

Geochemistry of Water–Rock Interaction in the Area of the Khibiny Alkaline Massif

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Abstract—The interaction of natural and industrial waters with the rocks and apatite ores of the Khibiny alkaline massif was studied to estimate the extent of anthropogenic influence on natural processes. The abundance of the major rock-forming elements of the nepheline syenites and foidolites in the natural waters indicates that dissolution of nepheline and feldspathoids in natural water plays a significant role under the conditions of slow weathering in the Far North. Experiments showed that fine nepheline particles are transformed into amorphous phases at a fixed water volume at 18–20°C and pH 7.5–8.1. This process became observable already within the first day and continued for months. It is possible in stagnant reservoirs of natural waters and clearly expressed in industrial settling tanks. This is supported by the high content of amorphous phases enriched in Na, K, Al, and Si in the top layer of lacustrine sediments at the zone affected by the sewage of a concentrating mill.

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INTRODUCTION

Under the conditions of slow weathering in the regions of the Far North, different processes of water–rock interaction must be clearly expressed [1]. Many minerals of Khibiny rocks actively interact with water [2–5]. Mining and concentrating operations extract tremendous volumes of bedrocks into the supergene zone, where the surface area of their exposure to atmospheric agents increases considerably. Using the available data, we attempted to determine the conditions of water saturation in the major elements of a number of rock-forming minerals, taking into account the role of fine mineral particles.

We studied the rocks of the Khibiny apatite–nepheline deposits, whose compositions were studied in detail in [2, 4]. The following element groups were analyzed in waters [6, 7]: weakly mobile major elements (Al, Si, and Ca); highly mobile major elements (Na and K); and minor components not very common in the Khibiny rocks but showing the highest mobility (SO₄ and Cl) [8]. The choice of these elements is justified by Table 1. The available data indicate insignificant chemical variations in the surface waters of the Khibiny Massif and adjacent areas (Table 1, an. 3, 4). Underground waters have elevated contents of Na, Al, and Si (Table 1, an. 5, 6). Hence, the discharge of underground waters can significantly affect the composition of surface waters. However, anomalously high concentrations of Na (up to 16 mg/l), K (up to 3.8 mg/l) [7], and

Al (up to 0.096 mg/l) were also detected in some cases in the surface waters collected far from mines and concentrating plants. These contents are close to the constantly high contents of these elements in the water of Lake Imandra near the site of sewage discharge from concentrating mills [6] (Table 1, an. 7, 8).

INTERACTION OF MINERALS AND NATURAL WATERS

It is usually thought that the main geochemical factor of water–mineral interaction in the supergene zone is the formation of weathering crusts. Weathered rocks were first reported in the Khibiny Massif by Chirvinskii [9]. Fissure (infiltration) weathering residues of preglacial origin were found and studied in detail by Dorfman [2]. Their age was estimated as Pleistocene–Miocene on the basis of their hydromica–montmorillonite composition [10].

Topographically, the fissure residues are expressed as ravines, creek beds, and mountain valleys overlain by glacial deposits. They are composed at depth of hydromica, montmorillonite, and iron hydroxides replacing the rocks, and their fissures are mainly filled with montmorillonite (Fig. 1). There are also zeolites, secondary carbonate–hydroxide–fluorapatite, and minor opal and kaolinite [3]. In addition, a wide diversity of supergene minerals replace pyroxene, titanite, and accessory minerals of the agpaitic association [2, 4].

Table 1. Compositions of lacustrine, riverine, and underground waters in the region of the Khibiny alkaline massif and the area affected by the discharge of the OAO Apatit concentrating mill (mg/l)

Component	1	2	3	4	5	6	7	8
pH	7.2	7.08	7.16	7.08	6.9	8.1	7.7	7.43
Ca	4.0	3.30	0.63	0.44	1.2	0.5	3.65	4.01
Mg	1.3	1.02	0.07	0.11	0.24	0.16	1.03	1.03
Na	7.5	5.52	4.5	6.40	6.44	9.43	16.2	17.0
K		1.17	1.17	0.76	–	–	2.54	2.74
SO ₄	3	9.41	2.05	2.8	2.88	3.25	26.9	26.9
Cl	1.8	2.28	0.52	1.4	1.07	1.35	5.29	5.03
PO ₄	0.008	0.002	–	–	–	–	0.001	0.001
Si (NO ₃ + NO ₂)	0.6	1.46	1.3	1.44	1.75	1.75	0.14	0.23
Al	–	0.022	0.03	0.054	0.087	0.074	0.085	0.091
Fe	–	0.022	0.02	0.28	–	–	0.034	0.055
Cu	<0.005	0.004	–	–	–	–	0.004	0.004
Zn	<0.005	0.007	–	–	–	–	0.001	0.015
Mn	–	0.022	0.003	0.002	–	–	0.009	0.014
Sr	–	0.042	0.005	0.056	–	–	0.063	0.070

Note: (1) Limiting natural composition of Lake Imandra waters estimated by Moiseenko et al. [6]; (2) composition of Lake Imandra waters in the control zone located in the area of the combined influence of local industrial enterprises, after Moiseenko et al. [6]; (3) and (4) the minimum and maximum contents of mineral components in the surface waters far away from plants and sites of industrial water discharge [7]; (5) and (6) the same for underground waters [7]; (7) and (8) compositions of Lake Imandra waters in the zone affected by the discharge of concentrating mills (7) near the surface and (8) at the bottom according to our data, analyst L.P. Kudryavtseva (Institute of the Industrial Ecology Problems of the North, Kola Scientific Center, Russian Academy of Sciences).

Previous physicochemical modeling by means of the Selector program [11, 12] showed [13] that the composition of the Khibiny fissure (infiltration) weathering crusts corresponds to the humid conditions of midlatitudes [14]. However, an increase in water pH up to 7.5–8.1 depresses the replacement of primary minerals with depth even in the ground nepheline sands produced as tailings from apatite concentration. The calculated rates of the formation of supergene phases under the conditions of the Far North suggest that the first traces of presently forming hydromica–montmorillonite weathering residues will be visible after 300–400 years [13].

Physicochemical computer simulation showed [13] that, during the formation of secondary phases under the influence of atmospheric waters percolating through nepheline sands, the composition of water must be less saturated in the rock components than that observed in present-day natural waters. This once more indicates that water–rock interaction is not limited to the formation of weathering crusts [1, 15].

The dissolution of Khibiny minerals, including nepheline, could exert a significant influence on the water composition [2, 4, 5]. Nepheline crystals are covered by a thin film of gray or grayish brown halloysite (or metahalloysite) and iron hydroxides at the drying rocky surface subjected to the maximum atmospheric influence, with no visible alteration beneath it. The rock remains fresh beneath the film. However, deep hollows at the place of nepheline crystals can be observed on the bottom of permanent streams and run-

ning-water lakes. In such cases, the slow dissolution of nepheline is obvious.

The content of rapidly dissolving minerals [2, 5] in the Khibiny is not significant in general. At relatively low pH values of 5.8–6.5, significant amounts of Na, K, and Ca can be extracted from abundant nepheline and feldspathoids, and S and Cl are released from sodalite [2, 4]. The Khibiny rocks usually contain no more than 0.01% S and Cl and occasionally up to 0.10% SO₄.

The content of F, the most mobile element of the Khibiny apatite deposits, is often 0.04–0.40%. It occurs in fluorapatite, amphiboles, biotite, and easily soluble natural NaF (villiaumite). When a borehole penetrates a local villiaumite accumulation, the F content in the water may initially increase up to 0.4–2.25 mg/l and then decrease rapidly.

The main repository of Cl and S in the Khibiny rocks is sodalite, including sulfate-sodalite. According to Dorfman [2], the indications of sodalite dissolution appear very rapidly, within a few hours. Sulfate-sodalite is a rare mineral of alkaline pegmatites, while significant amounts of chlorine-sodalite occur as rims replacing nepheline. According to Kostyleva-Labuntsova et al. [4], the content of sodalite in the Khibiny rocks locally reaches 2%. Detailed mineralogical analysis showed that the ijolites, urtites, and apatite–nepheline rocks contain 0.2–0.7% sodalite [16]. The Khibiny sodalite contains 5.66–6.55% Cl, and rare sulfate-sodalite (hackmanite) contains 6.05–6.92% Cl and 0.29–0.77% S [4].

To test the hypothesis of rapid saturation of natural waters in sodalite constituents, including S and Cl, its interaction with distilled water was experimentally modeled using three samples of unaltered rock (Table 2). The samples were taken in 1959 from depths of 130–240 m in the boreholes located above mining pits and far away from possible industrial and domestic discharges and have been stored since then in a dry room for 36 years. The samples were crushed in a water environment, with the minimum yield of fine-grained fractions. The 1–3 cm rock fragments were splintered to 5.0–0.3 mm to obtain no more than 10% of the <0.315 mm fraction. Then, the rock chunks were washed to remove dust and fine particles.

A 10-g aliquot of crushed rock was loaded into a large agate mortar, mixed with 150 cm³ distilled water, and carefully crushed. The sample was kept for 10 min, after which water was collected, examined for visible suspensions, filtered through a 0.45 μm membrane filter, and analyzed (analyst L.P. Kudryavtseva).

It was planned that the time of water–rock interaction would be increased. However, the compositions of the obtained solutions (Table 3, an. 1a–3a) appeared to be similar to that of natural waters (Table 1). The contents of SO₄ and some cations (Na, K, Mg, and Al) in the experimental solutions were weakly dependent on the presence of sodalite in the samples, which presumably indicates the presence of concentrated liquid inclusions or easily soluble salts in the pores of rocks. The possible role of the so-called buried waters (capillary or film water [1]) in the modern system of water monitoring was noted during the hydrogeological work in the Kola Peninsula.

The easily soluble pore phases could be formed in the rocks owing to the penetration of drill mud during prospecting operations; on the other hand, they could occur as inclusions retained from the time when the rock was located at a considerable depth. The elevated contents of hydrocarbon gas phases in the Khibiny rocks were in some cases accompanied by the occurrence of soda [17]. Physicochemical computer modeling showed the principal possibility of soda formation in the Khibiny rocks during slow interaction of nepheline with hydrocarbon gases in a moist environment [18].

It is possible that the recent natural waters inherit in part the composition of waters buried during the preglacial period simultaneously with the development of

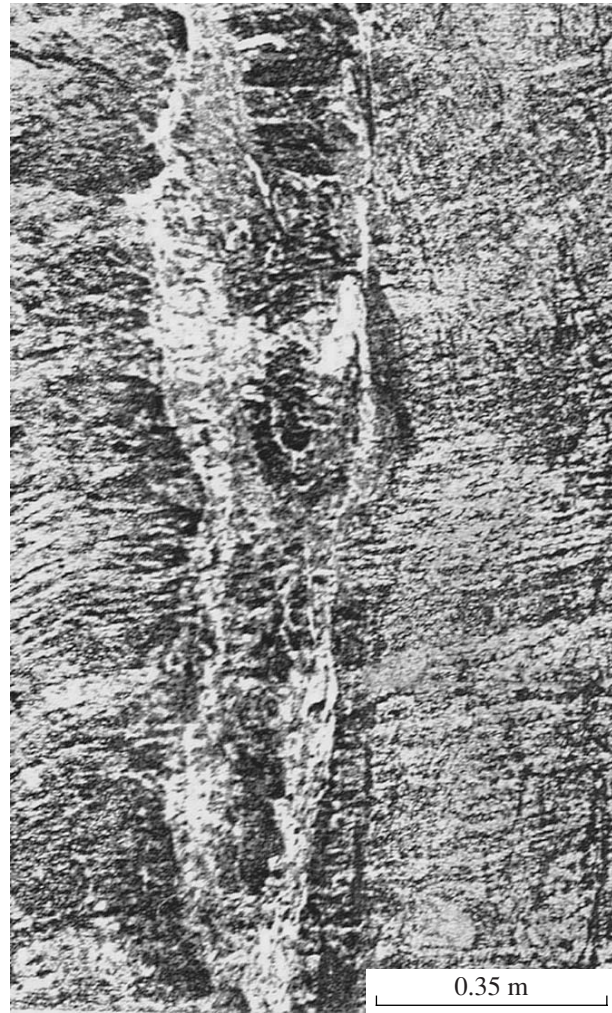


Fig. 1. Steeply dipping supergene fissure zone in the lens-banded ore of an apatite–nepheline deposit. The light-colored veinlets are mainly composed of montmorillonite with small grains of opal and secondary apatite. The lens-banded ore is replaced by hydromica, montmorillonite, and iron hydroxides in the fissure zone.

areal weathering mantles, which preserved as relics of infiltration fissure residues. The repeated formation and thawing of ice sheets in the Khibiny Massif had to affect the state of the pore space of the rocks and result in the redeposition, filtration, and drying of pore inclusions in the rocks. Currently, the most active exogenous process in the Khibiny Massif is the disintegration of

Table 2. Mineral compositions of the rock samples (wt %)

Rock	Nepheline	Feldspar	Pyroxene and amphibole	Sodalite	Apatite	Other minerals
Banded ore of the Yukspor deposit	48	2	8	<1	33	8
Urtite, Mt. Yukspor	65	5	21	<1	3	5
Sodalite zone of pegmatite in Yukspor nepheline syenite	0	21	7	70	0	2

Table 3. Composition of water (mg/l) after experiments (a) on the opening of rock pores in water and (b) on the interaction of finely ground apatite–nepheline rock with a fixed water volume

Component	1a	2a	3a	4b	5b
pH	7.31	7.74	7.48	7.94	8.05
Ca mg/l	2.83	5.36	0	2.87	3.05
Mg mg/l	0.30	0.42	0.03	0.19	0.04
Na mg/l	11.3	12.6	12.8	2.63	10.1
K mg/l	6.4	7.4	4.2	4.4	2.91
SO ₄ mg/l	2.75	2.98	2.52	0.43	0.2
Cl mg/l	3.38	2.1	4.8	0.39	0.30
P _{tot} µg/l	–	–	–	1.94	3.2
Si µg/l (NO ₃ + NO ₂)	–	–	–	0.62	4.77
Al µg/l	2.15	2.11	1.88	0.59	0.76
Fe µg/l	0.45	0.74	0.84	0.058	0.11
Cu µg/l	0.010	0.010	0.003	0.002	0.001
Zn µg/l	0.045	0.047	0.008	0.003	0.001
Mn µg/l	0.019	0.037	0.027	0.002	0.001
Sr µg/l	0.216	0.845	0.019	0.28	0.19

Note: The compositions of water after interaction: (1a) with apatite–nepheline ore, (2a) with urtite, and (3a) with sodalite pegmatite. The compositions of water after interaction with a finely ground sample of apatite–nepheline ore: (4b) for three days and (5b) for three months.

bedrocks, which leads to the extensive opening of previously closed pores.

There is another physical factor related to rock disintegration that could provide a rapid saturation of natural waters in the components of endogenous minerals. It is well known that fine particles (nanoparticles) can be decomposed in water within minutes or even seconds [19, 20, etc.]. According to the available data, this process can be expected for the rock-forming minerals of the Khibiny apatite deposits, primarily, for nepheline. Under natural conditions, mud-sized (dust) mineral particles can be formed during rock collapses, avalanches, and mudflows. In addition to these natural factors, which may control the composition of surface waters already at the heads of mountain streams, of great importance must be the anthropogenic factor, the crushing of minerals during mining operations and ore concentration.

The behavior of fine mineral particles of apatite ore in water was studied by the example of a banded ore from the Yukspor deposit of the following composition (wt %): nepheline 42, apatite 38, pyroxene 12, titanite 3, Ti-magnetite 1, and feldspar 2. The major-element composition of this ore is (wt %) SiO₂ 25.50, TiO₂ 0.52, Al₂O₃ 18.90, Fe₂O₃ 2.29, CaO 19.00, Na₂O 10.82, K₂O 3.12, and P₂O₅ 16.63.

Small portions of the sample were ground in an agate mortar. The 5-g powder aliquots were mixed with 250 ml of distilled water and periodically stirred. The experiments lasted three days and three months. At the end of experiments, the products were settled for a day, without the addition of any reagents. The obtained solu-

tion was filtered through a 0.45-µm membrane filter and analyzed. The compositions of solutions obtained by the interaction of finely ground samples with water (Table 3, an. 4b and 5b) are comparable with that of natural waters (Table 1). An X-ray amorphous precipitate was retained on the filter after water purification. Its emission spectral analysis revealed high contents of Si, Al, and Na. The weight loss of powders obtained by drying at room temperature varied from 10 to 18%. Their X-ray diffraction patterns showed the presence of dispersed phases, which were especially abundant in experiments with a fixed water volume contacting the sample for 3 months (Fig. 2).

The presence of dispersed phases was confirmed by IR spectrometry (O.A. Zalkind, Institute of Rare Element and Mineral Chemistry and Technology, Kola Research Center, Russian Academy of Sciences). The X-ray diffraction patterns of the powders showed that an increase in the extent of dispersion was accompanied by a decrease in the content of crystalline nepheline relative to apatite. This observation was confirmed by the analysis of pelleted samples using an MS-46 microprobe (Fig. 3). The samples were analyzed with a 100-µm beam in ten points, and the average composition was then calculated. The obtained data showed that fine nepheline particles are unstable in atmospheric water even at high pH values, when they transform slowly into amorphous phases.

The lake waters of the Khibiny Massif contain 0.001–0.003 mg/l phosphorous, which is only slightly higher than the average content in natural waters [21]. It can be suggested that apatite particles smaller than

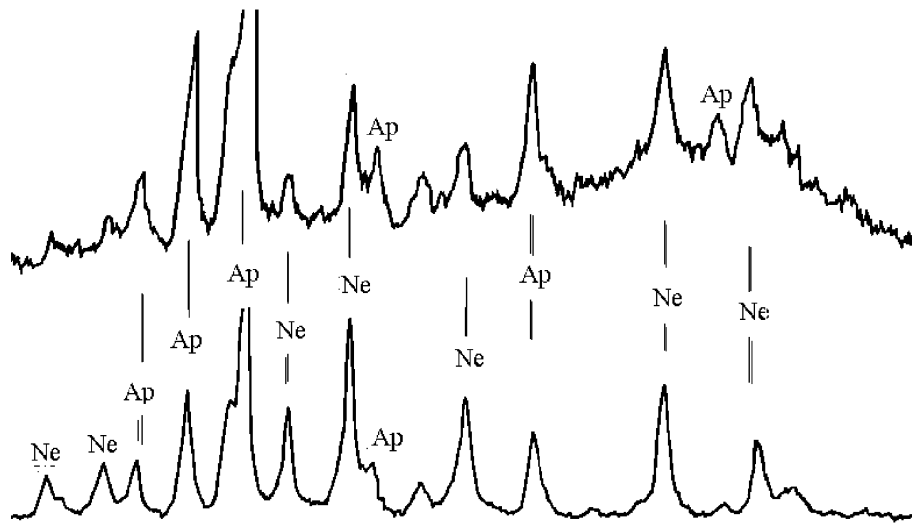


Fig. 2. X-ray diffraction patterns of ground apatite–nepheline ore before (bottom) and after (top) a three-month experiment with water. Ap, apatite; Ne, nepheline. The diffraction patterns were recorded at the Geological Institute of the Kola Scientific Center, Russian Academy of Sciences, analyst T.A. Selivanova

0.5 μm are better preserved in alkaline water than nepheline particles of the same size.

Our results showed that the interaction of the mineral matter of Khibiny rocks with natural waters is a complex process involving weathering, slow dissolution of nepheline and feldspathoids, rapid dissolution of fine mineral particles, formation of amorphous phases at the expense of the decomposition of fine nepheline particles, and possible activation of buried waters. Of course, this list is not complete.

MINERAL COMPOSITION OF BOTTOM SEDIMENTS AT THE REGION OF INDUSTRIAL WATER DISCHARGE FROM THE CONCENTRATING MILL INTO LAKE IMANDRA

The apatite–nepheline deposits of the Khibiny Massif are the greatest source of phosphates. Apatite concentrate is produced by flotation with crushing up to the <0.3-mm fraction. This process results in the influx of huge masses of mineral ore particles smaller than 1 μm into the environment. After ore crushing, the mill tailings containing the finest fraction are stored in a depository of sands, which remained after apatite extraction and supply industrial wastes into Lake Imandra.

The Belaya River basin is mainly located outside the Khibiny Massif, among the Proterozoic volcanosedimentary country rocks of the Imandra–Varzuga Formation and Archean granite gneisses. The bottom sediments of Lake Imandra were sampled near the mouth of the Belaya River, which receives industrial waters from the concentrating mill of OAO Apatite. The top layer of the lacustrine sediments 7.8 cm thick was sampled in two

parallel columns. The composition of water at the sampling site is shown in Table 1 (an. 7 and 8).

The investigation of the inorganic matter of bottom sediments is a difficult task, because it is dominated by nanoparticles [22]. The samples are dark brown muds cementing during drying. Their chemical compositions were analyzed on an MS-46 electron microprobe (analyst Ya.A. Pakhomovskii), using the aforementioned

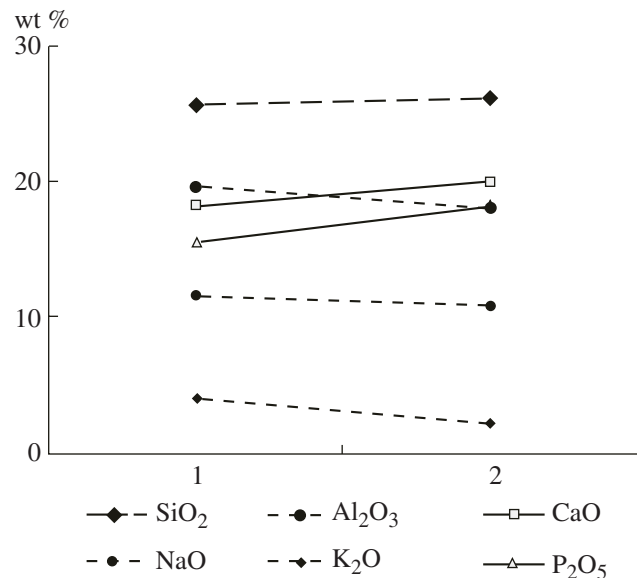


Fig. 3. Main changes in the composition of ground apatite–nepheline ore (1) after its storage in water for three months (2). The finest suspensions were partially removed with water. Analyst Ya.A. Pakhomovskii, Geological Institute, Kola Scientific Center, Russian Academy of Sciences.

Table 4. Major-component composition of the bottom sediments (wt %)

Oxide	1	2	Oxide	1	2
SiO ₂	37.4	39.2	MnO	0.2	0.2
TiO ₂	1.5	1.5	SrO	0.6	0.6
Al ₂ O ₃	17.4	19.3	Na ₂ O	5.2	6.6
CaO	10.8	8.9	K ₂ O	3.5	4.5
MgO	1.4	1.5	P ₂ O ₅	8.0	7.1
FeO	6.3	6.3	Total	93.7	96.7

Note: (1) Whole-rock analysis and (2) fraction <0.002 mm. Analyst Ya.A. Pakhomovskii, Geological Institute, Kola Scientific Center, Russian Academy of Sciences.

technique without reagents or additional grinding and heating. The results are given in Table 4.

Standard grain-size analysis was used for the density separation of solid particles in a control sample in water without precipitating fine fraction by reagents. The fraction >0.01 mm accounted for 32.5%; fraction 0.01–0.002 mm, for 35.3%; fraction <0.002 mm, only for 0.07%; and the loss was 32.1%. The significant loss could be caused by the large volume of distilled water that was used in this method. This could lead to the loss and dissolution of low-density fine solid particles and colloidal phases. The X-ray diffraction patterns of the whole-rock sample of bottom sediments and all its fractions revealed a high content of dispersed phases, which was confirmed by IR spectrometry (O.A. Zalkind, Institute of Rare Element and Mineral Chemistry and Technology, Kola Research Center, Russian Academy of Sciences). The microscopic examination of the >0.01 mm fraction in immersion oils confirmed the presence of an isotropic phase with a low refractive index. It is evident that the amorphous phase was partially retained in all size fractions.

In addition to nepheline and apatite, the examination of the >0.01 mm fraction in immersion oil revealed significant amounts of quartz and feldspars and the presence of amphibole and chlorite. This suggests that considerable amounts of the material of the country rocks of the Khibiny Massif were delivered by the river to the lake. However, the major components of the sediments are nepheline and apatite (Table 1, Fig. 4). The X-ray diffraction patterns (Fig. 4) indicate that the maximum effect of apatite production is confined to the fine fractions of the top layer of lake sediments.

The microprobe analyses of pressed pellets showed that the composition of the <0.002 mm fraction (Table 4, an. 2) is close to the bulk composition of the suspensions. At the same time, this fraction has elevated content of nepheline constituents (Table 4). The intensity of nepheline lines in the X-ray diffraction pattern of this fraction decreases sharply relative to the apatite lines (Fig. 4). The observed features of the composition of the fine fraction are similar to those in the experiments

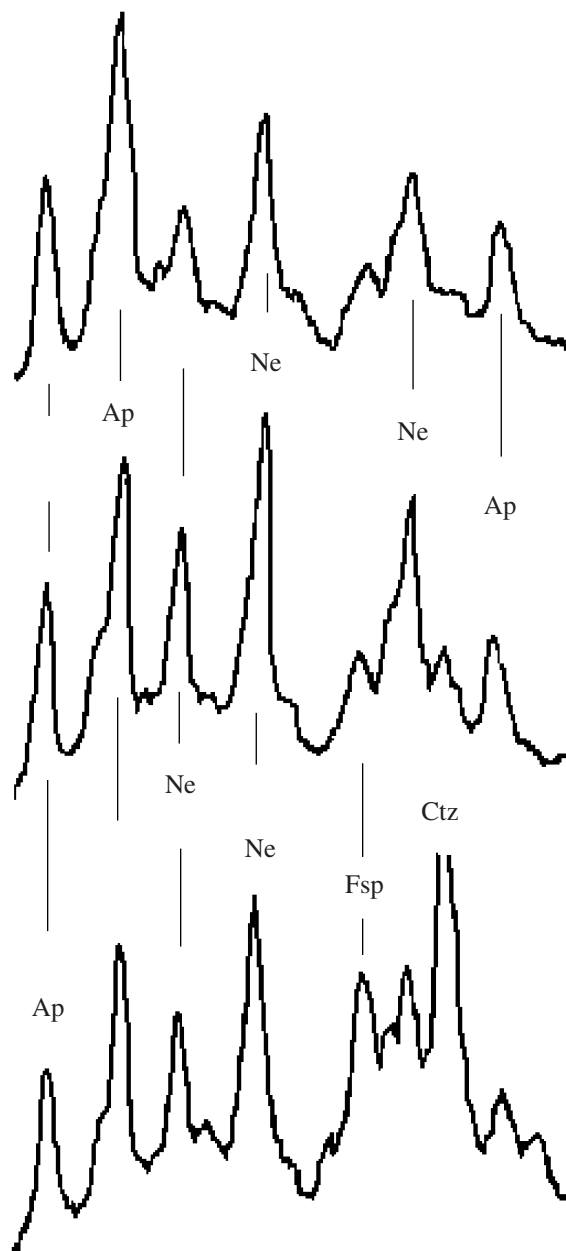


Fig. 4. Fragments of X-ray diffraction patterns of bottom sediments with particles >0.01 mm (lower), 0.01–0.02 mm (middle), and <0.002 mm (upper).

on the decomposition of nepheline into dispersed phases.

DISCUSSION AND CONCLUSIONS

The contents of the major elements of the Khibiny rocks increase sequentially from the surface water of the Khibiny Massif to underground waters and to the lacustrine waters of the zone affected by industrial wastes (Table 1). An exception is SiO₂, whose content decreases in the waters of the mixing zone, although the

SiO₂ content of the industrial water is 9–10 mg/l [7]. This fact is confirmed by numerous analyses obtained in different years ([6, 7], Table 1, an. 7 and 8) and can be explained on the basis of natural observations.

White crusts consisting mainly of silica (spectral analyses) were described in the beds of small streams in the Khibiny Mountains already in the 1930s [9]. White foamlike sediments were repeatedly observed by us on the banks of Khibiny streams. They were analyzed twice, and it appeared that they consist of almost pure silica in an X-ray amorphous state. In some cases, this sediment was observed on the banks of streams whose beds contained rock with “pocks” at the place of nepheline crystals. This leads to the conclusion that silica released during slow nepheline dissolution in the beds of perennial streams is transported as a gel by water flows. The same phenomenon must take place during the opening of natural stagnant reservoirs.

The possible existence of underground reservoirs of stagnant waters in the Khibiny Massif is suggested by the occurrence of gently sloping infiltration weathering crusts (“pockets”) [2]. During their exposure and erosion by atmospheric waters, alkalis and Al colloids could be transformed into dissolved species, while silica is removed as an amorphous phase. This may be responsible for the short-term anomalous increase in the contents of major rock-forming elements of nepheline syenites and foidolites in the waters. In the relatively calm setting of lacustrine waters, silica gel could form the amorphous component of the upper sedimentary layer.

The anomalous contents of SO₄ and Cl disagree with the compositions of underground waters and the results of our experiments (Table 3). It can be supposed that SO₄ and Cl were accumulated in a natural way as salt sediments in the pores of rocks, but the influence of anthropogenic factors is probably more significant. The snow cover is the main concentrator of anthropogenic atmospheric sulfur under the conditions of the Far North. There are sources of industrial sulfur in the Khibiny area. Significant amounts of SO₄ and Cl can be supplied by mines, concentrating mills, towns, and mining settlements.

Mining and concentrating plants significantly affect the content of alkalis and aluminum in waters (Table 1). In such a case, the role of interaction between fine mineral particles (primarily, rock-forming nepheline, which is suggested by the obtained data) and water increases dramatically. The main anthropogenic sources of fine mineral particles are the tailings of the concentrating mills.

Mill tailings containing the finest fraction after ore crushing are transported to the depository of sands remained after apatite extraction and to the settling tanks of industrial waters. The colloidal phases contained in them cause local effects of quicksand. Owing to the disturbance of dams or during floods, the concentration of colloids in the settling tanks may cause satu-

ration of surface and underground waters in the major rock-forming elements. At the same time, colloidal phases play a positive role as sorbents accumulating heavy and trace elements [6].

The following conclusions can be drawn.

1. Under the conditions of retarded weathering in the Far North, the slow dissolution of rock-forming nepheline and feldspathoids in the Khibiny alkali massif plays a significant role in the water–rock interaction. Intense processes of disintegration in the mountain mass and mining activity suggest that the rapid dissolution of dusty particles of some minerals strongly affects the composition of waters. The liquid and easily soluble phases extracted from rock pores, which were previously formed under different geologic conditions, could also affect the composition of underground and surface waters.

2. It was shown that nepheline particles smaller than 0.02 mm are transformed into amorphous phases at $t = 18^{\circ}\text{--}20^{\circ}\text{C}$ and $\text{pH} = 7.5\text{--}8.1$. This process becomes observable already in the first day and continues for months. It is possible in natural stagnant water reservoirs and much more pronounced in the settling tanks of concentrating plants. This is confirmed by the comparison of experimental data with the phase composition of the upper layer of lacustrine sediments at the site of industrial water discharge.

3. Using the alkaline rocks of the Khibiny Massif as an example, we can conclude that the interaction of minerals with a water environment is controlled by a combination of various exogenic processes proceeding with different rates. The study of these processes is of great importance for the protection of ecosystems and for the utilization of wastes, in particular, for the additional extraction of trace and noble metals.

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