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Nature of tonsteins in the Azeisk deposit of the Irkutsk Coal Basin (Siberia, Russia)

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ABSTRACT

In this paper data on the mineral and chemical composition of tonsteins from the Jurassic Azeisk deposit located in the Irkutsk Basin (South Siberia, Russia) are presented. The mineral composition includes kaolinite (87–89%); quartz (3.0–4.0%), cristobalite (4.9–5.3%), illite (1.9–2.1%) and feldspar (1.0–2.0%). Accessory minerals comprise zircon, monazite, uranium oxides, native minerals (gold, silver, nickel, zinc, tungsten, and silicon), sulfides and intermetallic compounds. The tonsteins and coals of the Azeisk deposit have high concentrations of REE, Y, Zr, Hf, U, Th, Ta, Sn, Ga, Cu, Pb, Se, Hg, Sb, and Te. The highest concentrations of these elements were found at the contact with coals. The enrichment of the coal with lithophile rare metals is possibly caused by their leaching from the tonsteins. The accumulation of these trace elements is a characteristic feature in coals both above and below the tonsteins. The width of the enrichment in the coal zone depends on the properties of chemical elements and features of the coal properties and character of interaction between the coals and tonsteins. The authors verify the pyroclastic nature of the initial matter of the tonsteins of the Azeisk deposit. Mineralogical and geochemical data from the tonsteins suggest a felsic (rhyolite) composition for the original volcanic matter that was altered in the aggressive acidic environments of the peat bogs. As a result of the burial of this material in a paleo-peatland some of the elements typical of felsic pyroclastics accumulated.

1. Introduction

Tonsteins occur in coal-bearing sequences worldwide. Typically the beds are thin (<10 cm), the contacts with the adjacent beds are sharp, the color is lighter than the adjacent mudrocks; and the appearance is flint-like, hence the name tonstein (claystone). Although known from the mid-19th century it was only some 30 years ago that it was generally accepted that tonsteins resulted from the alteration of volcanic ash in the coal swamp environment, which led to the formation of kaolinite (Spears, 2012 and references therein). Tonsteins were recognized because they proved to be of value in correlating coal seams and coal-bearing strata. This remains the case, but, in addition, since the beds are volcanic it has been possible to investigate the nature and periodicity of the volcanic activity, to determine absolute ages and establish the tectonomagmatic setting (Van, 1968, 1972, 1973; Spears, 1970, 2012; Bohor et al., 1979; Zarickiy, 1976, 1979, 1989; Crowley et al., 1989; Lyons et al., 1990, 1992, 1994; Admakin, 1991; Chernovyants, 1992; Eskenazy, 1996; Hower et al., 1999; Burger et al., 2000; Yudovich and Ketris, 2000, 2008; Zhou et al., 2000; Kramer et al., 2001; Creech, 2002; Dai et al., 2003, 2011, 2014a; Grevenitz et al., 2003). In addition, the volcanic ash from which the tonsteins formed introduced trace elements into the peat swamp, and in some cases this has led to commercial deposits (Vine, 1955; Hower et al., 1999; Dai et al., 2003, 2010, 2014b; Seredin, 2004; Arbuzov and Ershov, 2007; Seredin and Finkelman, 2008; Seredin and Dai, 2012).

Tonsteins in the Jurassic coals of the Irkutsk Basin were first noted by Chekin (1973) in the Aziesk deposit. The tonsteins were described in detail by Admakin and Portnov (1987), who proposed their derivation from weathered soils on the margins of the basin, which was one of the possible mechanisms for tonstein formation that had been considered by other workers (Spears, 2012).

The aims of the present study are to establish whether the tonsteins in the Irkustk Basin have a volcanic origin, and if so to investigate the mobility of the elements during alteration of the ash based on samples of the tonsteins and the enclosing coals.

The presence of high and often anomalous concentrations of lithophile rare metals (REE, Sc, Be, Y, U, Th, Zr, Hf, Ta), and also Cr, Fe, Co, Cu, Zn, Sb, and Au, is an important geochemical feature of the coals in the Irkutsk Basin in general and in the Azeisk deposit in particular (Arbuzov and Ershov, 2007; Arbuzov et al., 2011, 2014). The ash of individual coal samples has REE concentrations up to 0.3%, Sc – 490 ppm, U — 130 ppm, Th – 360 ppm, Hf – 164 ppm, Ta – 30 ppm, Zn – 0.13%, Co – 616 ppm, Sb – 64 ppm, and Au – 0.15 ppm. Such concentrations are indicative of unusual processes of coal formation and

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the possibility of significant amounts of volcanic ash entering the palustrine environment is one possible explanation.

2. Geological setting

From a geological perspective the region is an ancient Precambrian platform overlain by thick Paleozoic and Mesozoic–Cenozoic sequences. The tectonic–magmatic activity on the platform ended with Triassic trap volcanism. No post-Jurassic volcanism or hydrothermal activity has been recorded in the region.

The Azeisk deposit is located in the north-western part of the Irkutsk Basin (Fig. 1), positioned within the erosion-tectonic depression that developed on the mixed carbonate-siliciclastic Paleozoic rock. The Jurassic rocks are gently dipping (1–2°) towards the axial part of the depression in the northeast and southwest. The Triassic igneous rocks consist of fine-grained to coarse-grained dolerite and gabbro-dolerite. A thick weathering crust, developed on the Triassic and Paleozoic rocks, is recorded below the Jurassic rocks in the Azeisk deposit (Bessolitsyn and Fainshtein, 1963).

The Jurassic coal-bearing Cheremhkovskaya Formation ($J_{1\text{-}2}$čr) consists of about 70 m of friable fine-grained sandstones and siltstones (Cherepovskyi, 2002). Two main productive coal seams (I and II) and three lensoid seams (III, IV and "Verhkny") occur within the formation. The main commercial coal mining source is seam II, which comprises 75% of the coal resources of the Azeisk deposit. The thickness of this seam ranges in general from 3 to 6 m over the whole deposit, but bulges of up to 13 m have been recorded (Cherepovskyi, 2002). The coal is humic, subbituminous B, with low-sulfur content (<1%) and medium ash yield, generally in the range from 11 to 23%. Coal beneficiation in the Azeisk deposit is difficult because of the amount of fine-dispersed clay matter in the organic mass of the coal. Numerous siliciclastic (kaolinite) inter-layers of different thickness and composition occur within the coal seams (I and II). Seven kaolinite tonsteins, ranging in thickness from 0.1 to 20 cm, are documented in the succession, including four tonsteins in seam II (Admakin and Portnov, 1987). In the open-cut mine exposure the tonsteins are distinctive because they occur as thin beds with sharp contacts, their color is paler than the surrounding beds (Fig. 2) and they are lithified. The tonsteins are laterally continuous over a distance of 4 km in the exposed part of the Azeisk deposit.

3. Samples and analytical procedures

To determine the nature of the tonsteins and their role in the accumulation of rare metals and toxic trace elements in the coals of Azeisk deposit, we sampled and studied in detail both the tonsteins and the tonstein-bearing coals. Three tonsteins within seam II, with thicknesses of 1, 3 and 20 cm, were sampled. Fifty-eight tightly spaced samples were taken from four vertical cross-cut profiles in the seam II coal in a distance of 1 km from each other (Fig. 1). The samples include coal, fine-grained sandstone and clay within the coal, and seven samples of tonstein. The length of the sampling intervals ranged from 1 cm to 1 m, and the cross-sections of the channels were 0.05 × 0.03 m (Fig. 2). Tonsteins were found in all four sections sampled. All tonsteins found in the mined coal seam were sampled in detail in Section 3 (Fig. 1) (samples Az-21-09, Az-24-09, Az-26-09, Az-30-09). In Section 1 two tonsteins were sampled (samples Az-9-09 and Az-7-09). In Section 2 only one tonstein sample was collected (sample Az-16-09). Thus, tonsteins no. 1 (Az-7-09, Az-21-09), no. 2 (Az-16-09, Az-24-09) and no. 3 (Az-9-09, Az-26-09) are all represented by two samples and tonstein no. 4 (Az-30-09) by one sample. Tonstein samples and adjoining coals were collected in well exposed parts of the seam in the open pit coal mine. The sampling was undertaken with a steel knife and geological hammer. The upper part of the coal seam was firstly removed, then the coal samples were accurately cut into slices from 1

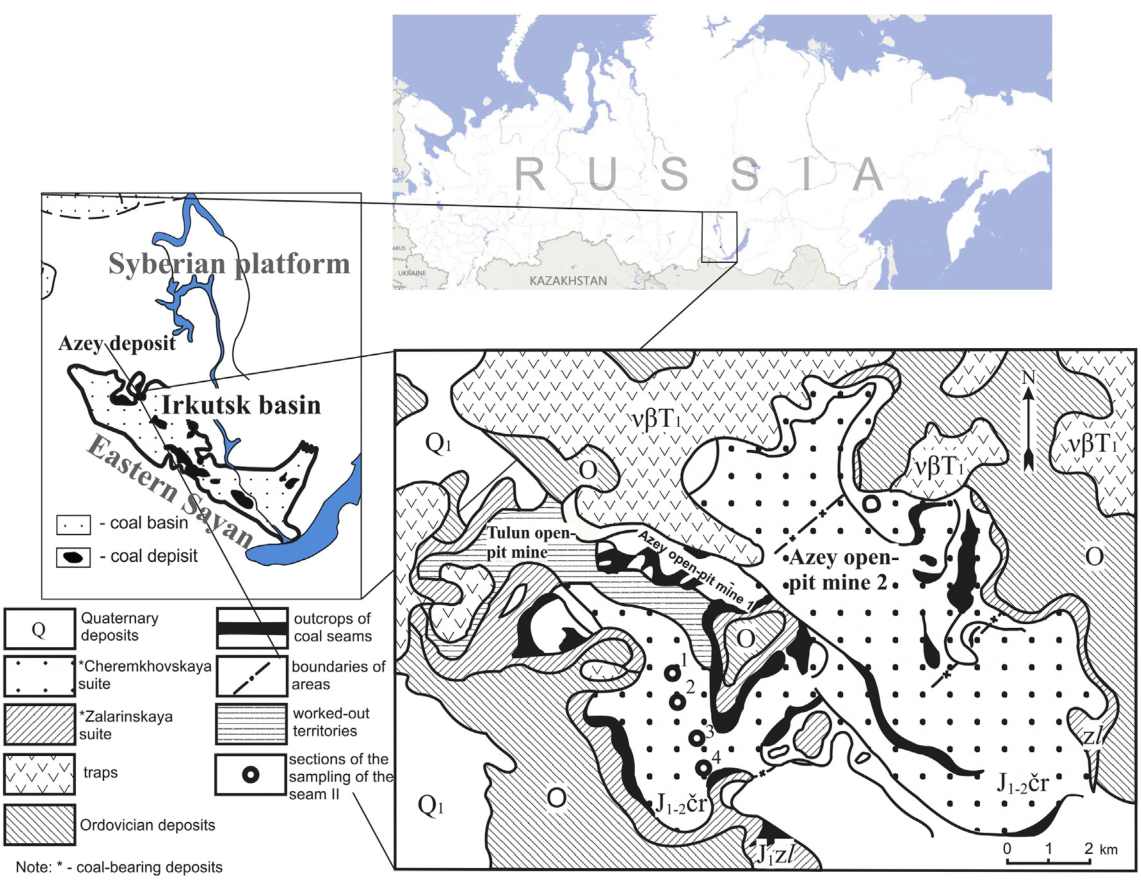

Fig. 1. Location and geologic maps of the Azeisk deposit region (from Coal base of Russia, 2002).

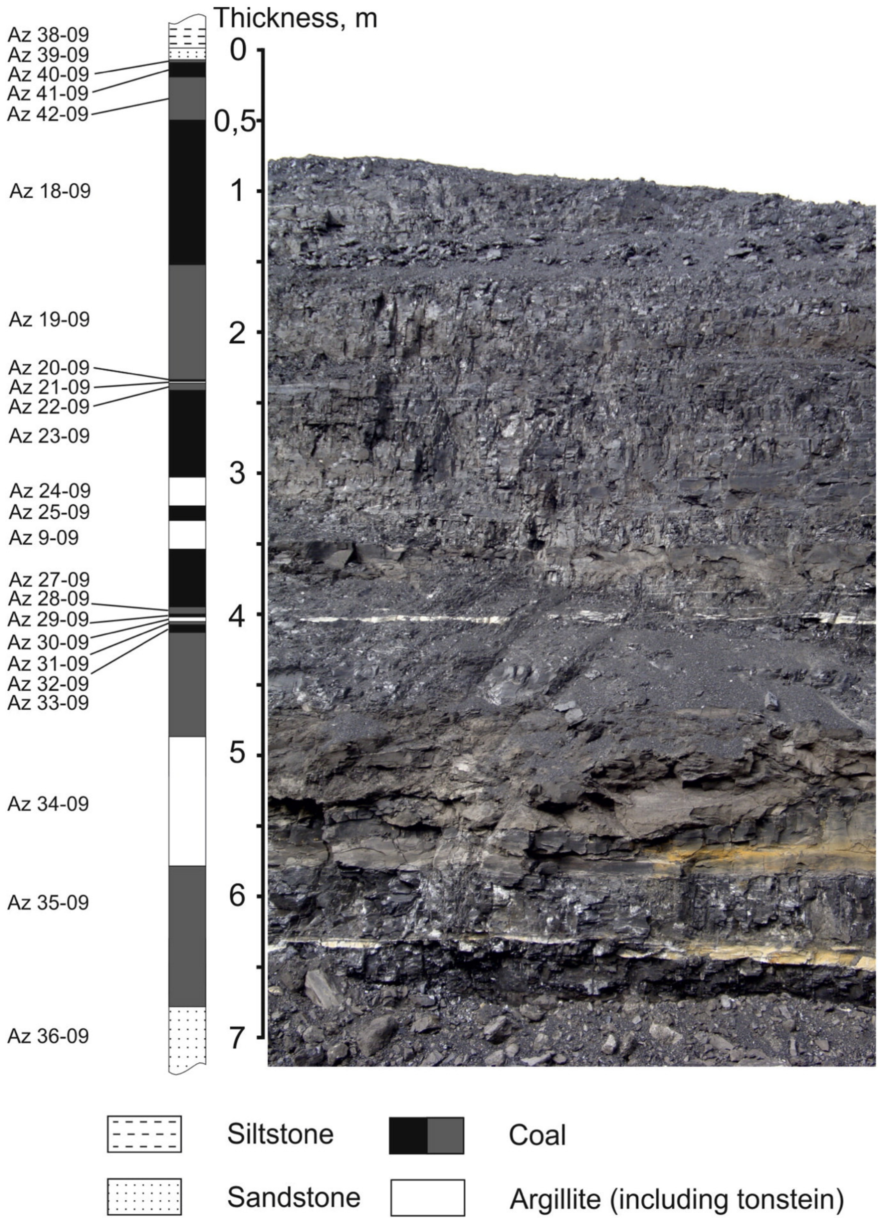

Fig. 2. Photo and the log of the seam II of the Azeisk deposit (sampling shown on the left of the log).White layers are the tonsteins (samples Az 9-09, Az 21-09, Az 24-09, Az 30-09). The coal sampling intervals on the log are colored as gray and black. Sample Az-34-09 is a coaly argillite.

to 5 cm and sample of tonstein of the visible thickness. All samples were packed into plastic bags.

The distribution of minerals and their composition, as well as the composition and structure of the tonsteins and the coal enclosing the tonsteins, were examined in the thin sections using a Zeiss Axioskop-40 petrographic microscope. Further analysis of the minerals was carried out by differential thermal analysis (DTA) and X-ray powder diffraction (XRD). Differential thermal analysis was carried out using an SDT Q600 V20.9 Build 20 at the Scientific-Analytical Center of Tomsk Polytechnic University. The temperature range for sample heating was 20 to 1200 °C, with a heating rate of 10 °C per minute and an airflow of 100 $ml \cdot min^{-1}$. The analyzed sample mass was 40 g. The XRD-patterns were recorded on a Rigaku Ultima IV X-ray diffractometer, using a Cu anode; the voltage of the X-ray tube was 40 kV and the current 30 mA, giving a power of 1.2 kW. Whole rock samples were scanned from 5 to 70° 2θ at a scanning speed 1° per minute with a step of 0.02°. In addition to the bulk samples, clay fractions were also separated by sedimentation following disaggregation and dispersion. In order to fully characterize the clay minerals present the clay fractions were scanned in the air-dried state, then after saturation with glycol overnight and after heat treatment at 350 °C for 1 h. Comprehensive identification of the clay minerals was made following procedures given by Moore and Reynolds (1997). Quantitative mineralogical analyses of the whole rock data were performed by a Rietveld analysis (Bish and Post, 1993) using PDXL and Siroquant software (Taylor, 1991). The composition and modes of occurrence of finely dispersed mineral matter were studied using a Hitachi S-3400N scanning electron microscope (SEM) with Bruker energy-dispersive X-ray analyzer and Oxford Inka Wave spectrometer in the Laboratory of Electron-Optical Diagnostics of Tomsk Polytechnic University. Micromineral phases were identified based on optical characteristics and chemical data.

The XRF analysis of major element oxides (SiO_2, Al_2O_3, CaO, MgO, Fe_2O_3, K_2O, Na_2O, TiO_2, MnO, and P_2O_5) was performed in the X-ray analysis laboratory at the Institute of Geology and Mineralogy in Novosibirsk (Siberian Department of Russian Academy of Sciences). Fused discs were prepared by drying the samples at 105 °C for 1.5 h, then mixing with a flux agent before igniting at 960 C for 2.5 h. The mixture was ignited in platinum crucibles in an inductive oven (Lifumat-2,0-Ox, Germany). The measurements were made on an ARL-9900-XP X-ray spectrometer. State standard rock samples were utilized as controls (MU-1, MU-3, MU-4, SA-1, SCHT-1, SCHT-2, SDO-1, SDU-1, SG-1A, SG-2, SG-3. SGD-1, SGD-2, SGX-1, SGX-5, SGXM-2, SGXM-3, SI-1, SI-2, SNS-1, SNS-2, SOP-1, ST-1) (Karmanova and Karmanov, 2011).

The concentrations of 29 elements (Table 1) in the majority of samples were determined using instrumental neutron-activation analysis (INAA) of the coal without preliminary organic matter ashing, thereby eliminating potential loss of volatile elements. Moreover the same elements were determined by INAA in the coal ash after the preliminary ashing at 815 ± 10 °C. Laboratory analyses of the coal, coal ash, and surrounding rocks were carried out at the Nuclear Geochemical Laboratory of the Department of Geoecology and Geochemistry of Tomsk Polytechnic University in Russia (NGL of TPU). The samples were exposed to radiation treatment in the IRT-T research nuclear reactor. The weight of each INAA sample ranged from 100 mg to 200 mg. The detection limits for these elements are shown in Table 1.

Traditional INAA without special sample preparation can reliably detect 29 elements only (Shtan, 1990). This is not enough for the thorough analysis and geochemical identification of tonsteins. Seven of 14 REE are absent from the range of elements detected: Nb, Y, Zr, Ti and some others, which are important for the identification of the initial tonstein composition. Thus, the tonsteins were additionally analyzed by ICP-MS (62 trace elements). The samples were ground to ≤0.071 μm and dissolved in a mixture of concentrated nitric, hydrofluoric, and hydrochloric acids. They were then subjected to a further nitric acid digestion following the methodology of Oleinikova et al. (2015). The ICP-MS analysis was done on the ELAN DRC-E equipment at the Chemical-Analytical Center "Plazma", Tomsk. The repeatability of the two methods of measurement for the studied group of elements was found to be satisfactory (Table 2).

4. Results and discussion

Although a volcanic source is indicated by the field characteristics of the tonsteins in this work, namely occurrence as thin, well lithified beds with a pale color and with lateral continuity, albeit over a distance of only 4 km, the evidence is by no means conclusive. Conclusive evidence, however, is provided by the textures and the mineralogical and geochemical compositions.

4.1. Mineralogical compositions

The XRD and DTA results show that kaolinite is the dominant mineral, with only small amounts of other minerals (Fig. 3). Furthermore the kaolinite is well ordered, which is a characteristic of tonsteins (i.e. altered volcanic ash), unlike the kaolinite found in the majority of seatearths and fireclays in coal-bearing sequences (Spears, 2012). In thin section the kaolinite is very fine grained and appears isotropic or

Table 1
Detection limits of INAA (ppm) for chemical elements in coal, coal ash and coaly rocks.

Element	Detection limit	Element	Detection limit
Na	20	La	0.03
Ca	300	Ce	0.05
Sc	0.02	Nd	2.0
Cr	0.2	Sm	0.01
Fe	100	Eu	0.01
Co	0.1	Tb	0.05
Rb	0.6	Yb	0.1
Cs	0.3	Lu	0.01
As	1	Hf	0.01
Sb	0.2	Ta	0.05
Ag	0.5	Au	0.01
Sr	7	Th	0.2
Ba	8	U	0.1
Zn	2.0	Br	0.3
Se	0.1		

Table 2
To show a comparison of trace element concentrations (ppm) determined by ICP MS and INAA methods.

Elements	Az-9-09		Az-24-09		Az-30-09	
	ICP Ms	INAA	ICP Ms	INAA	ICP Ms	INAA
Sc	11.8	7.4	24.9	18.1	19.6	12.5
Cr	10.3	12.7	33.0	23.0	12.3	8.4
Fe,%	0.43	0.42	1.21	0.66	1.78	1.88
Co	2.2	2.0	8.7	6.1	3.4	2.9
Rb	3,7	5.6	<0.1	4.7	<0.1	10.8
Sr	47	<25	9.4	<25	24.3	14.6
Sb	1.06	0.81	0.92	0.69	0.32	0.22
Cs	1.92	0.48	<0.1	0.93	0.79	0.88
Ba	51	107	65	78.4	62	70.3
La	30.1	34.6	52.0	50.9	81	90.3
Ce	67.0	66.9	108	90.3	163.0	157.6
Nd	30.4	22.8	48.0	34.3	78.0	58.7
Sm	5.9	5.9	8.4	7.8	13.4	14.2
Eu	0.83	0.87	1.87	1.50	2.6	2.6
Tb	0.82	0.76	1.51	1.39	1.47	1.67
Yb	1.55	1.6	3.8	3.4	2.17	2.2
Lu	0.15	0.20	0.42	0.45	0.30	0.25
Hf	4.5	5.2	4.7	5.0	4.8	6.2
Ta	3.0	2.9	1.5	1.6	1.8	2.0
Th	32.7	35.6	25.2	24.1	12.9	13.7
U	6.9	8.1	9.4	8.2	2.6	3.9

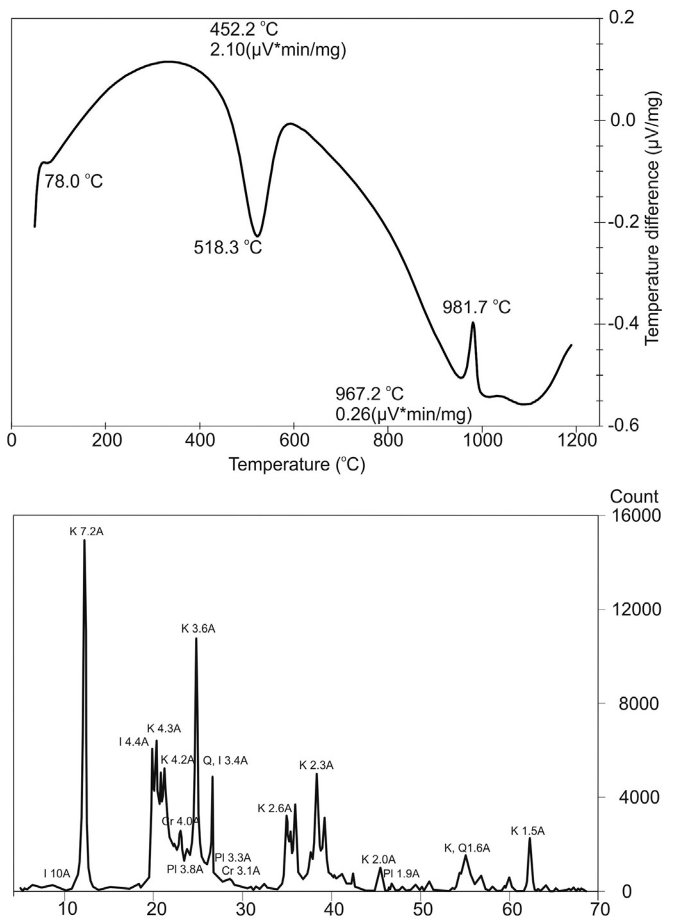

Fig. 3. Differential thermal analysis curve (A) and X-ray diffraction powder pattern (B) of the tonstein (Az-30-09) from the seam II. I: illite; K: kaolinite; Q: quartz; Cr: cristobalite; Pl: feldspar.

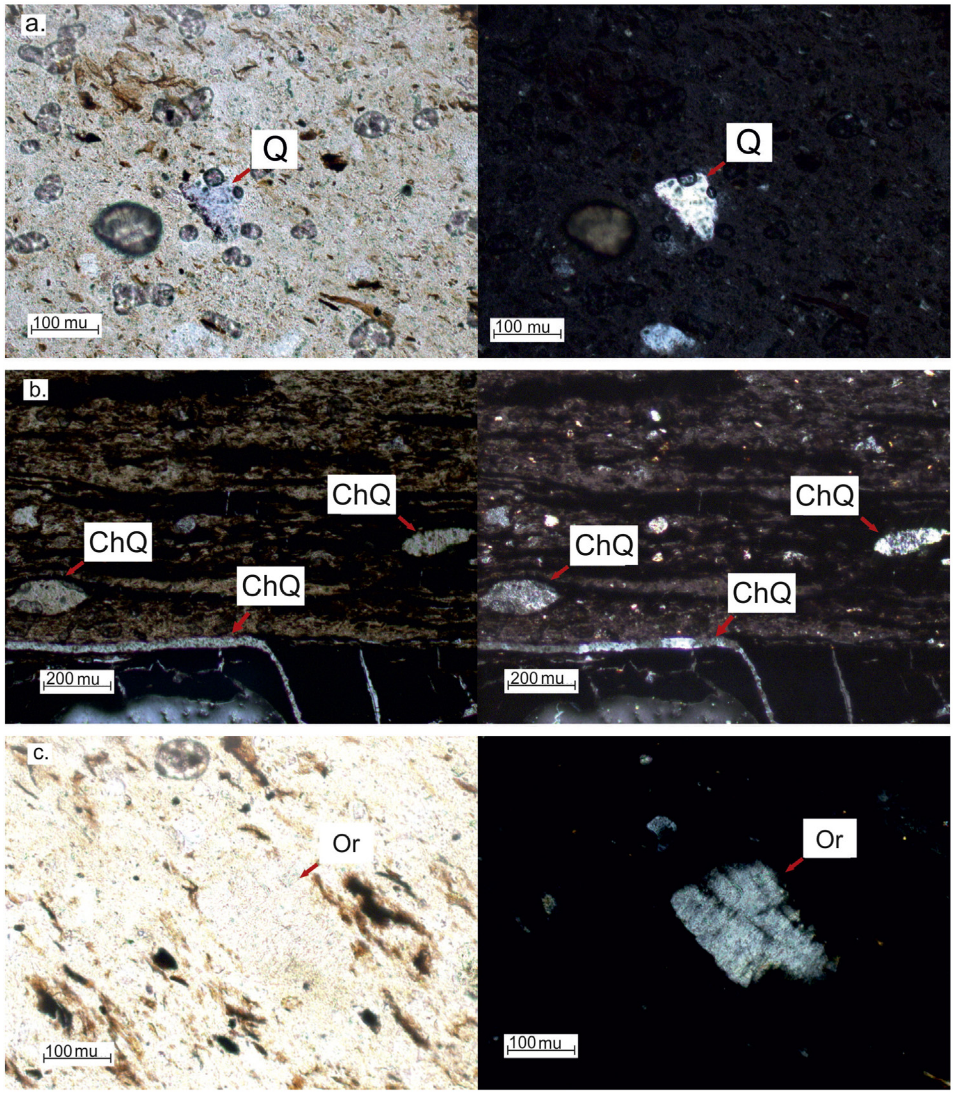

Fig. 4. Petrographic composition of the tonsteins (Az 30-09): a) quartz fragments in kaolinite matrix (Q); b) lens of chalcedony-type quartz (XQ); c) relics of feldspar (Or), replaced by kaolinite. Transmitted-light optical microscopy: open polars (left) and crossed polars (right).

with weak aggregate polarization (Fig. 4), showing that there is some orientation of the crystals.

According to the classification of Schuller and Hoehne (1956) and Burger (1979, 1985) the tonsteins of the Azeisk deposit belong to the group of cryptocrystalline (solid) kaolin tonsteins known as Dichte tonsteins. Although the classification is descriptive and based on petrography, there is a genetic basis. Volcanic tuffs are traditionally classified on the glass-mineral proportions and range from vitric tuffs to crystal tuffs (Pettijohn, 1975). Bouroz et al. (1983) and Bohor and Triplehorn (1993) compared the tonstein classification with tuff nomenclature and interpreted the Dichte tonstein as a clay-altered vitric tuff. The tonsteins in the present work consist almost entirely of kaolinite with a minor admixture (<5%) of allogenic silt-sized quartz particles, kaolinized feldspars (Fig. 4c) and biotite, both still recognizable from the preservation of the original grain shapes. Feldspar was also identified in the XRD scans, although the concentration was low (1.0–2.0%). The low percentage of these volcanogenic minerals is consistent with an altered vitric tuff. Small pyrite and leucoxene grains were also noted under the microscope, and presumably these formed during diagenesis.

The quartz grains are irregular in shape and generally sub-isometric and sharp (Fig. 4a). This form is associated with explosive volcanism rather than normal sedimentary processes and is another indicator of the volcanic origin of the tonsteins. However, there is also evidence of silica precipitation during diagenesis in the form of chalcedony-type cryptocrystalline quartz in the kaolinite matrix and in fissures along and across the bedding. Small lens-shaped cryptocrystalline quartz inclusions were also observed (Fig. 4b). Quartz (3.0–4.0%) and cristobalite (4.9–5.3%) were noted in the XRD scans.

Opal-cristobalite is quite widely spread in sedimentary sequences, due to the transformation of volcanic ash under alkaline or weakly alkaline conditions (Yudovich and Ketris, 2010). Most often it forms an opal–cristobalite–zeolite association. Such an association has not been described, however, in the acid conditions of peat bogs and coal seams. In the Azeisk deposit it has not been fully developed but the presence of α-cristobalite was confirmed by XRD. A fibrous variety of α-cristobalite, called lussatine, is known in rhyolites and felsic lavas (Deer et al., 1963). Opal is a common authigenic mineral in peat and coal conditioned by the redistribution of biogenic and chemogenic silica (Lukashev et al., 1971; Finkelman, 1981; Ruppert et al., 1985). Conditions for the formation of even metastable α-cristobalite (Deer et al., 1963) are substantially different from those which could exist in the brown coals of the Azeisk deposit. Many researchers (Mizota and Aomine, 1975; Mizota et al., 1987; Wallace, 1991; Mizota and Itoh, 1993, Shane, 1996) have found that cristobalite commonly occurs in modern soils formed on tuffs of various composition and that it has a volcanogenic rather epigenetic origin. X-ray diffraction and oxygen isotope data indicate that the cristobalite was inherited from primary volcanic ash rather than formed during pedogenesis (Mizota et al., 1987). This allows presumption of an initial volcanogenic origin and enables it to be studied together with zircon, quartz, sanidine, and apatite as a volcanically-derived feature in tonsteins (Bohor and Triplehorn, 1993, Spears, 2012).

In addition to the kaolinite, minor amounts of illite (1.9–2.1%) were detected by X-ray diffraction. Small proportions of detrital sediment are common in tonsteins (Spears, 2012) and this is thought to be the origin of the illite, which is typically detrital in origin. Admakin and Portnov (1987), in their earlier work on these tonsteins, noted the presence of angular quartz and kaolinized feldspar and biotite grains in a fine grained matrix of kaolinite. They also recorded heulandite, a zeolite, but this has not been confirmed in the present work. One reason why Admakin and Portnov (1987) did not favor a volcanic origin for the tonsteins was the absence of volcanic activity in Central Siberia during the Jurassic.

Euhedral crystals of zircon with well-developed crystal faces were identified using SEM techniques (Fig. 5). Such crystals are characteristically volcanogenic. Zircon is a common accessory mineral in felsic igneous rocks and because it is a resistant mineral it is common in felsic tonsteins. However, zircon is rare in alkali tonsteins (Zhou et al., 2000; Dai et al., 2011). The tonstein terminology reflects the original ash

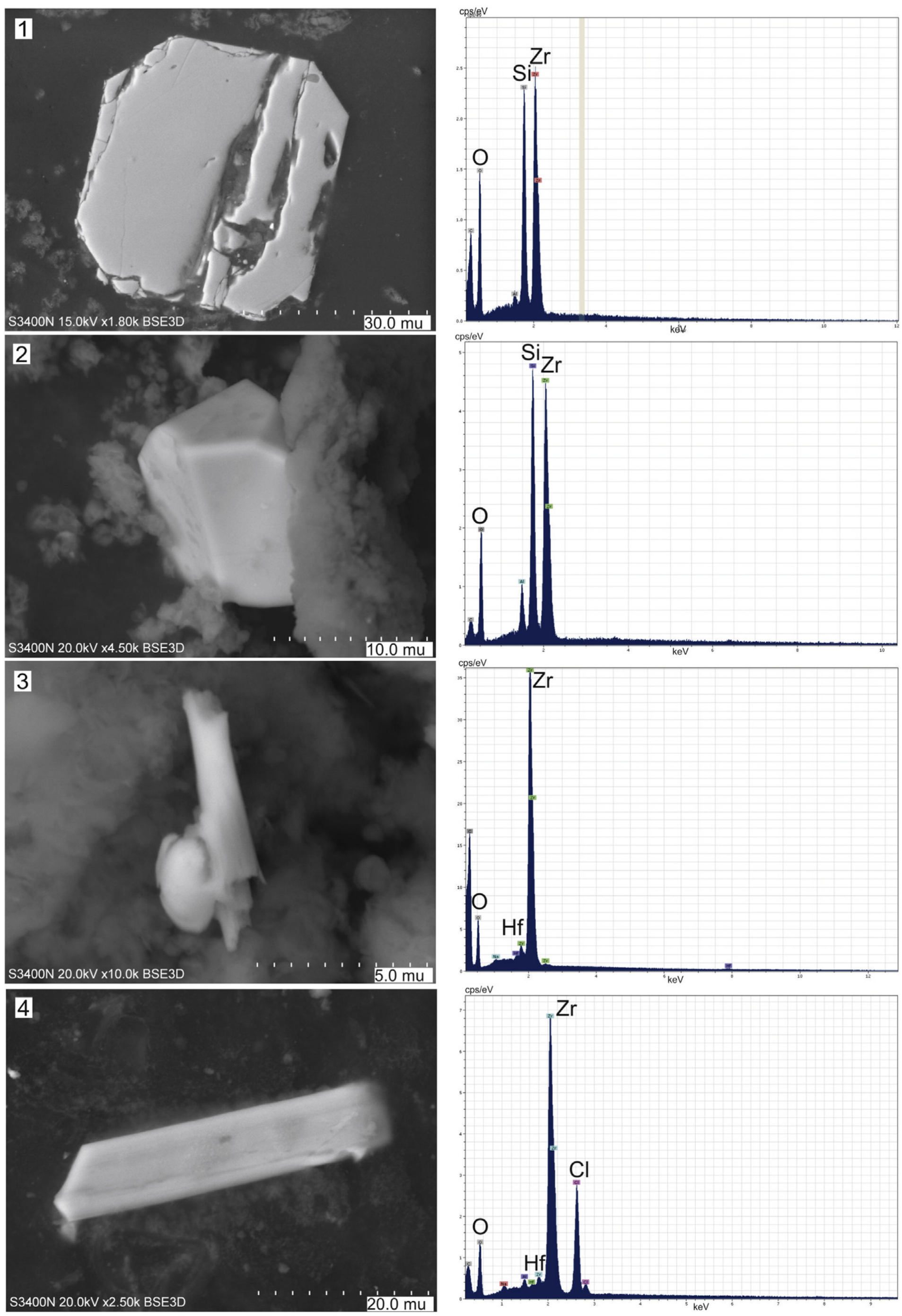

Fig. 5. Zircon and baddeleyite crystals in tonsteins and coal ash. Images and EDS spectra. 1 — zircon crystals in the tonsteins (Az 21-09), polished sections, backscattered electron image; 2 — zircon crystals (Az 30-09) in dust, backscattered electron image; 3 — baddeleyite crystal in coal ash over a tonstein (Az 29-09), backscattered electron image; 4 — baddeleite crystal with Cl in coal ash under the tonstein (Az 31-09), backscattered electron image.

composition expressed in somewhat broad categories. In a group of Euramerican tonsteins studied by Lyons et al. (1994), zircon was present in all samples. Those tonsteins formed from a high-silica rhyolitic ash, based on analyses of glass inclusions in volcanic quartz grains; that is, they are felsic tonsteins. The presence of zircons in the Irkutsk coals suggests that the original ash composition was also possibly felsic.

Pyrite and other sulfides, including chalcopyrite, galena and sphalerite, were identified using SEM techniques, but not in the XRD scans, presumably because of low abundance. These minerals are thought to be diagenetic. Heulandite was recorded in tonsteins by Admakin (1991), and this mineral is thought to be present in the current samples based of the recognition of a calcium aluminosilicate using the electron microscope.

In the coal, directly at the contact with the tonsteins, we observed well faceted crystals and tube formations of baddeleyite (Fig. 5). Even though baddeleyite (ZrO_2) was not found in the tonsteins, its occurrence in the coal would appear to be directly connected with tonstein formation. The appearance of the baddeleyite crystals indicates very limited transportation (input with volcanic ash) or formation in situ. Because baddeleyite was only found in coals near their contact with the tonsteins an authigenic formation is more likely. It seems that some zirconium migrated from the tonsteins into the adjoining coal, thus forming the unusual baddeleyite. The weak migration ability of Zr and the absence of visible relics of zircon destruction in the tonsteins of seam II in the Azeisk deposit permits us to postulate that less stable zirconium-bearing minerals were present in the initial volcanic ash. The presence of different zirconium-bearing minerals of complex composition in the coal and coal ash is indicative of such a possibility (Arbuzov et al., 2014, 2015).

4.2. Geochemical compositions

The major element analyses of three tonstein samples are shown in Table 3. Silica and alumina are the major components, as would be expected from the kaolinite composition. In comparison with an idealized kaolinite (Table 3) the tonsteins contain proportionally more SiO_2 compared with the Al_2O_3, which is due the small amount of quartz and cristobalite detected in the tonsteins. The total concentration of the other major elements, i.e. TiO_2, F_2O_3, MnO, CaO, MgO, K_2O, Na_2O, and P_2O_5, ranges from 3 to 6% in the tonsteins of the present study. A small amount of Fe^{3+} may present in the kaolinite structure substituting for Al^{3+} (Deer et al., 1962) but iron minerals, notably pyrite, are known to be present. There is also an excess of Ca, which can be accounted for by carbonates and heulandite. Although there is a small deviation from the idealized kaolinite, major differences occur between the tonstein analyses and those of possible source volcanics. To illustrate this a representative analysis of a rhyolitic magma is also given in Table 3. This analysis is of glass inclusions within volcanic quartz from a tonstein petrographically similar to those in the present work (analyses from Lyons et al. (1992), Table 4). What this demonstrates is the

Table 3
Major element concentrations (%) in tonsteins from seam II.

Components	Tonsteins*			Glass inclusions**
	Az-9-09	Az-24-09	Az-30-09	
SiO_2	46.38	46.53	46.21	73
Al_2O_3	34.49	36.09	33.61	11.7
CaO	1.51	1.15	0.89	0.5
MgO	0.40	0.29	0.52	0.02
Fe_2O_3	2.12	0.91	3.47	0.7
Na_2O	0.16	0.09	0.16	2.8
K_2O	0.21	0.19	0.45	4.1
TiO_2	0.52	0.34	0.31	0.07
MnO	0.02	0.01	0.01	0.02
P_2O_5	0.07	0.04	0.14	n.d.
LOI	13.88	14.32	14.05	n.d.
Sum	99.77	99.96	99.82	94.7
SiO_2/Al_2O_3	1.34	1.29	1.37	6.24
TiO_2/Al_2O_3	0.015	0.0094	0.0092	0.006

*Based on organic-free basis. ** Lyons et al. (1994); Table 4 lot 169).

Table 4
Trace element concentrations (ppm) in the tonsteins of seam II.

Elements	Tonsteins[1]			Clay shale[2]
	Az-9-09	Az-24-09	Az-30-09	
Sc	11.8	45.5	23.7	15.0
Cr	20.2	57.5	15.8	76.0
Co	3.2	15.3	5.4	19.0
Ni	43.1	40.0	6.6	47.0
Cu	73.0	118.0	22.0	36.0
Zn	42.1	37.3	285.0	52.0
Ga	62.0	58.3	43.5	16.0
Ge	2.2	2.5	<0.1	2.0
As	3.3	4.8	3.7	9.3
Se	1.3	8.0	<0.5	0.36
Br	7.7	4.3	<0.1	57
Rb	8.9	11.8	20.5	130
Sr	50.9	108	38.4	240
Y	38.2	118	44.8	31.0
Zr	293	500	402	190
Nb	10.8	30.3	4.3	11.0
Sn	30.2	23.0	14.6	3.5
Sb	1.3	1.7	0.4	1.0
Te	0.2	<0.1	<0.1	0.01
Cs	0.8	2.3	1.6	10.0
Ba	170	196	133	460
La	47.9	130	130	48.0
Ce	107	270	261	75.0
Pr	12.9	32.0	34.1	10.0
Nd	48.3	120.0	124.8	36.0
Sm	9.4	21.0	21.4	8.0
Eu	1.3	4.7	4.2	1.2
Gd	8.3	26.3	21.8	5.8
Tb	1.3	3.8	2.4	0.83
Dy	6.7	22.0	12.8	4.4
Ho	1.1	3.6	1.8	0.7
Er	2.5	9.9	4.1	1.9
Tm	0.4	1.9	0.5	0.6
Yb	2.5	9.5	3.5	2.5
Lu	0.2	1.05	0.48	0.39
Hf	8.3	12.5	11.7	5.0
Ta	4.1	4.8	3.8	1.4
Au	0.031	0.015	0.0093	0.0065
Hg	0.074	0.26	0.31	0.089
Pb	142.0	71.2	15.0	14.0
Th	56.6	60.3	25.9	10.0
U	12.9	20.5	7.5	4.5

Note: 1, Based on organic-free basis; 2, according to Grigor'ev, 2003.

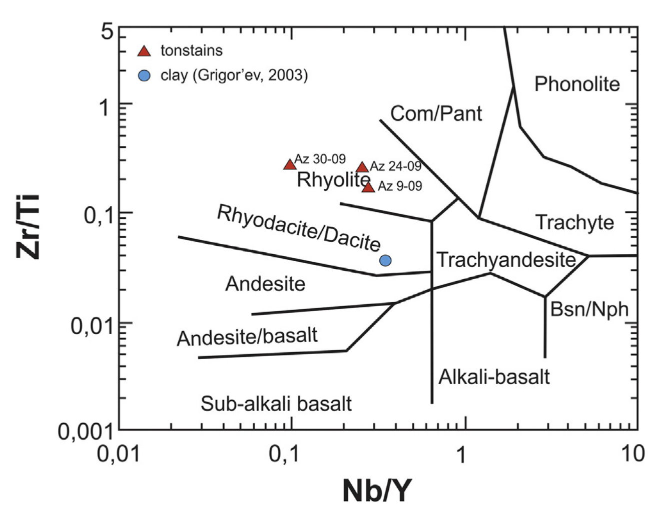

Fig. 6. Nb/Y and Zr/Ti classification diagram of the tonsteins in the Azeisk deposit according to Winchester and Floyd (1977).

Table 5
Trace element concentrations (ppm) in the tonstein (Az-30-09) and the ash of the associated coal.

Elements	Element content						
	Az-27-09	Az-28-09	Az-29-09	Az-30-09	Az-31-09	Az-32-09	Az-33-09
Sc	330	448	185	23.7	298	425	268
Cr	293	660	321	15.8	404	470	374
Co	275	322	148	5.4	234	272	118
Rb	<10	43.9	9.6	20.5	48.1	<10	<10
Sb	4.4	7.1	3.7	0.4	5.9	8.8	4.7
Ba	667	616	1384	133	660	898	225
La	143	145	521	130	328	133	162
Ce	250	166	673	261	462	205	224
Nd	247	128	345	125	218	172	83.6
Sm	37.2	40.5	72.9	21.4	59.8	43.0	32.4
Eu	13.8	17.6	20.2	4.2	19.8	14.3	11.7
Tb	15.0	9.8	15.5	2.4	19.9	18.7	10.0
Yb	39.8	60.8	35.5	3.5	55.6	51.9	27.1
Lu	6.1	9.3	4.1	0.48	6.4	7.0	3.6
Hf	29.9	164	103	11.7	137	29.7	12.3
Ta	<0.1	8.6	17.4	3.8	27.9	<0.1	1.5
Au	0.065	0.059	0.086	0.0093	0.120	0.105	0.056
Th	72.6	360	228	25.9	340	85.1	60.8
U	22.6	93.5	54.5	7.5	81.9	48.5	22.2
Th/U	3.2	3.9	4.2	3.5	4.2	1.8	2.7
Sum of REE	752	577	1687	548	1170	645	554
Distance from tonstein, cm	40	5	2	Tonstein	2	5	100

Note: Az-27-09, Az-28-09, and Az-29-09 –– samples of coal ash over the tonstein; Az-31-09, Az-32-09, and Az-33-09 — samples of coal ash under the tonstein.

concentration of Al_2O_3 relative to the other elements and, in particular, loss of SiO_2, Na_2O and K_2O during the alteration process. In order to prove the volcanic origin and to characterize the composition of the original volcanic ash it is necessary to focus on elements known to be immobile in the alteration process, and whose concentrations differ with magma type and at the same time differ to normal sediments. Immobility may be due to the resistate nature of the volcanogenic minerals, such as zircon, or the low solubility of elements during the alteration process. Aluminum is one example of the latter, but there are less obvious possibilities, including the precipitation of elements such as Pb and Zn because of the presence of reduced sulfur species during diagenesis. Retention of elements is not restricted to the tonstein, and the adjacent coal may also play an important role, as discussed later in the text.

Aluminum and other hydrolysate elements, including Ti, Zr, Hf, Y, Nb, Ta, REE, would be expected to be relatively immobile in the alteration process. In order to establish the volcanic origin and composition from the element concentrations, it is desirable to use element ratios rather than absolute concentrations, to overcome concentration effects due to loss of mobile elements in the alteration process. The TiO_2/Al_2O_3 ratio is one such parameter that has been used. Spears and Kanaris-Sotiriou (1979) showed that this ratio was less than that in normal sediments for a tonstein which had formed from acidic volcanic ash and greater in one which had formed from basic ash. TiO_2/Al_2O_3 values of <0.02 have been suggested for felsic tonsteins (Yudovich, 1981; Addison et al., 1983; Yudovich and Ketris, 2000; Burger et al., 2002). This ratio in the tonsteins of acid, alkaline and mafic composition from the Permian coals of China has confirmed values of <0.02 for TiO_2/Al_2O_3 in silicic tonsteins (Dai et al., 2011). The tonsteins of the Azeisk deposit have values of this ratio between 0.0094 and 0.015, which appears to indicate a felsic volcanic origin. Other element ratios that have been used to characterize the tonsteins include Zr/Al, Cr/Al and Ni/Al (Spears and Kanaris-Sotiriou, 1979), which were used with the Ti/Al ratio in a discriminant function analysis to improve the volcanic designation. However, greater subdivision of the volcanic ash was achieved in the classification diagram of Winchester and Floyd (1977), based on Zr/Ti and Nb/Y, and this diagram has been widely used in tonstein studies (Spears, 2012). In the present work, the analyses of the three tonsteins all fall in the rhyolite field (Fig. 6), which is consistent with the petrographic evidence discussed above.

The geochemical characteristics of the tonsteins in this study indicate an acidic or subalkaline composition of the initial volcanic material. Such volcanics are substantially enriched in REE, Y, Zr, Hf, U, Th, Ta, Sn, Ga, Cu, Pb, Se, and Te, compared with the mean composition of clay shale (Table 4).

The coals, and especially the coals adjacent to the tonsteins, are anomalously enriched in the above-mentioned elements (Table 5; Fig. 7). Concentrations of lanthanides in the coal ash of individual samples reach up to 0.1–0.2%, thorium – 360 ppm, uranium – 130 ppm, and tantalum – 28 ppm. Accumulation of these trace elements is characteristic of the coal immediately above and below the tonsteins.

Possible leaching of REE from tonsteins and the formation of authigenic minerals near the contact with tonsteins have been recognized in some studies (Crowley et al., 1989; Hower et al., 1999; Dai

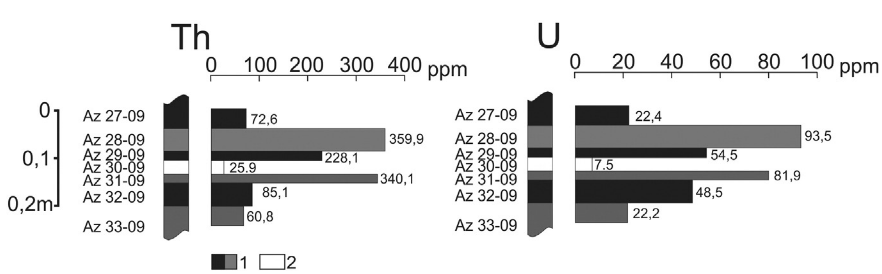

Fig. 7. Distribution of U and Th in the ash of coal from the middle part of seam II, close to the tonstein: 1) coal, sampling intervals; 2) tonstein; figures on the right of the diagram refer to the concentrations of U and Th; H = length of the sampling interval.

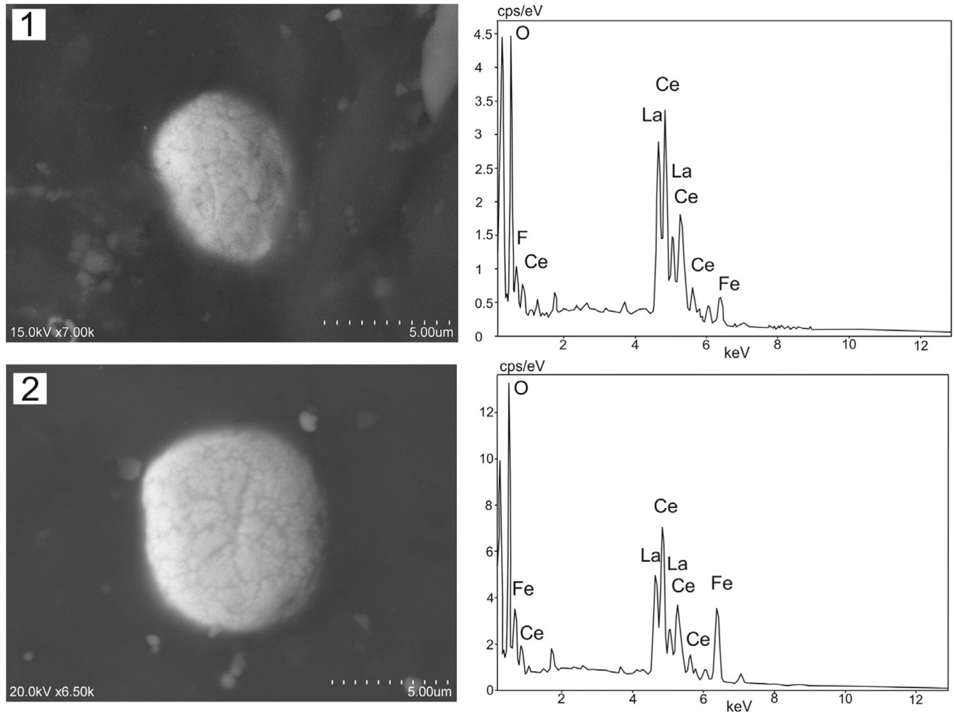

Fig. 8. Carbonates of rare-earth elements in coal of seam II in the Azeisk deposit. Images and EDS spectra. 1 — Polished sections of the coals, bastnaesite in the coal, backscattered electrons image (Az 26-09); 2 — Polished sections of the coal, bastnaesite with FeO in coal, backscattered electron image (Az 27-09).

et al., 2006, 2008; Wang, 2009). Explaining the nature of anomalous REE enrichment of coal adjoining the Fire Clay tonstein in the Appalachian Basin, Hower et al. (1999) pointed to monazite as the main mode of occurrence for the REE. In the Azeisk deposit, REE carbonates as well as monazite also commonly occur (Fig. 8). The occurrence of rare earth carbonates is only possible if there is an excess of REE, presumably leached from the tonstein and reacting with carbonate-bearing water. Clastogenic input of rare earth carbonates (bastnaesite) into the coal seams is unlikely because of weak carbonate stability during transportation under surficial weathering conditions in a humid climate. However, rare-metal carbonatite deposits do occur in the folded margins of the Irkutsk coal basin, 100–150 km to the south of the Azeisk open-cast mine. These deposits (Belosiminskoe, Bolshetagninskoe, and Sredneziminskoe) are enriched with rare earth carbonates (Frolov and Belov, 2000).

The substantial enrichment of rare earth elements in the coal at the contact with the kaolinite (tonstein) layers clearly suggests that the tonsteins were responsible, and possibly indicates their original composition (felsic), rather than that the REEs originated from weathered crust

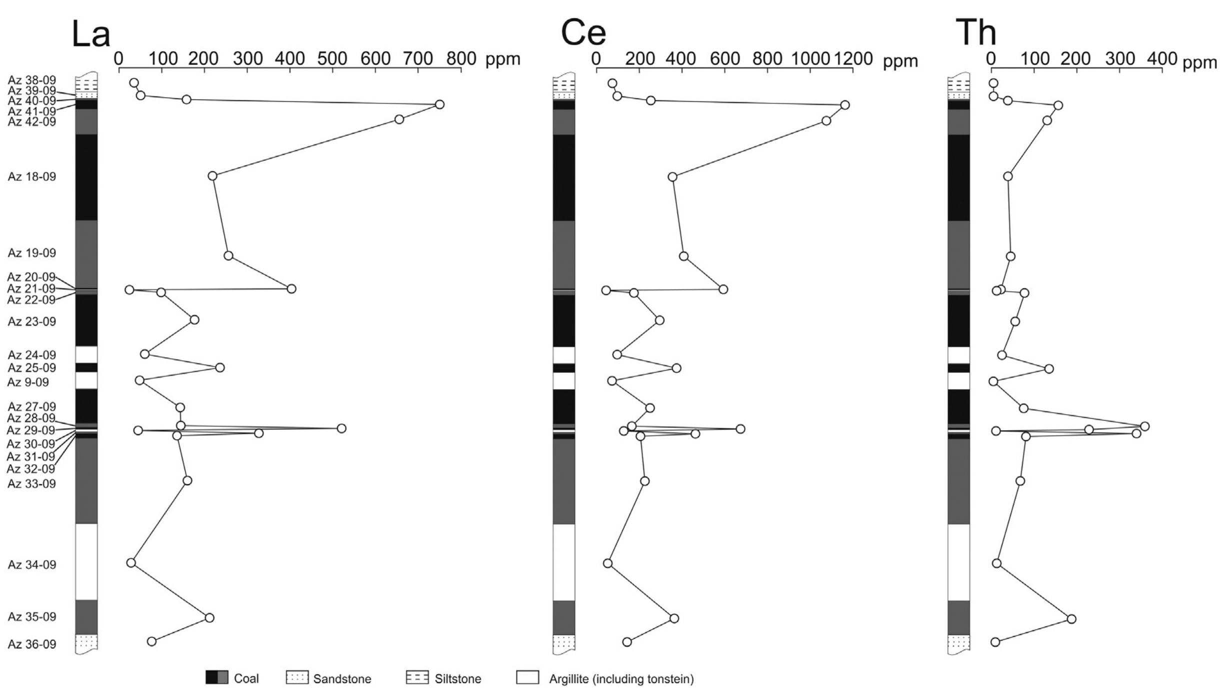

Fig. 9. Distribution of La, Ce, and Th in the vertical section of seam II: 1) coal, sampling intervals; 2) sandstone; 3) siltstone; 4) intra-formational rock layers to McDonough and Sun (1995).

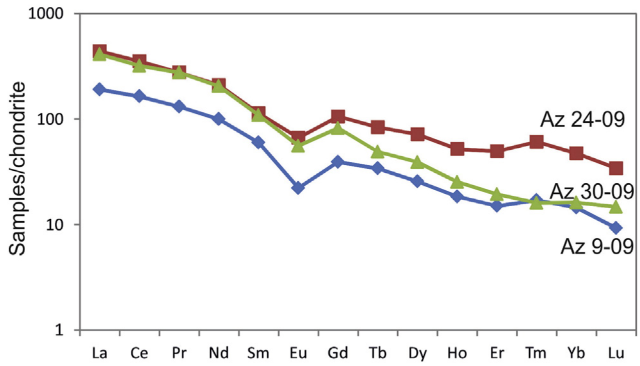

Fig. 10. Normalized curves of the REE distribution in tonsteins of seam II of the Azeisk deposit. Normalized to coaly chondrites according.

material. If the tonsteins had formed from re-deposited material derived from weathered crust, which has given the evidence considered earlier in the paper is not thought to be the case, most of the rare elements would have been lost during weathering and transportation of the clastic matter. The study of ancient and modern crustal weathering (Balashov, 1976) shows that residual products are usually somewhat enriched in REE. Zones of weathering profiles enriched in authigenic clay minerals tend to have low concentrations of REE in comparison with the substrate rocks and the eluvial zone (Alfimova et al., 2011). Therefore, kaolinites re-deposited from crustal weathering zones are always poor in lithophile rare metals in comparison with the initial substrate. This provides further evidence demonstrating that the pre-Mesozoic and early Mesozoic weathered crust in the margins of the Azeisk deposit could not have been a source for the anomalous concentrations of REE, Th, U, Y, Zr, Hf, Sn, and Ta in the tonsteins and the near-tonstein parts of the coal seam.

The rock composition in the main source area for the coal basin (north and east margins) also indicates the impossibility for accumulation of anomalous concentrations of rare earth elements in the tonsteins and coals of the Azeisk deposit (Timofeev, 1970). The weathered crust at the margins of the Azeisk deposit is developed on mixed terrigenous-carbonate sedimentary rocks of Ordovician age and on the Triassic traps of the Siberian platform. Both rock types have low concentrations of lanthanides and other lithophile rare metals. The sedimentary and trap rocks on the Azeisk deposit margins can, however, be considered as a source for anomalous concentrations of scandium and cobalt in the coals. Mafic rocks are generally enriched in Sc compared to other types of rocks, but they have low concentrations of lithophile rare metals, including lanthanides (Grigor'ev, 2003; Kopylova and Tomshin, 2011). The tonsteins of the Azeisk deposit are notable for the high concentrations of lithophile rare metals, but have low concentrations of Sc, Ni, Co, Ti, and Cr (Table 4). This also proves that the tonsteins could not have been derived from basic igneous rocks, which is consistent with the conclusion reached earlier in the text of a felsic (rhyolitic) origin.

Tuffs and tuffites of rhyolitic composition have been found in the Jurassic deposits of the Cheremkhovskaya and Kudinskaya Formations in the south of the basin in the Priirkutskaya depression (Kiziyarov and Meshalkin, 1978; Meshalkin et al., 1983). Although the rare-metal composition of these rhyolitic rocks has not been studied in detail, it is known that they are enriched in U, Th and Sn, and have the same age as the tonsteins of the Azeisk deposit (Kiziyarov and Meshalkin, 1978). Therefore, these pyroclastics could also be a source for the high concentrations of lithophile rare metals in the tonsteins and adjacent coal layers in the Azeisk deposit.

The study of a limited range of major and trace elements in modern volcanic ash formed from the eruption of a central type volcano in Italy (Albert et al., 2012), showed that the ash, of rhyolite composition, had anomalously high concentrations of Th, U, Y and Ta, and also a negative Eu anomaly. The geochemistry allows these ashes to be distinguished from tuffs of trachyandesite, andesite and more basic composition. The criterion of a pronounced negative Eu anomaly is clearly present in the tonsteins of the Azeisk deposit (Fig. 9). The Eu/Eu* ratio in the studied tonsteins ranges from 0.46 to 0.61. Such a coefficient of Eu

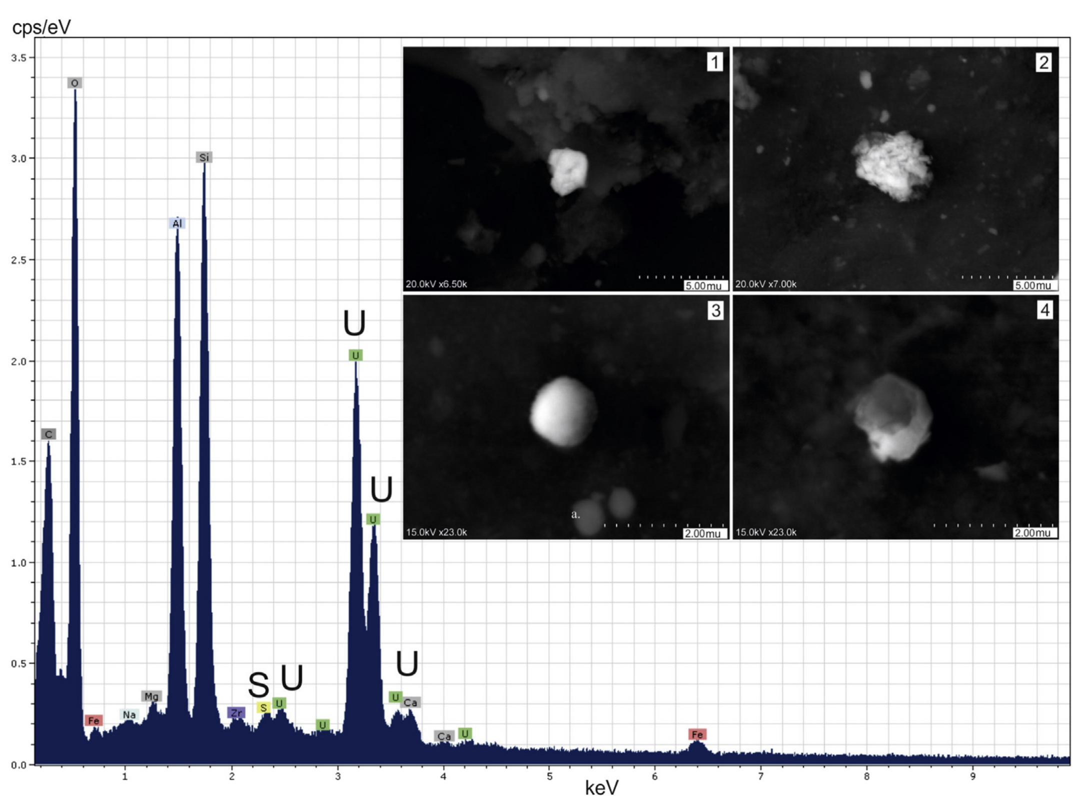

Fig. 11. Images and EDS spectra of spherical bodies of uranium oxides in the tonsteins (Az 30-09). Polished sections of the tonstein, backscattered electron image.

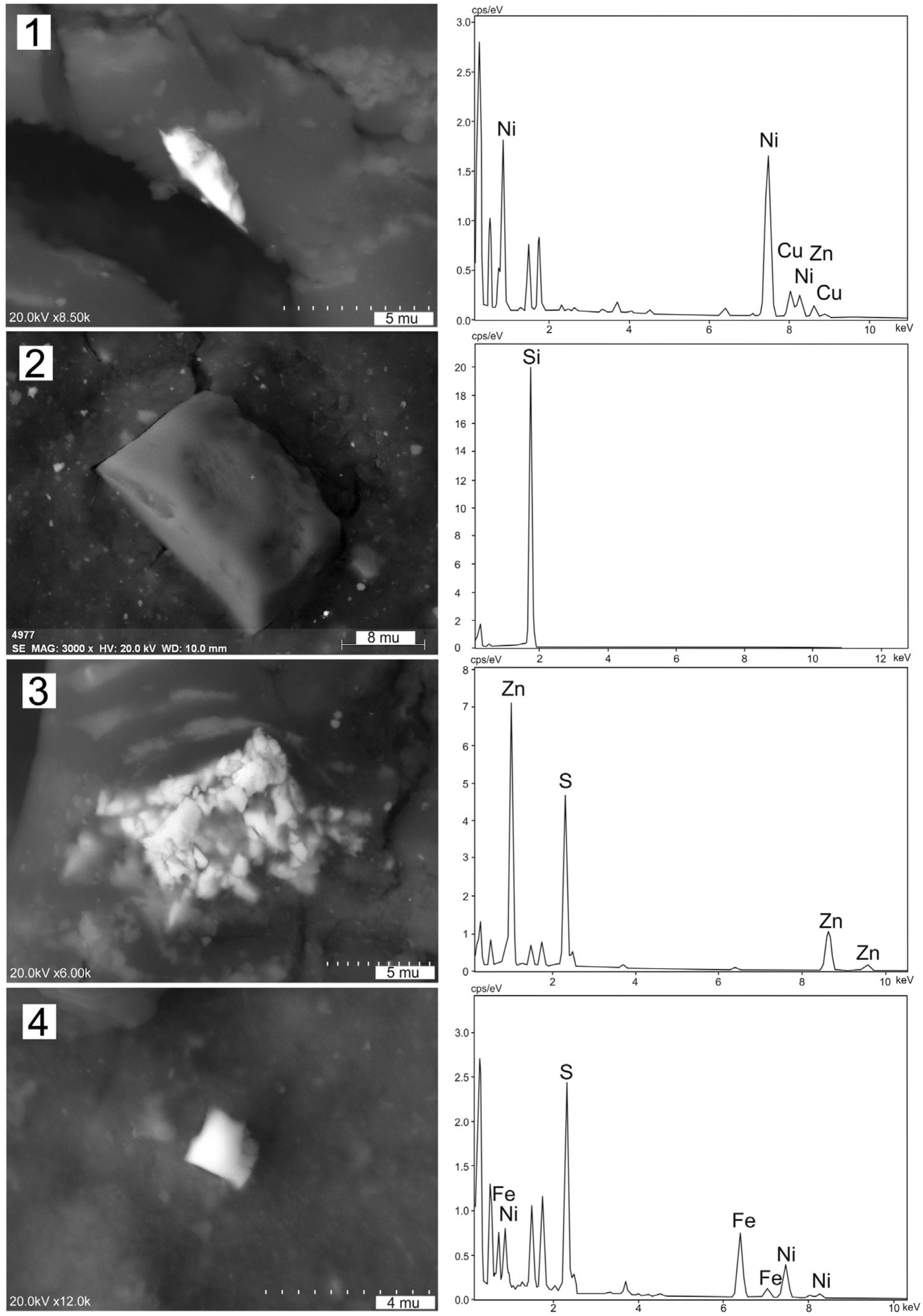

Fig. 12. Native elements, intermetallic compounds and sulfides in the tonsteins of the Azeisk deposit (Az 30-09). Images and EDS spectra. 1 — intermetallic compounds of Ni, Cu and Zn; 2 — native Si; 3 — ZnS (sphalerite); 4 — Fe-Ni sulfide. Polished sections of the tonsteins, backscattered electron image.

depletion is characteristic for Phanerozoic I-type granitoids (Taylor and McLean, 1985) and is consistent with a rhyolitic composition for the initial material of the tonsteins as deduced earlier in this paper.

An intensive alteration of the pyroclastics in an aggressive peat-forming environment may lead to migration of REE, U, Th, Ta, Sn and other chemical elements and to their enrichment in the nearest peat layers (Fig. 10). An acidic peat environment would be favorable for the formation of authigenic minerals in the tonstein as well. For example, spherical bodies of uranium oxide 1–2 μm in diameter were observed in the tonsteins under the SEM, as well as sulfur in the EDS spectrum (Fig. 11). These could have been formed by a process of uranium reduction involving H_2S bubbles, possibly similar to the mechanism described by Kochenov et al. (1977). The penetration of H_2S bubbles into unconsolidated ash horizons probably occurred when the horizons were still permeable to gases, and may have stopped before the total alteration of the tonsteins to kaolinite had been completed. This may explain the high uranium content in the tonsteins.

Widespread occurrence of native elements (gold, silver, nickel, tungsten, and silicon), sulfides and inter-metallic compounds (Il'enok, 2013) also points to a reducing environment (Fig. 12). The latter is characteristic of the alteration process of the volcanic ashes into the tonstein in the Azeisk deposit.

Another geochemical feature indicating a possible role of pyroclastics in formation of the tonsteins is the high Hg and Sb concentrations in both the tonsteins and the coals of the Azeisk deposit. The Hg concentration in some tonstein samples reaches up to 0.84 ppm, and in the coal 1.2 ppm; the Sb concentration in the coal ash reaches up to 64 ppm. Some tonsteins also have anomalous Cu concentrations (up to 0.06%).

A study of the composition of condensates and magmatic gases, new-fallen ash and magma, atmospheric fallout and aerosols close to gas outlet and under the tail area of gas–ash clouds during the eruption of Tolbachik volcano in Kamchatka in 1976 (Miklishansky et al., 1979), showed enrichment of volatile elements (As, Sb, Hg, Cu, and others) in the atmosphere in the region of the eruptions. These elements associate with the steam–gas phase and become concentrated on the surface of sub-micrometer ash particles, which are in turn able to reach stratosphere layers and influence the global input of elements on to the Earth's surface. This mechanism may explain the high concentrations of Hg, As and Cu in some tonsteins of the Azeisk deposit. However, such anomalies in the Azeisk deposit are not necessarily proof of the pyroclastic occurrence and may also be connected with other sources, such as hydrothermal activity. Such Hg occurrences are known in the western margin of the Irkutsk Basin, and numerous manifestations of Cu mineralization (copper-bearing sandstones and siltstones) have been found in the basement of the Riphean Platform terrigenous deposits (Domarenko and Arbuzov, 1989).

5. Conclusion

The study of mineral and chemical composition of the tonsteins of the Azeisk deposit in the Irkutsk Basin has revealed their mineral composition, namely the predominance of kaolinite (87–89%), quartz (3.0–4.0%), cristobalite (4.9–5.3%), illite (1.9–2.1%) and feldspar (1.0–2.0). Zircon, monazite, baddeleyite, bastnaesite, uranium oxides, native minerals (gold, silver, nickel, zinc, tungsten, silicon) and inter-metallic compounds were found in minor concentrations.

The tonsteins and coals of the Azeisk deposit have high concentrations of REE, Y, Zr, Hf, U, Th, Ta, Sn, Ga, Cu, Pb, Se, Hg, Sb, and Te. The highest concentrations of these elements were identified in the ash of coals at contacts with the tonsteins, and enrichment of the coal in lithophile rare metals is attributed to leaching from the tonsteins. The enrichment of trace elements in the coals occurs in a narrow zone both above and below the tonstein layers. The width of the enrichment zone depends on the properties of the element, the coals and the migration environment.

The pyroclastic nature of the initial matter of the tonsteins in the Azeisk deposit has been identified. The mineralogical and geochemical data indicate a felsic (rhyolite) composition of the initial volcanogenic material. This is determined from the presence of relic feldspars, biotite, and cristobalite grains, a typical range of accessory minerals (zircon, monazite), and the geochemistry of the tonsteins, particularly of those elements considered immobile in the alteration process. The tonsteins have low TiO_2/Al_2O_3 ratios (<0.02), which is characteristic for felsic pyroclastics, and are enriched in REE, Y, Zr, Hf, U, Th, Ta, Sn, Pb, Cu, Au, and Hg. In the volcanic discrimination diagram of Winchester and Floyd (1977), based on Zr/Ti and Nb/Y ratios, the tonsteins fall within the rhyolite field.

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