

## Composition and Physicochemical Properties of Natural Blue Clays

L. G. GILINSKAYA, T. N. GRIGORIEVA, L. I. RAZVOROTNEVA and L. B. TROFIMOVA

*Institute of Geology and Mineralogy, Siberian Branch of the Russian Academy of Sciences, Pr. Akademika Koptyuga 3, Novosibirsk 630090 (Russia)*

*E-mail: lgilinskaya@uiggm.nsc.ru*

(Received July 27; revised January 18, 2008)

### Abstract

Physical and chemical features of natural clays have been studied using the methods of X-ray diffraction, chemical, thermal and spectral analyses, ESR and IR spectroscopy; the nature of their medical properties being considered. The composition of macro and trace impurities in the clays has been analysed. The medical properties of the clays are determined by the presence of almost all the chemical elements necessary for normal functioning of a living organism as well as by sorption features due to a specific character of crystal structure. Using ESR technique, the forms of occurrence for some trace impurities ( $\text{Mn}^{2+}$ ,  $\text{Fe}^{3+}$ ) and for paramagnetic centers (PC) of the radiation nature have been determined. The intensity of PC response has been shown to correlate with the content of actinoid ions such as U and Th in the samples. Basing on the ESR spectral data it has been established that blue color of the clays is caused by  $\text{V}^{4+}$  impurity ions  $\text{V}^{4+}$  in the form of vanadyl  $\text{VO}^{2+}$ . The content of the microelements such as vanadium, boron and chromium in blue kaoline глинах has been demonstrated to be 10–15 times higher as compared to clay samples of another coloring. An important role of complex influence of macro- and microelements (silicon-boron, vanadium-chromium, manganese, etc.) on the enzymes and hormones in various organs, as well as the presence of such combinations of chemical elements in blue clays have been noted.

**Keywords:** natural clays, physicochemical features, medical properties

### INTRODUCTION

Medical (therapeutic) mineralogy that deals with the questions of the fundamental problem “Minerals and Human’s Health”, at all times, since 1838 [1], holds a steady position in the structure of mineralogy as an independent section. It is supplemented in a natural manner with a consistent field of medical geology formed in the beginning of 21th century to study the influence of the geological environment upon the health of humans and animals [2, 3]. The investigation of minerals’ medical properties, the knowledge on their nature represents a principal condition for a competent, science-based application of the minerals in medicine, especially concerning the field of mineralogical pharmacology [4].

Natural clays are most widely used for medicinal purposes in medical practice. However,

the nature of their healing properties, and particularly the differences in the effect of clay varieties, is not established till now. Traditionally the physicians who use clays in their practice pay attention to their pollution and prefer to choose “pure” (monophase) clay specimens. To all appearance, such the clays have just named as “medical clays”. Any choice of clays according to their properties is out of the question, since there are no particular data concerning one or the other properties of clays at this moment.

Red, green, brown, white and blue clays are mainly used in Russia for the treatment; however the causes of variety in the coloration of clays are not clear from the literature data available. Blue clay, its healing properties and treatment methods based on the use of it are most often mentioned in the publications. At the resort places of Altai, in the Tula Re-

gion and in other places there are Blue lakes whose names are due to the color of their beaches formed by blue clay.

It is well known from the general concepts of crystal chemistry that differences in the coloring of clays could be caused by the presence of color centers whose occurrence might be connected with impurity ions ( $\text{Cu}^{2+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Ti}^{3+}$ ) or with the structure defects of a mineral (for example,  $\text{SiO}_3^-$ ,  $\text{SO}_3^-$  radicals, *etc.*). It is obvious that the medical properties of clays depend on the presence of certain macro elements (K, Mg, Ca, Fe) and microelements (Mn, Cu, Zn, Al, *etc.*, altogether about 20 elements) whose influence on the functional abilities of a living organism is actively studied [5]. The detailed investigation of clays as well as of their physicochemical and structural features is of current importance since just the latter determine the properties of clays including medical varieties. The publications available at present time mainly deal with the consideration of the properties of clays as sorption agents or indicator minerals with respect to geological processes, with no concern of medical aspects of this natural material. We

have made an attempt to compensate this deficiency.

## EXPERIMENTAL

Seven samples natural clays taken from various territories of West Siberia (the Novosibirsk Region, Iskitim and Cherepanovo districts), Eastern Siberia (the Troshkovo deposit), Altai, the Volga region (Naberezhnye Chelny) were investigated. According to the genetic type the clays under investigation from Western Siberia, Altai and from the Volga region belong to sedimentary clays (samples Nos. 1–4, 6), whereas the clays of Troshkovo (Angara) deposit are attributed to secondary redeposited clays (samples Nos. 5, 7).

The formation of the clays of the Troshkovo deposit occurred due to the redeposition of fine-particle products of crust-forming eluvium developed over crystalline rocks of the Precambrian folded substratum. Among the samples under investigation four specimens were blue in color (samples Nos. 1–4), two ones were light-beige (samples Nos. 5, 7) and one specimen was dark-brown in color (sample

TABLE 1

Phase composition of the clays under study

Sample No.	Content, mass %		Quartz	Mica	Quartz to mica ratio*	Other minerals	Sample colour	Sampling place
	Kaolinite	Smectite						
1	30	–	+	+	>	PF**, hematite	Blue	Altai
2	37	Traces	+	+	≡	–	«	Cherepanovo
3	40	–	+	+	<	Pyrite	«	Iskitim (Novosibirsk Region)
4	50	–	+	+	>	Pyrite, hematite	«	Lozhok (Novosibirsk Region)
5	72	28	–	–	–	–	Light-beige	Troshkovo deposit
6	15	80	Traces	Traces	>	Peach, plagioclase	Dark-brown	Naberezhnye Chelny
7	20	80	–	–	–	–	Light-beige	Troshkovo deposit

Note. “+” means the presence of a mineral in a sample, “–” stands for the absence.

\* According to ESR spectra.

\*\* PF – potash feldspar.

No. 6). The results obtained were approved on a plenty of samples, and a comparative analysis with white and red clays being carried out.

Clays were investigated with the use of X-ray diffraction, chemical, thermal and spectral analytical methods. In addition, IR and ESR spectra as well as sorption properties were studied for the clays under investigation, and uranium and thorium content was determined for all the samples.

The minerals inherent to the majority of clays belong to lamellar silicates. It is a matter of general experience that it is best to use for medical purposes the minerals of montmorillonite group (montmorillonite, beidellite, nontronite, hectolite and saponite) and of kaolinite group (kaolinite, dickite, nacrite, halloysite) [6] whose structures are well-known and described. The composition of the minerals of the kaolinite group corresponds to the formula such as  $Al_4Si_4O_{10}(OH)_8$ , whereas that of the montmorillonite group minerals corresponds to the formula such as  $(Na,K,Ca,Mg)_{0,33}(Al,Mg)_2Si_4O_{10}(OH)_2 \cdot nH_2O$  [7].

The details of experimental studies on physicochemical properties of clays are presented in [25].

## RESULTS AND DISCUSSION

### *Physicochemical properties of clays*

Table 1 demonstrates the data on the phase composition of natural clays obtained using the methods of X-ray and thermal analysis as well as IR spectroscopy. It is apparent that all the samples represent a polymineral mixture of clay and non-clay minerals. The basic mineral clay component in five samples is presented by kaolinite (samples Nos. 1–5), in two samples it is

presented by smectite (samples Nos. 6, 7), whereas in some samples illite was revealed in trace amount. Furthermore, a higher content of such impurities as quartz, mica  $2M_1 + 1M$ , and trace amount of potash feldspar, pyrite, hematite and peach are inherent to the samples. Secondary redeposited clays (samples 5 and 7, kaolinite and smectite, respectively) are the closest to a monomineral material.

It should be noted that mainly these two phases (kaolinite and smectite) are present in clays simultaneously in various proportions. For the clay samples of sedimentary genesis (blue clays) the content of the basic mineral clay component (kaolinite) varies within the range from 30 to 60 %. For the secondary clays (samples Nos. 5, 7) the content of the basic phase being as much as 95–98 %, these clays are characterized by a high degree of crystallinity. The percentage of quartz and mica impurities is especially high for sedimentary clays (30–70 %).

Chemical composition of the clays under investigation is presented in Table 2. According to the ratio of the basic components ( $SiO_2$  и  $Al_2O_3$ ) and to presence of exchangeable Ca, Mg, Fe, K cations these minerals could be classified as kaolinite and smectite. It should be noted that the balance between basic elements (Al, Si) in blue clays (samples Nos. 1, 2) differs from the standards generally adopted in mineralogy (for example, sample No. 5): there is considerably higher silicon content, the content of aluminium being lower and the percentage of potassium impurity is much higher. For smectites (samples Nos. 6, 7) the content of the basic components and exchangeable cations meet the standard mineralogical characteristics [7].

TABLE 2

Results of chemical analysis for natural clays under study

Sample No.	Content, mass %											CL*	Sum
	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	P <sub>2</sub> O <sub>5</sub>	Na <sub>2</sub> O	K <sub>2</sub> O	MnO	H <sub>2</sub> O		
1	69.81	19.72	1.09	0.32	n/r	0.36	0.098	0.54	2.55	<0.003	0.14	5.39	100.02
2	72.42	18.24	0.95	0.26	n/r	0.32	0.066	0.59	2.36	<0.003	0.21	4.97	100.39
5	50.55	32.53	0.64	1.10	0.50	0.64	0.11	<0.03	0.29	<0.03	0.01	13.70	100.13
6	59.89	15.86	0.88	6.60	1.69	2.32	0.16	1.62	2.05	0.074	2.88	6.58	100.60
7	57.51	19.60	0.26	2.00	2.03	4.47	0.03	<0.03	0.37	<0.03	0.14	13.03	99.50

Note. n/r – not revealed.

\*CL – calcination loss.

TABLE 3

Impurity content in the clays under study according to spectral analysis, mass %

Sample No.	B	Pb	Ga	Mn	Ni	Mo	V	Zr	Ti	Cr	Cu	Sc
1	0.010	0.0015	0.00086	0.0086	0.0013	<0.0001	0.0072	0.021	0.47	0.005	0.002	0.002
2	0.011	—	0.0010	—	0.0010	<0.0001	0.0080	0.025	0.51	0.005	0.001	0.003
3	0.0096	—	0.0009	—	0.0012	<0.0001	0.0068	0.024	0.52	0.005	0.001	0.002
4	0.010	—	0.0010	—	0.0019	<0.0001	0.0084	0.025	0.36	0.006	0.005	0.003
5	0.0045	0.010	0.0015	—	0.0010	<0.0001	0.0014	0.035	0.23	—	0.0009	0.0007
6	0.0056	0.0011	0.0009	0.048	0.0066	<0.0001	0.0090	0.020	0.36	0.01	0.005	0.001
7	0.0016	0.0015	0.00088	~0.001	0.0011	0.0001	0.00056	0.033	0.072	—	0.002	—

Note. Ba, Be, Co, Y, Sn, Sr, Yb, La, Zn, Li, Rb, Cs were found out in the samples, too.

The data of the spectral analysis of the samples indicate a high content of trace impurities (more than 20 chemical elements) whose biological role in a human and animals' organism, as mentioned earlier, could be of an important value. In Table 3 the results of quantitative spectral analysis are presented for the most significant of them. From the data shown in Table 3 one can see that for the three trace impurity elements (boron, vanadium and chromium) some laws of their display could be deduced. So, the content of boron and vanadium in sedimentary clays (the samples of blue colour, Nos. 1–4) is an order of magnitude higher than that in secondary clays (samples Nos. 5, 7), and there being no chromium revealed in the latter.

The other elements, except for lead and manganese, are present in all the samples and the content of those changes insignificantly from sample to sample. As far as lead and manganese are concerned, no laws due to the presence of those in clays connected either with genesis or with clay coloring can be found out.

Owing to the fact that macro and micro impurities are mainly in the form of transition metal ions (see Tables 2, 3) we have used an electronic paramagnetic resonance (ESR) technique.

The features of ESR spectra inherent to the clays under investigation (Figs. 1, 2) are determined by the following paramagnetic centers (PC):

1. In the spectra of all the samples within the range of magnetic field  $H \approx 70$  mT,  $g = 9.0$  and  $H \approx 170$  mT,  $g = 4.2$  the lines of isomorphous high-spin ions  $\text{Fe}^{3+}$  ( $S = 5/2$ ) in orthorhombic octahedral positions ( $\text{Al}^{3+}$ ) are registered.

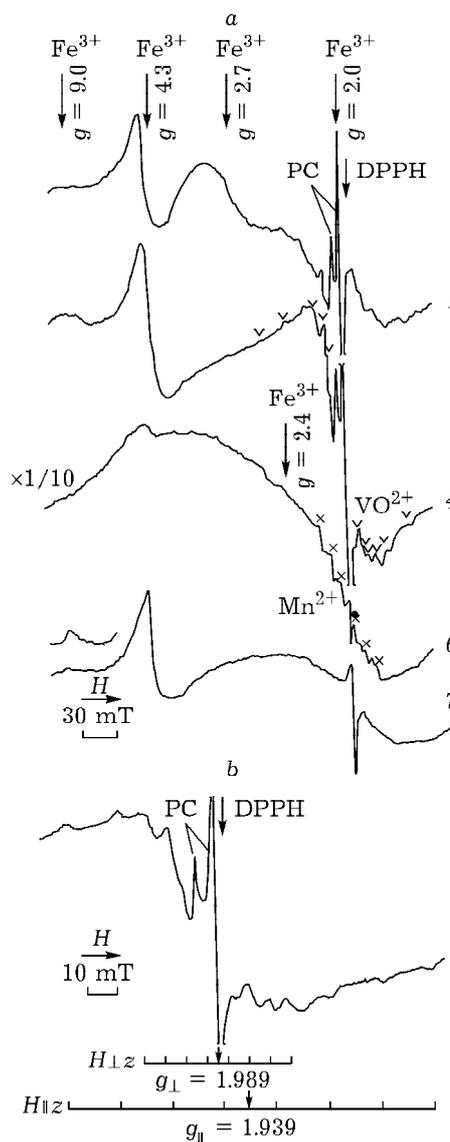


Fig. 1. Survey ESR spectra of some clays under study (samples Nos. 1, 4, 6, 7) over the magnetic field range from 0 to 700 mT (a) and ESR spectrum of vanadyl ( $\text{VO}^{2+}$ ) complexes in blue clay (sample No. 4) (b).

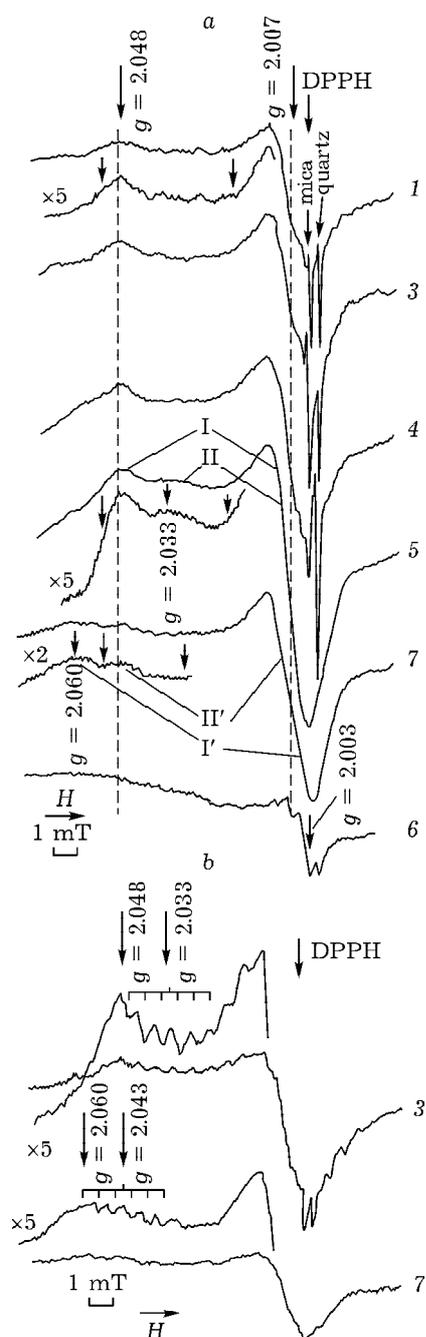


Fig. 2. ESR spectra of paramagnetic centres for clay samples under study (samples Nos. 1-7) over the range of  $g = 2.00$ . T, K: 293 (a), 77 (b).

2. Broad signals with  $g = 2.0$  and  $2.7$ ,  $\Delta H = 60$  and  $90$  mT have been attributed to  $\text{Fe}^{3+}$  ions those could interact among themselves either in the neighbouring cationic positions or in the magnetic impurity phases. Such PC use to be observed only for the samples those contain any impurities of ferriferous minerals according to XRD analysis. These PC were not revealed in

the ESR spectra of washed clays, which confirms the fact that the PC observed belong to impurity phases.

3. Six narrow lines of hyperfine structure (HFS) due to nuclear spin  $J = 5/2$  in the range of  $g = 2.00$ , caused by ions  $\text{Mn}^{2+}$  ( $S = 5/2$ ) have been registered only for sample 6.

4. The spectrum of vanadyl complexes  $\text{VO}^{2+}$  ( $S = 1/2$ ) consisting of 16 HFS lines in polycrystalline samples for two orientations of its magnetic axes ( $H \parallel z$  and  $H \perp z$ ), caused by unpaired electron ( $S = 1/2$ ) coupling with  $^{51}\text{V}$  nucleus ( $J = 7/2$ ) was observed in ESR spectra of samples Nos. 1-4. The spectrum of  $\text{VO}^{2+}$  complexes inherent to the clays under investigation exhibited the following parameters:  $g_{\parallel} = 1.939$ ,  $g_{\perp} = 1.989$ ;  $A_{\parallel} = 184$  mT,  $A_{\perp} = 73$  mT, which is in a good accordance with the data available from the literature [8].

It should be noted that the spectrum of vanadyl  $\text{VO}^{2+}$  complexes was observed only for the samples of blue clays, whereas in the ESR spectrum of sample No. 6 it has not been registered, though, according to the data of spectral analysis, the content of vanadium in this sample is comparable to the vanadium content in the samples of blue clays.

It is common knowledge that vanadium ions can exist in the following valent states:  $\text{V}^{4+}$  ( $3d^1$ ,  $S = 1/2$ ),  $\text{V}^{3+}$  ( $3d^2$ ,  $S = 1$ ),  $\text{V}^{2+}$  ( $3d^3$ ,  $S = 3/2$ ). Their ESR spectra are distinctly in the value of spin moment  $S$ .  $\text{V}^{4+}$  ions can form stable vanadyl complexes at room temperature through the reaction such as  $\text{V}^{4+} + \text{O}^{2-} \rightarrow \text{VO}^{2+}$ . A typical ESR spectrum of these complexes is registered in the samples of blue clays under our investigation, and the signal intensity correlates with the content of kaolinite phase. The highest intensity of the ESR signal from vanadyl complex is registered for sample No. 4 with a maximal content of kaolinite. The absence of  $\text{VO}^{2+}$  ESR spectrum for sample No. 6 indicates vanadium to be in another valent state.

The studies carried out earlier demonstrated that chemical compounds and minerals with  $\text{V}^{4+}$  use to exhibit dark blue, blue and green colours [8]. The minerals those simultaneously contain  $\text{V}^{4+}$  and  $\text{V}^{5+}$  simultaneously, are usually of dark-brown or black colour [9].

The valent state of vanadium impurity in blue clays under our investigation ( $\text{V}^{4+}$  in the

form of vanadyl  $\text{VO}^{2+}$ ) has been established from ESR spectrometry data. Basing on the correlation between the presence of vanadyl ions in the samples studied and their blue colour, as well as on the data presented in [8, 9] one may propose that the blue colouring of clay samples could be caused by vanadyl complexes.

5. In the range of  $g = 2.00$  the spectra of all the clays demonstrate rather narrow (1.8 mT) lines caused by electron-hole centres of radiation origin (see Fig. 2). In most cases the spectrum in this area represents a superposition of several (from two to five) lines from different centres, both of electronic and hole nature [10–13].

Some lines manifested in the ESR spectra of clays are corresponding to impurity phases such as quartz and mica (see Fig. 2, *a*). Furthermore, there are electron centres ( $E'_1$ ) widespread in natural samples of these minerals whose ESR parameters are:  $g_{\parallel} = 2.0008$ ,  $g_{\perp} = 2.0000$  for quartz [14] and  $g = 2.0027$  for mica [15].

ESR spectra of clay minerals (kaolinite and smectite) are caused by two types of the centres (I, I', II, II') whose paramagnetism is determined by ionic oxygen species  $\text{O}^-$  such as ( $S = 1/2$ ) in the complex with two or one aluminium atom ((Al–O<sup>−</sup>–Al, type I, and Al–O<sup>−</sup>, type II, respectively). The parameters of ESR spectra for kaolinite and smectite are presented below:

Kaolinite	type I $g_{\parallel} = 2.048$ , $g_{\perp} = 2.007$
	type II $g_{\parallel} = 2.033$ , $g_{\perp} = 2.007$
Smectite	type I' $g_{\parallel} = 2.060$ , $g_{\perp} = 2.005$
	type II' $g_{\parallel} = 2.050$ , $g_{\perp} = 2.008$

At the temperature of 77 K for the centres II and II' six HFS lines are observed due to one  $^{27}\text{Al}$  nucleus ( $J = 5/2$ ) with the  $A$  parameter values  $A = 0.74$  and  $0.82$  mT for kaolinite and smectite, respectively. Centres I and I' also exhibit an additional splitting (to all appearance, due two  $^{27}\text{Al}$  nuclei (11 lines)) which splitting in the pure state was not possible to be selected up till now because of spectra transposition (see Fig. 2, *b*).

It is well known, that PC in natural minerals are mainly of the radiation-induced origin, being formed as a result of the irradiation whose sources are mostly presented by actinoid ions such as U and Th those are contained in these minerals. Thus, the fact that ESR centres are registered in the samples under investigation

TABLE 4

Signal intensity from paramagnetic centres and mass fraction of actinoid ions in the clays studied

Sample No.	Intensity, rel. units	Content, mass %	
		U	Th
1	128	$0.9 \cdot 10^{-6}$	$2.7 \cdot 10^{-6}$
2	81	$1.8 \cdot 10^{-6}$	$3.4 \cdot 10^{-6}$
3	58	$1.1 \cdot 10^{-6}$	$3.4 \cdot 10^{-6}$
4	42	n/d	n/d
5	359	$7.3 \cdot 10^{-4}$	$4.2 \cdot 10^{-3}$
6	11	$0.7 \cdot 10^{-6}$	$2.7 \cdot 10^{-6}$
7	66	$9.2 \cdot 10^{-4}$	$7.1 \cdot 10^{-3}$

Note. n/d – not detected.

indicates the presence of these ions in the mineral, whereas the signal intensity of ESR spectra is determined by the content of such ions. This conclusion was confirmed in [12, 13], too.

For all the samples under our investigation the presence of PC was registered, but their amount being considerably different depending on a genetic type of the samples. So, for sedimentary clays (samples Nos. 1–4, 6) the intensity of PC response is much lower as compared to that for secondary clays (samples Nos. 5, 7) (Table 4). Furthermore the signal intensity from PC observed for smectites is lower as compared to with that for kaolinites, which is in a good accordance with U and Th content in the latter (see Table 4).

The sorption properties of clay minerals are studied well enough by present time [16, 17]. A high exchange capacity of clays is considered to be caused by their internal structure and the properties of the surface of grains. The cation exchange capacity of clays could be determined by the two factors.

1. The substitution inside the structure over tetrahedral ( $\text{Si}^{4+} \rightarrow \text{Al}^{3+}$ ) and octahedral ( $\text{Al}^{3+} \rightarrow \text{Mg}^{2+}$ ) lattices can result in the occurrence of a non-compensated negative charge of a structural cell. As a rule, this charge is compensated by extra-structural exchangeable cations located on the basal planes of the particles of clay minerals. Isomorphic substitution causes ~80 % of the cation exchange capacity.

2. The presence of Si–OH and Al–OH groups on lateral faces and edges. The breaking of chemical bonds in tetrahedral and octa-

hedral lattices results in the occurrence of the hydroxyl groups on the lateral faces whose hydrogen atoms under certain conditions could enter into an exchange reaction. About 15 % of cation exchange falls to "dangling bonds".

Exchangeable cations are not the unique active centres of lamellar silicates. A great variety of chemical reactions at the surface of them use to proceed with the participation of the hydroxyl groups, coordinatively unsaturated ions, and adsorbed water molecules. The role of structural defects such as negatively charged centres arising due to heterovalent isomorphism (for example,  $\text{OH}^- \rightarrow \text{O}^{2-} \rightarrow \text{O}^-$ ) should be considered, too. The oxygen species such as  $\text{O}^-$ , occurring in minerals (including clays) as a result of radiation effect, exhibits paramagnetic properties ( $S = 1/2$ ) being observed in ESR spectra. It is well known, that this oxygen species exhibits a very high reactivity.

Sorption properties of the clays under investigation were considered by the example of such elements as Co, Ni, Sr, Cs, Ca, Mg. The last two among them are vitally important for normal functioning of living organisms. In this connection, the maintenance of their balance in an organism due to the treatment with clays is of important value, particularly upon clay ingestion. Other elements can be accumulated copiously in living organisms in the case of dwelling in difficult environment. Thus there is a necessity to remove these elements from an organism, perhaps, with the help of clay, too. There are examples available from the literature concerning the studies on the sorption of such heavy metals as Cu, Zn, Fe, Cd and Pb on illite [18], as well as of radionuclides on natural clays (kaolinites, montmorillonite) [19].

The results of the studies on the sorption properties of clay samples are presented in Table 5. One can see that samples Nos. 5 and 7 (kaolinite and smectite respectively) demonstrate a significant difference from other samples in the sorptive capacity value. Moreover, differences in sorptive capacity values between kaolinites of sedimentary genesis (blue clay) and secondary kaolinite (sample No. 5) were found out. According to ESR spectrometry data, for the sample No. 5 a very intense PC spectrum ( $\text{O}^-$ ) has been registered, which, to all appearance, could determine its sorption properties.

TABLE 5

Percentage of cations absorbed from solutions by clay minerals studied, %

Sample No.	Ca	Mg	Sr	Cs	Ni	Co
1	4.8	5.4	9.7	24.5	44.1	39.5
2	4.8	0	24	12.6	40.5	39.0
4	H. o.	H. o.	35	164	0	43.8
5	18.0	23.2	41.6	57.2	84	91.3
6	0	15.1	54.0	65.5	95.2	92.1
7	25.7	34.0	88	94.5	89	95

Note. n/d - not detected.

A higher sorptive capacity of smectite against kaolinite is likely to be determined by the presence exchangeable cations, OH groups and  $\text{H}_2\text{O}$  molecules of in the former. A considerable effect on the sorption is exerted by radiation-induced electron-hole centres in the structure those are accompanied by radioactive elements. The sorption of Ca and Mg on secondary clays is almost an order of magnitude higher than the sorption on sedimentary clays.

It should be noted that in the course of the studies, no distinctive features inherent to red, white and other natural clay varieties were found out.

It was established that sedimentary clays are severely contaminated with non-clay phases, whereas secondary clays are much more pure, but they use to contain a lot of radioactive elements.

The data obtained indicate that preliminary detailed and comprehensive analysis of natural clays is necessary to perform in order to use them for medical purposes. The priority for to use clay either as a sorption agent or as a source of microelements should be determined in each particular case basing on the data obtained from the analysis.

#### Role of microelements

The teaching about the biological role of microelements (ME) in organisms of animals and humans is connected in Russia with the name of V. I. Vernadsky. The world literature concerning ME is very voluminous, and during the last years the number of the publications devoted to ME is increasing in an avalanche-like manner. According to the opinion of medical scientists, "ME are not casual ingredients

of the tissues and liquids of living organisms, but they are the components of a naturally existing, very ancient and complex physiological system that participates in the regulation of the living functions of organisms at all the stages of their development" [20]. At the same time the medical aspects of the doctrine about ME are still insufficiently considered.

Microelements represent a group of chemical elements those are contained in the organisms of humans and animals in very small amounts within the range of about  $10^{-3}$  to  $10^{-12}$ %. The twelve most widespread elements (C, O, N, H, P, K, S, Na, Cl, Mg, Ca, Fe) are the basic, or "structural", elements whose presence in living matter is connected with the fact of their predominant content in the biosphere. Furthermore, there is a small amount of heavier elements contained in all the organisms (microelements and ultra-microelements). From the 92 elements those occur in the nature, there are as much as 81 elements in a human organism found out, and 15 elements among them are recognized to be vitally important (essential), as it follows: iron, iodine, copper, zinc, cobalt, chromium, molybdenum, nickel, vanadium, selenium, manganese, arsenic, fluorine, silicon, lithium [3, 20].

It should be noted that an original discovery of the role of ME has been made accidentally, in connection with the eruptions of inexplicable diseases (endemic adenomatous goiter, iron-deficiency anemia, fluorosis, silicosis, aluminosis). Systematic studies on the role of

ME began only since 1957, and two last decades were marked by a vigorous burst of research in this field and by a scientific importance of the results obtained [20].

The excess, deficiency or disbalancement of ME in the organisms of humans and animals use to result in the occurrence of various diseases, syndromes and pathological states (microelementoses), with respect to both an organism as a whole and various systems and organs. Table 6 demonstrates the results of the studies on the blood of patients suffering from the most widespread in the present time diseases [5], indicate a considerable disbalancement of ME.

Mineral substances those are the constituents of plants are also presented by macro elements and microelements. Just like as physiologically active compounds, they form the basis of the healing properties of herbs comprehensively investigated by present time [21]. Alongside with the sorption properties, «the healing factor» of natural clays, is likely to be determined also by the micro- and microelements included in the clay composition. In particular, clay (of any colouring) is a source of such a microelement as silicon.

Silicon represents an important bio-element for higher organisms. The essential role of silicon for a human organism became known in 1972. First of all, silicon is necessary for the formation of cartilage, bone and connective tissue; it plays an immediate part in the process of osseous tissue mineralization. The physiolog-

TABLE 6

Content of microelements in whole blood of patients with affection of liver and alimentary organs as well as coronary heart disease,  $\mu\text{g } \%$  [5]

Disease	Nickel	Chromium	Manganese	Iron	Barium	Strontium	Lead	Copper	Vanadium
No disease	100	47	145	365	78	76	298	128	46
Stomach ulcer	14.6±1.8	4.5±1.1	38.6±6.2	34.4±2.6	5.2±1.0	4.5±0.8	15.4±0.5	79.3±10.0	3.7±1.1
Chronic									
cholecystitis	4.4±1.6	2.5±0.9	25.4±8.4	44.2±5.9	4.5±1.0	2.4±0.8	17.0±2.2	91.5±11.1	3.0±1.5
Primary cancer									
of liver	80	33	42	167	31	102	272	725	130
Hepatic cirrhosis	Trace	Trace	51	270	40	52	306	126.9	Trace
Atherosclerotic									
cardiosclerosis	4.5±1.1	2.6±0.8	22.6±3.3	45.3±3.2	5.3±0.4	5.39±1.3	27.1±8.5	85.5±8.4	3.6±1.0
Chronic coronary									
deficiency,									
acute condition	4.1±1.1	2.5±0.1	26.8±2.8	41.2±5.1	4.6±0.5	4.7±1.1	27.8±5.5	108.2±13.4	3.7±0.9

ical role of silicon is connected mainly with the synthesis of glycosaminoglycans and their protein complexes those form a framework of the connective tissue to impart them both durability and elasticity. The deficiency of silicon in an organism results in thinning and deformation of bones, and, moreover, a full loss of silicon could result in the softening of bones (osteomalacia) [20]. Derangement of silicon metabolism in an organism can result in the disturbance of mineral and acid-base balance in biological electrolytes and tissues, which is fraught with various diseases.

A great variety of macro- and microelements in clays capable to exhibit medical effect on a human organism includes almost all the essential elements. The physiological role of many of these elements in an organism [5] is well established. So, it is known, that copper forms the renal and hepatic enzyme (urinase), the cardiac enzyme (cytochrome oxidase) and others; manganese is included in the structure of hepatic enzyme (arginase), *etc.* Moreover, it is found that very low concentrations of the salts of such metals as Mo, Cu, Zn, Co, Fe, *etc.* can activate about 200 enzymes. However, the role of the majority of chemical elements is as yet under study.

The presence of radioactive elements in clays gives rise to one more problem unsolved up till now. From the data presented in Table 4 one can see that U and Th amount in the samples of clays may differ between each other within the range of three orders of magnitude. Depending on the dose of "natural irradiation" such clay used for treatment can result, to all appearance, in the fact that either a tumour mass in an organism to disappear or, on the contrary, to its growth to be promoted (at high irradiation doses). An especially great hazard could be posed due to ingestion of clays.

As mentioned above, among the clays under our investigation the blue varieties differ from the others by an increased content of vanadium, boron and chromium. The physiological role of these microelements in an organism is not established comprehensively up till now. The laboratory experiments demonstrated that vanadium plays an active role in a number of chemical reactions proceeding in an organism, in particular, in redox processes.

Vanadium exhibits an important biochemical feature from the viewpoint of medicine since this element participates in the regulation of heartbeat strength and frequency, thus influencing the biochemical activity of corresponding enzymes those participate in the regulation of sodium-potassium-ATPase system functioning. Due to these properties the salts of vanadium are used for the treatment of cardiac insufficiency. The form of vanadium occurrence in an organism is of important value: inside the cells it is bound with proteins in the form of vanadyl complex; owing to this fact it is passive and harmless for  $\text{Na}^+ - \text{K}^+ - \text{ATPase}$ . However, the presence of vanadium in the form of vanadate  $\text{V}_2\text{O}_5$  ( $\text{V}^{4+}$  oxidized in blood) exhibits a negative effect on this system. The vanadate to vanadyl ratio to all appearance could represent a main mechanism for the regulation of the "sodium pump" [20, 22].

Chromium represents a variable-valence metal with an especial reactivity in the complex formation necessary for normal vital functions. The important role of chromium for human health became known as late as 1959. Pronounced changes in the content of chromium in whole blood were found out at all the stages of the development of coronary heart disease, atherosclerotic cardiosclerosis, chronic coronary deficiency and, in particular, in patients with myocardial infarction (see Table 6). The biological role of this element important for an organism is, undoubtedly, the subject of the further studies.

The essentiality of boron for a living organism was for a long time refused being revealed as late as the beginning of 1980s. This ME has a considerable effect on calcium, phosphorus and especially magnesium exchange since it participates in the regulation of the activity of parathyroid hormone [20]. The role of boron in an organism is poorly understood up till now, but it is established that the deficiency of this element can dull the thinking and ability for concentration, disturbing the coordination of eyes and hands. Boron was shown to promote the prevention of osteoporosis and rheumatoid arthritis. Antiseptic properties of boron compounds are well-known, too. A unique known boron compound occurring in nature, is the antibiotic boromycine ( $\text{C}_{45}\text{H}_{74}\text{O}_{15}\text{NB}$ ) iso-

lated from the culture of streptomycetes [20]. Many medicinal antiseptic preparations contain boron: boromenthol, borated petrolatum, sodium tetraborate, "bicarmine" tablets, borneol, boranes (boron hydrides), *etc.* Boranes  $B_4H_{10}$ ,  $B_{10}H_{16}$ ,  $B_2H_6$  are used in order to obtain antineoplastic preparations.

It seems reasonable to say that the well-known antiseptic properties of blue clays are determined by the presence of boron in their composition. Therewith the boron content in the blue clays under our investigation is 10–15 times higher as compared to the content of boron in other clay varieties.

Successful use of clays is well known with respect to the treatment of such diseases as quinsy, stomatitis, mucous tunic affections in the nasopharynx, in the upper air passages, in the gastrointestinal tract, in the urinary tracts due to microscopic fungi of *Candida* genus as a disease-producing factor. These pathogenic agents, as well as the poisons of organic origin could form complex compounds with microelemental impurities of clays (such as zinc, copper, iron, nickel, chromium, *etc.*) which compounds are then sorbed and removed from an organism [6].

The capability of clays to interact with various microorganisms is used at present time for solving some practical problems in biology, *e.g.*, when the accumulation of a certain biomass amount is needed [23] or when creating efficient biosorbents for radionuclides and heavy metals on the basis of clays [24] whose sorptive power is much higher than that of natural sorption agents.

In the publications devoted to the studies of ME, a necessity is emphasized for their complex use upon treatment. For example, for the treatment of arthritis and osteoporosis, silicon should be necessarily used in combination with boron. The complex use of vanadium in combination with chromium, zinc, manganese, magnesium and other elements was demonstrated to be of most efficiency for treating 2-type diabetes. It is just these combinations of microelements which were found out in blue clays. Moreover, as compared to other clays, an increased content of potassium and a decreased that of aluminium are typical for the blue clays

(see Table 2), which could also play a certain part in the medical effect.

Thus, blue clays exhibit a number of advantages over the others, both in composition, amount and occurrence forms of the macro- and microelements necessary for normal functioning of an organism, and in their combination. The sorptive capacity of blue kaolinite clays is lower as compared to smectites (see Table 5). At the same time, to judge from publications, blue clays are more actively used for treatment. To all appearance, a primary factor determining medical properties of blue clays is the presence of macro- and microelements in the clay composition.

## CONCLUSIONS

The natural clays under investigation are presented by kaolinite and smectite with the traces of illite. Kaolinite is a prevailing matter in the composition of blue clays, and other samples represent a mixture of these clay phases in various proportions. In all the samples of sedimentary genesis besides the main clay components, certain non-clay phases (quartz, mica) are observed in the amount up to 70 % those could become a source of fibrous and carcinoid tissues growth in an organism due to ingestion of clays. Secondary redeposited clays do not contain impurity phases, but they are much more polluted with radioactive elements.

The studied composition of clays indicates that there are almost all the essential macro- and microelements necessary for normal functioning of organism. A great variety of these elements provides a complex effect on the enzymes and hormones inherent in various organs, which is important from the viewpoint of medicine. The presence of radioactive elements in clays allows to use the latter for the treatment of tumour mass in organism providing a meticulous examination and fitting the dose of irradiation.

According to the results of ESR spectrometry studies blue clays were shown to contain vanadium in the form presented by  $V^{4+}$  complex with oxygen  $O^{2-}$  such as vanadyl ( $VO^{2+}$ ). Just such a form of vanadium occurrence determines a blue colouring of clays being most "plausible" for the normal functioning of a living organism. In comparison with the other clays

the blue variety is characterized by a higher content of boron and chromium.

Due to the specific character of the structure, clay represents an active sorbent. Sorptive activity of clays is connected with the presence of OH groups and H<sub>2</sub>O molecules in their structure, which provides the occurrence of various types of chemical bonding (such as hydrogen intermolecular bond, hydrogen hydroxyl bond) and results in the formation of hydrated ion interlayers, multilayered aqueous spheres with exchangeable cations, and so on. The microelements presenting in the clay could form complexes with microorganisms and with the poisons of organic origin such as toxic products of metabolism to be then eliminated from an organism. The paramagnetic centers identified in the clays those are of more intense response for the secondary clay samples than for the sedimentary clays, give rise to a considerable change in the sorptive capacity of clays. The latter fact could result in a loss of such important elements for an organism as Ca and Mg due to a long-term ingestion of clays. In this connection the analysis of the genesis of natural clays used for treatment is of currently central value.

### Acknowledgement

The authors express sincere gratitude to the researchers of the Institute of Geology and Mineralogy, SB RAS, T. A. Korneva, V. N. Stolpovskaya, I. M. Fominykh for the assistance in this work.

### REFERENCES

- 1 A. Lovetskiy, *Nachalnye osnovaniya mineralogii*, part 1: Oriktoznoziya, Moscow, 1832.
- 2 R. B. Finkelman, H. C. W. Skinner, G. S. Plumlee *et al.*, *Geotimes*, November (2001) 20.
- 3 M. M. Komatina, *Medical Geology. Effect of Geological Environments on Human Health*, Elsevier, Amsterdam *etc.*, 2004.
- 4 N. P. Yushkin, *Zap. Vseros. Mineral. Ob-va*, CXXXIII 4 (2004) 92.
- 5 L. R. Nozdryukhina, *Biologicheskaya rol' mikroelementov v organizme zhivotnykh i cheloveka*, Nauka, Moscow, 1977.
- 6 V. V. Krivenko, A. V. Khmelevskaya, G. P. Potebnya, *Litoterapiya, Pedagogika-Press*, Moscow, 1994.
- 7 A. G. Betekhtin, *Kurs mineralogii*, Gosgeoltekhizdat, Moscow, 1961.
- 8 G. P. Vasyanov, G. R. Bulka, in: *Fizika mineralov i gornykh porod*, Izd-vo Kazan. un-ta, Kazan, 1985, p. 52.
- 9 A. N. Platonov, *Priroda okraske mineralov*, Nauk. dumka, Kiev, 1976.
- 10 V. V. Mazykin, E. V. Polshin, I. V. Matyash, *Geokhim.*, 4 (1976) 634.
- 11 V. I. Ivchenko, *Zap. Vseros. Mineral. Ob-va*, 2 (1988) 230.
- 12 J. P. Muller, G. Calas, *Econ. Geol.*, 84 (1989) 694.
- 13 J. P. Muller, Ph. Ildefonse, G. Calas, *Clay and Clay Minerals*, 6 (1990) 600.
- 14 I. O. Matyash, A. B. Brik, A. P. Zayats, V. V. Mazykin, *Radiospektroskopiya kvartsa*, Nauk. dumka, Kiev, 1987.
- 15 I. V. Matyash, A. M. Kalinichenko, A. S. Litovchenko *et al.*, *Radiospektroskopiya slyud i amfibolov*, Nauk. dumka, Kiev, 1980.
- 16 Yu. I. Tarasevich, *Stroyeniye i khimiya poverkhnosti sloistykh silikatov*, Nauk. dumka, Kiev, 1988.
- 17 Yu. I. Tarasevich, F. D. Ovcharenko, *Adsorbtsiya na glinistykh materialakh*, Nauk. dumka, Kiev, 1975.
- 18 H. G. Cho, *Neues Jahrbuch für Mineralogie. Monatshefte*, 1 (2000) 34.
- 19 L. I. Razvorotneva, V. P. Kovalev, L. G. Gilinskaya *et al.*, *Mineralogiya tekhnogeneza (A Collecton of Papers)*, Izd-vo UrO RAN, Miass, 2002, p. 141.
- 20 A. P. Avtsyn, A. A. Zhavoronkov, M. A. Rish, L. S. Strochkova, *Mikroelementozy cheloveka (etiologiya, klassifikatsiya, organopatologiya)*, Meditsina, Moscow, 1991.
- 21 M. Ya. Lovkova, A. M. Rabinovich, S. M. Ponomareva, *Pochemu rasteniya lechat*, Nauka, Moscow, 1989.
- 22 E. E. Sigulya, *Khim. i Zhizn'*, 6 (1989) 84.
- 23 M. A. Fomina, V. M. Kadoshnikov, E. N. Gromozova, V. S. Podgorskiy, *Mineralogiya i zhizn': biomineralnye gomologii (A Collecton of Papers)*, Geoprint, Syktyvkar, 2000, p. 146.
- 24 V. Kadoshnikov, B. Zlobenko, M. Fomina, Yu. Fedorenko, *Ibid.*, p. 207.
- 25 L. G. Gilinskaya, T. N. Grigorieva, L. I. Razvorotneva, L. B. Trofimova, *Zh. Neorg. Khim.*, 50, 4 (2005) 689.