

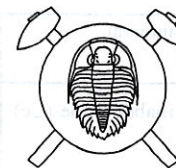
Rhabdophane group minerals in the uranium ore district of northern Bohemia (Czech Republic)

Minerály skupiny rhabdofanu v oblasti uranových ložisek v severočeské křídě (Czech summary)

(2 text-figs., 6 plates)

MARTA SCHARMOVÁ - BOHDAN SCHARM

Diamo s. p., 471 27 Stráž pod Ralskem



Four mineral species of the rhabdophane group, namely: ningyoite, brockite, rhabdophane-(Ce), and rhabdophane-(Nd) are found in the sandstone type uranium ore district in the Bohemian Cretaceous Basin. Electron microanalyses indicate the existence of a continuous isomorphic series between ningyoite and brockite which is manifested by the unlimited mutual substitution of U and Th. However, there are pronounced differences in the habit and dimensions of the Th-bearing members on the one hand and the Th-free member ("pure" ningyoite) on the other. Rhabdophanes are characterized by a wide range of REEs proportions. The occurrence of rhabdophane-(Nd), unusual La-free rhabdophane-(Ce) together with the earlier discovered phosphates, arsenates, and fluorocarbonates with Nd- and La-dominated composition indicate a distinctive fractionation of rare earth elements during exogenic processes.

Introduction

Economic uranium concentrations in northern Bohemia occur within sedimentary rocks of Upper Cretaceous age belonging to platform units of the Bohemian Massif (the so-called Bohemian Cretaceous Basin). All uranium concentrations have been classified as uranium deposits of the peneconcordant sandstone type, but with an unusual association of the elements: U-Zr-P-Ti (Čadek et al. 1975). Although it would be possible to consider the uranium concentrations occurring in the above mentioned ore district as a single major deposit, for practical reasons several sections, for example Hamr, Stráž, Břevniště, Holičky, Hvězdov, Osečná - Kotel, are being distinguished as independent "deposits".

The ore district is remarkable by the occurrence of the unique mineral assemblage. One of the striking features of this ore district is the occurrence of the rhabdophane group phosphates. The general formula for these phosphates may be written as $AXO_4 \cdot 1-2 H_2O$, where A = Ca, REE, Th, U, Fe^{3+} , and X = P, (S). It has been proposed by several authorities that also fluorine (Dorfman et al. 1993) as well as (PO_3OH) -ions (Dojnikova et al. 1993) and $(CO)_3$ -ions (Fisher - Meyrowitz 1962) may enter as minor constituents in the structure of these minerals. Dojnikova et al. (1993) put forward the idea about the possibility of the extended or even complete miscibility between the cations Ca, REE, U, and Th in this mineral group.

In general, hexagonal symmetry and the space group $P6_22$ are assumed for these phosphates. An exception represents only ningyoite whose structure is not known till now. An actual compilation of the natural phases of the rhabdophane group is given in Table 1.

The other phosphates which according to some sources (Fleischer - Mandarino 1991) belong to this

mineral group, *i.e.* tristramite, smirnovskite, and grayite, represent problematic mineral species. Tristramite, described by Atkin et al. (1983) from old dumps of the Trewevas mine (Cornwall, U. K.), seems to be actually ningyoite. Belova et al. (1987) re-evaluated data of this mineral given by Atkin et al. and came to the conclusion that some optical properties of this phosphate might be influenced by oxidation processes of the original ningyoite in the surficial environment of dumps where it occurs. Similarly, new investigations of so-called smirnovskite carried out by Dojnikova et al. (1993) revealed that it is really an analogue of brockite. The third of the mentioned problematic species, grayite, unsufficiently described by Bowie (1957) from the former Southern Rhodesia, seems to be brockite, too (see Dojnikova et al. 1993).

In the Cenomanian sedimentary rocks of the uranium ore district of northern Bohemia, the following unique association of the rhabdophane group phosphates have been identified: ningyoite, brockite, rhabdophane-(Ce), and rhabdophane-(Nd).

Since the original discovery of ningyoite in the Ningyo-Toge mine, Japan (Muto et al. 1959), the mineral has also been reported from the former U.S.S.R. (Belova et al. 1978a, b), Canada (Boyle et al. 1981), and Bulgaria (Belova et al. 1986). A compilation of selected data referring to ningyoite is listed in Table 2. According to Belova et al. (1985) uranium is predominantly pentavalent in this mineral.

In addition to the above-mentioned uranium ore district of northern Bohemia, in the Czech Republic this phosphate has also been discovered in the Horní Slavkov-, Jáchymov-, and Rožná-deposits (Dymkov et al. 1986). It occurs also in Miocene sediments at the locality Kocourek in the Otovice part of the Sokolov-basin (Litochlebová et al., unpublished report).

The aim of this paper is to give a short character-

mineral	formula	symmetry space group	cell dimen- sions [Å]	source
rhabdophane-(Ce)	(Ce,...)PO ₄ .H ₂ O	hexagonal P6 ₂ 22	a 6.98(3), c 6.39(3)	1
rhabdophane-(Nd)	(Nd,...)PO ₄ .H ₂ O	hexagonal P6 ₂ 22	a 6.96(3), c 6.372(6)	2,3
rhabdophane-(La)	(La,...)PO ₄ .H ₂ O	hexagonal P6 ₂ 22		4
ningyoite	Ca _{2-x} U _x [P(O,OH) ₄] ₂ .nH ₂ O	hexagonal P6 ₂ 22, P622 or P6mm	a 6.86(3), c 6.38(3)	5
brockite	(Ca,Th)PO ₄ .H ₂ O	hexagonal P6 ₂ 22	a 6.98, c 6.40	6
			a 7.03, c 6.40	5
	Ca _{2-x} Th _x [P(O,OH) ₄] ₂ .nH ₂ O			7

Table 1
Natural mineral phases of the rhabdophane group

1 - Muto et al. (1959), 2 - Bowles - Morgan (1984), 3 - Atkin et al. (1983), 4 - Fleischer - Mandarino (1991), 5 - Dojnikova et al. (1993), 6 - Fisher - Meyrowitz (1962), 7 - this paper

ization of the rhabdophane group phosphates occurring in northern Bohemia, namely: (1) to show the various forms of their occurrence, (2) to display the frequent chemical (micro)-inhomogeneity of ningyoite crystals, and (3) to demonstrate the existence of a continuous series between ningyoite and brockite and to show differences between Th-free and Th-bearing members of this series.

Rhabdophane group minerals in northern Bohemia

As already mentioned, *ningyoite*, *brockite*, *rhabdophane*-(Ce), and *rhabdophane*-(Nd) occur in the above-mentioned ore district.

Ningyoite and brockite

A short characterization of ningyoite and brockite, including X-ray powder data, has been presented by Scharm et al. (1980). As pointed out by Scharmová and Burda (1979, unpublished report) and Scharmová (1980), some electron probe analyses indicate that, in addition to ningyoite and brockite, also intermediate members between these phosphates probably occur in this ore district. Subsequent mineralogical studies carried out in the course of the years of 1980-1994 by Scharmová, Sulovský, Půlpán and Kundrát and presented in unpublished reports, brought additional evidence for the existence of a continuous series between ningyoite and brockite. Our studies revealed, however, that there are pronounced differences in the habit and dimensions of the Th-bearing members on the one hand and the Th-free member ("pure" ningyoite) on the other.

Ningyoite occurs as grain coatings, void fillings, and

accretionary masses in the sedimentary rocks of both the marine and freshwater Cenomanian (sandstones, siltstones, conglomerates, breccias) mainly in the deposits of Stráž, Holičky, Hvězdov, and - in a lesser extent - Hamr and Břevniště, too. It occurs closely associated with Fe-sulphides, hydrozircon, and other components of the cement. It was found also intimately intergrown with *vyacheslavite* (Scharmová et al. 1990). Various intimate intergrowths of ningyoite with pyrite belong to the striking features of this phosphate. Beside Cretaceous sediments, ningyoite has also been found in hematitized phyllitic rocks of the immediate basement of the Cenomanian in the Stráž deposit. This phosphate occurs here accompanied by rhabdophane-(Nd) and churchite-(Y) (Scharmová et al. 1993).

In Cretaceous sediments of northern Bohemia ningyoite is found in several forms, namely: (1) euhedral columnar crystals (10-50, exceptionally up to 100 micrometers in length) and their aggregates (Pls. I/1, II/1, III/1-3, V/1), (2) very fine needle- and spindle-shaped crystallites (usually up to 3-4 micrometers in length), sometimes forming asterisk-shaped aggregates (Pls. V/6, VI/1-2), (3) mineral bodies preserving indications of their gel-like nature (Pl. II/2), (4) rarely filling cells of macerals in coal substance (e.g. "sieve structure" of fusinite) (Pl. V/2), and (5) overgrowth rims on monazite grains (Pl. IV/5). While ningyoite of the types 1, 3, and 4 does not contain any admixtures of Th, variable amounts of Th may be present in the type 2 and 5 (up to the atomic proportions U : Th = 1 : 1).

A discrepancy appears between the clearly defined rhombohedral crystal faces as observed on some columnar ningyoite crystals (Pl. III/2) and the hexagonal symmetry of the mineral as assumed by Belova et al. (1985) and Dojnikova et al. (1993). It seems, that the trigonal symmetry is more probable.

Table 2

Ningyoite - summary of selected data from different sources

Sources: 1 - Muto et al. (1959), 2 - Belova et al. (1978a), 3 - Boyle et al. (1981), 4 - Belova et al. (1986), 5 - Belova et al. (1985, 1987), 6 - Dojnikova et al. (1993).

formula	symmetry	space group	unit cell dimensions [Å]		source
			X-ray	cl. diffr.	
$\text{Ca}_{1-x}\text{U}_{1-x}\text{TR}_{2x}(\text{PO}_4)_2 \cdot 1,5 \text{H}_2\text{O}$ $x \leq 1$	orthorhombic (primitive cell)	P222	a 6.78(3) b 12.10(5) c 6.38(3)		1
$\text{Ca}_{2-x}\text{U}_x(\text{PO}_4)_2 \cdot n \text{H}_2\text{O}$ $x \leq 1$	orthorhombic (C-centered cell)	Cmmm or C222, Cmm2, Cm2m		a 6.77 b 12.10 c 6.37	2
$\text{Ca}_{2-x}\text{U}_x(\text{PO}_4)_2 \cdot n \text{H}_2\text{O}$ $x \leq 1$	orthorhombic (C-centered cell)		a 6.75(1) b 12.00(1) c 6.38(1) V 516.78 Å ³		3
$\text{Ca}_{2-x}\text{U}_x[\text{P}(\text{O},\text{OH})_4]_2 \cdot n \text{H}_2\text{O}$ $x \leq 1$	orthorhombic (C-centered cell)	Cmmm or Cmm2, Cm2m, C222		a 6.76 b 12.00 c 6.37	4
$\text{Ca}_{2-x}\text{U}_x[\text{P}(\text{O},\text{OH})_4]_2 \cdot n \text{H}_2\text{O}$ $x \leq 1$	hexagonal	P6/m or P6mm, P6̄	a 6.87 c 6.40	a 6.86(3) c 6.38(3)	5
$\text{Ca}_{2-x}\text{U}_x[\text{P}(\text{O},\text{OH})_4]_2 \cdot n \text{H}_2\text{O}$ $x \leq 1$	hexagonal	P6 ₂ 22 or P622, P6mm	a 6.87 c 6.40	a 6.86 c 6.38	6

Brockite is mainly found finely dispersed in the cement of the freshwater and marine Cenomanian. It occurs only in trace amounts closely associated with other minerals of the cement, particularly with pyrite and hydrozircon. Till now, this phosphate has been discovered in a number of samples from the Stráž- and Hamr-deposits. Unlike Th-free ningyoite, the length of brockite crystals only rarely exceeds 10 micrometers. There are several commonly encountered forms of brockite, namely: (1) minute acicular crystals occurring individually or as small asterisk-shaped aggregates (Pls. V/6, VI/1, 2), (2) acicular crystals growing from a gel-like matter of the same composition (Pl. V/3), and (3) euhedral parallelly intergrown columnar crystals forming tubular aggregates. A colloform (papillary) matter, the composition of which is identical with the adjacent columnar brockite, fills usually the space inside these aggregates (Pl. V/4, 5).

Chemical composition

Although several tentative formulas of ningyoite appeared in some studies (see Table 2), no satisfactory analysis of this phosphate had been published till now. According to Muto et al. (1959), the X-ray data indicate the identity of the crystal structures of natural ningyoite, a synthetically prepared compound of the similar composition, and rhabdophane. This suggested that ningyoite had probably the formula close to $\text{CaU}(\text{PO}_4)_2 \cdot 2 \text{H}_2\text{O}$, in which the rare earth elements of rhabdophane were substituted by equivalent amount of calcium and quadrivalent uranium. The surplus of Ca

in the microchemical analysis is ascribed to apatite in the concentrate analysed. Later, Belova et al. (1978a) revealed that the predominance of calcium over uranium is not caused by heterogeneous admixtures but it represents a characteristic property of ningyoite.

Ningyoite and brockite from the ore district of northern Bohemia have been analysed using combined backscattered electron imagery (CamScan-4 DV) and electron-microprobe techniques (LINK AN 10 000) under the following conditions: accelerating voltage - 20 kV, standards: apatite (for Ca, P), UO_2 (U), FeS_2 (Fe, S), ThO_2 (Th). The analyses have been computed using the programme ZAF-4/FLS. In order to ascertain the presence of CO_3 -ions, selected polished sections have been studied by the analyser Microspec WDX-2A. Qualitative analyses showed considerable differences in the CO_3 -content and sometimes an admixture of fluorine in some ningyoite crystals, too.

Till now, many hundreds of EDX analyses of ningyoite and brockite from different parts of the ore district have been carried out. The common features of both ningyoite and brockite analyses may be summarized as follows: (1) nearly in all analyses Ca prevails over U (or U+Th), (2) most of the analyses exhibit deficiency of P as compared with the cations, (3) in addition to Ca, U (Th), and P also Fe and S appear usually in the EDX spectra (see below). Beside these common features concerning both ningyoite and brockite, the following specific properties have been observed in ningyoite: (1) there are two kinds of ningyoite, namely: (a) ningyoite without any admixture of Th, and (b) ningyoite containing variable amounts of Th, (2) most

Analyses	CaO	UO ₂	ThO ₂	P ₂ O ₅	Fe	S	Al ₂ O ₃	SiO ₂	TiO ₂	ZrO ₂	Σ
1	15.83	49.87	-	26.14	1.26	1.06	-	1.03	-	-	95.19
2	14.49	49.13	-	25.18	3.27	2.15	-	-	-	-	94.22
3	12.74	44.64	-	21.32	3.88	4.31	-	-	0.26	2.05	89.20
4	14.11	45.09	-	23.05	2.42	3.43	-	-	-	-	88.10
5	15.79	47.10	-	21.35	1.36	1.86	-	3.54	-	-	91.03
6	11.59	46.55	-	22.07	6.02	6.73	-	-	-	-	92.96
7	14.73	46.54	-	25.09	0.33	1.07	0.87	0.62	-	-	89.25
8	10.09	45.63	-	19.98	-	-	1.03	0.12	-	-	76.85
9	11.94	48.92	-	23.05	1.96	2.09	-	-	-	-	87.96
10	11.80	48.36	-	20.81	2.17	2.11	0.28	0.67	0.69	0.78	86.87
11	13.00	42.54	-	25.95	1.83	1.16	-	-	-	-	84.48
12	12.68	46.25	-	21.96	1.80	0.78	-	-	-	-	83.47
13	9.05	38.08	0.67	21.08	2.15	1.74	-	-	-	-	72.77
14	12.71	44.21	2.50	21.63	1.32	1.06	0.50	0.76	-	0.83	85.52
15	12.72	43.03	1.60	24.39	2.08	1.64	-	-	-	-	85.46
16	9.50	30.63	7.17	17.42	8.20	7.90	-	4.31	-	-	85.13
17	13.20	40.24	2.14	23.72	5.27	4.17	-	-	-	-	88.74
18	9.80	31.76	4.55	19.46	2.20	1.80	0.76	4.32	-	-	74.65
19	13.44	34.72	9.93	24.75	1.70	1.71	-	1.19	-	-	87.44
20	14.21	32.71	11.39	24.90	0.55	1.59	-	3.63	0.66	-	89.64
21	11.60	26.12	16.19	22.48	1.83	2.14	-	-	3.81	-	84.17
22	12.39	14.71	29.10	23.08	1.08	1.98	1.02	0.38	0.31	0.98	85.03
23	13.95	11.04	36.66	27.30	1.12	0.64	-	-	-	-	90.71
24	13.67	4.90	46.14	27.04	0.61	0.76	-	-	-	-	93.12
25	12.13	7.17	40.77	24.17	0.26	0.45	0.26	0.48	-	1.80	87.49
26	12.10	0.55	49.20	25.89	1.56	0.24	0.99	2.11	-	1.56	94.27

Table 3

Selected electron microanalyses (EDX) of the minerals of the ningyosite - brockite series

*Analyses - samples: 1 - 256 107/4; 2 - 272 105/7; 3 - 220 099/41731; 4 - 220 099/41744; 5 - 220 099/41745; 6 - 320 123/6; 7 - 240 099/6; 8 - 312 115/7; 9, 10 - 009 009/45484; 11 - 220 099/41761; 12 - 220 099/41753; 13 - 308 197/7; 14 - 300 181/11; 15 - 268 095/44293; 16 - 232 103/1; 17 - 268 095/44293; 18 - 224 103/4; 19 - 256 107/15; 20 - 240 091/6; 21 - 336 131/31; 22 - 336 131/10; 23 - 280 103/13; 24 - 308 197/19; 25, 26 - 3493/20565.

crystals of the Th-free ningyosite exhibit distinct chemical (micro-)inhomogeneity (see e.g. Pls. I/1, II/1, III/3-5, IV/1-3), (3) some ningyosite crystals exhibit partial or complete pseudomorphic replacement by pyrite or/and uranium oxide (Pls. II/1, III/3-5, IV/1-4). In brockite, the following features have been revealed: (1) a considerable compositional variation in the Th/U proportions (in comparison with the frequent occurrence of Th-free ningyosite, no U-free brockite has been found till now), (2) in comparison with (Th-free) ningyosite, brockite appears chemically more resistant (it does not exhibit any features of replacement by uranium oxides). The small size of brockite crystallites and Th-bearing ningyosite, too, usually does not allow to check their chemical homogeneity.

The (micro-)inhomogeneity of ningyosite is apparent from the differences in the mean atomic-number contrast in the backscattered electron image (BEI). It consists first of all in the presence of pyrite particles embedded in ningyosite crystals. Several forms of the incorporation of pyrite particles inside the ningyosite crystals could be attributed to the replacement of this phosphate by pyrite, often along growth zones of ningyosite. The chemical composition and backscattered images sometimes remind of different stages of the development of the particular type of pseudomorphs, called *shadow pseudomorphs* (see e.g. Česnokov 1974). It is the case, when inside a ningyosite crystal in BEI somewhat darker bodies appear in which concentration levels of Fe and S are higher than those in the surrounding ningyosite (see Pl. II/1). This appears to be

caused by the presence of densely disseminated FeS₂-particles inside the ningyosite matter. Some pseudomorphs of uranium oxides developed after earlier ningyosite remind of *shadow pseudomorphs*, too (Pl. IV/3). Elemental maps made by electron microanalysis revealed the identical distribution of (dominant) uranium and (minor) phosphorus and calcium.

Due to the very intimate intergrowth of both ningyosite and brockite with pyrite the analysed spot size often precluded analysis of only the phosphate. Consequently a problem arises, namely to determine precisely which parts of Fe and S in an analysis represent isomorphic admixtures in the phosphate and which parts of the same elements belong to Fe-sulphide. The analyses given in Table 3, therefore, were not recalculated and they are presented as measured. The differences in the totals are attributed to the uneven exposed surfaces because of their multiparticulate nature, to the void spaces in the aggregates, and to the influence of other mineral phases in the volumes analysed, as well.

The predominance of Ca over the sum of U+Th in ningyosite complies well with the formula of this phosphate as suggested by Belova et al. (1978a). According to Dojnikova et al. (1993) the charge difference caused by the variation in the Ca²⁺- and U⁴⁺- contents may be balanced by the presence of (PO₃OH)²⁻-ions. It seems that the Ca/Th variations in brockite are balanced by (PO₃OH)²⁻-ions, too.

Phosphorus deficiency and the related charge difference probably is balanced by the partial substitution of (PO₄)⁻-ions for (CO₃)⁻- or/and (SO₄)⁻-ions.

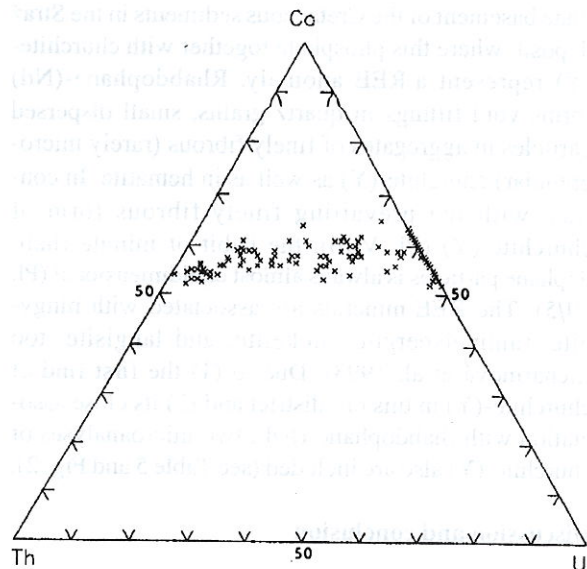


Fig. 1. Ca-U-Th-plot for members of the ningyuite-brockite series. The diagram demonstrates (1) distinct continuous field between the end-members of both the phosphates and (2) the predominance of Ca over U+Th

As shown in Fig. 1, the continuous mutual substitution of U and Th, revealed in many crystals, indicates the existence of a continuous series between ningyuite and brockite. The Ca-U-Th plot demonstrates a distinct uninterrupted field between the end-members of both the phosphates. The plot has been made using two hundred microanalyses carried out on samples from different parts of the ore district.

Some analyses showed that, beside dominant constituents of ningyuite and brockite, minor amounts of other elements as for example Zr, Si, Sr, Ba, Al, and REEs appear in analysed volumes. In the majority of cases they probably represent heterogeneous components immediately intergrown with ningyuite or brockite (hydrozircon, crandallite group minerals, kalinite, monazite, etc.).

Rhabdophane

Rhabdophane is a hexagonal hydrous phosphate with the ideal formula REE(PO₄) · H₂O. Dorfman et al. (1993) described a Ca-bearing variety of rhabdophane with tetravalent cerium of the composition Ca_{0.5}Ce⁴⁺_{0.5}(PO₄) · H₂O. According to Vlasov (1964) rhabdophane dehydrates at about 400 °C and changes to monazite. Nekrasova (1990) reports, however, that the transition of a synthetically prepared hydrated REE-phosphate, *i.e.* rhabdophane, to monazite does not necessitate higher temperature. She found that the change takes place under normal conditions in the course of several months.

With regard to the nomenclatoric system originally proposed by Levinson (1966) and later recommended for general usage by the I.M.A. Commission on New

Minerals and Mineral Names, two mineral species of rhabdophane may be distinguished according to the predominant rare earth element in the above-mentioned ore district, namely: (1) rhabdophane-(Ce) and (2) rhabdophane-(Nd). Beside these minerals, several small grains of a La-dominated REE-phosphate have been found in this ore district but it is not sure whether they represent rhabdophane-(La) or monazite-(La). The probably widespread occurrence of rhabdophane in the ore district could not be checked up due to the disseminated nature of the mineral and small size of its crystallites.

The same microanalytical techniques as in the cases of ningyuite and brockite have been used to identification of rhabdophane. The following standards were used for the REEs : LaB₆ (for La), CeAl₂ (Ce), PrF₃ (Pr), NdF₃ (Nd), SmF₃ (Sm), GdF₃ (Gd), metallic Tb, DyF₃ (Dy), HoF₃ (Ho), ErF₃ (Er), metallic Yb, YAG (Y). The microanalyses on apparently homogeneous areas of the mineral usually produced totals of about 94 wt %. The difference to 100 wt % corresponds well to 1 molecule of H₂O in the accordance with the formula of rhabdophane. Unfortunately, due to the lack of material, no X-ray studies could be done on rhabdophane.

Table 4
Electron microanalyses (EDX) of rhabdophane-(Ce)

	1	2		3	4
Ce ₂ O ₃	31.58	36.27	Ce ₂ O ₃	53.22	54.34
La ₂ O ₃	11.08	9.53	La ₂ O ₃	-	-
Pr ₂ O ₃	4.41	1.73	Pr ₂ O ₃	-	-
Nd ₂ O ₃	13.62	12.39	Nd ₂ O ₃	1.69	1.19
Gd ₂ O ₃	1.00	1.63	Sm ₂ O ₃	0.69	-
Dy ₂ O ₃	0.34	-	Eu ₂ O ₃	0.53	-
CaO	0.89	1.25	Gd ₂ O ₃	2.60	-
ThO ₂	1.50	1.73	Tb ₂ O ₃	-	0.55
UO ₂	1.19	0.40	Dy ₂ O ₃	-	0.20
P ₂ O ₅	28.32	29.12	Ho ₂ O ₃	-	0.39
SO ₃	0.40	-	Yb ₂ O ₃	-	0.46
H ₂ O*	5.67	5.95	Lu ₂ O ₃	-	0.43
	100.00	100.00	CaO	2.89	2.38
			SrO	0.43	0.45
			ThO ₂	1.23	0.68
number of ions on the basis of 4 (O)			UO ₂	0.83	0.81
Ce ³⁺	0.477	0.546	P ₂ O ₅	27.46	27.31
La ³⁺	0.169	0.145	Al ₂ O ₃	0.72	0.53
Pr ³⁺	0.066	0.026	Fe ₂ O ₃	0.44	0.55
Nd ³⁺	0.201	0.182	SO ₃	1.37	1.20
Gd ³⁺	0.014	0.014			
Dy ²⁺	0.004	-			
Th ⁴⁺	0.014	0.016			
U ⁴⁺	0.011	0.004			
(PO ₄) ³⁻	0.989	1.014			
(SO ₄) ²⁻	0.012	-			
				94.10	91.62

1) Analyses - samples: 1 - 007 017/45315 (Hamr-deposit); 2 - 296 091/6 (Stráž-deposit); 3, 4 - 320 123/30 (Stráž-deposit)
2) The analyses 3 and 4 presented as measured (they are influenced by surrounding minerals)

As can be seen in Tables 4 and 5, the analysed rhabdophanes are characterized by a wide range of proportions of REEs.

Rhabdophane-(Ce) occurs sporadically as an authigenic constituent in the cement of clastic rocks, mainly in those which exhibit apparent signs of alteration associated with oxidation processes. It occurs in small irregular aggregates of fine-grained crystallites (Pl. VI/4), which only rarely exhibit clearly defined crystal faces (with regularly hexagonal sections perpendicular to *c*). Some electron microanalyses also indicate the presence of an unusual La-free type of rhabdophane-(Ce) (see Fig. 2 and Table 4).

Rhabdophane-(Nd), as already mentioned, has been discovered in hematitized phyllitic rocks of the imme-

diolate basement of the Cretaceous sediments in the Stráž deposit, where this phosphate together with churchite-(Y) represent a REE anomaly. Rhabdophane-(Nd) forms void fillings in quartz grains, small dispersed particles in aggregates of finely fibrous (rarely microgranular) churchite-(Y) as well as in hematite. In contrast with the prevailing finely-fibrous form of churchite-(Y) (Pl. VI/6), the habit of minute rhabdophane particles is always almost equidimensional (Pl. VI/5). The REE-minerals are associated with ningyosite, rammelsbergite, nickelite, and langisite, too (Scharmová et al. 1993). Due to (1) the first find of churchite-(Y) in this ore district and (2) its close association with rhabdophane-(Nd), two microanalyses of churchite-(Y) also are included (see Table 5 and Fig. 2).

Discussion and conclusion

Unfortunately, no crystal structure determinations of ningyosite nor brockite, seems, have been made till now. Moreover, no perfect determination of the chemical composition of these minerals, probably has been published. Due to the inhomogenities and/or small size of crystallites no reliable analyses of the minerals of the ningyosite - brockite series could be obtained by our study, too. Consequently, many questions remain to be solved. However, our studies showed that the general formula of ningyosite as suggested by Belova et al. (1978a) and confirmed by Boyle et al. (1981) and Dojnikova et al. (1993) corresponds well with our analytical results. Besides, we also believe that the formula of brockite may be written correspondingly $Ca_{2-x}Th_x[P(O,OH)_4] \cdot n H_2O$ (see Fig. 1 and Table 3).

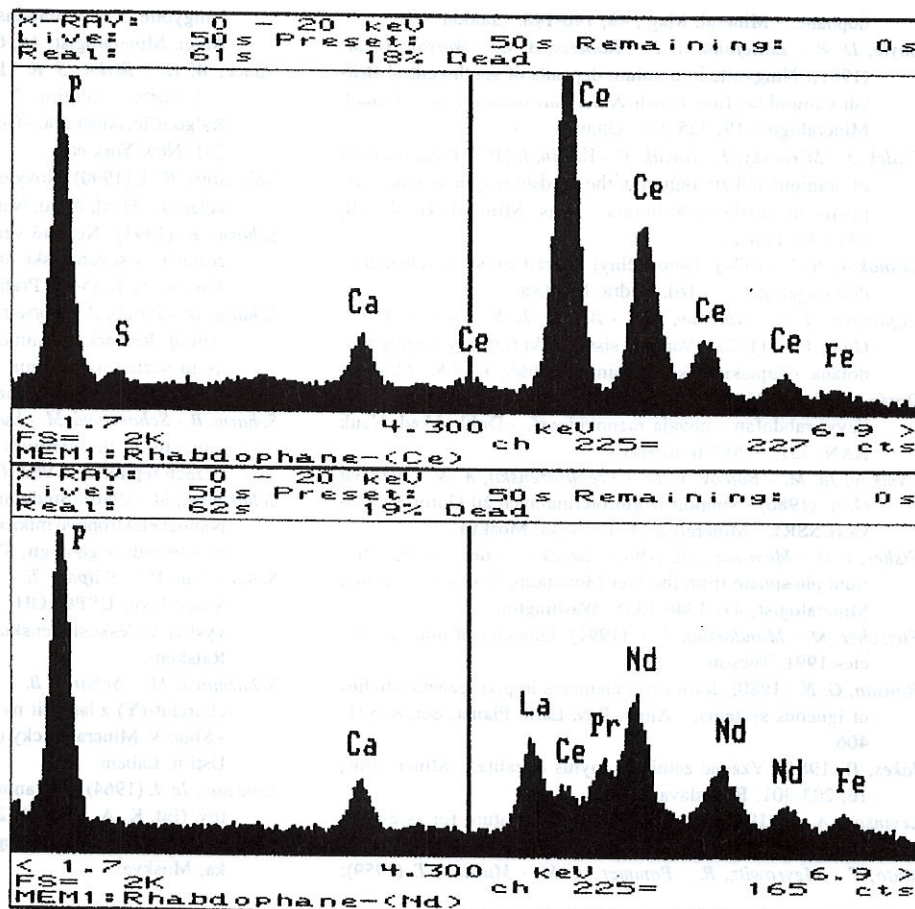
As already mentioned, Dojnikova et al. (1993) consider that there is a possibility of an extended or even complete miscibility between the Ca, REE, U, and Th in the minerals of the rhabdophane group. However, as follows from our experience, we are able to confirm only the existence of a continuous mineral series between ningyosite and brockite. The idea about the extended miscibility between the minerals of the ningyosite-brockite series on the one hand and rhabdophane on the other, seems, to be not well-founded till now. For example, according to Boyle et al. (1981) the REEs reported in ningyosite from Japan by Muto et al. (1959) are due to the presence of another mineral in a finely dispersed state. Electron microanalyses of ningyosite from Ningyo-Toge mine mentioned by Boyle et al. (1981) showed that the distribution of REEs does not correspond to uranium. A similar observation regarding to the relation between the REEs and ningyosite has been made by the study of specimens from the Tye deposit in British Columbia, Canada, too (Boyle et al. 1981). In the uranium ore district of northern Bohemia, the REEs occasionally appear in the EDX-spectra of some ningyosite aggregates, too, but as revealed by detailed studies, the occurrence of these elements usu-

Table 5
Electron microanalyses (EDX) of rhabdophane-(Nd) and churchite-(Y)

	rhabdophane-(Nd)			churchite-(Y)	
	1	2	3	4	5
La ₂ O ₃	12.56	12.14	12.11	-	-
Ce ₂ O ₃	8.80	6.88	7.60	-	-
Pr ₂ O ₃	3.91	4.12	4.16	0.42	-
Nd ₂ O ₃	19.91	19.89	20.41	0.96	0.32
Sm ₂ O ₃	4.65	5.47	4.84	0.64	0.95
Eu ₂ O ₃	1.98	2.81	1.38	0.48	-
Gd ₂ O ₃	3.88	3.94	3.99	2.79	2.28
Tb ₂ O ₃	1.05	1.12	0.58	1.07	-
Dy ₂ O ₃	1.34	0.92	1.77	5.05	5.16
Ho ₂ O ₃	0.15	-	0.27	-	1.00
Er ₂ O ₃	0.77	0.55	0.90	2.57	2.60
Yb ₂ O ₃	-	-	0.75	2.14	3.68
Y ₂ O ₃	1.66	0.17	1.51	36.98	36.79
CaO	2.49	2.72	2.40	1.49	1.46
FeO	0.16	-	-	-	-
P ₂ O ₅	30.47	30.83	30.99	30.80	31.89
H ₂ O	6.22	8.44	6.34	14.61	13.87
	100.00	100.00	100.00	100.00	100.00
number of ions on the basis of 4(O)					
La ³⁺	0.186	0.181	0.177	-	-
Ce ³⁺	0.129	0.102	0.111	-	-
Pr ³⁺	0.057	0.060	0.060	0.006	-
Nd ³⁺	0.285	0.286	0.290	0.013	0.004
Sm ³⁺	0.064	0.076	0.066	0.008	0.012
Eu ³⁺	0.014	0.039	0.019	0.006	-
Gd ³⁺	0.052	0.053	0.052	0.036	0.028
Tb ³⁺	0.014	0.015	0.008	0.013	-
Dy ³⁺	0.017	0.012	0.023	0.062	0.063
Ho ³⁺	0.002	-	0.003	-	0.012
Er ³⁺	0.010	0.007	0.011	0.031	0.031
Yb ³⁺	-	-	0.009	0.025	0.042
Y ³⁺	0.035	0.004	0.032	0.756	0.738
Ca ²⁺	0.107	0.117	0.102	0.061	0.059
Fe ²⁺	0.005	-	-	-	-
(PO ₄) ³⁻	1.035	1.053	1.042	1.001	1.018

- 1) All analyses carried out in the sample 336 131/903 (Stráž deposit);
- 2) H₂O - content calculated from the difference to the sum of 100 wt %.

Fig. 2. Comparison of the EDX-spectra of La-free rhabdophane-(Ce) and rhabdophane-(Nd) (compare with Table 4 and 5). Stráž-deposit



ally reflects the intimate intergrowths of ningyoite with another mineral (Pl. IV/6). An exception may represent yttrium which appears in some ningyoite analyses (up to 4 wt % Y_2O_3), probably as an isomorphic constituent.

Although many authorities (Nance - Taylor 1977, Hanson 1980, Jakeš 1984) believe that the REEs are not readily fractionated under supergene conditions, other (e.g. Semenov 1964, Vlasov 1964, Bowles - Morgan 1984, Banfield - Eggleton 1989) have demonstrated that especially some exogenic processes may be responsible not only for a significant mobility of

these elements but also for their fractionation and for the precipitation of minerals with Nd- and/or La-dominated composition instead of Ce-dominated phases. The occurrence of rhabdophane-(Nd), the unusual La-free rhabdophane-(Ce) together with the earlier discovered phosphates, arsenates and fluorocarbonates with Nd- and La-dominated composition (e.g. Scharm 1993, Scharm et al. 1994) indicate a distinctive fractionation of rare earth elements during exogenic processes.

Submitted August 19, 1994

Translated by the authors

References

- Atkin, D. - Basham, I. R. - Bowles, J. F. W. (1983): Tristramite, a new calcium uranium phosphate of the rhabdophane group. - *Mineral. Mag.*, 47, 393-396. London.
- Banfield, J. F. - Eggleton, R. A. (1989): Apatite replacement and rare earth mobilization, fractionation, and fixation during weathering. - *Clays and Clay Miner.*, 37, 2, 113-127. New York.
- Belova, L. N. - Gorškov, A. I. - Ivanova, O. A. (1978a): Pervaja nachodka ningioita v SSSR. - *Dokl. Akad. Nauk SSSR*, 238, 1, 215-216. Moskva.
- (1978b): Novyje dannye o ningioite: železosodëržaščij ningioit. - *Dokl. Akad. Nauk SSSR*, 243, 4, 1022-1023. Moskva.

- Belova, L. N. - Gorškov, A. I. - Ivanova, O. A. - Dikov, Ju. L. - Sivcov, A. V. (1985): Ningioit v svete novych eksperimentalnykh dannych. - *Izv. Akad. Nauk SSSR, Ser. geol.*, 3, 101-109. Moskva.
- Belova, L. N. - Gorškov, A. I. - Ivanova, O. A. - Fedorov, O. V. - Zelenova O. I. - Filipova, M. I. - Dragomanov, L. V. (1986): Ningioit v Bolgarii. - *Crystal Chemistry of Minerals*. 773-779. Proc. of the I. M. A. in Sofia, 1982. Sofia.
- Belova, L. N. - Gorškov, A. I. - Ivanova, O. A. - Sivcov, A. V. (1987): Ob analogii tristramita i ningioita. - *Izv. Akad. Nauk SSSR, Ser. geol.*, 11, 136-137. Moskva.
- Bowie, S. H. U. (1957): Summary of progress of the Geological survey of Great Britain and the Museum of practical geology for the year 1956. London.
- Bowles, J. F. W. - Morgan, D. J. (1984): The composition of rhab-

- dophane. - Mineral. Mag., 48, 146-148. London.
- Boyle, D. R. - Littlejohn, A. L. - Roberts, A. C. - Watson, D. M. (1981): Ningyoite in uranium deposits of south-central British Columbia: first North American occurrence. - Canad. Mineralogist, 19, 325-331. Ottawa.
- Čadek, J. - Mirovský, J. - Novák, F. - Vavřín, I. (1975): Association of uranium and zirconium in the sandstone type uranium deposits in northern Bohemia. - Čas. Mineral. Geol., 20, 131-140. Praha.
- Česnokov, B. V. (1974): Otnositel'nyj vozrast mineralnyh individov i agregatov. - Izd. Nedra. Moskva.
- Dojnikova, O. A. - Gorškov, A. I. - Belova, L. N. - Sivcov, A. V. - Gulij, V. N. (1993): Voprosy sistematiki fosfatov grupy rabdofana. - Zapiski Vsesojuz. mineral. Obšč., 3, 79-88. Moskva.
- Dorfman, M. D. - Gorškov, A. I. - Nečeljustov, G. N. (1993): Kalcijevyj rabdofan - novaja raznovidnost'. - Dokl. Akad. Nauk RAN, 331, 5, 583-6. Moskva.
- Dymkov, Ju. M. - Bojcov, V. Je. - Preobraženskij, A. N. - Ivanova O. A. (1986): Ningioit iz gidrotermal'nyh žil Gorni Slavkova (ČSSR). - Mineral. Ž., 8, 6, 34-43. Moskva.
- Fisher, F. G. - Meyrowitz, R. (1962): Brockite, a new calcium thorium phosphate from the Wet Mountains, Colorado. - Amer. Mineralogist, 47, 1346-1355. Washington.
- Fleischer, M. - Mandarino, J. A. (1991): Glossary of mineral species 1991. Tucson.
- Hanson, G. N. (1980): Rare earth elements in petrogenetic studies of igneous systems. - Amer. Rev. Earth Planet. Sci, 8, 371-406.
- Jakeš, P. (1984): Vzácné zeminy - mýtus a realita. - Miner. slov., 16, 283-301. Bratislava.
- Levinson, A. A. (1966): A system of nomenclature for rare-earth minerals. - Amer. Mineralogist, 51, 152-158. Washington.
- Muto, T. - Meyrowitz, R. - Pommer, A. M. - Murano, T. (1959): Ningyoite, a new uranous phosphate mineral from Japan. - Amer. Mineralogist, 44, 633-650. Washington.
- Nance, W. H. - Taylor, S. R. (1977): Rare earth element patterns and crustal evolution. 2. Archean sedimentary rocks from Kalgoorlie, Australia. - Geochim. Cosmochim. Acta, 41, 225-231. New York etc.
- Někrasova, R. A. (1990): Novyje dannyje o sostave fosfatnoj matricy kularita. - Dokl. Akad. Nauk SSSR, 312, 2, 464-467. Moskva.
- Scharm, B. (1993): Někteří vzácné minerály provázající uranové zrudnění v severočeské křídě. - Bull. mineral.-petrogr. Odd. Nár. Muz., 1, 45-48. Praha.
- Scharm, B. - Burda, J. - Hofreiter, V. - Sulovský, P. - Scharmová, M. (1980): Remarkable mineral assemblage on uranium deposits in northern Bohemia (the Stráž block). - Čas. Mineral. Geol., 25, 2, 113-124. Praha.
- Scharm, B. - Scharmová, M. - Kundrát, M. (1994): Crandallite group minerals in the uranium ore district of northern Bohemia (Czech republic). - Věst. Čes. geol. Úst., 69, 1, 79-85. Praha.
- Scharmová, M. (1980): Studium ložiska Stráž-Noviny pod Ralskem pomocí elektronové mikroskopy. - Sbor. Aplikace elektronové mikroskopy v geologii, 87-92. ČSVTS, Ústí n. Labem.
- Scharmová, M. - Půlpán, T. - Sulovský, P. - Scharm, B. (1990): Vjačeslavit, $U^{IV}PO_4 \cdot OH \cdot H_2O$, ze severočeské křídě - první výskyt v Československu. - MEGA, 14, 3, 81-87. Stráž p. Ralskem.
- Scharmová, M. - Scharm, B. - Rutšek, J. (1993): Rabdofan-(Nd), churchit-(Y) a langisit na ložisku Stráž v severočeské křídě. - Sbor. V. Mineralogický cyklický seminář, 97-99. Audit VT, Ústí n. Labem.
- Semenov, Je. I. (1964): Lantanoidy. In Geochimija redkich elementov. (Ed. K. A. Vlasov), 210-283. Nauka. Moskva.
- Vlasov, K. A. (1964): Mineralogija redkich elementov. - Izd. Nauka, Moskva.

Minerály skupiny rabdofanu v oblasti uranových ložisek v severočeské křídě

Součástí minerální asociace nacházející se v oblasti uranových ložisek v severočeské křídě (Hamr-Stráž pod Ralskem) jsou také fosfáty skupiny rabdofanu. Doposud byly identifikovány: ningyoit, brockit, rabdofan-(Ce) a rabdofan-(Nd). Tyto minerály se nacházejí především v pojiu sedimentů cenomanského stáří (pískovce, prachovce, brekcie). Ningyoit a rabdofan-(Nd) byly nalezeny také v podložních fylitech.

Jak ningyoit, tak brockit, se vyskytují v několika formách. Podrobné studium těchto minerálů pomocí skenovací elektronové mikroskopie a elektronové mikroanalýzy prokázalo existenci plynulé izomorfní řady mezi oběma minerály (viz obr. 1 v textu a tab. 3). Z několika set elektronových mikroanalýz vyplynuly některé obecné poznatky týkající se chemismu jak ningyoitu, tak brockitu. Je to např. 1. převaha Ca nad U, resp. U+Th, 2. deficit P oproti kationtům projevující se u většiny analýz (valenční kompenzaci patrně zajišťují ionty CO_3 a snad i SO_4) a 3. vedle dominantních prvků, tj. Ca, U (Th) a P se téměř ve všech spektrech objevují linie Fe a S (z větší části patrně odrážejí vliv FeS_2 , zčásti snad odpovídají také iontům Fe^{3+} a $(SO_4)^{2-}$ jako izomorfních příměsí).

Byly zjištěny dva typy ningyoitu, a to a) ningyoit bez (stanovitelné) příměsí Th a b) ningyoit s velmi variabilními obsahy Th (až po U : Th = 1 : 1). Oba typy se zpravidla liší rozměry krystalů a habitem. Pro většinu ningyoitových krystalů je příznačná chemická nehomogenita, časté je jejich zatlačování disulfidy železa, příp. i oxidy uranu. Přes problémy spojené s interpretací výsledků elektronových mikroanalýz, u nichž analyzované objemy zpravidla zasahují i vedlejší minerální fáze, se zdá, že vzorec ningyoitu, udávaný Belovou et al. (1978a, 1982 aj.) a Boylem et al. (1981) v podobě $Ca_{2-x}U_x[P(O,OH)_4] \cdot nH_2O$, lze považovat za reálný. Vzhledem k existenci izomorfní řady mezi ningyoitem a brockitem a také k tomu, že rovněž u brockitu se projevuje převaha Ca nad Th, resp. Th+U, lze soudit, že vzorec tohoto fosfátu bude adekvátní vzorci ningyoitu, tj. $Ca_{2-x}Th_x[P(O,OH)_4] \cdot nH_2O$.

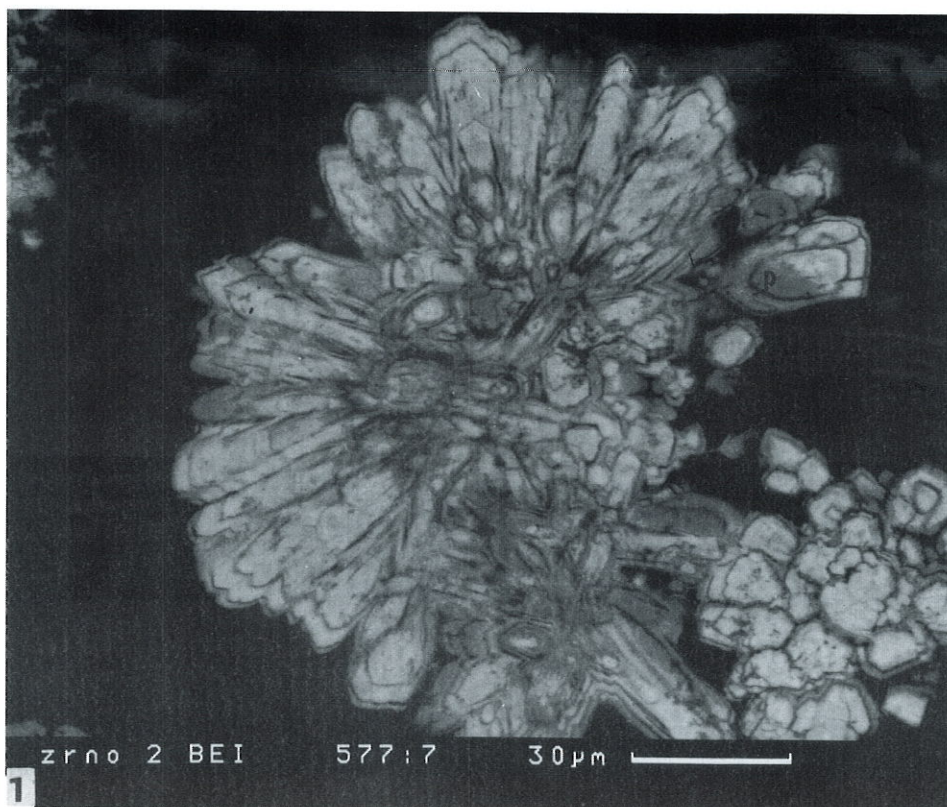
Vzácný akcesorický rabdofan-(Ce) se nachází v pojiu pískovců, většinou s více či méně zřetelnými znaky oxidace. Vytváří jemnozrné agregáty, u nichž lze pouze ojediněle pozorovat automorfní krystalové částice šestiúhelníkového průřezu. Pozoruhodné je, že obsah La v některých agregátech je pod mezí detekce EDX-analýzy.

Rabdofan-(Nd) byl nalezen v tektonicky podcračených a hematitizovaných fylitech v přímém podloží cenomanu, kde vytváří velmi jemnozrné agregáty. V asociaci s ním byly identifikovány churchit-(Y), ningyoit, rammelsbergit, nikeln a velmi vzácný arzenid niklu a kobaltu - langisit.

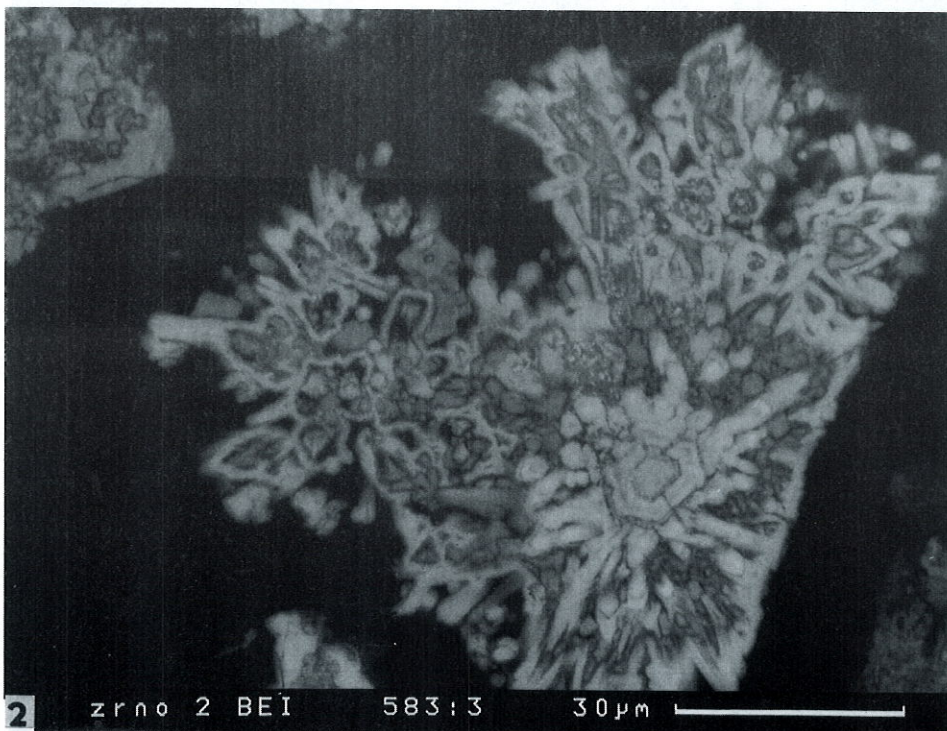
Výskyt rabdofanu se značně variabilními poměry mezi prvky vzácných zemin, spolu s fosfáty, arzenáty a fluorokarbonáty vzácných zemin, u nichž dominantním prvkem není Ce, ale La nebo Nd, nalezenými v této rudní oblasti již dříve (např. Scharm 1993, Scharm et al. 1994), svědčí o zřetelných projevech frakcionace prvků vzácných zemin v exogenních podmínkách.

M. Scharmová - B. Scharm: Rhabdophane group minerals in the uranium ore district... (Pl. I)

1. Rosette-like aggregate of euhedral ningyoite crystals. Dark zones and grey parts of some ningyoite crystals (P) represent FeS_2 . Polished section, backscattered electrons. Stráž-deposit

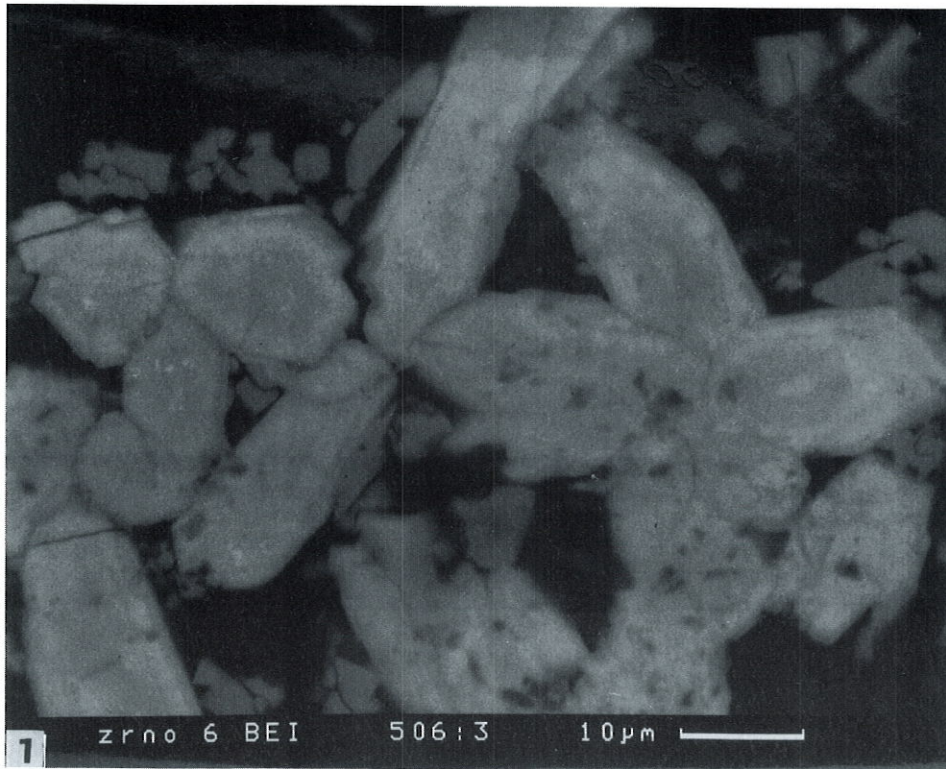


2. Ornamental texture composed of intimately intergrown ningyoite (light) and pyrite (grey). Polished section, backscattered electrons. Stráž-deposit

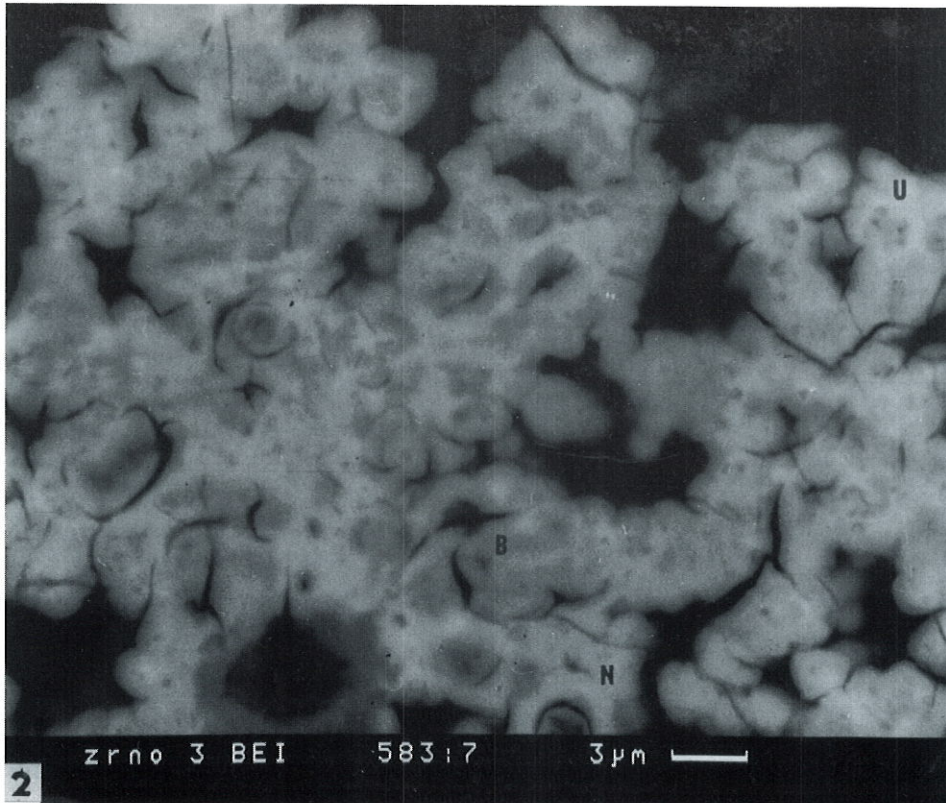


All SEM-micrographs, with the exception of V/1, 4, 5 (made by J. Burda) and III/2 (made by T. Půlpán), were taken by M. Scharmová

M. Scharmová - B. Scharm: Rhabdophane group minerals in the uranium ore district... (Pl. II)

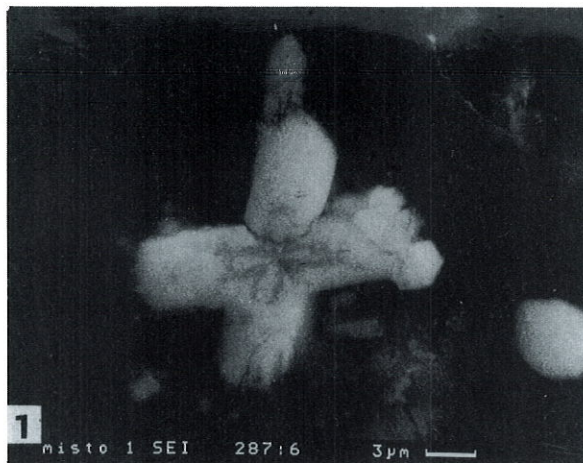


1. An example of the chemical (micro-)inhomogeneity of ningyoite crystals reflecting variable Fe- and S-contents inside the crystals. It is probably caused by the densely disseminated FeS_2 -particles inside the ningyoite crystals. Polished section, backscattered electrons. Stráž-deposit

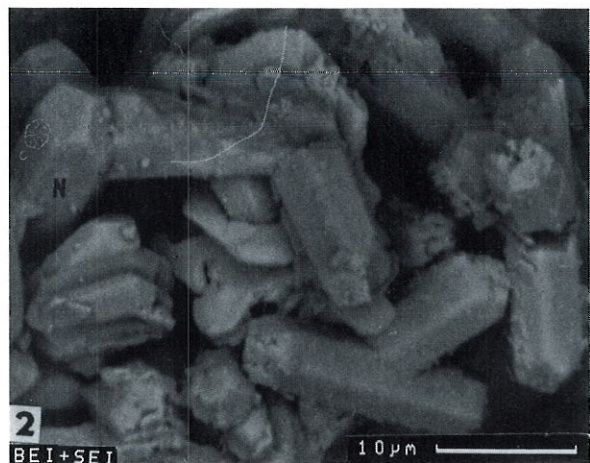


2. Poorly differentiated mineral matter of gel-like appearance. The main components are close to baddeleyite (B), ningyoite (N), and uraninite (U). Locally indications of hexangular cross-section of ningyoite are visible. Polished section, backscattered electrons. Stráž-deposit

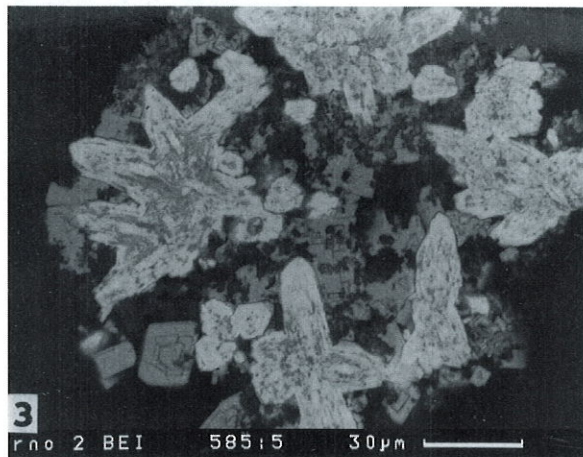
M. Scharmová - B. Scharm: Rhabdophane group minerals in the uranium ore district... (Pl. III)



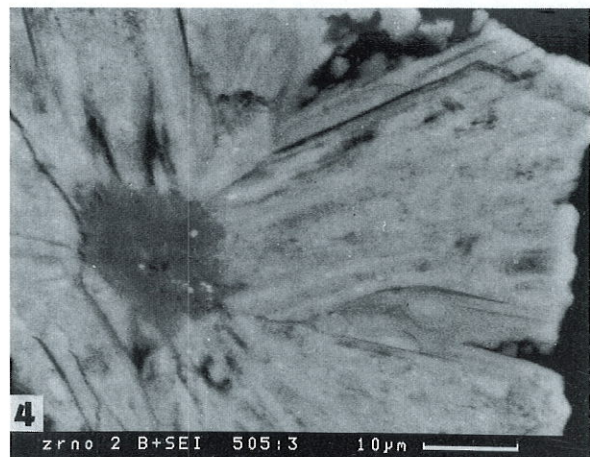
1. Cruciform twins of ningyoite. The darker double cross inside the intergrowth consists of FeS_2 . Polished section, secondary electrons. Stráž-deposit



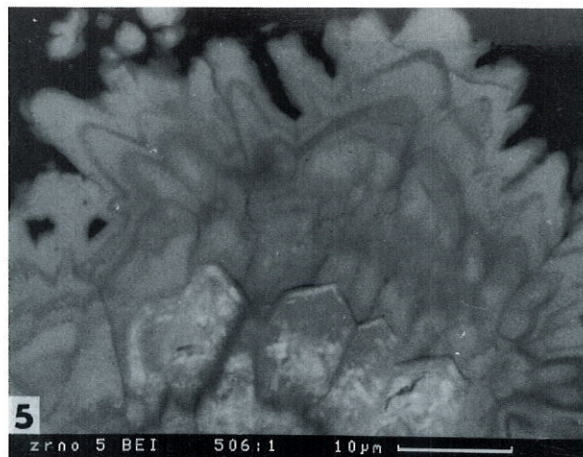
2. Columnar crystals of ningyoite intergrown with platelets of vyacheslavite. Rhombohedral crystal faces are observable on one of the ningyoite crystals (labeled N). Combination of secondary and backscattered electrons. Stráž-deposit



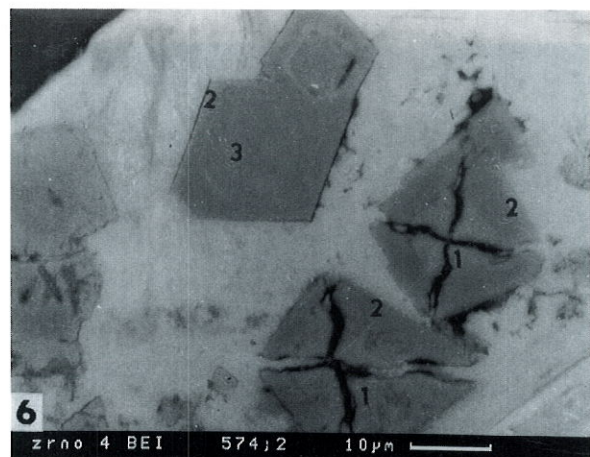
3. Aggregates of ningyoite crystals containing minute FeS_2 -inclusions and surrounded by the same sulphide. Polished section, backscattered electrons. Stráž-deposit



4. Close-up of a ningyoite aggregate with distinct chemical (micro-)inhomogeneity caused by many minute inclusions of FeS_2 . Polished section, backscattered electrons

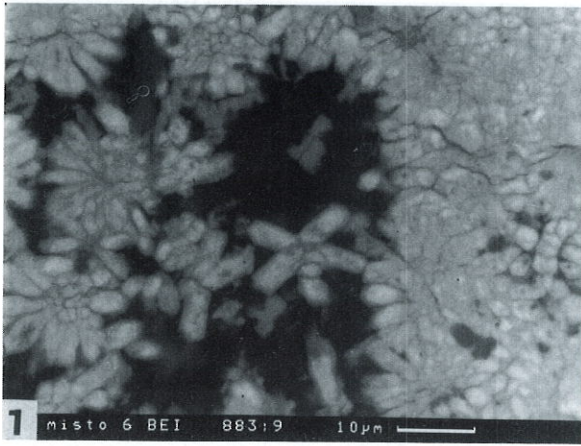


5. Another example of chemical (micro-)inhomogeneity of ningyoite. Dark zones - FeS_2 , white spots - uranium oxide. Polished grain section, backscattered electrons. Stráž-deposit

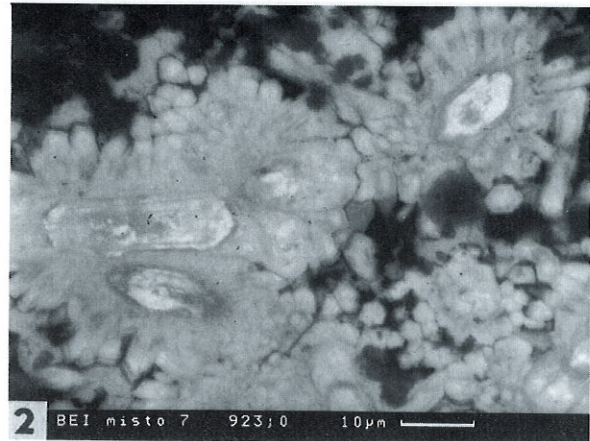


6. Sulphides (1 - siegenite, 2 - bravoite, 3 - vaesite) enclosed by ningyoite (light grey). Polished section, backscattered electrons. Stráž-deposit

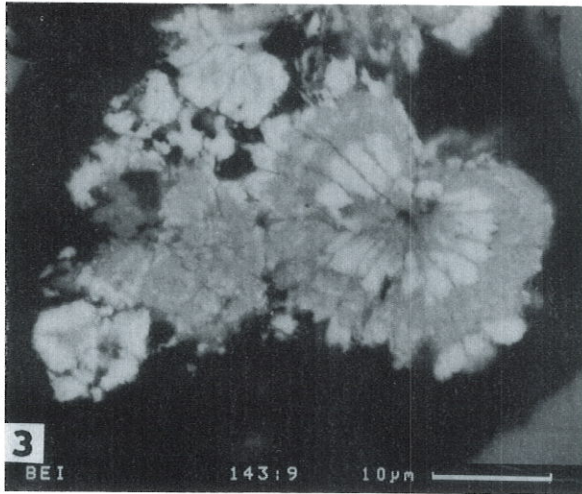
M. Scharmová - B. Scharm: Rhabdophane group minerals in the uranium ore district... (Pl. IV)



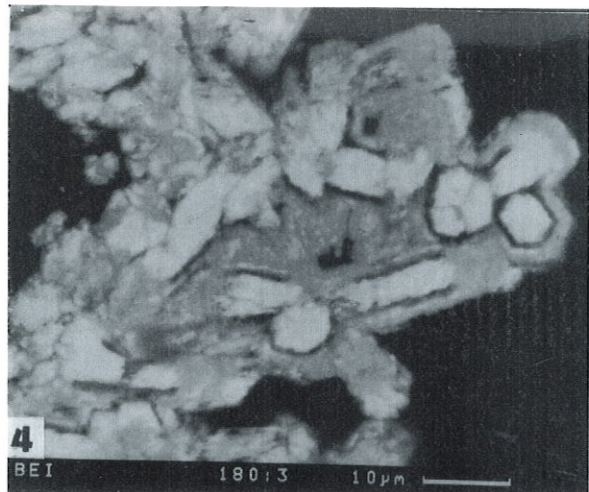
1. Aggregates of ningyoite crystals with distinct chemical (micro-)inhomogeneity. Stráž-deposit



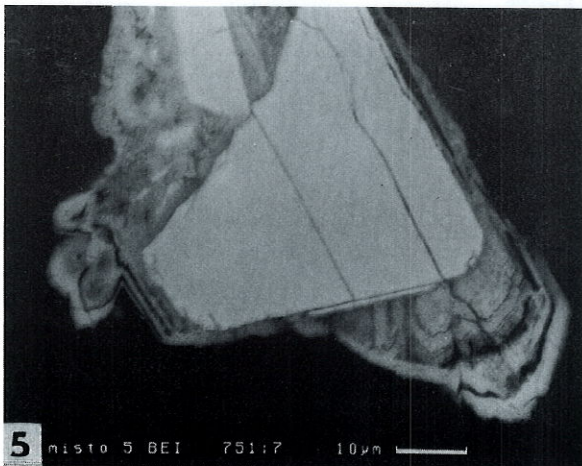
2. Example of the replacement of ningyoite by uranium oxide (white, central parts of the ningyoite aggregates). Polished section, back-scattered electrons. Stráž-deposit



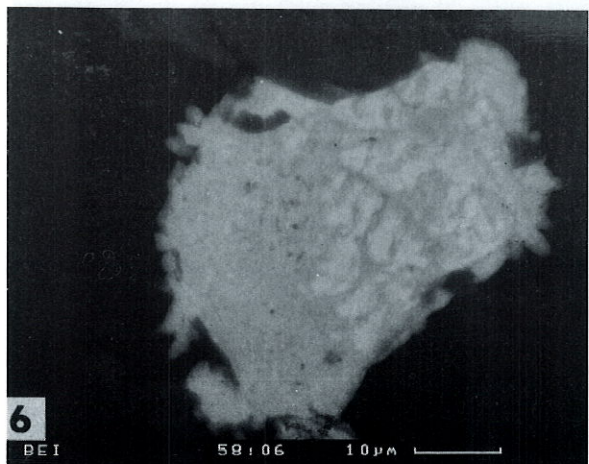
3. Pseudomorphs of pyrite (light grey) and uraninite (white) after earlier ningyoite. Polished section, backscattered electrons. Hvězdov-deposit



4. Example of the progressive replacement of ningyoite (white) by FeS_2 (grey). Polished section, backscattered electrons. Hvězdov-deposit

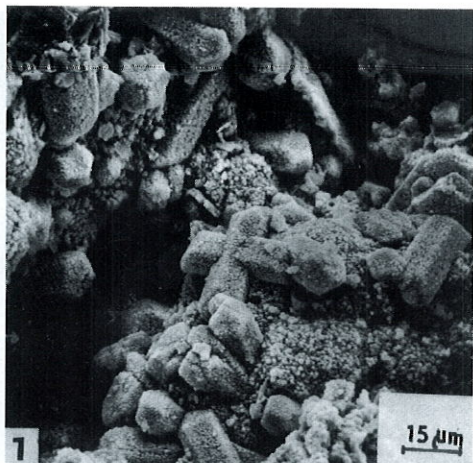


5. Clasts of monazite-(Ce) rimmed by ningyoite (zonal, inhomogeneous). Polished section, backscattered electrons. Stráž-deposit

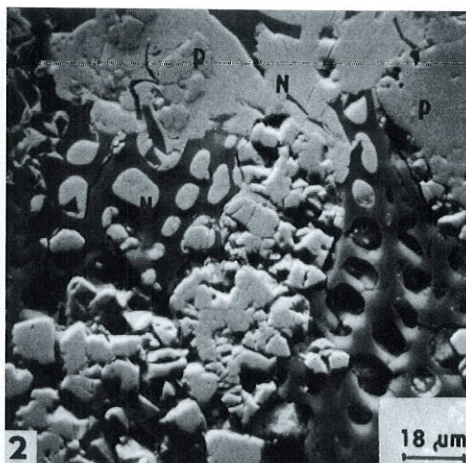


6. Example of the resorption of a REE-phosphate (chemically close to rhabdophane and monazite, light grey) by ningyoite (grey). Polished section, backscattered electrons. Stráž-deposit

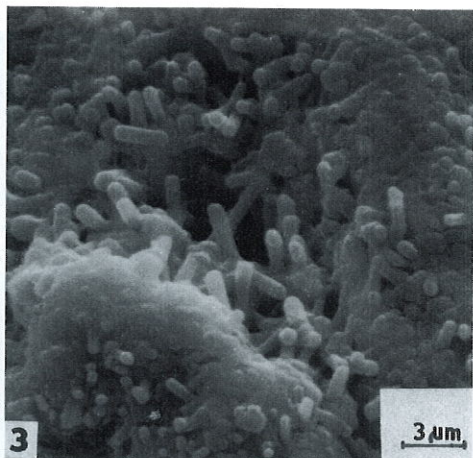
M. Scharmová - B. Scharn: Rhabdophane group minerals in the uranium ore district... (Pl. V)



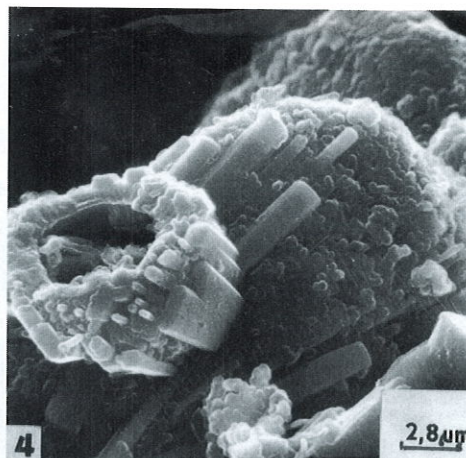
1. Euhedral crystals of ningyoite coated by microgranular hydrozircon. Secondary electrons. Hamr-deposit



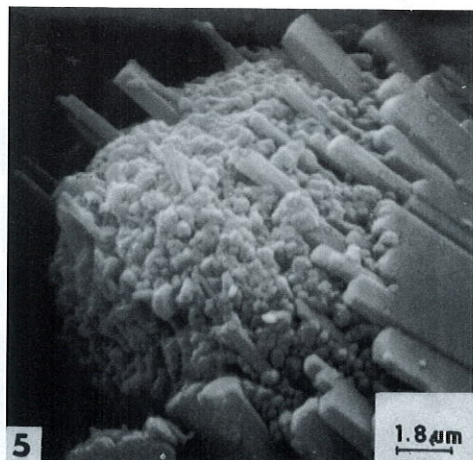
2. Ningyoite (N) occurring as irregular grains and as filling of some cells in coalified organic substance (fusinite). P = pyrite. Polished section, secondary electrons. Holičky-deposit



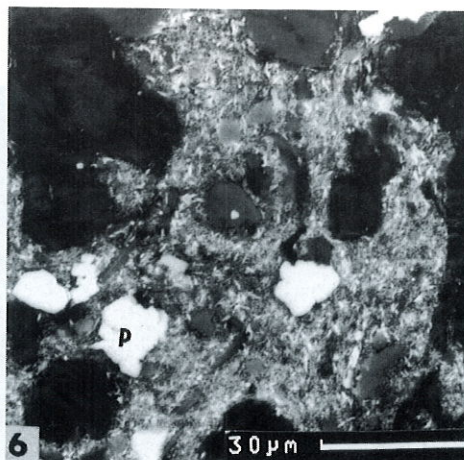
3. Acicular crystals of brockite growing from a gel-like matter of the same composition. Secondary electrons. Hamr-deposit



4. Sheaf-like aggregates of brockite built of both distinctly crystalline and colloform forms. Stráž-deposit

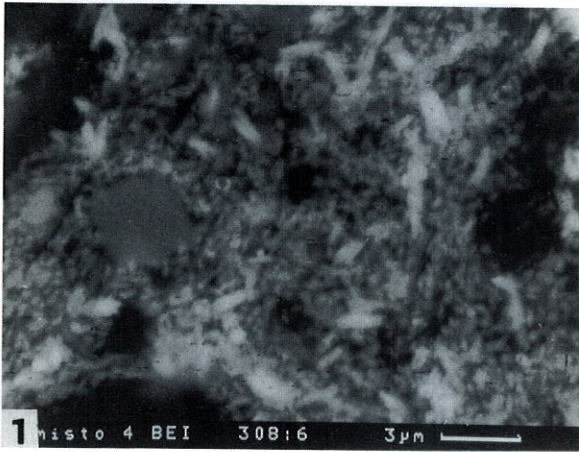


5. Detailed view of a sheaf-like aggregate of brockite showing the distinctly crystalline and colloform types of this mineral. Secondary electrons. Stráž-deposit

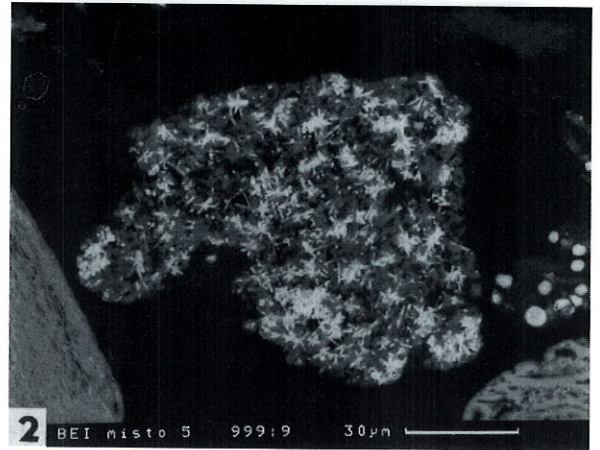


6. Minute needle-shaped inclusions of Th-bearing ningyoite up to brockite (Th prevails over U in some mineral particles) in a hydrozircon aggregate (light grey, prevailing). P - pyrite. Polished section, backscattered electrons. Stráž-deposit

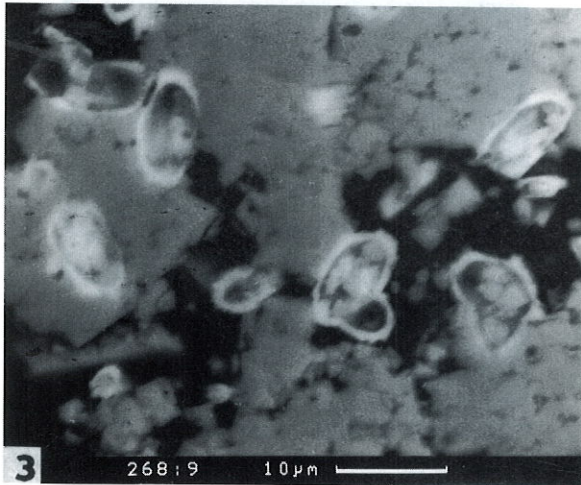
M. Scharmová - B. Scharn: Rhabdophane group minerals in the uranium ore district... (Pl. VI)



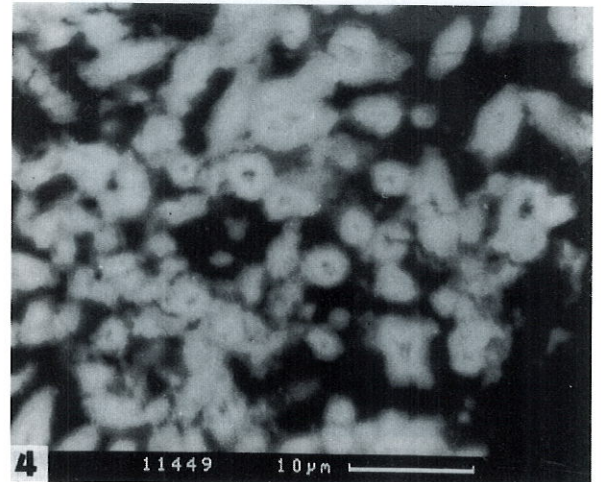
1. Detailed view of the fig. V/6: Small elongated crystallites of U-Th-phosphates enclosed by microgranular hydrozircon. Polished section, backscattered electrons. Stráž-deposit



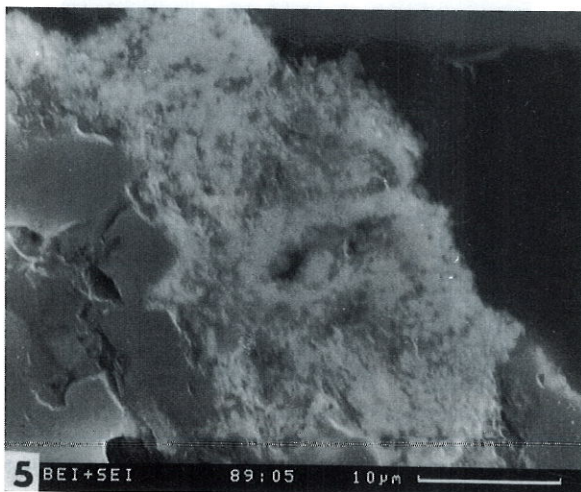
2. Asterisk-shaped aggregates of an intermediate member between ningyoite and brockite (U : Th up to 1 : 1) closely associated with strontian crandallite (grey). Polished section, backscattered electrons. Stráž-deposit



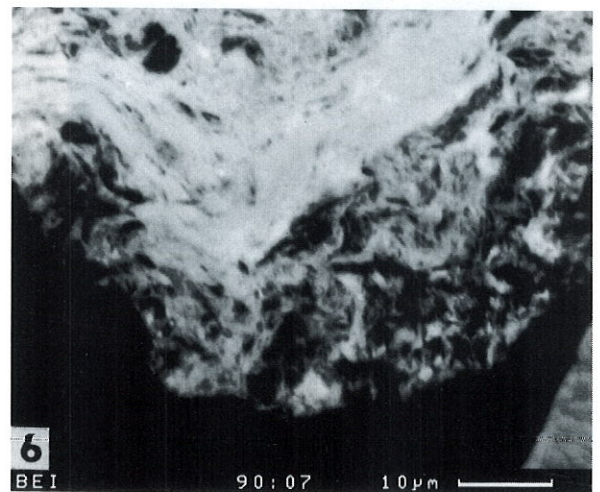
3. Brockite (white elliptical forms) in pyrite aggregate (grey, predominant). Polished section, backscattered electrons. Stráž-deposit



4. Crystallites of rhabdophane-(Ce) embedded in strontian crandallite (in the used conditions of SEM-observations crandallite appears black in colour). Polished section, backscattered electrons. Stráž-deposit



5. Finely grained aggregate of rhabdophane-(Nd) filling a void in a corroded quartz grain. Polished section, backscattered electrons. Stráž-deposit



6. Fibrous churchite-(Y) (light, predominant) enclosing minute particles of rhabdophane-(Nd) (almost white). Polished section, backscattered electrons. Stráž-deposit