ON THE IDENTIFICATION OF Ti-Ta-Nb-OXIDES
IN “WIIKITES” FROM KARELIA

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ABSTRACT

Purpose. With respect to the nature of Ti-Ta-Nb-oxides, which are included in the mineral associations that have historically gone by the now outdated name of “wiikites”, there is no unanimity of opinion. The main difficulty in identifying them is associated with the complexity of their chemical composition, their metamict structure and the substantial changes in their initial mineral form due to the effects of natural weathering. The aim of this work is the development of methodology to identify Ti-Ta-Nb-oxides corresponding to the mineral formulas AB₂O₆ and A₂B₂O₇.

Methods. The methodology developed in the work includes two experimental approaches: 1) electron probe microanalysis of phases revealed through use of the SEM-BSE method. Based on the resulting data, a hypothesis about the nature of the Ti-Ta-Nb-oxides in a number of wiikite samples is proposed. 2) XRD analysis of those phases that are formed in the course of thermal annealing of samples from 200 to 1000°C. Based on the resulting data here, the previous hypotheses are either accepted or rejected for each sample.

Findings. Using this methodology, three “wiikite” samples were analyzed (the experimental codes were Wk-2, Wk-3 and Wk-7). The Ti-Ta-Nb-oxides in two of these wiikites (Wk-2 and Wk-3) were preliminarily determined to be hydroxyyttropyrochlore and hydroxycalciobetafite, respectively. In the third sample (Wk-7), the Ti-Ta-Nb-oxide was classified as polycrase. The results of XRD phase analysis of the annealed samples were compatible with the primary hypotheses that hydroxycalciobetafite and polycrase were the initial minerals in “wiikites” 3 and 7, respectively.

Originality. The paper considers the issue of the chemical conditions necessary for the recovery of the original Ti-Ta-Nb-oxide during recrystallization of the metamict structures. This is a problem that has not been substantively addressed in the literature. Also for the first time experimentally proved the existence of the polycrase in “wiikites”.

Practical implications. Completed work expands our knowledge of the mineral composition of the granitic pegmatites of the Baltic shield and the possibility of their use both for research purposes and for needs of national economy.

Keywords: Ti-Ta-Nb-oxides, polycrase, pyrochlore supergroup minerals, isochronous thermal annealing, SEM-BSE analysis, EMP analysis

1. INTRODUCTION

Granite pegmatites of the Baltic shield are of considerable practical interest, since they are characterized by the presence of a peculiar accessory mineralization. The pegmatites of the Neulanniemi Peninsula (North Ladoga area), which are rich in the rare-earth accessory minerals niobium and tantalum, the so-called “wiikites” (Kalita, 1961) are very interesting in this respect.

According to Lokka (1950), a wiikite was discovered in 1889 by a mining engineer, G. Lisitzin, in the Lokaansaari feldspar quarry. He found three different varieties: a black crystalline one, a dark brown, partly crystalline one and a brown amorphous one. He considered this mineral to be a euxenite. In 1895, W. Ramsay described the dark “euxenite” of Lokansaari as a “euxenite-like mineral”, and he gave the name of wiikite to a similar, but yellow, mineral that he had found in 1894 at Nuolainiemi, in honor of his teacher Professor F.J. Wiik.

Since X-ray diffraction methods of analysis were unavailable at the time, researchers focused on their appearance, crystal habit and coloration. Attempts have been made to connect the coloration of the minerals with their chemical composition. Notably, Ant-Wuorinen (1936) divided all of the wiikites into two groups: those that were calcic, with a density of 3.23 – 3.73 g/cm³, and those that were yttrical, with a density of 4.01 – 4.7 g/cm³.
The first group consisted of wiikites that were predominantly light-colored. The second included those that were dark-colored, and they were thought to be samarskite-like varieties. This last supposition, however, was not upheld by further chemical analyses. In their chemical composition, the dark-colored wiikites turned out to be closer to euxenite, since, in both cases, the content of Ta, Nb, REE and U varied within the same range. But, in their content of Ti, wiikites differ from both euxenite and samarskite. The amount of TiO₂ in wiikites fluctuates between 2.3 and 23.8 percent, while in euxenite it ranges from 17.0 and 26.4 percent and in samarskite it does not exceed 4.3 percent. It has likewise been impossible to find a distinct correlation between the coloration of wiikites and the lanthanide content (Soboleva & Pudovkina, 1957). Light-colored varieties have been discovered with both a high and a low content of rare earth elements. This also applies to dark-colored varieties. In light of what is known at present, it can be said that the original colorations of wiikites are black and dark brown. Lighter tones are a result of metamictisation, hydrothermal effects and other harsh environmental factors (Kalita, 1961). For this reason, the surface of the minerals is frequently covered with a yellow film or crust that varies in thickness from a fraction of a millimeter to several millimeters. The intergranular spaces can also be filled with modified mineral matter, which makes it more difficult to interpret the results of a chemical analysis.

In addition to the many different effects of incongruent dissolution, there is another difficulty in identifying the specific tito-tantalo-niobates in any wiikite, and that is its metamict state. The diffraction pattern can be obtained only after thermal recrystallization of a metamict structure, but its connection with the original crystal structure of a tito-tantalo-niobate is not obvious. This is rather convincingly shown in the works of Cao, Krivovichev, Burakov, & Liu (2014) and Qixiang, Isakov, Xiaodong, Krivovichev, & Burakov (2014). The authors of these articles had studied the annealing of a metamict mineral of the Y-samarskite type (ICDD No. 00-052-1651). After annealing in a vacuum at 400°C for three hours, the X-ray diffraction spectrum did indeed show peaks corresponding to the samarskite phase. But when the temperature was increased to 750°C, phases with columbite-(Fe) and fergusonite-(Y) structures appeared. At temperatures from 1000 to 1200°C, the columbite-like phase disappeared, and fergusonite-beta-(Y) and tapiolite-(Fe) became the main phases.

Most likely, similar effects can, to some extent, explain the differences that are encountered in various literary sources concerning the identification of Ti-Ta-Nb oxides. In their chemical composition, the dark-colored wiikites of the first post-Ladoga group. They form large rectilinear veins 3 – 5 m thick, gradually wedging out in length and depth. Very large feldspar precipitates are observed in them – solid or sprouted with quartz. In the latter case, a so-called graphic pegmatite is formed. Biotite in these pegmatites forms large saber-like plates, and sometimes large clusters of irregular shapes or nests. These pegmatites often have a zonal structure. They are also of interest because they include such comparatively rare minerals as ortite, monazite, xenotime, cirtolite, wiikite (yttropyrochlore) (Kalita, 1961) and others.

The corresponding samples of wiikites were obtained from the Department of the Geology of Mineral Deposits (the Faculty of Geology), Saint Petersburg State University and designated as Wk-1, Wk-2, Wk-3 and Wk-7 in the mineral collection of the department (the Wk-1 sample mentioned here will be discussed in section 3.1.).

Appearance of the minerals:
The samples were crushed in a metal mortar and separated using a set of sieves into several granulometric fractions. In this research, the following fractions were used: 0.12 – 0.25 mm and 0.25 – 0.5 mm.

2.2. Experimental procedure

Identification of the wiikites was carried out in two stages. The first stage included the following procedures:

– determination of the elemental composition of the samples at a qualitative level using X-ray fluorescence analysis. Spectrometer: Oxford Instruments. X-supreme 8000. Operating voltage to generate the primary spectrum: 5 kV for light elements, 30 kV for heavy elements;

– X-ray phase analysis of powdered samples conducted on a Diffray-401 diffractometer according to the Bragg-Brentano method in reflection geometry. Detector: gas-filled proportional (flow-through). X-ray tube type: BSV-33. Anode material: chrome. Tube operating mode: 16 kV/6 mA. The limits of absolute error when measuring the angular positions of the diffraction peaks do not exceed ±0.02 degrees;

– scanning electron microscopy and electron micro-probe analysis (EMPA). Equipment used: The SEM model TESCAN VEGA II LMH with Oxford Instruments Inca X-act, a system of energy-dispersive X-ray microanalysis. Photofixation of phases was performed in the backscattered electron regime, making it possible to identify the phases that differ in the “average” atomic number (“compositional contrast”). The sections were covered with a layer of carbon that was 5 nm thick. An additional layer of carbon covering (2 – 5 Wt % depending on the density of the phase being analyzed) was measured according to the internal standard method when analyzing the carbonates. Spatial resolution of the BSE image with 20 kV accelerating voltage in the high vacuum mode was about 10 nm. Standards used: MAC (Micro Analysis Consultants Ltd., United Kingdom) “Reference standards for X-ray microanalysis” Std. UNI532 (55 standards universal block, C as (C Graphite), O (SiO2 Quartz), Mg (MgO Periclase), Al (Al2O3 Corundum), Si (Silicon Si), K (KBr), Ca (CaF2 Fluorite), Sc (Scandium wire 99.9%), Ti (Titanium wire 99.99%), V (Vanadium wire 99.9%), Mn (Manganese pieces 99.99%), Fe (Iron wire 99.99%), Br (KBr), Y (Yttrium rod 99.9%), Nb (Niobium wire 99.8%), La (LaB6 99.5%), Ce (CeO2 99.9%), Ta (Tantalum wire 99.9%), Pb (PbTe Pb = 61.89%), Std. REE32 (18 rare earth standards block, Nd (NdF3 99.9%), Sm (SmF3 99.9%), Std. SMH32 (30 standards heavy metals block, U (Uranium glass UO2 = 4.94%), Th (Thorium glass ThO2 = 5.96%);

– preliminary identification of metamict minerals. The assignment of the metamict phases detected in wiikites to a specific natural Ti-Ta-niobate was made by comparing the elemental composition that was found with known mineral compositions, which are indicated in numerous papers (for example, (Ercit, 2005; Atencio, Andrade, Christy, Giere, & Kartashov, 2010; Christy & Atencio, 2013), as well on the http://www.webmineral.com/ website, the New IMA List of Minerals et al. For each of the hypothesized mineral compositions, the range of contents for the basic elements was identified on this site, and a table of the maximum and minimum values of these contents was made. In these tables took into account the variations of the elemental composition in the following sets of minerals: minerals of the pyrochlore supergroup – 13 samples, euxenite-like minerals – 8 samples, and samarskite – 6 samples.

Comparison of the composition of the unknown mineral with the real compositions of natural Ti-Ta-niobates and subsequent classification of the Ti-Ta-niobate under study to a particular mineral in a selected mineral group was accompanied by the following calculation. The sum of the modules of the differences between the atomic % of all the elements in the minerals under study and those in the comparison minerals included in this group was calculated. The minimum sum of the modules was considered as a specific parameter that characterizes the proximity of the two compositions: that of the minerals under study and that of the comparison minerals. The minimum sum was one of the criteria used to identify the corresponding Ti-Ta-Nb-oxide.

As a result of the first stage of the research, the titan-tantaloidiobates were preliminarily identified and the elemental composition of the corresponding mineral associations was determined.

The second stage consisted of thermal annealing of the wiikites and X-ray diffraction control of the phases in the samples to ascertain their composition at each annealing temperature. For the thermal annealing, an amount of a wiikite weighing 100 mg was placed in a quartz tube evacuated with a roughing pump. The temperature range was from 200 to 1000°C in increments of 200°C. The annealing time for each temperature was 10 minutes. The temperature was monitored by chromel-copel and chrom-alumel thermocouples and an OVEN TRM-1 thermoregulator (Russia). The relatively short annealing time was chosen so that the formation of the phases in the study samples could be observed in greater detail. It is assumed that brief exposure to higher temperatures causes changes in polyhedra that are relatively limited in volume. At the same time, the spatial diffusion of atoms accompanying the formation of new mineral phases has only a limited impact on the recrystallisation processes, especially at lower annealing temperatures.

At this stage, X-ray phase analysis of the samples was performed using a Bruker D2 Phaser, an automated powder diffractometer. The X-ray tube radiation was CoKα1 (λ = 1.78900 Å) and CoKα2 (λ = 1.79283 Å). The tube operating regime was 30 kV/10 mA. The sample rotation speed was 20 rpm; the shooting temperature was 25°C, and it was done in air. A position-sensitive detector was used; reflection geometry and a Bragg-Brentano focusing scheme were adopted. Identification of the phases was carried out using the Rigaku PDXL2 software package and the Powder Diffraction File (PDF-2 ICOO, 2011) database. Quantitative phase analysis was performed using the TOPAS software package and resorting to Quantitative Rietveld phase analysis, taking into account the Inorganic Crystall Structure Database (2012) for each phase.

3. RESULTS AND DISCUSSION

3.1. Chemical composition of the wiikite samples

The X-ray diffraction patterns of study samples Wk-1, Wk-2, Wk-3 and Wk-7 are presented in Figure 1. The spectra show several diffraction maxima belonging to the silicate (aluminosilicate) phases growing on the X-ray amorphous halos that are characteristic of metamict structures.
For the Wk-3 spectrum, the most characteristic minerals are those of the chlorite group (chamosite) and the mica group (presumably celadonite or polytitionite). The portion of chamosite in Wk-7 is significantly lower than in Wk-3, and the main silicate phase is represented here by quartz. As the results of X-ray fluorescence analysis showed, wiikites 3 and 7 have the necessary elements of the compounds of the general type $A_xB_yO_z$, namely Ti, Nb, Ta, Y, U, Th, Ca, as well as several others. Wk-2 exhibits very little Ti and no Th at all. Wk-1 has a high amount of rare earth elements and thorium, but Ti, Nb, Ta are completely absent.

Scanning electron microscopy of the samples in back-scattered electrons (Fig. 2 – 5), followed by quantitative electron microprobe analysis made it possible to determine the elemental composition of the phases that were detected. According to the methodology described above in 2.2.d, preliminary identification of the Ti-Ta-Nb-oxides contained in the mineral associations under investigation (Table 1) was made.
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Table 1. Elemental composition (Wt %) and phase composition of the metamict samples studied, according to EMPA.
EMPA was performed according to the concentration of the spectrum over the entire area of the phase (in the picture) in one measurement. Calculation of the surface area is carried out by calculating the number of pixels in the BSE image within the range of a definite brightness/contrast characteristic for each of the phases. When determining the area, the relative error does not exceed 1.0 – 1.5%.

As is known, Ant-Wuorinen (1936) believed that wiikites constitute a continuous series of niobates between α-wiikite Ca₃U(HNbO₅) and β-wiikite Y₄(HNbO₅). According to Lokka (1950), wiikites are silico-titanotantalooxides. Therefore, if the word “wiikite” is understood in the traditionally accepted sense as a synonym for “titanotantalooxide” (or, more correctly, as including a Ti-Ta-Nb-oxide in the contents of its mineral association), then sample Wk-1 cannot be classified as a wiikite. The main mineral in this sample (about 98 percent) is allanite-(Ce) (orthite). Its metamictization was brought about by the nuclear decay of radioactive nuclides of the Th-232 series.

The content of Y, Ti, Ta, Nb, U, and some rare earth elements (Table 1), made it possible to identify the Ti-Ta-Nb-oxides in Wk-2 as hydroxytortopyrochlores with small variations in the amounts of yttrium and uranium. In the same way, the Ti-Ta-Nb-oxide in Wk-3 was designated as hydroxyyttropyrochlore, a mineral of the pyrochlore supergroup (the betafite was one of the minerals identified by the Bjørlykke (1931) in “wiikites”). Its overall content in the sample is 56.5 percent, two-thirds of which belongs to the common betafite and the remaining third to a less reliably identified hydroxycalciosilicate that is more enriched with tantalum.

Given a significant deficit of cations in Position A, we can calculate the corresponding formulas of Ti-Ta-Nb-oxides in Wk-2 and Wk-3.

**Pyrochlore-1** (hydroxytortopyrochlore): (Y₀.₂₂U₀.₂₂C₀.₄₁P₀.₆₀G₀.₆₀Sm₀.₀₃As₀.₀₂)(0.₇₅)(Nb₁.₃₅Ta₀.₂₇
T₁₀.₂₁Fe₀.₁₇)₂.₀₀(O₁.₇₇OH₂.₃₇)₇.

**Pyrochlore-2** (hydroxytortopyrochlore): (Y₀.₃₆C₀.₁₂G₀.₁₄P₀.₆₀Sm₀.₀₅As₀.₀₃)(0.₈₈)(Nb₁.₁₂Ta₀.₁₉
T₁₀.₂₂Fe₀.₁₇)₂.₀₀(O₁.₄₆OH₂.₆₆)₇.

**Hydroxycalciosilicate**: (Ca₀.₃₈Y₀.₂₂U₀.₁₇)₁(Fe₀.₀₉Ti₀.₀₄Mn₀.₀₂)(0.₉₂)(Ti₀.₇₆Nb₀.₄₈Ta₀.₃₁
Fe₀.₃₂Al₀.₃₂)₂.₀₀(O₁.₇₇OH₁.₈₇)₇.

**Hydroxycalciosilicate--extraordinary (?)**: (Ca₀.₇₀U₀.₃₄Ti₀.₀₁F₀.₀₂Mn₀.₀₄)(1.₃₃)(Nb₀.₀₆Ta₀.₆₇Ti₀.₄₄Fe₀.₂₀)₂.₀₀
(O₁.₇₇OH₁.₃₀)₇.

The deficit of positive charges in these formulas is offset by the inclusion of the hydroxyl group (OH)⁻ in the oxygen position.

In contrast to these two wiikites, Wk-7 contained a Ti-Ta-Nb-oxide that was classified at this stage of our research as belonging not to the pyrochlore supergroup but to the group of euenite-like minerals, and it was determined to be polycrase. We can assume that 36 percent of it can be attributed to polycrase-(Y)-1 and 17 percent to polycrase-(Y)-2 unusually enriched in Fe and U.

**Polycrase-(Y)-1**: (Y₀.₂₄Fe₀.₁₀C₀.₄₀G₀.₆₀Sm₀.₀₄Th₀.₀₄Y₀.₀₁)(0.₅₈)(Ti₀.₅₈A₀.₄₄Nb₀.₃₉
Si₀.₁₃Fe₀.₂₃Ta₁.₁₅)₂.₀₀(O₁.₄₃OH₂.₅₇)₇.

**Polycrase-(Y)-2**: (Mg₀.₃₈C₀.₄₀Y₀.₀₆Fe₀.₀₆Mn₀.₀₂)(0.₆₉)(Ti₁.₉₅Fe₀.₆₀Si₀.₃₄Nb₀.₂₁
Al₀.₁₈Ta₀.₁₀)₂.₀₀(O₂.₈₈OH₁.₁₄)₇.

Note: the authors suppose that the hematite phase in wiikites was formed as a result of leaching and oxidation of divalent iron atoms originally included in group A of Ti-Ta-Nb-oxides. Therefore, when calculating the mineral formulas in group A, iron was included in amounts corresponding to the amount of hematite in the sample and the phase area of the particular Ti-Ta-Nb-oxide. It should also be noted that, as minor uranium-bearing phases, urancalcarite and liandratite are present in Wk-3 and Wk-7, respectively.

### 3.2. XRD research of annealing products of the wiikite samples

#### 3.2.1. Wiikite-3

We begin an analysis of the results here by examining the XRD spectra obtained in the process of isochronous annealing. Figure 6 shows the X-ray diffraction spectra of Wk-3, both the original sample and the sample annealed at several different temperatures (at $T = 1000^\circ C$, in addition to 10-minute annealing, 30-minute annealing was also performed).
represented by chamosite in the amount of 22.5 percent, although it is possible that this is clinochlore (in the figures, for the sake of brevity, these minerals are labeled as mica and chlorite). The content of hematite and calcite are equal to 6.5 percent and 13 percent, respectively. The presence of tapiolite-(Fe) in small amounts (not more than 3 percent) cannot be ruled out as well. It can be assumed that this mineral does not show marked isomorphism in relation to uranium and thorium, and is able to remain in a crystalline state. The X-ray diffraction method could not confirm the presence of uranocalcrite.

The following changes are observed in the X-ray diffraction spectra with an increase in the annealing temperature. The diffraction maxima of chlorite and calcite disappear at temperatures higher than 600°C. When exposed to a higher temperature, minerals from the mica group are not altered and are observed to remain steadily at 1000°C. Furthermore, mainly at temperatures higher than 800°C, a rutile phase gradually forms. It is also possible to assume that small amounts (approximately 2 percent) of perovskite and columbite may build up. Due to the low content of these phases, however, it is not easy to note the beginning of the crystallization process.

As can be seen from the data in Table 1, betafite is the only Ti-Ta-Nb-oxide in Wk-3. X-ray diffraction analysis confirmed the identification made during the first stage of the study, i.e., when the chemical composition of this mineral was analyzed. Indeed, on the XRD powder pattern of the sample annealed at 1000°C, calcio-betafite lines are clearly observed, with interplanar spacing $d_{220} = 2.97$ Å and $d_{400} = 2.57$ Å. The content of the phases is as follows: calcio-betafite – 50 percent; rutile – 20 percent; hematite – 14 percent; celadonite (polylithionite) – 12 percent; perovskite and columbite – 4 percent. It is noteworthy that the betafite phase begins to form relatively early – in the temperature range of 200 – 400°C, while recrystallization of metamict betafite, as it is pointed out in the monograph “Thermal Studies of Uranium and Uranium-bearing Minerals” (Ambartsuyan, Basalova, Gorzhevskaya, Nazarenko, & Hodzhava, 1961), occurs in a temperature range of 650 – 730°C. The early crystallization that we observed allows us to propose that the Wk-3 sample retained a sufficient amount of crystalline domains from the original betafite phase, giving rise to the corresponding epitaxial process with relatively low activation energy.

Further transformation of the spectrum resulting from conversion of the calcio-betafite phase at higher temperatures was not studied, since this process, in our view, is not relevant to this study.

3.2.2. Wiikite-7

Figure 7 illustrates a series of X-ray diffraction spectra of Wk-7 samples, including both the initial one and others that were annealed at several different temperatures. The XRD pattern of the original sample allows us to identify the following phases: quartz – 64.5 percent; mica (celadonite or polylithionite) – 2.5 percent; hematite – 13.5 percent; goethite – 4 percent; a mineral from the chloride group – 8 percent; and anatase – 8 percent. These contents pertain solely to the crystalline phases of the sample and have been calculated without taking the metamict phase of the Ti-Ta-Nb-oxide into account.

For this reason, they are different from the data in Table 1 for Wk-7. Moreover, three additional mineral phases, not previously identified by electron microprobe analysis, were discovered in the composition of the mineral association.

As the annealing temperature is increased, growth of the diffraction maximum in the range of $d = 3.00$ Å is observed. It can be considered that the corresponding phase begins to form at 400°C. In conjunction with other XRD diagnostic maximums of lower intensity, this phase, just as during the first stage of our study, was identified as polycrase-(Y). But as analysis of X-ray diffraction spectra of the annealed samples shows, polycrase is not the only Ti-Ta-Nb-oxide in Wk-7. Fergusone-beta-(Y) and calcio-betafite are probably present as well, and the asymmetry of the polycrase diffraction maximum can be explained by the close proximity ($d = 2.94$ Å) of their lines. The sample annealed at 1000°C contains approximately 17.4 percent of polycrase, 3 percent of fergusite-beta-(Y), 9 percent of fergusone-beta-(Y), 3 percent of tapiolite and 14 percent of calcio-betafite, which makes a total of around 50 percent of Ti-Ta-Nb-oxide phases (with a 37 percent content of quartz, 12 percent of hematite and around 5 percent of minerals from the mica group). These values are different from the data in Table 1, where the percentage of the Ti-Ta-Nb-oxide phase, in the form of polycrase, is given as 53 percent. It is rather difficult to make a correct comparison, though, as the values in the table were determined by the size of the area occupied by the corresponding phase in the SEM – BSE image. Furthermore, X-ray diffraction was unable to confirm the 0.7 percent of lineadrite found during the first stage of our study.

If we isolate the heavy fraction from the mineral composition of Wk-7, using bromoform to free it from silicates, a significant enrichment of Ti-Ta-Nb-oxides can be observed. When annealed at 1000°C, this fraction has the following mineral composition: polycrase-(Y) – 31 percent; fergusone-beta-(Y) – 18 percent; calcio-betafite – 11 percent; fergusite-alpha-(Y) – 7 percent; and tapiolite – 8 percent, making a total of 75 percent (the remaining 25 percent is hematite). Detection of fergusite and tapiolite cannot be considered as resulting
from recovery of the original crystalline structure of the Ti-Ta-Nb-oxide when the sample is annealed. Such a recovery is typical for an operating temperature of around 400°C. It is clearly shown in the studies of Cao, Krivovichev, Burakov, & Liu (2014) and Qiu, Isakov, Xiaodong, Krivovichev, & Burakov (2014) that in the case of these two minerals, this only concerns the formation of new phases in a temperature range of 750 – 1000°C. Clearly, fergusonite-alpha-(Y) and fergusonite-beta-(Y) are observed only after annealing at 1000°C. It is possible that fergusonite-(Y) is present at lower temperatures, but we do not see it because there is so little of it and its most intensive diffraction maximum \( d_{112} = 3.05 \) Å is superimposed on the most intensive maximum of polycrase \( d_{111} = 2.99 \) Å, which, in turn, has a large half-width at 600 and 800°C. Thus, it can be concluded that the main initial phase of the Ti-Ta-Nb-oxide in Wk-7 was polycrase. It cannot be ruled out that there were small amounts of fergusonite-alpha(beta)-(Y) and calciobetafite among the initial minerals.

### 3.2.3. Wiikite-2

This sample, according to Table 1, consists almost entirely of a Ti-Ta-Nb-oxide phase (97 percent). Based on an analysis of its chemical composition, it was identified as pyrochlore, i.e., not just any member of the pyrochlore supergroup, but hydroxyyttrropyrochlore with a high content of uranium. XRD phase analysis, however, did not confirm the formation of this mineral during recrystallization of the metamict structure when it was annealed. Instead, as can be seen in Figure 8, starting from a temperature of 400°C (or somewhat earlier), two minerals form – a member of the microlite group (conditionally uranomicrolite) and liandratite.

**Figure 8. XRD powder patterns of Wk-2 at room temperature and when annealed in the range of 200 – 1000°C:**

![Image](image.png)

It can be assumed that their synthesis comes from material that does not require chemical transformation and is located rather compactly in the metamict structure. The formation of liandratite points to a high level of hexavalent uranium, which arose during metamictization and also under the effect of other natural processes on Wk-2. Therefore, its discovery does not raise any questions. But it is not entirely clear why microlite formed instead of yttrropyrochlore, since, according to EMPA analysis, the Nb content in Wk-2 is three times higher than the Ta content. As a possible explanation, it can be assumed that the early formation of the liandratite phase creates a certain spatial deficiency of niobium, thereby initiating the formation of microlite. It is difficult to calculate the precise phase relations in the 400 – 600°C temperature range. With an increase in the annealing temperature, the relative proportion of liandratite in Wk-2 should obviously decrease. But at a temperature of 800°C the liandratite content (42 percent) is still a bit higher than the microlite content (38 percent). At the same temperature, the lines of two more minerals, fergusonite and ixiolite, appear in the spectrum. When the temperature is raised to 1000°C (and the annealing lasts for 30 minutes), the liandratite content drops to 16 percent. As is easily seen, this is connected with the high-temperature reduction of uranium U(VI) to the U(IV) state as a result of Le Chatelier’s principle. Simultaneously, the formation of phases of several tantalum-niobates is observed in the following amounts: fergusonite-Y – 10 percent; fergusonite-beta-(Y) – 30 percent; ixiolite – 10 percent; and tapiolite – 5 percent. Since the content of microlite at this temperature does not exceed 30 percent, it should be supposed that the uranium that has been reduced to the tetravalent state is distributed in varying degrees between the newly formed minerals. Thus, we can conclude that recovery of the original crystalline structure in the process of thermal annealing of a metamict mineral requires certain chemical conditions. Apparently, the conditions necessary for the formation of yttrropyrochlore were not present in Wk-2.

### 3.2.4. Liandratite – Questions and Hypotheses

When analyzing the patterns involved in the formation of Ti-Ta-Nb-oxides in metamict structures, it is quite reasonable to ask: if liandratite forms in Wk-2, why doesn’t it form in Wk-7?? Especially since, according to a recent radiochemical study (Hosseinpour Khanmiri, Goldwirt, & Bogdanov, 2015), the content of hexavalent uranium in Wk-7 is not less than 60 percent. In response to this question, there are several possible explanations, but they require experimental verification. In a study by Bogdanov, Batrakov, Puchkova, Sergeev, & Burakov (2002), it was shown that all of the hexavalent uranium in some pyrochlore and beta-fite samples is present in the form of uranyl-ions. Taking into account the significant changes in polycrase under the influence of natural solutions and self-irradiation, it can be expected that the hexavalent uranium in Wk-7 also acquired the form of uranyl-ions. Its conversion into the form of oxide ions probably occurs above 600°C, while liandratite forms in the Wk-2 metamict structure starting at a temperature of no higher than 400°C. Due to this temperature delay, liandratite cannot be observed in the XRD spectra of Wk-7.

As an alternative explanation, the possible role of quartz should be pointed out in determining the “fate” of liandratite during thermochemical processes in the metamict structures. We have already seen that a significant portion of uranium in Wk-7 and Wk-2 is in the hexavalent state. But it is impossible for liandratite to form if the reduction of uranium to the tetravalent state occurs at
4. CONCLUSIONS

Hydro-chemical processes significantly alter the original composition of metamict minerals. It is therefore difficult to attribute metamict minerals to a specific group of minerals or to identify a metamict mineral as part of a particular group. The reasons for this are clear: two key parameters that are essential for conclusive identification are missing, namely the crystalline structure of the mineral and its original chemical composition. This is especially true for the titano-tantalo-niobates (compound Ti-Ta-Nb-oxides) which make up several groups of minerals and isomorphous series.

In the present work, a methodology was developed to identify Ti-Ta-niobates in mineral associations that go by the name of “wiikites”, now considered to be outdated. This methodology involves two complementary approaches. The first is based on an EMPA of the basic chemical elements in the niobate under study and a step-by-step comparison of the composition thus obtained with literature data of the real chemical composition of Ti-Ta-Nb-oxides found in nature. The second is built upon observing the dynamics of how the crystalline phase is formed using an X-ray diffraction analysis during isochronal annealing of the sample study at different temperatures.

Using this methodology, the Ti-Ta-niobates in three “wiikite” samples were identified. The corresponding Ti-Ta-Nb-oxide in Wk-3 is represented by hydroxyocalciobetafite (of two different chemical compositions), substantially depleted by the cations of group A. A small amount of betafite is observed in Wk-7, but the main Ti-Ta-niobate here is Polycrase-(Y) (also of two different chemical compositions). The XRD powder patterns of polycrase presented in this work are the first experimental proof that polycrase is contained in “wiikite” samples taken from granite pegmatite of the Noyalynniemi Peninsula, since all the values of the interplanar spaces cited in the work of Kalita (1961) based on XRD powder patterns of “black wiikites” or species with a pitchy luster and are attributed exclusively to euxenite.

Thus, the apparent contradiction that, “in the Ti-content, wiikites differ from both euxenite and samarskite” becomes clear. It is the elevated level of uranium that identifies a euxenite-like mineral as polycrase. That being said, the widespread occurrence of betafite in granite pegmatite veins that cut the Svekofenian granite-geiss of the Ladoga region make it possible to speak of the potential mining not only of niobium, tantalum and rare-earth elements but “in passing” also uranium (Nettleton, Nikoloski, & Da Costa, 2015).

As already noted, the results of SEM-EDS and EMP analysis of Wk-3 and Wk-7 were confirmed by XRD-experiments. By contrast, such results were not obtained for Wk-2. Instead of pyrochlore, which was expected based on the results of SEM-EDS and EMPA, isochronal annealing of samples led to the formation of microilte. In the opinion of the authors, the formation of microilte in place of pyrochlore was connected with two circumstances:

1) the hexavalent state of uranium, which results in the synthesis of liandratite;
2) the deficit of niobium, caused by its entering into liandratite.

The absence of liandratite in the sample of Wk-7, despite the high content of hexavalent uranium, can be explained by its effective reduction by electrons released from \( E_1 \) centers of quartz at 400°C. In Wk-2, this process cannot take place due to the absence of quartz. It is also impossible in some instances to exclude the influence of oxidic or uranyl forms of uranium (in the composition of metamict Ti-Ta-Nb-oxides) on the possible re-arrangement of the initial crystalline structure of minerals.

It should be noted that an analysis of the circumstances and conditions accompanying or impeding the formation of the initial Ti-Ta-niobate in the course of thermal recrystallization of metamict structures was carried out for the first time in this work.

ACKNOWLEDGEMENTS

The study was conducted using equipment of the Center of X-ray Diffraction Studies and the Center for Microscopy and Microanalysis of the Research Park at Saint Petersburg State University, as well as the analytical laboratory of OJSC MMC Norilsk Nickel in Saint Petersburg.

REFERENCES


ДО ПИТАННЯ ІДЕНТИФІКАЦІЇ Ті-Ta-Nb-ОКСІДІВ У “ВІІКІТАХ” КАРЕЛІЇ

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Мета. Розробка методології ідентифікації Ti-Ta-Nb-оксидів складного хімічного складу з метаміктною структурою, що відповідає мінеральним формулам АВ₂О₆ та А₂В₂О₇.

Методика. Для розробки методології ідентифікації у роботі використано два експериментальних підходи: 1) рентген-спектральний мікроаналіз фаз, виявлених методом скануючої електронної мікроскопії зразків у процесі термічного відпалу від 200 до 1000°C. На основі отриманих результатів для кожного зразка первинна гіпотеза приймалася або відкидалася.

Результати. 3 використання даної методики були виявлені три зразки “війкіт” (шарф зразків: Wk-2, Wk-3 i Wk-7). Наявність Ti-Ta-Nb-оксидів попередньо визначено в двох зразках (Wk-2 і Wk-3) відповідно, як гідроксітропохлор та гідроксікапляйобетафіт. У третьому зразку (Wk-7) Ti-Ta-Nb діагностовано як полікраз. Результати рентген-дифракційного аналізу відповідних зразків підтвердили гіпотези про те, що початковими мінералами у Wk-3 i Wk-7 були гідроксікапляйобетафіт і полікраз відповідно.

Наукова новизна. Визначена хімічна умови, необхідні для виявлення мінералів в ізоктонному проміжку від 200 до 1000°C.

Ключові слова: Ti-Ta-Nb-оксиди, полікраз, мінерали супергрупи пірохлору, ізоктонний термічний відпал, скануюча електронна мікроскопія, рентгеноспектральний мікроаналіз

К ВОПРОСУ ИДЕНТИФИКАЦИИ Ti-Ta-Nb-ОКСИДОВ В “ВИКИТАХ” КАРЕЛИИ

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Цель. Разработка методологии идентификации Ti-Ta-Nb-оксидов сложного химического состава с метамиктовой структурой, соответствующих минеральным формулам АВ₂О₆ и А₂В₂О₇.

Методика. Для разработки методологии идентификации в работе использовано два экспериментальных подхода: 1) рентген-спектральный микронализ фаз, выявленных методом сканирующей электронной микроскопии образцов в обратно отражённых электронах. На основе полученных результатов выдвинута гипотеза о природе Ti-Ta-Nb-оксидов. 2) рентген-дифракционный анализ фаз, образующихся в процессе термического
отжиг образцов от 200 до 1000°С. На основе полученных результатов для каждого образца первоначальная гипотеза принималась или отвергалась.

Результаты. С использованием данной методики были изучены три образца “виикитов” (шифры образцов: Wk-2, Wk-3 и Wk-7). Наличие Ti-Ta-Nb-оксидов предварительно определено в двух образцах (Wk-2 и Wk-3) соответственно, как гидрокситтрапирохлор и гидроксикальциобетафит. В третьем образце (Wk-7) Ti-Ta-Nb диагностирован как поликраз. Результаты рентген-дифракционного анализа отожженных образцов подтвердили гипотезы о том, что первоначальными минералами в Wk-3 и Wk-7 были гидроксикальциобетафит и поликраз соответственно.

Научная новизна. Определены химические условия, необходимые для образования первоначального Ti-Ta-Nb во время рекристаллизации метамиктовой структуры, что ранее не рассматривалось в соответствующих тематических научных литературе. Впервые экспериментально выявлена присутствие в “виикитах” поликраза.

Практическая значимость. Полученные результаты расширяют и дополняют знания о минеральном составе гранитных пегматитов Балтийского щита и дают возможности их использования в исследовательских целях и нуждах народного хозяйства.

Ключевые слова: Ti-Ta-Nb-оксиды, поликраз, минералы супергруппы пирохлора, изохронный термический отжиг, сканирующая электронная микроскопия, рентгеноспектральный микроанализ

ARTICLE INFO
Received: 14 November 2017
Accepted: 5 January 2018
Available online: 10 January 2018

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