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ORIGINAL PAPER

ZEOLITE-BEARING ROCKS FROM ELUVIAL DEBRIS OF SHCHUCHINSKIJ SYNCLINORIUM (POLAR URAL, RUSSIA): NEW PETROGRAPHICAL AND MINERALOGICAL DATA

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ABSTRACT

The territory of the Polar Urals is characterized by significant forecast resources of natural zeolites. In case of their successful development, the resources of the zeolite deposits can provide a positive impact on the development of a number of industries in the adjacent regions of the Urals and Western Siberia. At the same time, the available data about the zeolite-bearing rocks of the Polar Urals present in published research paper and materials of geological funds is rather contradictory. The results of research performed by different scientific groups often contain opposed conclusions on the mineralogical composition, the content of the commercial component in the ore, as well as on the ore reserves calculation and the potential of commercial exploitation for the same mineral occurrences. In many respects, this situation can be explained by the complexity of the geological and geomorphological conditions of the territory under consideration, the remoteness of the promising mineral occurrences from large scientific and industrial centers, and the variety of ore occurrences. This work presents the study results of lithological–petrographic features and the material composition of the eluvial debris of the Middle–Late (Givetian–Frasnian) Devonian zeolite-bearing rocks of the volcanogenic-sedimentary origin within the Naunpe area of the Polar Urals. The main objective of the proposed research was to evaluate the economic feasibility of their development and possible directions for commercial exploitation of this type of ores. Research methods included petrographic study of samples of zeolite-bearing rocks in thin sections, SEM-EDS, determination of the total mineral composition by XRD and the chemical composition by XRF. Within the Naunpe area, the outcrops of zeolite-bearing rocks on the surface are represented by blankets and debris of small lumpy–gravel eluvial deposits with indistinct outlines. Macroscopically, zeolite-bearing eluvial deposits are represented by reddish or pinkish in color, massive and relatively homogenous rocks. The ore occurrences are well interpreted based on the remote sensing data. According to the results of petrographic, lithological, and mineralogical studies, three main rock types were distinguished among the eluvial debris deposits: zeolite-bearing crystallo–lithoclastic tuffs of the mafic, intermediate, and felsic composition, and also tuffoargillites, and siliceous rocks. Crystallo–lithoclastic tuffs and tuffoargillites contain Ca-zeolites, represented mainly by laumontite (13.8–18.9 %), which fill small open spaces between crystallites and lithoclasts. Volcanic glass fragments and feldspars from tuffoargillites are replaced partially or completely by zeolites. The content of zeolites in these rocks is even lower (less than 10 %). The characteristic features of the studied zeolite-bearing rocks from the ores of the known deposits of the Polar and Subpolar Urals have higher contents of Fe_2O_3, CaO и Na_2O and lower content of K_2O. The obtained results show that the studied rocks are quite complex, diverse, and polygenetic, as well as their formation is a result of several stages of post-volcanic authigenic mineral formation. The rather low content of zeolite minerals in these rocks and high variability of the material composition decrease the industrial potential of that eluvial debris deposits as an object of mineral raw material base. At this, they can be considered as prospecting indicator for prospecting the areas with a similar geological structure.

1. INTRODUCTION

Determining the most efficient use of a local raw material base is a modern trend in the development of global industry (Hilson and Murck, 2000; Moran and Kunz, 2014). The reasons for this phenomenon include the depletion of a large number of mineral deposits and the improvement of technologies for the extraction and processing of raw materials and the

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greening of most areas of life, including industrial production (Azapagic, 2003). This situation suggests cardinal rethinking of existing raw material resources in the context of global economic development trends, which are especially important for regions with historically developed heavy mining industries (Carvalho, 2017).

The Ural Federal District of the Russian Federation is a good example of such a region. Since the sixteenth century, the Ural territory has been one of the most important and stable raw material bases of Russia, facilitating the social and economic development of the whole country. The mining industry, as well as the related metallurgy and heavy engineering industries, have been a tremendous competitive advantage of the Ural region for a long time (Pakhomov and Dushin, 2008). In the second half of the twentieth century, the situation significantly changed. Due to the depletion of ore reserves, the production of many types of raw materials decreased, while the import dependence of the region, as well as the discrepancy between production and processing, increased. At present, an industrially developed region is at risk of transforming into a depressive, old industrial region. This problem is urgent for the Southern and Middle Urals, which are characterized by a high degree of industrial development, since the main regional mining and processing centers are located within these territories. This situation requires new sources of mineral resources capable of maintaining and developing the industry of the Urals and adjacent regions.

One of the possible ways to solve this problem is the development of natural resources from the Polar and Subpolar Urals (Pakhomov et al., 2010), which are characterized by their substantial potential and are in relative proximity to the existing transport infrastructure of the Urals and Western Siberia. The territory of the Polar and Sub-Polar Urals is characterized by the presence of numerous deposits of rare and non-ferrous metals, high-quality quartz raw material, and industrial minerals, including natural zeolites (Tabakov, 2005). The latter is of special interest, as well. Although Russia contains one of the world's largest zeolite raw material reserves, with total resources of 1800 million tons and forecast resources of 750 million tons, deposits with the highest industrial potential are characterized by irregular geographical distribution (Ablyamitov et al., 2009). The mineral resources from the majority of large deposits of high-quality zeolite ores are located in Eastern Siberia and the Russian Far East, at a considerable distance from the industrially developed regions of European Russia and the Urals. In this regard, the relevance of industrial exploration of natural zeolite deposits located within the Polar and Subpolar Urals is becoming progressively more urgent.

Zeolites belong to several universal-type economic mineral classes, which are in demand for both traditional and high-tech industries (Distanov and Konyukhova, 2009). The existing experience of natural zeolite's industrial applications shows the effectiveness of this type of raw material for purifying waters (Margeta et al., 2013), producing organo–mineral fertilizers (Rehakova et al., 2004) and powder adsorbents for oil-associated gas dehydration (Ackley, 2003), and for use as fillers and additives in the construction industry (Stamatakis et al, 1998; Perraki et al., 2003; Colella, 2005; Mertens et al., 2009; Snellings et al., 2012). These trends of using zeolites are extremely relevant for Western Siberia and the Urals, as these territories are characterized by the presence of developed oil-and-gas, chemical, and heavy industries, as well as an agricultural sector.

The first zeolite ore occurrences within the territory of the Subpolar Urals were discovered in the 1960s as a result of large-scale geological surveys (Smirnov, 1999). Studies continued into the 1990s, resulting in the discovery of numerous deposits of zeolite in the Subpolar and Polar Urals. Despite the high potential of this territory, data on its the potential for natural zeolite described in geological reports and (rare) published research is often contradictory, and the number of properly studied deposits and mineral occurrences is negligible. This situation negatively affects the investment attractiveness of the zeolite deposits of the Subpolar and Polar Urals.

The zeolite ore occurrences and deposits in the Polar Urals are essentially different in their structures and resources due to the complex and diverse geological and geomorphological conditions of the area. As a rule, large ore occurrences have been selected as objects for detailed studies. One of these objects located in the territory of the Polar Urals is the Naunpe ore occurrence of chabazite-bearing rocks (up to 95 % chabazite, on average 50 % – 75 %), discovered in Middle–Upper Devonian deposits within the Shchuchinskij structural and formational zone. Limited data on this occurrence are available in only a few scientific reports and papers published in Russian. At the same time, the results of geological surveys and remote sensing have revealed significant eluvial debris composed of zeolitized rocks in the immediate vicinity of the Naunpe ore deposit area. The industrial potential of this type of mineral occurrence remains unexplored.

This work aims at studying the type of zeolitization and the content of zeolite-bearing rocks from the eluvial debris mineral occurrences within the Naunpe area of the Polar Urals.

2. ZEOLITE RESOURCES OF THE SUBPOLAR AND POLAR URALS

The zeolite deposits of the Subpolar Urals and Polar Urals are of a volcanogenic–sedimentary (diagenetic) type (Ablyamitov et al., 2009). Zeolites of the Subpolar and Polar Urals are secondary minerals, which formed as a result of the epigenetic transformation of volcanic ash under the action of hydrothermal solutions (Voronov, 2001; Nefedov and Valieva, 2011). The considerable remoteness of some zeolite-bearing beds from sources of volcanogenic hydrothermal solutions supports the hypotheses proposed by a number of researchers that zeolitization is related not to hydrothermal activity but to the influence of large high-amplitude tectonic fault zones, close to which zeolite-bearing ore bodies are formed (Ugryumov et al., 2010). The most intensive zeolitization (up to 50 %–90 %) is characteristic of the fine-grained ash tuffs in the outcrops of the Polar Urals (Kostyuk and Sokolova, 2006).

The ore bodies are lenticular or stratified in shape (Voronov, 2006). The beds with the highest degree of zeolitization are, as a general rule, from the Devonian age (Nefedov and Valieva, 2011). Partial zeolitization and its signs are also noted in Carboniferous and Upper Paleozoic deposits, Triassic sandstones of the Shchuchinskij synclinorium, and adjacent tectonic structures (Ugryumov et al., 2010). The ore occurrences and deposits of the Polar and Subpolar Urals are characterized by clinoptilolite–montmorillonite (Mysovskoe, Beregovoe, Severo-Sosvinskoe, and Lyulinskoe) and clinoptilolite–mordenite ores (Yanganape, Toupugol, and Dorozhnoe) (Smirnov, 1999; Kostyuk and Sokolova, 2006; Nefedov and Valieva, 2012). Zeolites from the mineral occurrences of the Polar Urals are mostly represented by chabazite (Voronov, 2001) and, to a lesser extent, by other minerals, such as heulandite, laumontite, natrolite, phillipsite, and analcime (Nefedov and Valieva, 2011). In zeolite-bearing deposits of the Shchuchinskij synclinorium, the individual zeolite grains vary in size from 0.1 to 3 mm (Ugryumov et al., 2010). It should be noted that data on the mineral composition of zeolite-bearing rocks of the Ural Region (especially for the Polar Urals) is rather contradictory. Different ore-forming minerals are often listed for the same objects of the raw material base.

The main mineral occurrences of the Subpolar Urals are Mysovskoe, Beregovoe, and Lyulinskoe deposits, as well as a Severo-Sosvinskoe ore occurrence (Nefedov and Valieva, 2012). In terms of tectonics, this group of occurrences and deposits is confined to the Lyulinskoe uplift. As noted above, ores of these deposits belong to the clinoptilolite–montmorillonite group. The rocks in these deposits include grains of feldspar, pumpellyite, volcanic glass, and iron hydroxides. The resources of the most explored Mysovskoe deposit constitute 44 thousand tons, and the forecasted resources throughout the Lyulinskoe uplift as a whole total 10 million tons.

The zeolite deposits and ore occurrences of the Polar Urals are confined to a large tectonic structure, the Shchuchinskij synclinorium, where the Upper Paleozoic zeolitized tuffs crop out within the Naunpe area. The most important objects of the raw materials base of the territory are the Naunpe and Yanganape deposits. Zeolites are mainly represented by chabazite and laumontite, and finely dispersed iron hydroxides, chlorite, pumpellyite, and feldspar clasts are often found among the inclusions. The ore bodies are simple in their structure, which makes open-pit mining possible; the thickness of the ore-bearing horizon, as a rule, does not exceed 5–7 m. According to preliminary estimates of the forecast resources, the reserves of the Naunpe structure are 1–3.2 million tons and those for the whole Shchuchinskij synclinorium total 18 million tons (Voronov, 2001; Ugryumov et al., 2010).

In summary, zeolite ore occurrences of the Subpolar Urals are studied much better in terms of the geology, resource potential, and mineralogy of the ores. For the entire territory under consideration, there is a significant discrepancy between the proven reserves of concrete deposits and the overestimated forecast resources, although the mineral and raw material potential of Polar and Sub-Polar zeolites is currently estimated at only 2.76 million tons.

3. MATERIALS AND METHODS

3.1. GEOLOGICAL SETTINGS

The study area is located in the northeastern spurs of the Naunpe Ridge, on the watershed between the right tributaries of the Yun-Yakha River, 4 km northwest from Lake Yun-to and 15 km northeast from Laborovaya trading post. This area is a part of the Shchuchinskij geological and economic region (Fig. 1). Geologically, the study area resides in the Shchuchinskij structural and formational zone, localized in the volcanogenic–sedimentary strata of the Givetian–Frasnian age, which constitutes the eastern flank of the Prirazlomanaya volcanoplutonic structure. The Shchuchinskij synclinorium (allochthon) is the northernmost separated part of the Tagil–Magnitogorsk megasynclinorium. Therefore, the Shchuchinskij synclinorium is better known in the scientific literature as the morphostructural continuation of this geological structure. The zeolite-bearing formations within the study area are confined to the Middle–Late (Givetian–Frasnian) clastic volcanogenic–sedimentary strata.

In terms of geomorphology, the study area is the zone of residual low mountains in the northern part of the Naunpe Ridge. In addition, the study area is characterized by undulating hilly reliefs with gentle slopes and flat watersheds between small streams. The tops of small hills are often represented by limestone and tuff cliffs.

The first findings of zeolite outcrops in the Naunpe area of the Polar Urals date back to the 1970s and are related to the studies performed by V.N. Voronov (Voronov, 2001, 2006). The materials obtained during the geological mapping of the territory and general exploration of the resource potential of the territory have shown that zeolite formations occur in the detrital strata of volcanogenic–sedimentary origin of the middle-late (living-fran) Devonian. Two main zeolite group minerals were identified within the ore occurrences of the territory under consideration: laumontite and

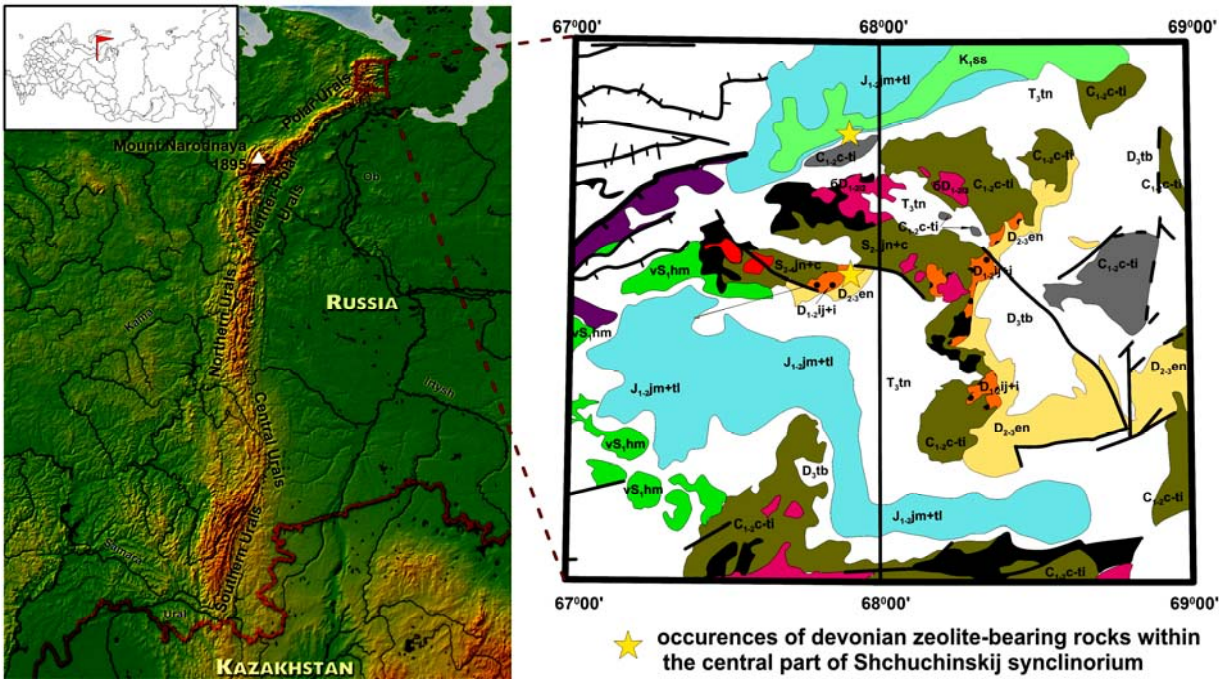

Fig. 1 Simplified map showing the location of study area within the territory of Russian Federation and Polar Urals and simplified geological map of the central part of Shhuchinskij ore district (from geological map of Russia, list Q-42).

chabazite (Report, 2008). Further research on the Naunpe outcrops of zeolites was performed by V.A. Nefedov and V.V. Nikolayev in the 1990s according to the recommendation of V.N. Voronov. As a result of these studies, three beds extending a total length of up to 5 km as a chain of ore debris were identified as potential objects for further exploration. Based on the eluvial debris outlines, the width of zeolite-bearing bodies was estimated as 6 m. The studies performed by V.A. Nefedov and V.V. Nikolayev showed that zeolite-bearing rocks are distinctly different from their enclosing strata and vegetation in terms of their spectral characteristics. Therefore, the eluvial debris of ore bodies are easily recognizable on high-resolution satellite images as NE-striking narrow lenticular zones.

The proposed paper presents the results of studies performed during the summer field season of 2008 within the area previously selected based on an analysis of remote sensing data and the materials of previous studies. Three samples of zeolite-bearing rocks from the eluvial debris of the Naunpe area were selected for further detailed analytical investigations.

3.2. ANALYTICAL METHODS

Studies of the chemical, elemental, and mineral compositions of zeolite-bearing rocks were performed at the Laboratory for Isotope and Element Analysis of the Institute of Geology and Petroleum Technologies of Kazan Federal University (Kazan) and the "West Siberian Geological Center" (Tyumen). The lithological and microscopic studies were carried out at Tyumen Industrial University (Tyumen).

The determinations of bulk chemical composition were performed on an 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). This method allows one to measure elements in solid, powdery, and liquid samples in a range from B to U in vacuum or a helium atmosphere. The device was equipped with a rhodium anode 4 kW SST-mAX tube. The sample was placed in the grinding jar of a planetary ball mill and ground for over 10 minutes to achieve particle sizes of less than 10 μm. A sample of 0.5 g was placed in a ceramic crucible and calcined at 1100 °C for over two hours to determine the loss on ignition (LOI). Then, another quantity of the 4 g test sample weighed on analytical balance with an accuracy of 100 mg was mixed with organic wax and pressed into a boric acid substrate with a force of 300 kN. The obtained pellet was placed in a spectrometer, and further processing was performed using GeoQuant software. The recorded spectrum was processed with the fundamental parameter method to eliminate automatic recognition errors and spurious peaks. In addition, diffraction phenomena and matrix effects were taken into account, and the LOI value was used to account for indefinable elements.

A semi-quantitative analysis of the mineral composition was carried out via X-ray diffractometry using a DRON-4 X-ray diffractometer with CuKα source at the "West Siberian Geological Center" (Tyumen). The diffractograms obtained were

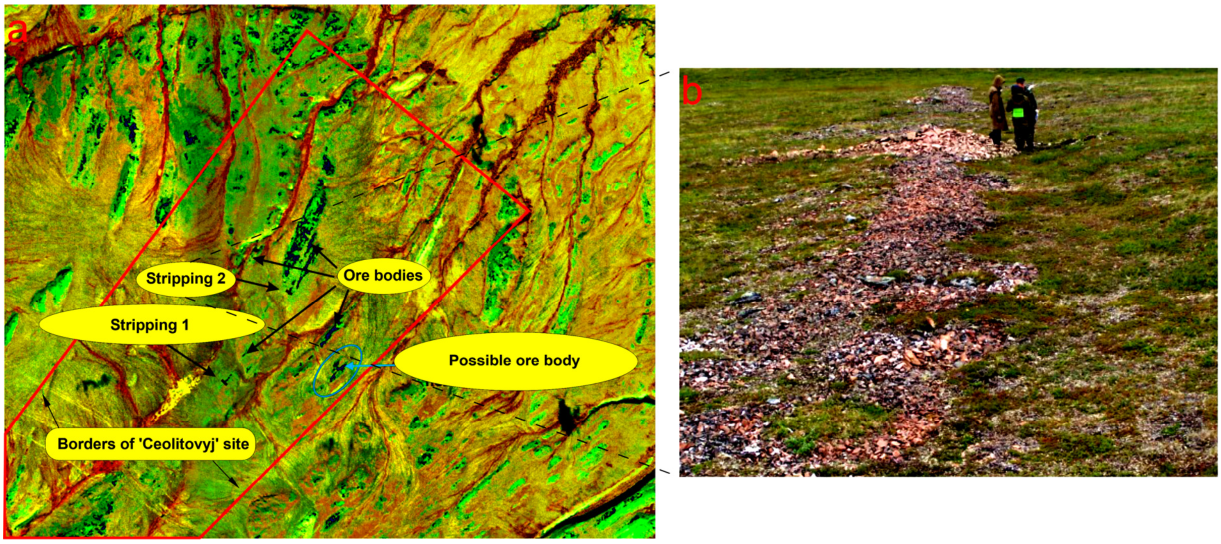

Fig. 2 Eluvial debris of zeolite-bearing rocks of Naunpe outcrop, a - in the satellite image of the Zeolite site, b - in its natural form.

processed with the GeoQuant software to eliminate automatic recognition errors and spurious peaks. A lithological and petrographic study of the samples was carried out under a microscope in sections that were made thin according to the standard methodology. The SEM study of individual samples was performed using a JEOL JSM 6510A scanning electron microscope, equipped with an EDS system for elemental analysis.

4. RESULTS

4.1. FIELD GEOLOGY AND GEOMORPHOLOGY

According to the results of the field studies, six bodies of zeolite-bearing tuffs were discovered within the study area. The zeolite-bearing rocks represent the material of eluvial debris with indistinct boundaries (Fig. 2). The ore bodies are traced along the debris at a distance of 150–250 mm and a width of 3–6 (up to 10 m) m, with a depth greater than 1 m. At the bottom, eluvial deposits are composed of large boulders, while the bedrocks have never been opened. The ore bodies are interrupted along the strike by swampy depressions 50–150 m long. Macroscopically, the zeolite-bearing eluvial formations represent massive and relatively homogenous rocks colored reddish-pink, dark pink, or brownish-red, depending on the degree of ferruginization. The ore bodies are well recognizable from the background limestones and schists as magnetic anomalies due to in an increase in the local magnetic field intensity. In terms of their morphology, magnetic anomalies have inherited the structure of the volcanogenic–sedimentary strata, having both a similar strike and distribution (Voronov, 2001).

4.2. PETROGRAPHIC STUDIES

Three main rock varieties were distinguished among the eluvial debris rocks based on the results of microscopic studies: zeolite-bearing crystallo–lithoclastic tuffs of mafic, intermediate, and felsic composition, tuffoargillites, and siliceous rocks. Zeolite-bearing crystallo–lithoclastic tuffs are composed of angular, poorly sorted clasts of 0.07–0.9 mm in size. Crystalloclasts are represented by single fused quartz grains, plagioclase, and orthoclase. Lithoclasts of tuffs are represented by rhyolites (dacites) with felsic, porphyritic, perlitic textures, as well as andesites with pilotaxitic and andesitic textures. In addition, lithoclasts of mafic rocks, including basalts with hyaline and intersertal textures of the groundmass, were identified. Pyroxene and amphibole (2.4 % and 1.5 %, correspondingly), as well as epidote, were also found. The proportion of ore minerals (mainly oxidized magnetite grains and hematite) varied from 4.4 % to 11.2 %. Rocks are irregularly carbonatized; the proportion of carbonates is 3.8 %–5.3 %, while that of celadonite in tuffs is 4 %–6 %. The latter fills thin spaces between crystalloclasts and lithoclasts and often occurs inside pelitic structures together with zeolites. The rocks show signs of the mechanical deformation of clasts, which is expressed in their crushing and fracturing. The degree of deformation in the studied rock samples is variable. The tectonic activity and hydrothermal processes contribute to intensive post-volcanic authigenous mineral formation, which occurs over several stages.

Tuffoargillites are composed of devitrified volcanic glass fragments, angular grains of quartz and feldspar (8 %–10 %) of 0.025–0.13 mm in size, and small (0.047–0.087 mm) partly chloritized round clasts of felsic effusives. Clasts of volcanic glass are also felsic in composition. This is indicated by the bubbly structure of individual highly altered clasts. The fragments are angular, forked, crescentic, and filamentous in shape. Almost all ash particles were

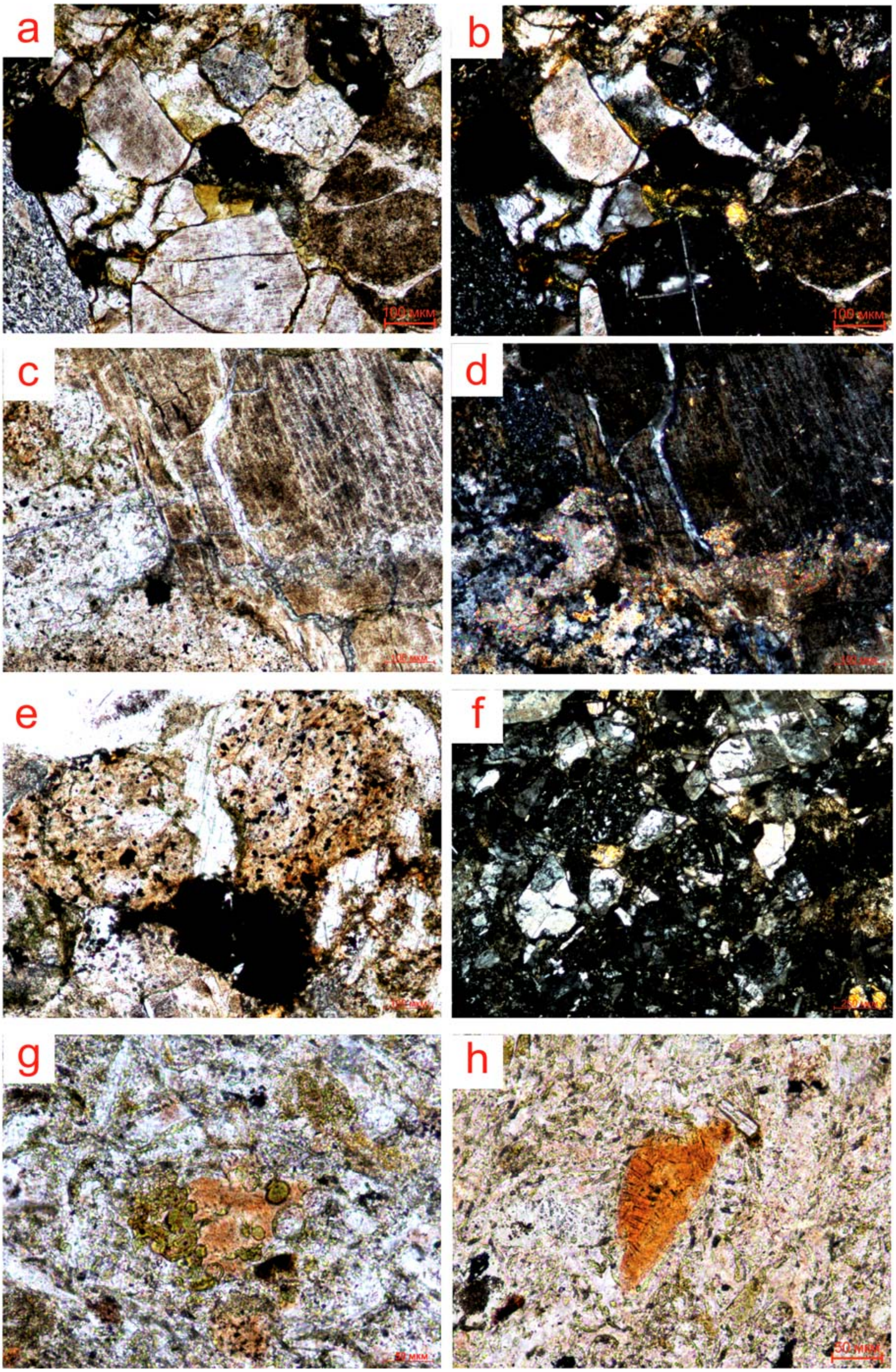

Fig. 3 Mineral components and textural–structural features of zeolite-bearing rocks: a, c, e, g, parallel nicols; b, d, f, h, crossed nicols; a, b, zeolites with corrosion signs (yellow grains) in the porous space between crystallites and lithoclasts; b, c, d, zeolites in fractures of cataclazed fragments; d, intensive carbonatization; e, development of zeolite along the fracture in a clast; f, development of zeolites on feldspar; g, h, zeolitization of volcanic glass fragments in tuffoargillites.

subject to secondary alterations, which are expressed in their claying: montmorillonitization, silification, and zeolitization. There are flocculent light green segregations of montmorillonite, while very small flakes of illite are scattered throughout the rock volume. The occurrence of organic remains (radiolarians) is typical for the studied rocks. Radiolarian shells, varying in size from 0.07 to 0.18 mm, have skeletons with internal cavities incrusted with chalcedony. Their thin outer outlines are emphasized by a yellowish-green rim of illite–chlorite. Grains of pyrite and hematite represent Ore minerals. In addition, there are small grains of zircon, apatite, and epidote.

Siliceous rocks are represented by tuffosilicites with cryptocrystalline, relic structures, and banded structures. These bands, reddish–brown in color, are probably the relics of siliceous tuffoargillites. The cryptocrystalline siliceous groundmass contains crystallo-lithoclastic tuff zones. As in tuffoargillites, this groundmass contains organic remains represented by rounded silicified radiolarian shells. Rocks are fractured, and multidirectional fractures are filled with carbonates.

The crystallo–lithoclastic tuffs and tuffoargillites contain Ca-zeolites. Zeolites of the first-type rocks fill small open spaces between crystallites and lithoclasts (Figs. 3a, 3b), which were initially filled with volcanic glass or feldspar crystals (Fig. 3f). In addition, these zeolites occur in fractures of cataclazed rock fragments (Figs. 3c, 3d, 3e).

Volcanic glass fragments in tuffoargillites are partially or completely replaced by zeolites. In this way, they, as well as feldspars, preserve their original shape (Figs. 3g, 3h). Zeolites are orange–red in color due to the presence of iron oxide and hydroxide film and are regularly distributed throughout the rock groundmass. The content of zeolites in some tuffoargillites range up to 10 %.

4.3. SEM-EDS ANALYSIS

The results of studies using scanning electron microscopy have revealed that the structure of all studied samples is heterogeneous. The most easily recognizable mineral components are K-feldspars, which are often zeolitized to a different extent (Fig. 4). The latter occur in association with aggregates of laumontite-type zeolites. Rare grains of Fe-rich monoclinic pyroxene are also present in the studied samples. The matrix has a clay composition. Single grains of quartz, apatite, mica, fragments of volcanic glass, etc. are locally distributed. Carbonatization is irregularly developed; calcite usually dominates in the composition of the carbonate portion of rocks.

4.4. XRD ANALYSIS

Zeolites from studied rocks are represented by laumontite, which is determined by X-ray analysis based on the parameters of the most intensive diagnostic reflexes d (110) = 9.4 Å; d (130) = 4.16 Å; d (002) = 3.51 Å. Certain values differ from the reference in the range of d (110) = 9.4 Å (reference value = 9.5 Å). This difference is likely because laumontite is partially dehydrated in air and turns into leonhardite. According to measurements, this type of rock contains from 13.8 % to 18.9 % zeolite minerals. Intense reflexes of quartz were fixed in the individual samples, which suggests that silicified fragments of rock were analyzed. The average content of quartz in the considered tuffs is 12 %–15 %.

4.5. CHEMICAL COMPOSITION

Table 1 presents the contents of the main oxides in zeolite-bearing rocks from the eluvial debris, as well as the chemical composition of zeolites from the main deposits of the Polar and Subpolar Urals and important volcanogenic and volcanogenic–sedimentary deposits in Russia. The characteristic features of the studied zeolite-bearing rocks include higher contents of Fe_2O_3, CaO, and Na_2O. The elevated contents of iron oxides are reflected in the pinkish and reddish color of the rocks. Based on the SiO_2/Al_2O_3 ratio, the rocks under consideration are ascribed to low-Si formations (4.1) and are similar to the zeolite ores from the main ore occurrences of the Subpolar Urals (4.1–4.3). At the same time, this ratio in zeolites of the Polar Urals is slightly higher. Among the chemical composition features, the predominance of CaO and Na_2O over MgO and K_2O potentially affects the ion-exchange properties.

Figures 6 and 7 present CaO–SiO_2–Al_2O_3 and K_2O/Na_2O diagrams of the studied zeolite-bearing rocks and data on zeolite-bearing rocks from different deposits in the Urals and other regions of Russia. The CaO–SiO_2–Al_2O_3 diagram demonstrates the similarity in the genesis of all objects under consideration. At the same time, the K_2O vs. Na_2O diagram shows a significant difference between the studied rocks and other volcanogenic and volcanogenic–sedimentary zeolite-bearing ores. It is possible that this fact can be explained by the results of the petrographic and mineralogical studies. In all studied samples, Na-feldspars (albite $NaAlSi_3O_8$), sometimes with the inclusion of an orthoclase component, were dominant, while K-feldspars ($KAlSi_3O_8$) occurred in much smaller amounts. The results of the microscopic studies also showed that zeolites have a calcium composition. Among other Ca-bearing mineral components, monoclinic pyroxenes of the diopside–hedenbergite series (identified in Samples 4–59) and carbonate minerals, such as calcite and ankerite, were identified. Potassium-bearing minerals, however, are scarce both in feldspars and zeolites.

5. DISCUSSION

The results of previous studies devoted to the ore occurrences in rocks from the Naunpe area, performed

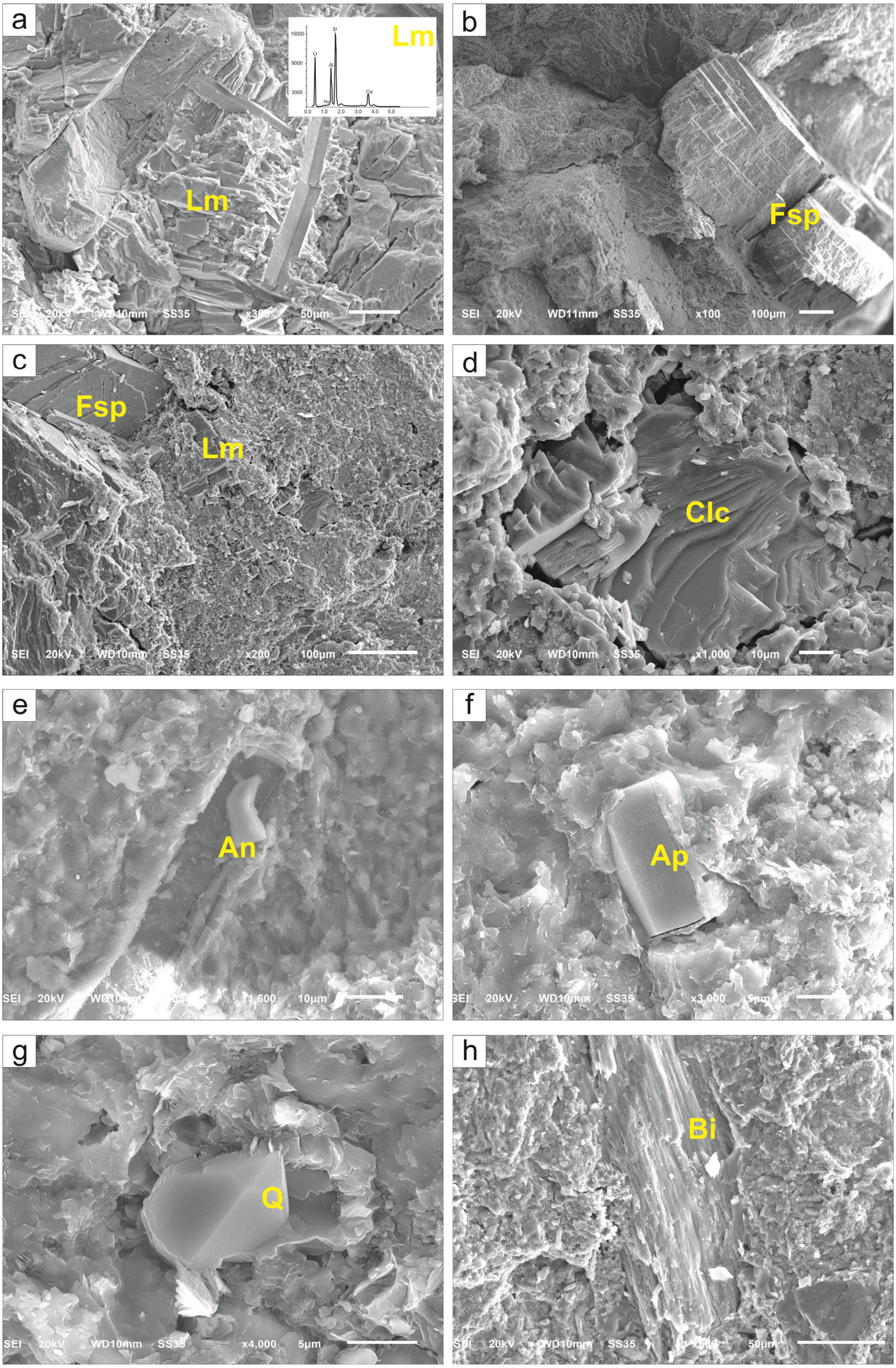

Fig. 4 a - lomontite (4-59); b, an albite clast with inclusion of the orthoclase component; b - large aggregates of feldspars; c - lomontite and feldspars; d - calcite; e - illite on the surface of ankerite-type Fe-carbonate; f - apatite; g - regenerated quartz crystallite; h - scaly aggregates of biotite
Fsp, feldspar; Lm, lomontite; Clc, calcite; An, ankerite; Ap, apatite; A, quartz; Bi, biotite.

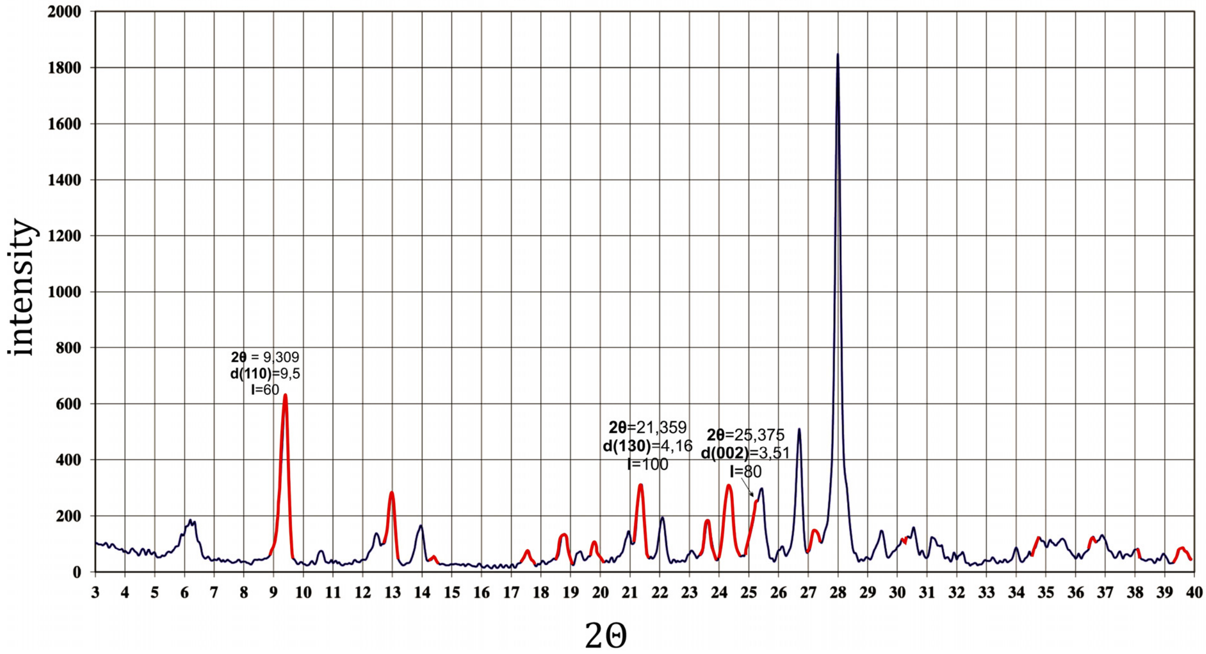

Fig. 5 Diffraction pattern and their inserts of zeolite-bearing rock (sample No. 4-59) with the region between 3 to 40°2θ (CuKα). Red marked peaks of laumontite; numerically signed - the most intense peaks.

Table 1 Chemical composition of the studied zeolite-bearing rocks of similar genesis from different deposits of the Urals and other regions of Russia.

Object of study	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	MnO	K_2O	Na_2O	P_2O_5	TiO_2	SO_3	LOI
Studied samples												
4-59	57.02	13.87	4.92	9.95	1.43	0.12	0.38	3.40	0.58	0.51	0.12	7.64
4-60	58.24	14.08	4.87	7.21	1.34	0.11	0.61	3.66	0.59	0.48	0.29	8.45
Zeolite-bearing rocks from deposits of the Polar and Subpolar Urals after (Nefedov, Valieva, 2011)												
Mysovskoe	59.30	14.50	3.10	3.77	1.63	0.14	0.86	0.82	-	0.52	0.03	-
Beregovoe	60.18	13.90	2.60	1.93	1.81	0.14	1.65	1.07	-	0.63	0.01	-
Average for Yamal Nenets Autonom. District	71.33	11.98	1.43	4.0	0.72	0.04	0.41	0.8	-	0.22	-	-
Zeolite-bearing rocks from large volcanogenic and sedimentary–volcanogenic deposits of the Russian Federation after (Ablyamitov, 2009)												
Kholinskoe	67.66	11.97	1.04	1.37	0.42	-	3.63	2.52	-	0.09	-	11.39
Chuguevskoe	67.36	12.74	1.18	1.46	0.12	-	3.15	2.29	-	0.08	-	11.42
Pegasskoe	62.91	11.96	3.34	4.49	1.25	-	1.17	0.41	-	0.29	-	13.97
Khonguruu	67.28	11.12	1.55	3.31	1.49	-	1.00	1.39	-	0.12	-	12.33
Shivyrtui	61.38	13.20	1.21	3.28	1.20	-	2.66	1.56	-	0.33	-	14.23

by geologists from the Siberian Scientific Analytical Center and the Central Research Institute of non-metallic minerals, have shown that all samples of zeolite-bearing rocks from the territory under consideration can be divided into two groups. The first group consists of samples in which the zeolite phase is represented by laumontite (in the range of 40 %–60 %). Rocks in which the zeolite phase is represented by clinoptilolite comprise the second group. The insignificant presence of a clay mineral also appeared in all samples (likely from the smectite group), which was recorded in the diffraction patterns as a weak peak with a value of d =14.2 A, though a more accurate identification of the minerals from the clay fraction was not performed. These data are well correlated with the results obtained in the present work.

In the investigated samples, there is a deficit (up to 100 %) in the concentrations of the crystalline phases, which significantly exceed the experimental errors. The latter circumstance indicates the presence of an X-ray amorphous phase in these samples (most likely an uncrystallized volcanic glass). The presence of chabazite in all investigated samples was excluded

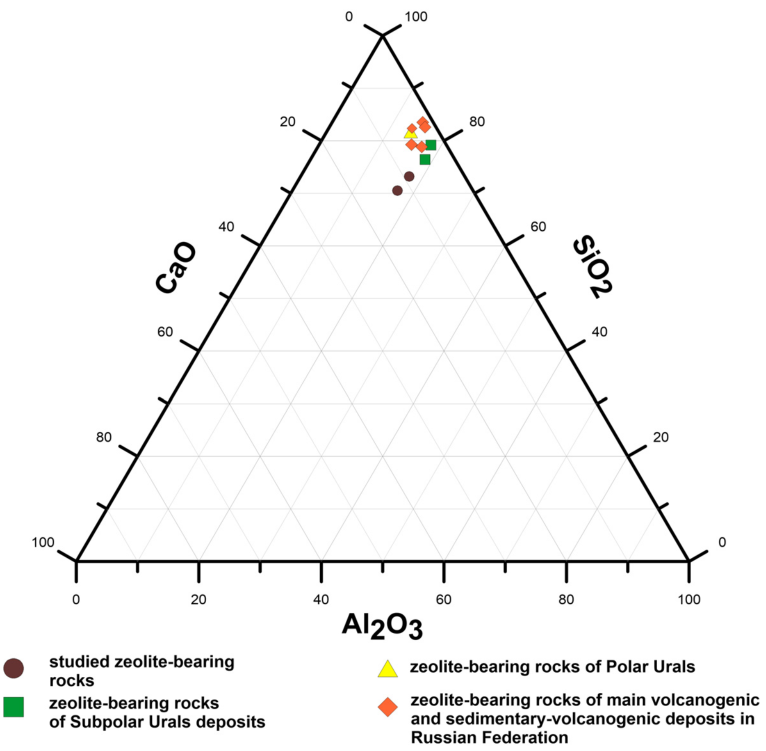

Fig. 6 Ternary CaO-SiO_2-Al_2O_3 diagram (wt% based) illustrating the distribution in chemical composition of studied samples as well as different zeolite-bearing rocks of Polar and Subpolar Urals and main volcanogenic and sedimentary volcanogenic deposits in Russian Federation.

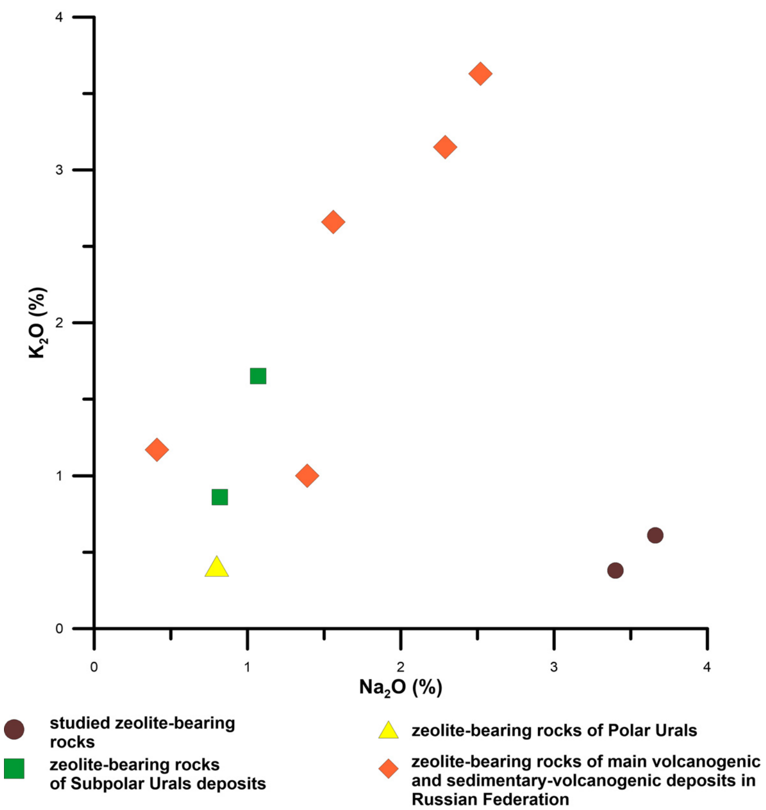

Fig. 7 K_2O versus Na_2O diagram (wt% based) illustrating the distribution in chemical composition of studied samples as well as different zeolite-bearing rocks of Polar and Subpolar Urals and main volcanogenic and sedimentary volcanogenic deposits in Russian Federation.

since its diffraction patterns on the diffractograms are absent in the areas of the two most intense diagnostic chabasite reflexes: d = 4,324 A, J = 76 and d = 2,925 A, J = 100, which also supports the results of previous studies.

Consequently, it is possible to agree with Report (2008), who preliminarily classified the Naunpe zeolite manifestation as a volcanogenic–sedimentary hydrothermal–diagenetic type. This interpretation is in good agreement with the results of the following studies and successfully describes the history of the formation of the rocks. Petrographic studies in thin sections, as well as the scanning electron microscopy performed during our research, convincingly indicate that the studied rocks feature diverse and polygenetic formations, as their evolution is associated with several cycles of secondary postvolcanic processes and authigenic mineral formation stages. Apparently, in the originally volcanogenic or volcanic–clayey substrate, the processes of zeolitization proceeded both due to their formation in the pore space and due to the transformation of feldspar minerals. Moreover, the silicification of previously-zeolitized tuffs and tuffargillites occurred, which resulted in the destruction of part of the previously formed zeolites and their replacement by various forms of silica. Thus, it is possible to conclude that the studied rocks are characterized by a high degree of heterogeneity; moreover, the nature of the zeolitization of the initial strata was complex.

The results of field studies have not identified the pertinent complex geological and geo-morphological conditions: The overburden rocks are absent, the parent rock is already fragmented to a certain degree, and the relief is relatively calm. In this context, a significant challenge for the practical development of eluvial debris is the high heterogeneity of the strata and low contents of zeolite minerals in such occurrences. In general, the absence of chabazite mineralization in the zeolite ores of the Naunpe area significantly limits the areas of their possible use. As noted above, two types of zeolite ores can be distinguished in this manifestation: medium laumontite and poor clinoptilolite. Laumontite is considered to be a prospective industrial zeolite; it is significantly inferior to clinoptilolite in its adsorption and ion exchange properties and is characterized by low thermal and acid resistance. The content of laumontite zeolites in the studied eluvial debris samples is significantly lower than that in the rocks of the ore-bodies examined in previous studies, and the industrial exploration prospects of such occurrences are significantly low. At the same time, the eluvial debris of zeolite-bearing rocks can act as a deciphering search feature, which allows one to distinguish the individual presumptive boundaries of large ore bodies.

6. CONCLUSIONS

(1) Outcrops of zeolite-bearing rocks are blankets and debris of small lumpy–gravel eluvial deposits. Based on their outlines, the length of the ore bodies is 150–250 m at a width of 3–6 m. The zeolite-bearing rocks are traced in the debris to a depth of 1 m. The width of the eluvial debris in the mine openings reaches up to 10 m. The debris deposits are well defined on the surface and can be easily deciphered based on the remote sounding data.

(2) Petrographic and microscopic studies enabled us to reveal the significant heterogeneity of the eluvial debris deposits. Because of these microscopic studies, three main rock varieties were distinguished in the samples under examination: zeolite-bearing crystallo–lithoclastic tuffs of mafic, intermediate, and felsic composition; tuffoargillites; and siliceous rocks. These rock varieties are essentially different in their mineralogical composition, expressiveness of their manifestations of authigenic mineral formation, and their content of zeolites.

(3) According to the X-ray analysis data, Ca-zeolites, represented by laumontite, were found in crystallo–lithoclastic tuffs (13.8 %–18.9 %) and tuffoargillites (less than 10 %). The composition of zeolite minerals is consistent with the results of previous studies conducted within the study area, except for the fact that clinoptilolite zeolites were absent.

(4) The distinctive features of the studied zeolite-containing rocks from the fields of the Polar and Subpolar Urals include higher contents of Fe_2O_3 and CaO, as well as Na_2O; and the predominance of CaO and Na_2O over MgO and K_2O. Apparently, these features are due to the fact that sodium feldspar noticeably predominates over potassium in the studied rocks, and zeolites are represented almost exclusively by Ca zeolites.

(5) The low content of useful components in rocks of eluvial debris and the heterogeneity of their material composition make their industrial use unpromising. On the other hand, eluvial debris are well characterized on the ground and can be used to identify and delineate more promising ore bodies.

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