

## Clays of the Navbakhor Deposit, Uzbekistan

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**Abstract**—A new deposit of high-quality bentonites and carbonate–palygorskite clays was discovered in the Paleogene section of the southwestern foothill of Southern Nuratau Range. The bentonites have a substantially montmorillonitic composition. Minor and admixture components are represented by illite, palygorskite, quartz, iron hydroxides, and other minerals. In terms of physicochemical properties, the bentonites are subdivided into the alkaline and alkaline-earth varieties. The carbonate–palygorskite clays possess a calcite–montmorillonite–palygorskite composition. The bentonites and carbonate–palygorskite clays formed in the alkaline medium of a marine basin. The major rock-forming montmorillonite formed as a result of the transformation of structurally similar clay minerals, while calcite and palygorskite are authigenic minerals. The bentonites and carbonate–palygorskite clays have been ascertained as a material suitable for the preparation of drilling muds, as adsorbents for the bleaching of cotton oil and purification of alcoholic products, as ointment bases and the principal component for medicinal preparations, and for other purposes.

We discovered the Navbakhor deposit of bentonites and carbonate–palygorskite clays in 1998. It is situated at the southwestern foothill of the Southern Nuratau Range of the Tien Shan mountain system. The mineral deposit occupies a favorable economic–geographical position: it is situated at a distance of only 35 km from the railroad station of the city of Navoi near the Navoi–Nurata highway.

### GEOLOGICAL FEATURES OF THE MINERAL DEPOSIT

The Navbakhor deposit area is composed of the weakly dislocated Meso–Cenozoic sedimentary cover lying with a sharp angular unconformity upon metamorphosed and strongly dislocated rocks of the basement.

The sedimentary cover includes four (Upper Cretaceous–Eocene, Oligocene–middle Miocene, upper Miocene–lower Quaternary, and Holocene) structural stages separated by erosion and minor unconformities.

The sedimentary cover of the deposit area is complicated by small folds and faults related to the Alpine folding. They are observed as simple brachyanticlinal uplifts located between synclinal depressions. The disjunctive dislocations are predominantly normal or reverse faults.

Folds and faults of the sedimentary cover and basement are characterized by predominantly sublatitudinal and northwestern strikes. The folds arranged into an echelon system.

Productive units of bentonite and carbonate–palygorskite clays of the Navbakhor deposit are confined to the lower Eocene sequence that makes up the

northern limb of a synclinal fold in the Upper Cretaceous–Eocene structural stage. This syncline has an asymmetric structure with a gentle ( $5^{\circ}$ – $7^{\circ}$ ) northern and relatively steep ( $20^{\circ}$ – $25^{\circ}$ ) southern limbs. Its eastern segment is complicated by a submeridional normal fault. Its eastern block is subsided and overlapped by a thick cover of the Quaternary diluvium–proluvium.

The Upper Cretaceous–Eocene section of the Navbakhor deposit is composed of the following units: rudist limestones and quartz sandstones of the Maestrichtian, sandy dolomites and dolomites of the middle Paleocene Bukhara Formation, quartz sandstones of the middle–upper Paleocene Kazakhtau Formation (Thanetian Stage), bentonites of the early Eocene Nura Formation, carbonate–palygorskite clays of the early–middle Eocene Sugrali Formation (Ypresian Stage), and bentonite-type clays of the middle–upper Eocene Kul'taban Formation (Lutetian–Bartonian stages).

The Maestrichtian light gray limestone contains abundant remains of rudist shells, such as *Praeradiolites* ex gr. *Boucheroni bayle* in Toucas, *Orbignya vlasovi* Bobkova, *Gyropleura* sp., *Apricardia* sp., and *Biradiolites* sp. (determinations by I.M. Abdusamratova), which are typical Maestrichtian forms for Central Asia. Quartz sandstones lack fossils, but have a sharp contact with the rudist limestones. The Maestrichtian unit is 4–6 m thick.

Rocks of the Bukhara Formation overlap the Maestrichtian rocks with an erosion surface and has a two-member structure. The lower member is composed of sandy dolomites, while the upper one consists of pure white flourey dolomites containing shells of mollusks: *Corbula* (*Coneocorbula*) *angulata* Lam. and *C. (C.) biangulata* Sesh. According to A.A. Abdusamratov,

these mollusks are typical of the Thanetian Stage. The thickness is 3–5 m.

The Kazakhtau Formation is composed of quartzose, friable, and well sorted sands with subordinate feldspars (5–8%) and rare phosphorite grains. The thickness is 5 m.

The Nura Formation is composed of bentonite clays. Its lower contact is sharp and conformable. Depending on the erosional downcutting, the thickness varies from 2 to 13 m.

Carbonate–palygorskite clays of the Sugrali Formation contain phosphate matter and remains of microorganisms (foraminifers and nannoplankton), such as *Neococcolithus dubius*, *Marthasterites tribrachitus*, *Discoaster barbadiensis*, *D. lodoensis*, and *Coccolithus lopelogicus* (determination by A.R. Kushakov), which are assigned to nannoplankton zones *Marthasterites tribrachitus* (NP 12) and *Discoaster lodoensis* (NP 13) and typical of the early Eocene. The maximal thickness is 12 m.

The Eocene section is completed by greenish gray and grayish green platy bentonite-type clays of the Kul'taban Formation. Their incomplete thickness is up to 40 m.

Bentonite clays of the Nura Formation and carbonate–palygorskite clays of the Sugrali Formation of the Eocene form commercial-grade units in the Navbakhor deposit. Their explored and proven reserves amount to 7.1 Mt, while the potential resources are more than 150 Mt.

#### *Chemical–Mineral Composition and Physicochemical Properties of Clays*

The chemical–mineral composition and physicochemical properties of the bentonites and carbonate–palygorskite clays were studied using a complex of modern laboratory methods (chemical, thermic, electron microscopic, X-ray diffraction, electron microprobe, and mass spectrometric analyses). In addition, we determined the dispersity, swelling capacity, exchange capacity, and compositions of the absorbed complex of clays and their aqueous extract.

The bentonites are gray, light gray, sometimes brown in color. All of them are fine-dispersive, elastic in the wet state, and wax-type and greasy appearance. They yield fine translucent soap-type shavings upon scratching by a nail.

The clays have a pelitic texture and homogeneous-massive or laminated structure. The laminated structure is underlined by the presence of thin lenticular interlayers of brownish red or reddish yellow iron hydroxides.

On drying, bentonite samples become lighter colored and are easily split into hard scaly or platy fragments with smooth surfaces.

The mineral composition of bentonites is sharply dominated by montmorillonite (as high as 80%). Illite

is minor (10–25%). Quartz, cristobalite, iron hydroxides, calcite, palygorskite, halloysite, alunite, jarosite, and other minerals are admixtures (Mirzaev and Chini-kulov, 1999).

The bentonites are divided into alkaline and alkaline-earth varieties. The alkaline bentonites are confined to the middle section of the Nura Formation. Their dry samples slowly swell in water to form a fluffy velvety rim on the surface. The swelled mass resembles an open rose.

The alkaline-earth bentonites are confined to the lower and upper sections of the Nura Formation. In contrast to the alkaline varieties, they have a monotonous light gray color and more massive structure. They are characterized by slight swelling upon disintegration into small plates in water.

The carbonate–palygorskite clays make up the entire section of the Sugrali Formation. They are gray or light gray in the wet state. On drying, they turn white and are split into oval and oval-plane fragments with smooth surfaces and peculiar concentric structures. The dry samples are compact, relatively light in weight, strongly sticky, which is evidence for a high effective porosity of the rock.

The carbonate–palygorskite clays are composed of palygorskite, calcite, and montmorillonite as rock-forming minerals. The admixtures are represented by illite and quartz.

The alkaline and alkaline-earth bentonites of the Navbakhor deposit are similar to bentonites from other deposits in the chemical composition (Table 1). The only difference is the minimal alumina content, which is probably related to a substitution of  $Al^{3+}$  for  $Fe^{3+}$  in octahedral layers of the montmorillonite (Ginzburg and Rukavishnikova, 1951; Millo, 1968).

Results of the chemical analysis of bentonites were recalculated to the structural crystallochemical formula based on the theoretical structural formula of montmorillonite,  $R^{3+}(Si_4O_{10})(OH)_2$ , where  $R^{3+}$  is  $Al^{3+}$  and  $Fe^{3+}$ . The crystallochemical formula of alkaline bentonites and alkaline-earth bentonites corresponds to  $Na_{0.22}K_{0.17}Ca_{0.04}(Mg_{0.20}Fe_{0.280}^3Al_{1.17})[Si_{4.20}O_{10}](OH)_2 \cdot 3.91H_2O$  and  $Na_{0.14}K_{0.20}Ca_{0.05}(Mg_{0.41}Fe_{0.36}^3Al_{1.15})[Si_{4.05}O_{10}](OH)_2 \cdot 3.38H_2O$ , respectively. The calculated crystallochemical formulas of the clays confirm their montmorillonitic composition. An excess negative charge appearing upon the substitution of  $Al^{3+}$  for  $Mg^{2+}$  in octahedrons is compensated by exchange cations  $Na^+$ ,  $K^+$ , and  $Ca^{2+}$ .

The molecular  $SiO_2/(Al_2O_3 + Fe_2O_3)$  ratio in the alkaline and alkaline-earth bentonites of the Navbakhor deposit is 5.8 and 5.5, respectively, suggesting the presence of a significant amount of quartz and cristobalite.

The dominating mineral in bentonites of the Navbakhor deposit is *montmorillonite*. On X-ray diffraction

**Table 1.** Chemical composition of bentonites from different mineral deposits, wt %

Mineral deposit	SiO <sub>2</sub>	TiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	FeO	MgO	CaO	Na <sub>2</sub> O	K <sub>2</sub> O	P <sub>2</sub> O <sub>5</sub>	SO <sub>3</sub>	L.O.I.	Total
Biklyan, Russia	56.94	0.36	20.35	7.22	–	2.42	2.03	2.79	1.69	–	0.50	7.59	99.89
Cherkassk, Ukraine	52.82	0.35	19.27	7.58	–	1.80	1.53	0.20	traces	–	traces	16.78	100.33
Keles, Kazakhstan	65.67	–	14.34	6.74	–	1.66	1.32	2.27	1.35	–	–	5.78	99.13
Oglanly, Turkmenistan	56.07	–	15.18	1.03	–	3.10	3.58	0.74	0.28	–	–	19.63	99.61
Khanlar, Azerbaijan	53.64	0.26	16.39	2.73	–	4.32	2.12	1.19	0.77	–	0.06	18.40	99.88
Sarigyukh, Armenia	50.96	0.42	15.36	6.73	0.06	traces	4.78	0.84	3.35	–	0.06	17.92	100.47
Gumbria, Georgia	56.94	0.31	15.15	2.57	0.12	2.59	1.36	0.14	1.06	–	0.50	19.55	100.29
Askan, Georgia	53.14	0.38	17.54	4.08	0.22	4.64	2.91	10.82	10.64	–	0.07	14.86	100.30
Azkamar, Uzbekistan	57.92	–	18.89	5.77	–	0.01	0.72	2.63	2.63	–	–	11.52	100.09
Navbakhor:													
Alkaline bentonite	57.91	0.35	13.69	5.10	–	1.84	0.48	1.53	1.75	0.43	0.75	16.17	100.00
Alkaline-earth bentonite	56.23	0.61	13.56	6.50	–	3.76	0.69	0.98	2.20	0.92	0.49	14.06	100.00
Carbonate-palygorskite clay	46.79	–	8.63	–	3.44	2.74	10.08	–	1.60	1.99	–	24.33	99.94

Note: (–) Not detected.

**Table 2.** X-ray diffraction data on bentonites from the Navbakhor deposit

Sample no.																	Minerals	
Alkaline bentonites								Alkaline-earth bentonites										
SSH-2a		SSH1		SK-3		10ShR-1		10ShR-2		NL1-3		NL1-4		NL2-1		NL2-2		
<i>i</i>	<i>d</i> , Å	<i>i</i>	<i>d</i> , Å	<i>i</i>	<i>d</i> , Å	<i>i</i>	<i>d</i> , Å	<i>i</i>	<i>d</i> , Å	<i>i</i>	<i>d</i> , Å	<i>i</i>	<i>d</i> , Å	<i>i</i>	<i>d</i> , Å	<i>i</i>		<i>d</i> , Å
4	12.50	3	12.50	5	12.50	10	12.50	3	12.07	1	11.66	3	12.22	10	12.0	10	12.0	Montmorillonite
–	–	–	–	–	–	–	–	–	–	–	–	–	–	4	10.27	9	10.69	Palygorskite
2	9.87	1	10.07	2	10.07	–	–	–	–	1	10.17	3	10.07	8	9.87	–	–	Illite
5	8.93	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	Clinoptilolite
–	–	–	–	–	–	–	–	–	–	–	–	–	–	3	6.39	2	6.43	Palygorskite
1	4.95	–	–	1	4.95	3	4.95	1	4.95	1	5.05	2	5.00	6	5.00	3	5.03	Illite
2	4.48	2	4.49	1	4.49	2	4.49	1	4.49	2	4.49	2	4.49	2	4.49	1	4.49	Montmorillonite
2	4.23	3	4.23	2	4.23	–	–	2	4.23	5	4.28	4	4.28	3	4.27	3	4.30	Quartz
–	–	2	4.07	–	–	–	–	2	4.07	3	4.10	3	4.08	–	–	–	–	Cristobalite
2	3.92	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	Clinoptilolite
9	3.32	8	3.32	8	3.32	6	3.32	4	3.32	8	3.32	9	3.32	10	3.32	9	3.32	Quartz
3	3.17	2	3.17	3	3.17	6	3.15	3	3.17	5	3.21	6	3.20	10	3.19	9	3.19	Montmorillonite
2	1.98	1	1.98	2	1.99	2	1.99	1	2.00	1	1.99	3	1.99	8	1.96	4	1.99	Quartz
1	1.82	1	1.81	1	1.81	–	–	–	–	2	1.81	2	1.80	1	1.79	2	1.81	Quartz

(XRD) patterns of oriented preparations, it is identified by the principal basal reflections with the interplanar spacing (*d*) equal to 12.5 and 3.17–3.19 Å for the alkaline bentonites and 11.5–12.2 and 3.15–3.19 Å for the alkaline-earth bentonites (Table 2). When the preparation is saturated with ethylene glycol, the former basal reflection is shifted toward low reflection angles with *d* up to 16.8 Å and distinctly separated from the illite reflection with *d* = 10 Å.

The first basal reflection of montmorillonite with *d* = 12.5 Å indicates its alkaline nature (Zakirov, 1977), i.e., a sharp predominance of Na cations in the exchange complex. This is also confirmed by values of the exchange capacity and absorbed base complex (Table 3).

Variations in the interplanar spacings of the first basal reflection of montmorillonite in the alkaline-earth bentonites from 11.5 to 12.2 Å are related to the com-

**Table 3.** Exchange capacity and composition of the absorbed complex of bentonites and carbonate–palygorskite clays from the Navbakhor deposit, mg-equiv/100 g

Clay	Sample no.	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Na <sup>+</sup>	K <sup>+</sup>	Total	Alkalinity coefficient
Alkaline bentonite	SK1-1	2.37	12.38	60.00	0.74	75.49	4.12
"	SK1-2	2.88	13.13	60.00	0.78	76.79	3.80
"	SSh1-1	1.75	7.85	67.14	1.00	77.77	7.07
"	NL1-1	4.00	25.5	47.00	11.26	78.26	1.50
Alkaline-earth bentonite	14ShR-3	5.00	18.50	20.45	0.60	44.55	0.89
"	12ShR-4	13.00	17.75	15.41	0.49	46.65	0.52
"	11ShR-10	11.00	18.50	23.30	0.91	53.71	0.82
"	11ShR-5	10.00	25.50	31.30	0.85	62.65	1.05
"	8ShR-1	13.00	25.00	23.80	0.91	63.21	0.67
"	4ShR-1	10.00	25.50	18.25	0.57	54.32	0.53
"	4ShR-3	11.50	19.00	21.20	0.84	52.54	0.72
"	NL1-2	4.5	31.50	34.00	1.10	71.10	1.00
"	NL1-3	2.00	29.00	23.30	0.85	55.15	0.80
"	NL1-4	6.00	40.00	19.30	1.31	66.61	0.43
"	NL1-5	5.00	38.00	20.00	1.10	64.10	0.50
"	NL2-1	6.00	39.00	25.60	1.23	71.33	0.60
"	NL2-2	4.00	38.00	19.00	1.05	62.05	0.50
"	9ShR-1	7.00	42.5	19.3	0.87	69.17	0.40
Carbonate–palygorskite clays	5ShR-1	11.00	25.50	2.60	1.46	40.56	0.11

position of the absorbed complex of clays. It has been established that the sharp predominance of the absorbed cation of Mg over that of Na yields a basal reflection with  $d = 11.5 \text{ \AA}$ . The  $d$  value has a positive correlation with the amount of absorbed Na cation. The predominance of the absorbed cation of Na over Mg with the alkalinity coefficient of more than unity is accompanied by an increase in  $d$  up to  $12.2 \text{ \AA}$ .

It is necessary to note that samples taken from deep sections of exploration pits show a very intense first basal reflection of montmorillonite that forms a unified common peak with the illite reflection. In contrast, this peak is less intense in samples taken from near-surface sections of the pits, but basal reflections of these minerals are distinctly separated. In intensely weathered sections, the principal basal reflections of both montmorillonite and illite are faintly visible; only intense narrow basal reflections of quartz are noted against the general low background. This is most probably related to a significant reduction of particle sizes of clay minerals and partial destruction of their crystalline lattice under the action of hypergene processes. Hence, the intensity of peaks on the XRD patterns primarily depends on the structural perfection of minerals rather than their contents. This circumstance requires a more careful approach to the deciphering of XRD patterns of clayey

rocks. At the same time, it allows us to distinguish the most weathered parts of clays in the rock section.

Montmorillonite makes up the background on SEM images of suspension sample. It is observed as irregular-isometric cloudlike particles with blurred edges. The crystals vary in size from  $0.1$  to  $1.0 \text{ \mu m}$ , sometimes to  $1.5 \text{ \mu m}$ . Crystals  $0.3$ – $0.5 \text{ \mu m}$  in size are predominant. Deformed montmorillonite crystals are well seen on electron photomicrographs of replicas of sample surface.

Derivatograms of the bentonites exhibit all of the three endothermic peaks inherent in montmorillonite clays. The first (most intense) peak related to release of the adsorbed water shows a maximum at  $90$ – $120^\circ\text{C}$ . The second (maximum at  $510$ – $530^\circ\text{C}$ ) and third ( $820$ – $860^\circ\text{C}$ ) peaks are also registered. The second and third peaks are related to the release of hydroxyl water and destruction of the montmorillonite crystal structure. The slightly decreased temperature of the second peak is probably caused by the presence of illite.

*Illite* is the second in abundance mineral of the bentonites. It is distinguished by intense basal reflections with  $d = 9.87$ – $10.17 \text{ \AA}$  on XRD patterns of the oriented samples (Table 2). Their position does not change upon saturation of the preparation with ethylene glycol and quenching at  $550^\circ\text{C}$  during 1 h. On SEM images, illite is observed as transparent or translucent isometric

plates up to 1–2  $\mu\text{m}$  in size. Edges of the particles are generally distinct. Broken crystals are also encountered.

*Palygorskite* is present as a minor mineral in alkaline-earth bentonites. Sometimes, however, it is observed as a major mineral, and the share of illite simultaneously decreases in the rock. In such cases, the contents of illite and palygorskite are comparable well with each other, and an intense peak of palygorskite with  $d = 10.27\text{--}10.50$  Å and relatively low peaks at  $6.39\text{--}6.43$  Å appear on the XRD patterns.

Electron-microscopic images of palygorskite demonstrate that it forms intricate fibrous aggregates of narrow, elongated-lamellar crystals up to  $1.0\text{--}1.2$   $\mu\text{m}$  in length and  $0.01\text{--}0.02$   $\mu\text{m}$  in width.

*Halloysite* is present in some samples and detected only found on SEM images of the suspension as rare hollow tubes that are light-colored in the central sections and dark-colored on the edges.

*Clinoptilolite* was identified on the XRD patterns of several samples by narrow intense basal reflections with  $d = 8.93$  and  $3.97$  Å. Electron-microscopic images demonstrate that it is present as well-developed botryoidal segregations of water-transparent crystals.

*Free silicon oxides* are represented by quartz and cristobalite. Quartz is commonly encountered as a terrigenous micrometer-sized admixture. It is identified on the XRD patterns by the basal reflections with  $d = 4.21\text{--}4.30$ ,  $3.32$ ,  $1.98\text{--}2.00$ , and  $1.79\text{--}1.81$  Å. On SEM images, it is seen as angular particles uniformly dispersed in the clayey mass.

Cristobalite is identified on the XRD patterns by the basal reflection  $4.07\text{--}4.10$  Å. In common with the terrigenous quartz, it is an ordinary admixture in the bentonites.

*Iron hydroxides* are present in the clay as fine reddish lenticular laminas, or pervasive fine dispersion. Under electron microscope, they are seen as fine dissemination or stellate segregations. Iron hydroxides are hypergene neogenic minerals related to the leaching of fine-dispersed pyrite, which is evident from their coexistence with sulfate minerals.

*Sulfates* are present in the bentonites as gypsum, celestine, barite, jarosite, and alunite. Gypsum is found as two genetic types. The first (sedimentary) type is observed as floury gypsum on the interfaces of clay microlaminas. The second (hypergene) type is related to the leaching of fine-dispersed pyrite in the rock and associated with iron hydroxides along with jarosite and alunite.

Jarosite and alunite are found under electron microscope as rare rectangular crystals. Celestine and barite often form large ( $1\text{--}5$  cm, sometimes up to  $20$  cm) nodules and concretion-type intergrowths.

*Carbonates* are only represented by rare calcite identified under electron microscope by the typical rhombic shape.

Manganese and phosphorus compounds are not registered by the X-ray structural and electron microscopic analyses. They are only detected by results of the chemical analysis.

Electron probe microanalysis of the bentonites demonstrates that their matrix is composed of montmorillonite. At high magnification, the surface of deformed montmorillonite crystals resembles the astrakhan fur-type structure (Fig. 1a).

Dispersed angular micrometer-sized quartz grains, rather large deformed illite plates (Fig. 1b), and rare pseudo-hexagonal kaolinite crystals are noted against the background of the montmorillonite matrix (Fig. 1c).

The electron probe microanalysis allows one to determine the shape and relationships between the crystals, their chemical compositions, and thus identify with certainty minerals (in our case, illite and montmorillonite) in a rock. This is not always possible by other laboratory analytical methods, particularly with respect to the identification of mixed-layer minerals. Judging from the chemical composition, these minerals vary from almost pure illite to montmorillonite.

Carbonate-palygorskite clays of the Navbakhor deposit are characterized by a decreased contents of silica ( $\text{SiO}_2$ ) and alumina ( $\text{Al}_2\text{O}_3$ ) and elevated contents of CaO owing to the presence of carbonate material. The average CaO content is 10.5%, which corresponds to almost 19% of  $\text{CaCO}_3$  (Table 1).

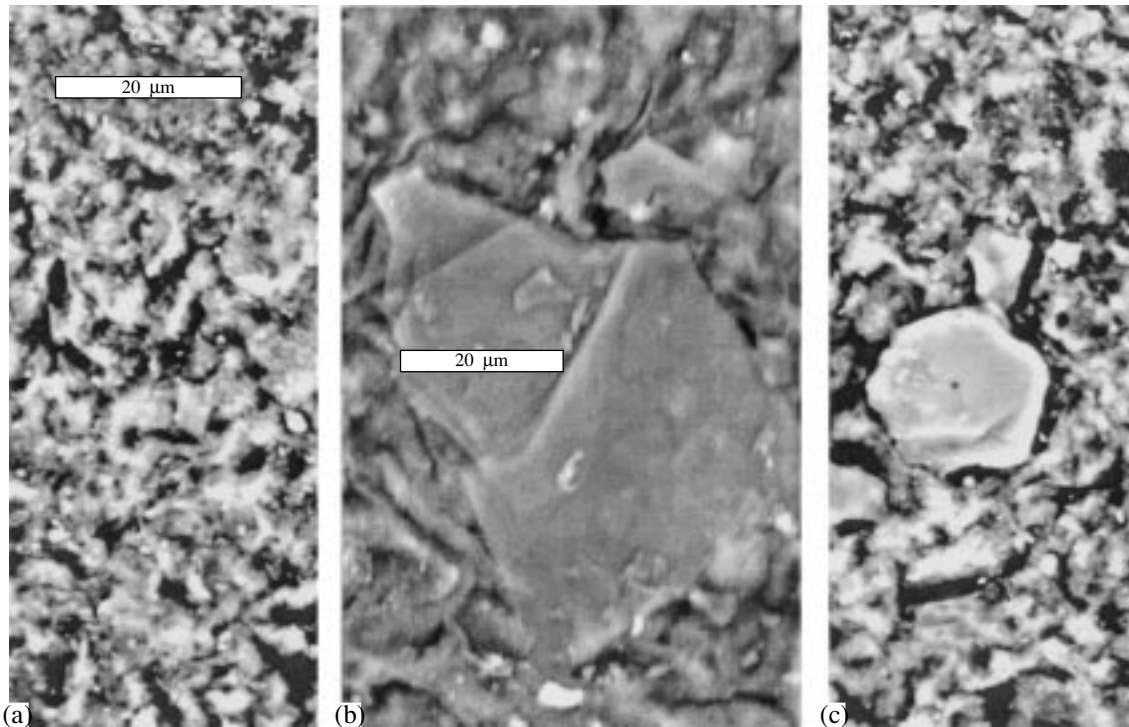
The elevated  $\text{P}_2\text{O}_5$  content (2 wt %) attracts our attention. In contrast to the bentonites, the carbonate-palygorskite clays predominantly contain divalent Fe, which is responsible for the light, almost white color of the rock.

The X-ray structural analysis of the carbonate-palygorskite clays reveals palygorskite, calcite, and montmorillonite, which are rock-forming minerals. Illite, quartz, and cristobalite are admixtures. Palygorskite is identified by basal reflections  $10.27\text{--}10.47$  and  $6.35\text{--}6.39$  Å; montmorillonite, by basal reflections  $12.0$ ,  $4.49$ , and  $3.17\text{--}3.19$  Å. Calcite (>10%) is clearly detected by narrow basal reflections  $2.99$ ,  $1.91$ , and  $1.86\text{--}1.87$  Å (Table 4).

Electron-microscopic images of clay suspension preparations show abundant dispersed palygorskite crystals. At high magnification ( $\times 60000$ ), its crystals are translucent and exhibit an elongated ribbon morphology, often with concave ends. When superimposed, the underlying individuals are also visible.

Irregularly oriented bundles of fibrous palygorskite crystals are well seen on carbon replicas of the sample surfaces.

As is seen on SEM images of the preparation, montmorillonite and, especially, illite play a subordinate role in the composition of the carbonate-palygorskite clays. One can sometimes see relatively large (roll-shaped) halloysite rods formed as a result of the piling of lamellar crystals.



**Fig. 1.** Microprobe images of the bentonite surface: (a) astrakhan fur-type structure; (b) large illite crystal; (c) pseudo-hexagonal kaolinite crystal.

Calcite is found as opaque (rhombic or rectangle) crystals commonly grouped into clusters of two or three crystals.

Derivatograms of the carbonate–palygorskite clays exhibit two endothermic peaks. The first one (maximum at 120°C) is related to the removal of adsorbed water. The second peak (maximum at 780–820°C) corresponds to the calcite decomposition. The presence of sufficient amounts of carbonate material disguises the second and third endothermic peaks inherent in montmorillonite. The montmorillonite, in its turn, reduces the dissociation temperature of calcite. Judging from the loss on ignition, the carbonate material content sometimes reaches 30%.

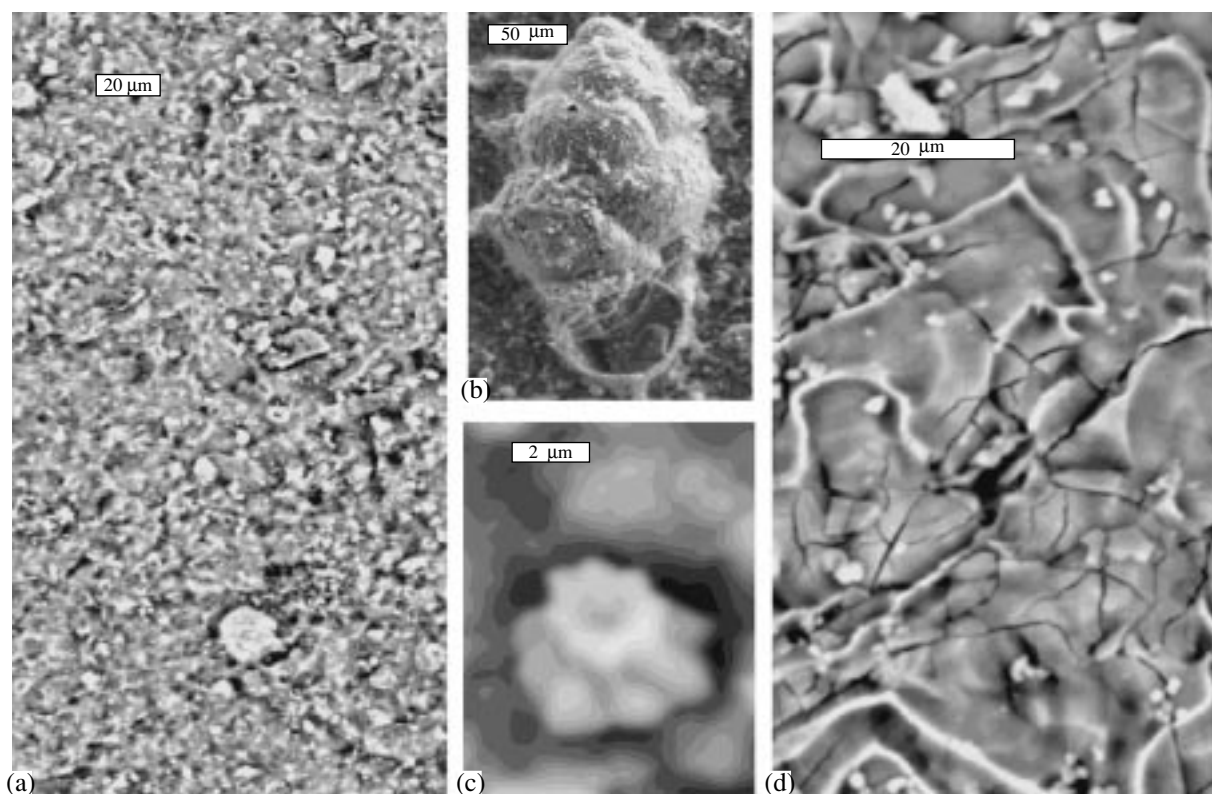
Images of fracture surface of the carbonate–palygorskite clay sample obtained using a JXA-8800R Superprobe clearly demonstrate an intricate morphology of diverse particles and highly porous structure of the rock (Fig. 2a). Rounded-oval, stellate, elongated, foliated, and angular particles are most often encountered. Angular-oval particles commonly characterized by a concentric structure generally represent organic remains of carbonate or siliceous composition. Foraminifers (Fig. 2b) and nannoplankton shells (Fig. 2c) 5 × 5 µm in size are discernible at high magnification.

The bentonites also contain relatively large concretions of phosphate matter (phosphatized organic remains) and barite crystals. The phosphatized remains are highly porous, with numerous tortuous canals widen-

ing toward one end. The widening part grades to a segment-type plane with smooth surface (Fig. 2d). Individual rhombic calcite crystals 2–3 µm in size are well seen against the background of the phosphatized material.

**Table 4.** X-ray diffraction data on carbonate–palygorskite clays from the Navbakhor deposit

Sample no.								Minerals
3K1-0		5ShR-2		NL2-3		KT-1		
<i>i</i>	<i>d</i> , Å	<i>i</i>	<i>d</i> , Å	<i>i</i>	<i>d</i> , Å	<i>i</i>	<i>d</i> , Å	
–	–	1	12.00	3	12.00	3	12.00	montmorillonite
2	10.27	2	10.27	7	10.47	7	10.37	palygorskite
1	6.39	–	–	2	6.35	1	6.36	illite
–	–	–	–	1	4.98	1	4.98	illite
–	–	–	–	1	4.49	1	4.49	montmorillonite
1	4.23	1	4.23	1	4.25	1	4.25	quartz
1	4.05	–	–	–	–	–	–	crystalite
1	3.89	2	3.89	1	3.83	1	3.85	dolomite
3	3.32	3	3.34	9	3.32	9	3.33	quartz
1	3.17	1	3.19	6	3.19	5	3.19	montmorillonite
5	3.03	8	2.99	10	3.01	9	3.02	calcite
–	–	1	2.84	1	2.83	2	2.84	dolomite
1	1.91	2	1.91	4	1.91	2	1.91	calcite



**Fig. 2.** Microprobe images of the carbonate–palygorskite clay: (a) porous surface; (b) foraminifer shell; (c) nannoplankton shell; (d) phosphatized organic remain.

Barite is observed as crystals up to 1.5  $\mu\text{m}$  in size that often form separate segregations.

All organic remains composed of calcium carbonate are seen on the SEM images (Fig. 3). They are distinguished by a light color against the background of Ca and dark color against the background of other elements. The SEM images demonstrate a rather uniform distribution of Si, Mg, Fe, and K owing to their introduction into the crystalline lattice of clay minerals. The light-colored spots against the Si distribution pattern are related to the presence of terrigenous quartz or siliceous organic remains (Fig. 3).

The alkaline bentonites, alkaline-earth bentonites, and carbonate–palygorskite clays sharply differ from each other in the exchange capacity and absorbed complex composition (Table 3). The total exchange capacity of the alkaline bentonites is, on the average, equal to 74.3 mg-equiv/100 g of clay, and the alkalinity coefficient is 4; i.e., they are assigned to strong alkaline varieties.

The total exchange capacity of the alkaline-earth bentonites is significantly lower and averages 52.0 mg-equiv/100 g of clay, while the alkalinity coefficient is 0.9. Significant variations in the total exchange capacity of the alkaline-earth bentonites (from 44 to 71 mg-equiv/100 g) and the alkalinity coefficient (from 0.4 to 1.0) indicate a

variability of the mineral composition and dispersity of the clays.

The carbonate–palygorskite clays are characterized by the lowest value of the exchange capacity among all natural varieties of the clays. They are assigned to the alkaline-earth type with a very low alkalinity coefficient. The sharp predominance of alkaline-earth cations in the absorbed complex composition is well registered on derivatograms as an additional break at 220°C complicating the shape of the first endothermic peak.

The polymineral calcite–montmorillonite–palygorskite composition of these clays predetermines their rather low exchange capacity, because palygorskite has an elongated-ribbon crystal shape with small effective surface and calcite crystals lack the surface energy at all.

#### *Conditions of Clay Formation*

Paleogene bentonites of the Navbakhor deposit formed under calm platformal marine conditions with a highly smoothed topography of denudation areas and arid climate. All these factors predetermined the insignificant share of coarse-clastic particles and high content of clayey fractions and dissolved components in the material supplied to the sedimentary basin.

Hydrodynamic and hydrochemical conditions of sedimentation were important for the bentonite accu-

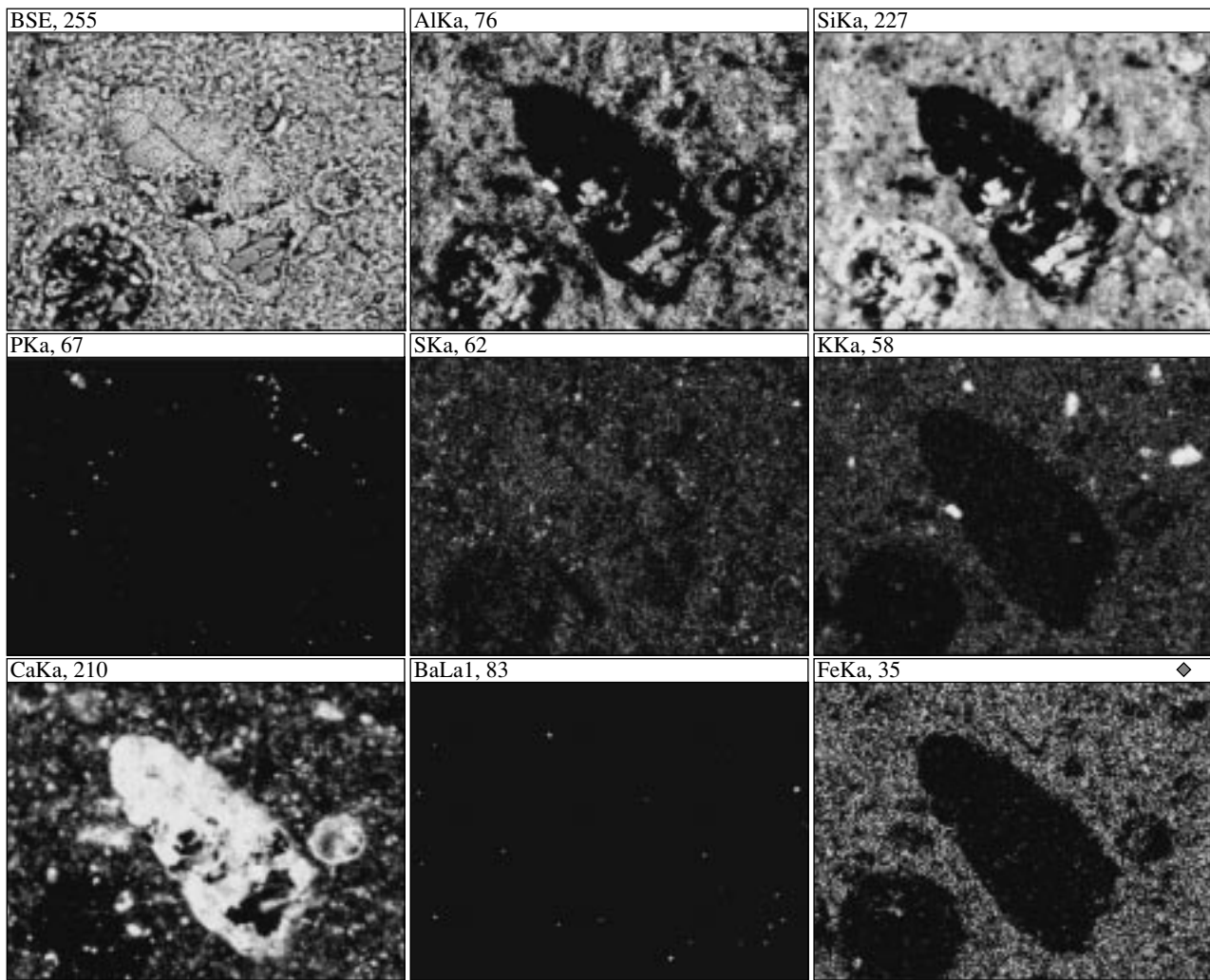


Fig. 3. SEM images showing the distribution of major elements in the carbonate-palygorskite clay.

mulation. The influence of these factors on the formation and preservation of clayey minerals was elucidated in many works (Grim, 1967; Kossovskaya and Shutov, 1963; Vikulova, 1957; Zkhus, 1966).

The bentonites accumulated under calm hydrodynamic conditions beyond the domain of sea waves and currents. This is evidenced by the high dispersivity of clayey material and lack of benthos microorganism remains. One can only see rare remains of plankton microorganisms (foraminifers, radiolarians, diatoms, and nannoplankton) precipitated from upper seawater layers.

Montmorillonite in the bentonites of the Navbakhor deposit is both allochthonous and autochthonous. The influence of ash material on its formation is not excluded as well.

The microlaminated structure of bentonites becomes very distinct upon their drying. Bentonite samples slightly moistened with water are split into thin parallel laminae in the course of drying. However, ben-

tonites related to halmyrolysis of volcanic material lack such a structure. They are massive and lumpy.

The Paleogene marine basin was characterized by a peculiar chemical composition of water. This is reflected in the exchange complex of bentonites and the formation of alkaline and alkaline-earth varieties. It must be noted that such alkaline (allothigene transformed) bentonites are unknown in the literature.

The marine basin is distinguished by the presence of sodium salts (chloride and sulfate compounds). In the case of high salinization of waters,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  cations are driven out from the absorbed complex by  $\text{Na}^+$  cations, and the clay becomes sodic. In this case,  $\text{Mg}$  cations are tightly bonded and more difficult to drive out. Therefore, relative concentration of  $\text{Mg}^{2+}$  in the absorbed complex is higher than that of  $\text{Ca}^{2+}$  (Perel'man, 1972).

The existence of salinized conditions during the formation of alkaline bentonites is confirmed by the sul-



fate—chloride sodic composition of their aqueous extract.

Most researchers consider palygorskite and sepiolite in clayey rocks as indicator minerals of an evaporite process, which is confirmed by their confinement to carbonate and clayey deposits formed under arid conditions (Millo, 1968; Rateev, 1964; Strakhov, 1963).

The formation of Paleogene carbonate—palygorskite clays of the Navbakhor deposit was accompanied by a significant shallowing of the marine basin and substantial variations in hydrodynamic and hydrochemical conditions of the sedimentation environment. These circumstances facilitated the concurrent precipitation of terrigenous, chemogenic, and biogenic material with the predominance of a certain material in each specific case.

The presence of sufficient amounts of dissolved silica and Mg cations in seawater is favorable for synthesis of magnesium silicates, including palygorskite. The authigenic genesis of palygorskite is confirmed by its occurrence as bundles distinctly registered on the carbon replicas.

Hence, the high-quality bentonites formed under calm hydrodynamic conditions in marine basin with water characterized by an alkaline reaction and elevated salinity. Such conditions favored the transformation of terrestrial clay minerals and formation of authigenic montmorillonite. The subsequent significant shallowing of the marine basin led to a concurrent precipitation of chemogenic and biogenic materials. The supply of terrigenous material to the sedimentation basin was limited. The carbonate—palygorskite clays accumulated under platformal tectonic and arid climatic conditions.

#### *Technological Properties of Clays*

Laboratory-technological and industrial testings of the bentonites and carbonate—palygorskite clays of the Navbakhor deposit demonstrated a high quality of the raw material. These clays can be used for the production of drilling suspension used in oil and gas wells. The production can be as much as 14–15 m<sup>3</sup>/t from the alkaline clays and 12–13 m<sup>3</sup>/t from the alkaline-earth bentonite varieties (specific weight of the drilling mud is 1.04 and 1.05 g/cm<sup>3</sup>, respectively; viscosity is 25 s). Other exploitation parameters also correspond to the standard requirements. Muds obtained from the bentonites can efficiently be used for drilling wells in low-pressure horizons. The drilling mud is easily subjected to chemical treatment and loading. Thus, one can regulate exploitation parameters of the wells in response to changes of geoenvironmental conditions during the drilling.

The carbonate—palygorskite clays also have a high output of the drilling mud (10 m<sup>3</sup> from 1 t of the raw material). Moreover, all exploitation parameters,

except the filtration (water yield), fit the requirements to drilling muds.

Reduction of water yield of the drilling mud suspension can be achieved by the addition of NaCl. The addition of 5% NaCl to the suspension reduces the filtration from 40 to 5 cm<sup>3</sup>/30 s.

During the drilling of boreholes through salt-bearing rock sequences, the drilling mud salinity can rise up to more than 20%. In order to elucidate the carbonate—palygorskite clay behavior in the presence of electrolytes, we prepared clay suspensions with a salinity of 10 and 20%. In the mineralized suspension of the carbonate—palygorskite clay, values of the viscosity and static shear stress increase and the water yield decreases, whereas all other parameters do not substantially change.

Hence, carbonate—palygorskite clays of the Navbakhor deposit are salt-resistant, and the presence of salts improves their mud suspension quality.

Another advantage of the carbonate—palygorskite clay over other varieties is the presence of a sufficient amount of calcite in its mineral composition. Intensely reacting with acids, calcite facilitates the opening of pathways for hydrocarbon fluids infiltrating from productive rock units to the boreholes.

The facts presented above show that the mud prepared from the bentonites and carbonate—palygorskite clays is suitable for drilling boreholes under various geoenvironmental conditions without its treatment by chemical reagents.

The bentonites and carbonate—palygorskite clays of the Navbakhor deposit were used for bleaching cotton oil and alcoholic products. The obtained results satisfied industrial requirements.

For the adsorption bleaching, we used refined cotton oil with the acid number equal to 0.58 mg KOH and the color index equal to 20.0 red units in a 13.5-cm layer. The sorbent amount varied from 1 to 2 wt % of the oil preliminarily activated by acidic and thermal methods.

The best adsorption capacity is registered in the carbonate—palygorskite clays and alkaline bentonites. If 2% of this material is used, the color index of the cotton oil reduces by 8–9 red units, which are equal to the bleaching degree of 40–45% corresponding to the industrial requirements. The use of the clays after thermal processing decreases the acid number to the standard value. Conversely, the use of the acid-activated clays increases the acid number. The bleaching degree in these cases is nearly the same. Hence, the clays studied are suitable for bleaching cotton oil after their simple thermal processing. This method sharply reduces the net cost of production, is safe with respect to acid activation, and creates no environmental problems.

Alkaline bentonites of the Navbakhor deposit can be used as a structure-forming doping in the production of dyes and active component of cleaning agents. Thanks to high thixotropy and dispersity, the alkaline bento-

nites are better than the synthetic agent T-80 (polyethylene glycol) for the structurization of enamel. Laundry soap, detergent pastes, and high-quality cleaning powders were produced from the alkaline bentonites.

Investigations conducted at the Tashkent Pharmaceutical Institute demonstrated that the bentonites can be used as subsidiary (even principal in some cases) active components in the production of medicinal preparations. A preparation with strong antiseptic and adsorption properties was obtained from the bentonites after special processing. Clinical tests demonstrated its high efficiency in the treatment of wounds and burns.

The bentonites and carbonate–palygorskite clays of the Navbakhor deposit can also be used in the construction and perfume industry, agriculture, and others.

### CONCLUSIONS

(1) The bentonites and carbonate–palygorskite clays of the Navbakhor deposit are confined to the lower Eocene section (Ypresian Stage).

(2) The bentonites are composed of the major montmorillonite. Illite, palygorskite, quartz, iron hydroxides, and other minerals are minor and trace components. According to the physicochemical properties, the bentonites are subdivided into the alkaline and alkaline-earth varieties.

(3) The carbonate–palygorskite clays are mainly composed of calcite, montmorillonite, and palygorskite. They conformably overlie the bentonite unit.

(4) The bentonite and carbonate–palygorskite clay deposits formed in the alkaline medium of a marine basin. Their principal rock-forming mineral (montmorillonite) was formed by both allothigenic and authigenic processes, whereas the calcite and palygorskite were produced by only authigenic processes.

(5) The bentonites and carbonate–palygorskite clays are suitable for the preparation of drilling muds, as well as for the purification of cotton oil and alcoholic prod-

ucts. They can also be used in household chemistry, medicine, cosmetics, construction industry, and others.

### REFERENCES

- Ginzburg, I.I. and Rukavishnikova, A.I., *Mineraly drevnei kory vyvetrivaniya Urala* (Minerals of Ancient Weathering Crust in the Urals), Moscow: Akad. Nauk SSSR, 1951.
- Grim, R.E., *Clay Mineralogy*, New York, 1953. Translated under the title *Mineralogiya i prakticheskoe ispol'zovanie glin*, Moscow: Mir, 1967.
- Kossovskaia, A.G. and Shutov, V.D., Clay Minerals as Indicators of Depth Alteration of Terrigenous Rocks, *Geokhimiya, petrografiya i mineralogiya osadochnykh obrazovaniy* (Geochemistry, Petrography, and Mineralogy of Sedimentary Formations), Moscow: Akad. Nauk SSSR, 1963.
- Millo, Zh., *Geologiya glin* (Clay Geology), Leningrad: Nedra, 1968.
- Mirzaev, A.U. and Chinikulov, Kh., The Navbakhor Deposit: A New Bentonite Deposit, *Geologiya i mineral'nye resursy* (Geology and Mineral Resources), 1999, no. 5, pp. 23–30.
- Perel'man, A.I., *Geokhimiya elementov v zone gipergenez* (Geochemistry of Elements in the Hypergenesis Zone), Moscow: Nedra, 1972.
- Rateev, M.A., *Zakonomernosti razmeshcheniya i genezis glinistykh mineralov v sovremennykh i drevnykh morskikh basseynakh* (Distribution Patterns and the Genesis of Clay Minerals in Recent and Ancient Marine Basins), Moscow: Nauka, 1964.
- Strakhov, N.M., *Tipy litogeneza i ikh evolyutsiya v istorii Zemli* (Types of Lithogenesis and Their Evolution in the Earth's History), Moscow: Gosgeoltekhizdat, 1963.
- Vikulova, M.F., *Metodicheskoe rukovodstvo po petrografo-mineral'nomu izucheniyu glin* (Methodical Manual on Petrographic–Mineralogical Study of Clays), Moscow: Gosgeoltekhizdat, 1957.
- Zakirov, M.Z., *Gipergenez glinistykh otlozhenii Uzbekistana i ego mineral'nye indikatory* (Hypergenesis of Clayey Sediments in Uzbekistan and Its Mineral Indicators), Tashkent: Physical Inst., 1977.
- Zkhus, I.D., *Glinistye mineraly i ikh paleogeograficheskoe znachenie* (Clay Minerals and Their Paleogeographic Implication), Moscow: Nauka, 1966.