First data on the chemical composition of natural waters at the gold deposit "Novye Peski" (South Karelia, Russia)

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Abstract. Actual analytical methods make it possible to precisely determine a of chemical elements contained in water, including for the purpose of assessing the ecological state of the environment in connection with mining activities. The object of this research is the natural waters of the gold deposit "Novye Peski" located in the Pryazhinsky region (Republic of Karelia, Russia). Analytical data indicate that the geochemical background of the region is exceeded for most of the chemical elements. Research results indicate that the geochemical background of the region is exceeded for most of the considered chemical elements and ions, which can be divided into three groups: 1) the highest concentrations were determined in quarry water (Zn, As, Mo, U, Ni, Cu, Sr, Li, B, as well as Ca and other cations, HCO_3^- , SO_4^{2-}); 2) the content is at the same level in all samples (Al, Si, V, Ti, Ba); 3) the highest content in stream and tailing pond (Fe, Mn). We assume that the main factor influencing the behavior of elements of the first group is mining, and for the third is the presence of dissolved organic matter high content with the formation of metal-organic species in water.

1 Introduction

The gold deposit "Novye Peski" is located in the Pryazhinsky region of the Republic of Karelia near the settlement of the same name (Figure 1). This deposit is associated with the southern part of the Vedlozero-Segozero greenstone belt of the Fennoscandian shield. The host rocks are represented by gabbro-dolerites metamorphosed into amphibolites and amphibole schists and schists over tuffaceous-sedimentary rocks of intermediate composition of the Shotozero sequence (AR_2 *st*) [1-2].

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The gold-bearing sulfide–arsenide mineralization was identified in 1988 [3]. As a result of the work of "Onego-Zoloto" in 2007-2013, "Novye peski" was transferred to the rank of a deposit with Au in proved reserves 0.97 t, Au 2.7 g/t, probable reserves 4.18 t, Au 2.9 g/t and inferred exploration potential 10.8 t Au [4]. Mineralization is limited to metasomatized rocks that have undergone cataclasis and foliation. These zones are spatially connected with submeridional fracture systems. The width of the ore zone is 200-250 m in the central part of the deposit. Ore metasomatites are represented by ilmenite-quartz-garnet-amphibole, ilmenite-quartz-garnet-feldspar-amphibole, and titanite-carbonate-biotite-chlorite-epidote (clinozoisite) metasomatites [5].

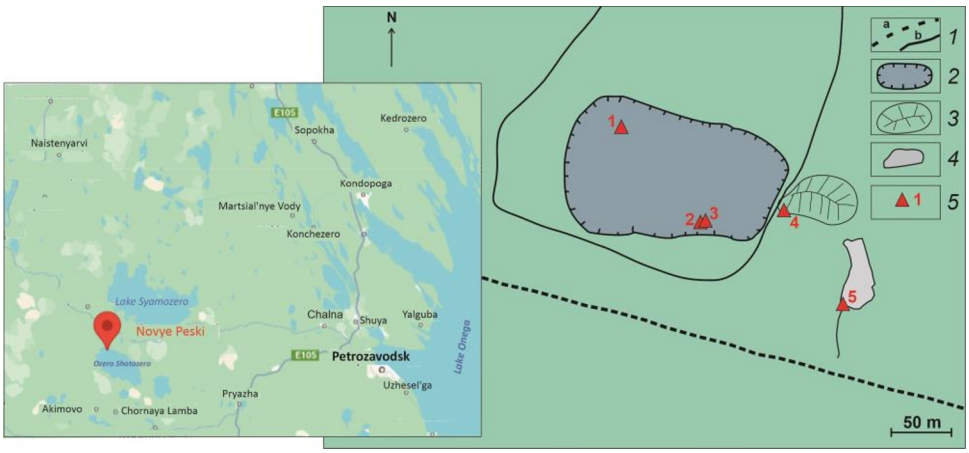

Fig. 1. Location of the study area and sampling scheme. Legend: *1* – roads: *a*- railway line; *b* – soil road; *2*- flooded quarry; *3*- dumps; *4* – settling pond; *5* – sampling points.

The mineral composition of ore zones according to our data, as well as according to a literature review [2, 4] is presented:

- Silicates: quartz, feldspar (albite), amphibole (ferrochermakite, ferroactinolite, grunerite, Fe-hornblende), pyroxene (ferropijonite, ferroaugite), chlorite (brunswigite-chamosite), garnet (pyralspite-ugrandite series with a high content of grossular minal (20-50 %)), epidote (clinozoisite), biotite, titanite.
- Oxides: magnetite, ilmentite, scheelite, wolframite.
- Sulfides: marcasite, pyrite, pyrrhotite, chalcopyrite, sphalerite, galena, bismuthine.
- Arsenides and sulfo-arsenides: arsenopyrite, loellingite, glaucodotus, pharmacosiderite, cobaltite, gersdorffite, glaucodot.
- Native metals: bismuth, gold, maldonite, electrum, jonassonite.
- Halogenides: zavaritskite, bismoclite.
- Phosphates: F-apatite.
- Carbonates: calcite, siderite.
- Supergene minerals: goethite, hydrogeothite, scorodite, zykaite, preisingerite, bismite.

A test quarry has been developed in 2018-2021 on the territory of the deposit, but currently there is no mining. A feature of this object is the widespread occurrence of As-containing mineralization, which is associated with an increased Au content. When carrying out strip mining, rocks are crushed, resulting in access of atmospheric air and natural waters into contact with ore-containing rocks. In other words, the processes of water-rock interaction are intensified and the risk of potentially toxic elements entering the natural waters of the area increases. This primarily applies to a wide range of heavy metals and metalloids: As, Pb, Fe, Ni, Zn, W. Therefore, studying the chemical composition of the natural waters of the deposit "Novye Peski" is an actual challenge.

2 Materials and methods

Samples of natural waters and rocks were collected in 2022. A total of five water samples were taken at different points (Figure 1): 1 and 2 samples were collected from the surface (0.2 m) from opposite sides of the quarry; sample 3 was collected from a depth of 2 meters in the same point as sample 2; sample 4 represented water from a small stream flowing out under the dump, sample 5 was collected from the tailing pond. A temporary watercourse flows from the pond into Lake Shotozero, which is important as a source of fresh water and fish for the local settlement. Additionally, two rock samples were selected. Both are amphibolite schist. In the first case, the rock is in contact with the 10-15 cm thick arsenopyrite vein, in the second, at a distance from it. Sample taken from the near of the vein is presented at the (Figure 2).

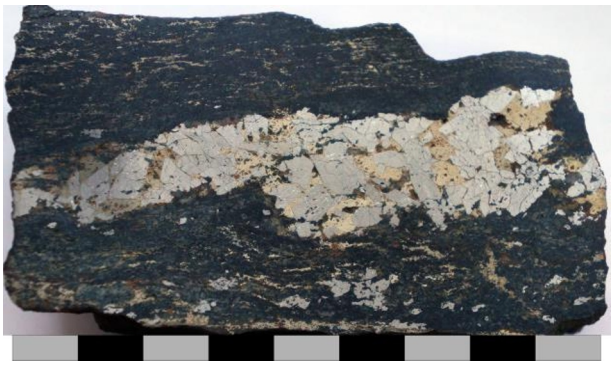

Fig. 2. Sample of amphibole schist with arsenopyrite (white) and pyrite (yellow) mineralization. Scale in cm.

In-situ measurements included the determination of values of pH, Eh, and temperature (PH200 meter, ORP-200 meter (HM Digital)). Water samples for elemental analysis were passed through acetate-cellulose membranes with a 0.45 μm pore size and transferred to 15-mL polypropylene vials with 0.45 mL of ultratrace grade HNO_3 for preservation. For the analysis of carbonate system components, chloride, and sulfate ions, the samples were collected in 300-mL plastic bottles that had been thoroughly washed three times with water from the study area.

The concentrations of Ca, Mg, Na, K, Fe, and Al were determined by ICP-AES (iCAP 6500 DUO, Thermo Scientific), while the concentrations of trace elements were analyzed by ICP-MS (X-series 2, Thermo Scientific). The contents of CO_2, HCO_3^-, and CO_3^{2-} were determined by potentiometric titration using Expert-001 (Econix-Expert). Furthermore, Cl and SO_4^{2-} concentrations were quantified by ionic chromatography (ICS-3000, Thermo Scientific).

Mineralogical composition was determined by scanning electron microscopy (SEM) using a Mira3 instrument (Tescan) coupled to an X-ray microanalysis spectrometer (X-MAX, Oxford Instruments).

3 Results and Discussion

The water samples collected at various points at the gold deposit “Novye Peski”.have low levels of salinity and very close pH values (7.76 – 7.92). Some differences were noted in the measured Eh values. The identical value (220 mV) was measured in three samples taken from the quarry. In 4 and 5 samples the Eh values were slightly lower (152 and 138 mV, respectively). In addition, some differences were observed in the temperature conditions.

The water taken from the quarry is colder (13.5ºC) than at other points (16.8 and 18.8ºC). The shallow depth of small stream and tailing pond probably contributes to more intense heating.

All sampled waters are of the HCO_3-Ca chemical type. High values of sulfate were also determined in the anionic composition. The highest value of SO_4^{2-} were measured in water samples taken from the quarry. The content of macro cations (Ca, Mg, Na, K) is also higher in samples collected from the quarry. The concentration of Al and Si are low and do not show any differences related to the sampling location. On the contrary, significant differences were noted in the Fe concentrations. In 4 and 5 samples, the Fe content (1.09 – 1.15 mg/L) is on an order greater than in quarry water (0.03 – 0.53 mg/L). Elevated Fe levels in water may likely result from its accumulation due to complexation with dissolved organic matter (DOM). We did not determine the DOM content in the samples. However, the yellowish color of the 4 and 5 water samples indirectly indicates the presence of organic substances of humic nature. In previously studied water objects with similar geochemical conditions, the interaction of Fe with DOM was identified as a key mechanism in its accumulation [6].

Table 1. Chemical composition of natural water sampled at the gold deposit "Novye Peski".

Chemical elements/Ions	Units	Samples					Geochemical background [7]
		1	2	3	4	5	
Ca		14.8	14.9	14.8	9.57	9.17	2.32
Mg		4.76	4.71	4.66	3.27	3.24	0.77
Na		3.7	3.62	3.69	2.69	2.64	1.04
K		1.73	1.71	1.70	1.31	1.35	0.34
Fe	mg\L	0.53	0.03	0.04	1.15	1.09	0.0716
Si		5.52	5.57	5.57	5.12	5.6	-
HCO_3^-		59.6	59	59.3	42	42.4	-
Cl^-		2.05	1.84	1.75	1.00	1.41	0.857
SO_4^{2-}		15.7	15.2	15	10.8	8.77	2.23
Li		1.34	1.52	1.31	1.02	0.97	-
B		6.36	6.51	6.55	5.36	5.48	1.25
Ti		2.32	1.95	2.29	2.10	2.59	-
V		0.25	0.21	0.24	0.29	0.43	0.19
Mn		2.94	0.63	0.32	123.4	77.2	-
Al		91.1	48.7	69	46.6	56	34.4
Ni		1.29	0.14	-	-	-	0.278
Cu		2.04	0.84	0.99	0.83	0.52	0.525
Zn	µg/L	50.26	52.8	6.7	13.59	11.7	0.964
As		1.76	1.81	1.9	1.06	1.4	0.082
Rb		1.64	1.65	1.68	2.2	2.26	0.536
Sr		38.17	38.61	40.17	28.64	29.54	14.7
Mo		0.18	0.16	0.17	0.05	0.04	0.108
Ba		13.48	13.34	14.73	14.86	23.33	-
U		0.463	0.456	0.458	0.155	0.109	0.01

Excesses of the geochemical background are highlighted in italics.

Depending on the behavior of trace elements in the studied water samples, three groups of elements are divided:

- Group of elements with the highest concentrations in quarry water – Zn, As, Mo, U, Ni, Cu, Sr, Li, B.
- Group of elements with concentrations of the same level in all selected samples – V, Ti, Ba.
- Group of elements with the highest contents in the stream and tailing pond – Mn, Rb.

Most of the measured concentrations of chemical elements exceed the geochemical background values, which are taken to be the mean contents of the elements in the surface waters of Karelia and adjacent territories [7]. The highest excesses were observed in the first group of chemical elements, indicating a negative impact of mining. In other words, the accumulation of these elements most likely occurs during interaction with exposed rocks in a quarry. As a rule, in the case of quarrying, an intensive accumulation of elements occurs during the interaction with the crushed rock fraction, in other words, at higher rock-water ratios [8]. The original source of most of the chemical elements of the first group (Zn, Ni, Cu, As, Mo) is the most widespread in the object ore minerals: Zn - sphalerite; Ni - pyrite (up to 3.5 wt.% Ni is contained in pyrite according to [4]; Cu - chalcopyrite; Mo - probably also sulfides; As - arsenopyrite and loellingite.

In contrast to the mining of building stone in Pitkäranta, North-Eastern Russia, Karelia [8], the rocks of this quarry contain a lower concentration of uranium by 1-2 orders of magnitude, probably, and are also more resistant to weathering and produce drainage with significantly lower U content than in the previously studied quarry. Other minerals containing As, Ni, and Cu have an extremely low distribution in rocks. However, it is necessary to take into account, minerals such as skorodite are supergene, so the interaction of primary minerals with waters occurs through the formation of these phases.

We assume that the main mechanism for the accumulation of elements of the third group (at least Fe and Mn) is complexation with DOM, which inhibits the precipitation of secondary mineral phases containing these metals. This mechanism has been studied under different geochemical conditions [9-10].

4 Conclusion

The contents of most major and trace elements in the natural waters of the deposit “Novye Peski” exceed the regional geochemical background abundancies. Among these elements there are potentially toxic to humans. All the chemical elements considered are divided into three groups:

- Elements with the highest concentrations in quarry water - Zn, As, Mo, U, Ni, Cu, Sr, Li, B, as well as Ca and other cations, HCO_3^- , SO_4^{2-}. We assume that the elements on this list have undergone the greatest changes due to mining operations.
- Elements with the same content level in selected samples – Al, Si, V, Ti, Ba.
- Elements with the highest contents in the stream and tailing pond – Fe, Mn. For this group, the main mechanism of accumulation in water is supposedly complexation with DOM.

In summary, we note the necessity to assess the risks of natural water pollution and organize monitoring of the state of environmental conditions during the mining of the deposits.

Due to the high resistance to weathering of the quarry's bedrock, the ecological consequences of the mining turned out to be not so dramatic. But nevertheless, taking into account the fact of the high fragility of the northern ecosystems, it is difficult to say that the environment of the influence zone of the mining operations remained untouched and completely without damage.

In the case of research area, a larger sampling is needed to assess the accumulative effect of water-rock interactions.

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