



## ORIGINAL PAPER

**THE LATE MIOCENE PELITIC SILTSTONE OF THE ISHIM FORMATION (SOUTHWESTERN SIBERIA): MINERALOGICAL AND GEOCHEMICAL CHARACTERIZATION AND PROSPECTS FOR FURTHER USE****Alexander O. Konstantinov<sup>1)</sup>, Pavel V. Smirnov<sup>1,2)</sup>\*, Olga B. Kuzmina<sup>3)</sup>, Irina V. Khazina<sup>4)</sup>, Georgii A. Batalin<sup>4)</sup> and Bulat I. Gareev<sup>4)</sup>**<sup>1)</sup> Tyumen Industrial University, St. Volodarsky 38, 625000 Tyumen, Russia<sup>2)</sup> Clausthal University of Technology, Adolph-Roemer-Straße 2A, 38678 Clausthal-Zellerfeld, Germany<sup>3)</sup> Trofimuk Institute of Petroleum Geology and Geophysics, Siberian Branch of Russian Academy of Sciences, Ac. Koptyuga ave 3, 630090 Novosibirsk, Russia<sup>4)</sup> Kazan Federal University, Kremlyovskaya St. 18, 420008 Kazan, Russia\*Corresponding author's e-mail: [geolog.08@mail.ru](mailto:geolog.08@mail.ru)**ARTICLE INFO****Article history:**

Received 4 April 2018

Accepted 24 August 2018

Available online 25 September 2018

**Keywords:**Late Miocene  
Sedimentary rocks  
Pelitic siltstone  
Western Siberia  
Mineral addition  
Filler**ABSTRACT**

The Miocene Ishim Formation is characterized by a considerable distribution area within the southwestern Siberia. These deposits are highly dispersed and are composed mainly of angular quartz grains of aleuritic and pelitic fractions. The study of the Ishim Formation is of interest both for investigating the origin of the sediments, and for justifying these rocks as a new type of mineral raw material for the local construction materials industry. This paper presents the results of first complex studies of the Ishim Formation deposits from two outcrops Masali and Bigila. The studies included determination of the particle size distribution on the laser particle analyzer, semiquantitative determination of the mineral composition (X-ray diffraction analysis), as well as, determination of contents of sesquioxides (X-ray fluorescence analysis), rare and trace elements (Inductively Coupled Plasma Mass Spectrometry) and measurement of specific surface area. The most representative samples were chosen for petrographic studies. In certain extent these deposits are characterized by quite high degree of homogeneity of the mineral, chemical, and granulometric compositions. The main component is SiO<sub>2</sub> (about 70 %); other most important components are Al<sub>2</sub>O<sub>3</sub> (about 14 %) and Fe<sub>2</sub>O<sub>3</sub> (2–5 %). At the same time, deposits of the upper part of the Ishim Formation are depleted in CaO, MnO, MgO, TiO<sub>2</sub>, and P<sub>2</sub>O<sub>5</sub>. This is probably due to the fact that the proportion of clayey minerals in the upper part of the formation is lower than that in the lower one. The contents of trace elements in the Ishim Formation are lower or close to their clark values in the Earth's crust. This is with the exception of such elements as Eu, Tb, Cr, and Sb, which form a strong anomaly and, to a lesser extent, a number of other elements that is probably related to the tectonic setting during the period of sedimentation. The CIA values vary from 68–70 in the lower unit of the Ishim Formation at the transition to the sandy facies to 75–80 in the upper one, which indicates a moderate weathering of rocks. The results obtained testify to the fact that these deposits were formed under the conditions of degrading shallow water bodies. A distinct geomorphological confinement to boundaries of the Neogene river paleovalleys, continuity, high dispersion and, predominantly, quartz composition allow us to consider these deposits as a promising type of filler for construction materials industry.

**INTRODUCTION**

The use of mineral additions such as natural and artificial pozzolanic materials and fillers is one of the most effective ways of reducing consumption of materials and energy in construction materials industry (Meyer, 2002). Active mineral additives are finely ground natural or man-made materials introduced into calcareous binding agents and cements to improve their properties for proofing special qualities (Maria, 2016). In most cases, the reaction of lime with active mineral additives is based on the fact that active (amorphous or finely dispersed) silica reacts with lime in the presence of water and forms calcium hydrosilicate that provide ability to hydraulic

hardening (Mehta, 1987; Afanasiev and Tseluiko, 1988; Snellings et al., 2012). Inactive mineral additives-fillers (crystalline materials or fillers) are finely ground or finely dispersed substances of natural origin or industry waste, consisting of crystalline silica, alumina and other substances that do not have latent hydraulic activity. The action mechanism of such additives is based on an increase in the specific surface area of the components of the cement paste components and, in this connection, the volume of firmly retained adsorption water (Rahhal and Talero, 2005). Inactive additives-fillers of natural origin are including fine-dispersed materials and fine-grained substances.

It should be noted that most of the areas rich in deposits of natural mineral additions (especially pozzolanic materials) are confined in terms of geology to the manifestation areas of ancient and modern volcanism, the active-type continental margins, and rift zones (Snellings et al., 2012). At this, such deposits are generally uncommon for the passive-type (Atlantic) margins and ancient platforms. A similar situation, due to the features of the geological structure, is also characteristic of the southwestern Siberian Plain, which is underlain by the epi-Hercynian West Siberian plate and the basement is composed of intensively dislocated Paleozoic deposits and is covered by loose marine and continental Mesozoic–Cenozoic deposits with a total thickness of above 1000 m (Rostovtsev, 1964).

Thus, the peculiarities of the geological development of the southwestern Siberia determine the traditional low potential for searching a number of types of construction materials, including natural mineral additives (Botvinnikov, 1961; Vaneev, 1968). A substantial deficit of high-quality construction materials is one of the factors constraining the development of the construction sector in the regions of the southwestern Siberia. The reduction of the material consumption when producing construction materials is possible due to searching for new types of raw materials, including additives that allow one to reduce the cement consumption. The Upper Miocene Ishim Formation, the outcrops of which are well represented within the southwestern Siberian Plain is one of the potential sources of raw materials for local construction materials industry.

Ishim Formation serves as a regional stratotype of the southwestern part of the West Siberian Plain (Tobol–Ishim interfluvium), which recorded the sedimentation conditions close to Miocene–Pliocene boundary. These deposits are usually described as bleached or mealy silts (Astapov, 1977). In some works, outward similarity of these deposits with Eocene diatomites and tripolite of the Transuralian Region was mistakenly noted (Kuznetsov, 1963). The results of the previous studies of pelitic siltstone of the Ishim Formation made it possible to establish that these siliceous deposits are characterized by high dispersion and can be described as a natural silica (quartz) flour or “marshallite” (a term, which is predominantly used in the countries of the former USSR for pelitic size-grained quartz) (Smirnov et al., 2016; Novoselov, 2016). At the same time, despite their significance for stratification of the continental Neogene of the Western Siberia, the deposits of the Ishim Formation, especially in the northern distribution areas, are still insufficiently studied, their genesis is controversial, and the real potential for industrial use is not defined.

The paper purpose is to present the results of lithological, mineralogical, geochemical, microscopic structural and texture features of the highly dispersed siliceous Upper Miocene rocks of the Ishim Formation at the territory of the Tobol–Ishim

interfluvium. The studies are intended to identify general trends for further use in local industry.

## GEOLOGICAL SETTINGS

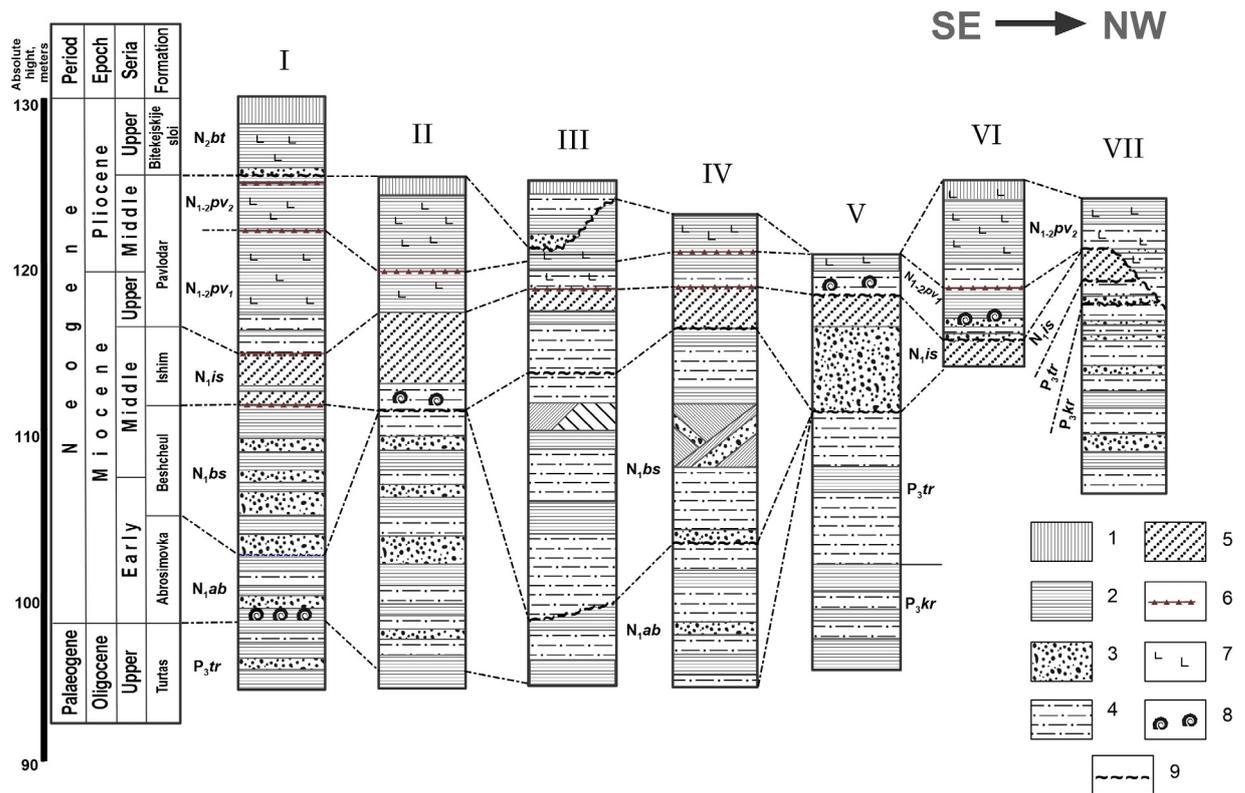
### REGIONAL STRATIGRAPHY

In terms of geology, the area of study is located in the southwestern part of the West Siberian Platform. The southern part of the West Siberian Plain is characterized by the three-unit structure: the lower level is composed of highly dislocated metamorphosed sedimentary and effusive-sedimentary Paleozoic rocks; the second level is composed of dislocated continental Triassic–Jurassic sometimes coal-bearing deposits, filling the submeridional narrow depressions emplaced on the Paleozoic basement. The third level is the platform cover with a thickness of up to 1.5 km and more, composed of near-horizontal laying Jurassic, Cretaceous, Lower to Middle Paleogene marine, predominantly clayey deposits and Middle to Upper Paleogene and Quaternary continental clayey deposits. In terms of tectonics, the area of study is confined to the Transuralian monocline (Nalivkin and Ingerson, 1960; Rostovtsev, 1964; Clarke, 1994).

According to the modern regional lithostratigraphy (“Unified 2001”) Eocene–Quaternary deposits within the area of study (Fig. 1) are represented by green and greenish-gray clays of up to 70–120 m thick (Middle–Upper Eocene, Tavda Formation ( $P_3tv$ )), the alternating sequence of brownish-gray to gray silty clays and gray ultrafine- to fine-grained sands (Lower Oligocene, Kurtamysh Formation ( $P_3kr$ )), alternation of silts, sands, and silty–sandy clays varying from 10 to 40 m in thickness (Upper Oligocene, Turtas Formation ( $P_3tr$ )), conformably laying on deposits of the Kurtamysh Formation, the alternating sequence of brownish-gray silty clays, siltstones, and uneven-grained sands, containing detrital and lignite fragments, up to 20 m thick (Lower Miocene, Abrosimovka Formation ( $N_1ab$ )), sands, tripolite-like mealy siltstones of up to 20 m thick (Upper Miocene, Ishim Formation ( $N_1is$ )), and poorly defined variegated clays (8–10 m thick) with carbonate nodules and sands (Upper Miocene, Tavoljan and Pavlodar formations). Quaternary sediments are represented mainly by clays, loams, sandy loams, sands, clayey sands, boggy sediments (silt, sapropel, peat) in local lake depressions. The thickness of Quaternary deposits varies considerably depending on the relief.

### ISHIM FORMATION

The Ishim Formation or deposits of Ishim sedimentary rhythm are well distributed within the Ishim–Irtysh and Tobol–Ishim interfluviums of the West Siberian Plain. This formation was distinguished for the first time by V.A. Nikolaev in 1947 and had not considered as an independent stratigraphic unit for a long time (Unified, 2001). The section in the outskirts of the town of Petropavlovsk is regarded as the stratotype of the Ishim Formation (Zykin, 2012).



**Fig. 1** Correlation of Neogene deposits in the south of the Tyumen region and northern Kazakhstan according to Astapov (1976); from southeast to northwest I - Petropavlovsk, II - Arhipovka, III - Ragozino, IV - Klepikovo, V - Masali (Khryaschyovka), VI - Pyatkovo, VII - Khorzovo. 1 - cover loams, 2 - clays, 3 - silt, 4 - sands, 5 - aleurolites, 6 - paleosols, 7 - calcification, 8 - fauna of mollusks, 9 - line of erosion.

The general information about the distribution of the Ishim Formation within the Tobol–Ishim interfluvium is given mainly in Astapov’s works, released in the 1970s (Astapov, 1977; Astapov et al., 1979).

In the lower part (0.5–2.3 m), the Ishim Formation is represented by pale gray to white sands, from fine-grained to coarse-grained down section with gravel, clayey nodules, and pebbles (up to 3–4 cm thick). The bedding in sandy deposits is cross-bedding, lenticular–cross, lenticular, and diagonal. Up the section sands become fine-grained. In some places the sandy unit is crowned by subparallel alternation of pale gray to white sandy loams and greenish-gray silty-sand clays. In the upper part of the Ishim Formation and at the contact with the overlying sediments, Ishim mealy pelitic siltstones are with Fe-Mn hydroxide and oxide nodules. The thickness of the flood plain facies is 0.5–1.5 m. In many outcrops, the unit of channel sands is missed in the section and the overlying lacustrine mealy pelitic siltstone lie on more ancient various deposits (up to the Turtas Formation) (Unified, 2001).

The Ishim sedimentary rhythm is crowned by a quite distinct unit of lacustrine fine-dispersed (“mealy”) pelitic siltstones, pale gray to nearly white, velvety soft, massive without visible bedding or with indistinct irregular parallel bedding. The transition from sands to pelitic siltstone is gradual. As usual, the

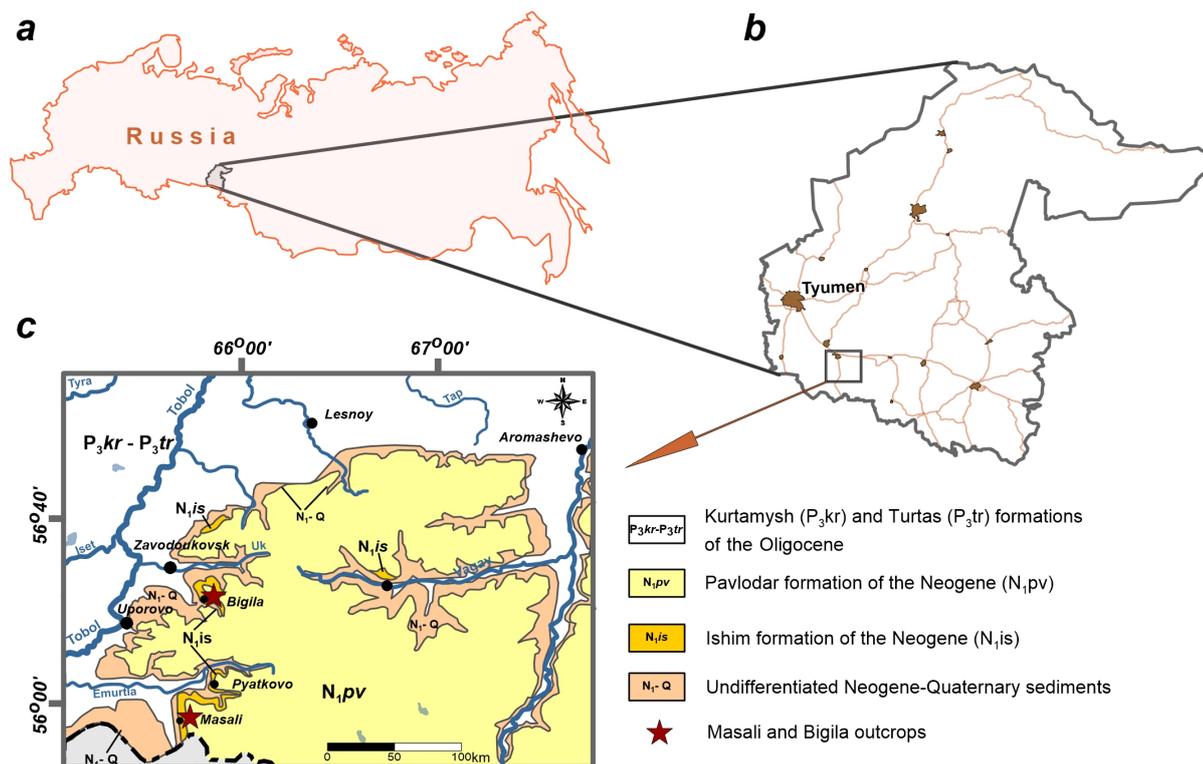
lower boundary is distinct, flat with signs of insignificant areal erosion. In the stratotype section, the Ishim Formation lies unconformably on the Lower–Middle Miocene deposits of the Bescheul Formation, and is overlain by the Upper Miocene–Lower Pliocene deposits of the Novaya Stanica Formation (Martynov and Nikitin, 1967; Zykin, 2012).

Sands and siltstones that compose the Ishim Formation are hardly considered as objects of the mineral raw material base for the local construction materials industry with the exception of some sandy deposits confined to the lower unit of the Ishim Formation, which were developed or are still under development by manual method.

**MATERIALS AND METHODS**

**AREA OF STUDY AND SAMPLING SITES**

The field studies were performed in 2014–2016 at the territory of Zavodoukovsk and Uporovo districts of the Tyumen region within two reference sites of Bigila (N 56°24'34.59"; E 66°40'26.19") and Masali (N 56° 5'25.56"; E 66°35'6.16"), located in environs of the same-name localities (Fig. 2). According to the geomorphologic zoning of the southwestern Siberia, the area of field works is located within the Ishim denudation inclined plain (Varlamov, 1972) with absolute elevations of 50–150 m above sea



**Fig. 2** a, b – the location of the study area within the Russian Federation and the Tyumen region, c - is the simplified geological map of the study area.

**Table 1** The sampling depth as well as some general characteristics of the samples from Masali and Bigila outcrops.

Sample	Depth (m)	Summary description	Sample	Depth (m)	Summary description
M1	0.3-0.4	Aleurite	M10	4.2-4.4	Pelitic siltstone
M2	0.7-0.8	Aleurite	B1	1.2-1.3	Pelitic siltstone
M3	1.3-1.4	Aleurite	B2	1.7-1.9	Pelitic siltstone
M4	1.7-1.8	Aleurite	B3	2.0-2.2	Pelitic siltstone
M5	1.9-2.0	Pelitic siltstone	B4	2.5-2.7	Pelitic siltstone
M6	2.3-2.4	Pelitic siltstone	B5	3.1-3.3	Pelitic siltstone
M7	2.7-2.8	Pelitic siltstone	B6	3.5-3.8	Pelitic siltstone
M8	2.9-3.1	Pelitic siltstone	B7	4.5-4.7	Pelitic siltstone
M9	3.5-3.6	Pelitic siltstone	B8	5.5-5.8	Fine Sand

level (Zemtsov et al., 1988). The study area is characterized by quite a high degree of relief roughness in the south of the Tyumen Region: the linear dismemberment by ravines, gulches, and small river valleys is 0.6–1.2 (Ogorodnov, 1971). The river network of the area of study belongs to the Kara Sea basin; the main river is Tobol. The valleys of small rivers – Begila, Kizak, and Kurchigai – are included in the paleovalleys of the Neogene river network.

Eighteen samples from different intervals were selected out of the examined exposures for further geochemical, mineralogical, and lithological studies. The most representative samples of pelitic siltstone and overlying deposits were chosen for microscopic studies. The list of samples, their brief lithological description, as well as depths of sampling sites are presented in Table 1.

#### ANALYTICAL METHODS

The complex of analytical research methods included the particle size distribution measurement using a laser particle analyzer, the semiquantitative determination of the mineral composition by the X-ray diffractometry, the determination of 10 major oxides by X-ray fluorescence, and determination of rare and trace elements by inductively coupled plasma mass spectrometry (ICP-MS). Microscopic investigations included the study of thin sections of rocks using classical light microscopes and electron microscopy.

The particle size distribution measurement of the rock samples was performed using a Microtrac S3500 (USA) laser particle analyzer in the laboratory of lithology of OOO “Tyumen Central Laboratory”. Sample preparation included the rock drying at

a temperature of 105 °C, grinding with a rubber pestle to avoid a damage of mineral grains. Then, a 5 g rock sample was kept within 24 hours in a 5 % HCl solution, *filtered, washed with distilled water, and water-oven dried during 6 hours at a temperature of about 100 °C.*

A semi-quantitative analysis of the mineral composition was carried out with the X-ray diffractometry using a DRON-2 X-ray diffractometer at OOO “Zapadno-Sibirsky Geological Center” (Tyumen).

The contents of major oxides were measured on the S8 Tiger high-end *wavelength dispersive* X-ray fluorescence spectrometer (Bruker, Germany) in the Laboratory for Isotope and Element Analysis of the Institute of Geology and Petroleum Technologies of Kazan Federal University (Kazan).

Elemental analysis of samples was performed using inductively coupled plasma mass spectrometry (ICP-MS) in the Analytical Centre of the Institute of Geology and Mineralogy of the Siberian Branch of Russian Academy of Sciences. For the determination of elements, samples were mixed with lithium metaborate and fused in platinum crucibles at 1050 °C in a muffle furnace. The resulting melt was dissolved in dilute HNO<sub>3</sub> with the addition of trace amounts of HF; before ICP-MS measurement solutions were diluted by adding the internal standard. The required level of acidity (4 % HNO<sub>3</sub>) for dissolution of the melt and implementation of all stages of dilution was established by experiment (Nikolaeva et al., 2008, 2012). All measurements were performed on Element 2 Finnigan MAT Inductively Coupled Plasma Mass Spectrometer. The validity of the developed method was confirmed by comparing the results obtained with certified standard samples BCR-1, JG-1A, the SRS-1A. The error analysis did not exceed 10 %.

The specific surface of selected samples was estimated by the BET method. The measurements were performed on an automated ASAP-2400 device from Micromeritics (USA), controlled by a personal computer. The method for determining the specific surface area of the samples is based on an analysis of nitrogen adsorption isotherms at 77 K.

The lithological and petrographic studies of samples was carried out under microscope; thin sections were prepared according to the Shevtsov’s standard methodology (Shevtsov, 1958). Microscopic morphological studies of samples have been performed using JEOL JSM-6510 scanning electron microscope.

For better understanding the origin and provenance of sediments  $K_2O/Na_2O$ ,  $SiO_2/Al_2O_3$ ,  $Al_2O_3/TiO_2$ , CIA were calculated.

## RESULTS

### LITHOLOGY

Within the outcrops under consideration, the Ishim Formation combines beds of uneven-grained sands and bleached pelitic siltstone and represents an

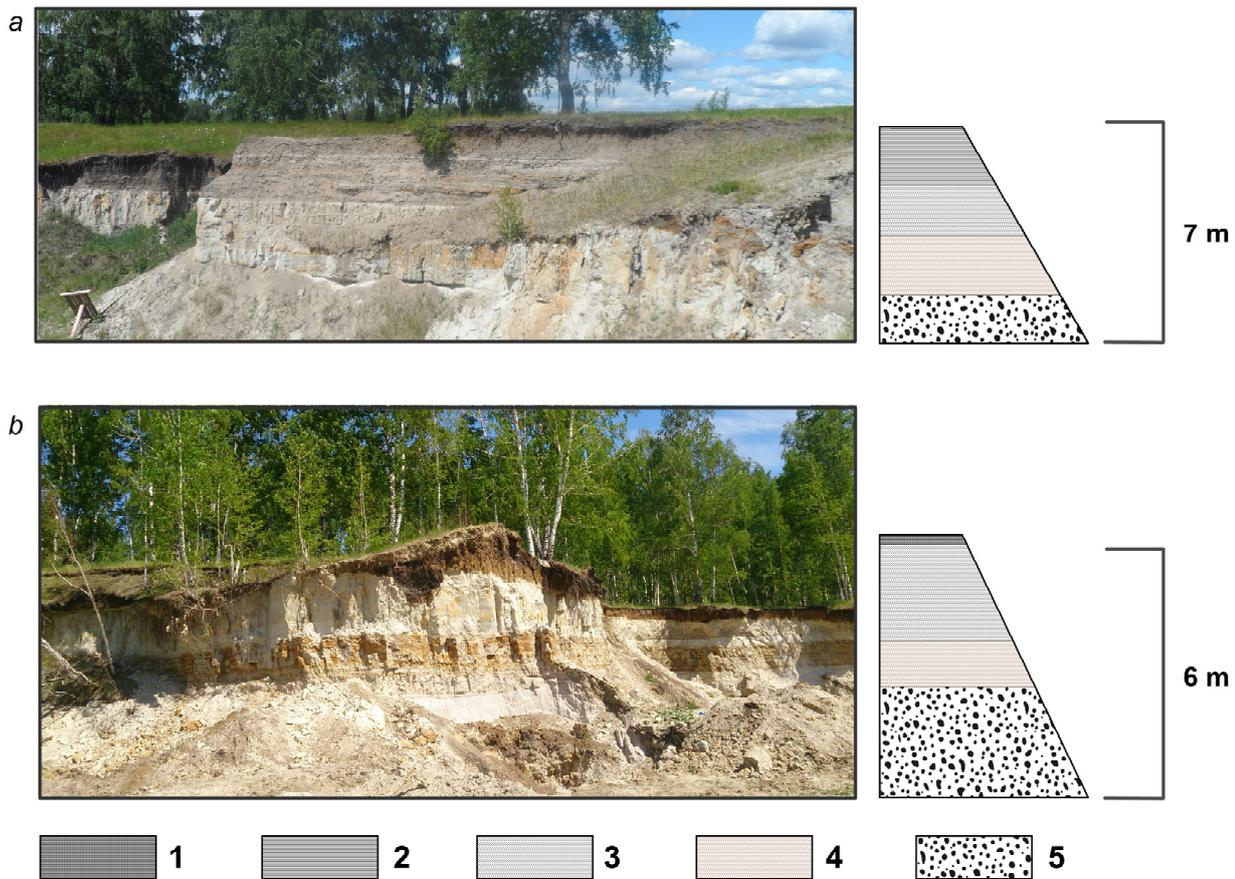
unified formation of up to 20 m thick (Astapov, 1977). The transition from sandy alluvium to siltstone is gradual; the lower contact is usually distinct, even with signs of slight erosion. The presence of the basal horizon, which is composed of coarse-grained, sometimes gravel sands with dark-colored minerals and quartz pebbles, with cross, ribbon, diagonal bedding, with a thickness of 5–10 cm, was established in the outcrops studies. The pelitic siltstone sequence in outcrops is conditionally divided into two units: a ferruginous lower and bleached upper. Sometimes, pelitic siltstone of the upper unit contain small accumulations of black manganese concretions, rod-shaped, knotty, with a finely lumpy surface.

The upper pelitic siltstone unit of the Ishim Formation with a thickness of 5 m (a total thickness of the outcrop of 7–8 m), cropping out in the Bigila outcrop, is exposed within an abandoned quarry, which is currently used as a household waste dump (Fig. 3a). Deposits of the upper unit are pale gray to nearly white, very loose, with a massive structure. The rock is composed of fine-grained detrital material; there are rare small and very small black, less often brown, grains of carbonaceous plant detritus, clastic grains of ore minerals and iron-manganese concretions. Deposits of the underlying stratum are darker and are characterized by platy parting; along the planes of which there are signs of ferrugination (thin films of iron hydroxides).

The Masali outcrop is exposed in an abandoned quarry 1.5 km to the north-east from the village of Masali (Fig. 3b). The visible thickness of rocks of the Masali outcrop is 4.5 m; the total thickness together with overlapping deposits is 6–9 m. In the lower part of the outcrop are light, almost white, pelitic siltstone. The pelitic siltstone sequence is overlain by Quaternary clayey–silty rocks with a considerable proportion of sandy material and organic matter (Kuzmina et al., 2016). Pelitic siltstone are pale gray, homogeneous, weakly cemented, loose, micaceous, and light. The texture of deposits is pelitomorphous; the structure is uniform.

### TEXTURE AND MINERALOGY

In accordance with the results of the granulometric analysis, almost all samples from the upper unit of the Ishim Formation are characterized by a marked predominance of aleuritic and pelitic fractions (Table 2). There no significant variations in the granulometric composition of deposits through the section: the silt content varies insignificantly in ranges of 79.97–87.68 % (Bigila outcrop) and 88.08–91.13 % (Masali outcrop). The major fractions of rocks of the upper aleuritic and pelitic fractions are characterized by full absence of coarse- (0.63–2.0) and average-grained (0.2–0.63) sandy material and almost complete absence of fine-grained sand (0.063–0.2). There is a rather low proportion of aleurite fraction (from 1.14 to 7.92 %), the content of which increases down section as a whole. The proportion of a clayey fraction varies from 6.03 to 12.46 % that is, in



**Fig. 3** Outcrops schemes (sections A - "Masali" B - "Bigila"); 1 - soil-spreading layer; 2 - Quaternary clayey-silty rocks that overlap the aleuropelites of the Ishim Formation; 3 - upper (light) bundle of aleuropelitic strata; 4 - lower (ferruginous) bundle of aleuropelitic strata; 5 - sand of the Ishim suite.

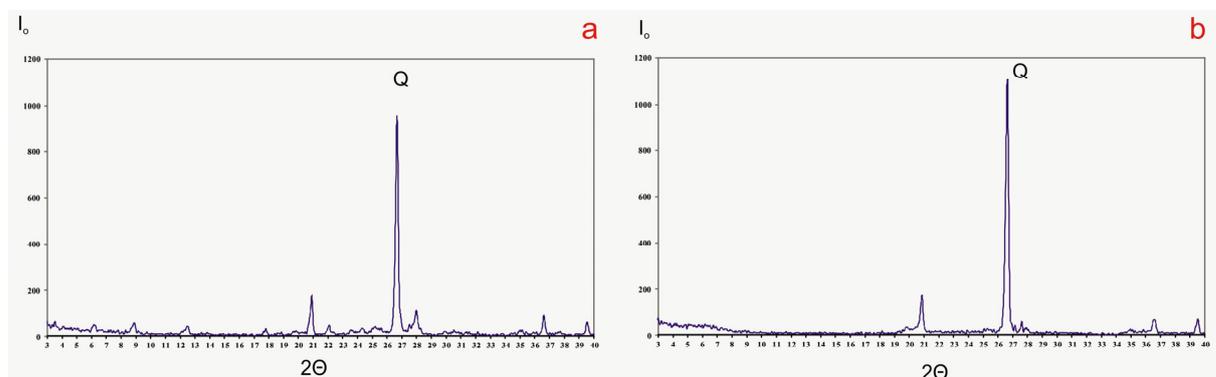
**Table 2** Distribution of main granulometric fractions of the studied sediments.

Depth (interval. m)	Very coarse sand	Coarse sand	Medium sand	Fine sand	Alevrite	Silt	Clay	
Bigila outcrop								
1	1.5	0.00	0.00	0.00	1.85	87.54	10.61	
1.5	2	0.00	0.00	0.00	1.14	87.68	11.18	
2	2.3	0.00	0.00	0.00	1.88	87.68	10.44	
2.3	2.9	0.00	0.00	0.00	1.65	85.89	12.46	
2.9	3.4	0.00	0.00	0.00	2.15	79.97	9.96	
3.4	4	0.00	0.00	0.00	0.52	6.27	84.18	9.03
4	5	0.00	0.00	2.00	39.31	24.42	29.38	4.89
5	5.8	0.00	0.00	9.90	83.03	5.55	1.52	0.00
Masali outcrop								
0.3	0.4	0.00	0.00	0.60	7.56	17.74	64.71	9.39
0.7	0.8	0.00	0.00	0.00	1.43	6.48	70.68	21.41
1.3	1.4	0.00	0.00	0.00	0.98	5.87	67.98	25.17
1.7	1.8	0.00	0.00	0.00	0.98	5.56	74.69	18.77
1.9	2	0.00	0.00	0.00	0.07	3.39	88.49	8.05
2.3	2.4	0.00	0.00	0.00	0.06	2.78	91.13	6.03
2.6	2.7	0.00	0.00	0.00	0.44	3.07	87.79	8.70
2.9	3	0.00	0.00	0.00	0.42	3.04	88.15	8.39
3.5	3.6	0.00	0.00	0.00	0.06	2.53	88.08	9.33
4.1	4.2	0.00	0.00	0.00	0.44	3.22	88.58	7.76

\*Very coarse sand (2-1 mm); coarse sand (1.0-0.5 mm); medium sand (0.5-0.25 mm); fine sand (0.25-0.1 mm); alevrite (very fine sand) (0.1-0.05 mm); silt (0.05-0.005 mm); clay (< 0.005 mm).

**Table 3** Semi-quantitative (wt. %) mineralogical composition of bulk sample. Qz = quartz; K-Fds = K-feldspar; N-Fds = Na-feldspar; K = kaolinite; Chl = chlorite; M/I = mica/illite; ML = mixed layers; MM – montmorillonite; +++++ - dominant (>50 wt.%), +++ - abundant (20-50 wt.%), ++ - subordinate (5-20 wt.%), + - low (1-5 wt.%), tr - traces (<1 wt.%).

Depth (interval. m)	Qz	K-Fds	N-Fds	K	Chl	M/I	ML	MM
<b>Bigila outcrop</b>								
B1 1.2-1.3	++++	+	++	+	+	++	-	+
B2 1.7-1.9	++++	+	++	tr	+	+	+	-
B3 2.0-2.2	++++	+	++	+	+	+	-	+
B4 2.5-2.7	++++	+	+	+	+	+	-	-
B5 3.1-3.3	++++	+	++	+	+	+	+	+
B6 3.5-3.8	++++	+	++	+	+	+	+	-
B7 4.5-4.7	++++	+	++	-	+	++	+	-
B8 5.5-5.8	++++	+	+	+	+	+	-	+
<b>Masali outcrop</b>								
M1 0.3-0.4	++++	+	+	+	=	+	-	+
M2 0.7-0.8	++++	+	+	tr	+	+	-	+
M3 1.3-1.4	++++	+	+	tr	+	+	-	+
M4 1.7-1.8	++++	+	++	+	-	+	-	+
M5 1.9-2.0	++++	+	++	+	+	+	-	-
M6 2.3-2.4	++++	+	++	tr	+	+	+	=
M7 2.7-2.8	++++	+	++	+	+	+	-	+
M8 2.9-3.1	++++	+	++	tr	+	+	+	+
M9 3.5-3.6	++++	+	++	+	+	+	+	+
M10 4.2-4.4	++++	+	++	-	+	+	tr	tr



**Fig. 4** Representative diffractograms with strong quartz peak. objects: a – Bigila; b – Masali.

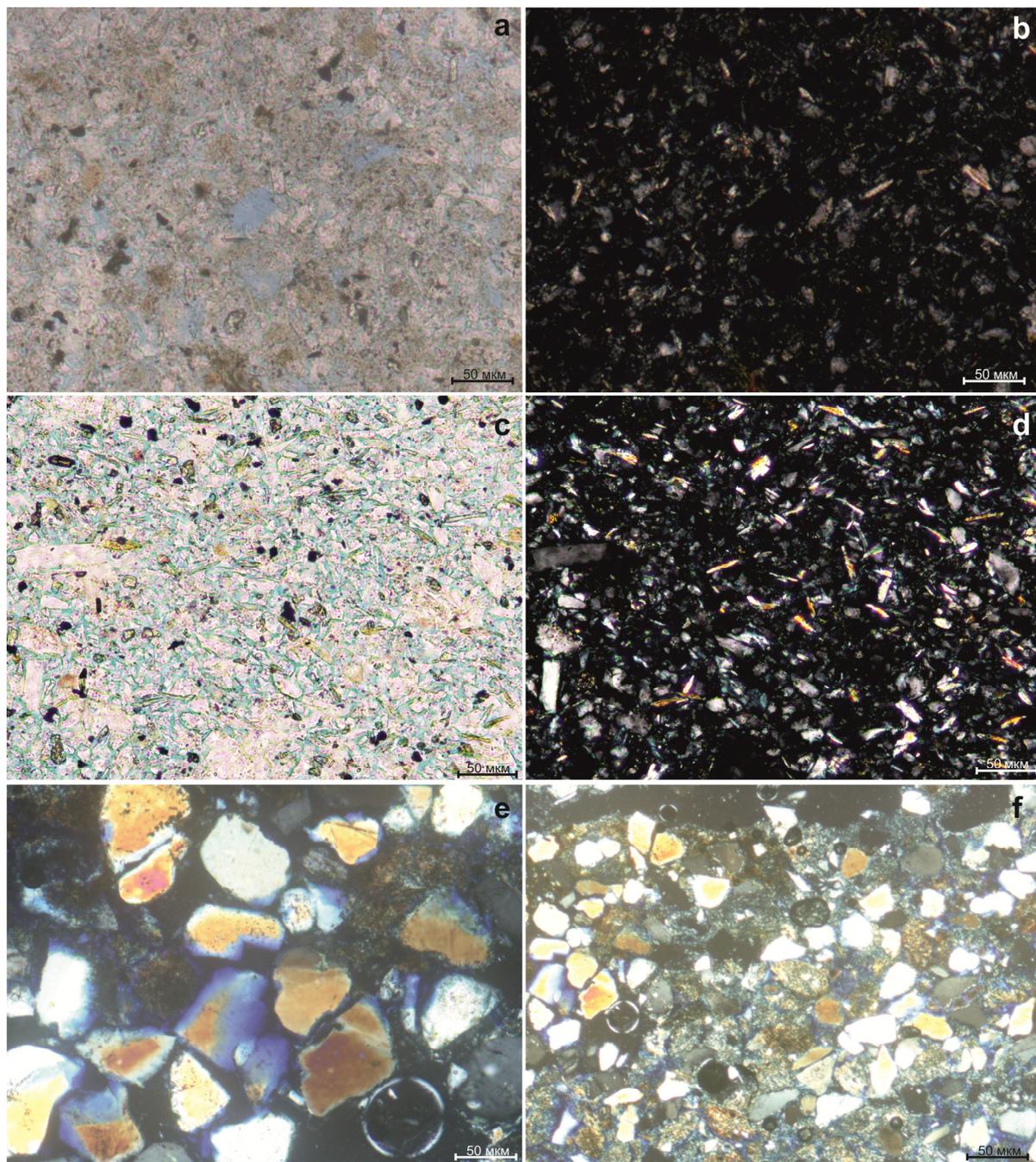
general, slightly higher than that in the upper unit of the Bigila outcrop. The deposits overlaying pelitic siltstone unit of the Ishim Formation is more heterogeneous and characterized by increased clayey fraction content (up to 25.17 %). The sands of the lower unit of the Ishim Formation are fine-grained, homogeneous in terms of granulometry, and are characterized by an absence of the clayey fraction and insignificant content of silt.

In terms of bulk mineralogical composition, quartz is the main component in all samples studied (Fig. 4). The quartz in the siltstone unit of the Ishim Formation is dominant (up to 70–90 %), slightly decreasing down section in both outcrops (Table 3). Among other minerals are potassium and sodium feldspars, kaolinite, chlorite, hydromica, mixed-layer minerals, and montmorillonite. As shown in previous studies (Smirnov et al., 2016), the content of clay

minerals in the pelitic siltstone rocks is insignificant (about 5 %). Clay minerals in its composition are represented by kaolinite (0.4 %), chlorite (1.0 %), corrensit and / or tosudite (0.8 %), hydromica (3.1 %) and mixed layers or MCO (0.7%). It is necessary to pay special attention to the fact that not only the clay minerals from the smectite group themselves are included in the concept or term of hydromica, but also small, quite numerous terrigenous fragments of hydrolyzed micas. The same applies to chlorites, which can also be represented by terrigenous small debris, which have hydrolyzed micas, magmatogenic or metamorphic origin.

#### PETROGRAPHIC DESCRIPTION

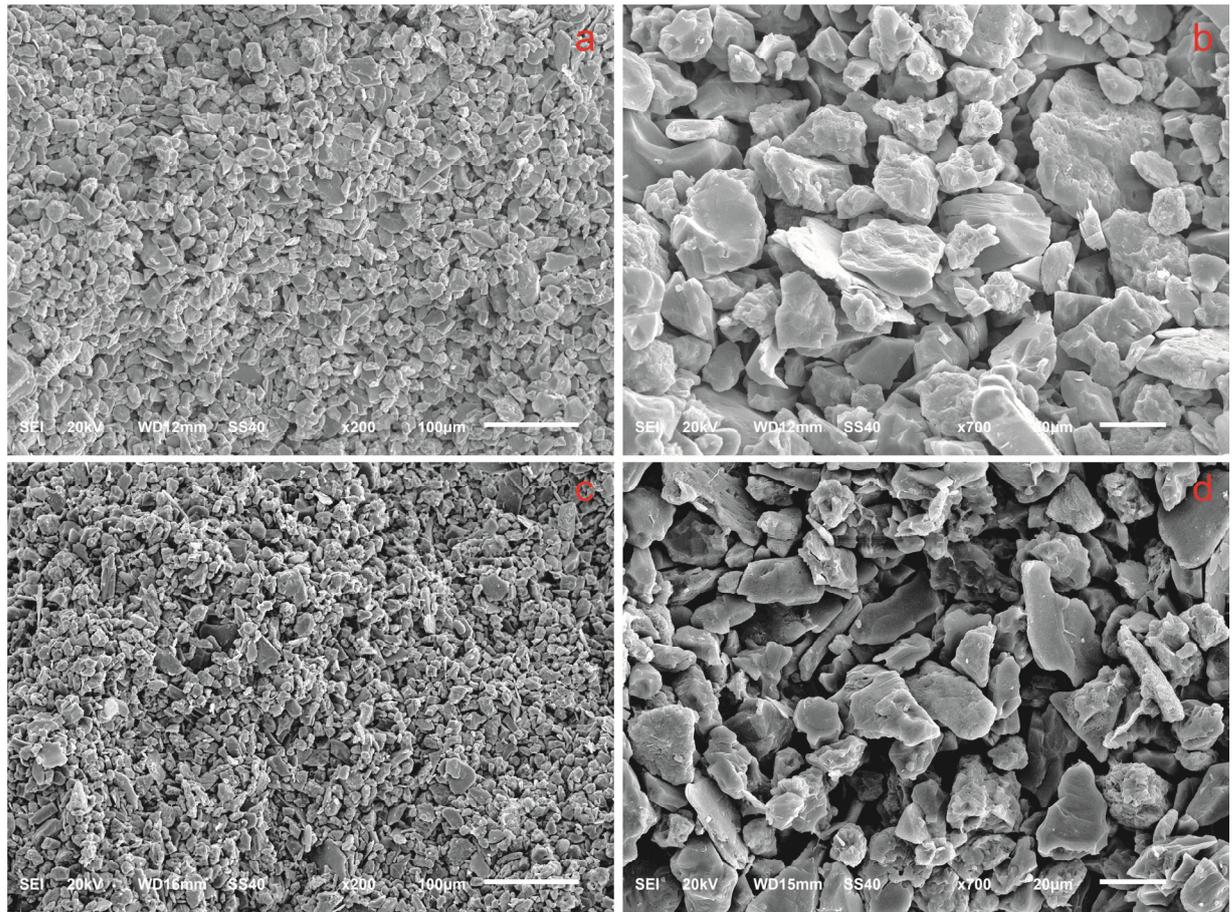
According to the petrographic analysis, sediments from the Bigila outcrop have pelitic siltstones texture with a particle size of less than



**Fig. 5** a, b - General view of the Ishim Formation's aleuopelites: from the outcrop of Bigil in the parallel and crossed Nicols, c, d - aleuopelites from the Masali Outcrop in parallel and crossed Nicols, e, f-aleurites, overlapping the Ishim Formation in the Masali Outcrop (thin section image).

0.01–0.001 mm, single grains being up to 0.03 mm. The rock mass is represented mainly by quartz and admixture ultra-thin hydromica flakes (Figs. 5a–5b). Rounded grains of up to 0.03 mm in size belong to mixed-layer minerals. Under microscope they are yellowish in parallel nicols. Ore minerals are represented by more or less evenly disseminated pyrite (as much as 1–2 %) and an ore mineral indefinable due to complete chemical alteration (about 5 %). Accessory minerals are represented by titanium minerals (4–5 %) of up to 0.01 mm in size.

In terms of mineralogical and petrographic features, deposits of the upper pelitic siltstone unit of the Ishim Formation (Masali outcrop) look alike and they are composed of 90 % of angular quartz grains reaching 0.12 mm in size. Quartz particles with an average diameter of more than 0.05 mm make up 3–5 % of the bulk rock volume; the prevailing size of grains is 0.005–0.012 mm (Figs. 5c–5d). Feldspar and mica (mostly heavily hydrated) occur in small amounts. Feldspars are represented by acid plagioclase. Hydromica occurs as thin flakes with



**Fig. 6** a, b – SEM images of aleuropelites from the outcrops of Masali and Bigila x 200 and c, d – x 700.

a bright interference color. There are rare small rounded yellow-green glauconite grains. Samples contain rounded segregations, consisting of quartz grains of the same size as the rock as a whole, cemented with an amorphous substance, seemingly represented by opal/chalcedony. Clayey minerals are represented by chlorite flakes. Quite small black grains (<0.005 mm in size) are scattered throughout the sample. The mineral composition of these grains cannot be reliably determined due to their small size (presumably ore minerals). The rock is weakly cemented and loose due to a small amount of cement (3–5 %) with contact and porous types of distribution, and consists of authigenic silica, chlorite, and hydromica. The rock sample has a rather high degree of microporosity, formed by intergranular pores of less than 0.005 mm in diameter. According to studies in thin-sections under microscope the rock became intensively colored in blue. In addition, there are trace fossils filled with a coarser-grained material and highly ferruginized.

Clayey–silty deposits, overlaying siltstone unit in the Masali outcrop, are pale gray to dark brown, sometimes almost black, often ferruginous, with a large amount of sand and organic material. They are composed of clayey minerals (mainly hydromica) with an admixture of fragments of sandy fraction. Quartz fragments of the fine-grained sandy fraction

are 0.05–0.16 mm in size; silt admixture is less than 5 %. The presence of carbonaceous plant detritus is universal in occurrence. The hydromica clay contains an admixture of grains of the sandy fraction. Quartz fragments of the fine-grained sandy fraction are of 0.05–0.16 mm in size; aleuritic admixture is less than 5 %. The rest is hydromica clay and, possibly, kaolinite–hydromica rock occurring as rounded or irregular grains (Figs. 5e–5f).

The study results of the collected samples with scanning electron microscope also indicate that rocks of the upper unit of the Ishim Formation are composed of angular fine quartz grains with an insignificant content of the clayey cement (Fig. 6b).

#### MAJOR OXIDES

The measurement results show that the contents of major oxides are largely consistent with the mineral composition of deposits (Table 4). The relationships between major oxides and  $Al_2O_3$  are shown in diagrams (Fig. 7). Quartz is the main rock-forming component in all studied samples. It should be noted that the  $SiO_2$  content in almost all pelitic siltstone samples of the Ishim Formation is higher than their Clarke values in the Earth's crust and varies in a significant range from 63 % to 78 %. A significant relationship between the content of the silt fraction and the  $SiO_2$  content was revealed. The  $SiO_2$  content

**Table 4** Major element concentration of the samples from Masali and Bigila outcrops; all values in wt. % oxide. LOI = loss on ignition; CIA = Chemical index of alteration; CC = Continental Crust (Wedepohl, 1995), PAAS = post-archaeon Australian shale (Taylor and McLennan, 1985).

Sample	M1	M2	M3	M4	M5	M6	M7	M8	M9	M10
SiO <sub>2</sub>	69.14	71.17	57.46	64.63	73.22	73.08	72.35	71.87	72.50	78.99
Al <sub>2</sub> O <sub>3</sub>	15.35	13.65	17.95	11.52	13.60	13.77	13.89	14.18	13.69	10.19
Fe <sub>2</sub> O <sub>3</sub> (T)	3.66	5.11	7.48	6.44	2.55	2.31	2.51	2.61	2.57	2.22
MnO	0.04	0.08	0.05	0.03	0.03	0.03	0.03	0.03	0.04	0.03
MgO	1.06	0.99	1.37	1.03	1.13	1.24	1.42	1.42	1.47	0.79
CaO	0.81	0.71	1.07	0.94	1.00	0.60	0.65	0.60	0.72	0.53
Na <sub>2</sub> O	0.56	0.38	0.23	0.23	2.27	2.21	2.12	2.14	2.25	2.04
K <sub>2</sub> O	1.45	0.88	1.07	1.02	1.82	1.88	1.92	1.88	1.85	1.45
TiO <sub>2</sub>	1.12	1.00	0.98	1.13	0.96	0.96	0.99	0.97	1.05	0.95
P <sub>2</sub> O <sub>5</sub>	0.03	0.07	0.07	0.09	0.05	0.05	0.05	0.04	0.05	0.04
LOI	6.59	5.71	12.01	99.77	3.57	3.69	3.85	4.05	3.63	2.56
Total	99.81	99.76	99.73	285.97	99.79	99.81	99.79	99.80	99.81	99.77
K <sub>2</sub> O/Na <sub>2</sub> O	122.76	185.23	252.99	5.61	32.21	33.13	34.14	33.63	32.17	38.65
SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub>	4.50	5.21	3.2	10.20	5.38	5.31	5.21	5.07	5.29	7.76
Al <sub>2</sub> O <sub>3</sub> /TiO <sub>2</sub>	13.73	13.65	18.38	84.05	14.15	14.30	14.00	14.57	13.10	10.78
CIA	84.46	87.35	88.35	1.17	74.34	74.61	74.79	75.41	73.93	71.67

Sample	B-1	B-2	B-3	B-4	B-5	B-6	B-7	B-8	CC	PAAS
SiO <sub>2</sub>	71.43	72.03	72.82	76.63	63.67	64.21	87.82	91.47	61.50	62.80
Al <sub>2</sub> O <sub>3</sub>	14.35	13.81	13.48	11.28	17.12	16.99	6.78	4.47	15.1	18.90
Fe <sub>2</sub> O <sub>3</sub> (T)	2.66	2.61	2.58	2.72	5.08	4.79	0.68	0.61	6.28	6.50
MnO	0.03	0.03	0.04	0.03	0.09	0.13	0.0	0.01	0.10	0.11
MgO	1.55	1.39	1.41	1.07	1.45	1.47	0.15	0.09	3.7	2.20
CaO	0.91	0.82	0.80	0.61	0.76	0.77	0.14	0.10	5.5	1.30
Na <sub>2</sub> O	1.99	2.14	2.04	1.51	1.01	1.10	0.93	0.71	3.2	1.20
K <sub>2</sub> O	1.91	1.85	1.85	1.50	1.82	1.81	1.58	1.23	2.4	3.70
TiO <sub>2</sub>	0.97	0.99	1.01	0.93	0.96	0.99	0.38	0.27	0.68	1.00
P <sub>2</sub> O <sub>5</sub>	0.05	0.05	0.05	0.04	0.06	0.05	0.02	0.01	0.18	0.16
LOI	3.96	4.12	3.75	3.42	7.79	7.47	1.41	0.92	-	-
Total	99.82	99.84	99.83	99.73	99.82	99.77	99.89	99.89	-	-
K <sub>2</sub> O/Na <sub>2</sub> O	35.85	33.65	35.70	50.88	63.14	58.24	94.05	128.36	-	-
SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub>	4.98	5.21	5.40	6.79	3.72	3.78	12.95	20.46	-	-
Al <sub>2</sub> O <sub>3</sub> /TiO <sub>2</sub>	14.87	14.03	13.34	12.13	17.84	17.00	17.65	16.57	-	-
CIA	74.85	74.17	74.15	75.75	82.66	82.21	71.83	68.63	48.6	70.5

in deposits overlaying pelitic siltstone in the Masali outcrop is a bit lower on average than in the underlying rocks. It varies from 57 % to 71 % that reflects the heterogeneity of these deposits (alternation of clayey silts and humus interlayers).

The content of Al<sub>2</sub>O<sub>3</sub> in the Masali outcrops is varied insignificantly - from 13 to 14 %, and somewhat higher due to the greater content of clay minerals in the overlapping sediments. In the rocks of the Bigila outcrop, the Al<sub>2</sub>O<sub>3</sub> content varies in a large range (from 11 to 17 %) and increases in the lower part of the pelitic siltstones pack. An analogous distribution along the section is also characteristic for Fe<sub>2</sub>O<sub>3</sub>: in the Masali outcrop, 2–2.5 % for pelitic siltstones and up to 7 % for overlapping deposits, in the Bigila outcrop, as well as for Al<sub>2</sub>O<sub>3</sub>, there is a tendency to increase the content at the boundary with the sand bud - from 2–3 % to 5–6 %.

The content of iron oxides is noticeably higher in the lower ferruginous part of the upper unit of the

Ishim Formation and, overall, is somewhat higher in deposits of the Bigila outcrop. The low CaO and MgO contents are resulted in almost complete absence of carbonates and gypsum. The low TiO<sub>2</sub> content (lower than in the Earth's crust) is most likely due to the low proportion of illite and kaolinite with which it is associated. In general, low contents of MnO, P<sub>2</sub>O<sub>5</sub>, as well as CaO and Na<sub>2</sub>O suggest that deposits are quite weathered and probably have been redeposited (Lisboa et al., 2015). This dependence on the whole confirms a number of hypotheses that both the channel and lacustrine facies of the Ishim Formation were formed due to erosion and redeposition of more ancient deposits of the Turtas Formation.

#### TRACE ELEMENTS

Table 5 and Figure 8 show the measured contents of trace elements. Deposits exposed in the Bigila outcrop are characteristic of the following regularities in contents of trace elements. The contents

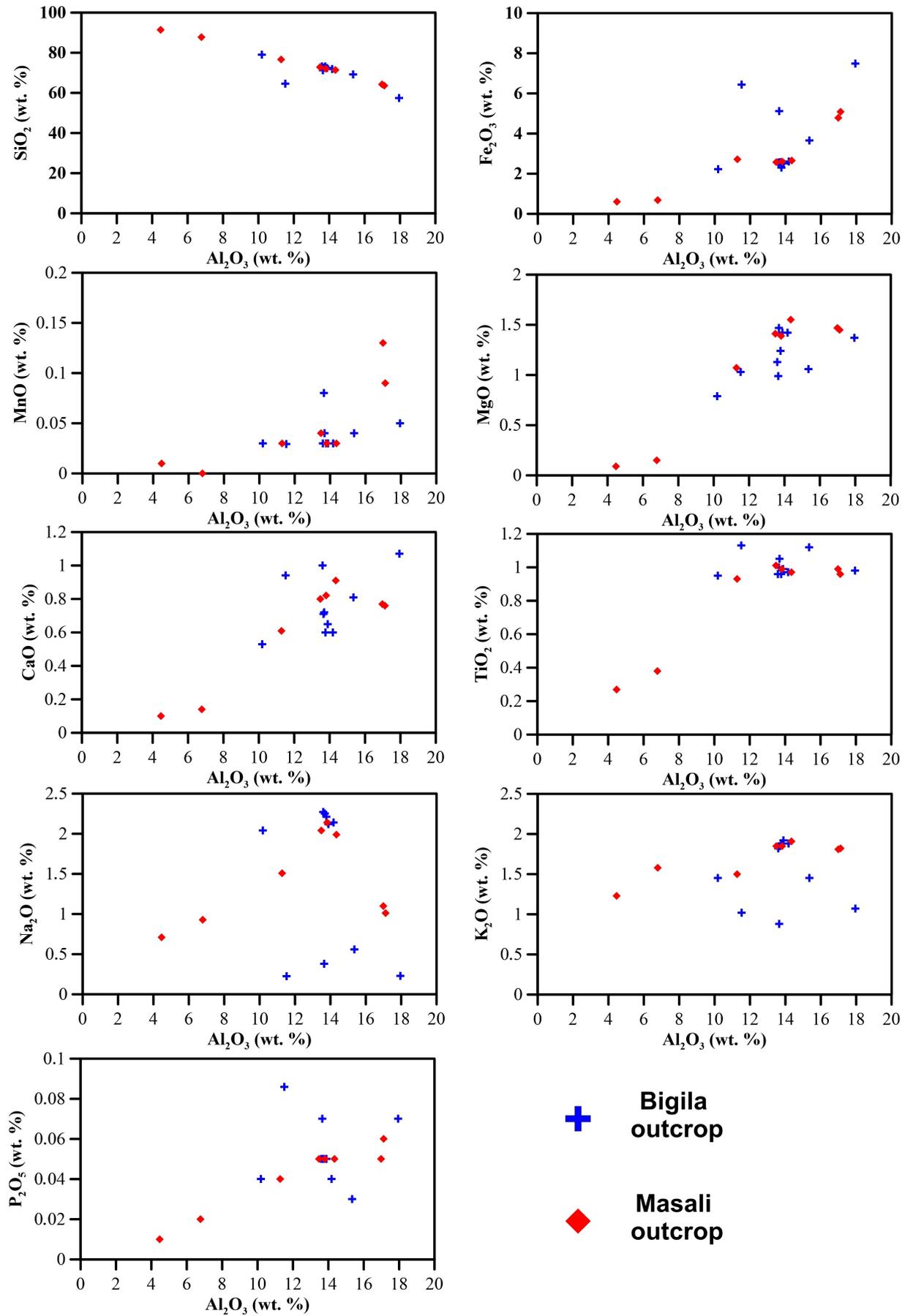


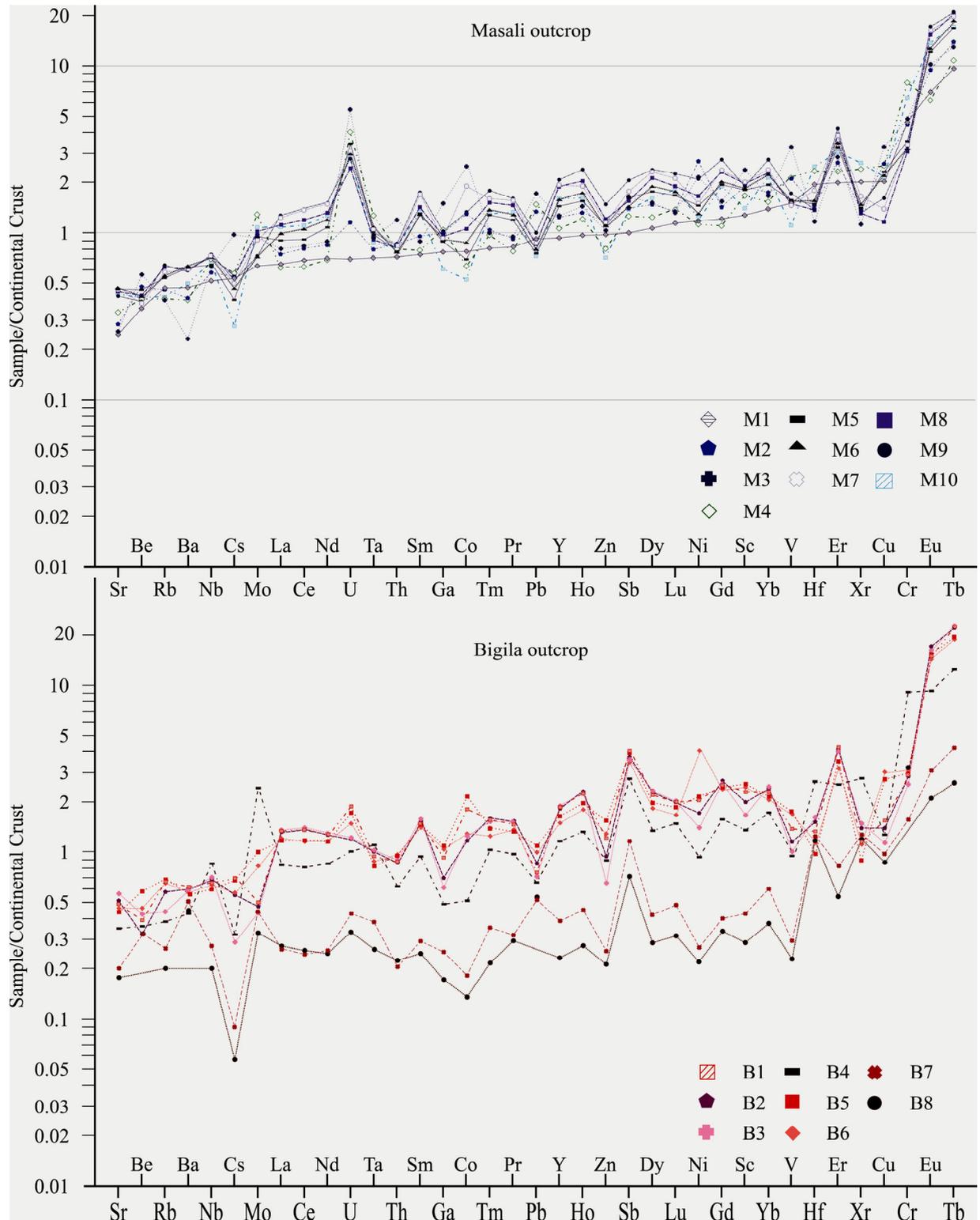
Fig. 7 Discrimination plots of major element oxides and  $Al_2O_3$

**Table 5** Trace and REE concentration of the samples from Masali and Bigila outcrops; all values in ppm. CC = Continental Crust (Wedepohl, 1995), PAAS = post-archaeon Australian shale (Taylor and McLennan, 1985).

	M1	M2	M3	M4	M5	M6	M7	M8	M9	M10
Be	1.10	1.47	1.74	1.22	1.43	1.29	1.19	1.29	1.21	1.26
Sc	9.0	13.6	16.6	11.7	12.9	13.1	13.8	13.7	13.2	9.8
V	79	113	173	113	82	78	78	79	91	59
Cr	159	157	169	277	121	111	117	107	116	226
Co	9.0	15.3	29	7.3	8.1	10.2	22	12.2	15.5	6.1
Ni	22	50	40	21	27	24	28	31	39	23
Cu	29	37	47	36	33	20	19.8	16.6	23	31
Zn	51	61	54	42	59	57	61	63	77	37
Ga	10.8	14.3	21	14.6	12.4	12.6	12.4	13.4	14.5	8.5
Rb	51	50	44	44	60	61	64	69	70	45
Sr	79	90	81	106	140	143	142	139	133	136
Y	19.4	26	26	22	30	33	40	39	43	33
Zr	477	333	268	573	332	347	390	312	317	618
Nb	13.4	15.0	16.8	18.4	16.8	18.3	18.9	18.7	19.2	17.4
Mo	0.89	1.36	1.31	1.80	1.32	1.02	1.28	1.43	1.02	1.52
Sb	0.31	0.44	0.51	0.39	0.49	0.44	0.55	0.48	0.64	0.43
Cs	3.1	3.2	5.7	3.3	2.3	2.7	2.9	3.2	3.1	1.61
Ba	314	270	155	263	410	415	409	409	399	333
La	21	24	26	20	29	32	40	36	41	35
Ce	45	53	55	41	60	69	91	79	91	73
Pr	5.2	5.9	6.0	4.9	7.6	8.2	9.9	9.2	10.1	8.4
Nd	18.0	22	23	17.9	28	31	39	34	39	33
Sm	3.5	4.5	4.2	3.7	5.3	6.2	8.1	6.7	8.2	6.3
Eu	0.66	0.90	0.97	0.59	1.16	1.21	1.56	1.47	1.64	1.31
Gd	3.4	4.0	4.3	3.1	5.4	5.6	6.6	6.5	7.7	5.3
Tb	0.48	0.70	0.65	0.54	0.86	0.93	0.99	1.02	1.05	0.86
Dy	3.1	4.3	4.3	3.6	5.1	5.5	6.7	6.2	6.9	4.7
Ho	0.60	0.82	0.89	0.75	0.96	1.07	1.18	1.26	1.48	1.00
Er	1.90	2.5	2.7	2.2	3.1	3.3	3.7	3.7	4.0	2.9
Tm	0.30	0.38	0.37	0.36	0.48	0.50	0.59	0.56	0.66	0.48
Yb	2.1	2.6	2.5	2.3	2.9	3.3	3.6	3.4	4.1	3.2
Lu	.31	0.36	0.36	0.37	0.45	0.48	0.57	0.51	0.61	0.49
Hf	11.3	8.5	6.8	13.6	8.6	9.0	10.4	8.0	8.0	14.5
Ta	1.07	1.19	1.40	1.91	1.49	1.60	1.58	1.37	1.52	1.31
Pb	15.7	23	29	25	12.6	13.4	14.6	14.6	17.1	12.4
Th	7.4	8.8	12.3	8.3	8.0	8.0	8.8	8.6	8.6	8.4
U	1.74	2.9	13.7	10.0	8.6	7.4	7.7	6.1	6.9	7.1

	B1	B2	B3	B4	B5	B6	B7	B8	CC	PAAS
Be	1.21	1.00	1.32	1.11	1.79	1.43	<1	<1	3.10	–
Sc	16.1	13.9	11.6	9.5	17.9	17.1	3.0	2.0	7.00	16
V	73	61	53	50	92	90	15.5	12.1	53.00	150
Cr	106	99	89	320	103	108	55	112	35.00	110.0
Co	21	13.6	14.5	5.9	25	14.9	2.1	1.57	11.60	23
Ni	38	32	26	17.2	40	75	5.0	4.1	18.60	55.0
Cu	22	20.0	16.2	18.1	39	43	13.9	12.4	14.30	–
Zn	63	49	34	46	80	67	13.2	11.0	52.00	85
Ga	12.9	9.8	8.5	6.8	15.3	14.5	3.5	2.4	14.00	–
Rb	73	63	48	42	75	71	29	22	110.00	–
Sr	155	161	177	110	139	146	63	56	316.00	–
Y	39	38	39	24	34	31	8.0	4.8	20.70	–
Zr	278	329	354	656	210	262	302	283	237.00	–
Nb	16.9	17.8	17.8	22	15.5	16.4	7.1	5.2	26.00	–
Mo	0.70	0.66	0.61	3.4	1.39	1.15	0.61	0.46	1.40	–
Sb	1.23	1.21	1.12	0.85	1.21	1.07	0.36	0.22	0.31	–
Cs	4.0	3.2	1.67	1.86	3.9	3.3	0.52	0.33	5.80	–
Ba	406	400	398	287	372	381	335	298	668.00	–
La	43	43	43	27	38	39	8.4	8.8	32.30	38.2
Ce	90	90	90	53	77	76	16.1	16.9	65.70	79.6
Pr	9.3	9.6	9.6	6.1	8.4	8.6	2.0	1.85	06.30	8.8
Nd	33	33	33	22	30	30	6.7	6.4	25.90	33.9
Sm	6.9	7.2	7.4	4.4	6.9	6.6	1.37	1.16	4.70	5.6
Eu	1.35	1.62	1.52	0.88	1.44	1.35	0.29	0.20	0.10	1.08
Gd	7.2	7.5	7.2	4.4	6.8	6.7	1.12	0.94	2.80	4.7
Tb	1.13	1.10	1.13	0.62	0.97	0.94	0.21	0.13	0.05	0.8
Dy	6.5	6.6	6.7	3.9	5.7	5.3	1.26	0.83	2.90	4.7
Ho	1.42	1.42	1.41	0.82	1.22	1.11	0.28	0.17	0.62	1.0
Er	4.0	3.8	3.8	2.4	3.3	3.0	0.78	0.51	0.95	2.9
Tm	0.59	0.59	0.56	0.38	0.51	0.46	0.13	0.080	0.37	0.4
Yb	3.5	3.6	3.7	2.6	3.2	3.1	0.90	0.56	1.50	2.8
Lu	0.54	0.54	0.54	0.40	0.50	0.45	0.13	0.085	0.27	0.4
Hf	7.7	8.8	9.4	15.3	5.6	6.6	7.2	6.8	5.80	–
Ta	1.40	1.52	1.52	1.64	1.23	1.31	0.57	0.39	1.50	–
Pb	12.7	14.5	12.1	11.1	18.5	16.9	8.8	09.1	17.00	20.0
Th	8.9	8.9	9.2	6.4	9.7	9.9	2.1	2.3	10.30	14.6
U	4.7	3.0	3.0	2.5	4.3	3.7	1.07	0.83	2.50	3.1



**Fig. 8** Trace and REE elements normalized to continental crust.

of large ion lithophile elements (LILE) Rb, Sr, Cs, and Ba are markedly lower than those in the Earth's crust (Wedepohl, 1995). It is generally believed that elements with a large ionic radius are actively captured by clay minerals (Nesbitt et al., 1980; Wronkiewicz and Condie, 1987). Accordingly, their low contents are associated with insignificant

proportion of the clayey fraction (clay minerals) and high quartz content in the silty fraction of deposits under consideration. For both outcrops, the contents of Ba, Sr, and Rb remain practically unchanged in the section, except for Cs. The content of the latter in the deposits, enriched in clay minerals and organic matter, overlapping the Ishim Formation is close to that in the

Earth's crust. In turn, the Cs content in deposits of the lower part of the Ishim Formation lying at the contact with the sandy unit is 3–10 times lower.

The next group of high field strength elements (Y, Th, U, Pb, Zr, Hf, Nb, and Ta (HFSE)) shows a low degree of mobility and insignificant involvement in the processes of sedimentogenesis (Lisboa et al., 2015). In general, the contents of almost all above elements in deposits of the Ishim Formation are close to those in the Earth's crust. In addition, the high uranium contents in Quaternary siltstones overlying pelitic siltstone of the Ishim Formation should be noted. Probably, the higher U contents can be explained by its intensive accumulation by organic matter. Such elements as V, Cr, Mn, Co, Ni, Cu, Zn, Ga, Ge, and Sb (transition trace elements and other post-transition metals) are characterized by rather a high content variability. In addition, it should be noted that Cr, Cu and Sb contents are much higher than those in the Earth's crust; there is a strong Cr anomaly at all. Most of rare earth elements (REE) are characterized by contents close to those in the Earth's crust; the only exception is Eu and Tb, forming strong anomalies (20 times greater than those in the Earth's crust).

#### **SPECIFIC SURFACE AREA**

Analysis of the obtained data indicates that the samples studied have a large specific surface area varying from 5.2 to 31.5 m<sup>2</sup>/g. There is a directly proportional dependence of the specific surface area of the samples on the content of aluminum oxides in them, the concentration of which, in turn, is directly related to the content of clay minerals in the composition of the samples studied.

#### **DISCUSSION**

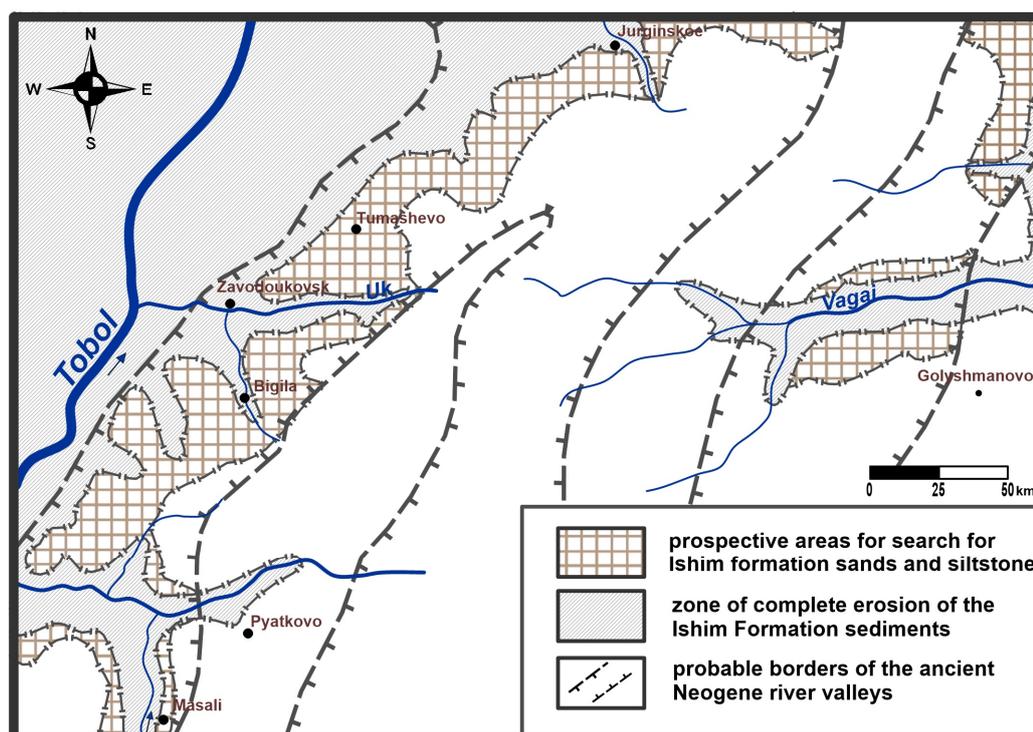
By the Early Miocene a lacustrine basin, which occupied the vast territory in the West Siberian Plain in the Late Oligocene, had reduced (Shatsky, 1978). This was caused by activation of positive tectonic movements in the mountain frame of the West Siberian Plate. As a result, a large previously existing lacustrine basin was separated into a system of gradually degrading and eutrophic water bodies, and the sedimentation of the Ishim Formation occurred synchronously with subsequent slow subsidence and stabilization of the entire macroregion (Astapov, 1977). The tectonic activation continued in the Middle Miocene both in the frame and within the West Siberian Plate.

Some part of the clastic material was transported from the Urals through the net of large waterways to the western part of the Tobol–Ishim interfluvium. The river network in the Miocene was markedly different from the modern one by obviously non-transitive character, since the basis of erosion of rivers in that epoch was defined by weakly flowing and inactive lacustrine basins, confined to the surface of the partially replenished buried Late Oligocene relief.

Under such conditions any significant transportation of clastic material was hardly possible. Based on the results of the thickness analysis, distribution conditions, lithological and geochemical features there appears a possibility to make a conclusion that the sedimentation of the Ishim Formation occurred under the paleogeographic setting of the continental weathering. At this, based on the similarity in mineral and chemical compositions, the Ishim Formation is proposed to represent the neoeuvium developed from the Turtas Formation – the most obvious source for quartz material of Ishim Formation. Under the conditions of flowage and high oxygen potential of the surface waters the washing and eluvial bleach of deposits took place (Astapov et al., 1979). Another argument in favor of that the deposition of the upper unit of the Ishim Formation occurred under conditions of degrading oxbow water bodies are values of basic geochemical indices and ratios (K<sub>2</sub>O/Na<sub>2</sub>O, SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub>, CIA). For example, indices of chemical weathering calculated testify about moderate weathering of deposits of the Ishim Formation and vary in a range of 68–80. Apparently, the degradation of water bodies was reciprocating and lasted over a long period. Great Eu and Tb anomalies, possibly, evidence in favor of certain role of hydrothermalism.

An important source of information about the formation conditions of deposits of the Ishim Formation is their distinct geomorphological confinement. Pelitic siltstones are common in areas confined to buried river paleovalleys and they form a virtually continuous cover on the watershed plateau with elevations above 120 m. Both the sands of the lower channel unit and pelitic siltstone formed under the shallow lake conditions are exposed within the sites corresponding to the marginal parts of the Early–Middle Neogene paleoriver network. Within the territory of the Tobol–Vagai interfluvium being under consideration there are presumably three paleovalleys of the Ishim epoch (Fig. 9). In terms of lithology, this was a complex river net with numerous separate waterways. In general, the river valleys of modern waterways (Tobol or Vagai rivers, correspondingly, and, probably, smaller rivers) inherit the western and eastern river paleovalleys.

The conditions for the formation of deposits of the Ishim Formation predetermined the high dispersity and, accordingly, the possibilities of industrial use of these rocks. As shown in previous works (Novoselov, 2016; Smirnov et al., 2016), there is a real possibility of using deposits of the upper unit of the Ishim Formation as a source of raw material for manufacturing of foam glass-ceramic materials. Siliceous composition and high dispersion create premises for further use in other industries. At the same time, the use of these rocks as polyfunctional additives for mortars is a more promising trend of their practical application.



**Fig. 9** Scheme of distribution of the Ishim Formation (sands and aleuropelites) relatively Neogene and modern river network.

**Table 6** Sediments of the Ishim formation and several types of material additives of natural and man-made origin.

Material	Chemical composition (%)				Specific surface (m <sup>2</sup> /g)	Source
	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO		
Blast furnace slags	28-38	8-24	-	30-50	-	Regourd, 2001
Fly ash	Bituminous	20-60	5-35	10-40	1-12	Ahmaruzzaman, 2010
	Subbituminous	40-60	20-30	4-10	5-30	
	Lignite	15-45	20-25	4-15	15-40	
Gliez	72.8	12.4	5.1	2.8	-	Kantsepolsky et al., 1969
Diatomaceous earths	50-90	3-15	1-10	≤10	≥20	Distanov, 1976; Snellings, 2012
Rice husk ash and other burned organic matter residues	86-87	≤1	≤1	1-2	25-40	Siddique and Khan, 2011
Silica fume	85-90	≤1	≤1	≤1	20-22	ASTM C 1240
Marshallite	92-97	≤1-7	≤1	≤1	≥12	Krashennikova et al., 2007
Ishim formation siltstone	63-80	11-17	2-5	≤1	5.2-31.5	This study; Smirnov et al., 2016

The results of the comparative characteristics of Ishim Formation pelitic siltstones and materials of various origins used as additives are presented in Table 6. By their properties, deposits under consideration are close to silica flour or “marshallite”, natural ultradisperse quartz rock with a particle size of 0.07–0.03 mm, containing not less than 98 % SiO<sub>2</sub> is widely used in the production of construction materials (Molchanov and Yusupov, 1981). A market share of marshallite varies from 80 to 99 %, the surface area is not less than 12 m<sup>2</sup>/g. In this respect,

deposits of Ishim formation and marshallite are similar. An essential difference between marshallite and considered rocks is a significant content of oxides of Fe and Al oxides associated with clay fraction. However, marshallite can easily be processed by elutriation, air elutriation, and chemical processing with extraction of monomineralic fractions and a simultaneous decrease in Fe<sub>2</sub>O<sub>3</sub> to a tenth of a percent. This experience can be useful at the practical use of the deposits under investigation.

## CONCLUSIONS

- The deposits of the Ishim Formation have the material composition specific of rocks formed under the continental conditions. Quartz is the main rock-forming mineral in deposits of the upper part of the Ishim Formation. There is a small amount of feldspars, clayey minerals occur in minor amounts. According to the petrographic and SEM data, deposits are composed of angular quartz grains (90 %) of >0.05 mm in diameter on the average; the maximum size of particles is 0.12 mm;
- According to contents of the major oxides of SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, the upper unit of the Ishim Formation is characterized by a relatively high degree of homogeneity. An increase in the iron content is recorded in the lower ferruginous unit of the Ishim Formation. Low contents of MgO, P<sub>2</sub>O<sub>5</sub>, CaO, and MnO evidence a possible redeposition of deposits of the Ishim Formation;
- The contents of large ion lithophile elements (Rb, Sr, Cs, and Ba) in deposits of the upper unit of the Ishim Formation are markedly lower than those in the Earth's crust. In turn, the contents of high field strength elements such as Y, Th, U, Pb, Zr, Hf, Nb, and Ta, as well as the contents of transition trace elements and other post-transition metals V, Mn, Co, Ni, Zn, Ga, Ge, and Sb are close to those in the Earth's crust. There are positive anomalies of Eu, Tb, Cr, Sb, and Cu. Great Eu and Tb anomalies, possibly, evidence in favor of certain role of hydrothermalism and tectonic settings during the sedimentation period.
- The quartz composition, high dispersion and high specific surface area make it possible to consider deposits of the upper part of the Ishim Formation as a possible raw material base for the local construction materials industry mainly as a cheap natural filler for cement production.
- A distinct geomorphological confinement of outcrops of the Ishim Formation to paleovalleys of the Neogene river network greatly simplifies the prospecting works, reserve calculation, and development of deposits.

## ACKNOWLEDGMENTS

We are grateful to our colleagues I. I. Nesterov and A. A. Novoselov for valuable advices and recommendations during our investigation and V. T. Chernyshev for assistance in carrying out microscopic investigations. We thank D.V. Voroshchuk for translation an early version of the manuscript from Russian to English.

## REFERENCE

- Afanasiev, N.F. and Tseluiko, M.K.: 1989, Additives in concrete and mortars. Budivelnik Publishing House, Kyiv, 128 pp., (in Russian).

- Ahmaruzzaman, M.: 2010, A review on the utilization of fly ash. *Prog Energy Combust Sci.*, 36, 327–363. DOI: 10.1016/j.peccs.2009.11.003
- Astapov, A.P., Drozhashhikh, N.B. and Generalova, R.S.: 1979, Paleogeography of paleogene and neogene of Tyumen region in the connection with prospects non-metallic mineral raw materials. CF Rosgeolfond (Inv. no. 373894), Tyumen, 15–17, (in Russian).
- Astapov, A.P.: 1977, Continental Oligocene–Neogene of Tobol–Ishim interfluve. Dissertation, Novosibirsk, 185 pp., (in Russian).
- ASTM C1240-15: 2015, Standard specification for silica fume used in cementitious mixtures. ASTM Int West Conshohocken, PA. www.astm.org
- Botvinnikov, V.I. et al.: 1961, Mineral raw construction materials base of the Western Siberia. Gosgeoltekhizdat, Moscow, (in Russian).
- Clarke, J.W.: 1994, Genesis of the West Siberian Basin and its petroleum geology: A recent interpretation. *Int. Geol. Rev.*, 36, 11, 985–996. DOI: 10.1080/00206819409465500
- Distanov, U.G.: 1976, Siliceous rocks of USSR. Tatar Kn. Izd., Kazan, (in Russian).
- Gurari, F.G., Volkova, V.S., Babushkin, A.E., Golovina, A.G., Nikitin, V.P., Nekrasov, A.I., Kriventsov, A.V., Dolya, Zh.A., Kolykhanov, Yu.M. and Gnibidenko, Z.N.: 2001, Unified regional stratigraphic schemes of Paleogene and Neogene of the West Siberian Plain. SNIIGiMS, Novosibirsk, 13 pp., (in Russian).
- Kantsepol'sky, I.S., Terekhov, S.V., Khlebo, A.P. and Ronchinsky, E.M.: 1969, Frost and atmosphere resistance of solutions in pozzolan Portland cements. *Tr Alma-At Nauk Issled Proekt, Inst. Stroit. Mater.*, 9, 119–125, (in Russian).
- Krashennnikova, N.S., Kazmina, O.V. and Frolova, I. V.: 2007, Batch pulping on the basis of natural substandard siliceous materials. *Bull. Tomsk Polytech. Univ.*, 310, 1, 120–123.
- Kuzmina, O.B., Khazina, I.V., Smirnov, P.V. and Konstantinov, A.O.: 2016, New palynological data from Upper Miocene Ishim Formation (section Masali, West Siberian Plain). *Interexpo GEO-Siberia*, 1, 83–88.
- Kuznetsov, K.M.: 1963, An analysis of resources and perspectives of expansion of the local raw material base of nonmetallic mineral resources in the Ural part of the West Siberia Lowland. Geological report, Fil SNIIGIIMS, Tyumen.
- Lisboa, J.V., de Oliveira, D.P.S., Rocha, F., Oliveira, A. and Carvalho, J.: 2015, Patterns of rare earth and other trace elements in Paleogene and Miocene clayey sediments from the Mondego platform (Central Portugal). *Chemie der Erde – Geochemistry*, 75, 3, 389–401. DOI: 10.1016/j.chemer.2015.07.002
- Maria, S.: 2016, Use of natural pozzolans with lime for producing repair mortars. *Environ. Earth Sci.*, 75, 9, 1–8. DOI: 10.1007/s12665-016-5444-5
- Martynov, V.A. and Nikitin, V. P.: 1968, Stratigraphy of the Neogene sediments of the southern part of the West Siberian lowland. *Geol. Geofiz.*, 12, 3–15, (in Russian).
- Mehta, P. K.: 1987, Natural pozzolans: Supplementary cementing materials for concrete. *CANMET Spec. Publ.*, 86, 1–33.
- Meyer, C.: 2002, Concrete and sustainable development in the United States. In: *Spec Publ ACI*, 206, 1–12.

- Molchanov, V.I. and Yusupov, T.S.: 1981, Physical and chemical properties of finely divided minerals. Nedra, Moscow, (in Russian).
- Nalivkin, D.V., Ingerson, E. (eds): 1960, The Geology of the U.S.S.R. A short outline.
- Nesbitt, H.W., Markovics, G. and Price, R.C.: 1980, Chemical processes affecting alkalis and alkaline earths during continental weathering. *Geochim. Cosmochim. Acta*, 44, 11, 1659–1666. DOI: 10.1016/0016-7037(80)90218-5
- Nikolaeva, I.V., Palessky, S.V., Chirko, O.S. and Chernozhkin, S.M.: 2012, Determination of major and trace elements in silicate rocks after fusion with LiBO<sub>2</sub> by inductively coupled mass-spectrometry. *Anal. Control.*, 16, 2, 134–142, (in Russian).
- Nikolaeva, I.V., Palesskii, S.V., Kozmenko, O.A. and Anoshin, G.N.: 2008, Analysis of geologic reference materials for REE and HFSE by inductively coupled plasma-mass spectrometry (ICP-MS). *Geochem. Int.*, 46, 10, 1016–1022.
- Novoselov, A.A.: 2016, Lithological and petrographic characteristics of aleuropelitic Ishimskian deposits in the western part of Tobol–Ishim interstream area. *Georesources*, 18, 3, Part 2, 206–211. DOI: 10.18599/grs.18.3.10
- Ogorodnov, E.A.: 1971, Morphostructural zoning of the West Siberian Plain. Atlas of the Tyumen region. Moscow, Tyumen, GUGK Publ., 45 pp, (in Russian).
- Rahhal, V. and Talero, R.: 2005, Early hydration of portland cement with crystalline mineral additions. *Cem. Concr. Res.*, 35, 7, 1285–1291. DOI: 10.1016/j.cemconres.2004.12.001
- Regourd, M.: 2001, Cements made from blast furnace slag. In: Hewlett, P.C. (ed.), *Lea's Chemistry of Cement and Concrete*, 4th edn., Butterworth-Heinemann, Oxford, 637–678.
- Rostovtsev, N.N. (ed): 1964, West Siberian Lowland. In: Sidorenko, A.V. (ed.), *Geology of the USSR*. Moscow, Nedra Publ., 44, 550 pp., (in Russian).
- Shatsky, S.B. (ed.): 1978, Paleogene and Neogene of Siberia: Paleontology and stratigraphy. Nauka, Novosibirsk, 3–21, (in Russian).
- Shvetsov, M.S.: 1958, Petrography of sedimentary rocks. Moscow, Nedra Publ., 412 pp., (in Russian)
- Siddique, R. and Khan, M.I.: 2011, Supplementary cementing materials. *Engineering Materials*, Springer-Verlag Berlin. DOI: 10.1007/978-3-642-17866-5\_5
- Smirnov, P.V., Konstantinov, A.O. and Ivanov, K.S.: 2016, Composition and physical properties of the aleuropelitic rocks of Ishim formation (southern part of Tyumen region). Prospects for their industrial application. *Bull. Tomsk Polytech. Univ., Geo Assets Eng.*, 327, 1, 40–45, (in Russian).
- Snellings, R., Mertens, G. and Elsen, J.: 2012, Supplementary cementitious materials. *Rev Miner Geochem*, 74, 1, 211–278. DOI: 10.2138/rmg.2012.74.6
- Taylor, S. R. and McLennan, S. M.: 1985, The continental crust: its composition and evolution. Blackwell Sci, Oxford.
- Unified regional stratigraphic schemes for Neogene and Paleogene deposits of the West Siberian Plain. Explanatory Notes: 2001, Siberian Nauchno-Issled. Inst. Geol. Geofiz., Mineral. Syr'ya, Novosibirsk, (in Russian).
- Vaneev, V.A.: 1968, Mineral raw construction materials base of the Western Siberia and trends of its rational use. Novosibirsk.
- Varlamov, I.P.: 1972, Geomorphology of the West Siberian Plain. Geomorphological map of the West Siberian Plain. Western Siberia Publ., Novosibirsk, 111 pp., (in Russian).
- Vereshchagin, V. I., Melnikova, I. G. and Mogilevskaja, N. V.: 2014, Activation of sintering of construction ceramics based on refractory and fusible clay raw material with additives of marshallite. *Vestn TSUAB*, 6, 109–117, (in Russian).
- Wedepohl, K.H.: 1995, The composition of the continental crust. *Geochim. Cosmochim. Acta*, 59, 7, 1217–1232. DOI: 10.1016/0016-7037(95)00038-2
- Wronkiewicz, D.J. and Condie, K.C.: 1987, Geochemistry of Archean shales from the Witwatersrand Supergroup, South Africa: source-area weathering and provenance. *Geochim. Cosmochim. Acta*, 51, 9, 2401–2416. DOI: 10.1016/0016-7037(87)90293-6
- Zemtsov, A.A., Mizerov, B.V., Nikolaev, V.A., Sukhodrovskiy, V.L., Beletskaya, N.P., Gritsenko, A.G., Pilkevich, I.V. and Sinelnikov, D.A.: 1988, Relief of the West Siberian Plain. Nauka, Novosibirsk, 192 pp., (in Russian).
- Zykin, V.S.: 2012, Stratigraphy and evolution of environment and climate in the Late Cenozoic in the southwestern Siberia. *Akad. Izd. GEO*, Novosibirsk, (in Russian).