MINERALOGIA POLONICA
Vol. 6, No 2 — 1975

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NIOBIUM-BEARING RUTILE, ILMENORUTILE AND IRON MOSSITE(?) FROM PEGMATITES OF THE MARGINAL ZONE OF THE ŁUŻYCE GRANITOIDS

UKD 546.882/.883:[549.514.63.08.+549.752.31.08]:552.322.2:552.321.1/.4(234.565—192.2)

Abstract. A number of titanium minerals that are associated with pegmatites of the marginal zone of the Łużyce granitoids have been analysed for the niobium and tantalum content. Two generations of rutile have been distinguished. Rutile of the first generation originated immediately after albitization and contains, on the average, several per cent of niobium, the content of this element being highly variable. Rutile of the second generation is connected with the process of prochloritization. It is ilmenorutile characterized by a high and constant niobium content, amounting to approx 10 wt.%. Besides, a mineral corresponding to the formula $FeNb_2O_6$ with the properties similar to mossite has been recorded. It may owe its origin to the replacement of ilmenorutile by iron compounds.

INTRODUCTION

In the Łużyce granitoids, occurrences of titanium- and niobium-bearing pegmatites have been noted. The granitoids are represented by alkaline varieties, consisting mainly of potassium feldspars, quartz, plagioclases and mica. In the marginal zones they show substantial contact changes. There are tectonic zones there that are associated with veined or vein-nest-like pegmatite bodies. The granitoids adjoining the latter bodies are free of biotite, which has been probably replaced by prochlorite. The quantitative mineral composition of the granitoid and pegmatite, as determined by microscopic examinations, is presented in Table 1. It is evident from the table that the mineral composition of pegmatites differs conspicuously from the wall rock. The content of feldspars in the former is much higher, prochlorite appears in substantial amounts, while mica is missing altogether.

The main components of the ore-bearing pegmatites crystallized in the following approximate sequence:

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1) muscovite,
2) orthoclase,
3) microcline,
4) albite,
5) niobium-bearing rutile,
6) zircon,
7) quartz,
8) hematite,
9) prochlorite,
10) ilmenorutile,
11) niobium-bearing iron minerals and $FeNb_2O_6$ (associated with thorium mineralization).

It may be assumed that the development of pegmatites was accompanied by a drop in temperature. This fact was favourable for the activation of hydrothermal processes. The subsequent, post-magmatic stages of mineralization with niobium, thorium and rare earths as well as with trace amounts of native copper were presumably associated with these processes.

Table 1

Mineral composition of granitoid and pegmatite (vol. %)

Minerals	Granitoid %	Pegmatite %
Quartz	59,7	21,2
K-Feldspars	26,8	56,6
Muscovite	9,5	—
Plagioclases	3,9	5,9
Prochlorite	—	14,9
Total	99,9	98,6

The secondary processes, i.e. albitization (weakly manifested), sericitization, prochloritization, mineralization with quartz and iron, remain in intimate association with the development of pegmatites and the following stages of their mineralization and alteration. Albitization gave rise to the oldest niobium-bearing rutile (Černy 1964, Collective work 1964), prochloritization, as appears from further discussion, to ilmenorutile, and enrichment in iron — to iron mossite.

NIOBIUM-BEARING RUTILE

Originally, rutile formed presumably grains up to 4 mm in size. Due to the secondary processes, it was intensely corroded so that today only its relics may be observed. Rutile is replaced by quartz, anatase, rarely by sphen or hydrated iron oxides (Phot. 1, Fig. 1). The latter form psedomorphs after rutile, and not seldom do they contain relics that, considering their chemical composition, should be regarded as a transitional form between ilmenorutile and iron mossite (Phot. 1, Fig. 1, Tab. 2, point *A*). Compared with the isotropic matrix of hydrated iron oxides, the ilmenorutile relics show a higher reflectance and dark, hardly discernible internal reflections. The larger and better preserved rutile crystals have heterogeneous internal reflections, varying from almost colourless through yellow-brown to hardly visible dark-brown or grey-black. Microprobe analyses (Phot. 2, Tab. 2, point *B*, *C*) have shown that the darkening of the internal reflections attends on an increase in the niobium content. The amount of niobium also determines the lowering of reflectance, relative to rutile, seen in immersion. The results of observations are in accord with the optical features reported by Ramdohr (1960) for rutile and ilmenorutile. Niobium is randomly distributed in rutile, and it is difficult to determine any preferential directions. It has been noticed in some cases that the more fissured rutile is, the less intensive its internal reflections; it may be inferred therefore that it contains more niobium. There is in this point certain analogy with the experimental data of Hutchinson (1955). The rutile under study is characterized by a widely variable Nb content, low Fe content and, practically, the lack of Ta, Mn and Sn.

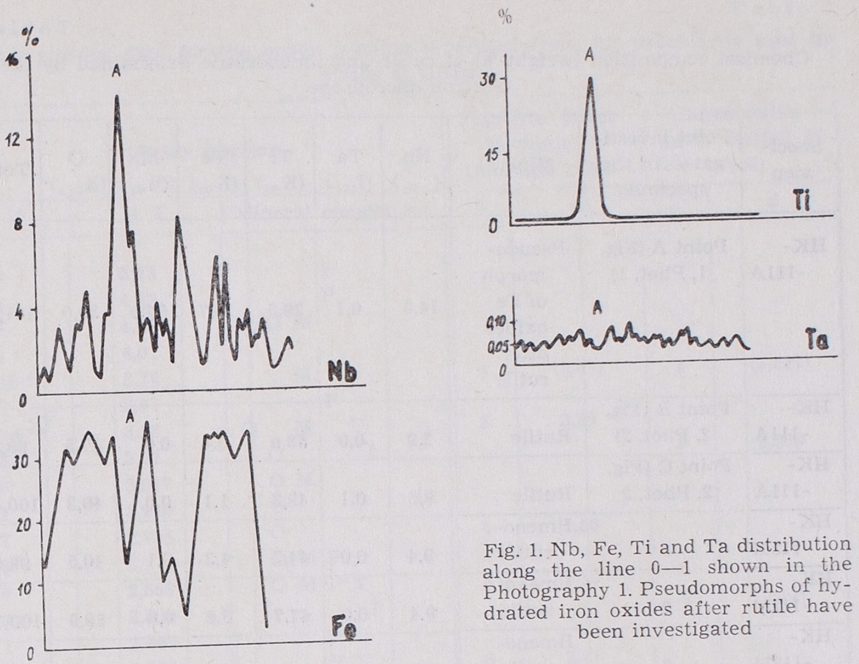

Fig. 1. Nb, Fe, Ti and Ta distribution along the line 0—1 shown in the Photography 1. Pseudomorphs of hydrated iron oxides after rutile have been investigated

Summarizing the results of microprobe analyses and microscopic investigations, it is interesting to note the following facts:

1. The investigations failed to show any columbite or mossite secretions in the niobium-bearing rutile.

2. The original Nb concentration in rutile is associated with an insignificant amount of iron (Tab. 2, point *B*, *C*). The iron content increases substantially in the process of replacement of rutile by iron compounds (Tab. 2, point *A*). It appears, therefore, that the association of ilmenorutile with mossite is a secondary feature.

3. Not all the niobium must have entered the rutile lattice simultaneously with titanium.

Table 2

Chemical composition (weight-%) of rutile and ilmenorutile determined by the electron microprobe

Specimen	Point investigated in the specimen	Mineral	Nb ($_{\alpha_1}$)	Ta (L_{α_1})	Ti (K_{α_1})	Fe (K_{α_1})	Mn (K_{α_1})	O ($K_{\alpha_{1,2}}$)	Total
HK--111A	Point A (Fig. 1, Phot. 1)	Pseudomorph of Fe oxides after rutile	14,0	0,1	29,5	18,7	0,00	39,0	101,3
HK--111A	Point B (Fig. 2, Phot. 2)	Rutile	2,9	0,0	58,0	0,4	0,0	37,5	98,8
HK--111A	Point C (Fig. 2, Phot. 2	Rutile	9,6	0,1	49,3	1,1	0,0	40,3	100,4
HK--112M	1	Ilmenorutile	9,4	0,0	44,7	4,3	0,1	40,5	99,0
HK--112M	2	Ilmenorutile	9,4	0,0	47,7	3,8	0,0	39,9	100,8
HK--112M	3	Ilmenorutile	9,6	0,0	45,8	4,2	0,0	40,0	99,6
HK--112M	4	Ilmenorutile	9,7	0,0	45,0	3,8	0,0	39,8	98,3

Experimental conditions: accelerating voltage 20 kV, standard of spectral purity: Nb, Ta, Ti, Fe, Mn, Fe_2O_3, counting time 100 sec.

ILMENORUTILE

Ilmenorutile is associated with the prochloritization zones adjoining directly the pegmatite bodies. The amount of prochlorite in the rock increases to 70 vol.%, and so does, proportionally, the content of ilmenorutile.

Ilmenorutile forms idiomorphic crystals averaging 0.03 mm, sometimes up to 0.1 mm in size. They are very well preserved and, in contradistinction to niobium-bearing rutile, are not subject to replacement. The crystal habit is dipyramidal, prismatic or tabular, uncommonly needle-like. The crystals often form twins, similar to the varieties reported from the Ilmeńskie Mts. (Minieraly 1965, vol. 11). Occasionally, regular octagons formed by eight intergrown pyramidal crystals (with very regular structure) may be observed microscopically. Under the ore microscope the mineral shows weak bireflectance on the grain boundaries, conspicuous in the intergrowths, colourless. The anisotropy ranges from weak to distinct, being visible in intergrowths. In immersion bireflectance is distinct on the grain boundaries and strong in the twin intergrowths, varying in colour from grey-pink to grey-blue and violet. The internal reflections are dark brown,

Table 3

X-ray powder data for the heavy fraction separated from the prochlorite zone by means of $CHBr_3$

Heavy fraction			Tapiolite (after Michiejev, Dubinina 1939)		Ilmenorutile (after XRDC II 1944)	
I	*d* Å	Mineral component	*I*	*d*	*I*	*d*
2	5,73	P				
4	4,43	P				
5	4,23	Q O M				
1	4,01					
1*b* *	3,78	M	4	(3,67)	2	(3,617)
8	3,47	P				
3*d* **	3,38	Q M T	8	3,33		
10	3,27	O I			8	3,269
10	3,017	O M				
2	2,910	O				
7	2,835	O	4	2,85		
3	2,772	O M P				
6	2,569	O M P T	8	2.57		
7	2,500	I			6	2,497
1	2,447	Q P				
1	2,374	P T	6	2,37		
4	2,283	O T	2	2,26	2	2,305
2*d*	2,203	I			2	2,185
7	2,154	O M				
1	2,064	O	2	2,11		
1	1,988	O M?P				
5	1,919	O M?	6	(1,94)		
6	1,864	T	2	1,86	2	(1,872)
4	1,806	Q?O?M				
3	1,766	O				
2	1,748	M? T	10	1,75		
7	1,700	I			10	1,695
2	1,678	Q? T	6	1,68		
1	1,632	I			6	1,626
1	1,570	P	4	(1,552)		
1	1,547	P?T	4	1,543		
			6	1,502	2	1,483
1	1,459	M I			4	1,456
3	1,432	M T	4	1,432		
			7	1,405		
1	1,385	Q I			4	1,386
1	1,367	Q I			2	1,360
4	1,337	P?T	2	1,344		
1	1,292	Q? T	4	1,293		
1*b*	1,222		6	1,214		
			4	(1,200)		
1	1,184	Q?	4	(1,190)		
			6	1,138		

Table 3 ct

Heavy fraction			Tapiolite (after Michiejev, Dubinina 1939)		Ilmenorutile (after XRDC II 1944)	
I	*d* Å	Mineral component	*I*	*d*	*I*	*d*
2*b*	1,120		2	1,121		
1	1,080	Q	7	1,070		
1	1,048	Q?	4	1,064	6	1,047
2	1,042					
2	1,022	Q	4	1,007		
					4	0,895
					4	0,881

Explanation: Q — quartz, O — orthoclase, M — microcline, P — prochlorite, T — iron mossite (tapiolite), I — ilmenorutile
* *b* — broad line.
** *d* — double line.

in air visible only on the grain boundaries on the contact with gangue minerals; in immersion they are somewhat stronger.

It has been found that the investigated ilmenorutile contains no inclusions that have been frequently reported in literature (Ramdohr 1960; Uytenbogaardt & Burke 1971). This mineral, associated genetically with prochloritization, may be a stable compound, not subject to decomposition. This fact is additionally confirmed by the stability of its chemical composition, which has been established during microprobe analyses (Tab. 3). It is interesting to note that ilmenorutile is practically free of Mn, Ta and Sn and has a relatively low Fe content compared with that of Nb. Fe deficiency in relation to Nb may be a factor precluding the precipitation of columbite or mossite in the process of decomposition of ilmenorutile. Such low Fe : Nb and Fe : Ta ratios (Tab. 2) are rather uncommon (Collective work 1964, vol. 2).

Ilmenorutile and the co-occurring gangue minerals were subjected to X-ray examinations using CoK_{α_1} radiation. Natural samples and the separated fractions lighter and heavier than $CHBr_3$ were investigated. The X-ray powder pattern (Tab. 3) shows a similarity to that of ilmenorutile from the Ilmeńskie Mts. (Michiejev 1957).

IRON MOSSITE (?)

Table 3 gives an interpretation of the X-ray powder pattern of the fraction heavier than bromoform, obtained from the investigated mineral assemblage. After eliminating the reflections of ilmenorutile, prochlorite, orthoclase, microcline and quartz, there still remain several interplanar spacings that correspond to none of the afore-named minerals. The results of microprobe analyses (Fig. 1, 3) together with the X-ray powder data indicate that it may be mineral of the topiolite-mossite series with a specific chemical composition corresponding to iron mossite ($FeNb_2O_6$).

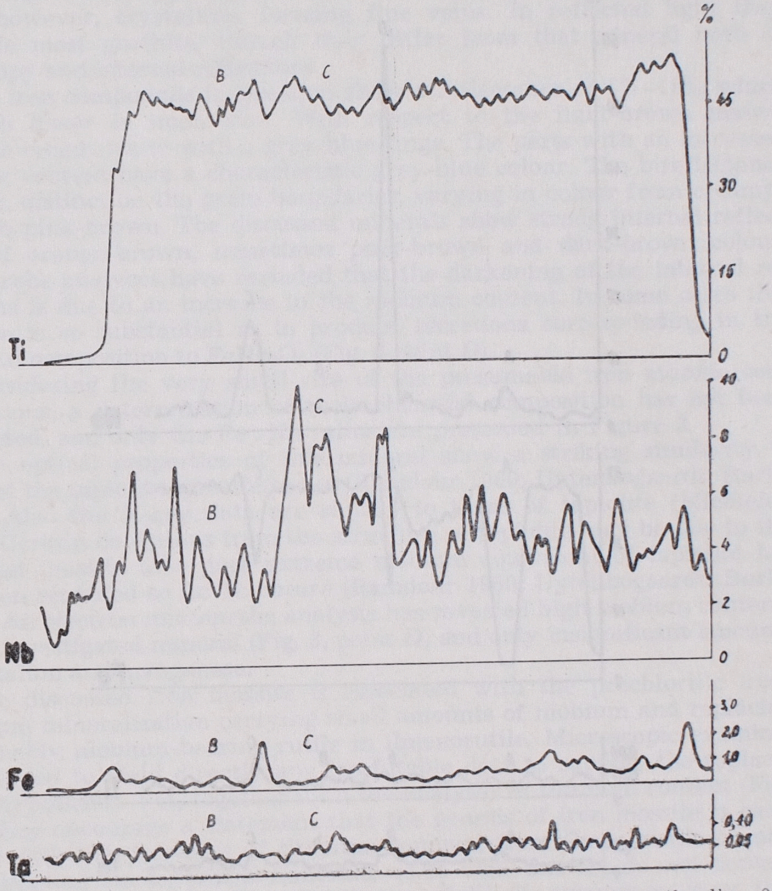

Fig. 2. Ti, Nb, Fe and Ta distribution in Nb-bearing rutile along the line 0—1 shown in the Photography 2

Microscopic examinations of ilmenorutile derived from the prochlorite zones have revealed the presence of a rim with dark-brown, indistinct internal reflections on some grains of this mineral. Anisotropy of the mineral forming this rim is hard to identify considering its small size. The reflectance lower by about 5% than that of ilmenorutile would correspond to a member of the tapiolite-mossite series (Uytenbogaardt, Burke 1971). Similar rims with unidentified chemical composition have been noted on strüverite from Mongolia (Minieraly 1965, vol. 2, part II). The rims in question contain sometimes microinclusions of ilmenorutile *. Their small size, however, makes microscopic and chemical analyses extremely difficult. Genetically, the rims follow prochloritization, being associated with the stage of iron-thorium mineralization that also carries a certain, though rather insignificant, amount of niobium. In the prochlorite zones this mineralization is weakly developed, being limited to very fine veiny secretions of hydrated iron oxides with a reflectance of 14—15% and with dark-brown, intensive internal reflections. The latter darken in the case of occurrence of minute secretions with a slightly higher R which may belong to mossite. The hydrated iron oxides are isotropic and have increased contents of Th, Si and P. Somewhat larger grains of iron oxides are associated with the stage of hydrothermal iron-thorium mineralization recorded in the feldspathic cores of pegmatites. They correspond in time to the compounds of that type reported from the chlorite zone. They are frequently, however, crystalline, forming fine veins. In reflected light they resemble most goethite, though they differ from that mineral both in anisotropy and internal reflections.

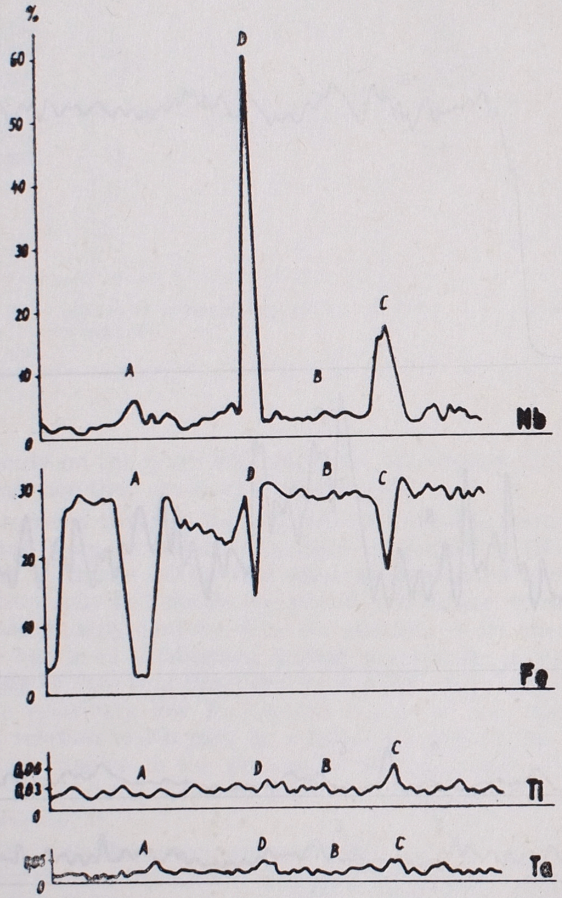

Fig. 3. Nb, Fe, Ti and Ta distribution of goethite-like mineral along the line 0—1 shown in the Photography 3. In point *D* there are inclusions corresponding in the chemical composition to iron mossite

The iron compounds in question show a reflectance of 17—19%, which is much lower in immersion. With respect to the light-brown matrix they are cream-white with a grey-blue tinge. The parts with an increased niobium content have a characteristic grey-blue colour. The bireflectance is weak, distinct on the grain boundaries, varying in colour from creamy-grey to pink-brown. The discussed minerals show strong internal reflections of orange-brown, sometimes pink-brown and dark-brown colour. Microprobe analyses have revealed that the darkening of the internal reflections is due to an increase in the niobium content. In some cases this increase is so substantial as to produce secretions corresponding in the chemical composition to $FeNb_2O_6$ (Fig. 3 point *D*).

Considering the very small size of the presumable iron mossite concentrations, a determination of their chemical composition has not been attempted, and only the Fe : Nb ratios are presented in Figure 3.

The optical properties of this mineral show a striking similarity to those of the tapiolite-mossite series (Ramdohr 1960; Uytenbogaardt, Burke 1971). Also the X-ray data are similar to those of tapiolite (Michiejev 1957). Certain deviations from the structure of tapiolite may be due to the fact that mossite as a pure extreme niobium equivalent of tapiolite has not been recorded so far in nature (Ramdohr 1960; Uytenbogaardt, Burke 1971). An electron microprobe analysis has revealed high niobium contents in the investigated mineral (Fig. 3, point *D*) and only insignificant amounts of tantalum and manganese.

The discussed iron mossite is associated with the prochloritic iron-thorium mineralization carrying small amounts of niobium and replacing presumably niobium-bearing rutile in ilmenorutile. Microscopic examinations failed to yield directly any irrefutable data to support the replacement hypothesis. Yet, together with the analyses of titanium content (Figs 2, 3) they encourage a statement that the genesis of iron mossite is associated with the processes of titanium removal from ilmenorutile or niobium-bearing rutile, which minerals, as is well known, do not contain tantalum or manganese. For that reason $FeNb_2O_6$ appears as very fine secretions in iron minerals.

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[*] Some authors (e.g. Strunz 1970) regard ilmenorutile as a member of the rutile-mossite series.

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RUTYL NIOBOWY, ILMENORUTYL I MOSSYT ŻELAZOWY(?) Z PEGMATYTÓW BRZEŻNEJ STREFY GRANITOIDÓW ŁUŻYCKICH

Streszczenie

Kilka minerałów tytanu związanych z pegmatytami brzeżnej strefy granitoidów łużyckich zbadano pod kątem zawartości niobu i tantalu. Wyróżniono dwie generacje rutylu. Rutyl pierwszej generacji powstał bezpośrednio po albityzacji i zawiera średnio do kilku procent niobu, przy czym zawartość tego pierwiastka jest zróżnicowana. Druga generacja rutylu związana jest z procesem prochlorytyzacji. Jest to ilmenorutyl, zawierający około 10% wagowych niobu. Zarejestrowano również minerał odpowiadający formule $FeNb_2O_6$ zbliżony własnościami do mossytu. Mógł on powstać przez oddziaływanie związków żelaza na ilmenorutyl.

OBJAŚNIENIA FIGUR

Fig. 1. Wykres koncentracji Nb, Fe, Ti i Ta wzdłuż profilu zaznaczonego na fotografii 1. Dane otrzymano w wyniku badań w mikroobszarze pseudomorfozy uwodnionych tlenków żelaza po rutylu

Fig. 2. Wykres koncentracji Ti, Nb, Fe i Ta w mikroobszarze rutylu niobonośnego wzdłuż odcinka zaznaczonego na fotografii 2

Fig. 3. Wykres koncentracji Nb, Fe, Ti i Ta w mikroobszarze minerału żelaza przypominającego goethyt zaznaczonego na fotografii 3. W punkcie *D* minerał ten zawiera wydzielenie odpowiadające składem chemicznym mossytowi żelazowemu

OBJAŚNIENIA FOTOGRAFII

Fot. 1. Elektronowy, absorpcyjny obraz pseudomorfozy uwodnionych tlenków żelaza po rutylu (100 × 100 µm). W punkcie *A* dokonano analizy składu chemicznego (tab. 3). Wzdłuż odcinka 0—1 analizowano koncentrację Nb, Fe, Ti i Ta (fig. 1)

Fot. 2. Elektronowy, absorpcyjny obraz rutylu niobonośnego (200 × 200 µm). W punktach *B* i *C* dokonano analizy składu chemicznego. Wzdłuż odcinka 0—1 badano koncentrację Ti, Nb, Fe i Ta (fig. 2)

Fot. 3. Elektronowy, absorpcyjny obraz niobonośnego minerału żelaza zbliżonego do goethytu (150 × 150 µm). *A*, *B*, *C* i *D* oznaczają punkty w których stwierdzono podwyższone zawartości niobu. W punkcie *D* występuje wrostek mossytu żelazowego. Wzdłuż odcinka 0—1 badano koncentrację Nb, Fe, Ti i Ta (fig. 3)

Марян БАНАСЬ, Хенрик КУХА

НИОБИСТЫЙ РУТИЛ, ИЛЬМЕНОРУТИЛ И ЖЕЛЕЗИСТЫЙ МОССИТ (?) ИЗ ПЕГМАТИТОВ КРАЕВОЙ ЗОНЫ ЛУЖИЦКИХ ГРАНИТОИДОВ

Резюме

Несколько минералов титана, связанных с пегматитами периферической зоны лужицких гранитоидов, анализировались на содержание ниобия и тантала. Определены две генерации рутила. Рутил первой генерации образовался непосредственно после альбитизации и содержит в среднем до нескольких процентов ниобия. Вторая генерация рутила связана с процессом хлоритизации. Кроме того, был определен минерал, соответствующий формуле $FeNb_2O_6$ и по своим свойствам сходный с мосситом. Этот минерал образовался, вероятно, при воздействии соединений железа на ильменорутил.

ОБЪЯСНЕНИЯ К ФИГУРАМ

Фиг. 1. График содержания Nb, Fe, Ti и Ta вдоль отрезка, показанного на фото 1. Данные получены в итоге анализа микроучастка псевдоморфоза гидроокислов железа по рутилу

Фиг. 2. График содержания Ti, Nb, Fe и Ta на микроучастке ниобистого рутила, вдоль отрезка, показанного на фото 2

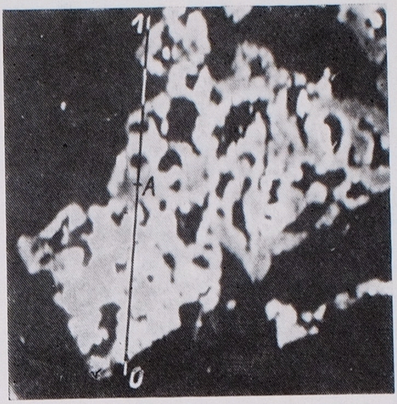
Фиг. 3. График содержания Nb, Fe, Ti и Ta на микроучастке минерала железа, напоминающего гётит. В точке *D* минерал содержит включение, по химическому составу соответствующее железистому мосситу

ОБЪЯСНЕНИЯ К ФОТОСНИМКАМ

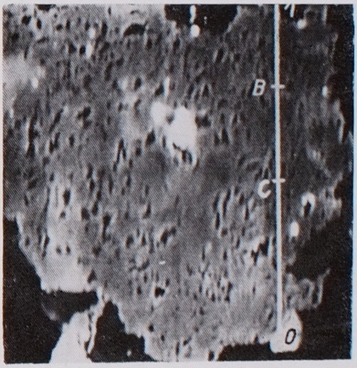
Фото 1. Электронный, абсорбционный вид псевдоморфоза гидроокислов железа по рутилу (100×100 µм). В точке *A* был произведен анализ химического состава (табл 3). Вдоль отрезка 0—1 анализировалось содержание Nb, Fe, Ti и Ta (фиг. 1)

Фото 2. Электронный, абсорбционный вид ниобистого рутила (200×200 µм). В точках *B* и *C* были произведены анализы химического состава. Вдоль отрезка 0—1 анализировалось содержание Nb, Fe. Ti и Ta (фиг. 2)

Фото 3. Электронный, абсорбционный вид ниобистого минерала железа, сходного с гётитом (150×150 µм). *A*, *B*, *C* и *D* — точки с повышенным содержанием ниобия. В точке *D* располагается включение железистого моссита. Вдоль отрезка 0—1 анализировалось содержание Nb, Fe, Ti и Ta (фиг. 3)



Phot. 1. Absorbed electron image of pseudomorph of hydrated iron oxides after rutile (100 × 100 μm). Analysis of chemical composition was performed in point *A* (Tab. 3). Scan along the line 0—1 for Nb, Fe, Ti and Ta (Fig. 1)



Phot. 2. Absorbed electron image of Nb-bearing rutile (200 × 200 μm). Analysis of chemical composition was performed in points *B* and *C*. Scan along the line 0—1 for Ti, Nb, Fe, and Ta (Fig. 2)

Phot. 3. Absorbed electron image of Nb-bearing goethite-like mineral (150 × × 150 μm). In points *A*, *B*, *C* and *D* — Nb content is higher. In point *D* is inclusion of iron mossite. Scan along the line 0—1 for Nb, Fe, Ti and Ta (Fig. 3)

Marian BANAŚ, Henryk KUCHA — Niobium-bearing rutile, ilmenorutile and iron mossite (?) from pegmatites of marginal zone of the Łużyce granitoids