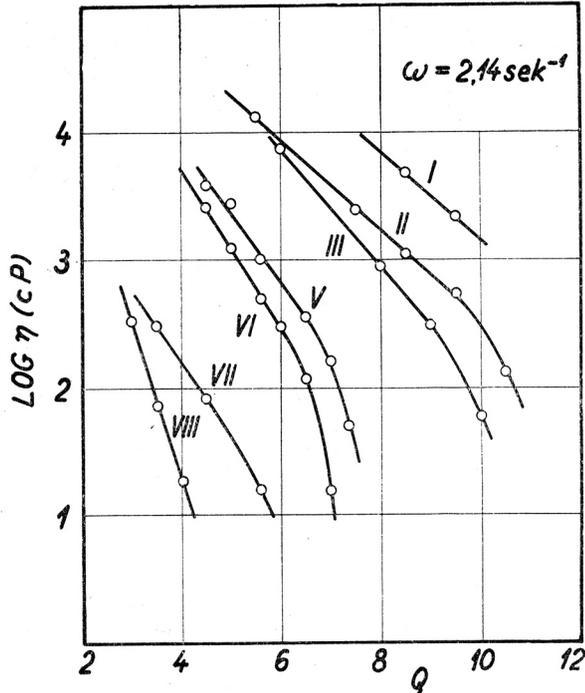


Fig. 2. Viscosity of bentonite suspensions in water at a different Q and at an angular velocity $\omega = 2.14 \text{ sec}^{-1}$ (20°C). Bentonites I Vrtnik, II Ginovci, III Smartna ob Paki, sample G. 51, V Rankovci, VI Klanjec, VII Smartna ob Paki, sample G. 31, VIII Petrovac na Moru.

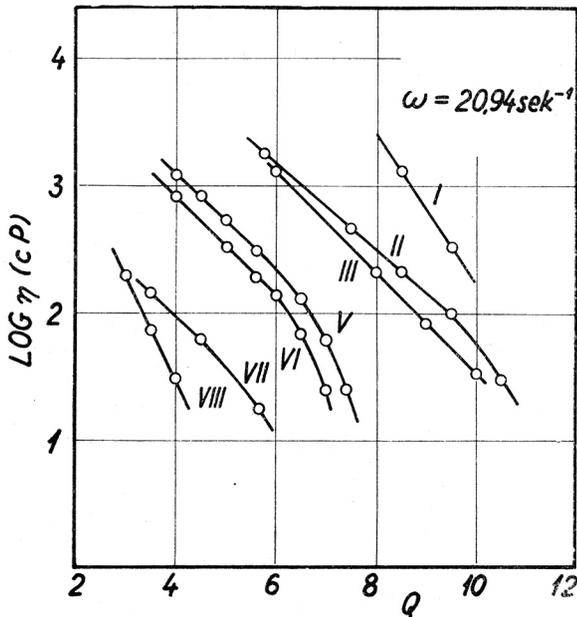


Fig. 3. Viscosity of bentonite suspensions in water at a different Q and at an angular velocity $\omega = 20.94 \text{ sec}^{-1}$. (20°C). Bentonites I Vrtnik, II Ginovci, III Smartna ob Paki, sample G. 51, V Rankovci, VI Klanjec, VII Smartna ob Paki, sample G. 31, VIII Petrovac na moru.

warmed at 90°C for an hour, after which the suspension was left in the pipette to cool to 20°C. This treatment resulted in the maximum possible dispersion as compared with the effect of other dispersing electrolytes. The distribution of the particle sizes of the particular bentonites is shown in Fig. 4 (bentonites containing quartz), and Fig. 5 (bentonites containing crystobalite and quartz). The particle size was computed from Stokes' law which is valid for spheric particles; consequently the particle radii given correspond to the diameter of spheric particles which are supposed to settle with the same speed as the non-spheric particles examined in this case⁴.

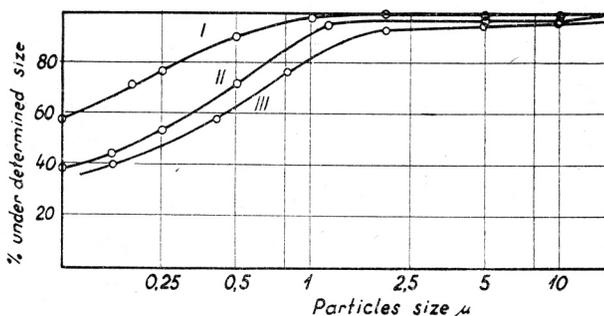


Fig. 4. Particle size distribution of bentonites containing free silica in the form of quartz. Bentonites I Vrđnik, II Ginovci, III Smartna ob Paki, sample G. 51.

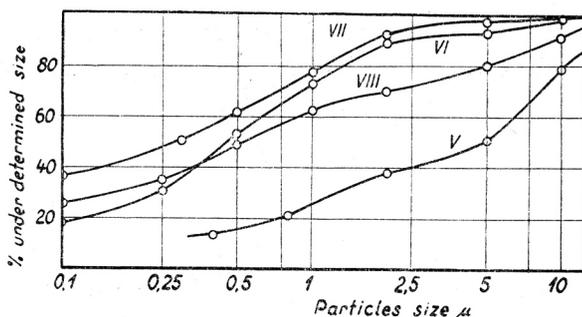
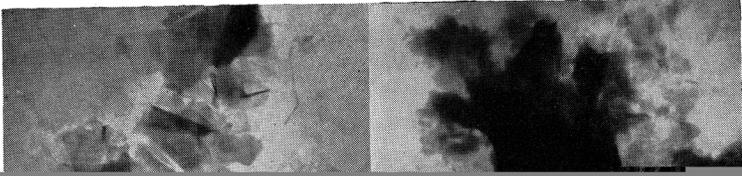


Fig. 5. Particle size distribution of bentonites containing free silica predominately as crystobalite. Bentonites V Rankovci, VI Klanjec, VII Smartna ob Paki, sample G. 31, VIII Petrovac na moru.

A general insight into the size and morphology of the particles of the bentonites investigated was obtained through photographs made by means of an electronic microscope. The bentonites were previously converted into the sodium form by treatment with solutions of sodium chloride of various concentrations. The excess of sodium chloride was removed by dialysis until the disappearance of the chlorine ions. Highly diluted suspensions of Na-montmorillonite were then subjected to intensive mixing and left for a certain time to settle. The electron micrographs (Figs. 6 and 7) were give a magnification of 10.000 times (electronic microscope Täubner & Co.).

DISCUSSION

Applying their observations based on investigations of the graphite oxide to montmorillonites, U. Hoffman, K. Endell and D. Willm⁶ have proved that the swelling of montmorillonite results from the formation of layers of mole-





cules of water between the silicate layers. Thus the authors cited have solved the basic problem of the structure of montmorillonite. C. E. Marshall⁷ and W. Noll⁸ have explained the base exchange capacity of montmorillonite crystals by the neutralization of electric charges caused by the substitution of aluminium ions for a part of silicon ions in the tetrahedral coordination of the crystal lattice, and of magnesium ions for aluminium ions in the octahedral sheet.

The swelling of montmorillonite, displayed by the increase of the elementary cell in the direction of the axis *c*, greatly depends on the nature of the exchangeable cations in the variable space; thus according to J. Mering⁹ the distance between layers of montmorillonites saturated with Ca⁺⁺ ions reaches 20 Å as a maximum; according to the investigations of K. Norrish¹⁰ in Na-montmorillonites this distance even exceeds 100 Å. This capacity of the Na-montmorillonites to divide their particles into very thin laminae endows them with precious properties of a high sedimentation volume, high thixotropy and structural viscosity.

Considerable differences however, exist in the above properties even among particular Na-montmorillonites. In her endeavours to explain this phenomenon M. D. Foster¹¹ concludes from measurements of swelling, precise analyses and structural formulae that swelling also depends on the degree of dissociation of the exchangeable ions, which increase with the decrease of the substitution in the octahedral coordination.

According to U. Hoffmann¹² the high structural viscosity and thixotropy of bentonite suspensions are caused by the formation of a special structure in the suspension (Kartenhausstruktur). Complementing this notion of thixotropy A. Buzágh¹³ has shown that an essential difference exists between highly and slightly dispersed systems, because in thixotropy the proportion between the adhesion and sedimentation capacities respectively is decisive. Steric hindrance, caused by anisodimensional forms and the cohesion of particles, acts adversely to sedimentation.

The montmorillonites investigated by the authors contained greater or lesser amounts of free silica. Bentonites with crystobalite frequently contain considerable amounts of impurities, as has been proved by the chemical and X-ray analysis, as well as by the results of the application of the solution method. Thus, for instance, bentonite VIII contains to 40 per cent of free silicic acid in the form of structurally distorted crystobalite, quartz and highly dispersed amorphous silica of which the primary particles do not exceed the size of 100 Å¹⁴.

Investigations of the dependence of viscosity on the degree of dilution have shown that bentonites containing chiefly crystobalite possess considerably poorer properties of structural viscosity (Figs. 2 and 3, bentonites V, VI, VII, and VIII).

Such a behaviour may be caused 1. by the dilution and by the negative influence of free silica, 2. by the unfavourable size and morphology of montmorillonite crystals, 3. by the number and kind of isomorphic substitution in the montmorillonite space lattice.

It is not easy to conclude which of these effects is decisive in each particular case, and this problem requires a prolonged study. In the first paper,

where the results of the investigations of the properties of free silica were given, the authors have shown that in the case of some bentonites containing cristobalite the use of the electronic microscope may reveal the adsorption of finely dispersed silica on the edges of the montmorillonite crystals, which phenomenon cannot fail to affect the thixotropic properties of these montmorillonites. In the present paper special attention should be devoted to the investigation of the size of particles and to the morphology of montmorillonite crystals.

It is clear from the distribution of particle sizes (Figs. 4 and 5) that among the bentonites investigated those containing quartz contain also a higher percentage of particles with a small equivalent spheric radius. This need not be generalized, especially with respect to the facts that quartz is usually found in coarser fractions than the structurally distorted cristobalite^{14, 15}, and that investigations by means of an electronic microscope have shown that montmorillonites in bentonites which do not contain any considerable amounts of cristobalite crystallize in well developed, highly anisometric platelets.

Fig. 6 shows electronic microscope photographs of such bentonites, Fig. 7 those of bentonite with cristobalite. If we compare these photographs a great difference in the structure of montmorillonite platelets can be observed. Thus, for instance, the specially dispersed, highly diluted preparations of Vrđnik bentonite have shown that a great part of montmorillonite platelets has dimensions of 500—700 $m\mu$ in the direction of the greater axis, and 300—500 $m\mu$ in the direction of the lesser axis, and that the platelets are very thin and translucent (probably not exceeding 2 $m\mu$ in thickness). The other bentonites shown in fig. 7 also contain montmorillonite particles of the above order of magnitude, often with their rolled edges which can be observed on the edges of incompletely dispersed specimens (Fig. 6d).

Such a highly anisometric shape is one of the favourable factors for thixotropic gel formation, as results from the geometric relationships in the notion of thixotropic gels evolved by U. Hoffmann¹².

On the other hand, the montmorillonite particles of the bentonites in Figs. 7a, b have either a flocculent appearance, or considerably smaller dimensions Figs. 7c, d (a large percentage of particles not exceeding 200 $m\mu$). In the diluted highly dispersed specimens of bentonite from Šmartna ob Paki (sample G 31) and from Petrovac na moru it is also possible to distinguish a considerable number of very small montmorillonite crystals of small thickness and also of small dimensions in the direction of both axes (50—100 $m\mu$).

It is particularly interesting to compare Figs. 6c and 7c, where two bentonites from the same area are presented, the former containing quartz and well-developed big montmorillonite crystals, the latter cristobalite with montmorillonite crystals on an average, of considerably smaller dimensions.

At present it is believed that bentonites derive from volcanic ashes of a definite composition by the process of weathering or under hydrothermal conditions. The synthesis of montmorillonite under laboratory conditions, either by hydrothermal¹⁶ or by normal action¹⁷ point out the conditions of the formation of that mineral. It is formed at a definite relationship Al_2O_3/SiO_2 in an alkaline medium and in the presence of magnesium and sodium ions. On the other hand, numerous investigations¹⁸ indicate that the formation of a definite

crystal form of silica is influenced by pH, the presence of certain catalyzers (halogens), by pressure and its duration, and by the concentration and the temperature gradient.

It is very probable that similar conditions, favouring the formation of quartz in bentonites often also favour the growth of big highly anisodimensional montmorillonite crystals.

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IZVOD

Studije bentonita. II

Morfologija montmorilonitnih čestica i kristalna modifikacija kremične kiseline u nekim bentonitima

V. Stubičan, N. Lisenko i M. Wrischer

Nastavljajući svoja istraživanja ispitali smo kemijski i mineraloški sastav, viskozitet suspenzija, veličinu i morfologiju čestica bentonita iz nalazišta: I. Vrdnik (Vojvodina) II. Ginovci (N.R. Makedonija) III. Šmartna ob Paki (N.R. Slovenija) uzorak G.51 IV. Studene Bare (N.R. Makedonija) V. Rankovci (N.R. Makedonija) VI. Klanjec (N.R. Hrvatska) VII Šmartna ob Paki, uzorak G.31 (N.R. Slovenija) VIII Petrovac na moru (N. R. Crna Gora). (Rimski brojevi na slikama odnose se na bentonite, kako su ovdje navedeni.)

Bentoniti I, II, i III sadržavaju, pored montmorilonita, slobodnu kremičnu kiselinu u obliku kvarca; bentonit IV je čist montmorilonit, a bentoniti V, VI, VII i VIII sadrže strukturno poremećen kristobalit i manje količine kvarca uz veoma disperznu amorfnu kremičnu kiselinu [bentoniti VII i VIII (14)].

Mjerenja viskoziteta vodenih suspenzija alkalno aktiviranih bentonita, na uobičajen način, pokazala su, da bentoniti, koji sadrže kvarc (I, II, III) posjeduju veći strukturni viskozitet od bentonita, u kojima dolazi, uz montmorilonit, pretežno kristobalit (V, VI, VII, VIII) (sl. 1, 2, 3). Slab strukturni viskozitet vodenih suspenzija može uvjetovati više faktora i to: 1. razređujuće djelovanje i negativan koloidno-kemijski utjecaj slobodne kremične kiseline, 2. nepovoljna morfologija montmorilonitnih čestica, 3. količina i vrsta izomorfni supstitucija u montmorilonitnoj rešetci.

Na prvu smo se točku osvrnuli u prijašnjem radu (14), a u ovom je djelu posebna pažnja poklonjena točki 2. Elektronsko-mikroskopska snimanja pokazala su, da kod ispitivanih vrsta bentonita, koje ne sadrže veće količine kristobalita (sl. 6a, b, c, d) susrećemo lijepo razvijene montmorilonitne kristale s visokim stupnjem anisometričnosti.

Povezujući uvjete geneze montmorilonita s fizikalno-kemijskim faktorima, koji određuju kristalni oblik kremične kiseline, konstatirali smo veliku vjerojatnost, da slični uvjeti, koji pogoduju formiranju kvarca, često pogoduju rastu većih montmorilonitnih kristala s visokim stupnjem anisometričnosti.

Na osnovu rezultata iznešenih u ovoj i prijašnjoj studiji (14), vrše se i dalje pokusi radi poboljšanja svojstava viskoziteta alkalnih suspenzija onih bentonita, koji sadrže kristobalit i amorfnu kremičnu kiselinu.

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