

ON THE IDENTIFICATION OF Ti-Ta-Nb-OXIDES IN “WIKITES” 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to the nature of Ti-Ta-Nb-oxides, which are included in the mineral associations that have historically gone by the now outdated name of “wiikites”, there is no unanimity of opinion.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 AB_2O_6 and $A_2B_2O_7$.

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 hydroxytropyrochlore and hydroxycalcibetafite, 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 hydroxycalcibetafite 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 Lokansaari 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 Nuolainniemi, 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 yttric, 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 titano-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 titano-tantalo-niobate is not obvious. This is rather convincingly shown in the works of Cao, Krivovichev, Burakov, & Liu (2014) and Qiuxiang, 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-niobates of the formation under study. For example, in the Encyclopedia of Mineralogy (Frye, 1983), with reference to a work by Hogarth (1977), wiikites are deemed to be a “mixture of pyrochlores”. In works by Kalita (1961) and Beus & Kalita (1961), such designations as obruchevite, loranskite, nuolaite and a number of others are mentioned when describing the mineral composition of wiikites. According to Hogarth, however, wiikites are mixtures of yttropyrochlore or other members of the pyrochlore group with euxenite and silicate. Upon the recommendation of the Soviet Union’s Commission of New Minerals and Mineralogical Terminology, Hogarth

adopted the name yttropyrochlore for obruchevite. According to Hogarth, nuolaite (which had already been introduced into mineralogical terminology by Lokka (1928) is a mixture of yttropyrochlore and other niobium oxide minerals related to wiikites, and must be discredited as a species. As for loranskite-(Y), in the Glossary of Mineral Species (Fleischer, 1987) the following formula (followed by a question mark) is given for it: (Y, Ce, Ca) ZrTaO₆ (?). In contrast to this, the Encyclopedia of Mineralogy (Frye, 1983) contains this brief notation: loranskite = euxenite (?). Thus, despite over a century of research into “wiikites”, it cannot be said that all of the questions concerning their nature have been answered. For example, the *Mineralogichesky Slovar’* (The Glossary of Minerals) by Krivovichev (2008) still attributes wiikites to minerals of the pyrochlore supergroup. In the present work, the authors attempt to develop a methodology to identify metamict Ti-Ta-Nb-oxides in the composition of several Karelian “wiikites”. Two approaches are considered:

- 1) taking into account the chemical composition of the corresponding titanium-tantalum-niobate;
- 2) using X-ray diffraction phase analysis during the process of thermal recrystallization of the mineral structure.

2. EXPERIMENTAL

2.1. Description of samples

The object of research in this study was a specimen of a metamict mineral (Ti-Ta niobate) within a mineral association from granite pegmatites found on the Nuolaynniemi Peninsula, in Priladozhye, Karelia, (the Svekofenian granite-gneiss in the Ladoga region), Russia. According to the Sm-Nd geochronology method (Glebovickiy, 2005), it was determined that these pegmatites were formed 1.800 ± 30 million years ago. Pegmatites of the Nuolaniemi Peninsula are among the pegmatites 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:

Wk-1. Color: black. Luster: vitreous (glassy). Fracture: conchoidal.

Wk-2. Color: orange-brown, amber-brown. Luster: from resinous to vitreous. Fracture: conchoidal.

Wk-3. Color: olive brown. Luster: greasy, opaque. Fracture: conchoidal.

Wk-7. Color: mottled, from yellowish, grayish-brown to black. Luster: bright vitreous. Fracture: conchoidal, uneven.

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 Difrey-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 microprobe 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. UNI5532 (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 99.995%), Br (KBr), Y (Yttrium rod 99.9%), Nb (Niobium wire 99.8%), La (LaB₆ 99.5%), Ce (CeO₂ 99.9%), Ta (Tantalum wire 99.5%), 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 minerals, 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 titanotantaloniobates were preliminarily identified and the mineral 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 chromel-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 D2Phaser, an automated powder diffractometer. The X-ray tube radiation was CoK α 1 ($\lambda = 1.78900$ Å) and CoK α 2 ($\lambda = 1.79283$ 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 ICDD, 2011) database. Quantitative phase analysis was performed using the TOPAS software package and resorting to Quantitative Rietveld phase analysis, taking into account the Inorganic Crystal 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.

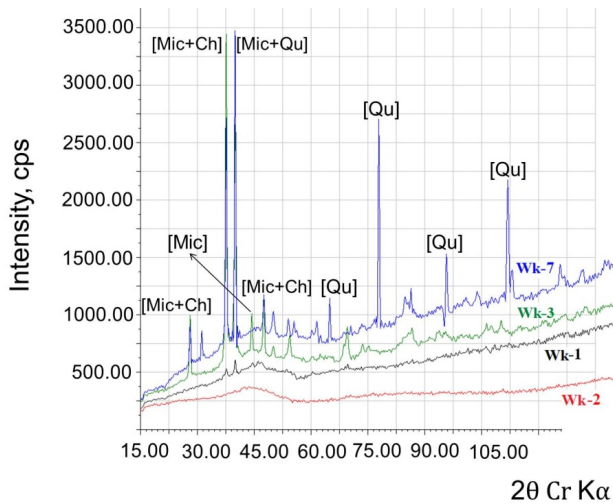


Figure 1. XRD powder patterns of wiikite samples: [Ch] – a mineral of the chlorite group; [Mic] – a mineral of the mica group; [Qu] – quartz

For the Wk-3 spectrum, the most characteristic minerals are those of the chlorite group (chamosite) and the mica group (presumably celadonite or polyilitonite). 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 backscattered 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.

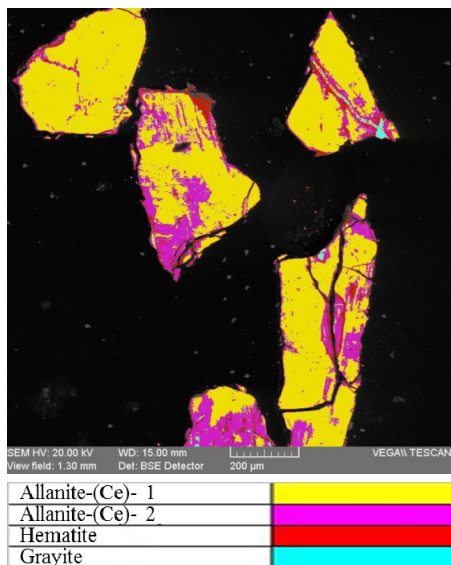


Figure 2. SEM-BSE image of Wk-1

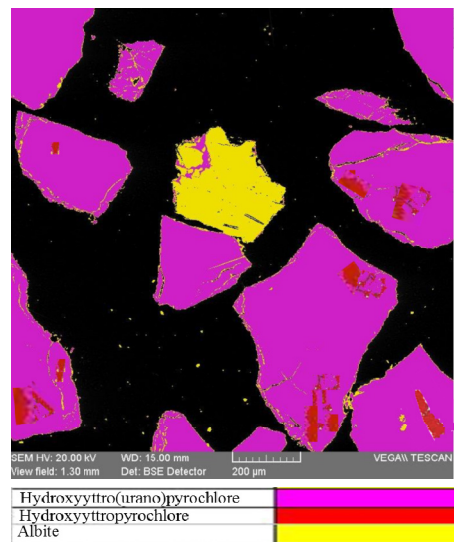


Figure 3. SEM-BSE image of Wk-2

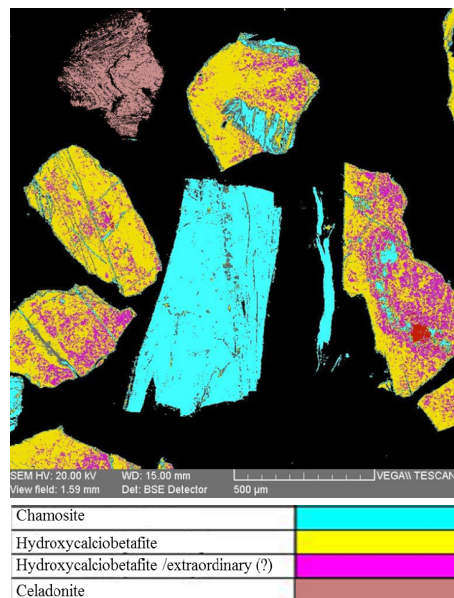


Figure 4. SEM-BSE image of Wk-3

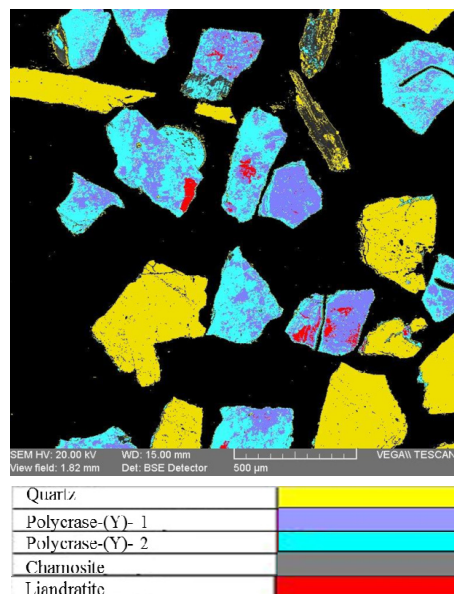


Figure 5. SEM-BSE image of Wk-7

*Notes:

Wk-1: allanite-(Ce)-2 differs from allanite-(Ce)-1 in that it contains more water;

Wk-2: in pyrochlore-2 (hydroxytropyrochlore) there is more Fe, Y, Gd than in pyrochlore-1 (hydroxytropyrochlore);

Wk-3: in the hydroxycalciobetafite/extraordinary (?) there is less Ti, but more Ca, U and Ta than in hydroxycalciobetafite. Despite the seeming discrepancy with the classification scheme, the authors presumed that it belonged to the betafite mineral species based on the closeness of its total elemental composition to that of the betafites. As a result, this hypothesis was experimentally confirmed;

Wk-7: polycrase-(Y)-2 enriched in Fe and U in comparison with Polycrase-(Y)-1.

The values of the square deviations were calculated in accordance with the guidelines (Reed, 2005).

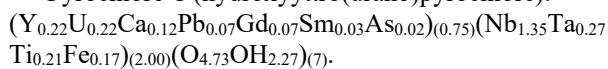
EMPA was performed according to the concentration of the spectrum over the entire area of the phase (in the picture) in one measurement. Calculation of the surface area is carried out by calculating the number of pixels in the BSE image within the range of a definite brightness/contrast characteristic 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 $\text{Ca}_3\text{U}(\text{HNbO}_3)$ and β -wiikite $\text{Y}_4(\text{HNbO}_5)$. According to Lokka (1950), wiikites are silico-titano-tantaloniobates. Therefore, if the word “wiikite” is understood in the traditionally accepted sense as a synonym for “titano-tantaloniobate” (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.

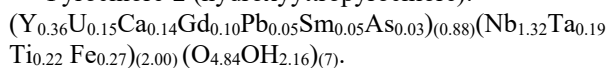
The content of Y, Ti, Ta, Nb, U, and some rare earth elements (Table 1), made it possible to identify the Ti-Ta-Nb-oxides in Wk-2 as hydroxytropyrochlores with small variations in the amounts of yttrium and uranium. In the same way, the Ti-Ta-Nb-oxide in Wk-3 was designated as hydroxycalciobetafite, 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 hydroxycalciobetafite 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.

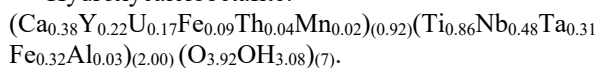
Pyrochlore-1 (hydroxytropyrochlore):



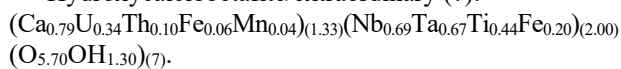
Pyrochlore-2 (hydroxytropyrochlore):



Hydroxycalciobetafite:



Hydroxycalciobetafite/extraordinary (?):

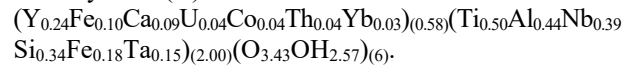


The deficit of positive charges in these formulas is offset by the inclusion of the hydroxyl group $(\text{OH})^{1-}$ in the oxygen position.

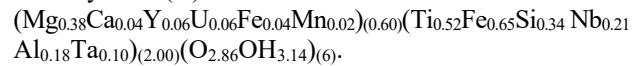
In contrast to these two wiikites, Wk-7 contained a Ti-Ta-Nb-oxide that was classified at this stage of our research as belonging to the pyrochlore supergroup

but to the group of euxenite-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:



Polycrase-(Y)-2:



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, urancalcrite 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 $T = 1000^\circ\text{C}$, in addition to 10-minute annealing, 30-minute annealing was also performed).

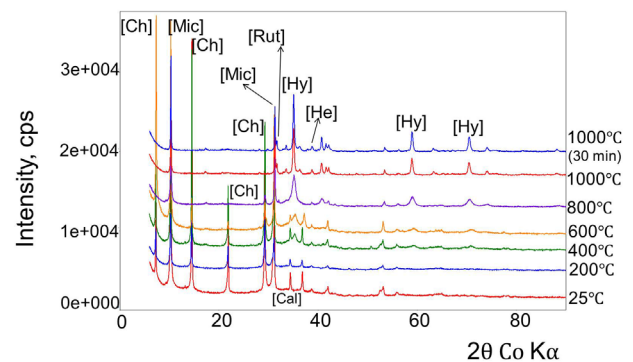


Figure 6. XRD powder patterns of Wk-3 at room temperature and when annealed in the range of 200 – 1000°C: [Mic] – mica; [Hy] – hydroxycalciobetafite; [He] – hematite; [Rut] – rutile; [Ch] – chlorite; [Cal] – calcite

The phase composition of the original sample (at $T = 25^\circ\text{C}$) is close, but not identical, to the one indicated in Table 1. A mineral from the mica group (celadonite or polyolithionite) makes up the bulk of the aluminosilicates (55 percent). The chlorite group, as noted in Table 1, is

represented by chamosite in the amount of 22.5 percent, although it is possible that this is clinocllore (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 urancalcite.

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, calciobetafite lines are clearly observed, with interplanar spacings $d_{222} = 2.97 \text{ \AA}$ and $d_{400} = 2.57 \text{ \AA}$. The content of the phases is as follows: calciobetafite – 50 percent; rutile – 20 percent; hematite – 14 percent; celadonite (polyolithionite) – 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” (Ambartsu-myan, Basalova, Gorzhhevskaya, Nazarenko, & Hodzhaeva, 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 calciobetafite 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 polyolithionite) – 2.5 percent; hematite – 13.5 percent; goethite – 4 percent; a mineral from the chlorite 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.

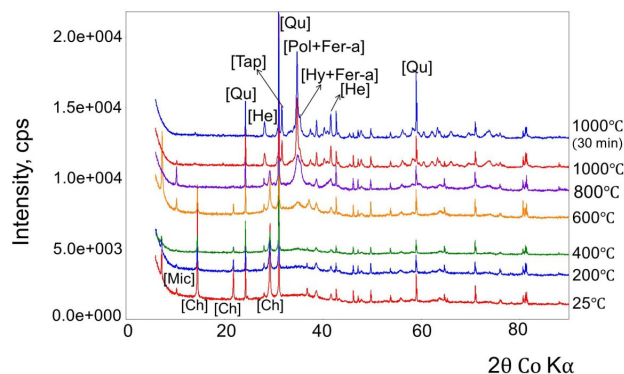


Figure 7. XRD powder patterns of Wk-7 at room temperature and when annealed in the range of 200 – 1000°C: [Qu] – quartz; [He] – hematite; [Tap] – tapiolite; [Pol + Fer-a] – polycrase + fergusonite-alpha-(Y); [Hy + Fer-a] – hydroxycalciobetafite + fergusonite-alpha-(Y); [Ch] – chlorite; [Mic] – mica

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 $d = 3.00 \text{ \AA}$ 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. Fergusonite-beta-(Y) and calciobetafite are probably present as well, and the asymmetry of the polycrase diffraction maximum can be explained by the close proximity ($d = 2.94 \text{ \AA}$) of their lines. The sample annealed at 1000°C contains approximately 17.4 percent of polycrase, 3 percent of fergusonite-alpha-(Y), 9 percent of fergusonite-beta-(Y), 3 percent of tapiolite and 14 percent of calciobetafite, 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 liandratite 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; fergusonite-beta-(Y) – 18 percent; calciobetafite – 11 percent; fergusonite-alpha-(Y) – 7 percent; and tapiolite – 8 percent, making a total of 75 percent (the remaining 25 percent is hematite). Detection of fergusonite 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 Qiuxiang, 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 ($d_{112} = 3.05 \text{ \AA}$) is superimposed on the most intensive maximum of polycrase ($d_{311} \sim 2.99 \text{ \AA}$), which, in turn, has a large half-width at 600 and 800°. 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 hydroxytropyrochlore 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.

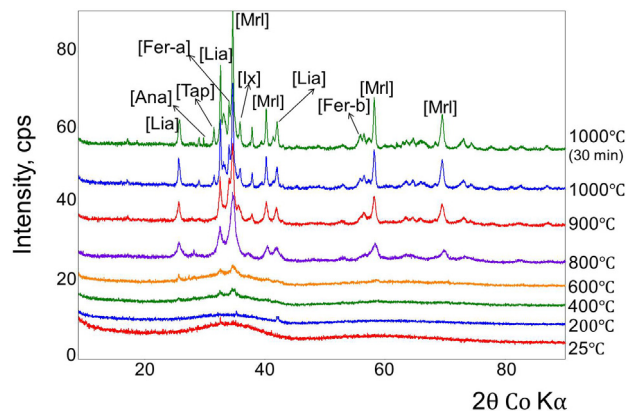


Figure 8. XRD powder patterns of Wk-2 at room temperature and when annealed in the range of 200 – 1000°C: [Lia] – liandratite; [Ana] – anatase; [Tap] – tapiolite; [Fer-a] – fergusonite-alpha-(Y); [Mr] – member of the microlite group; [Ix] – ixiolite; [Fer-b] – fergusonite-beta-(Y)

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 ques-

tions. But it is not entirely clear why microlite formed instead of ytropyrochlore, 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 ytropyrochlore 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 betafite 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

low temperatures. Electrons, thermally liberated from electron trapping centers of varying depth, may act as reducing agents. One of the prevalent electronic trapping centers is the (E_1)' center arising from the radiolysis of quartz (Moiseev, 1985; Rakov, 1989). It can be assumed that in Wk-7, where the quartz content is high, the heating of the sample to 350 – 400°C is accompanied by the appearance of a significant quantity of free electrons in the mineral association, which leads, in turn, to the reduction of uranium and formation of polycrase, instead of liandratite. The content of the silicate phases in the mineral association of the Wk-2 sample is no more than 3.5 percent. Due to this, the number of electrons is apparently not sufficient to reduce the uranium, which results in the formation of liandratite. It should be noted, however, that this mechanism for the reduction of the uranium can be realized under two conditions: first, the effective migration of free electrons across the interfase boundary of the quartz-metamict mineral; second, the motion of the electrons in the metamict structure where the zone model is not fully realized.

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 study sample 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 hydroxycalcibetafite (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 pegmatites of the Nuolaynniemi 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 titanium 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-gneiss 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 microlite. In the opinion of the authors, the formation of microlite 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 reconstruction 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.

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ДО ПИТАННЯ ІДЕНТИФІКАЦІЇ Тi-Ta-Nb-ОКСИДІВ У "ВІКІТАХ" КАРЕЛІЇ

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Мета. Розробка методології ідентифікації Ti-Ta-Nb-оксидів складного хімічного складу з метаміктною структурою, що відповідають мінеральним формулами AB_2O_6 та $A_2B_2O_7$.

Методика. Для розробки методології ідентифікації у роботі використано два експериментальних підходи: 1) рентген-спектральний мікроаналіз фаз, виявлених методом скануючої електронної мікроскопії зразків у надзад відображених електронах. На основі отриманих результатів висунута гіпотеза щодо природи Ti-Ta-Nb-оксидів. 2) рентген-дифракційний аналіз фаз, що утворюються в процесі термічного відпалу зразків від 200 до 1000°C. На основі отриманих результатів для кожного зразка первинна гіпотеза приймалася або відкидалася.

Результати. З використанням даної методики були вивчені три зразки "вікітів" (шифри зразків: Wk-2, Wk-3 і Wk-7). Наявність Ti-Ta-Nb-оксидів попередньо визначено є двох зразках (Wk-2 і Wk-3) відповідно, як гідроксіттропірохлор та гідроксікальціобетафіт. У третьому зразку (Wk-7) Ti-Ta-Nb діагностований як полікраз. Результати рентген-дифракційного аналізу відпалених зразків підтвердили гіпотези про те, що початковими мінералами у Wk-3 і Wk-7 були гідроксікальціобетафіт і полікраз відповідно.

Наукова новизна. Визначено хімічні умови, необхідні для утворення початкового Ti-Ta-Nb під час рекристалізації метаміктної структури, що раніше не розглядалось у відповідній тематичній науковій літературі. Вперше експериментально виявлено присутність у "вікітах" полікразу.

Практична значимість. Отримані результати розширюють й доповнюють знання щодо мінерального складу гранітних пегматитів Балтійського щита та надають можливість їх використання в дослідницьких цілях і потребах народного господарства.

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

К ВОПРОСУ ИДЕНТИФИКАЦИИ Ti-Ta-Nb-ОКСИДОВ В "ВИИКИТАХ" КАРЕЛИИ

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Цель. Разработка методологии идентификации Ti-Ta-Nb-оксидов сложного химического состава с метамиктной структурой, соответствующих минеральным формулам AB_2O_6 и $A_2B_2O_7$.

Методика. Для разработки методологии идентификации в работе использовано два экспериментальных подхода: 1) рентген-спектральный микроанализ фаз, выявленных методом сканирующей электронной микроскопии образцов в обратно отраженных электронах. На основе полученных результатов выдвинута гипотеза о природе Ti-Ta-Nb-оксидов. 2) рентген-дифракционный анализ фаз, образующихся в процессе термического

отжига образцов от 200 до 1000°C. 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 гидрокситропироклор 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 метамиктной структуры, что ранее не рассматривалось в соответствующих тематических научных литературе. Впервые экспериментально выявлено 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 пироклора, изохронный термический отжиг, сканирующая электронная микроскопия, рентгеноспектральный микроанализ*

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