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U-Ti MINERALS AT THE DEPOSIT NOVOVESKÁ HUTA (SLOVENSKÉ RUDOHORIE MTS.)

(Tab. 1, Figs. 6)



Abstract: Brannerite is together with pitchblende the mostly widespread mineral of uranium mineralization near Novoveská Huta. It is most often in mineralized rocks dispersed in close paragenesis with apatite. The chemical composition of brannerite on X-ray microanalyzer shows contents of TiO $_2$ 36–44 and UO $_2$ 47–53 specific gravity per cent. The average microhardness of analysed brannerites is 5266 MPa.

Резюме: Браннерит вместе с уранитом является самым распространенным минералом урановой минерализации у Нововеской Гути. Чаще всего он рассеянный в орудененных горных породах в тесном парагенезисе с апатитом. Химический состав браннерита на рентгеновском микроанализаторе дает отчет о содержании ${\rm TiO_2}$ 36—44 и ${\rm UO_2}$ 47—53 весовых процентов. Средняя микротвердость анализированных браннеритов 5266 MPa.

At the deposit of Novoveská Huta a more important uranium ore mineralization occurs in Permian rocks in two layers (I. Rojkovič - L. Novotný, 1981). The rocks of the upper, earlier known ore layer, is formed by psephite and psammite rocks with admixture of volcanoclastic material of rhyolite volcanism occurring in their close substratum (I. Rojkovič, 1968). The ore mineralization is represented mainly by pitchblende and molybdenite, accompanying chalcopyrite, pyrite, U-Ti minerals and galena. The mineralized rocks of the lower ore layer (150-200 m in the substratum of the upper) form highly altered rocks, which are of the character of quartzsericite schists. According to J. Gregorovič (1981) the original rocks are volcanics of intermediate character (dacites). The occurrence of abundant Fe-Ti oxides (magnetite, ilmenite and haematite) with structures of disintegration of solid solution in slightly altered andesites and dacites reflects their high-temperature magmatic origin. Fe-Ti oxides are often replaced by rutile (Fig. 1). Fragments of these rocks occur rarely in the upper ore layer. In mineralized altered rocks of the second ore layer the ore mineralization is represented by U-Ti minerals, apatite and pitchblende, accompanied by carbonates, tourmaline, pyrite, chalcopyrite and galena. Characteristic are higher concentrations of apatite, mainly in the upper parts of the lower ore layer in the central and eastern part of the deposit (I. Rojkôvič, 1981). The ore mineralization is polygenetic. During the Permian accumulation of ore mineralization by exogenic processes and post-volcanic hydrothermal activity was taking place. Further remobilization and concentration of ore mineralization took place during the Alpine orogenesis (I. Rojkovič - L. Novotný, 1981).

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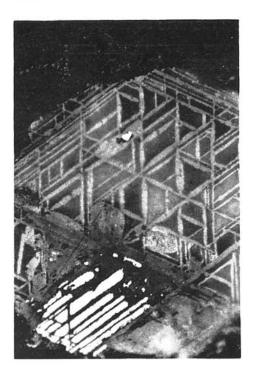


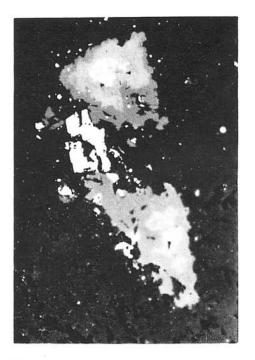
Fig. 1. Lattice structure of rutile (grey), which originated by replacement of ilmenite, is replaced by pyrite (white). Unmixing of ilmenite in the original magnetite took place in consequence of desintegration of solid solution. Sample UH 839/127, reflected light, magnification 1200 × in immersion oil.

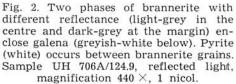
U-Ti minerals were established first at the deposit by V. I. Žukov (1976) and documented by qualitative analysis on the X-ray microanalyzer. In the Slovenské rudohorie Mts. the first to describe brannerite was C. Varček (1977) in association with pitchblende and gold in quartz veins and stockwork zones of the Gelnica group of the eastern part of the Slovenské rudohorie Mts. Here it forms columnar crystals and to various extent is secondary--altered into inhomogeneous leucoxene product (C. Varček, l. c.). The average chemical composition (C. Varček, l. c.) is U 42.48, Ti 20.82, Fe 0.76,

Ca 1.18, Si 0.27 and O 34.48 of specific gravity per cent. O is calculated completely and its increase in comparison with reality C. Varček (l. c.) explains in a way that it includes also weaker admixed components. After recalculation to oxides the above mentioned analysis is as follows: UO_2 48.19, $(UO_3$ 51.05), TiO_2 34.73, FeO 0.98, $(Fe_2O_3$ 1.09), CaO 1.65, SiO_2 0.58 with sum 86.13 (89.10) specific gravity per cent.

Brannerite (U, Ca, Th, Y) (Ti, Fe) $_2$ O $_6$ was established in the studied samples from both ore layers. In reflected light it has a lower reflectance than rutile. Mostly it forms allotriomorphic, 0.01-0.1 mm grains (Fig. 2), even colloform stratified structures. Idiomorphic grains are more rare, of columnar form and mostly not exceeding 0.005-0.01 mm (Fig. 3). Allotriomorphic, also idiomorphic grains are isotropic under microscope in consequence of metamictization and relatively often inner reflexes of brown or yellowishbrown colour are observed in them. Similarly as rutile, it appears also in hexagonal, tetragonal and trapezoid up to 0.1 mm sections, which mostly represent polymineral aggregates and they are obviously pseudomorphs after original magnetite and ilmenite. Irregular grains sometimes concentrate into clusters bands and veins. Hems and irregular formations with lower reflectance, which are an evident alteration product of the lighter phase, are observed in them (Fig. 2).

From the description of brannerite it is obvious that the allotriomorphic types correspond to "brannerite B" of K. G. Korolev et al. (1979). Most often it occurs in close association with rutile, which it replaces along the borders bet-





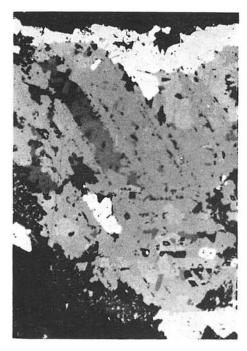
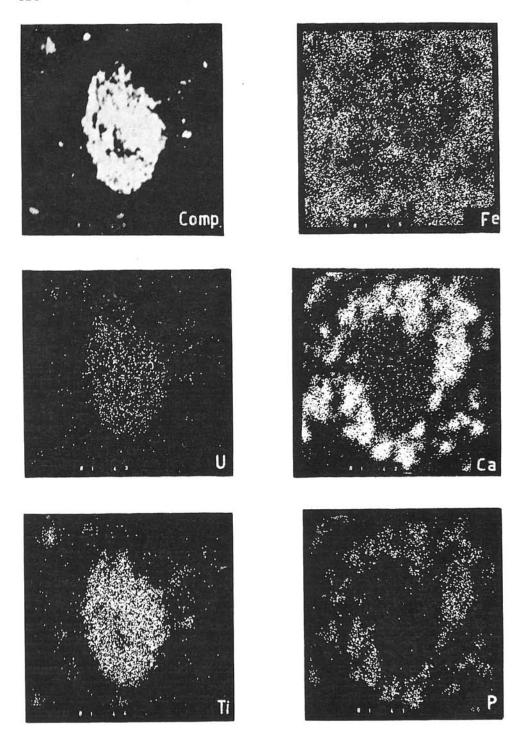


Fig. 3. Cut of rutile aggregate with hexagonal delimitation (light-grey), in which only indications of lattice structure are observed, along this it is replaced by crystalline brannerite (dark-grey). Metacrysts of brannerite are also dispersed. The whole aggregate of rutile is fringed and replaced by pyrite (white). Sample UH 27/135, reflected light, magnification 660×1 nicol.

ween grains, or fills up lattice structures of rutile and forms metacrysts in them. Rutile is often closed in it as small relict grains. U-Ti minerals from often also hems around rutile or leucoxene, sometimes together with pyrite. Pyrite forms very often fringes around aggregates of rutile and sometimes also around rutile-brannerite aggregates. More often, however enclosing or intergrowing of sulphide grains in brannerite and other U-Ti minerals can be observed. Enclosures of pyrite, galena and chalcopyrite were established. The enclosures of galena, mainly in darker phase at the rim of aggregates, are of spherical shape with a diameter about 0.001 mm. In the lower ore layer it is found very often mainly in samples rich in apatite. The grains of brannerite, sometimes also their fringes in apatite, are dispersed, even enclosed in apatite aggregates. Apatite is in rocks of the upper ore layer accessory but in proximity of brannerite its accumulation and fringing of brannerite with apatite is observed (Fig. 4).

The chemical composition of brannerite was confirmed by X-ray microanaly-zer MS-46 of the Cameca firma. The voltage kV was used. Natural uraninit



at U and Ca, rutile at Ti, quartz at Si and metallic Fe at Fe were applied as standards. The quantitative analyses was recalculated with corrections to the atomic number, absorption, fluorescence and dead time. From the analysis results that the content of TiO2 fluctuates within the range 36-44 and UO2 44-53 specific gravity per cent (Tab. 1). The mutual ratio of UO₂/TiO₂ shows a relatively wide variability from 1.08 to 1.48. The sum of all analysed components is highest (98.4 specific gravity per cent) in the crystalline variety. In other samples the sum varies from 91.0 to 95.7 per cent. When we also admit that the whole Fe is in form of Fe₂O₃ and U as UO₃, the sum varies from 93.8 to 99.0 specific gravity per cent. When analysing, evaporation of the material is observed. A volatile component is obviously water, which the X-ray microanalyzer cannot analyse. K. G. Korolev et al. (1979) mention in brannerite B, analysed chemically, 6.02-7.35 specific gravity per cent of water (p. 45) and the low sums (up to 93.3 specific gravity per cent) of analysis on the X-ray microanalyzer they substantiate by the content of water (p. 50). In the products of brannerite alteration represented by the darker phase, mainly at the rim of grains and aggregates, an increase of Si (Ca) content and on the contrary, sinking U and Fe may be observed.

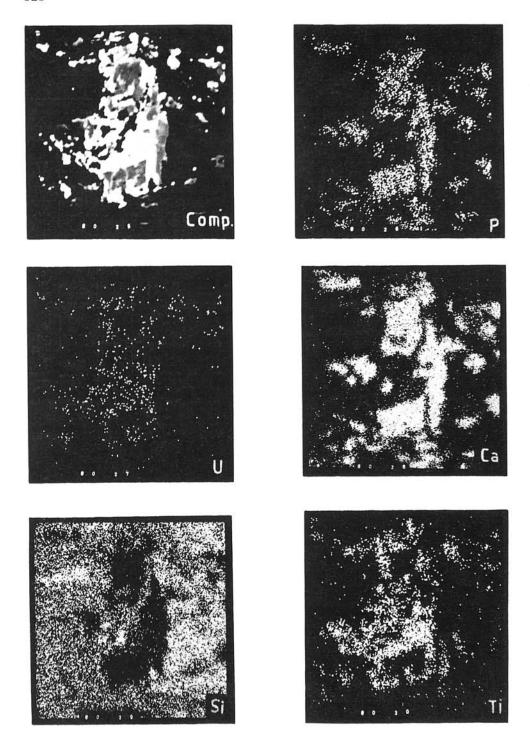
As a consequence of matemictization of brannerite it is not possible to determine its structure without heating. Under the electron microscope in no one phase crystalline shapes were found and the microdiffraction testified the amorphous character of both phases.

The average microhardness of the measured brannerites is 537 kp/mm², or 5266 MPa. The measured values show a relatively wide variability, equally as chemical composition. They are varying from 297 to 843 kp/mm² or from 2912 to 8270 MPa, exceeding the lower boundary 387–907 kp/mm², mentioned by W. Uytenbogaardt—E. A. J. Burke (1971), K. G. Korolev et al. (1979) mention for brannerite B the microhardness of 387 kp/mm². The darker phases in the measured samples have by 3 to 6 $^{0}/_{0}$ lower values of microhardness than the light phases only.

Brannerite B of colloform type was established by J. D. Gotman et al. (1968, 1971) at medium low-temperature hydrothermal deposits associated with metasomatites with composition pyrite-carbonate- potassium feldspar. In the last time numerous geological finds of brannerite concentrations in various also low-temperature mineral associations were observed and experimental data have shown that there exist varieties of uranium titamates, which are formed at temperatures lower than 200 °C. This confirms the possibility of uranium titanates formation in a wider range of geological conditions. K. G. Korolev et al. (1979) clear up the concentrations of brannerite B mostly as hydrothermal-metasomatic, linked with K or Na metasomatism.

R. B. Finkelman - H. Klemic (1976) supose in brannerite from Penn Haven Junction from uranium-bearing sandstones, close to the Colorado Plateau type, besides a detrital origin also its formation by impregnation of original porous leucoxene by uranium from solution and alteration by uranium-

Fig. 4. Composition (comp.) and areal distribution of Fe, Ti, Ca, U and P in brannerite fringed with apatite shown by X-ray microanalyzer. Sample UH 5256, magnif. $300 \times$.



-saturated with leucoxene into brannerite during following metamorphism. The origin of uranium titanates by the action of uranium-bearing solutions on titanium minerals is also supposed by L. V. Grigorjev et al. (1976) and N. A. Kulik et al. (1975). According to S. S. Adams et al. (1974), R. L. Reynolds — M. B. Goldhaber (1978), P. Ramdohr (1979) and N. J. Theis—1979) brannerite (or uranium titanates of variable composition) found in association with Ti or Fe-Ti oxides is not clastic but originated during further geological processes, whether already under the influence of groundwater or hydrothermal solutions. According to N. J. Theiss (1979) the presence of phase rich in uranium at the margin of granular aggregates rather testifies to absorption than to leaching.

Besides brannerite, U-Ti minerals were established distinguishing of which was possible by X-ray microanalyzer only.

U-Ti mineral $-X_1$. The optical properties of the mineral are similar as in brannerite (lighter phase), thus it is isotropic with abundant inner reflexes of yellowish-brown colour with reflectance close to the light phase of brannerite. It forms up to 0.05 mm irregularly bordered grains, dispersed in the rock. It is found in close paragenesis with apatite, intergrowing and replacing it (Fig. 5). The chemical composition of U-Ti mineral X_1 shows an essentially higher content of TiO_2 to the detriment of UO_2 and the ratio of $UO_2(TiO_2)$ in comparison with brannerite decreased to 0.43.

U-Ti mineral $-X_2(?)$ is probably a mixture of uranium, titanium minerals and quartz. Its reflectance is lower than at U-Ti minerals mentioned before. The heterogeneity of the material and unevenness of the surface hinder to obtain a reliable quantitative analysis on the X-ray microanalyzer. From the illustration of the composition and areal distribution of elements is, however, clear that uranium concentrates in the fringe around rutile, which encloses galena, chalcopyrite and pyrite (Fig. 6). It is probable, that there is an aggregate of brannerite with other Ti and Si minerals.

On the basis of the mentioned photographic and analytic documentation it results that at the locality Novoveská Huta an abundant uranium mineral of ore layers is brannerite (brannerite B in the sense of K. H. Korolev et al. l. c.). Its occurrence indicates that it is not an allothigenic mineral but a product of the action of uranium-bearing solutions on titanium oxides.

Translated by J. Pevný

Fig. 5. Composition (comp.) and areal distribution of P, U, Ca, Si and Ti U-Ti mineral- X_1 (white in the centre in the illustration of the composition) enclosing and replacing apatite (grey) surrounded by silicate minerals (black). Sample UH 706/355.3, magnification 300 \times .

Table 1 Chemical composition of brannerite and U-Ti mineral- \mathbf{X}_{I} (specific gravity per cents)

No of sam- ple UH	27/135		291		706A/124.9	706A/124.9 839 127		5256		706 355.3	No of sam- ple UH		27 135	291	706/125.2	706A 124.9	839/127		5256		706 355.3
pol.	ଟା	ଚୀ	1	1	H		1	-	1	61	pol.	2	61	-	-	1	н	1	1	1	6
min.	bra	bra	bra	bra	bra	bra	bra⁺	bra	bra'	UTi-X,	min.	bra	bra	bra	bra	bra	bra	bra ⁺	bra	bra	IITI X.
Si			0.7	1.3	1.9	1.4	2.4	9.0	1.5	3.3	SiO.			1.5	2.7	4.1	3.0	5.2	1.3	3.3	7.0
Ξ	24.8	23.5	22.6	26.1	21.6	22.8	23.2	22.4	21.9	34.1	TiO2	41.4	39.2	37.7	43.6	36.0	38.0	38.8	37.3	36.5	56.9
D	46.1	43.5	43.7	41.6	47.1	44.1	39.2	44.3	44.0	21.6	rou.	52.3	49.4	49.6	47.2	53.4	50.0	44.4	50.3	50.0	94.5
											(ΩO_3)	(55.4)	(52.3)	(52.5)	(20.0)	(26.5)	(23.0)	(47.1)	(53.2)	(52.9)	(26.0)
	2.2	1.1	2.5	6.0	1.3	1.2	0.8	2.9	2.0		FeO	2.8	1.4	3.2	1.2	1.7	1.6	1.0	3.7	2.5	1.8
Fe										1.4	(Fe ₂ O ₃)	(3.2)	(1.6)	(3.6)	(1.3)	(1.9)	(1.7)	(1.1)	(4.2)	(5.9)	(5.0)
Са	1.3	8.0	1.9	9.4	0.4	0.5	1.2	1.3	1.0	6.0	CaO	1.9	1.1	2.6	9.0	0.5	0.7	1.6	1.9	1.5	1.3
Sum	74.4	68.9	71.4	70.3	72.2	70.0	64	71.5	70.4	61.3	Sum	98.4	91.1	94.6	95.3	95.7	93.3	91.0	94.5	93.8	91.5
							64.4	ıc.			Sum	(101.9)	(94.2)	(6.79)	(98.2)	(0.66)	(96.4)	(93.8)	(67.6)	(97.1)	(93.2)
U Ti	1.86	1.85	1.93	1.59	2.18	1.93	1.69	1.98	2.01	0.63	UO ₂ /TiO ₂	1.26	1.26	1.32	1.08	1.48	1.32	1.15	1.35	1.37	0.43

Explanations: pol.-layer: min.-mineral; bra-brannerite; UTi-X₁ – UTi mineral-X₁; + – darker phase; (..) – sum with UO₂ and Fe₂O₃

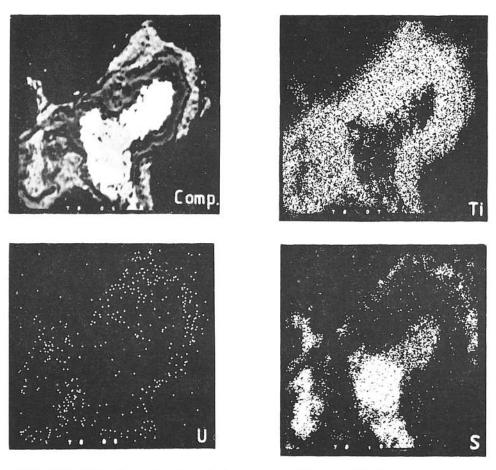


Fig. 6. Composition (comp.) and areal distribution of Ti, U and S. Rutile (dark-grey in illustration of the composition) enclosing galena, chalcopyrite and pyrite (white) is bordered by U-Ti mineral- X_2 (light-grey). Sample UH 706/125.2, magnification 300 \times .

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