Modification of the adsorption properties of montmorillonite by the thermochemical treatment

Zakusin S.V.1,2, Krupskaya V.1,2, Dorzhieva O.V.1,3, Zhuhlistov A.P.1, Tyupina E.A.4

1Institute of Geology of Ore Deposits, Petrography, Mineralogy and Geochemistry, Russian Academy of Sciences, Moscow
2Lomonosov Moscow State University, Moscow
3Geological Institute of the Russian Academy of Sciences, Moscow
4Baykov Metallurgy and Materials Institute, Moscow

The results of the study on changes in the structure and surface properties of montmorillonite from Tagansky deposit from exposure to nitric acid of varying duration at an elevated temperature are presented in this work. Treatment with 1M HNO3 solution causes partial leaching of octahedral and interlayer cations which leads to protonation of internal surfaces and to an increase in microporosity as a result of octahedral OH-groups protonation and change of octahedral Al coordination. The result of the exposure to acid solutions is a change of layer charge and interaction between the sheets and layers with each other which in turn leads to a significant increase of the specific surface area. Also, a reduction in the cation exchange capacity occurs due to the deposition of amorphous silica from disintegrated tetrahedral sheets on the particle surfaces as well as a reduction of the layer charge.

Keywords: montmorillonite, bentonite clays, Tagansky deposit, structure modification, thermochemical treatments, adsorption properties, engineering barriers.

Modifikasiya adsorbsionnykh svoistv montmorillonita pri termohimicheskom vozdeystvii

Закусин С.В.1,2, Крупская В.В.1,2, Доржиева О.В.1,3, Жухлистов А.П.1, Тюпина Е.А.4

1Институт геологии рудных месторождений, петрографии, минералогии и геохимии Российской академии наук, Москва
2Московский государственный университет имени М.В. Ломоносова, Москва
3Геологический институт Российской академии наук, Москва
4Институт металлургии и материаловедения им. А.А. Байкова, Москва

В работе рассмотрены особенности модификации строения и поверхностных свойств монтмориллонита Таганского бентонита в результате его обработки раствором азотной кислоты при повышенной температуре. Изучение особенностей состава и строения исходных и модифицированных образцов бентонита выполнено комплексом методов, включающим в себя рентгеновскую дифракцию, ИК-Фурье спектроскопию, электронную микроскопию, рентгенофлуоресцентный анализ. В качестве показателей поверхностных свойств были определены величины удельной поверхности и емкости кационного обмена. Показана стадийность преобразования строения монтмориллонита под воздействием кислотной обработки. Выявлено, что под воздействием растворов 1M HNO3 происходит частичное вымывание межслоевых и октаэдрических катионов, что приводит к протонированию внутренних поверхностей, а также появлению микропор, возникающих за счет частичной деградации структуры вследствие протонирования OH-групп октаэдрических сеток, изменения координации Al в
Introduction

Clay minerals are widely used in various industries, including nuclear power and particularly radioactive waste management as a component in engineered barrier systems for radioactive waste disposal. Systems of this kind are used in different countries for high-level radioactive waste disposal to ensure the repository safety for hundreds or even tens of hundreds of years due to the high sorption properties and low permeability of clay-based barriers [1, 2].

Filling the gap between the waste canisters and walls with bentonite allows to isolate waste from groundwater, limit the mass transfer between the waste and the groundwater to only diffusion, prevent the intake of radionuclides in colloidal form to the groundwater, ensure efficient sorption of radionuclides after a possible leakage of a radioactive waste canister, seal cracks and large cavities in rocks due to high swelling ability, dissipate the heat from the high-level waste into the geological environment. An important question in the study of bentonite clay is a modification of its properties under thermochemical treatments.

The major component (70-95%) of bentonite clay is montmorillonite, a smectite-group 2:1 (or TOT) mineral. Its structure consists of two tetrahedral sheets and a central octahedral sheet enclosed therebetween. Montmorillonites are characterized by a swelling structure, high number of isomorphous substitutions in octahedral sheets and an occupation of interlayer space by counterions (Na\(^+\), Ca\(^{2+}\), Mg\(^{2+}\), etc.) which are usually hydrated in normal conditions [3,4]. The features of the montmorillonite structure determine specific properties of bentonite clays, especially its high sorption capacity, specifically for heavy metals, isotopes of cesium, plutonium and other components of the radioactive waste. However, during a long term usage of bentonite clay, such engineered barriers can be influenced by highly reactive solutions, which leads to deterioration of the insulating properties. The aim of this research is to assess the mechanism of montmorillonite's structure and the adsorption properties transformation in the process of a long-term interaction with nitric acid solution. Nitric acid is often used, for instance, in the preparation of liquid radioactive waste for isolation by an injection in deep reservoir rocks [5,6]. High temperature at radioactive wastes injection spots is caused by radioactive decay [2,5].

Experimental

Experiments were carried out on bentonite clay powder samples from Tagansky deposit (Kazakhstan) containing up to 80% of montmorillonite. The impurities were represented by quartz (5-10%) and calcite (1-3%). Experiments were conducted in 1M HNO\(_3\) solution at 60 \(^\circ\) C for 12, 36, 50 and 108 hours. At a preliminary stage we used different solid/liquid ratios such as 1:10, 1:50 and 1:100. The greatest changes in the
structure and properties have been achieved expectantly at a 1:100 ratio, therefore, it is mainly used in this research to demonstrate the results.

The initial and modified samples were analysed applying a range of methods including X-ray diffraction, infrared spectroscopy, transmission electron microscopy, evaluation of the specific surface area and microporosity, and cation exchange capacity determination.

XRD patterns were obtained with the Rigaku Ultima-IV device (Cu-Kα, 1-D detector D/Tex-Ultra, scanning range: 3.6-65° 2θ, speed: 5°, step - 0.02° 2θ, the maximum intensity ~ 25,000 counts), acquired as part of Moscow State University Development Program. The specimens were prepared as "semi-oriented" mounts by pressing the powder samples in a sample holder. Excessive pressure and surface smoothing resulted in a partial orientation of montmorillonite particles in the substrate plane. In view of the fact that during the acid treatment samples underwent strong structural changes, standard approach to oriented mounts preparation failed. XRD patterns analysis was conducted according to [3, 4, 7].

IR absorption spectra were obtained using FTIR spectrometer Bruker VERTEX 80v company (Germany) equipped with a DTGS detector, and a KBr beam splitter. The analysis was carried out in the middle region (4000-400 cm⁻¹) in vacuum at 2 hPa with a resolution of 4 cm⁻¹. Specimens were prepared by mixing samples with KBr and pressing the mixture into pellets. Spectra were obtained for the air-dried specimens and after heating for 20-24 hours at 150 °C. Spectra processing was performed using the OPUS 7.0 software.

Initial samples and selected samples after treatment obtained (after exposure to 1M HNO₃ for 12 and 108 hours at a 1:100 liquid/solid ratio) were studied by high-resolution transmission electron microscopy (HRTEM) using the electron microscope JEM-2100 with an X-ray energy dispersive analysis attachment X-Max.

Chemical analysis of initial and treated samples was carried out by inductively coupled plasma atomic emission spectroscopy (ICP-AES). The results are presented with an account for loss on ignition and natural humidity of the samples. The choice of the method was motivated by the small amount of the samples.

Measurement of specific surface area was carried out with the Quadrasorb SI/Kr equipment, adsorption was conducted at liquid nitrogen temperature (77.35 K) with nitrogen of 99.999%purity; calibration of the measuring cells volume was performed with 6.0 helium (99.9999%). Calculation was carried out by the BET multiple point isotherm in the P/P₀ range from 0.05 to 0.30. Samples were pre-dried in vacuum at 100 °C. Pore size distribution was obtained according to the method of DFT "Monte Carlo" simulation in Quantachrome software.

Cation exchange capacity was determined using the method of Cu[(Trien)]²⁺ adsorption [8].

Results and discussion

Characteristics of natural montmorillonite. Raw bentonite sample (Fig. 1) is characterized by a predominance of montmorillonite (74%) with small amounts of quartz (22.5%), calcite (2.3%) and pyrite (1.2%). X-ray diffraction pattern of montmorillonite is quite typical and characterised by a series of reflections with d-values: 13.8, 6.3, 4.48, 3.14, 2.56, 1.70, 1.50 Å. The d-spacing value (13.8 Å) and a complex profile of the first basal reflection (001) are indicative of Ca-Mg-Na composition of the interlayer cation.
complex [9]. The domain size along the c-axis is an average of 8.2 nm (6 layers with interplanar spacing of 13.8 Å - 6N).

Fig. 1. X-ray diffraction patterns of non-oriented mounts of raw montmorillonite and montmorillonites treated with 1M HNO₃ with a solid/liquid ratio 1:100 for 12, 36 and 108 hours. The interlayer spacings are given in Angstroms. Mont - montmorillonite, Qu - quartz.

Chemical composition of natural and acid-modified montmorillonites shows two basic patterns associated with the increasing treatment duration (Tab. 1): 1) reduction of the content of Al₂O₃, Fe₂O₃, MgO, CaO, K₂O, and some other cations; 2) an increase of SiO₂ content.

Table 1. Changes in the chemical composition of Tagansky montmorillonite treated with nitric acid solutions. DL - detection limit, 1:10 and 1: 100 - solid/liquid ratio. 12, 36 and 108 hours - duration of treatment; LOI - loss on ignition

<table>
<thead>
<tr>
<th>Major oxides</th>
<th>DL, %</th>
<th>%</th>
<th>1:10 12 hours</th>
<th>1:10 108 hours</th>
<th>1:100 12 hours</th>
<th>1:100 36 hours</th>
<th>1:100 108 hours</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>0.01</td>
<td>62.09</td>
<td>65.63</td>
<td>71.71</td>
<td>65.82</td>
<td>67.93</td>
<td>75.22</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>0.006</td>
<td>16.48</td>
<td>16.61</td>
<td>12.70</td>
<td>16.45</td>
<td>14.91</td>
<td>10.67</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.2</td>
<td>2.20</td>
<td>&lt; DL</td>
<td>&lt; DL</td>
<td>&lt; DL</td>
<td>&lt; DL</td>
<td>&lt; DL</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>0.02</td>
<td>6.09</td>
<td>6.11</td>
<td>4.47</td>
<td>6.03</td>
<td>5.17</td>
<td>3.18</td>
</tr>
<tr>
<td>MgO</td>
<td>0.03</td>
<td>3.40</td>
<td>2.89</td>
<td>1.99</td>
<td>2.90</td>
<td>2.69</td>
<td>1.60</td>
</tr>
<tr>
<td>CaO</td>
<td>0.02</td>
<td>0.93</td>
<td>&lt; DL</td>
<td>&lt; DL</td>
<td>&lt; DL</td>
<td>&lt; DL</td>
<td>&lt; DL</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.009</td>
<td>0.04</td>
<td>0.03</td>
<td>0.03</td>
<td>0.02</td>
<td>0.03</td>
<td>0.02</td>
</tr>
<tr>
<td>Cr₂O₃</td>
<td>0.001</td>
<td>0.01</td>
<td>0.01</td>
<td>0.00</td>
<td>0.01</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>MnO</td>
<td>0.001</td>
<td>0.07</td>
<td>0.07</td>
<td>0.05</td>
<td>0.07</td>
<td>0.07</td>
<td>0.04</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.001</td>
<td>0.71</td>
<td>0.77</td>
<td>0.83</td>
<td>0.82</td>
<td>0.83</td>
<td>0.91</td>
</tr>
<tr>
<td>LOI</td>
<td>0.01</td>
<td>8.24</td>
<td>9.37</td>
<td>8.61</td>
<td>10.37</td>
<td>10.84</td>
<td>8.84</td>
</tr>
</tbody>
</table>

In the IR spectra (Fig. 2) raw montmorillonites are distinguished for Si-O vibrational bands observed in 1053 cm⁻¹, which corresponds to the tetrahedral sheet, and Al-O-Si and Si-O-Si vibrational bands at 523 and 470 cm⁻¹, respectively, which characterizes the interaction between tetrahedral and octahedral sheets and also at 925, 876
and 3634 cm\(^{-1}\) corresponding to the vibrations Al-Al-OH, Al-Fe-OH and OH-groups, respectively, in the octahedral mesh [9,10].

Fig. 2. The infrared spectra of (a) and the scaled fragments of the IR spectra (b) of the original montmorillonite and treated with 1M HNO\(_3\) with a ratio Tb:F 1:100 for 12, 36 and 108 hours.

Images of the initial sample obtained by transmission electron microscopy (TEM) give insights into the two phases of montmorillonite: coarse montmorillonite with a particles size of 1-2 micrometers and a fine-grained, probably Na-montmorillonite with a particle sizes in between 20-80 nm, which settle on larger particles and cover the space between them (Fig. 3a). The images obtained across the c-axis from the folded edges (Fig. 3b, c), show domains with a size of 23-32 nm, related to the basal planes of the individual layers with interlayer spacings of 10.5 Å (dehydrated in vacuum) to 11.8–12.3 Å (partially dehydrated). Domain sizes can also be evaluated using TEM as a size of an area with constant basal interlayer spacings (001); in the images from the folded particle edges it amounts to 4-7N.

Fig. 3. Electron microscopic images of particles of raw (a, b), and treated with 1 M HNO\(_3\) for 108 hours (c, d) montmorillonite; b and d - high resolution images from the folded edge of the montmorillonite particles (areas shown as white rectangles in Figures a and b, respectively).
Structural transformation of montmorillonite due to the acid treatment. Treatment of montmorillonite with 1M HNO₃ solution for 12 hours leads to a decrease of its basal spacing from 13.8 Å to 13.2 Å and to an increase of its XRD reflection intensity, which is probably the result of the defective montmorillonite phase dissolution and an increase of interlayer ordering due to partial leaching of Ca²⁺ and Mg²⁺. Further treatment leads to a reduction in the order of layers stacking and destruction of the 2:1 layer structure, which is manifested by a decrease in the intensity and broadening of the basal XRD reflections until almost complete disappearance of the basal reflections of all orders other than (001). The shift of (001) reflex to 13.9 Å after 36 and 108 hours reaction duration is the result of the dissolution of carbonates (mainly calcite) and the intake of calcium to the interlayer complex. This process is accompanied by a decrease of domain size to 4N (Tab. 2).

Table 2. Changes in the structural features: interplanar spacings (d₀₀₁), domain size determined from the size of the coherent scattering area (h₀₀₀₁), number of layers (N) and adsorption properties: specific surface area (S_BET), total pore volume (V_Σ), cation exchange capacity (CEC), of Tagansky montmorillonite under acid treatment.

<table>
<thead>
<tr>
<th>Treatment duration</th>
<th>d₀₀₁(Å)</th>
<th>h₀₀₀₁, nm</th>
<th>N</th>
<th>S_BET (m²/g)</th>
<th>V_Σ (cm³/g)</th>
<th>CEC, (meq/100g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw</td>
<td>13.7</td>
<td>8.2</td>
<td>6</td>
<td>67.1</td>
<td>0.085</td>
<td>86</td>
</tr>
<tr>
<td>12 hours</td>
<td>14.0</td>
<td>7.0</td>
<td>5</td>
<td>109.7</td>
<td>0.114</td>
<td>58</td>
</tr>
<tr>
<td>36 hours</td>
<td>14.0</td>
<td>7.0</td>
<td>5</td>
<td>191.2</td>
<td>0.192</td>
<td>56</td>
</tr>
<tr>
<td>108 hours</td>
<td>13.8</td>
<td>5.5</td>
<td>4</td>
<td>301.2</td>
<td>0.353</td>
<td>40</td>
</tr>
</tbody>
</table>

The domain size decrease, along with an expected specific surface area increasing can be tracked indirectly by the increasing intensity of the adsorbed water band in IR-spectra in the 4000-2500 cm⁻¹ region (Fig. 2a) a 108 hour treatment. Changes in the Si-O-Si band shapes in the range of 1100-1050 cm⁻¹(Fig. 2a) indicate a change of the way of interaction within the tetrahedral sheet. Also, a band shift from 1050 cm⁻¹ to 1095 cm⁻¹ for the initial samples and the ones treated for 108 hours indicates increasing the amount of the amorphous silica due to the partial destruction of the tetrahedral sheets [11, 12, 13]. The zoom-in fragment (Fig. 2c) illustrates a decrease in intensity of the 925 and 876 cm⁻¹ bands, corresponding to Al-Al-OH and Al-Fe-OH vibrations, respectively, in the structure of the octahedral montmorillonite sheets during nitric acid solutions treatment of different durations indicating leaching of Al³⁺ and Fe³⁺ from the octahedral sheet [11, 12, 13]. Octahedral cations leaching leads to modification of the interaction between the octahedral and tetrahedral sheets in the 2:1 layer and partial destruction of octahedral sheets.

108 hour treatment leads to microaggregates' surfaces becoming rough and pebbled which has been observed by the other researchers of Tagansky montmorillonite [14]; in the images of folded edges [15] only small fragments of parallel layers with a maximum length of 25 nm can be traced which corresponds to small packs of 2-3 layers (Fig. 3, g). The interplanar distance remained close to 12-14 Å which is typical for the natural montmorillonite and may be the result of the incomplete destruction of the montmorillonite structure.

Thus, the results of the montmorillonite structure exposure to thermo-chemical treatments are: partial destruction (dissolution) of relatively fine-grained clay particles, leaching of the octahedral cations and partial H⁺ substitution of the interlayer cations, changes in the interactions between octahedral and tetrahedral sheets and their partial destruction. Concurrently, the vast majority of the interlayer octahedral cations are leached
from the structure into the solution, however the vast amount of silicon is adsorbed on the surface which increases the content of amorphous silica.

**Modification of the montmorillonite adsorption properties during the acid treatment.** Adsorption properties of bentonite clays can be characterized by a specific surface area (SSA) and cation exchange capacity (CEC). It is widely thought (Osipov, Sokolov, 2013) that, in general, the value of SSA is in a direct proportion with the value of CEC, i.e. with an increase of SSA, CEC value rises and vice versa, which is true in most cases for natural soils [16] with a different mineral composition. However, the ratio of these parameters for montmorillonites with different composition may be in a more complex relationship. Table 2 shows the SSA and CEC values for raw and modified montmorillonites from Tagansky deposit. The following relationship can be observed: an increase in the specific surface area followed by a reduction of cation exchange capacity.

The vast majority of works dedicated to the transformation of microstructural characteristics of montmorillonite exposed to inorganic acids solutions are based on treatments with solutions of different concentrations [17-19]. These studies clearly show a similar trend: the increase of the SSA of montmorillonite with an increasing concentration of HCl or H$_2$SO$_4$. Researches that are focused on nitric acid effects are not so widespread in the press which is probably due to its greater toxicity and as a consequence, a rare application in technological processes. The research presented is focused on nitric acid effects because it is part of the liquid radioactive waste [6, 20].

Protonation of the Al$_3^+$ bond couple in octahedra transfers it from 4 to 6-coordinated [21], which, together with a decrease in the number of octahedral cations leads to a modification of octahedral and tetrahedral sheets and consequential appearance of micropores. Structural transformations are schematically shown in Fig. 4. Limit values for "micropores", "mesopores" and "macropores" dimensions may vary in different classifications developed for different fields of knowledge. In geology mesopore sizes lie in the range from 10 to 1000 micrometers, micropores - from 0.1 to 10 micrometers [22]. In the course of the detailed morphometric study of soils' microstructures V.I.Osipov and V.N.Sokolov [23] proposed more precise classification, subdivision of micropores into thin (0.1-10 µm), small (1-10 µm) and large (10-100 µm) whereas the lower limit of macropores is proposed at 100 µm.

![Fig. 4. Schematic representation of structural changes in natural montmorillonite due to treatment with solutions of inorganic acids: a - natural Ca-montmorillonite, b - partial interlayer protonation c - complete interlayer protonation (H-smectite), protonated OH-groups of the octahedral sheets and Al$^{3+}$ coordination change](image)

In other branches of knowledge there are other classifications of the pore sizes. For example, the International Union of Pure and Applied Chemistry (IUPAC) recommended...
the following classification: macropores (50 nm), mesopores (2 to 50 nm), micropores (2 nm) [24, 25, 26]. Micropores are subdivided into ultramicropores (less than 0.7 nm) and supermicropores having an intermediate size between ultramicropores and mesopores.

In fact, all the pore sizes in montmorillonite obtained due to the modification of the structure and which are predominantly involved in adsorption, do not exceed 6-9 nm for mesopores and 1-3 nm for micropores. The average pore size measured in the natural and modified montmorillonite is about 5 nm, which corresponds to the interparticle pores according to Sokolov and Osipov [23]. At the same time, acid treatment, as shown above, gives rise to pores in the layer structure (micropores) due to partial leaching of the octahedral cations, protonation of OH-groups and Al$^{3+}$ coordination changes that do not increase the average pore size, but the total pore volume (tab. 2).

Thus, cation exchange capacity (CEC) value naturally decreases from 86 meq/100 g for natural bentonite to 40 meq/100 g for the most heavily treated sample (Table 1). Such decrease in CEC values after a treatment with inorganic acids (e.g., HCl and H$_2$SO$_4$) was described in other researches [19]. The CEC value of bentonite is determined not only by the montmorillonite content, but especially its structure. As a result of the acid treatment, layer charge of montmorillonite decreased and amorphous silica appeared due to degradation of the tetrahedral sheets deposits on the particle surfaces that leads to a significant decrease of CEC.

**Conclusion**

The results of experiments allow us to describe the processes of transformation of the structure and adsorption properties of montmorillonite from Tagansky deposit due to a treatment with 1M HNO$_3$ solution at an elevated temperature for various durations.

Modification of the structure proceeds in several stages that partly overlap with each other: 1. Dissolution of the most defective nanoscale phase. 2. Leaching of interlayer cations and partial protonation of the interlayer. 3. Leaching of octahedral cations. 4. Changes in the interaction between octahedral and tetrahedral sheets. 5. Destruction of the tetrahedral sheet and partial deposition of amorphous silica on the particle surfaces.

Modification of the adsorption properties proceeds as in the following stages: 1. Increase of specific surface area due to the destruction of large aggregates and particles. 2. Increase of the total pore volume due to the appearance of micropores due to the protonation of OH-groups of the octahedral sheets and octahedral cations leaching. 3. Reduction of the cation exchange capacity due to reduction of the layer charge, and adsorption of amorphous silica, which appeared after the destruction of tetrahedral sheets.

Modification of the structural features due to acid treatment can be used to simulate the behaviour of physical and engineering properties of adsorption barriers for long operation periods.

*This work was financially supported by the Governmental Assignment #0136-2014-0009 (72-3).*

**References**

21. Krupskaya V.V. et al., Novoobrazovannyy smektit kak indikator preobrazovanii geologicheskoi sredy pod vozdeistviem vysokoreaktivnykh rastvorov, soprovodzayushchikh zhidkie radioaktivnykh otkhody [The newly-formed smectite as an indicator of changes of the geological environment under the influence of highly reactive fluids that carry liquid radioactive wastes] Reports of the Academy of Sciences, in print.
Zakusin Sergey V. - PhD-student of geological faculty at Lomonosov Moscow State University; Laboratory of crystal chemistry of minerals, Institute of geology of ore deposits, petrography, mineralogy and geochemistry of Russian Academy of Sciences, junior research fellow; Moscow, Russian Federation; zakusinsergey@gmail.com

Dorzhieva Olga V. - PhD-student at the Institute of geology of ore deposits, petrography, mineralogy and geochemistry of Russian Academy of Sciences; Geological Institute, Russian Academy of Science, Lead Research Trainee at Laboratory of Physical Methods for the Study of Rock-forming Minerals, junior research fellow; Moscow, Russian Federation; dorzhievaov@gmail.com

Tyupina Ekaterina A. - PhD in technical sciences, D. Mendeleyev University of Chemical Technology of Russia, Department of High-Energy Chemistry and Radioecology, associate professor, vice head of department; Moscow, Russian Federation; tk1972@mail.ru

Krupskaya Victoria V. - PhD in geological and mineralogical sciences, Laboratory of crystal chemistry of minerals, Institute of geology of ore deposits, petrography, mineralogy and geochemistry of Russian Academy of Sciences; geological faculty of Lomonosov Moscow State University, senior research fellow; Moscow, Russian Federation; krupskaya@ruclay.com

Zhuhlistov Anatoly P. - PhD in geological and mineralogical sciences, Laboratory of crystal chemistry of minerals, Institute of geology of ore deposits, petrography, mineralogy and geochemistry of Russian Academy of Sciences, leading research fellow; Moscow, Russian Federation; anzhu@igem.ru