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Vermiculite from the Koksharovsky Deposit (Primorsky Krai) and Its Properties

L. A. ZEMNUKHOVA[1], A. E. PANASENKO[1,2], N. V. POLYAKOVA[1], V. G. KURAVIY[1], O. D. AREF'EVA[2], V. A. ZEMNUKHOV[3]

[1]*Far Eastern Branch, Russian Academy of Sciences, Vladivostok, Russia*

E-mail: panasenko@ich.dvo.ru

[2]*Far Eastern Federal University, Vladivostok, Russia*

[3]*Alyumosilikat CJSC, Koksharovka Village, Primorsky Krai, Russia*

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Abstract

The results of the study of chemical and phase compositions, IR spectroscopy analysis, morphology, specific surface area, pH of aqueous extract, and magnetic susceptibility of vermiculite samples from the Koksharovsky deposit of Primorsky Krai (the mineral, concentrate, and intumesced product) are presented. Comparative analysis of samples of vermiculite from Koksharovsky and Kovdor deposits of different origins was carried out.

Keywords: vermiculite, Koksharovsky deposit, Kovdor deposit, elemental composition, morphology, phase composition, IR spectra, specific surface area, magnetic properties

INTRODUCTION

Vermiculite mineral is a part of a large group of layered crystals that find applications in a wide range of areas depending on physicochemical properties. In the territory of Russia, about 20 deposits of vermiculite ores are open to date. *Via* various techniques, concentrates are initially obtained from them, and further by their heating, exfoliated porous material having a number of useful properties. More than a hundred kinds of products are produced from expanded vermiculite in the industry of economically developed countries. On the contrary, this tendency in Russia is still in the formative stage [1]. Vermiculite minerals from different deposits differ among themselves genetically, therefore their chemical composition and properties are inconstant.

In the literature, there are data about vermiculite of Kovdor [2–4], Potaninsk [6], Karatas-Alt'ntask [7] and Tatarsk [8] deposits. In Primorsky Krai, there have periodically been made attempts on the processing of ore from the Koksharovsky deposit, information on which is poor [9, 10]. Air (dry) ore processing and the production of vermiculite concentrates of different grades (Large, Medium, Fine, and Super Fine) with a capacity to 700 t/month, and also expanded vermiculite (1000 m^3/month) was arranged in 2010. Vermiculite from the Koksharovsky deposit had earlier been regarded as a secondary mineral associated with the weathering crust of ultrabasic rocks and generated at the expense of biotite hydration. However, it has been currently established this is a mineral of endogenic (hydrothermal low-temperature) origin, unlike, for instance, vermiculite from the Kovdor deposit. Satellites minerals of vermiculite from the Koksharovsky deposit are titanomagnetite, sphene, and apatite [9].

The goal of the present work is the study of composition and physicochemical properties of vermiculite from the Koksharovsky deposit of Primorsky Krai (mineral, concentrate, and intumesced product).

EXPERIMENTAL

Study subject was vermiculite from the Koksharovsky deposit, *i.e.* a mineral (sample 1) and the intumesced product (sample 2). Expanded vermiculite from the Kovdor deposit (sample 3) and synthetic potassium aluminosilicate (sample 4) described in [11] were reference samples. Samples of expanded vermiculite corresponded to GOST 12865–67.

TABLE 1

Composition of the concentrate and vermiculite mineral from the Koksharovsky deposit, mass %

Indicators	Concentrate [10]	Mineral(Sample 1)
SiO_2	37.84–42.42	34.52
Al_2O_3	9.37–10.58	12.12
MgO	11.36–12.82	11.87
CaO	4.17–6.07	4.14
Fe_2O_3	12.98–15.57	25.05
FeO	1.71–1.78	
K_2O	0.66–1.68	4.61
Na_2O	0.97–0.98	–
TiO_2	2.76–4.59	5.21
Cr_2O_3	0.10	–
V_2O_3	0.094	–
MnO_2	0.13	0.21
S	0.017–0.025	0.51
H_2O total	1.89–16.74	N/d
pH	7.27–7.45	N/d
P	0.10	–
F	0.16	N/d

Note. 1. The dash indicates that the component was not detected. 2. N/d is Not determined.

Elemental analysis was performed by energy-dispersive X-ray fluorescence spectroscopy (Shimadzu EDX 800 HS spectrometer, Japan), Rh anode tube, the exposure time is 100 s. The concentrations of elements were computed using a calibration graph. Nitrogen content in the mineral from Koksharovsky vermiculite was determined by the Kjeldahl titrimetric method according to the standard procedure. X-ray diffraction patterns were recorded using Bruker D8 Advance diffractometer (Germany) in CuK_α-radiation. Identification of phases was carried out using the EVA program, the PDF-2 database. Infrared spectra of samples synthesized in vaseline oil were recorded in the 400–4000 cm^{-1} range on Shimadzu FTIR Prestige-21 spectrophotometer (Japan). Ignition losses (IL) were determined by sample calcination in a muffle furnace at 1000 °C for 1 h. The morphology of vermiculite samples was studied using a Hitachi S5500 (Japan) high resolution scanning electron microscope (SEM). Specific surface area (SSA) and porosity were determined according to nitrogen adsorption using Micromeritics Instrument Corporation ASAP 2020 analyser (USA). The values of SSA were computed using the BET method, while the pore size distribution – according to the BJH (Barrett-Joyner-Halenda) method. Magnetic properties of the samples were examined using a vibration magnetometer (VSM) that was a part of the system of measuring physical properties (Quantum Design PPMS 9T ECII) in the 3–300 K temperature range and within the limits of fields of ±5 T.

To determine the pH value of water extract, 5 g of a sample of expanded vermiculite was placed in a flask; 50 mL of distilled water was added and refluxed for 3 min in a flask. Thereafter, flask content was filtered off; the filtrate was cooled and the pH value was determined using Mettler Toledo FiveEasyPlus 20 pH meter (Switzerland).

RESULTS AND DISCUSSION

Vermiculite mineral

According to [12], vermiculite is a layered clay mineral with a total formula of $(Mg^{2+},Fe^{2+},Fe^{3+})_3[(Al,Si)_4O_{10}]\cdot(OH)_n\cdot 4H_2O$. Kok-

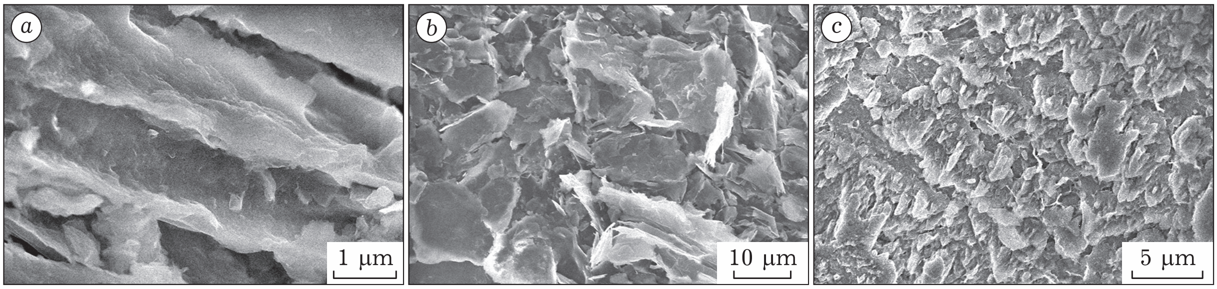

Fig. 1. Micrographs of vermiculite from the Koksharovsky deposit: mineral (*a*) and the intumesced product (*b*) and expanded vermiculite from the Kovdor deposit (*c*).

sharovsky vermiculite refers to bentonite series, however, unlike one from the Tatarsk deposit [8] (from this row too) is presented by average-flake vermiculite with a density of 2.7 g/cm^3 [9]. Vermiculite mineral from the Koksharovsky deposit is of brown colour and according to SEM data, has a layered structure (Fig. 1, *a*); the distance between layers is 1–1.5 μm.

Table 1 gives the composition of Koksharovsky vermiculite, concentrate [10], and mineral (sample 1). Compared with the concentrate from the Tatarsk deposit [8], it contains much more titanium and calcium and less magnesium and manganese. It is also worth noting that nitrogen (0.264 %) was detected in sample 1, which was probably due to mineral contamination with humic substances from soil.

Figure 2 presents the IR spectrum and the X-ray pattern of the mineral. In the 400–1200 cm^{-1} range, there are bands corresponding to stretching (1003, ~683 cm^{-1}) and bending vibrations of siloxane Si–O–Si and Si–O–M bonds (M = Al, Mg, Fe), typical for silicate compounds [13]. The absorption bands near 3200–3700 (stretching) and 1651 cm^{-1} (deformation) point to the presence of O–H bonds. The IR spectrum of synthetic sample 4 is given here too for comparison. It is characterised by the shape and the absorption band maximum of siloxane bonds. The X-ray diffraction pat-

TABLE 2

Composition of samples of expanded vermiculite from Koksharovsky and Kovdor deposits

Indicators	Deposit			
	Koksharovsky (Sample 2)		Kovdor (Sample 3)	
	2-005	2-025	3-005	3-025
SiO_2	30.30	30.59	31.64	33.46
Al_2O_3	18.75	18.49	11.73	17.34
MgO	21.53	21.16	36.21	37.87
CaO	1.87	1.62	9.55	0.54
Fe_2O_3	17.15	16.60	8.90	7.99
K_2O	4.54	5.10	0.08	0.05
Na_2O	0.28	0.25	0.49	1.27
TiO_2	4.33	4.77	0.86	1.12
MnO_2	0.11	0.12	0.20	0.09
BaO	1.42	0.88	н/о	н/о
IL*	7.5	3.7	9.5	7.7
pH**	6.69	6.77	11.04	7.67

Note. N/d is Not determined.

*IL is ignition losses at 1000 °C.

**pH of aqueous extract.

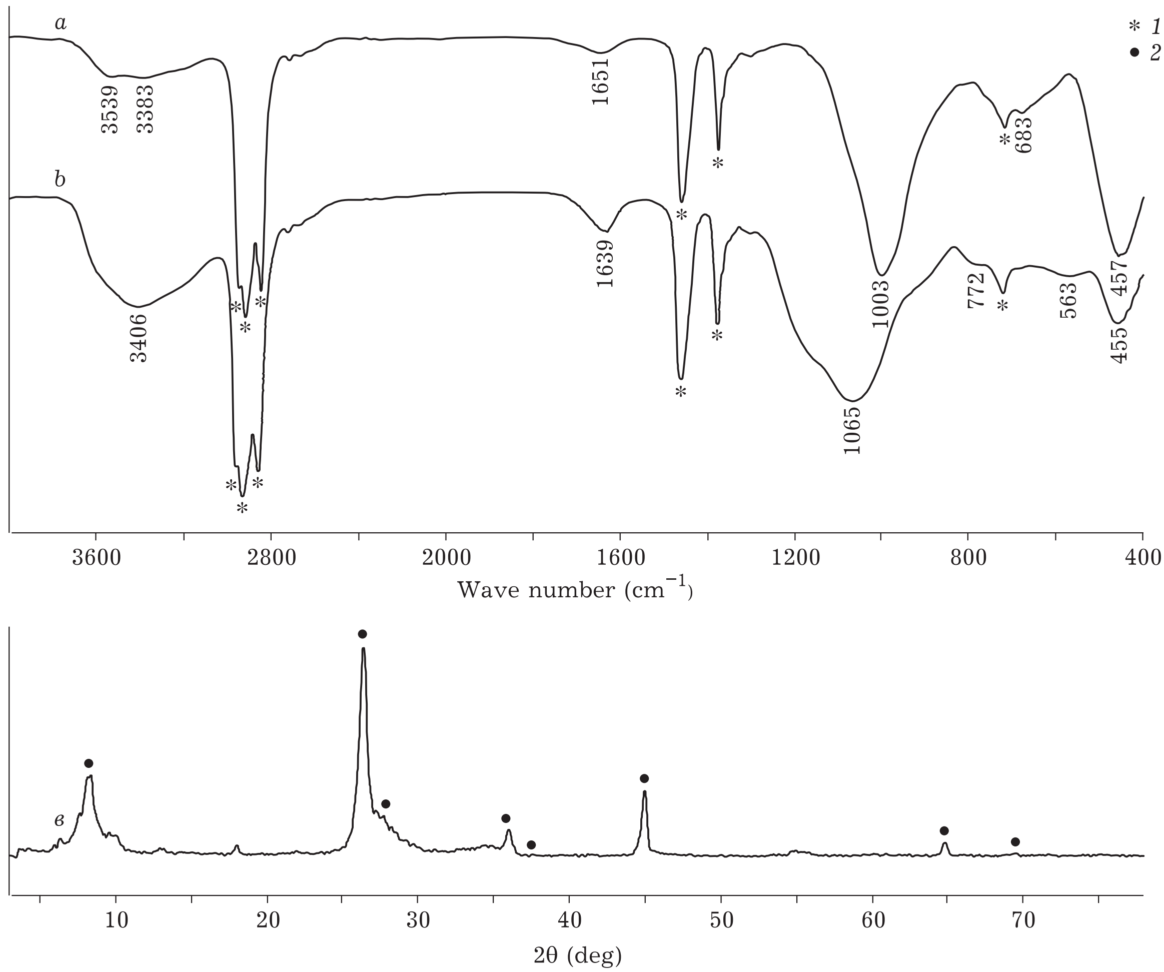

Fig. 2. IR spectrum (*a*) and X-ray diffraction pattern (*c*) of vermiculite mineral from the Koksharovsky deposit and IR spectrum of synthetic aluminosilicate (*b*) [10]. *1* – absorption bands of vaseline oil; *2* – position of the reflection of vermiculite according to the PDF 2 database.

tern of the mineral points to the crystal state of sample 1. According to the PDF-2 database, the main reflexes correspond to vermiculite ($(Mg,Fe,Al)_3(Al,Si)_4O_{10}(OH)_2 \cdot 4H_2O$).

It worth noting that the content of hydrated water in vermiculite from the Koksharovsky deposit in the oxidation zone (at a depth of 2–3 m from the ground) is 5–16.7 %, it is reduced to 1.9–3.7 % in deeper layers; there are no signs of the presence of other micaceous minerals. The bulk density of expanded vermiculite does not depend on water content and varies from 100 to 200 kg/m^3 [9, 10].

Process scheme for the preparation of vermiculite concentrate used during the development of the Koksharovsky deposit involves crushing and magnetic separation of raw materials. Vermiculite concentrate that is later exposed to fractionation is obtained from the non-magnetic product. Expanded vermiculite is produced from a fraction of less than 2 mm [10]. Flotation scheme is used during the preparation of Kovdor vermiculite concentrate, unlike Koksharovsky one.

Expanded vermiculite

Expanded vermiculite has thermal insulating and sorption properties, useful in practical terms, which determines its wide use in agriculture and industry. It is chemically inert, durable, and environmentally safe, of golden or silver colour, may be used at temperatures from −240 to 1100 °C [1].

Intumescence of vermiculite from the Koksharovsky deposit proceeds slowly at first (in the 150–350 °C temperature range), and then step-wise, right up to 900 °C. The volumetric bulk mass of expanded vermiculite varies from 98 to 342 kg/m^3. Its colour is gold, with brown shade [9, 10].

According to SEM, expanded vermiculite from Koksharovsky deposit (sample 2) is folded by chaotically oriented irregular shape plates of a size of 5–50 μm, with a thickness of 1 μm (see Fig. 1, *b*). The plates are partly connected into more massive aggregates; their thin parts are somewhat twisted, in other words, the material is elastic. Expanded vermiculite from the Kovdor deposit (sample 3) is generated by smaller plates of the elongated shape with a size of 0.5–5 μm. They are parallel to each other and are oriented in one direction (see Fig. 1, *c*). All samples contain a great number of small shapeless fragments located between larger species.

Figure 3 demonstrates X-ray diffraction patterns of samples 2 and 3 with well-resolved reflections pointing to their different phase compositions. The first reflection in the X-ray diffraction patterns of both samples corresponds to interlayer distances of 14.18 Å (sample 2) and 14.35 Å (sample 3). According to the PDF-2 database, sample 2 contains two main phases: phlogopite ($KMg_3(Si_3Al)O_{10}(OH)_2$) and vermiculite with a composition of ($Mg_x(Mg,Fe)_3(Si,Al)_4O_{10}(OH)_2 \cdot 4H_2O$), while sample 3 is vermiculite with a composition of ($Mg_{2.36}Fe_{0.48}Al_{0.16}$)($Al_{1.28}Si_{2.72}$)$O_{10}(OH)_2(H_2O)_{4.32}MgO_{0.32}$). Different phase compositions of samples 2 and 3 is also reflected in their IR spectra (Fig. 4, curves *a*, *c*): unlike sample 3, probe 2 is characterized by weak absorption bands in the range of stretching (3200–3600 cm^{-1}) and bending (1670 cm^{-1}) vibrations of OH groups, sharper bands in the area of vibrations of valence and deformation siloxane bonds, Si–O–Si(M) (1004 and 457 cm^{-1}), typical for silicates. (It should be noted that in [4], instead of the IR spectrum of expanded Kovdor vermiculite, a spectrum of a sample after acid treatment is mistakenly given.)

Natural vermiculite is always inhomogeneous by composition and may be contaminated by impurities that have different densities and hardnesses, therefore properties of expanded vermiculite will depend only on the size of its species. To highlight this dependence, samples of expanded vermiculite from Koksharovsky and Kovdor deposits were sieved and fractions smaller than 0.05 mm (samples 2-005 and 3-005) and larger than 0.25 mm (samples 2-025 and 3-025) were selected. Table 2 gives the elemental composition of these samples, IL values, and pH of aqueous extract. It can be seen that sample 2 is notable for significantly larger contents of iron, potassium, titanium and lower ones of magnesium compared to sample 3. There are considerable differences in the

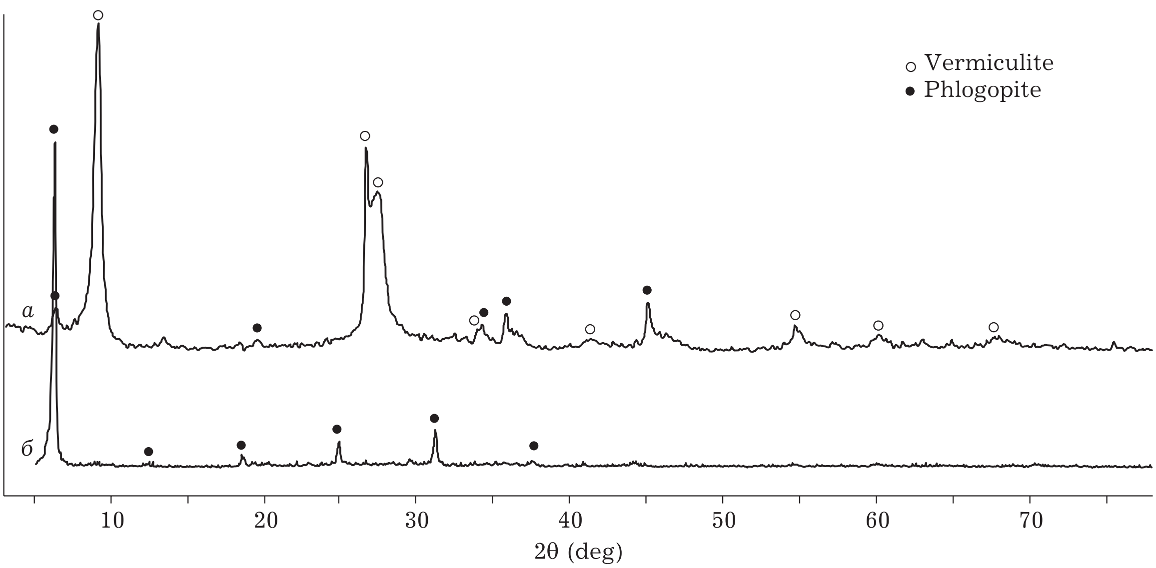

Fig. 3. X-ray diffraction patterns of expanded vermiculite from Koksharovsky (*a*) and Kovdor (*b*) deposits.

chemical composition of the fractions, especially for sample 3. For example, the content of aluminium, silicon, and sodium in a large fraction (3-025) is 1.3–1.5 higher than in the small one (3-005), while calcium content – 16 times smaller. Accordingly, the small fraction (3-005) has a much more alkaline pH value of aqueous extract than the large one.

X-ray diffraction patterns of samples 2 and 3 become more complicated after calcination at 1000 °C, as products are phase mixtures, mainly magnesium silicates identified by the PDF-2 database (Table 3). Crystallization of samples that happens at high temperatures is also reflected in a change of IR spectra, in the 400–1200 cm^{-1} long-wave region (see Fig. 4, curves *b*, *d*). In the IR spectrum of sample 2, absorption bands that correspond to hydroxyl groups disappear, unlike sample 3, in the spectrum of which, there are bands with maxima near 3177 and 1634 cm^{-1}. Apparently, this is due to the higher hygroscopicity of sample 3 driven by a high calcium content. It is known that in air, calcium oxide collects water to generate calcium hydroxide, the presence of which is confirmed by the appearance of an absorption band in the 3641 cm^{-1} range (see Fig. 4, curve *d*) corresponding to the

TABLE 3

Phase composition of samples of Koksharovsky (2-005, 2-025) and Kovdor (3-005, 3-025) expanded vermiculite after calcination at 1000 °C

Samples	Phase composition
2-005	Phlogopite $KMg_3(Si_3Al)O_{10}(OH)_2$
	Enstatite $MgSiO_3$
	Albite $Na(AlSi_3O_8)$
	Hematite Fe_2O_3
2-025	Phlogopite $KMg_3(Si_3Al)O_{10}(OH)_2$
	Enstatite $Mg_2(Si_2O_6)$
	Riebeckite $Na_2Fe_3Fe_2Si_8O_{22}(OH)_2$
	Diopside $CaMgSi_2O_6$
3-005	Enstatite $MgSiO_3$
	Olivine $Mg_{1.8}Fe_{0.2}(SiO_4)$
	Barbierite $2AlNaSi_3O_8/Al_2O_3 \cdot Na_2O \cdot 6SiO_2$
3-025	Enstatite $Mg_2(Si_2O_6)$
	Olivine $Mg_{1.784}Fe_{0.216}SiO_4$

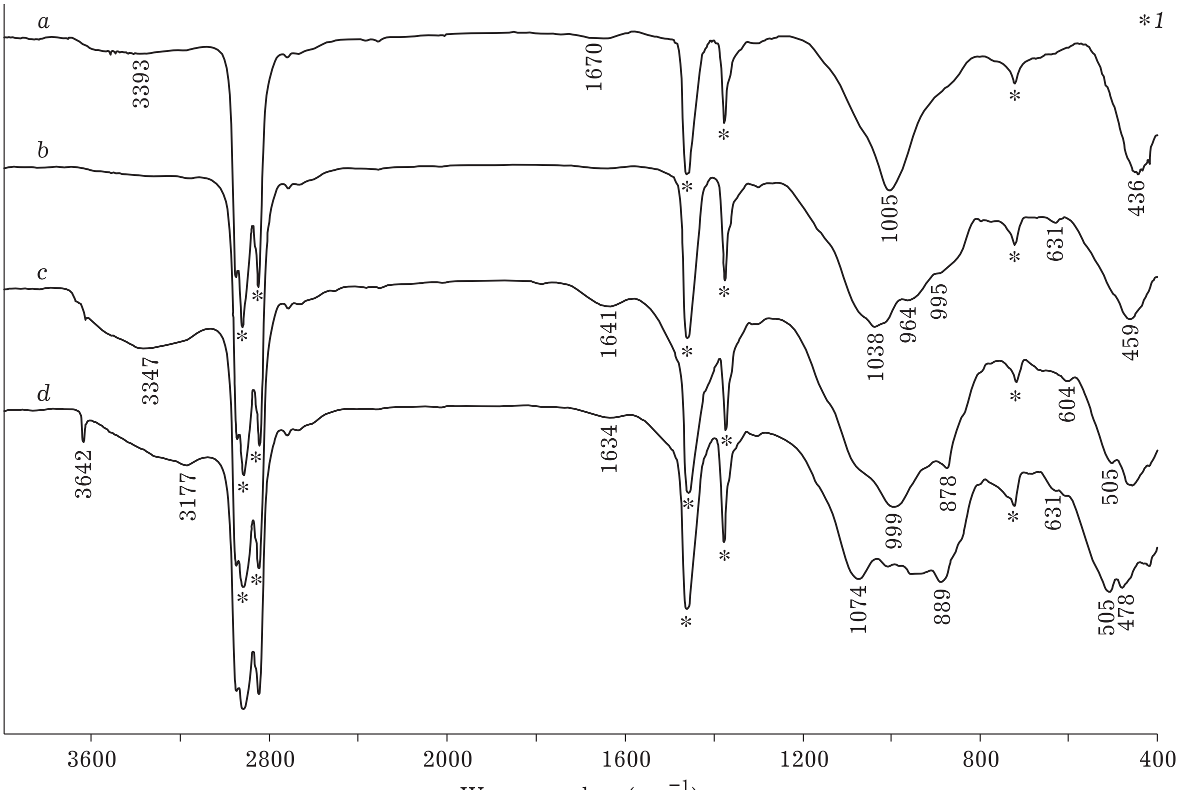

Fig. 4. IR spectra of samples (the <0.05 mm fraction) of expanded vermiculite from Koksharovsky (*a*, *b*) and Kovdor (*c*, *d*) deposits: *a*, *c* – initial, *b*, *d* – after calcination at 1000 °C. *1* – absorption bands of vaseline oil.

TABLE 4

Surface characteristics of samples of Koksharovsky (2-005, 2-025) and Kovdor (3-005, 3-025) expanded vermiculite

Samples	SSA, m^2/g	d, nm	V, cm^3/g
2-005	8.94	2.98	0.0470
2-025	8.07	2.97	0.0369
3-005	3.14	3.15	0.0196
3-025	8.14	5.34	0.0374

Note. SSA is specific surface area, d is pore diameter, V is specific pore volume.

stretching vibrations of OH group.

Surface characteristics of various functions of samples 2 and 3 examined according to nitrogen adsorption (Table 4) demonstrate that a small fraction of Kovdor vermiculite (3-005) has the minimum values of specific surface area, pore diameter and volume, while for Koksharovsky vermiculite, on the contrary, parameters for a small fraction (2-005) exceed the values for a large one (2-025).

High iron content in samples of expanded vermiculite from the Koksharovsky deposit (16.60–17.15 %, see Table 2) determines interest to its magnetic properties. As demonstrated by the study of the field dependence of magnetization, sample 2 demonstrates typically paramagnetic properties in the 3–300 K temperature range; the coercivity value is 50–66 Oe (Fig. 5). After calcination, reflections of hematite (Fe_2O_3) appear in the X-ray diffraction pattern of sample 2-005 (see Table 3), therefore one may assume that iron in expanded vermiculite is present as uncoordinated non-magnetic oxide centres located between aluminosilicate layers, similarly to [14]. Their crystallization occurs and the hematite phase is generated under high temperature effect.

CONCLUSION

The chemical and phase composition of the mineral, concentrate, and intumesced product from the Koksharovsky deposit of Primorsky Krai have been studied. The presence of nitrogen in the mineral has been detected. Comparative analysis of fractionated samples of expanded vermiculite from Koksharovsky and Kovdor deposits has been carried out. Their different origin determines the differences in the morphology of species, surface characteristics (specific surface area, diameter, and specific pore volume), elemental, and phase composition. Expanded vermiculite from the Koksharovsky deposit is a typical paramagnetic.

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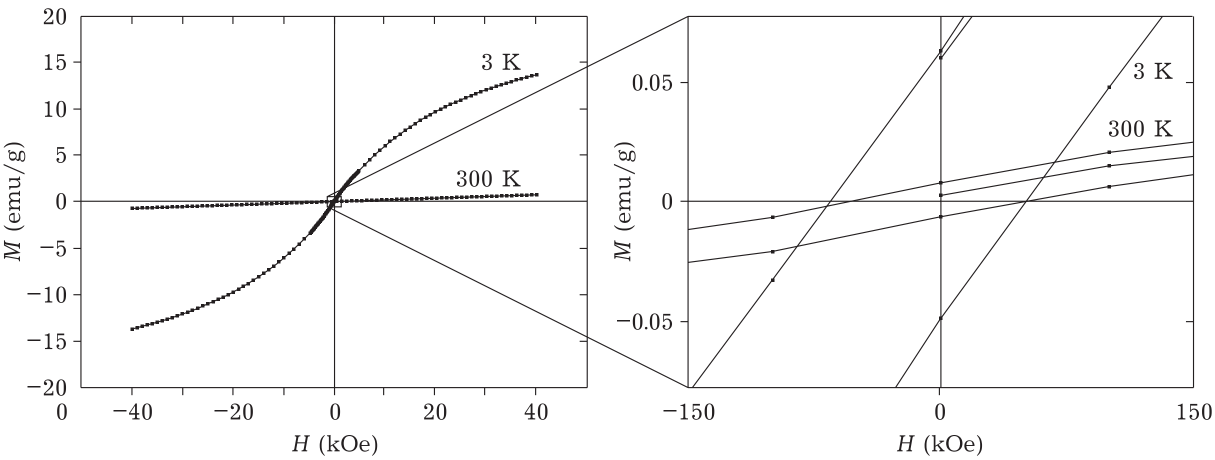

Fig. 5. Field dependencies of magnetization of expanded vermiculite (sample 2) from the Koksharovsky deposit at temperatures of 3 and 300 K.

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