

Article

Titanite Ores of the Khibiny Apatite-Nepheline-Deposits: Selective Mining, Processing and Application for Titanosilicate Synthesis

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Abstract: Geological setting and mineral composition of (apatite)-nepheline-titanite ore from the Khibiny massif enable selective mining of titanite ore, and its processing with sulfuric-acid method, without preliminary concentration in flotation cells. In this process flow diagram, titanite losses are reduced by an order of magnitude in comparison with a conventional flotation technology. Further, dissolution of titanite in concentrated sulfuric acid produces titanyl sulfate, which, in turn, is a precursor for titanosilicate synthesis. In particular, synthetic analogues of the ivanyukite group minerals, SIV, was synthesized with hydrothermal method from the composition based on titanyl-sulfate, and assayed as a selective cation-exchanger for Cs and Sr.

Keywords: apatite-nepheline-titanite ore; sulfuric-acidic decomposition; titanyl sulfate; hydrothermal synthesis; ivanyukite

1. Introduction

The world largest apatite-nepheline deposits of the Khibiny massif (NW Russia) host complex ores containing five economic minerals are: Fluorapatite, nepheline, titanite, aegirine and titanomagnetite. However, at present, only two of them (fluorapatite and nepheline) are economically attractive, while the rest are accumulated in tailings ponds [1]. Titanite, CaTiSiO_5 , is the most important mineral among them because titanium and its compounds are widely used in different industrial technologies.

In addition to titanite and titanomagnetite, the apatite-nepheline deposits contain numerous pegmatites with rare titanium minerals that have important functional properties, for example, ferroelectric loparite-(Ce) [2], molecular sieve chivruaiite [3,4] (Ca-analog of synthetic microporous titanosilicate ETS-4 [5,6]), cation exchangers kukisvumite and punkaruavite [7–10] (respectively, Zn and Li analogues of synthetic titanosilicate AM-4 [11,12]), cation exchangers sitinakite [13] (natural analogue of synthetic titanosilicate Ionsiv IE-911 [14–16]), and minerals of the ivanyukite group [17–20]. Besides, these and other synthetic titanium-based compounds (ETS-2, ETS-10, JDF-L1, LHT-9, MIL-125, etc.) are utilized as agents for cation relocation, hydrogen storage and heat transformation, dehydrating agents, drug nanocarriers, adsorbents and membranes [20–25].

In particular, ivanyukite-Na and its synthetic analogue SIV described herein have pharmacosiderite-related crystal structure consisting of Ti_4O_{24} -clusters coupled into a framework by single SiO_4 tetrahedra

(Figure 1). In this framework, there is a system of wide channels (≈ 6.1 Å), with extra-framework cations of K and Na and water molecules inside that can be easily exchanged with Rb^+ , Cs^+ , Tl^+ , Ag^+ , Sr^{2+} , Ba^{2+} , Cu^{2+} , Ni^{2+} , Co^{2+} , La^{3+} , Ce^{3+} , Eu^{3+} , Th^{4+} , etc. [18–20,26]. Moreover, (^{137}Cs , ^{90}Sr , ^{154}Eu)-exchanged forms of ivanyukite can be transformed by heating into stable SYNROC-like titanate ceramics for long-time immobilization of these radionuclides [20].

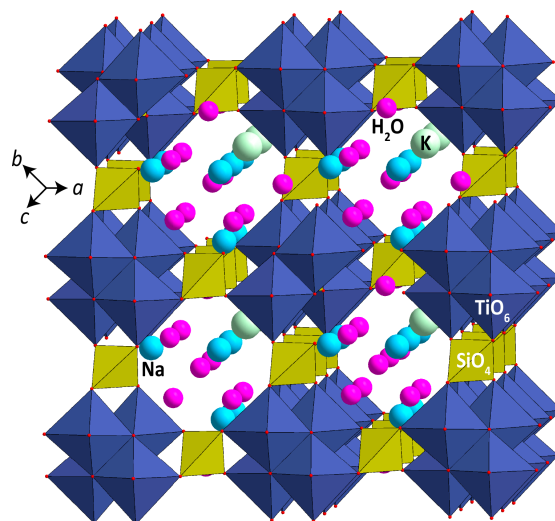


Figure 1. Crystal structure of ivanyukite-Na-T [17]: cubano-like clusters Ti_4O_{24} consisting of four edge-shared TiO_6 octahedra (dark-blue) are connected by vertexes SiO_4 tetrahedra (yellow) to form the microporous framework, with Na (cyan), K (pale green), and H_2O (magenta) in channels.

There are a lot of studies related to titanite concentrate chemical processing [27–29]. Among the known technologies, sulfuric-acidic ones are the most perspective because they enable to obtain a wide spectrum of materials including titanium pigments, fillers, adhesives, tanning agents, sorbents and molecular sieves. High titanite content is a typical property of apatite-titanite and nepheline-titanite rocks, which are currently stockpiled in dumps due to difficulties with titanite separation from apatite and nepheline by flotation. We would like to show herein new perspectives for production of synthetic ivanyukite-type compounds and other materials mentioned above with sulfuric-acidic cleaning followed by hydrometallurgical processing of ground apatite-titanite and nepheline-titanite ores. This approach features better productiveness in relation to a conventional technologies of titanite extraction by flotation and titanosilicate synthesis from compositions based on titanium chlorides.

2. Geological Setting

The world's largest Khibiny alkaline massif (35×45 km) is situated in the West of the Kola Peninsula (Murmansk Region, Russia), at the contact between low-metamorphosed volcano-sedimentary rocks of the Proterozoic Imandra-Varzuga greenstone belt and the Archaean ultra-metamorphic rocks of the Kola-Norwegian megablock (Figure 2). Its age is 380–360 million years [30]. The main rock of the massif is coarse-grained nepheline syenite (foyaite) that forms funnel-shaped homogeneous body divided into two parts by the Main Ring intrusion of foidolite (melteigite–urtite rock series), with related poikilitic (kalsilite)-nepheline syenites (rischorrite and lyavochorrite) and fine-grained alkaline syenite with xenolites of feinitized volcano-sedimentary rocks [31,32]. The Main Ring thickness on the day surface varies from 0.1 to 10 km, and rapidly decreases with depth. Within the outer part of the foyaite body, there is another one semi-ring zone of foidolites, alkaline syenite and fenite. In addition, monchiquite–carbonatite veins and explosion pipes occur in the Eastern part of the Main Ring.

The rock-forming minerals of foyaite include nepheline, microcline, orthoclase, albite, aegirine, augite, Na–Ca- and Na-amphiboles, aenigmatite, titanite, eudialyte, lamprophillite,

and annite. Rischorrite and lyavochorrite contain rock-forming nepheline, sodalite, orthoclase, aegirine, KNa-amphiboles, annite, titanite, aenigmatite, ilmenite, lamprophyllite, astrophyllite, and fluorapatite [31,32]. The main constituents of the foidolites are nepheline, clinopyroxenes of the diopside-aegirine-augite series, KNaCa-amphiboles (potassicrichterite, potassicferrorichterite, etc.), annite, titanite, fluorapatite, titanomagnetite (members of the magnetite-ulvöspinel series), ilmenite, and eudialyte, with wide-ranging relations between them (Figure 3).

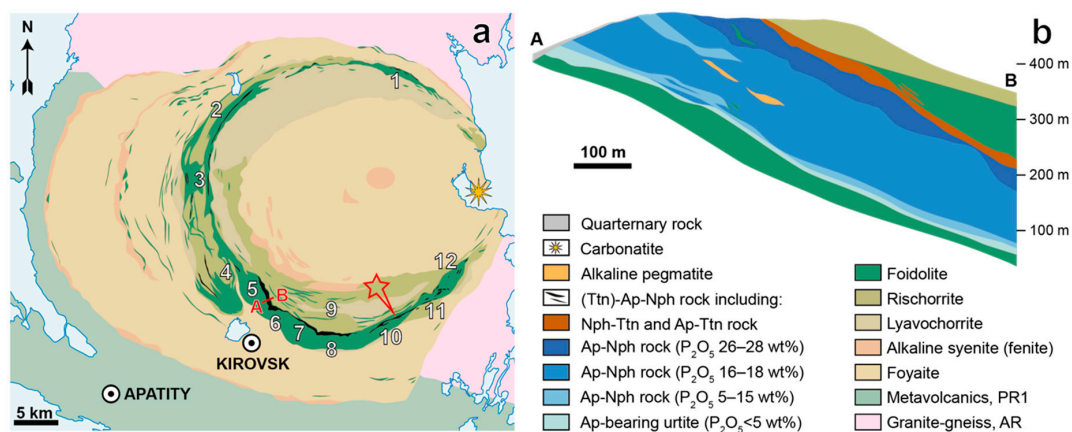


Figure 2. Geological map of the Khibiny massif (a, after [32]) and vertical section of the Kukisvumchorr titanite-apatite-nepheline ore body along A–B line (b, after F.M. Onokhin). Titanite-apatite-nepheline deposits: 1—Valepakhhk, 2—Partomchorr, 3—Kuelporr, 4—Snezhnyy Circus, 5—Kukisvumchorr, 6—Yuksporr, 7—Apatite Circus, 8—Plato Rasvumchorr, 9—Eveslogchorr, 10—Koashva, 11—Niorkpakhhk, and 12—OleniyRuchei. Red star indicates the place of titanite ore sampling.

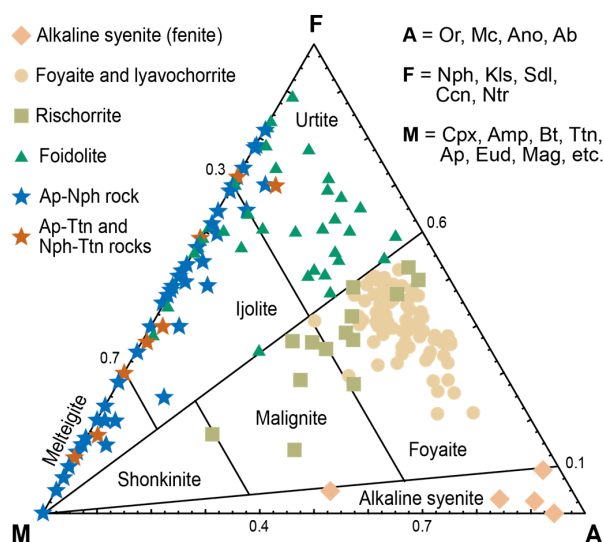


Figure 3. Modal composition of alkaline rocks estimated with grain squares of feldspars (A), feldspathoids (F), and dark colored minerals (M) in polished hand-sized specimens of the Khibiny massif (after [32,33], with additions). Ab—albite, Amp—amphiboles, Ano—anorthoclase, Ap—fluorapatite, Bt—biotite, Ccn—cancrinite, Cpx—clinopyroxenes, Eud—eudialyte, Kls—kalsilite, Mag—magnetite, Mc—microcline, Nph—nepheline, Ntr—natrolite, Or—orthoclase, Sdl—sodalite, and Ttn—titanite.

At apical parts of the Main Ring, there are fractal stockworks of specific apatite-rich foidolite, apatite-nepheline rock (see Figures 2 and 3), which form 12 apatite deposits developed by two mining

companies: JSC “Apatit”, and JSC “North-Western Phosphorus Company” [32]. Major minerals of apatite-nepheline rock are fluorapatite, nepheline, diopside–aegirine–augite, potassicrichterite, potassicferrorichterite, orthoclase, titanite, magnetite, and ilmenite, contents of that vary in a wide range of values (Figure 3).

Titanite is a typical apatite-nepheline rock mineral of accessory to minor rock-forming types (Table 1). It occurs as separate fine-grained lenses (up to 5 cm in diameter) within fluorapatite bands (Figure 4a). Content and size of titanite lenses increase towards the upper contact of apatite-nepheline rock covered by rischorrite–lyavochorrite that accommodates layers (up to 50 m thick) of titanite-dominant (up to 80 modal %) apatite-titanite and nepheline-titanite rocks (see Figure 2b). In these rocks, the main part of titanite is presented by brown prismatic crystals (up to 1 cm long) with lustrous faces (Figure 4b–d). Average chemical composition of such titanite (Table 2) corresponds to the formula: $(\text{Ca}_{0.95}\text{Na}_{0.04}\text{Sr}_{0.01})_{\Sigma 1.00}(\text{Ti}_{0.96}\text{Fe}^{3+}_{0.02}\text{Nb}_{0.01})_{\Sigma 0.99}(\text{Si}_{0.99}\text{Al}_{0.01})_{\Sigma 1.00}\text{O}_5$ [33].

Table 1. Titanite resources of the Khibiny titanite-apatite-nepheline deposits [33].

Deposit	Measured Ttn Resources, kt	Average Ttn Content in (Ttn)-Ap-Nph ore, wt %	Fraction of Ap-Ttn and Nph-Ttn Ores, vol %
Partomchorr	59,615	6.9	13.6
Kuelporr	995	5.2	4.3
Kukisvumchorr	17,550	4.2	6.9
Yuksporr	23,340	4.4	8.1
Apatite Circus	3840	3.2	1.9
Rasvumchorr	13,395	4.0	2.1
Eveslogchorr	45	8.9	27.7
Koashva	38,780	4.7	8.4
Niorkpakhk	1595	2.4	0.0
OleniyRuchei	12,075	3.1	0.0

Table 2. Chemical composition of titanite from titanite-apatite-nepheline rock, wt % [33].

Constituent	n	Mean	Min	Max	SD
Na ₂ O	15	0.61	b.d.	1.18	0.30
Al ₂ O ₃	15	0.24	b.d.	0.66	0.17
SiO ₂	15	30.31	29.61	32.38	0.62
K ₂ O	15	0.01	b.d.	0.20	0.05
CaO	15	27.16	25.22	28.04	0.95
TiO ₂	15	38.93	37.28	42.86	1.30
V ₂ O ₃	15	0.02	b.d.	0.15	0.04
MnO	15	0.01	b.d.	0.06	0.02
FeO	15	0.88	0.33	1.29	0.29
SrO	15	0.32	b.d.	0.53	0.15
ZrO ₂	15	0.14	b.d.	0.43	0.15
Nb ₂ O ₅	15	0.38	b.d.	1.35	0.41
La ₂ O ₃	15	0.05	b.d.	0.17	0.07
Ce ₂ O ₃	15	0.30	b.d.	0.68	0.16
Nd ₂ O ₃	15	0.04	b.d.	0.26	0.08

At the apatite deposits, content of (apatite)-nepheline-titanite rock reaches 30 vol % (Table 1) with average titanite content about 20 wt %. Taking into account stable position of this rock at the contact between bedding foidolite (including apatite-nepheline rock) and covering rischorrite–lyavochorrite, as well as significant thickness of these layers (Figure 2b), selective mining of titanite ores gains practical importance. Under the present studies, about 1.5 tons of nepheline-titanite rock were selectively mined from the apical part of the Koashva ore-body, and then processed with the sulfuric-acid method without preliminary concentration.

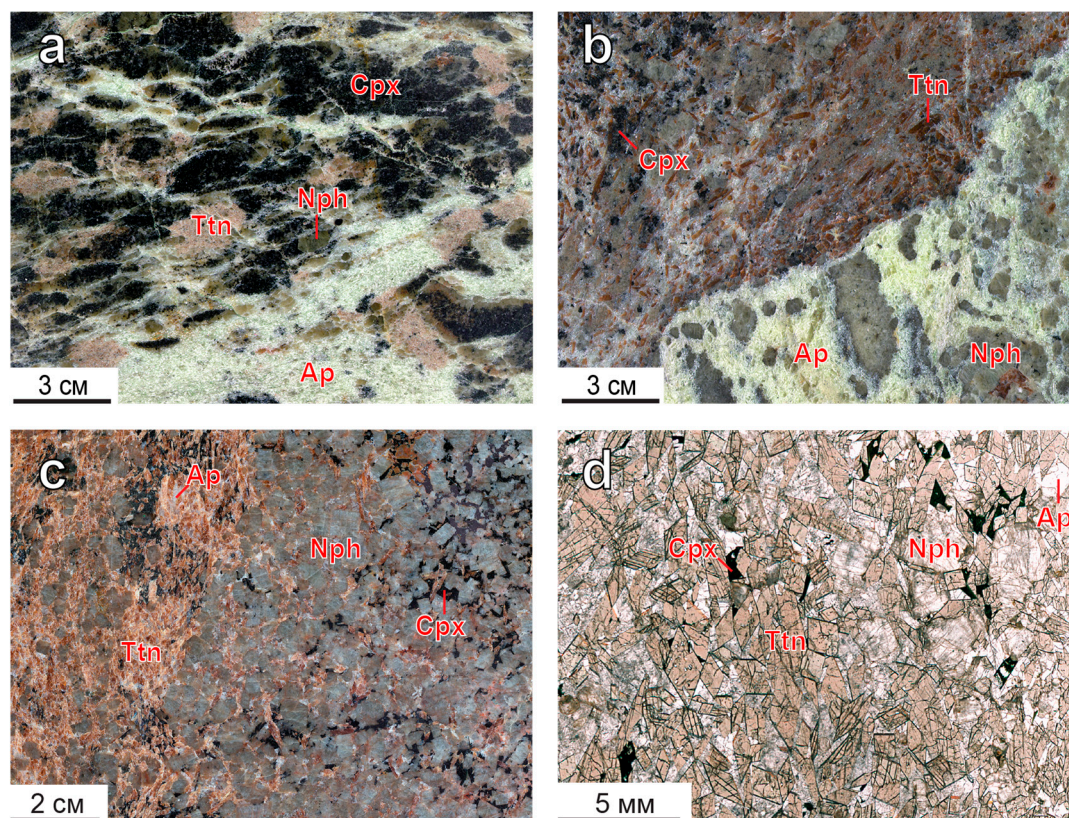


Figure 4. Titanite segregations in apatite-nepheline (a), apatite-titanite (b) and nepheline-titanite (c,d) ores of the Koashva apatite deposit, the Khibiny massif. Photos of polished samples (a–c) and thin section of the sample c in transmitted light (d). Ap—fluorapatite, Cpx—clinopyroxene, Nph—nepheline, Ttn—titanite.

3. Materials and Methods

For this study, we used blocks (up to 0.5 m in diameter) of (apatite)-nepheline-titanite ore, mined at the Koashva open pit. The reagents used included reagent-grade sulfuric and hydrochloric acids, sodium and potassium hydroxides (H_2SO_4 93.0%, HCl 37.5%, NaOH 99%, KOH 99%), analytical reagent grade pentahydrate sodium metasilicate, $\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$, and ammonium sulfate, $(\text{NH}_4)_2\text{SO}_4$, (Reachem, Moscow, Russia), and distilled water (Tananaev Institute of Chemistry, Apatity, Russia).

At first, ore blocks were crushed on a jaw crusher, and then in a 1.5 kW AGO-2 planetary mill (NOVIC, Novosibirsk, Russia) for 6 h, with the rock:balls ratio of 1:5 [34]. Then classification (dry sieving) was carried out (with separation of a powder fraction less than 40 μm). Modal and chemical composition of the crushed sample was determined by means of a FT IR 200 spectrophotometer (Perkin Elmer, Waltham, MA, USA).

The produced powder sample was separated from apatite and nepheline in H_2SO_4 or HCl dilute water solutions (50–100 g/L), with solid/liquid ratio S:L = 1:3–1:4 (Figure 5). The suspension was mixed in a magnetic stirrer at the temperature of 50 ± 5 °C for 2 h. After dissolution of apatite and nepheline, a purified titanite-aegirine concentrate was separated by filtration.

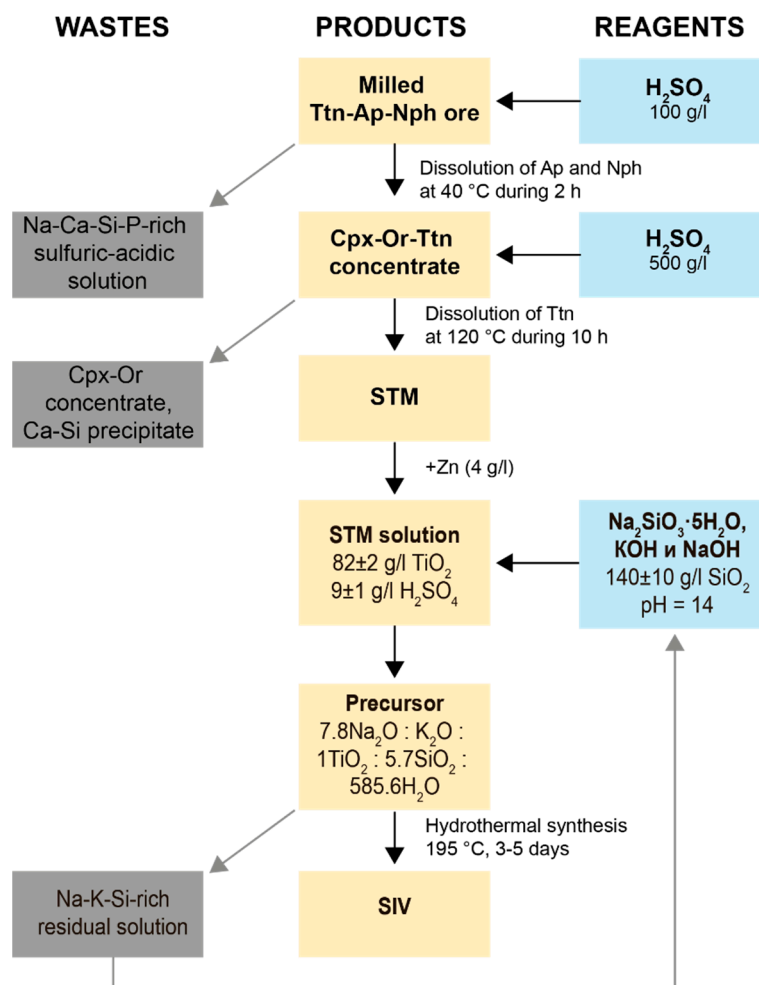


Figure 5. A principal scheme of apatite-nepheline-titanite ore processing for SIV synthesis. Mineral abbreviations see in Figure 3.

Then the concentrate was mixed with sulfuric acid (500 ± 100 g/L H_2SO_4) at the ratio of S:L = 1:3.5, and the mixture was poured into a flask equipped with a stirrer and a condenser [35]. The concentrate interacted with H_2SO_4 at the boiling point of the reaction mass for 9–10 h. The produced Ti-bearing sulfuric acid liquid phase was separated from insoluble aegirine by filtration, and used for crystallization of titanyl sulfates $\text{TiOSO}_4 \cdot \text{H}_2\text{O}$ (STM) and $(\text{NH}_4)_2\text{TiO}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$ (STA) [28,36]. The last compound was obtained by means of reaction of STM with ammonium sulfate.

Hydrothermal synthesis of microporous titanosilicates (ETS-4, SIV, AM-4, etc.) was performed by analogy with ETS-10 [37], with STM as Ti source. To prepare a titanium precursor, we used STM solution with concentrations of 82 ± 2 g/L TiO_2 and 9 ± 1 g/L H_2SO_4 . Four-valent titanium contained in the solution was partially reduced by addition of zinc powder (4.4 ± 0.1 g/L). Zinc consumption was assumed on the basis of Ti_2O_3 concentration of 5–10 g/L. Solution of sodium silicate $\text{Na}_2\text{SiO}_3 \cdot 7\text{H}_2\text{O}$ containing 140 ± 10 g/L of SiO_2 was also used. The reduced titanium solution was gradually dosed into the sodium silicate solution; after that, sodium and potassium alkali solutions were added to adjust pH. Total time for the mixture preparation was 3–3.5 h. The resulting gel-like suspension was placed in the Parr 4666-FH-SS autoclave (Parr Instrument, Moline, IL, USA) and held at 195 ± 5 °C for 3–5 days. The produced precipitate was separated and, after washing, placed in a drying cabinet. Drying time at the temperature of 70 ± 5 °C was 7–10 h.

Modal composition of the synthesized samples was determined by means of a XRD-6000 diffractometer (Shimadzu, Kyoto, Japan), with a Cu X-ray tube operated at 60 kV and 55mA.

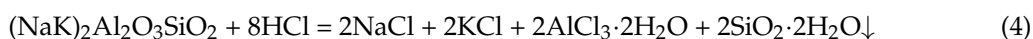
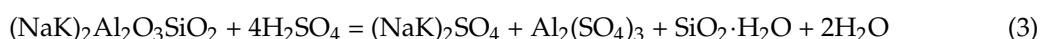
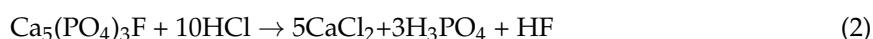
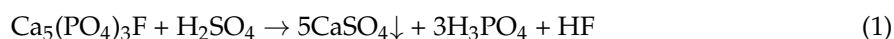
Bulk chemical compositions of the powder samples were determined using an X-ray fluorescence spectrometer Spectroscan MAK-S-GV (Spectron, St. Petersburg, Russia), operating in WDS mode at 40 kV. Morphology of the produced particles was analyzed with an optical microscope DM-2500P (Leica, Wetzlar, Germany) and a scanning electron microscope XL 30 (Philips, Amsterdam, The Netherlands) equipped with an Oxford INCA EDS analyzer (Oxford Instruments, Oxford, UK).

The BET surface properties and the porosity of the final products were characterized by nitrogen and adsorption/desorption method at 77 K using a surface area analyzer Micromeritics TriStar 3020. The average pore diameter (D_{av}) was calculated as 4 V/S. Prior to adsorption/desorption measurements the sample was degassed at 393 K for about 24 h. Low degassing temperature was chosen to avoid any structural changes of the material.

4. Results

4.1. STA and STM Production

Acidic cleaning of (apatite)-nepheline-titanite ore occurs due to consecutive fluorapatite and nepheline dissolution under the influence of diluted sulfuric or hydrochloric acids:



Because of close titanite intergrowth with nepheline and especially fluorapatite, it is necessary to ensure fine grinding of ore (<63 μm). It is obvious that at this stage we should rather use hydrochloric acid, which does not cause formation of silica and insoluble calcium compounds that can inhibit titanite dissolution at the next stage.

We found out that cold acidic cleaning of homogeneous finely ground ore was not very effective. Temperature increase up to 50 °C activates apatite dissolution with the corresponding phosphorus transfer into the liquid phase (Table 3); however, nepheline remains undissolved. Two-stage ore cleaning with cold and then heated sulfuric acid gives satisfactory results for both apatite (P) and nepheline (Al), without Ti losses. Addition of hydrochloric acid is the most effective for apatite separation; however, absence of insoluble secondary products compensates quite well slow dissolution of nepheline.

Table 3. Chemical composition of ground ore cleaned under different conditions.

Experiment	Conditions	Ore Composition, wt %		
		TiO ₂	Al ₂ O ₃	P ₂ O ₅
1	H ₂ SO ₄ , 80 g/L, S:L = 1:3, 4 h, 18 °C	30.5	0.97	4.23
2	H ₂ SO ₄ , 80 g/L, S:L = 1:4, 2h, 50 °C	28.0	2.69	1.00
3	1 stage: H ₂ SO ₄ , 80 g/L, S:L = 1:3, 4 h, 18 °C; 2 stage: H ₂ SO ₄ , 100 g/L, S:L = 1:4, 2 h, 50 °C	32.0	0.27	1.15
4	HCl, 50 g/L, S:L = 1:4, 2 h, 50 °C	31.5	1.62	0.21

Electron-microscope analyses showed that titanite grains cleaned with sulfuric acid were covered with the smallest particles of Ca sulfate and aluminum alum (Figure 6a). After cleaning with hydrochloric acid, they became free from any secondary phases, as we predicted (Figure 6b).

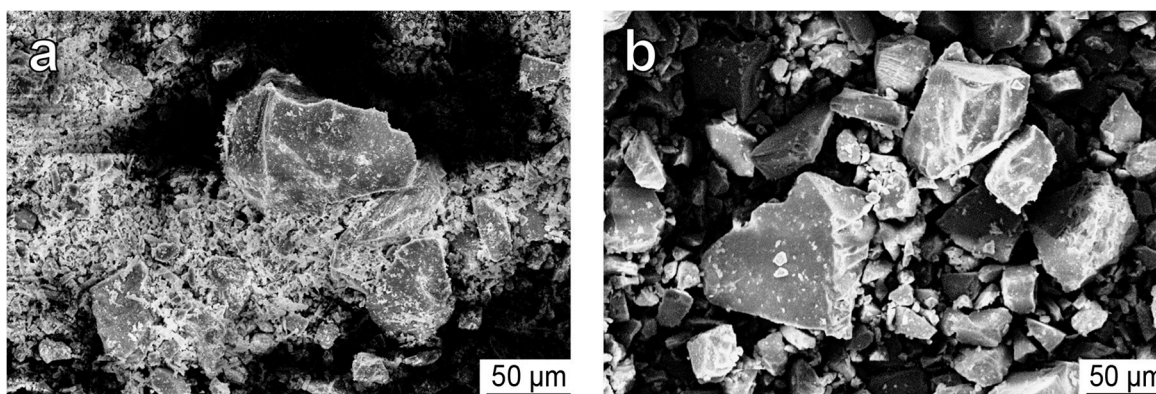
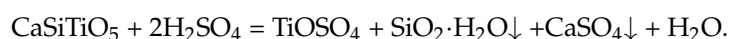


Figure 6. SE-images of titanite grains cleaned by sulfuric acid (a) and hydrochloric acid (b).

The titanite-aegirine concentrate processing stage included dissolution of titanite in heated concentrated sulfuric acid with formation of insoluble calcium sulfate and amorphous silica:



This reaction can be divided into two consecutive stages: kinetic stage and diffusion stage. The first stage gradually transforms into the second one due to accumulation of solid reaction products. Both stages, especially the second one, are diffusion limited. The mechanism of titanite dissolution is the same for both stages, but the dissolution rate is different (Figure 7). In practice, proportion of leached titanium (IV) in the liquid phase (i.e., proportion of dissolved titanite) ranges from 35 to 90% [28]. Optimal sulfuric acid concentration of 600 g/L prevents from precipitation of titanyl sulfate that exists in such solution only in a stable molecular-dispersive form.

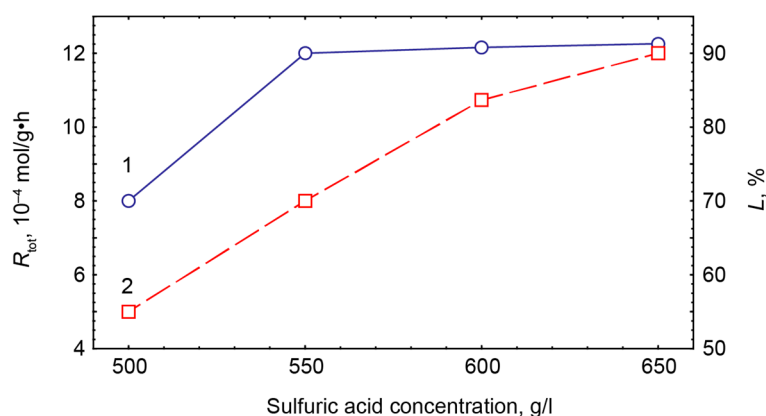
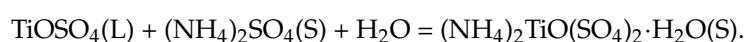


Figure 7. Ratio of Ti(IV) leaching from titanite (R_{tot} , line 1) and titanium recovery into the liquid phase (L , line 2) vs. sulfuric acid concentration at S:L = 1:3.5.

During the third stage of the experiment, the produced titanyl-sulfate solution was used to crystallize STA and STM salts. Their bulk crystallization from the solutions can be initiated by addition of salting-out reagents, in particular, ammonium sulfate [38]:



This composition becomes supersaturated when total concentration of ammonium sulfate and sulfuric acid in the solution reaches 550 g/L, with the ammonium sulfate:acid ratio to be 1.2:1. If this ratio decreases to the value of 1:2 due to growth of sulfuric acid concentration (400 g/L H_2SO_4

and 80–85 g/L TiO_2), another solid “acidic” compound $(\text{NH}_4)_2\text{TiO}(\text{SO}_4)_2 \cdot 0.15\text{H}_2\text{SO}_4 \cdot 0.89\text{H}_2\text{O}$ will precipitate instead of STA.

To produce STM, we pre-evaporated or diluted titanyl-sulfate solution with sulfuric acid up to 850–900 g/L H_2SO_4 . Crystalline STM precipitates during boiling of this solution for 5–7 h.

4.2. Synthetic Ivanyukite-Na (SIV) Synthesis

For hydrothermal synthesis of ivanyukite-Na (SIV), we used STM water solutions pre-reacted with metallic zinc to transform Ti^{4+} to Ti^{3+} [39]. The experimental conditions are shown in Table 4.

Table 4. Experimental conditions of SIV synthesis.

Experiment	Pre-Reaction with Zn	$\text{TiO}_2\text{:SiO}_2$, Moles	pH	T °C	Time, Day
1	+	1:4	11.5	200	3
2	+	1:5	12.5	190	3
3	+	1:4	12.5	200	5
4	−	1:4	11.5	200	5
5	−	1:5	12.5	200	3

Long-term crystallization of SIV occurs in the basic (pH up to 12.5) system $\text{Na}_2\text{O-K}_2\text{O-TiO}_2\text{-H}_2\text{SO}_4\text{-SiO}_2\text{-H}_2\text{O}$ supersaturated with Na and Si [39,40]. After a three-day synthesis (experiments 1 and 2), the precipitates consist of two SIV polymorphs: rhombohedral SIV-T, $\text{Na}_4(\text{TiO})_4(\text{SiO}_4)_3 \cdot n\text{H}_2\text{O}$, and cubic SIV-C, $\text{Na}_3\text{H}(\text{TiO})_4(\text{SiO}_4)_3 \cdot n\text{H}_2\text{O}$ (Table 5). Longer crystallization (experiment 3) causes protonation of SIV-T on the schema $\text{Na} + \text{TiO}_6 + \text{H}_2\text{O} \rightleftharpoons \square + \text{TiO}_5(\text{OH}) + \text{Na}(\text{OH})$, with the corresponding transformation of SIV-T into SIV-C (Figure 8) by analogy with natural ivanyukites [19]. When Ti^{4+} predominates over Ti^{3+} (experiments 4 and 5), ETS-4, $\text{Na}_6\text{Ti}_5\text{Si}_{12}\text{O}_{34}(\text{O},\text{OH})_5 \cdot 11\text{H}_2\text{O}$, crystallizes instead of SIV.

Table 5. Modal composition and surface properties of titanosilicate precipitates.

Experiment	Modal Composition	Surface Properties		
		S , m^2/g	V , cm^3/g	D_{av} , nm
1	SIV-T + SIV-C	148.0 ± 0.9	0.68	18.4 ± 0.2 (3.4–68.0)
2	SIV-T + SIV-C	158 ± 1	0.73	18.6 ± 0.1 (2.9–65.4)
3	SIV-C	143.3 ± 0.6	0.75	20.9 ± 0.1 (4.3–75.0)
4	70% ETS-4 + 30% SIV-T	81.0 ± 0.4	0.18	8.9 ± 0.1 (2.1–54.3)
5	65% ETS-4 + 30% SIV-T + 5% TiO_2	85.1 ± 0.5	0.22	10.3 ± 0.1 (1.8–58.2)

S —specific surface area, V —specific volume of pores, D_{av} —average diameter of pores, mean $\pm$ SD (min–max).

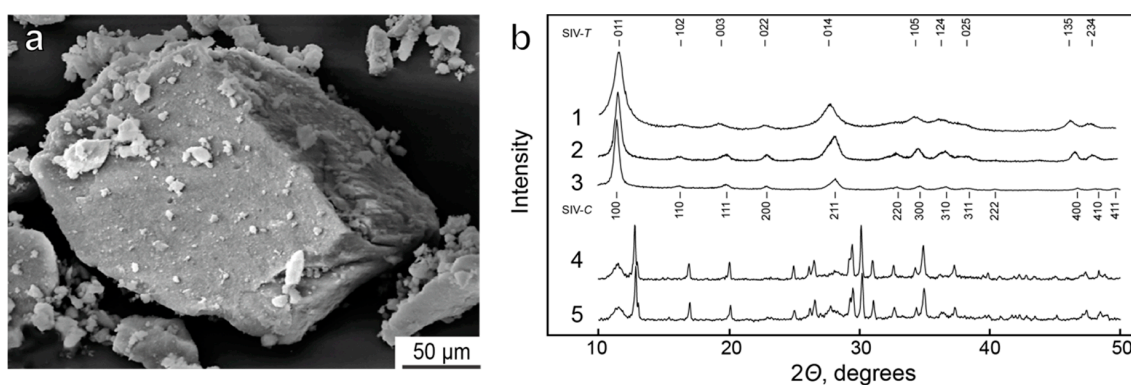


Figure 8. SE-image of SIV-C aggregates (experiment 3) (a) and powder X-Ray diffraction patterns of products obtained in experiments 1–5 (b).

Size of SIV particles varies from 2 to 15 μm . High specific surface area ($143\text{--}158\text{ m}^2/\text{g}$) and general pore volume ($0.68\text{--}0.75\text{ cm}^3/\text{g}$) of SIV aggregates as well as presence of extra-framework cations and water molecules in wide channels of SIV crystal structure (see Figure 1) result in impressive SIV cation-exchange properties [20,26].

5. Discussion

Environmental technologies play an increasingly important role in various industrial applications, including production of new materials. Being the main world suppliers of new zircon-, niobo- and titanosilicates, massifs of the Kola Alkaline Province are important sources of information on conditions of mineral formation and synthesis of the corresponding mineral-like functional materials. Again, we should like to emphasize that titanosilicate materials of practical importance, such as ETS-4, IE-911, SL3 and SIV, are complete analogues of zorite, sitinakite, punkaruaivite and ivanyukite-Na discovered in Lovozero and Khibiny massifs. On the other hand, synthesis of the natural minerals analogues allows us to study conditions of natural minerals formation for effective exploration of the minerals—prototypes of functional materials.

The Kola Science Center of the Russian Academy of Sciences has developed technologies for recovery of all listed mineral-like materials from the products of chlorine processing of the Lovozero's loparite, and sulfuric acid processing of the Khibiny's titanite (its resources is about 170 Mt [33]). The latest technology presented in this paper seems to be safer and more profitable, and enables to produce about 1 t of titanium tanning agent/precursor of sorbents, and then about 1 t of SIV from 1 t of titanite concentrate (1.5–2 t of apatite-nepheline-titanite ore), with simultaneous recycling of sulfuric acid produced by the Monchegorsk Copper-Nickel Combine.

The main consumer of SIV is the nuclear power industry (direct processing of liquid radioactive waste into titanate ceramics with reduction in waste volume by 2–3 orders). Precursor of STA/STM is used in the leather industry (due to higher safety of titanium tannic in comparison with chromium ones). Other potential applications of the developed materials are selective or collective extraction of non-ferrous and, especially, precious metals from process solutions and effluents, (photo)catalysis and medicine. In addition, during decomposition of titanite with sulfuric acid, a moist precipitate is produced. It contains calcium, silicon and titanium compounds (wt %): CaSO_4 40–45, SiO_2 15–20, TiO_2 5–10, and sulfuric acid. Neutralization of sediment with lime milk followed by annealing produces a titanium pigment filler, which is widely used in paint-and-varnish industry.

6. Conclusions

- (1) Large lenses and layers of (apatite)-nepheline-titanite ore, up to 50 m thick, are widespread in apical parts of the most apatite deposits in the Khibiny massif. This ore can be selectively mined and processed as a new kind of titanium raw materials;
- (2) This ore can be processed by acidic cleaning only, without a conventional flotation stage. With a new approach, the yield of Ti-salts becomes 5–6 times higher than in the known process flow diagram of titanite recovery from apatite-nepheline ore with flotation followed by sulfuric-acidic processing of titanite concentrate;
- (3) Sulfuric-acidic processing of titanite ore enables to recover up to 90% Ti into the liquid phase that becomes a common precursor for hydrothermal synthesis of functional titanosilicates, in particular, synthetic analogues of the ivanyukite-group minerals. To prevent from ETS-4 crystallization, the rate of titanium cations hydrolysis should be reduced by partial transformation of Ti^{4+} into Ti^{3+} ;
- (4) Perspectives of SIV application include recovering of liquid radioactive wastes into Synroc-type titanate ceramics, selective or collective extraction of non-ferrous and, especially, precious metals from process solutions and effluents.

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