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Niobium and titanium in the thorium-uranium albitites of the Novooleksiivka ore occurrence (Ukrainian shield)

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SUMMARY

The article presents the results of the study of the niobium and titanium distribution in the thorium-uranium albitites of the Novooleksiivka ore occurrence of the Partisan ore field of the Central Ukrainian uranium ore district of the Ukrainian Shield. Three investigated sections of thorium-uranium albitites of the actinolite-diopside group of facies of the cut of alkaline sodium metasomatites of the ore occurrence are characterized by the presence of titanium and niobium anomalies. The estimation of the average content of these chemical elements in albitites is much higher than the geochemical background. The estimate of the correlation coefficient of titanium and niobium content in albitites is very high - the Spearman rank correlation coefficient is 0.96, which is a consequence of the concentration of these chemical elements in one (total) mineral. Electron microscopic studies show that titanite is the main concentrator of both titanium and niobium in albitites . It was concluded that in the processes of pneumatolitho-hydrothermal rock formation, additional masses of titanium and niobium were brought and deposited together in the volume of the crust now occupied by thorium-uranium albitites. Titanium and niobium are paragenetic chemical elements in the thorium-uranium albitites of the Novooleksiivka ore occurrence.

Introduction. The works (Mihalchenko et al, 2015, 2016) present the results of the reconstruction of migration and deposition of chemical elements in the formation of thorium-uranium albitites of the diopside-actinolite facies group on the example of one section of the rocks of the rear zone of the metasomatic column of the Novooleksiivka ore occurrence of Central Ukrainian uranium ore district of Ukrainian shield.

Evidence has been obtained that K, Rb, Ba, Cu, Si, Pb were leached and removed and, respectively, Na, Ca, Mg, P (?), Ga, Y (?), Th, U were introduced and precipitated at the main stage of hydrothermal-metasomatic formation of Precambrian apogranite alkaline sodium metasomatites from the crust currently occupied by albitites. During the final (ore) stage of hydrothermal-metasomatic formation of metasomatites U, Th, Ti, Nb, Ca, Fe, Y, Mg, Mn, Ga, Rb, Ba were brought and deposited into the volume of the crust occupied by ore albitites. It was reconstructed that the main masses of these chemical elements were deposited in cavities of various origin. The results of the determination of the content (w), in particular, of Nb were verified by the ISP-MS method in the laboratory of the University of Tallinn (Estonia). In addition, it was found that the anomalous values of *w* (Nb) are not accompanied by the corresponding Ta anomalies. It should be noted that a systematic study of the distribution of Nb in the specific intersection of ore-bearing albitites of the Central Ukrainian region was performed for the first time.

To confirm the previous conclusion (Mihalchenko et al., 2015, 2016) on the reconstruction of the introduction and deposition of Nb and Ti during the formation of thorium-uranium albitites of the Novooleksiyiv ore manifestation a study of the distributions of these chemical elements in other sections of the body of ore-bearing albitites was performed. The determination of Nb concentrator minerals was also performed. Core material of two sections of the metasomatic body of thorium-uranic albitites (wells No. 10, No. 11) was provided for investigation by the Geological Service of Expedition No. 46 of Enterprise "Kirovgeology" (GSE No.46 of EK).

Method. The sequence of work: the finding of Nb mineral-concentrators in the cross-section of albitites; documentation of well cores; radiometric core measurements, sampling (GSE No.46 of EK); study of the chemical composition of albitites; assessment of the bonding power of chemical elements. Content of the main petrogenic components and trace elements in the three cross sections of the albitites, which are at different gypsometric levels of one body, was investigated in the laboratory of the scientific-educational institute "Institute of Geology" of Taras Shevchenko National University of Kyiv. The mass fraction (W) of the major petrogenic components was measured by X-ray fluorescence analysis on a “CPM-25” multichannel spectrometer, and trace elements by an energy dispersive X-ray spectrometer “CEP-01”. The chemical composition of minerals and the microstructural features of the rocks were investigated using a scanning electron microscope “PEMMA-202” with an energy dispersive X-ray spectrometer “Link Systems”. The power of the Ti and Nb statistical relationship was investigated using one of the non parametric correlation analysis methods, the Spearman rank correlation coefficient ($\boldsymbol{r_s}$). The verification of the estimation of the statistical relationship power is performed by calculating the Pearson correlation coefficient ($\boldsymbol{r}$) by the values of the coefficients $\mathbf{b_1}$ and $\mathbf{b_2}$ of the linear regression equations Nb on Ti and Ti on Nb. The constants and coefficients of the regression equations are calculated by the Legendre and Gauss method.

Results of investigation. The non-metallic and ore albitites, which were crossed by borehole 12, differ color, radioactivity, in structural and textural features: in the former, the relics of medium-coarse-grained structure and porphyry texture of granites of the Novoukrainsk massif are well identified; in the second - breccia structure. One of the features that distinguish these varieties of albitites is the size and volume fraction of crystals and splices of titanite. In non-metallic albitites, these are mainly small, rarely medium-sized titanite crystals. In ore albitites, the gray-white coarse crystals and germs (up to 1 cm) of titanite differ well against the gray-brown ore of albitite. The same peculiarity in the distribution and morphology of titanite is characteristic of the other two sections of ore albitites of wells №№ 10, 11. We pay special attention to the fact that in the original granites of the Novoukrainsk massif there is no titanite, it is a mineral formed in the processes of pneumatolitho-hydrothermal transformations of rocks. In addition to titanite, we found one small crystal of rutile and one small crystal of manganese ilmenite in the albitites.

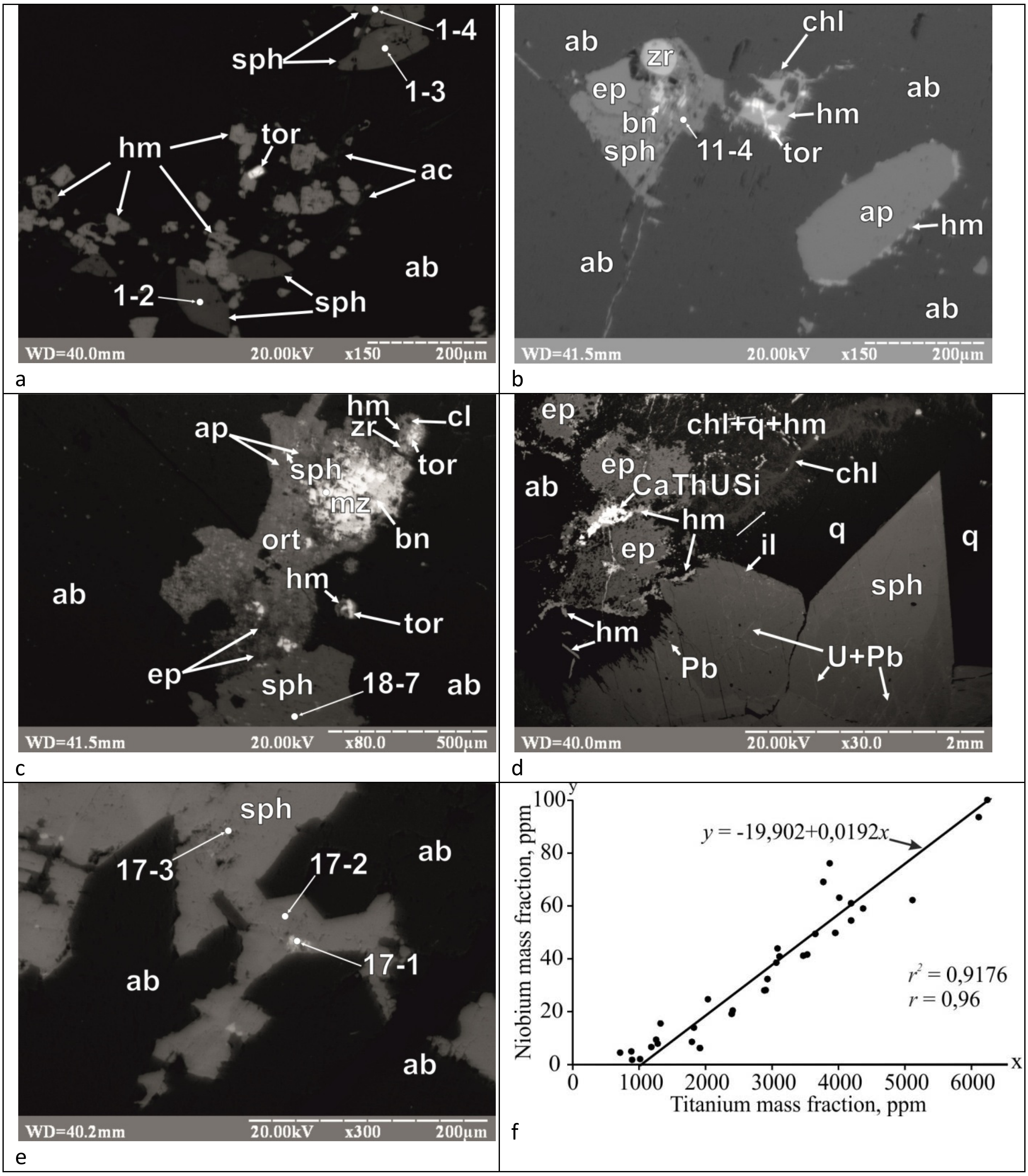

***Figure 1**. **a-e** are titanites in thorium-uranium-bearing albitites of the cross-section of the borehole 12 of the Novooleksiivka ore occurrence: **a** - cross sections of crystals of titanite in actinolite albitite; **b** - titanite growth with epidote, zircon and monazite residues with bastnesite; **c** - titanite, along with the remains of a large crystal of monazite, which decomposed into basnesite, torite, apatite, replaced by an epidote and orthite; **d** - fine manganese ilmenite in a large titanite crystal; **e** is the fine-phase growth of titanite crystals enriched in niobium and rare earth elements. The dots indicate the locations of measurements of the chemical composition of the minerals, the numerical designation is the number of the analysis.*
*Abbreviations of mineral names: ac - actinolite, ab - albite, ap - apatite, cl - chlorite, ep - epidote; sph - titanite, zr - zircon, tor - torite, hm - hematite, Ca-Th-U-Si - calcium-thorium-uranium silicate, il - manganese ilmenite, bn - basnesite. **f** is a correlation diagram of titanium and niobium content in the samples from the cross sections of the albitites of wells 10, 11, 12. y = -19.902 + 0.0192x - direct regression equation of titanium content on niobium content, r^2 - estimation of titanium and niobium coefficient of determination, r - estimation of pair Pearson correlation coefficient of titanium to niobium.*

According to the results of electron microscopic studies of the thin sections, we found an admixture of Nb in the chemical composition of the crystals of titanite of both ore and non-metallic albite , also there are crystals with *w*(Nb) less than the detection limit of the device (0.10%). The following is the chemical composition of titanites (wt.%). Fig. 1-a analysis 1-2: Nb_2O_5 0.77, P_2O_5 0.56, SiO_2 25.58, TiO_2 42.93, CaO 28.91, FeO 1.25; analysis 1-3: Nb_2O_5 0.59, P_2O_5 1.09, SiO_2 26.00, TiO_2 42.06, Al_2O_3 0.33, CaO 28.79, FeO 0.77, NaO 0.36; analysis 1-4: Nb_2O_5 0.16, P_2O_5 0.67, SiO_2 25.93, TiO_2 43.47, Al_2O_3 0.40, CaO 27.71, MgO 0.16, FeO 0.63, NaO 0.86. Fig. 1-b analysis 11-4: Nb_2O_5 0.18, P_2O_5 <0.10, SiO_2 26.03, TiO_2 42.43, ZrO_2 1.87, Al_2O_3 <0.10, CaO 28.22, MgO <0.10, FeO 1.26. Fig. 1-c analysis 18-7: Nb_2O_5 0.41, P_2O_5 <0.10, SiO_2 25.91, TiO_2 41.56, ZrO_2 2.27, Al_2O_3 <0.10, CaO 29.19, MgO <0.10, FeO 0.66. Figure 1-e analysis 17-2: Nb_2O_5 0.73, P_2O_5 <0.10, SiO_2 24.90, TiO_2 43.33, ZrO_2 0.73, Al_2O_3 0.80, La_2O_3 1.36, CaO 26.20, MgO <0.10, FeO 1.95. The large titanite growth (see Fig. 1-e) revealed a phase enriched in Nb and REE, analysis 17-3: Nb_2O_5 1.55, P_2O_5 <0.10, SiO_2 22.93, TiO_2 36.46, ZrO_2 0.86, Al_2O_3 0.90, La_2O_3 5.69. Ce_2O_3 7.35, Nd_2O_3 2.78, CaO 19.70, MgO <0.10, FeO 1.78. In other minerals, the content of *w*(Nb) is less than the detection limit of the instrument.

The content of Ti and Nb in the three sections of the albitites of the Novooleksiivka ore occurrence is given in tab. (for borehole 12, these data were published previously (Mihalchenko et al., 2015, 2016). Abnormal values of the content of these chemical elements were detected for all three cross sections studied, and estimates of arithmetic mean *w* (see tab.) were significantly higher than estimation of the geochemical background of these elements in the Novoukrainsk granites, which is evidence that during the processes of pneumotholite-hydrothermal formation of rock, additional masses of titanium and niobium were brought and deposited in the volume of the crust which now occupied by the thorium-uranium-bearing albitites ore occurrence.

The estimate of $\boldsymbol{r_s}$ Ti and Nb is 0.96 (see tab.), which is confirmed by the estimate of *r* Ti and Nb - 0.96 (see Fig.1-f). According to the Cheddock scale, the statistical relationship of these elements in albitites is estimated to be high. The estimate of r^2 Ti and Nb is 0.91 (see Fig.1-f) - the specific gravity of the variation is explained by the strong influence of the factor trait in the overall variation of the result trait. Respectively the factors that influenced the deposition of these elements were common, and led to the concentration of added mass Nb in titanite.

As part of the albitites of ore occurrence, we did not find brannerite, a mineral common in the albitites of the Kirovograd metallogenic zone (ore area) (Belevtsev et al, 1995). It is likely that the formation of titanite and thorium-uranium minerals occurred not at the same time and under different physical and chemical conditions.

Table. The results of the calculations of the estimates of the arithmetic mean values of measurements of mass particles ($\overline{w}$), the critical value of the correlation coefficient at the significance level of 0.05 ($\boldsymbol{r_{кр0,05}}$), the estimation of the Spearman rank correlation coefficient ($\boldsymbol{r_s}$) of sampling values of the mass parts of titanium dioxide (TiO_2, %) and niobium (Nb, ppm) in samples of three albite cross sections of the Novooleksiivka ore occurrence.

№	Bore-hole	$w(TiO_2)$, %	w(Nb), ppm	R_{Ti}	R_{Nb}	R_{Ti}-R_{Nb}	$(R_{Ti}-R_{Nb})^2$	№ з/п	Bore-hole	$w(TiO_2)$, %	w(Nb), ppm	R_{Ti}	R_{Nb}	R_{Ti}-R_{Nb}	$(R_{Ti}-R_{Nb})^2$
1	10	0.70	60.9	37.5	35.5	2.0	4.00	25	11	0.70	54.4	37.5	32.5	5.0	25.00
2	10	0.63	69.0	30.5	39.5	-9.0	81.00	26	11	0.61	49.3	28.5	28.5	0.0	0.00
3	10	0.52	40.8	23.5	22.5	1.0	1.00	27	11	0.58	41.1	25.5	24.5	1.0	1.00
4	10	0.66	49.7	33.5	30.5	3.0	9.00	28	11	0.32	6.1	11.5	5.5	6.0	36.00
5	10	0.70	54.4	37.5	32.5	5.0	25.00	29	11	0.40	19.1	14.5	13.5	1.0	1.00
6	10	0.61	49.3	28.5	28.5	0.0	0.00	30	11	0.49	32.2	19.5	19.5	0.0	0.00
7	10	0.58	41.1	25.5	24.5	1.0	1.00	31	12	0.31	13.9	10.0	11.0	-1.0	1.00
8	10	0.32	6.1	11.5	5.5	6.0	36.00	32	12	0.21	7.8	7.0	8.0	-1.0	1.00
9	10	0.40	19.1	14.5	13.5	1.0	1.00	33	12	0.15	4.8	2.0	4.0	-2.0	4.00
10	10	0.49	32.2	19.5	19.5	0.0	0.00	34	12	0.52	43.8	22.0	27.0	-5.0	25.00
11	11	0.21	9.3	6.0	10.0	-4.0	16.00	35	12	0.65	76.1	32.0	41.0	-9.0	81.00
12	11	0.15	1.7	3.0	1.0	2.0	4.00	36	12	1.04	100.0	43.0	43.0	0.0	0.00

13	11	0.17	2.0	4.0	2.0	2.0	4.00	37	12	1.17	136.4	44.0	44.0	0.0	0.00
14	11	0.30	8.5	9.0	9.0	0.0	0.00	38	12	0.85	62.1	41.0	37.0	4.0	16.00
15	11	0.59	41.5	27.0	26.0	1.0	1.00	39	12	0.48	27.9	17.0	17.0	0.0	0.00
16	11	0.34	24.6	13.0	16.0	-3.0	9.00	40	12	0.20	6.5	5.0	7.0	-2.0	4.00
17	11	0.12	4.4	1.0	3.0	-2.0	4.00	41	12	0.40	20.3	16.0	15.0	1.0	1.00
18	11	0.73	58.9	40.0	34.0	6.0	36.00	42	12	0.49	28.1	18.0	18.0	0.0	0.00
19	11	0.67	63.0	35.0	38.0	-3.0	9.00	43	12	0.51	38.4	21.0	21.0	0.0	0.00
20	11	1.02	93.5	42.0	42.0	0.0	0.00	44	12	0.22	15.4	8.0	12.0	-4.0	16.00
21	11	0.70	60.9	37.5	35.5	2.0	4.00	$\sum$	-	22.718	1734.04	-	-	-	548.00
22	11	0.63	69.0	30.5	39.5	-9.0	81.00	$\overline{w}$	-	0.52	39.4	-	-	-	-
23	11	0.52	40.8	23.5	22.5	1.0	1.00	r_s	-	-	-	-	-	-	0.96
24	11	0.66	49.7	33.5	30.5	3.0	9.00	$r_{кр}$	-	-	-	-	-	-	0.25

* **Note**. R_{Ti}, R_{Nb} - rank values of measurements w(TiO_2) and w(Nb)

Conclusions.

1. The presence of titanium and niobium anomalies is characteristic for the three investigated sections of thorium-uranium albitites of the actinolite-diopside group of the facies of the cut of alkaline sodium metasomatites of the Novooleksiivka ore occurrence.
2. The correlation of titanium and niobium content in albitites is very high - the Spearman rank correlation coefficient estimate is 0.96, which is a consequence of the concentration of these chemical elements in one (total) minerals.
3. Titanite is the main concentrator of both titanium and niobium in albitites. No brannerite, a characteristic mineral of the uranium ore albitites of the Kirovohrad metallogenic zone, was found in the albitites of the Novooleksiivka ore occurrence.
4. In the processes of pneumatolitho-hydrothermal formation, additional masses of titanium and niobium were brought and deposited in the volume of the earth's crust, which is now occupied by the thorium-uranium albitites of the Novooleksiivka ore occurrence. Titanium and niobium are paragenetic chemical elements in the thorium-uranium albitites of the Novooleksiivka ore occurrence.

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