Diatomaceous Clay of Shadrinsky deposit (Kurgan Region)

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Abstract. Kurgan region occupies a leading position among the regions of the Trans-Urals for reserves of opal-cristobalite rocks. Diatomaceous clay of Shadrinsky deposit is the largest object of the mineral resource base of the region, located in the 1-1.5 km south-west from the city of Shadrinsk, on the right bank of the river Iset at the deep erosional incision. The results of the research revealed that the rocks forming the productive strata of Shadrinsky deposits are represented with just diatomaceous clay, not tripoli, as previously thought. Diatomaceous clay of Shadrinsky deposit is characterized by diatom complex Pyxilla gracilis top of the upper part of Lower Eocene. The general chemical composition of the rocks is close to diatomite of the major deposits of Trans-Urals. The only significant difference is the lower content of the mineral phases SiO2 and greater clay components. The presence of zeolites, calcium-sodium composition (up to a few %) is detected as part of the impurities; the clay fraction is represented by smectite, kaolinite, mica. The bulk rock contains fragments of diatoms in size from 0.005 to 0.063 mm, fragments of siliceous sponge spicules in the size of 0.027 x 0.061 mm in various states of preservation. Features of material composition and microstructure of diatomaceous clay of Shadrinsky field allow us to consider them as a promising raw material for the production of building and insulating materials.

Key words: Kurgan region, Trans-Urals, Diatomaceous clay, opal-cristobalite rocks, lithology
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Introduction

Integrated use of local mineral resources base of solid non-metallic minerals is an important condition for the sustainable development of regions of Russia (Sadykov et al., 2004; 2015). The successful implementation of regional projects in the field of construction, transport infrastructure and agriculture depends largely on the efficiency of extraction, transportation, processing and use of solid non-metallic minerals.

The problem of low-degree involvement in the industrial use of local raw material base solid non-metallic minerals are relevant for the Urals Federal District (Pakhomov, Dushyn, 2008), and especially for the Kurgan region. Despite the favorable economic and geographical position, the presence of impressive and diverse mineral base, traditionally developed agriculture, Kurgan region is among depressed areas of agro-industrial type (Surkov, Shusharina, 2009).

Within the region large deposits are concentrated of bentonite clays, glass and molding sands, semi-precious stone materials, building stone, expanded clay and brick clay. Opal-cristobalite rocks occupy a special place among the objects of the mineral resource base of solid non-metallic minerals in Kurgan region, reserves of which in the region holds a leading position in the territory of the Trans-Urals. Shadrinsky tripoli field was previously explored and developed, balance reserves of 2.2 million m^3. Korablevsky tripoli field is known in the vicinity of Kataysk (4.5 million m^3), as well as Savinskiy promising area (presumably tripoli reserves – 6.2 million m^3) (Natural resources and environment ..., 2015).

Opal-cristobalite rocks are a perspective type of minerals, production and consumption volumes of which increased annually worldwide (U.S. Geological Survey, 2015). Due to a combination of physical properties, diatomite and diatomaceous clay may be in demand in the production of building materials (Nikitin et al., 2014; Radayev et al., 2013), fertilizers and ameliorants in agriculture (Loboda et al., 2014; Aksakal et al., 2012), natural sorbents for the purification of industrial and domestic waste water (Anisimov et al., 2010), etc.

Shadrinsky field is the largest object of the mineral resource base for opal-cristobalite rocks in Kurgan region. In the scientific literature and geological reports rocks that form the productive stratum of the field are described as 'tripoli' (The balance of mineral reserves of the USSR, 1984). The research results presented in this study demonstrate the need for further consideration of rocks from Shadrinsky field as diatomaceous clay, but not tripoli.

Objects and methods

Shadrinsky field is located in the 1-1.5 km south-west from the city of Shadrinsk, on the right bank of the river Iset, on a site immediately adjacent to the village Oseevo (Fig. 1). The field was discovered as a result of the work of the Ural exploration management in the 1930s of the XX century. Exploration was carried out in pits and wells in the area of 3 km^2.

In 1935, according to the passport, reserves were taken in the amount of 1.4 mln. m^3. In the 1950-60s additional exploration was carried out to identify new potential sites and recalculate reserves.

As of 2012 reserves of Shadrinsky field according to categories $A + B + C_1$ make 2246 thousand m^3. The field is located in the undistributed subsoil fund. Rocks are

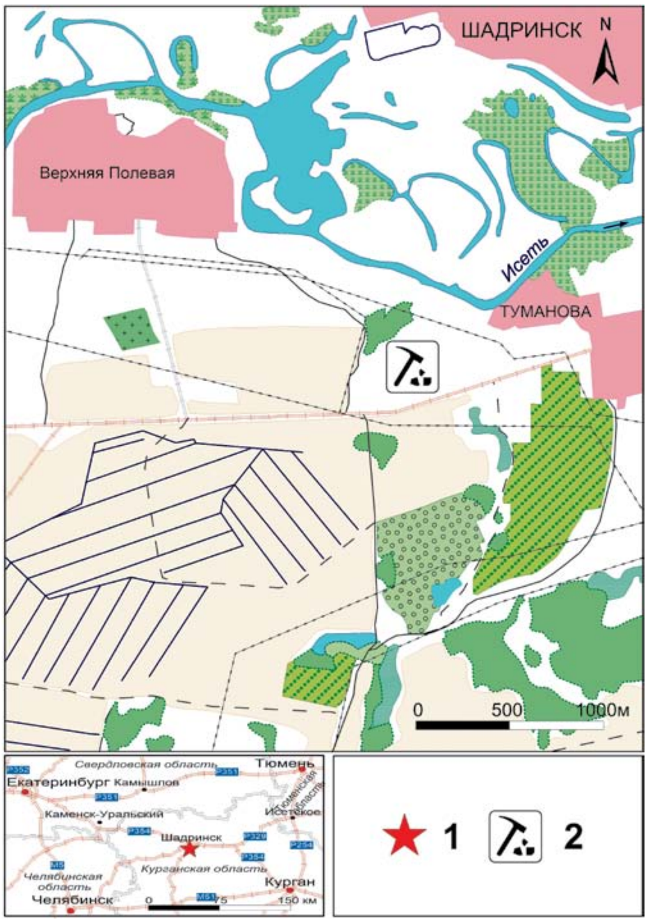

Fig. 1. Map of the actual material: 1 – location of the research site, 2 – location of an abandoned open-bit mine of Shadrinsky field.

suitable for the production of expanded clay gravel –filler of light concrete of brands 500, 600, 700. (Natural Resources and Environment ..., 2015). Form of the deposit is tabular, stretched from south-west to north-east. The field area is 1,812 km^2. Productive stratum lies directly on the surface of blue clay or thin layer of bluish quartz sand and related to the Irbitskian suite of Eocene; total thickness is up to 40-50 m in non-eroded state under interfluve areas, and from 10 to 30 m within the major erosional incision of river valleys (Vishnyak et al., 2011.); thickness on the Shadrinsky field reaches 12 m.

Stone material for the study was selected from the stripped walls of nonfunctioning open-pit mine. Analytical work included the study of elemental and mineral composition, lithological-petrographic and microprobe analysis, electron microscopy. Work was performed at the Center for collective use of multi-element and isotopic studies at the Institute of Geology and Mineralogy SB RAS (Novosibirsk), the Tyumen Industrial University and LLC "ZapSibGTs" (Tyumen). X-ray diffraction analysis of samples was carried out on the powder X-ray diffractometer ARL X'TRA of company Thermo Scientific ARL Products.

Elemental analysis of geological samples was carried out by mass spectrometry with inductively coupled plasma (ISP-MS) (Nikolaev, 2008; 2012). IR spectra were recorded in the range of wave numbers from 370 to 4000 cm^{-1} in the Fourier spectrometer VERTEX 70 FT IR of company Bruker. X-ray fluorescence analysis of the silicate samples was performed on the X-ray spectrometer ARL-9900-XP of company Applied Research Laboratories. The lithological and petrographic description was carried out in thin sections prepared by the standard method.

Results and discussion

According to the microscopic and lithological-petrographic research, the rock structure is biomorphic, fine-grained, pelitomorphic; texture – micro-layered, micro-lenticular, bioturbated. The rocks are characterized by diatomacaoues complex Pyxilla gracilis (upper part of the Lower Eocene) (Alexandrova et al., 2012). There are index-species Coscinodiscus payeri Grunow, as well as Paralia crenulata (Grunow) Gleser, Grunowiella gemmata (Grunow) Van Heurck, Pyxidicula moelleri (AS) Strelnikova et Nikolaev, Odontotropis carinarta Grunow, Stellarima microtrias (Ehrenberg) Hasle et Sims, Costopyxis broschii (Grunow) Strelnikova et Nikolaev, Stephanopyxis megapora Grunow, Vallodiscus lanceolata Suto. Presence of clearly defined biomorphic structure requires renounce of accepted in the literature and geological reports lithological description of the rock as 'tripoli' and characterize the rock as 'diatomaceous clay'.

The chemical composition of diatomaceous clay differs in content markedly from the basic components of Trans-Urals diatomite (%) (Table 1). By the general

Field	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	BaO	SO_3	V_2O_5	Cr_2O_3	NiO	Ignition loss, %
Shadrinsky (diatomaceous clay)	66,24	0,68	13,18	5,39	0,04	2,14	0,37	0,45	1,64	0,06	0,03	0,08	0,04	0,02	<0,01	9,55
Irbitsky (diatomite)	77,78	0,53	8,16	2,82	0,02	0,73	0,75	0,48	1,14	0,04	-	-	-	-	-	6,81
Kamyshlovsky (diatomite)	75,2	0,57	8,09	4,38	0,03	0,73	0,81	0,44	1,18	0,06	-	-	-	-	-	7,67

*Table 1. Common chemical composition of diatomaceous clay from Shadrinsky field and diatomite of Trans-Urals * (Sidorenkov et al., 1989). * Blanks – there are no data or below the detection limit.*

Be	Sc	Ti	V	Cr	Co	Ni	Cu	Zn	Rb	Sr	Zr	Nb
2,3	15,0	4600	300	118,0	12,0	17,1	37,0	100,0	80,0	105,0	120,0	11,3
Ga	**Sb**	**Ba**	**Pb**	**Y**	**Cs**	**La**	**Ce**	**Pr**	**Nd**	**Sm**	**Eu**	**Gd**
15,6	0,3	274,0	14,5	15,9	5,6	18,3	35,0	4,6	17,7	3,3	0,7	2,7
Dy	**Ho**	**Er**	**Tm**	**Yb**	**Lu**	**Hf**	**Ta**	**Th**	**U**	**Mo**	**Tb**	
3,0	0,6	1,7	0,3	1,6	0,3	3,5	0,9	8,3	1,6	1,8	0,5	

Table 2. The results of the elemental composition identification by ISP-MS method, g/t.

chemical composition, the rocks are close to diatomite from other deposits in the region, the only significant difference is the lower content of $Si0_2$ mineral phases, and more clay components.

The results of the microelement composition of diatomaceous clay from Shadrinsky field are shown in Table 2. The diatomaceous clays of Shadrinsky field are characterized with the values exceeding the clarke contents of the following elements: Mo, Yb, Hf, Cs, Sc and Zn.

As a result of X-ray diffraction (Fig. 2), the main component of diatomaceous clay is opal (amorphous silica) and smectite; there are quartz, mica, kaolinite, a small admixture of plagioclase, jarosite, traces of gypsum and anatase. However, the characteristic opaline halo is less pronounced than that of pure diatomite (Selyaev et al., 2014). Noteworthy is the presence of zeolites of calcium-sodium composition (up to a few %) as a part of impurities.

According to IR spectrometry (Fig. 3) the spectra of all samples exhibit a number of bands due to stretching and deformation vibrations of Si-O-Si bonds and OH groups. The most intense band of asymmetric stretching vibrations of Si-O-Si bonds is 1046 cm^{-1}. Shifting of the band (in comparison with typical diatomite) is due to the presence of clay fractions apart from diatome – smectite, kaolinite and mica.

According to the lithological and petrographic analysis, the bulk of the rock (Fig. 4) consists of partially optically oriented particles ranging in size from less than 0.001 to 0.005 mm, with gray and yellow interference color, having microgranular (microglobular), flaky and fibrous structure.

The bulk of rock has a significant number of fragments of diatoms in size from 0.005 to 0.063 mm, flint fragments of the spicules of sponges in size of 0.027 x 0.061 mm.

The clastic material is concentrated mainly in the form of thin micro lenses and intermittent layers, formed as a result of the activity of burrowing organisms, its content is not large in the range of 5-7 % of the area of the thin section; it is represented by grains of quartz, feldspar, biotite and muscovite flakes with grain size of 0.01-0.12 mm. Also the rock contains small, round, yellow-green glauconite grains, the size of 0.03-0.06 mm. Calcium-sodium zeolites, nontronite, pyrite, gypsum, pyrolusite, muscovite and biotite are among the main impurities. The rock is characterized by a high microporosity; pores prevail in size of less than 0.005 mm.

The research results under the electron microscope show that diatoms with a high degree of preservation are not numerous, some of them showing signs of losing its original structure: the bulk is composed of fine detritus (Fig. 4,5). Everywhere on the surface of biogenic residues small flakes of clay minerals are present. Due to the high degree of crushing, other minerals, except quartz are hardly diagnosed in a overall mass.

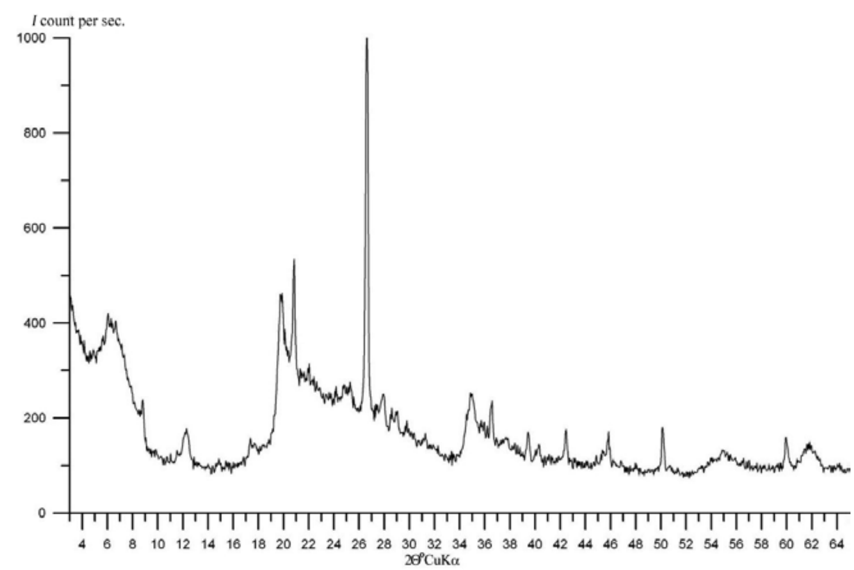

Fig. 2. Radiographs of diatomaceous clay from Shadrinsky field.

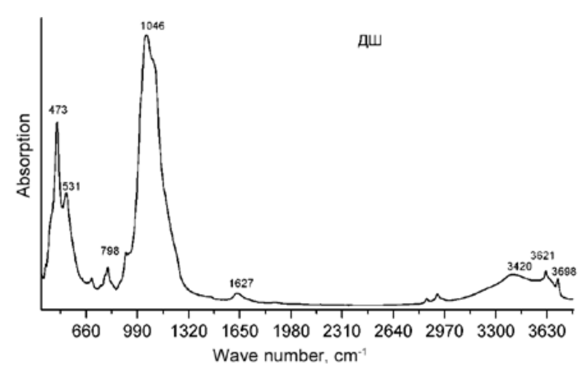

Fig. 3. IR spectrum of diatomaceous clay from Shadrinsky field.

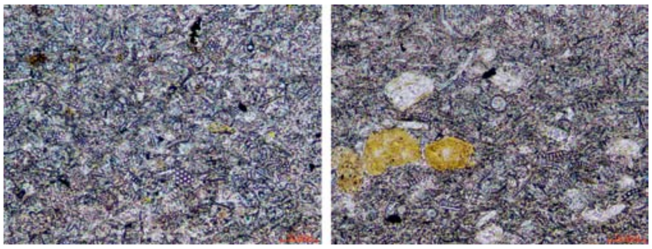

Fig. 4. Microstructure of diatomaceous clay from Shadrinsky field.

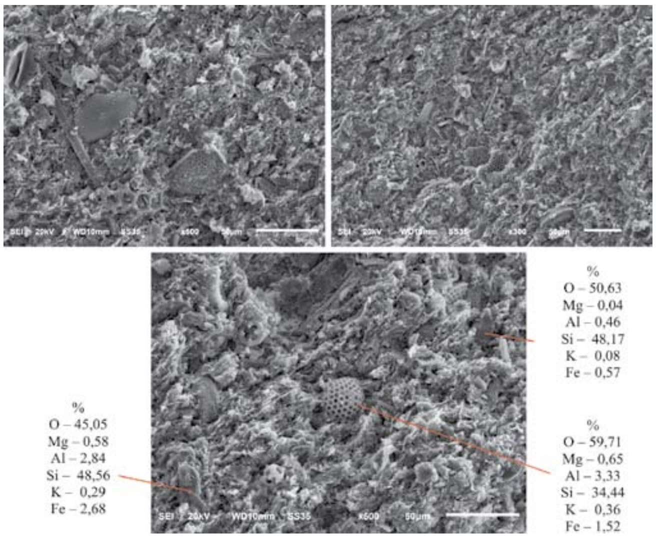

Fig. 5. Microscopic structure and results of microprobe analysis of diatomaceous clay from Shadrinsky field.

Conclusions

The presence of characteristic biomorphic structure of the studied rocks allows us to characterize the rock as ‘diatomaceous clay’. Diatomaceous clay of Shadrinsky field on the composition of the rock and quality of raw material is comparable to other fields of Trans-Urals. The main difference is the lower content of silica mineral phases, and large content of clay components. However, a significant argillization does not preclude their use in the production of building materials and thermal insulation; after heat treatment they can be used as an active additive in cement. Using diatomaceous clays in industries other than the construction involves more detailed studies of the physical properties of rocks, mineral composition, in particular of clay minerals and zeolites.

The Eocene diatomaceous clay of Shadrinsky field has signs of zeolite mineralization: studied rocks contain zeolites of calcium-sodium composition (up to a few %). It should be noted that the content of zeolite is much lower than in siliceous-carbonate sediments of the European part of Russia (Zorina, Afanasyeva, 2008; Zorina et al., 2008), and their origin is probably due to lithification and zeolitization of silicon gels at different stages of diagenesis.

References

Aksakal E.L., Angin I., Oztas T. Effects of diatomite on soil physical properties. *Catena.* 2012. Vol. 88. Is. 1. Pp. 1-5. DOI:10.1016/j.catena.2011.08.004.

Aleksandrova G.N., Oreshkina T.V., Iakovleva A.I., Radionova E.P. Late Paleocene-Early Eocene diatoms and dinocysts from biosiliceous facies of the middle Trans-Urals region. *Stratigraphy and Geological Correlation*. 2012. Vol. 20. Is. 4. Pp. 380-404. DOI: 10.1134/S0869593812030021 (In Russ.)

Anisimov V. S., Martynov P. N., Merkov S. M., Petrov K. V., Podzorova E. A., Chaban’ A. Yu., Shilina A. S. The Investigation of Tripoli Application for Water Mediums Purification. *Energotekhnologii i resursosberezhenie.* 2010. Is 1. Pp. 62-66.(In Russ.)

Balans zapasov poleznyh iskopaemyh SSSR. Kremnistoe (opal-kristobalitovoe) syr’e [Mineral resources of USSR (opal-cristobalite rocks). Report]. Moscow: Sojuzgeolfond. 1984. Is. 86. p. 213 (In Russ.)

Loboda B.P., Bagdasarov B.R., Fitsuro D.D. Effect of fertilizers based on zeolites and zeolite-containing tripolites from the Khotynetsky deposit on the yield and quality of potatoes. *Agricultural Chemistry.* 2014. Is 3. Pp.28-35. (In Russ.)

Nikitin A.I., Storozhenko G.I., Kazantseva L.K., Vereshchagin V.I. Teploizolyatsionnye materialy i izdeliya na osnove trepelov Potaninskogo mestorozhdeniya [Thermal insulation materials and products based on the Potanin tripoli field]. *Stroitel’nye materialy = Construction Materials.* 2014. № 8. Pp. 34-37(In Russ.)

Nikolaeva I.V., Palessky S.V., Chirko O.S., Chernonozhkin S.M. Determination of major and trace elements by inductively coupled mass-spectrometry in silicate rocks after fusion with $LIBO_2$. *Analitika i kontrol’ = Analytics and Control*. 2012. Vol. 16. Is 2. Pp. 134-142 (In Russ.)

Nikolaeva I.V., Palesskii S.V., Koz’menko O.A., Anoshin G.N. Analysis of geologic reference materials for REE and HFSE by inductively coupled plasma-mass spectrometry (ICP-MS). *Geochemistry International.* 2008. Vol. 46. Is. 10. Pp. 1016-1022.

Pahomov V.P., Dushin A.V. Analysis of the mineral-raw material safety in the Ural Federal District. *Economy of Regions*. 2008. No. 3. Pp. 129-143 (In Russ.)

Prirodnye resursy i okhrana okruzhayushchey sredy Kurganskoy oblasti v 2014 godu. Doklad [Natural Resources and Environmental Protection of the Kurgan region in 2014. Report]. Kurgan. 2015. 220 p. (In Russ.)

Radaev S.S., Seleznyova O.I. Ryasnaya N.Z., Zimakova M.V. Opaline rock- based building materials. *Bulletin of South Ural State University. Series «Construction Engineering and Architecture»*. 2010. Is. 15 (191). Pp. 11-12 (In Russ.)

Sadykov R.K., Vlasova R.G., Khaydarova N.Z. Mineral’no-syr’evoy potentsial regionov kak faktor ikh konkurentosposobnosti [Mineral and raw material potential of the regions as a competitive differentiator]. *Georesources*. 2004. Is. 1. Pp. 16-17 (In Russ.)

Sadykov R.K., Vlasova R.G., Muradymova V.M., Vyatkina L.Yu. Bulatova G.N. Solid Non-Metallic Minerals of the Republic of Tatarstan: Conditions, Problems in Subsoil Use and Prospects of Development. *Georesursy = Georesources*. 2015. Vol. 1. Is. 4(63). Pp. 13-20 (In Russ.)

Selyaev V. P., Neverov V. A., Kupriyashkina L. I. Rentgenostrukturnye i rentgenospektral’nye issledovaniya tseolitsoderzhashchikh porod Atyashevskogo i Tatarsko-Shatrashanskogo mestorozhdeniy Srednego Povolzh’ya [XRD and XRF studies of zeolite rocks of the Atyashevsky and Tatar-Shatrashanskoe fields of the Middle Volga region]. *Regional’naya arkhitektura i stroitel’stvo = Regional Architecture and Construction.* 2014. Is. 3. Pp. 13-18 (In Russ.)

Sidorenkov A.I., Zarubko N.S., Samoshin A.A. Model’ mehanizma obrazovanija trepelov i opok [Model of formation mechanism of tripoli and opoka]. Tyumen: ZapSibNIGNI. 1989. Pp. 46-63 (In Russ.)

Surkova S.A., Shusharina V.V. Depressivnye regiony: tipologicheskie osobennosti i mekhanizmy preodoleniya depressii [Depressive regions: typological features and mechanisms of depression overcoming]. *Regional’naya ekonomika: teoriya i praktika = Regional economics: theory and practice*. 2009. Is. 1(94). Pp. 25-37 (In Russ.)

Vishnyak A.I., Chetverkin I.A., Novikov V.P., Plotnikova R.I. Hydrogeolodical model of Shadrinsk groundwater deposit of carbonaceous mineral waters as the base of valuation of its reserves. *Prospect and protection of mineral resources.* 2011. Is. 11. Pp. 35-43 (In Russ.)

Zorina S.O., Afanas’eva N.I., Volkova S.A. Zeolite potential of Upper Cretaceous-Paleogene sedimentary rocks in the eastern and southeastern Russian Plate. *Lithology and Mineral resources*. 2008. Vol. 43. Is. 6. Pp. 577-587. DOI: 10.1134/S0024490208060059 (In Russ.)

Zorina S.O., Afanas'eva N.I. O rasprostranenii tseolitov v verkhnemelovykh i paleotsenovykh litostratonakh Russkoi plity [On the propagation of zeolites in the Upper Cretaceous and Paleocene lithostratigraphic units of the Russian Plate]. *Problemy mineralogii, petrografii i metallogenii. Nauchnye chteniya* [Problems of mineralogy, petrology and metallogeny. Proc. Sci. Conf.]. Perm: Perm University Publ. 2008. Pp. 43-49 (In Russ.)

U.S. Geological Survey. Mineral commodity summaries. 2015. 196 p. http://dx.doi.org/10.3133/70140094. (accepted: 31.05.2016).

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