

## THORITE, THOROGUMMITE AND XENOTIME-(Y) OCCURRENCE IN DITRAU ALKALINE INTRUSIVE MASSIF, EAST CARPATHIANS, ROMANIA

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Received July 10, 2013

The thorite and thorogummite, closely associated with the xenotime-(Y) represent the characteristic paragenesis of the Belcina type mineralization of the Ditrau alkaline intrusive massif. The Belcina vein mineralization is localized in the South-East of the massif, within the Cambrian metamorphic Tulghes Group. Genetically the Belcina mineralization is linked to the red alkaline syenites, the fluid responsible for the mineralisation belonging to the late-stage hydrothermal event. Late stage calcite, siderite, ferrodolomite veins and development of the Fe-oxides and hydroxides (hematite, goethite, lepidocrocite), minor sulphides of Fe, Pb, Zn, Mo and Hg, may be present. Also, REE-apatite, monazite-(Nd), monazite-(Ce), brabantite, ferrocolumbite, manganocolumbite, Nb-rutile, zircon, magnetite, thorianite, Y-fluorite are present as primary mineralization sequence. The gangue associated to the ore is represented by feldspars (microcline, albite, orthoclase), quartz, different common carbonates of at least two generations, natrolite, pectolite and different chlorites. Electron microprobe analyses of many individual grains of thorite gave mainly ThO<sub>2</sub>=70-80.00, SiO<sub>2</sub>=15-17.00, ZrO=0-6, FeO=0-4% and very little Ce<sub>2</sub>O<sub>3</sub>, UO<sub>2</sub>, Y<sub>2</sub>O<sub>3</sub>, PbO and P<sub>2</sub>O<sub>5</sub> contents. Thorogummite has less ThO<sub>2</sub>, more SiO<sub>2</sub>, ZrO, FeO, CaO, PbO and P<sub>2</sub>O<sub>5</sub>, than thorite. Thorite and especially thorogummite have an oscillatory chemical composition. The xenotime-(Y) has a constant composition, with of about Y<sub>2</sub>O<sub>3</sub>=60-62 and P<sub>2</sub>O<sub>5</sub>=38-40% (wt). Because of so many common carbonates, as mineral gangue, the Belcina Th-Y mineralization could be attributed to a carbothermal process more than to a hydrothermal one.

*Key words:* thorite, thorogummite, xenotime-(Y), Nb-rutile, monazite-(Ce), brabantite, apatite, ferrocolumbite, zircon, natrolite, pectolite, Fe oxides/hydroxides, hydrothermal/carbothermal activity.

### INTRODUCTION/GEOLOGICAL SETTING<sup>1</sup>

The Ditrau alkaline intrusive complex is situated within the Cambrian metamorphic Tulghes Group of the inner part of the East Carpathians. It has a distinct ring structure (Streckeisen, 1960), having a succession of magmatic events from gabbroic and dioritic magma to syenitic and various postmagmatic events as well, developed between a Triassic extensional stage and a Jurassic rifting stage (Krautner & Bindea, 1996). The succession of the magmatic events in Ditrau, could be completed with carbonatite intrusion that followed the alkaline intrusion and used the same pathways as the previous alkaline silicate melt. Its

affiliation to anorogenic alkaline magmas explains their general feature Nb>>Ta and the predominance of LREE in the first mineralization stages and the Th-Y one in the last hydrothermal /carbothermal stages. The Ditrau alkaline intrusive complex represents the end of a long lasting fractionation processes in the crust and deep upper mantle, respectively. This explains the modest dimensions of Ditrau intrusion and its enrichment with incompatible elements. The high petrographic complexity of Ditrau massif is doubled by a great diversity of mineral occurrences. In addition to the 85 minerals, previously mentioned (Jakab, 1998, Constantinescu, 1999), about 200 were recently identified, many of them being first occurrences in Romania (Hirtopanu *et al.*, 2003, Hirtopanu *et al.*,

2010a, 2010b). The rare element minerals determined in Ditrau complex intrusion, belong to the following 6 classes (in the predominant order): REE(Y) – Carbonates; Nb, Ta, REE(Y), Ti, Zr, Th, U – Oxides; REE(Y) – Phosphates; REE(Y), Th, Zr, Pb – Silicates; Halides and Tellurides (Hirtopanu *et al.*, 2010b). They occur in a small mineralization areas (Lazarea, Hereb-Cianod, Ditrau Valley/ Pricske, Aurora, Putna, Creanga Halasag) and in two big vein mineralization areas, Jolotca and Belcina (Fig. 1). The biggest Jolotca occurrence from the NV of the massif is of vein type and comprises a complex sulphides mineralization. The rare elements mineralizations followed after sulphides, almost all the rare element minerals being developed as veins in sulphides, as a late hydrothermal phase. They are represented by LREE-carbonates; Nb, Ta, REE(Y), Ti, Zr, Th, U oxides; REE(Y), Th phosphates; REE(Y), Zr, Th, Ti, REE silicates; Bi and Pb-Bi tellurides; and halides (Hirtopanu 2006, Hirtopanu *et al.*, 2010a, 2010b). The Jolotca rare elements mineralization has a gangue of ferrodolomite, ankerite, siderite and calcite. The other occurrence of vein type is the Belcina, less big than Jolotca, situated outside of the

Ditrau massif (SE), in the surrounding metamorphic rocks of the Tulghes Group, at 2.5 km distance of massif (Jakab, 1998) (Fig. 1). The Belcina occurrence comprises a complex mineralization, different from that reported in Jolotca. It is mostly constituted of Th silicates and Y-phosphates, less zircon, niobian rutile, ferrocolumbite, Y-fluorite, less sulphides, and almost no Nb-Ta pyrochlores (which occur frequently in Jolotca area), small/almost no REE(Y) – silicates (allanite, which has a big development in Jolotca area, chevkinite, etc), and small/no REE(Y)-carbonates (which also have a big development in Jolotca area). Also, there are present as accessory/ constituent primary minerals such as: Th-apatite, Fe-oxides and hydroxides (magnetite, hematite, goethite, lepidocrocite), some sulphides (pyrite, arsenopyrite, galena, sphalerite, chalcopyrite, tetrahedrite, molybdenite, cinnabar) and native mercury Hg, in the calcite-ferrodolomite-siderite and apatite gangue. The samples studied here (around 50) were collected from the vein situated at the confluence of Belcina Valley with Kisgyor Rivulet and were abbreviated with “Bel”. The samples collected from Jolotca were abbreviated with “Dt”.

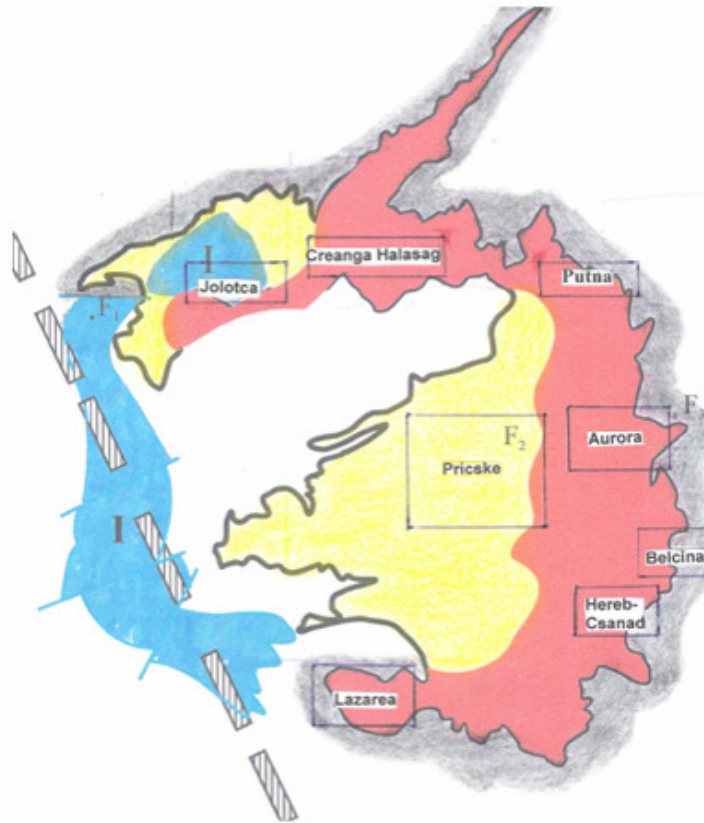


Fig. 1. The schematic geological map of Ditrau alkaline massif with **mineralization areas**: hornblendite-diorite complex (blue), red syenite (red), white nepheline syenite (yellow), Tulghes Group (grey), **F** = fault, **G8**=crustal fracture (hachure interrupted line), (acc. to Jakab, Gyula).

## MINERALOGY

The first and complete mineralogical description of Belcina mineralization belongs to Jakab (1982, 1998) who determined representative minerals of following mineral classes: a. silicates: K feldspar, albite, chlorite, biotite, sericite, thorite, zircon, epidote; b. oxides: ilmenorutile, rutile, anatas, columbite, pyrochlore, fersmite, magnetite, loparite, ilmenite, hematite; c. phosphates: xenotime, apatite, Y-fluorapatite; d. carbonates: calcite, ferrodolomite; sulphides: pyrite, arsenopyrite, galena, sphalerite, chalcopyrite, tetrahedrite, molybdenite. The mineral crystallization order (Jakab, 1998) is: Paragenesis I: pegmatitic quartz-feldspar gangue; ferrodolomite+quartz; niobotantalates+xenotime+ thorite+fluorapatite+arsenopyrite+sphalerite+molybdenite+pyrite+ chlorite; ferrodolomite; calcite+galena; Paragenesis II:pyrite+sphalerite+galena+calcite+quartz. The K/Ar microcline ages, shows for the Belcina mineralization the same age as the Ditrau rocks (Jakab, 1998). Also, the same author showed that the Jolotca mineralization, having the predominance of Y in respect to Ce, and high Th content, belongs genetically to the magmatic red syenites. The first modern study of the Belcina occurrence was made in laboratories of CSM, Exeter University (2007–2009). After a minutely optical study, the samples were analyzed chemically by microprobe and SEM. The electron microprobe data, which are presented below was collected on a JEOL8200 instrument located at Camborne School of Mines (CSM), University of Exeter, Cornwall, UK. Images and chemical analyses were collected using an accelerating voltage of 15KeV and 30nA beam current. The X-ray spectra were collected using EDS and WDS detectors calibrated with natural and synthetic standards. There were realized many backscattered electron images (BSEi), helping us to establish textural relationships, fine scale intergrowth of the thorite/thorogummite and xenotime-(Y), illustrated in the text. Also, the thorite, thorogummite, Th-apatite, apatite, Nb rutile, zircon oscillatory/ zoned compositions, can be seen in many optical and electronic images. The rare/common element minerals of the Belcina occurrence will be presented in the predominant order: **I. Th-Silicates; II. REE(Y) Phosphates; III. Other associated rare element minerals; IV. Gangue/common minerals.**

### Th-silicates: Thorite and thorogummite

**Thorite, ThSiO<sub>4</sub>**, tetragonal. Thorite is isostructural with zircon, with which it forms a

complete series. Also, thorite is related to a mineral called huttonite (ThSiO<sub>4</sub>). Thorite and huttonite are dimorphs. The two minerals have the same chemistry, they just have different structures. Huttonite is monoclinic and belongs to the Monazite Group, being related structurally to its members. Also, there is a close related mineral thorogummite, that was once considered a variety of thorite but it is a product of its hydrothermal alteration. Because thorite is highly radioactive, specimens are often metamictized. This is a state found in radioactive minerals and results from the destructive effects of their own radiation on their crystal lattice. The effect can lead to destroying completely its own crystal lattice while leaving the external appearance unchanged. In the Belcina area, thorite occurs as a constituent mineral, while the Jolotca thorite is an accessory mineral. The Belcina thorite occurs as irregular grains (Fig. 3) of a few mm and much longer up to 1cm in diameter. It could be massive and compact. The Jolotca thorite has idiomorph crystals with habits as square short prisms (Fig. 2), pseudooctahedral crystals. Macroscopically it is nearly opaque being transparent in thin fragments. In transmitted light it is yellow-orange, red, brownish yellow, brownish black, black (Figs. 2 and 3). It has a distinct, poor (110) cleavage (Fig. 2) and is uniaxial (+). The refringence ( $n \approx 1.85$ ), greater than that of the thorogummite, becomes lower when the thorite is metamictized ( $n \approx 1.65$ ). The metamictized areas are isotropic. The quantitative analyses of thorite give mainly ThO<sub>2</sub>, around 80.00 and SiO<sub>2</sub> around 17.00 (%wt) and very little Ce<sub>2</sub>O<sub>3</sub>, UO<sub>2</sub>, Y<sub>2</sub>O<sub>3</sub>, PbO and P<sub>2</sub>O<sub>5</sub> contents (Figs. 4 and 7, and Table 1). A thorite variety containing Ce was known as “freyalite”, actually a discredited mineral species. Other variety of thorite often called “uranothorite” is particularly rich in uranium and has been a viable uranium ore. The old mineral name “calciorthorite” is also discredited, it is an impure thorite variety with trace amounts of calcium. Often Belcina thorite has high Pb (Fig. 4), some Ce, Ca, Fe and Zr (Fig. 7), and very low U contents (Table 1). It is associated with apatite, forming veins or inclusions in it (Figs. 5 left and 6 right), zircon (Fig. 5 left), xenotime-(Y) (Fig. 5 right). The chemical composition of Belcina and Jolotca thorite determined with microprobe can be seen in Table 1 (Hirtopanu *et al.*, 2010a).

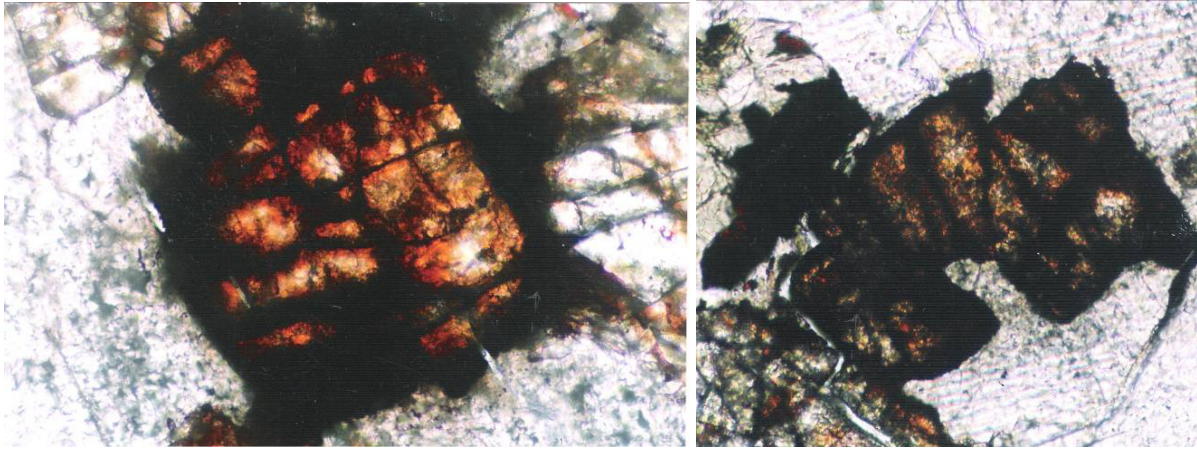


Fig. 2. Thorite (red, with distinct cleavage) in calcite (grey white), NII, sample Dt216, Jolotca area,  $\times 30$  (left); thorite (short prisms, high refringence) transformed central in thorogummite, aechynite-(Ce) (black prism) monazite (corner left, below), NII, sample Dt216A, Jolotca area,  $\times 30$ .

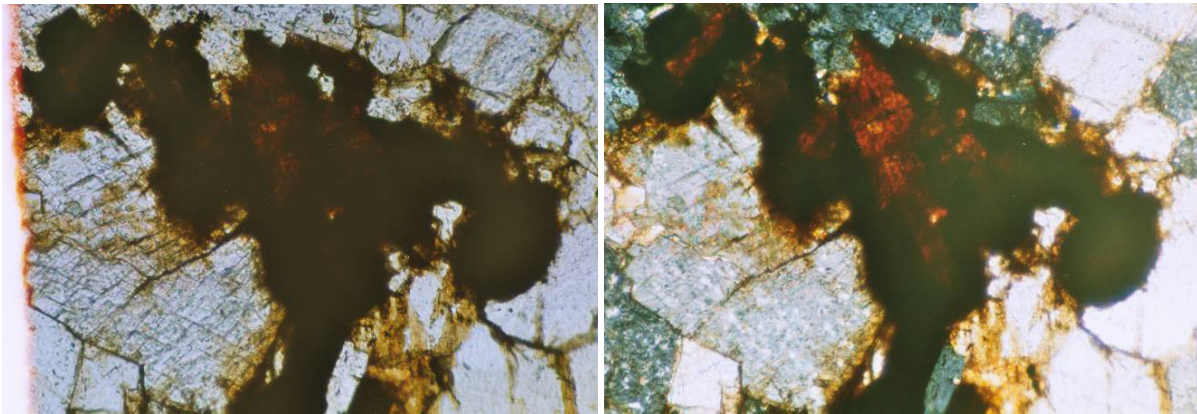


Fig. 3. Thorite (red black) in calcite (grey white), NII (left) and N+ (right), sample Bel 7, Balcina area,  $\times 30$ .

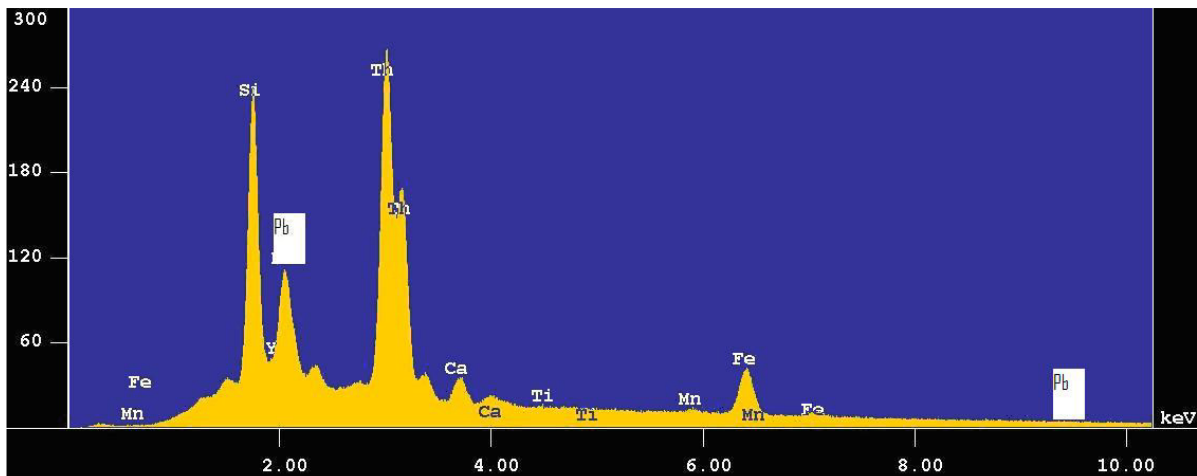


Fig. 4. EDS spectrum of thorite with Pb, Fe, Ca and Mn, sample Bel7/2, (see the BSE image in Figure 6 left).



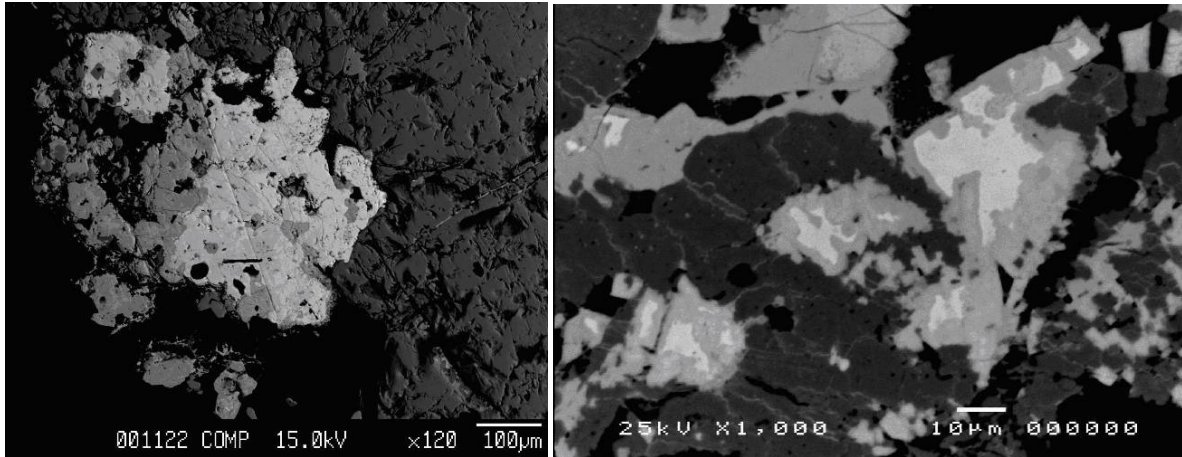


Fig. 5. Thorite (white), thorigummite (around, white grey with oscillatory composition), zircon (grey white, small and smooth, in apatite), apatite (grey dark) and calcite (black), sample 8Bel11/3 (left); Relics of thorite (white) in thorigummite (light grey), xenotime-(Y) (dark grey even), calcite (black), sample Belcina11 (right).

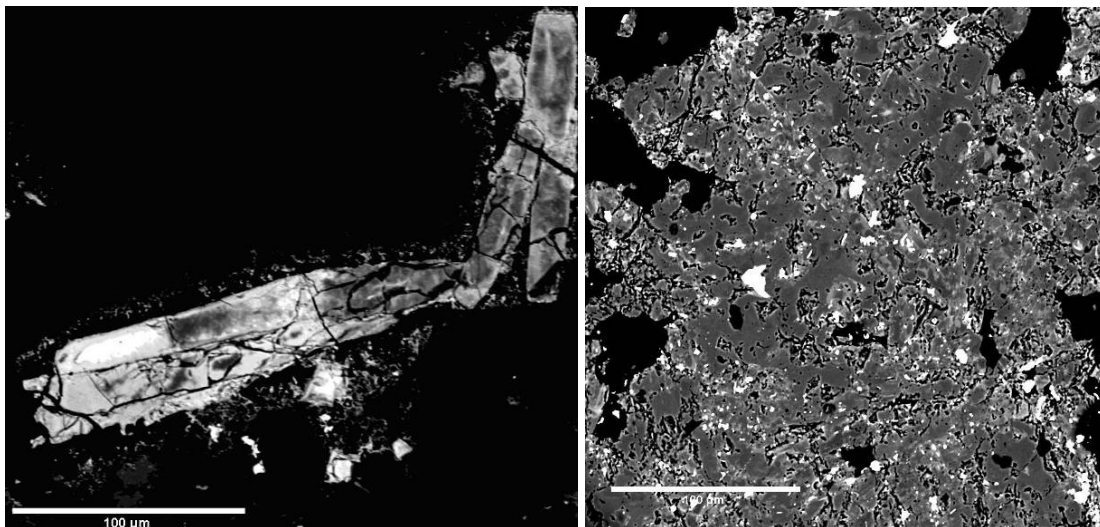


Fig. 6. BSE image of Pb-thorite (bright white) (see its EDS spectrum in Figure 4), thorite with high Si (grey dark) and thorite with high Si and Fe (grey white), sample Bel7/8 (left); BSE image of apatite with thorite (white) inclusions, sample Bel11 (right).

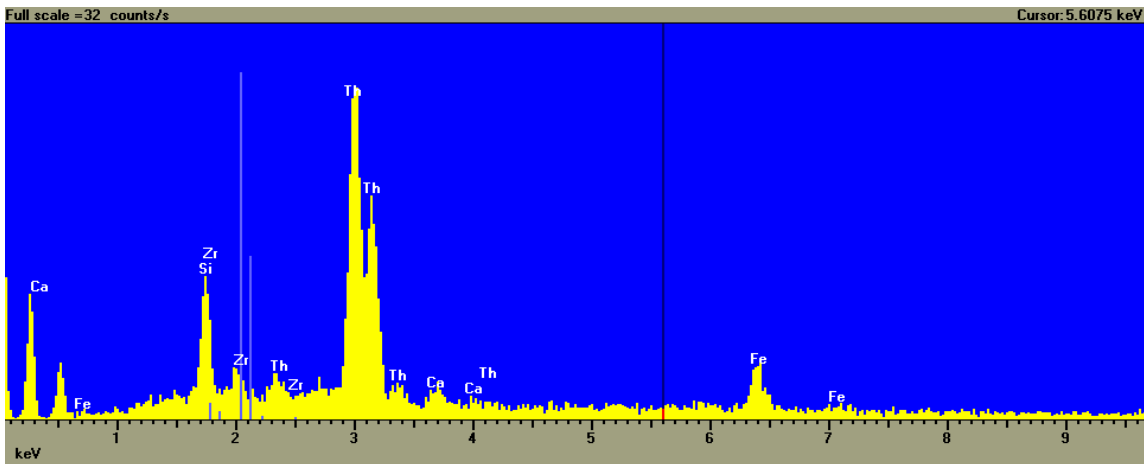


Fig. 7. EDS spectrum of thorite with Zr, Ca, Ce and Fe, sample Bel7/ca.

**Thorogummite**,  $(\text{Th,U})[(\text{SiO}_4)(\text{OH})_4]$ , synonym hydrothorite, tetragonal. It has a zircon structure type. Once it was considered a variety of thorite but is a product of its alteration. The thorogummite is believed to be formed from thorite by hydration which is facilitated by metamictization. Because the thorite is highly radioactive, the mineral is often metamictic. In the world the thorogummite is found in all localities containing thorite, and where the thorite has undergone metamictization. Inside the  $(\text{Th,U})_2(\text{SiO}_4)_{(2-x)}(\text{OH})_{4x}$  formula of thorogummite,  $x$  represents the conversion of one silicate tetrahedron with a negative four charge  $[\text{SiO}_4]^{4-}$  to four hydroxides with a single negative charge each,  $[\text{OH}]^{-1}$ . Thorogummite has some of the  $\text{SiO}_4$  tetrahedrons replaced by four hydroxides. So that, if half the silicate tetrahedrons are replaced by the four hydroxides, where  $X=1$ , the formula would look like this:  $(\text{Th,U})_2\text{SiO}_4(\text{OH})_4$ . In Belcina area the thorogummite occurs as microcrystalline, nodular masses, fine grain rounded aggregates, generally pseudomorphous after thorite (Fig. 8). The thorogummite is always pseudomorphous after thorite, and so it occurs in the same crystals/grains as thorite. Under the microscope it has a yellow, light red, light red yellow, red colour (Figs. 8, 9). Optically it has anomalous isotropy and it is slightly anisotropic. In transmitted light thorogummite differs from thorite by having lower refraction and no cleavage. The hydrothermal solutions have had a big oscillatory compositions, reflected in a compositional variations of thorogummite. It has many red shades (Figs. 8 and 9) in thin

sections or many grey shades in BSE images (Fig. 10). Thorogummite is closely associated/substituted with/by xenotime-(Y) (Figs. 8, 9, 10). Also, it is associated with Th-zircon, apatite, Nb-rutile hematite, goethite, magnetite, sulphides, in Belcina area, as a constituent mineral and with sulphides, LREE-carbonates, allanite-(Ce), monazite-(Ce), Nb rutile, as an accessory mineral in Jolotca area. In both occurrences thorogummite is always associated with thorite, as its secondary modification. The chemical variation of thorogummite, specially the FeO, ZrO, PbO, CaO contents one can see in their EDS spectra in Figs. 11, 12, 13 and 13A. Also, the representative microprobe chemical composition of Belcina thorogummite is displayed in Table 2, near the chemical composition of Jolotca thorogummite. The Belcina thorogummite has in its composition less  $\text{ThO}_2$  than thorite, and high PbO (sometimes more than 10%wt, sample Bel7, points 2 and 4), FeO (up to 20.14%wt, sample Bel11/5) and ZrO (up to 6%wt, Bel11/6) (Table 2). Generally, the  $\text{Ce}_2\text{O}_3$  content is low in both areas, but it is sensibly higher in the Jolotca area. It is interesting to notice the low/no  $\text{UO}_2$  in both areas. The relative high  $\text{P}_2\text{O}_5$  content (up to 1%wt) in the Jolotca thorite/ thorogummite, suggests the presence of a huttonite term in their composition. In the Jolotca area, the thorite is predominant over thorogummite, while in the Belcina area the thorogummite has a large development, the thorite occurring only as a relics in thorogummite.

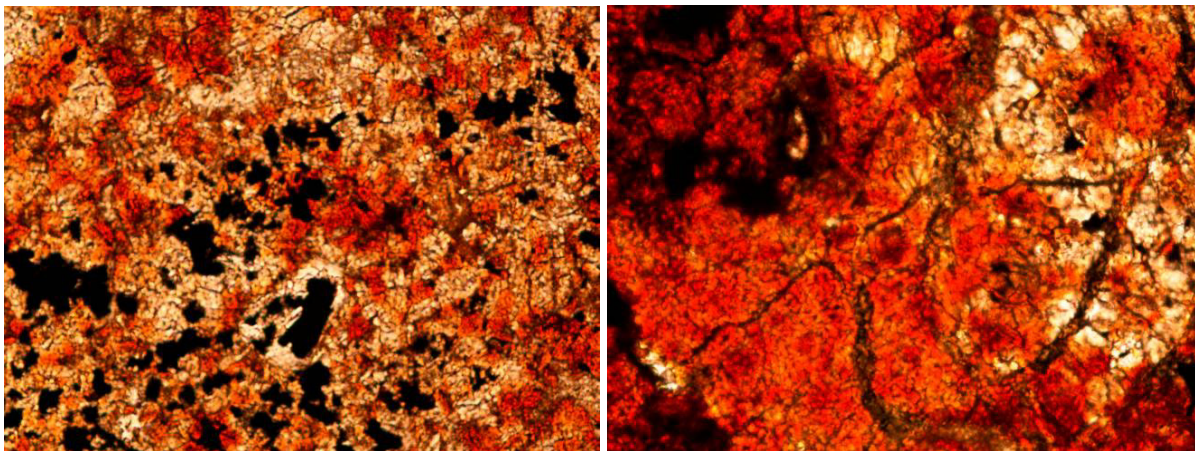


Fig. 8. Thorogummite (red, yellow, yellow red) grown on thorite (black), xenotime-(Y) (white, white-yellow), NII, sample Bel12 (left); thorogummite with oscillatory composition (many red shades), thorite (black, brown relics), xenotime-(Y) (white, white yellow), NII, sample 12B/1,  $\times 35$ .



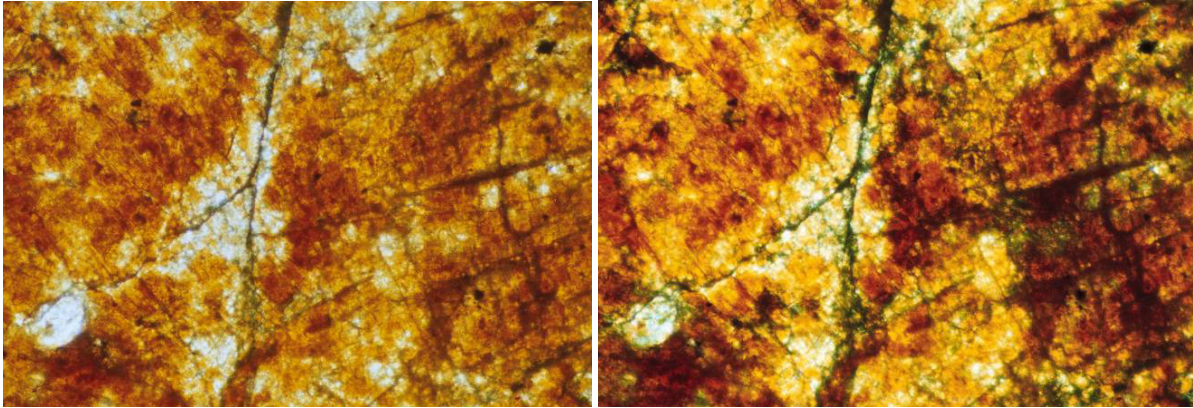


Fig. 9. Thorogummite (red, brown) intergrowth with xenotime-(Y) (white, white yellow, yellow), NII (left), N+ (right), sample Bel6,  $\times 35$ .

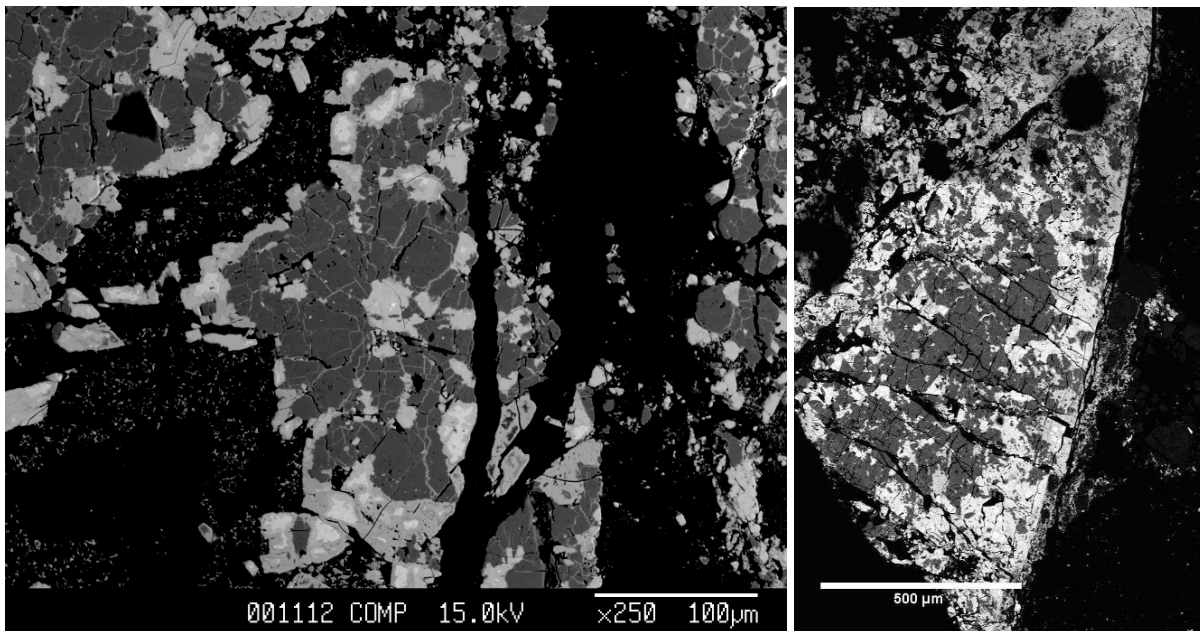


Fig. 10. Thorogummite (white grey) with thorite relics (white) and xenotime-(Y) (grey, big grains), calcite (black), sample Bel12A/2 (left); thorogummite, (light grey) with thorite relics (white), xenotime-(Y) (grey), Bel 12B/2.

The microprobe chemical analyses of Jolotca and Belcina thorite/thorogummite are different from those of Gradistea de Munte occurrence (GM, Sebes Mts, South Carpathians) (Hirtopanu *et al.*, 2012). Unlike the Jolotca and Belcina thorite/thorogummite, the GM thorite/thorogummite has a high  $UO_2$  content. The GM thorite has more than 30%  $UO_2$ , and the GM thorogummite has more than 20%  $UO_2$ . However, the  $UO_2$  content from GM thorite/thorogummite stays lower than  $ThO_2$ . Like the Belcina occurrence, the GM one has Y content much higher than Ce, both occurrences having in common the high Y content. But, unlike

Belcina occurrence, the Zr content is much higher in GM one. The mineralization of rare element minerals in Gradistea de Munte is linked with some alkaline granite (“hidden granite”), while de Belcina occurrence is for certain linked to alkaline intrusive magmatism of Ditrau massif, belonging to the latest hydrothermal/carbothermal event.

In the EDS-s spectra in Figures 11, 12, 13 and 13A can be seen the variations of Th, Si, Zr, Fe, Ca, Al and Pb contents in Belcina thorogummite. Big variations can be observed in Si, Th, Fe, Al and Zr contents.

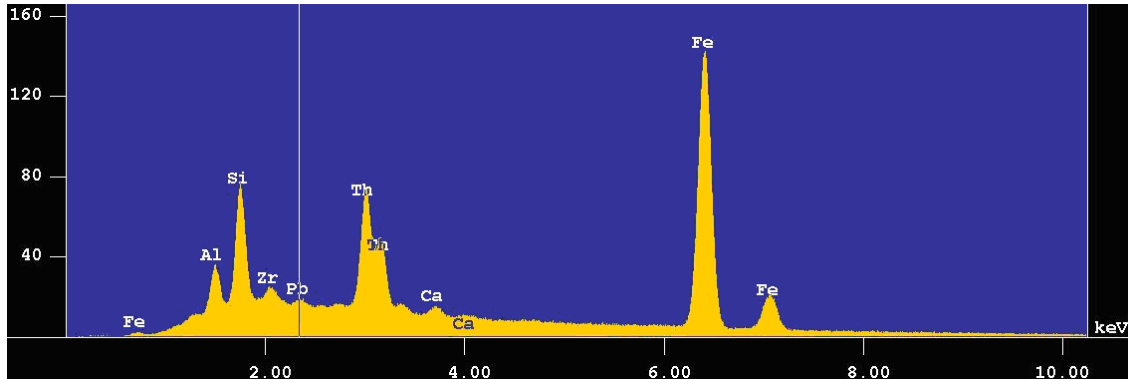


Fig. 11. EDS spectrum of thorogummite with high Fe, Al, and small Zr, Ca and Pb, sample 4Bel7/5.

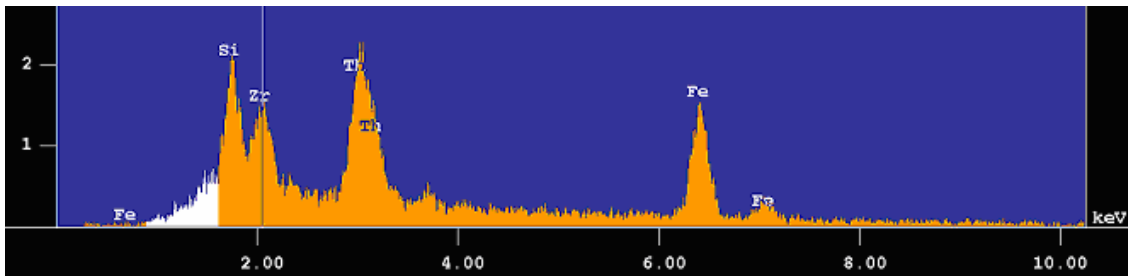


Fig. 12. EDS spectrum of thorogummite with high Zr and Fe, BEL7/ 2.

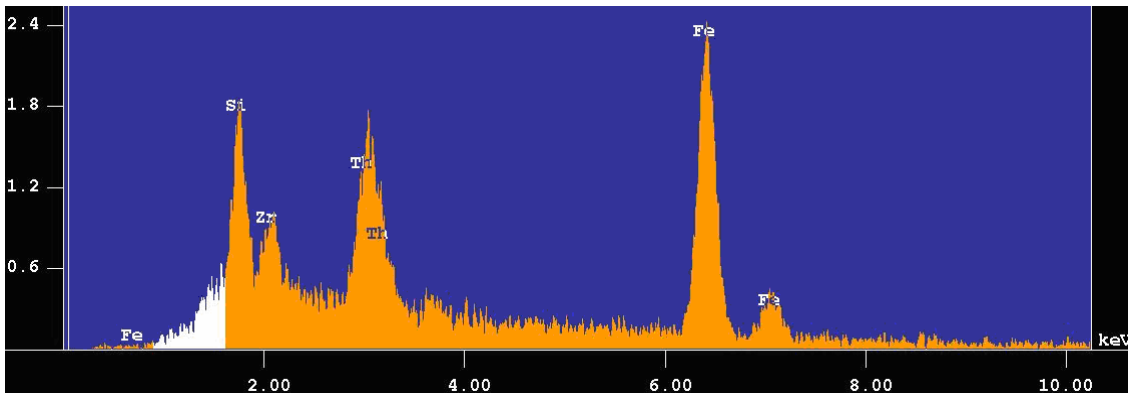


Fig. 13. EDS spectrum of thorogummite with very high Fe and high Zr, sample Bel7/4.

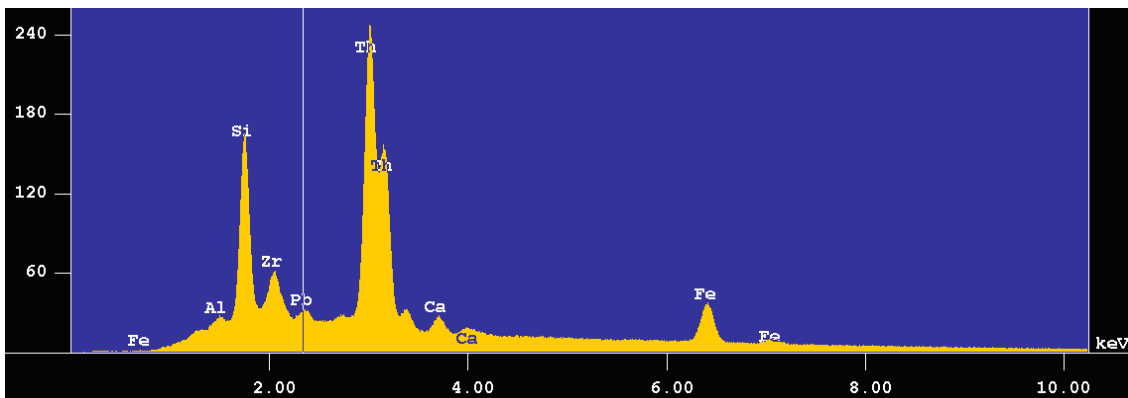


Fig. 13A. EDS spectrum of thorogummite with Zr, some Ca and Pb, and low Al and Fe, sample Bel11/6.



Table 1

The representative microprobe chemical composition of thorite: samples DT19/1, 12; DT212/46, 49; DT1/38, DT13/5; DT216/3 (Jolotca area); Bel12A/1 (Belcina area); sample DT216/25,26 (Jolotca area)

Oxides	1	12	46	49	38	5	3	1	25	26
SiO <sub>2</sub>	17.350	16.471	17.398	18.018	19.371	18.240	17.633	17.133	17.905	16.162
CaO	0.023	0.007	0.020	0.450	0	2.479	2.110	0	1.035	0.764
ZrO <sub>2</sub>	0	0	0	0	3.333	0.011	0	0	0	0
P <sub>2</sub> O <sub>5</sub>	0.584	0.563	0.708	0.035	0	0	0	0	0.489	0.403
MgO	0	0	0	0	0	0	0	0	0	0
La <sub>2</sub> O <sub>3</sub>	0	0	0	0	0	0.345	0	0	0.033	0.011
Ce <sub>2</sub> O <sub>3</sub>	0.087	0.139	0.552	0.017	0.028	1.343	1.001	0.201	0.040	0.073
ThO <sub>2</sub>	77.032	72.721	73.262	78.391	80.532	73.562	78.240	81.283	73.974	72.076
Y <sub>2</sub> O <sub>3</sub>	0.605	0.494	1.098	0	0.223	nd	nd	0	0.482	0.781
Al <sub>2</sub> O <sub>3</sub>	0.020	0	0.016	0.017	0.015	0.159	nd	0	0.006	0.001
Nd <sub>2</sub> O <sub>3</sub>	0.067	0.044	0.291	0.053	0.022	0.594	nd	0	0.126	0.135
UO <sub>2</sub>	0.291	0.269	0.216	0.314	0.298	nd	nd	0	0.234	0.266
F	0.214	0.211	0.088	0.096	0	0.058	nd	nd	0.252	0.405
Gd <sub>2</sub> O <sub>3</sub>	0.173	0.373	0.195	0.042	0.102	0.182	0	0	0.145	0.224
Dy <sub>2</sub> O <sub>3</sub>	0.275	0.313	0.280	0.057	0.071	0	0	0	0.320	0.368
Yb <sub>2</sub> O <sub>3</sub>	0.045	0.008	0.002	0	0.020	0	0	0	0.001	0.006
TiO <sub>2</sub>	0	0	0.007	0.011	0.020	0.004	0	0	0.002	0.001
PbO	nd	nd	nd	nd	nd	nd	0.966	0.924	nd	nd
FeO	nd	nd	0.075	0.119	0	4.047	0.051	0.660	0.150	0.257
MnO	0	0	0	0	0	0	1.000	0	0.228	0.174
Total	96.676	91.603	94.674	97.706	104.035	101.562	100.201	100.2	95.434	92.124

Table 2

The microprobe chemical composition of Belcina and Jolotca thorumite: samples Dt2007/10C/25; Dt212/45, 47, 48; (Jolotca); Bel7/2, 4; Bel11/5, 6; ; Dt216/ 23, 24

Oxides	25	45	47	48	2	4	5	6	23	24
SiO <sub>2</sub>	17.934	16.904	16.046	14.582	19.02	18.633	8.997	16.631	20.713	20.503
CaO	1.005	6.741	0.327	1.113	1.923	2.074	0.627	1.666	0.990	1.876
ZrO <sub>2</sub>	0	0.020	0	0	nd	nd	1.959	5.877	0	0.014
P <sub>2</sub> O <sub>5</sub>	0.673	0.553	0.243	0.149	0	0	0	0	1.083	0.974
MgO	0	0.002	0.030	0.020	nd	nd	0	0	0	0.027
Ce <sub>2</sub> O <sub>3</sub>	0.156	1.925	0	0.014	0	0	0	0	0.087	0.058
ThO <sub>2</sub>	68.493	56.610	58.956	60.563	57.821	65.832	62.840	64.177	66.229	63.849
Y <sub>2</sub> O <sub>3</sub>	1.456	1.075	0.138	0.249	0	0	0	0	0.099	0.246
Al <sub>2</sub> O <sub>3</sub>	0.045	0.249	0	0.027	nd	nd	4.236	0.806	0.153	0.217
Nd <sub>2</sub> O <sub>3</sub>	0.200	1.598	0	0.087	0	0	0	0	0.056	0.03
UO <sub>2</sub>	0.254	0.192	0.186	0.248	0	0	0	0	0.240	0.258
F	0.166	0	0.080	0.024	nd	nd	nd	nd	0	0
Gd <sub>2</sub> O <sub>3</sub>	0.387	0.555	0.034	0.031	0	0	0	0	0.040	0.083
Dy <sub>2</sub> O <sub>3</sub>	0.658	0.504	0.149	0.138	0	0	0	0	0.098	0.287
Yb <sub>2</sub> O <sub>3</sub>	0	0	0	0	0	0	0	0	0	0
TiO <sub>2</sub>	0	0	0	0	0	0	0	0	0	0
MnO	0.466	nd	0.190	0.453	0.757	0.597	0	0	0.300	0.192
FeO	2.797	4.314	0	0.605	9.519	1.322	21.140	10.788	9.410	7.390
PbO	n.d.	n.d.	nd	nd	10.034	11.541	0.201	0.054	Nd	nd
BaO	n.d.	0.475	0	0	nd	nd	0	0	0.119	0.124
Total	94.659	92.582	76.356	78.322	100.00	100.00	100.00	100.00	99.718	96.165

## II. REE(Y)-Phosphates

The phosphates certainly are the most widespread of all rare-earth elements minerals in Ditrau massif, especially the monazite, because this occurs as a constituent mineral in Jolotca area and as an accessory one in Belcina. Reversely, in the Jolotca area the xenotime-(Y) occurs as accessory mineral, and in Belcina area it occurs as an important constituent mineral phase. The Th-apatite as constituent mineral and the monazite-(Ce) and brabantite, as accessory one, are frequently present in Belcina area.

**Xenotime-(Y)**,  $\text{YPO}_4$ , tetragonal. The xenotime-(Y) forms isometric, short to long prismatic crystals sometimes in radial or rosette like aggregates. In transmitted light it is colorless to very pale yellow, yellowish green, yellow or golden yellow (Figs. 14, 15) with weak pleochroism and (100) good cleavage (Fig. 15). It

has high refringence and birefringence (Fig. 15) and it is uniaxial (+). The xenotime-(Y) in samples Bel12B (area 4, point 1), Bel12, Bel9, was investigated with microprobe and its chemical compositions showed only  $\text{Y}_2\text{O}_3$  and  $\text{P}_2\text{O}_5$ :  $\text{Y}_2\text{O}_3=61.40-62.00$  and  $\text{P}_2\text{O}_5=38.60-40.00$  wt(%). In the sample Bel7, xenotime-(Y) shows some Dy and Gd (Fig. 17). In the Belcina area xenotime-(Y) occurs as a constituent mineral always closely associated with thorite which forms relics in thorogummite (Figs. 14, 15, 16). Also, it is associated with zircon, Th-apatite, baddeleyite (?), Fe-oxides/hydroxides, chlorite, siderite, calcite. In the Jolotca area, when the Nb, Ta and LREE-element mineralizations are predominant, xenotime-(Y) occurs as accessory mineral, associated with LREE-carbonates and pyrochlore.

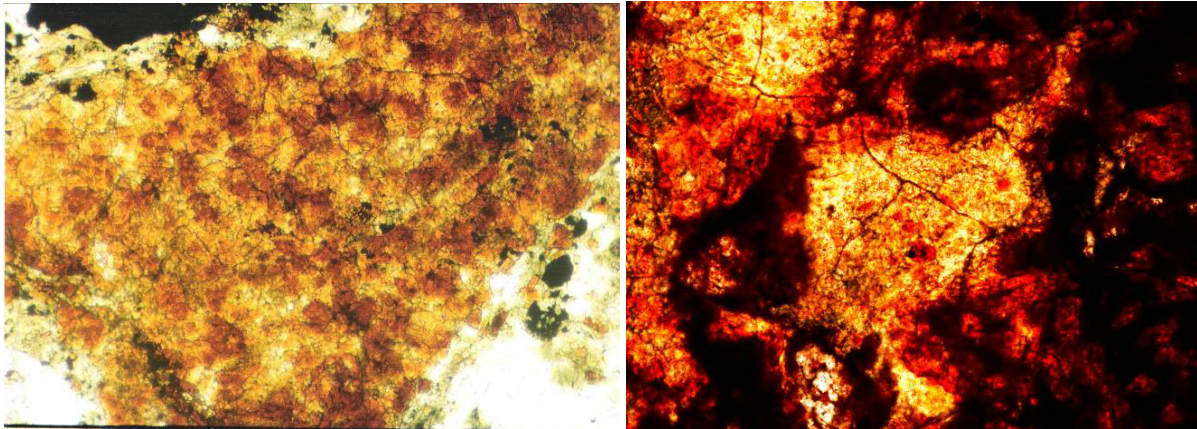


Fig. 14. Xenotime-(Y) (yellow) intergrowth with thorogummite (red) formed on thorite (red black), sample Bel9, NII (left); xenotime-(Y) (yellow-white), thorogummite (red) and thorite (black), NII, Bel/12B/3,  $\times 30$  (right).

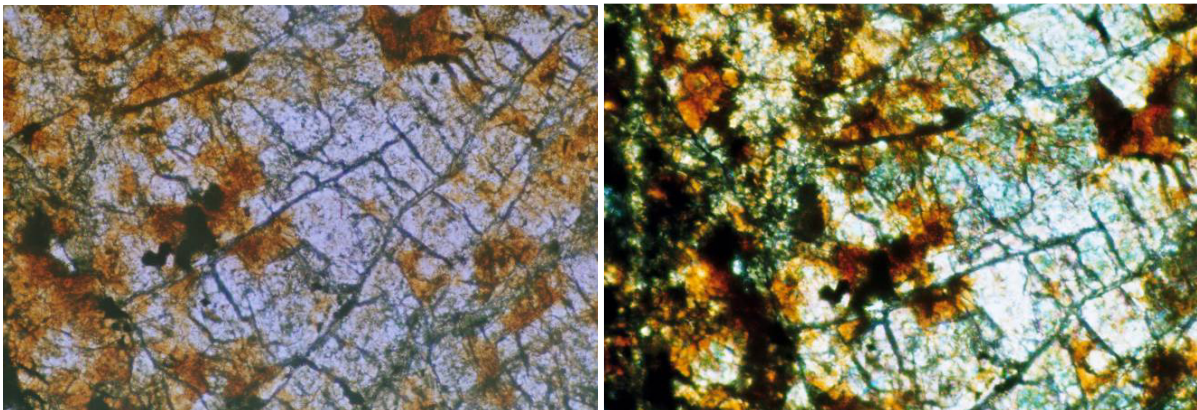


Fig. 15. Xenotime-(Y) (colorless, two good cleavages), thorogummite (red) and thorite (black), NII (left) and N+ (right), sample Bel/12B,  $\times 30$ .

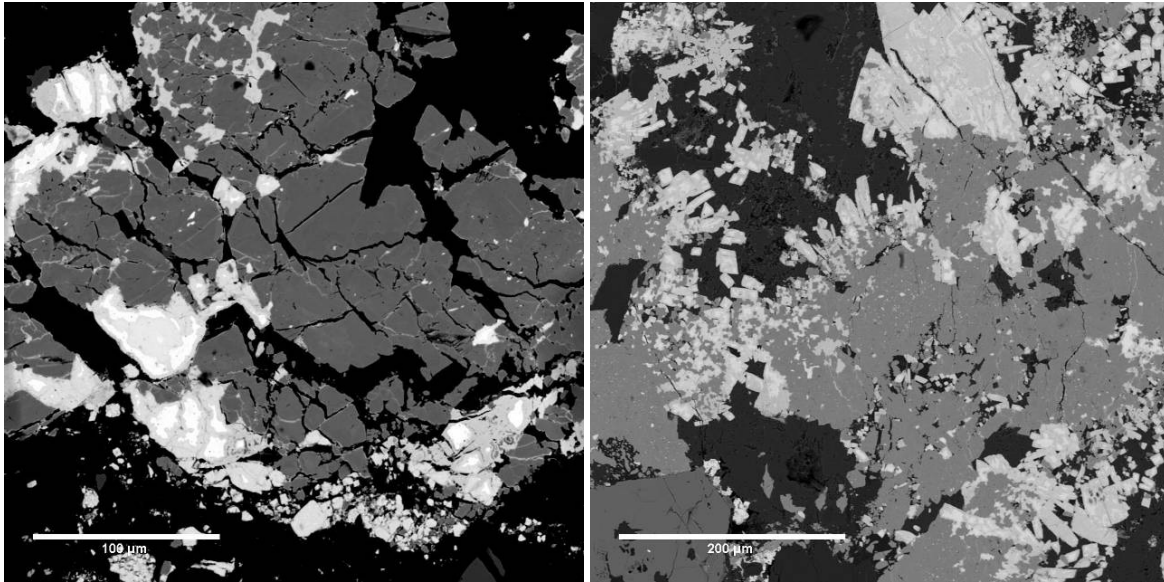


Fig. 16. BSE image of xenotime-(Y) (big grains, dark grey), thorite/thorigummite (with oscillatory composition: white more Th; white grey more Zr less Th; grey less Th, less Zr, more Fe), calcite (black), sample BEL12/5 (left); BSE image of xenotime-(Y) (big grains, grey), thorite/thorigummite with oscillatory composition (more Th, white and less Th light grey, grown on xenotime-(Y), pyrite (grey, left corner bottom) and calcite (black), sample Bell 1/3 (right).

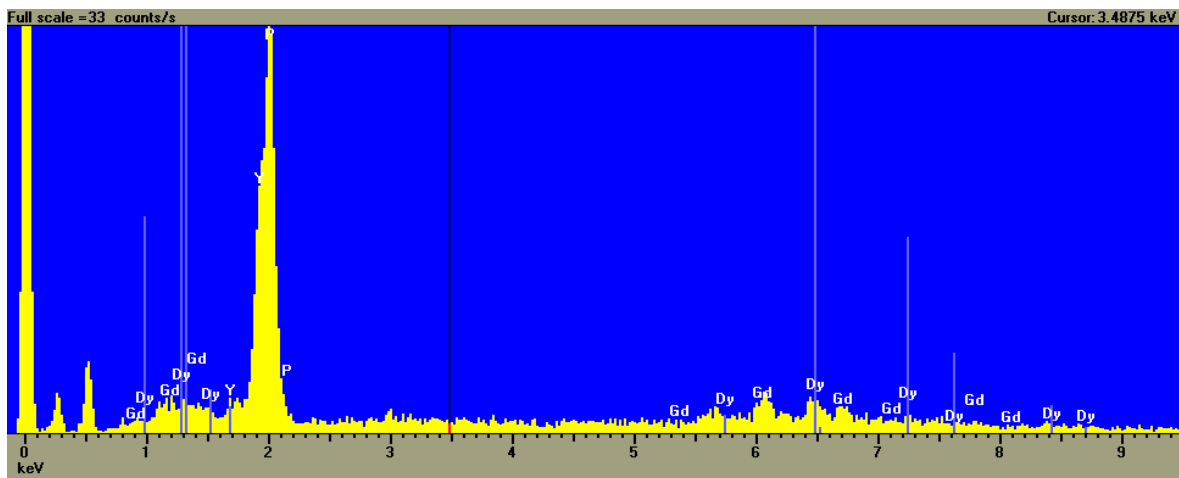


Fig. 17. EDS spectrum of xenotime-(Y) with some Dy and Gd, sample Bel7 /cd.

In the BSE images in Figure 16, the large xenotime-(Y) grains are surrounded by thorigummite with oscillatory composition, which is grown on it, the thorigummite (pseudomorph after thorite) being later than xenotime-(Y). Like monazite-(Ce), and unlike thorigummite, the xenotime-(Y) does not show oscillatory compositions (Fig. 16). The thorigummite in these figures has a compositional variation, with less Th than thorite (white areas on the figure), and with Zr and Fe-rich areas (grey on the figures).

**Th-apatite**,  $\text{Ca}_5(\text{PO}_4)_3(\text{F},\text{OH},\text{Cl})$ , hexagonal. In apatite the most common substitution is  $\text{Ca}^{2+} + \text{P}^{5+} \leftarrow \text{REE}^{3+} + \text{Si}^{4+}$ . A common characteristic of

apatite from Ditrau is its tendency to contain inclusions (or exsolutions?) of -REE, -Ta, -Nb -Y - Zr and Th minerals, such as xenotime-(Y), monazite-(Ce), bastnasite-(Ce), allanite-(Ce), thorite, but their presence is insufficient to account for the total rare elements content. In Belcina area, most frequently is the presence of thorite, zircon/baddeleyite and ferrocolumbite as inclusions. In Figure 6 (right, in the top) one can see inside apatite grains, many small grains of thorite/thorigummite with compositional variations as exsolutions/inclusions and in Figure 19, one can see oscillatory/zoned composition of apatite (variation in Ca and in Th contents of apatite). The Th element can enter the apatite structure (Fig. 18).



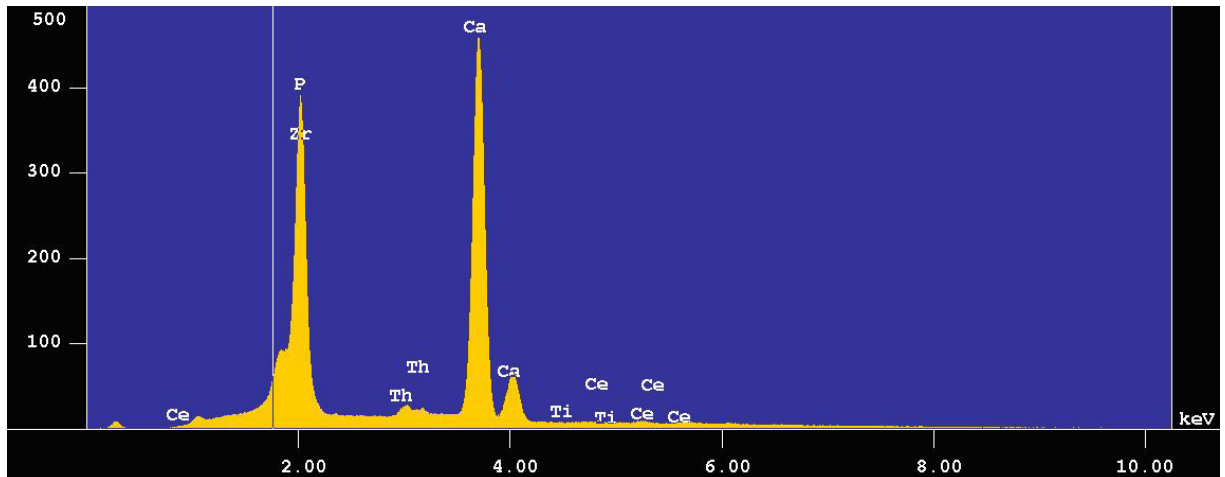


Fig. 18. EDS spectrum of Th apatite, with small Ce and Ti, sample Bel7/3.

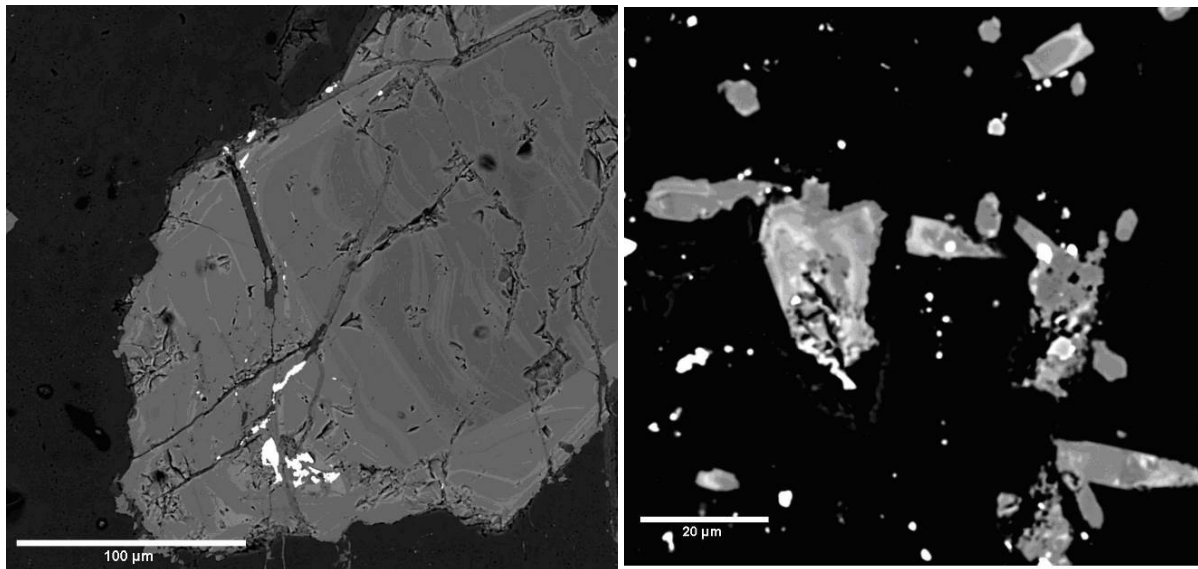


Fig. 19. BSE image of apatite with oscillatory composition (in Ca), monazite (white, small, inside), lepidocrocite (black, around), sample Bel3/2 (left); BSE image of zoned Th-apatite: apatite less Th (grey), apatite more Th (white grey), monazite-Nd (bright white), microcline (black), sample Bel4/3 (right).

**Monazite-(Ce)**,  $(\text{CeLaNdTh})\text{PO}_4$ , monoclinic. Monazite-(Ce) is the predominant phosphates in the Ditrau occurrences. In Jolotca area the big monazite grains/aggregates have a few cm with a specific brick-coloured and radial growth. It is colorless, light yellow or light brown in transmitted light, with weak pleochroism. The refringence and birefringence are high and they increase with Th content (more exactly, with Th silicate component huttonite) in the monazite structure. It has a (100) moderate and a (001) weak cleavages, sometimes fine twinned on (100). The chemistry of Jolotca monazite has a high contents of  $\text{Ce}_2\text{O}_3$ , followed by  $\text{La}_2\text{O}_3$ ,  $\text{Nd}_2\text{O}_3$ ,  $\text{ThO}_2$ ,  $\text{Pr}_2\text{O}_3$ ,  $\text{Sm}_2\text{O}_3$ ,  $\text{Gd}_2\text{O}_3$ ,

$\text{Yb}_2\text{O}_3$  si  $\text{Er}_2\text{O}_3$ , in decreasing order. The Belcina monazite has a higher  $\text{Nd}_2\text{O}_3$ , sometimes it could be **monazite-(Nd)**,  $(\text{NdCeThLa})\text{PO}_4$ , with less  $\text{Ce}_2\text{O}_3$  and high  $\text{ThO}_2$  and  $\text{CaO}$  contents (Fig. 20). It occurs sometimes in the same sample with monazite-(Ce), which has small Th content and no  $\text{CaO}$  (Fig. 21). In Jolotca area predominantly is monazite-(Ce). The Jolotca monazite occurs as a constituent mineral, being associated with LREE carbonates, especially bastnasite-(Ce), with allanite-(Ce) and calcite. The Belcina monazite occurs as accessory mineral, being associated with thorite/thorogumite, xenotime-(Y), allanite-(Ce) and apatite.

**Smirnovkite (?)**,  $(\text{Th,Ce,Ca})(\text{P,Si,Al})(\text{O,OH,F})_5$  is a not well-characterized mineral species. It is present in Belcina area and was determined with microprobe, in sample TDT, point 1b. Its representative chemical composition is:  $\text{Y}_2\text{O}_3=0.111$ ,  $\text{SiO}_2=11.783$ ,  $\text{P}_2\text{O}_5=8.058$ ,  $\text{ThO}_2=33.533$ ,  $\text{UO}_2=0.114$ ,  $\text{Nd}_2\text{O}_3=6.588$ ,  $\text{La}_2\text{O}_3=2.228$ ,  $\text{Ce}_2\text{O}_3=9.368$ ,  $\text{Yb}_2\text{O}_3=0.111$ ,  $\text{Dy}_2\text{O}_3=0$ ,  $\text{Gd}_2\text{O}_3=1.166$ ,  $\text{Al}_2\text{O}_3=0.599$ ,  $\text{ZrO}_2=1.055$ ,  $\text{CaO}=2.257$ ,

$\text{MnO}=0$ ,  $\text{FeO}=0$ ,  $\text{B}_2\text{O}_3=0$ ,  $\text{TiO}_2=0$ ,  $\text{F}=0.195$  (% wt), total=102.154.

**Brabantite,  $\text{CaTh}(\text{P,Si})\text{O}_4$** , monoclinic, partially metamict. It is present as elongated small crystals in crystalline or fine granular aggregates, associated with thorite, thoringummite, zircon, hematite, lepidocrocite and diverse carbonates. Its EDS spectrum can be seen in Figure 22.

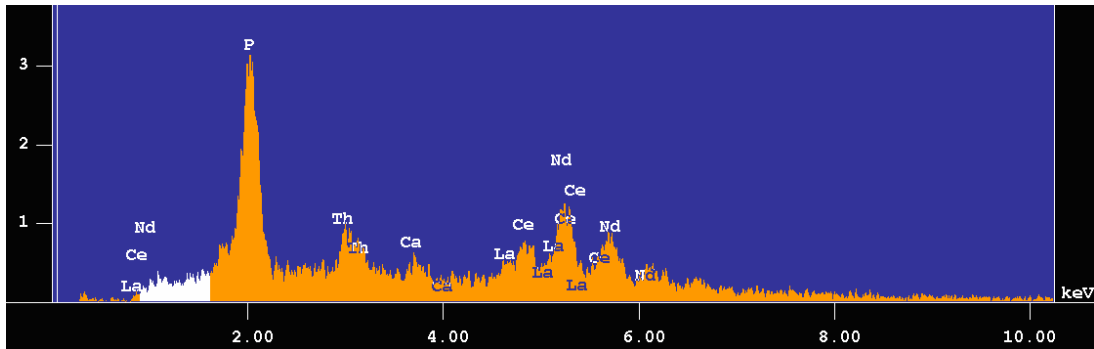


Fig. 20. EDS spectrum of Th monazite-(Ce), with high Nd content, sample Bel7/1.

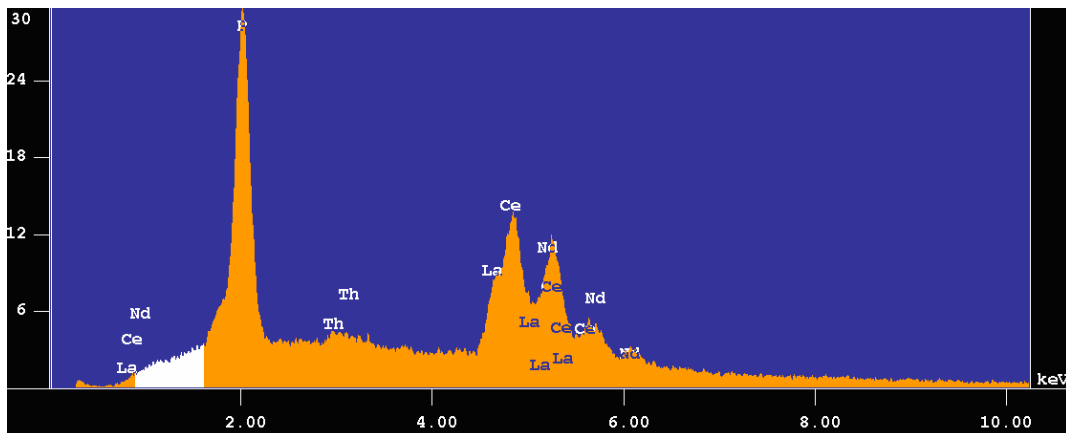


Fig. 21. EDS spectrum of monazite-(Ce), with low Th content, sample Bel4/2.

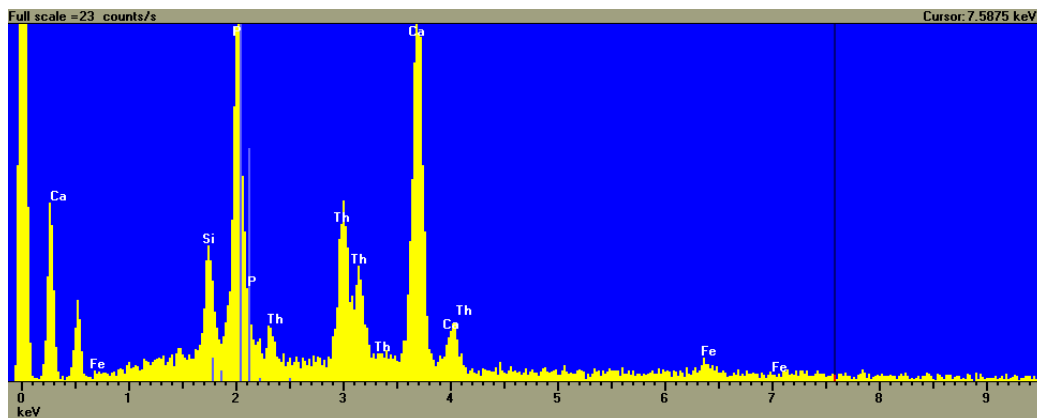


Fig. 22. EDS spectrum of brabantite, sample Bel 7/ce.

**III. Other associated rare element minerals:  
Zircon, Nb-rutile, ilmenorutile, ferrocolumbite,  
Thorianite, uraninite, baddeleyite, sulphides  
and native mercury**

**Zircon**,  $ZrSiO_4$ , tetragonal. In the Belcina area zircon occurs as an accessory mineral of a few mm and more. It has different chemical composition with respect to Jolotca zircon. The Jolotca zircon has little  $ThO_2$  (<1%wt), but the Belcina zircon, where the environment is rich in Th, the  $ThO_2$  content is very high (>20%wt) (Fig. 23). In both occurrences, the Hf and Y were detected in very small quantities. Also, the Belcina zircon has some Ca and Fe contents, as have the thorianite and thorogummite, with which it is isostructural and with which it forms a complete series. It is associated with magnetite, Th-apatite, thorite, thorogummite, molybdenite, Nb rutile, calcite,

siderite, goethite, lepidocrocite, natrolite and apatite. The Jolotca zircon grains have concentric zoning due to variation in the mineralizing hydrothermal fluid composition. In Fig. 24 left the core of zircon (grey in the picture) has Si, Zr little Th and Ca, the middle area (blue) has Si, more Zr little Hf, there follows an area with Si, Zr, little Ca and Fe (white red area), and a rim area which has again Si, Zr, little Hf. The Belcina zircon often alters chemically, because it contains Th, and cations of valence lower than four, and it transforms into cyrtolite, a variety with the formula  $Zr(SiO_4)(OH)_4$ . The cyrtolite is characterized by the presence of water and by a deficiency of silica. These features provide the proof for suspecting the existence of a substitution in zircon such as that indicated for thorianite substituted by thorogummite.

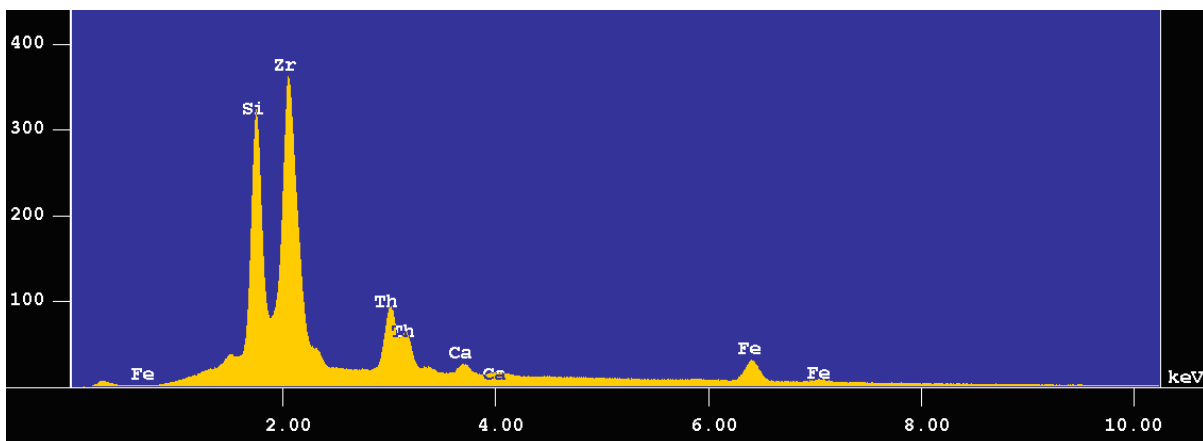


Fig. 23. The EDS spectrum of Th-zircon, sample Bel7/3.

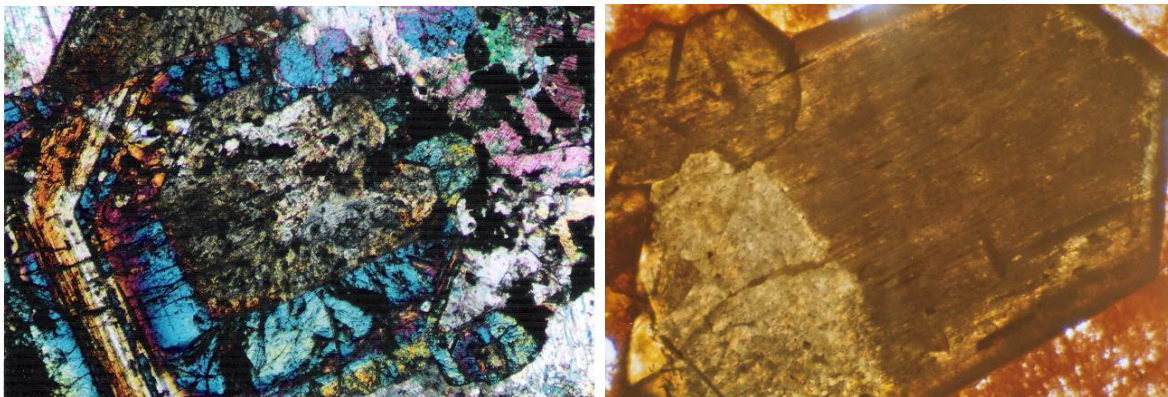


Fig. 24. Zircon (big grain zoned), thorite (black as inclusions), monazite (right, corner, top), in calcite (high birefringence), N+,  $\times 25$ , sample 17DtA/4 (left); Nb rutile (big grain, yellow-brown) altered in anatase (yellow-green), Fe-hydroxides (red), sample Bel13A,  $\times 30$ .



**Nb-rutile, (Nb,Ti)O<sub>2</sub>**, tetragonal. The grains of niobian rutile, less frequently than in Jolotca area, have a black bright colour. In transmitted light Nb rutile has brown, brown violet to yellow green, yellow reddish colour with great pleochroism and complex zonations. The zonation composition of Nb rutile can be seen in its BSE images (Fig. 25). The substitution in niobian rutile and ilmenite is due to the isomorphism of Ti<sup>4+</sup> with Nb<sup>5+</sup> and Fe<sup>2+</sup>, goes probably after the scheme:  $2\text{Ti}^{4+} \leftarrow \text{Nb}^{5+} + (\text{Fe}, \text{Al})^{3+}$ ;  $3\text{Ti}^{4+} \leftarrow 2\text{Nb}^{5+} + \text{Fe}^{2+}$ . The chemistry of niobian rutile shows omnipresent fluctuations because of variation of activity of components involved in the parental medium and thus the grains have an oscillatory zoning. The content of Nb<sub>2</sub>O<sub>5</sub> predominates over Ta<sub>2</sub>O<sub>5</sub>. The range of Nb<sub>2</sub>O<sub>5</sub> varies generally between 2-15% wt. Also, the content of FeO (1-15%wt) is much higher than that of MnO (0-0.1%wt). The Belcina Nb rutile has following microprobe representative

chemical composition: Nb<sub>2</sub>O<sub>5</sub>=25%, TiO<sub>2</sub>=64% and FeO=10% wt, total=99.00. Because of such a high Nb content, it could be termed ilmenorutile. Some low Cr<sub>2</sub>O<sub>3</sub> contents in niobian rutile were determined in the sample Bel13A (see its EDS spectrum in Fig. 26). The chemical composition of this point, determined with microprobe is: TiO<sub>2</sub>=87.626; Nb<sub>2</sub>O<sub>5</sub>=10.895; Cr<sub>2</sub>O<sub>3</sub>=1.478 (%wt), total = 99.999. The Cr<sub>2</sub>O<sub>3</sub> presence in its composition could suggest its mantle origin. The Nb rutile is associated with rutile (grown on it) (Fig. 25 right), apatite, thorite, thorigummitte, xenotime-(Y), zircon, goethite, hematite, monazite-(Ce), ferrocolumbite, calcite, siderite. The Belcina Nb rutile is sometimes transformed in secondary green-yellow grey anatase (Fig. 24 right), trimorphous with brookite and rutile. The anatase could be derived from Nb rutile through hydrothermal solution.

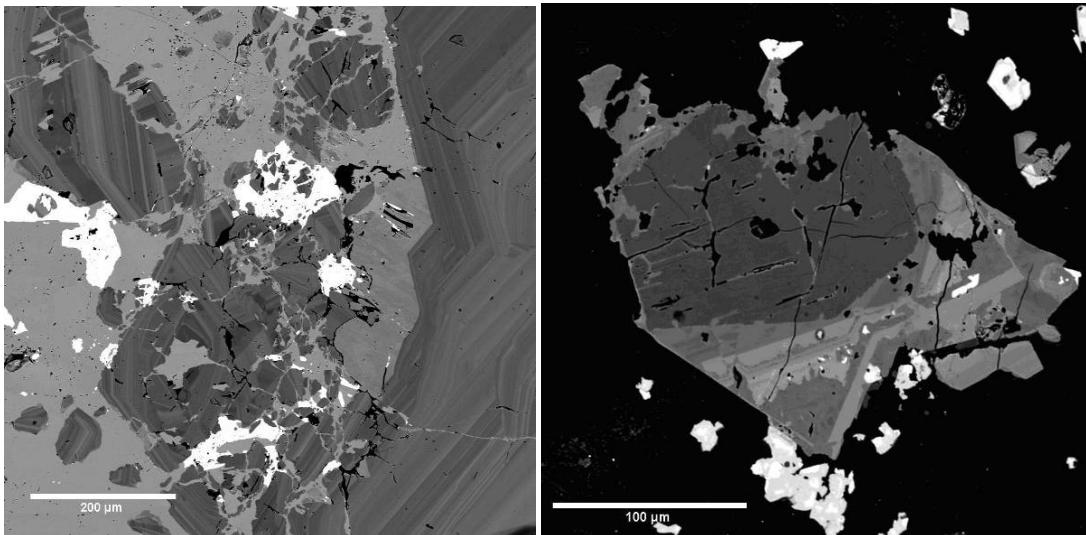


Fig. 25. BSE image of Nb rutile (dark grey with oscillatory composition), ferrocolumbite (white), ilmenite (grey), sample Dt214R (left); BSE image of rutile (centre, black grey), Nb rutile (around, grey light, oscillatory composition, with small white bright ferrocolumbite inside, thorite (white, around), quartz (black), Bel10A/4a.

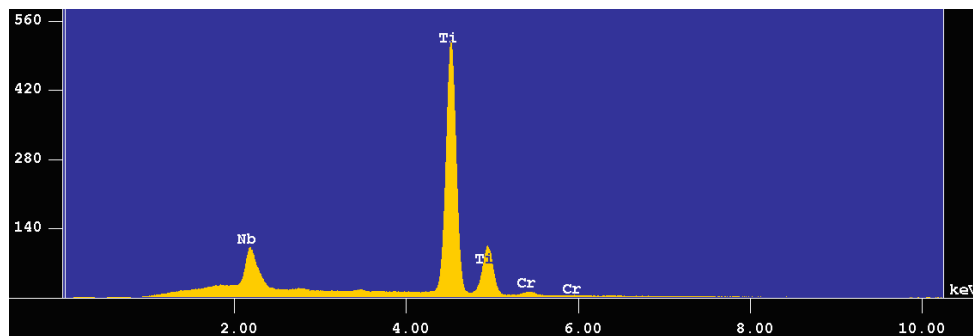


Fig. 26. EDS spectrum of Nb rutile with Cr, sample Bel/13A, point 1.

**Ilmenorutile**, (Ti,Nb,Fe)O<sub>2</sub>, tetragonal. The ilmenorutile has much more Nb and Fe than niobian rutile. It occurs typically intergrown with columbites, ilmenite, niobian rutile in large prismatic grain to a few mm and much more. In Belcina area it is less spread than in Jolotca. Black, dark yellow-green to red or reddish brown in transmitted light with distinct (110) and imperfect (100) cleavages. It is uniaxial (+) and has a strong pleochroism, from brown to dark bluish green or greenish blue. The Nb<sub>2</sub>O<sub>5</sub> content of ilmenorutile determined with microprobe analyses, has variations between 25-35%wt in Belcina area (Table 3) and between 35-38% in Jolotca area (Hirtopanu *et al.*, 2010a).

**Ferrocolumbite** (FeMnMg)Nb<sub>2</sub>O<sub>6</sub> and **manganocolumbite** (MnFeMg)Nb<sub>2</sub>O<sub>6</sub>, are orthorhombic. The orthorhombic minerals of this group have a general formula AM<sub>2</sub>O<sub>6</sub>, where A=Fe, Mn, Mg and M=Nb, Ta. Minor quantities of Fe<sup>3+</sup>, Sc, Ti, Sn and W are commonly present. End-member compositions include: ferrocolumbite (FeNb<sub>2</sub>O<sub>6</sub>), manganocolumbite (MnNb<sub>2</sub>O<sub>6</sub>), manganotantalite (MnTa<sub>2</sub>O<sub>6</sub>) and magnocolumbite(MgNb<sub>2</sub>O<sub>6</sub>). Compositions with a dominante ferrotantalite component (Fe>Mn) (Ta>Nb)<sub>2</sub>O<sub>6</sub> are also known but the end member FeTa<sub>2</sub>O<sub>6</sub> belongs to the tetragonal tapiolite series. The columbites-tantalites are decidedly the most widespread of the all Nb, Ta-bearing minerals, found in substantial quantities in most types of deposits in the world (Cerny & Ercit, 1985). At Ditrau, the columbites commonly occur as

a primary phase or it may originate as a secondary replacement product of earlier minerals. Metamictization of columbites occurs in the presence of U and Th, especially in the Belcina area. The composition of columbites is much more restricted to the Nb and Fe-rich ones (Table 4). The columbites have short prismatic or equal grains and form groups or aggregates of subparallel crystals of a few mm up to 1cm. It has a distinct cleavage on (100) and less distinct on (010). In transmitted light they are red to brown, brown black colour. The cleavages and the biaxial optical character differentiate them from the pyrochlores with the same colour. In transmitted light the manganocolumbite has a red light colour, while the ferrocolumbite has a dark red colour to black. Sometimes, the ferrocolumbite is opaque, especially when the Fe content is too high. In Jolotca area the columbites occur in many associations: (a) association with pyrochlore as little veins in alkaline rocks; (b) with LREE-carbonates, monazite-(Ce), pyrochlore and allanite-(Ce) in calcite carbonatite rocks; (c) with fluorite, Na-amphiboles and Na-pyroxenes in fenite rocks; (d) with Nb-Ti-Fe minerals like Nb rutile, ilmenorutile, ilmenite (Fig. 25 left), in calcite carbonate rocks. In the Belcina area the ferrocolumbite is much more frequently than in Jolotca one, where the manganocolumbite is predominant. The EDS spectrum of Belcina ferrocolumbite one can see in Figure 27. The Belcina ferrocolumbite is associated with apatite, Nb-rutile, thorite, throgummite, xenotime-(Y), monazite-(Ce), brabantite, zircon, magnetite.

Table 3

Representative microprobe composition of Belcina ilmenorutile, sample Bel/10A, points 1-4 and 9-10

Oxides%	1	2	3	4	9	10
Nb <sub>2</sub> O <sub>5</sub>	24.798	26.868	25.016	28.041	34.419	34.996
Ta <sub>2</sub> O <sub>5</sub>	0.061	0.157	0	0	0	0
MnO	0	0.011	0.033	0.013	0	0.065
FeO	9.383	9.784	9.115	9.636	6.141	6.52
MgO	0	0.205	0.158	0.057	0	0.122
TiO <sub>2</sub>	63.672	61.883	63.537	59.538	60.004	59.335
Total	98.907	98.703	97.859	97.285	100.564	100.973

Table 4

The microprobe chemical composition of Belcina ferrocolumbite, samples Bel12/1-9 and Bel10A/1A

Oxides%	1	2	3	4	5	6	7	8	9	1A
Nb <sub>2</sub> O <sub>5</sub>	73.566	71.537	73.43	71.329	73.904	74.071	73.125	73.809	71.434	74.427
Ta <sub>2</sub> O <sub>5</sub>	0	0	0	0	0	0.255	0	0	0	0
MnO	7.83	8.172	6.032	8.17	6.581	8.526	9.643	5.664	8.260	0
FeO	16.09	16.583	17.36	16.639	16.16	15.736	14.83	16.775	16.110	18.269
MgO	0.431	0	0.459	0.387	0.421	0.52	0.512	0.059	0.256	0
TiO <sub>2</sub>	2.213	2.196	2.586	2.151	2.611	2.30	2.283	3.149	3.544	3.077
Total	100.109	98.488	99.867	98.676	99.677	101.40	100.393	99.456	99.604	95.773

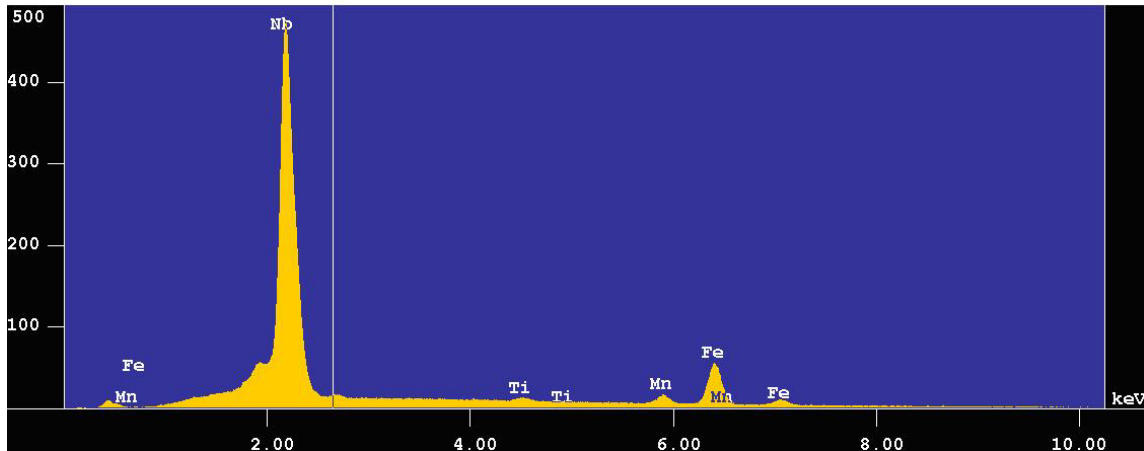


Fig. 27. EDS spectrum of ferrocolumbite, Bel/10A/2.

In the Jolotca area the columbites have a composition with high  $\text{Nb}_2\text{O}_5$ , varying between 70-80%wt. The  $\text{MnO}$  content (11-13%wt) is higher than  $\text{FeO}$  (6-7%wt), the columbite term being manganocolumbite.

**Thorianite**,  $\text{ThO}_2$ , and **uraninite**  $\text{UO}_2$ , (both cubic), form rounded very little grains of microscopic dimensions, of brown red, black colour. Thorianite forms a series with uraninite. They occur very rarely, as accessory minerals, in associations with thorite/thorogummite, zircon, monazite, brabantite.

**Baddeleyite**,  $\text{ZrO}$ , monoclinic, was determined only by microprobe. It has small Gd and Eu contents, as well as very low Th, Ca, Ce, Nd contents. It is associated with phlogopite and monazite-(Ce) in Jolotca area and with thorite/thorogummite, xenotime-(Y), calcite/dolomite, Nb rutile in Belcina area.

**Native mercury**, **Hg**, amorphous, was determined in Belcina area, with microprobe analyses, in close association with **cinnabar**, magnetite and galena, as very little veins in dolomite, calcite and apatite.

**Sulphides.** The Belcina sulphides, less common than in Jolotca area, are disseminated as small grains or form little veins in common carbonates. The mainly sulphides components are: pyrite, galena, sphalerite, chalcopyrite, tetrahedrite, arsenopyrite, molybdenite, pyrrhotite, arsenopyrite and cinnabar. The cinnabar/ metacinnabar (?), associated with native Hg were recently determined in Belcina area. They often are associated with galena, forming together little veins in dolomite, iron dolomite and ankerite.

#### IV. Gangue/common minerals: carbonates, natrolite, apatite, pectolite, goethite, lepidocrocite and chlorites

Several common carbonates, like ferrodolomite, dolomite, siderite, ankerite, calcite, occur as a large development, having crystals of decimeter dimensions and constituting the main gangue minerals. **Ferrodolomite I**, closely associated with thorite/thorogummite (Fig. 28 left) and xenotime mineralization ( $\pm$ some sulphides) was first, and **ferrodolomite II**, was formed later and it is "barren gangue", having no associated mineralization. **Calcite**, less spread than ferrodolomite, is the latest carbonate, having sphalerite and galena inclusions. Following carbonates, **the apatite** is the most widespread gangue mineral being closely associated with thorite/thorogummite (Fig. 29), diverse carbonates, Nb-rutile, xenotime-(Y), zircon. It occurs as a constituent mineral in the thorite/thorogummite associations.

**Natrolite**,  $\text{Na}_2\text{Al}_2\text{Si}_3\text{O}_{10}\cdot 2\text{H}_2\text{O}$ , orthorhombic, pseudohexagonal. It belongs to zeolite group. Natrolite has short to long prismatic crystals, up to 1cm and even more. It occurs as radiating or stellate groups, granular, fibrous, compact. In transmitted light it is colourless, has (110) perfect cleavage and parting on (010). It is biaxial positive, having a 2V around  $60^\circ$ . Its representative chemical composition, determined by microprobe is:  $\text{SiO}_2=55.01$ ,  $\text{Al}_2\text{O}_3=20.43$ ,  $\text{Na}_2\text{O}=14.30$ ,  $\text{H}_2\text{O}=10.00$ (%wt), total=99.74 (sample Bel11, point 4); the  $\text{H}_2\text{O}$  content was estimated through difference. In Belcina area natrolite is associated with thorite/thorogummite (Fig. 28 left), sphalerite and chamosite (Fig. 28 right).



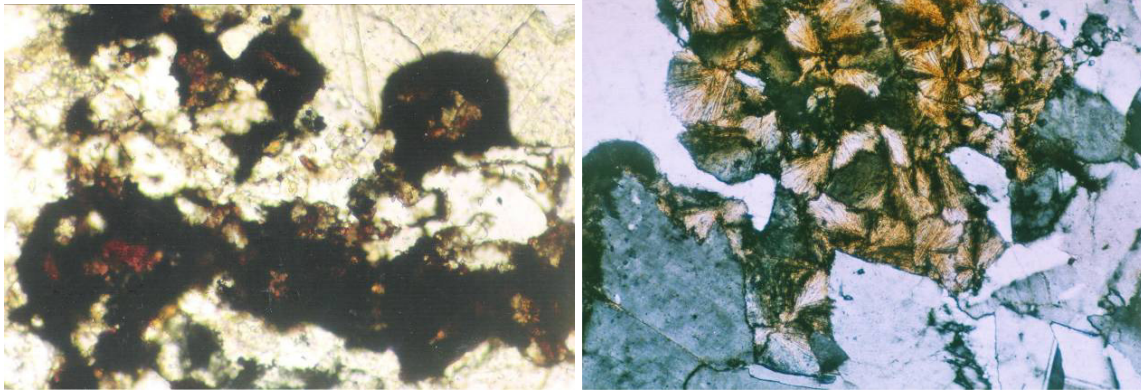


Fig. 28. Ferrodolomite I (pink light) with thorite/thorogummite (red black)+natrolite (white) vein, NII, sample Bel9, (left); radiary fibrous chamosite (yellow brown) in natrolite (white/gray, twinned), N+, sample Bel/7,  $\times 30$ .

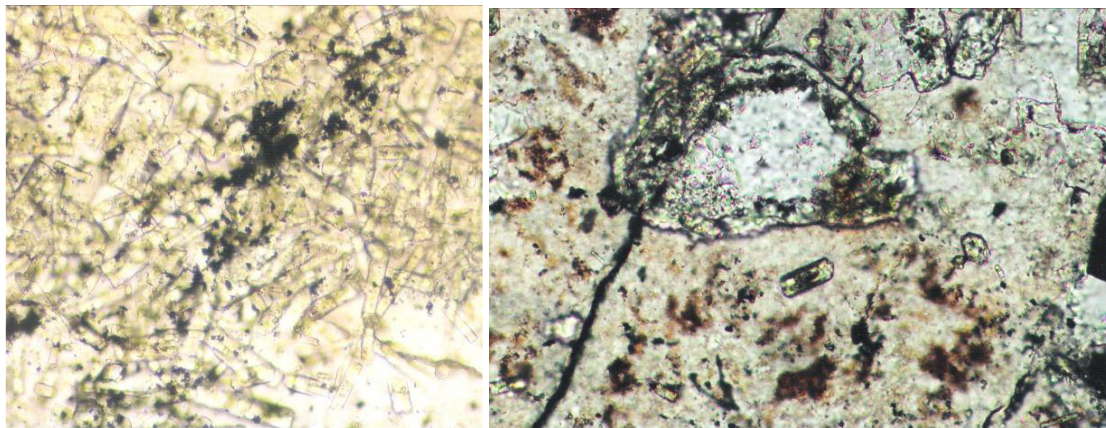


Fig. 29. Apatite (prisms) cut by thorite (small, black) vein, NII (left); zoned apatite with marginal small thorite inclusions, thorite/thorogummite (small red black) in a common carbonates/quartz mixture.

**Chamosite**,  $(\text{Fe}^{2+}, \text{Mg}, \text{Fe}^{3+})_5\text{Al}(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH};\text{O})_8$ , monoclinic, occurs as small radiating crystals or massive. It has one cleavage (001) perfect. Green, greenish grey, black, brown; in thin sections, colourless, yellowish, green (Fig 30, right), light brown. Optically it is biaxial, with 2V around  $20^\circ$ . The Belcina chamosite has a pleochroism weak to moderate; X=yellow-green, green, golden yellow to light brownish; Y=Z=green to dark green. It forms a series with clinochlore. Its representative chemical composition determined with microprobe is (%wt):  $\text{SiO}_2=26.101$ ;  $\text{Al}_2\text{O}_3 = 18.596$ ;  $\text{FeO}=33.968$ ;  $\text{MgO} = 10.334$  10.334;  $\text{H}_2\text{O}\approx 12.00$ , total=100.99. The chamosite is not a secondary mineral, being a late hydro- thermal mineral, later than the thorite, thorogummite and xenotime-(Y). Because of this association with Th and Y minerals, it can have some Y and Th in its chemical composition. This Y-Th chlorite has higher refringence and birefringence than common chamosite (Fig. 28, right).

**Clinochlore**,  $(\text{MgFe}^{2+})_5\text{Al}(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH})_8$ , forms a series with chamosite. It occurs as pseudo-

hexagonal grass green, olive green crystals, being more frequent in Jolotca area, where it is associated with LREE-carbonates, especially with bastnasite-(Ce), parisite-(Ce), synchysite-(Ce) and with some LREE-silicates. Also, in both areas, it is associated with monazite-(Ce) and allanite-(Ce).

**Pectolite**,  $\text{NaCa}_2\text{Si}_3\text{O}_8(\text{OH})$ , orthorhombic. It forms a series with serandite  $\text{Na}(\text{Mn}, \text{Ca})_2\text{Si}_3\text{O}_8(\text{OH})$  (triclinic). Pectolite develops as a good prismatic, tabular crystals (Fig. 30, left) of a few mm up to 3-4 cm in size. In thin sections it has perfect cleavage on (001) and (001) and it is colourless. Optically, the pectolite is biaxial positive having a 2V around  $60^\circ$ . It has a medium refringence and a high birefringence in bright multicolours and frequently is twinned with the twin axis (010) (Fig. 30 left). The Belcina pectolite occurs as a primary hydrothermal mineral. The representative microprobe chemical analyses of Belcina pectolite show  $\text{Na}_2\text{O}=8.44$ ,  $\text{CaO}=33.25$ ,  $\text{SiO}_2=58.30$  (% wt), total=99.99. It is closely associated with calcite and apatite, forming veins and nests accumulations in these minerals.



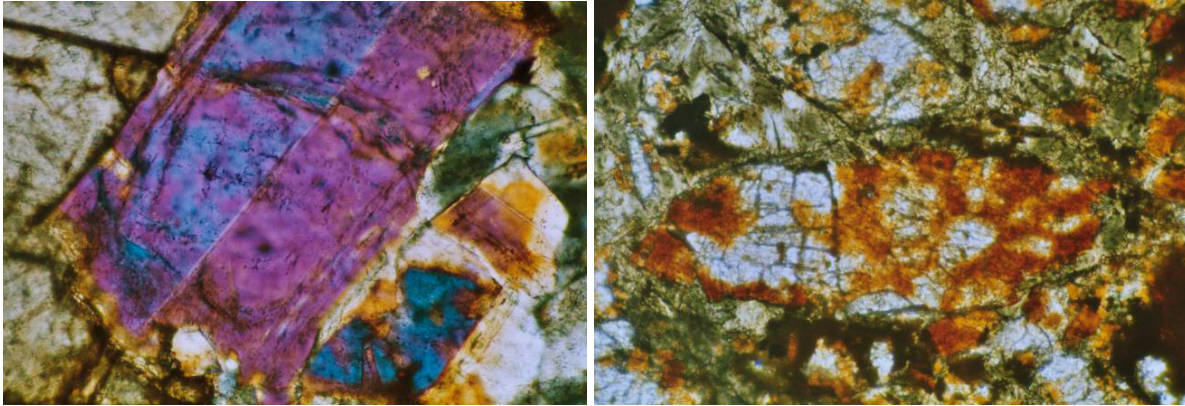


Fig. 30. Zoned and twinned pectolite (big grain) in calcite (white grey), N+, sample Bel13,  $\times 30$  (left); Th-Y chamosite (green) substitutes thorigummite (red)+xenotime-(Y) (white grey, two cleavages), NII, sample Bel12A (right).

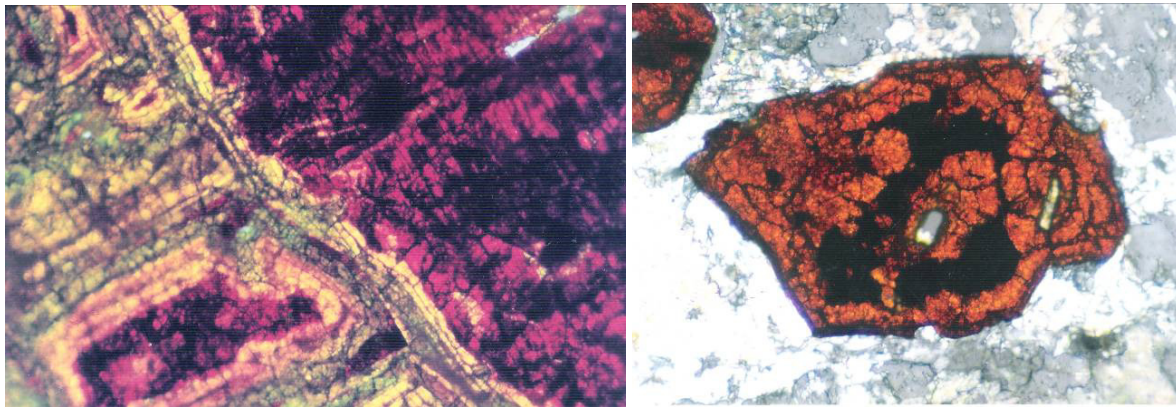


Fig. 31. Lepidocrocite, yellow red-ruby colour, NII, sample Dt215,  $\times 35$  (left); goethite (red, red light brown) grown on hematite (black) (right), N+, sample Bel10,  $\times 30$  (right).

Usually, the Belcina pectolite is altered to kaolinite, occurring as relics in the latter. Unlike the Jolotca pectolite, which has a radiary, fibrous growth, the Belcina pectolite has a good, nonfibrous, prismatic or tabular crystals (Fig. 30 left). Also, the Joltca pectolite is associated with aegirine and riebeckite, while the Belcina pectolite is closely associated with apatite and calcite.

**Lepidocrocite**,  $\gamma\text{-Fe}^{3+}\text{O(OH)}$ , orthorhombic, dimorphous with goethite. In thin sections has a flattened micaceous habit having three cleavages: perfect on (010), less perfect on (100) and good on (001) and a yellow ruby colour (Fig. 31 left). It has a strong pleochroism from yellow to ruby red, dark red orange, reddish brown. Optically it is biaxial negative, with high  $2V$  around  $80^\circ$ . Associated with pyrite, magnetite, goethite, siderite, Nb-rutile, thorite-thorigummite, xenotime-(Y). Lepidocrocite occurs as an oxidation product of other iron oxides (magnetite, hematite), but it could form as a hydrothermal product.

**Goethite**,  $\alpha\text{-Fe}^{3+}\text{O(OH)}$ , orthorhombic, dimorphous with lepidocrocite. It occurs as prismatic and tabular crystals, or as reniform, botryoidal masses. In thin sections is strong pleochroic from colorless, yellow, yellow reddish, yellow orange to deep reddish orange, reddish brown, brown. It is biaxial negative, with  $2V \approx 20^\circ$  and has two cleavages: perfect on (010) and less perfect on (100). In Belcina area it is associated with lepidocrocite, hematite, siderite, Nb-rutile, thorite/thorigummite. It could result by oxidation of other iron oxides (hematite, magnetite) (Fig. 31 right) or other iron bearing minerals (pyrite).

### SOME GENETICAL REMARKS

The magmatic/hydrothermal differentiation processes are responsible for the in-situ concentration of many varieties of the rare element minerals in Ditrau alkaline intrusive massif. The hydrothermal /carbothermal processes have played

the dominant role, being reflected in the common kind of mineral appearances: grains with marginal and sectorial zonations, oscillatory compositions in the same crystal/grain due to the sudden variation of hydrothermal mineralization solutions and very complicated compositions of some minerals. The mineralizing process was multi-stages; that is supported by textural relationships, where replacement of earlier REE minerals by later ones is common. Inside the Ditrau rocks, especially in the Jolotca area, there were concentrated many LREE-carbonates (bastnasite-(Ce), bastnasite-(La), parisite-(Ce), hydroxylbastnasite-(Ce), lanthanite-(Ce), etc), many terms of pyrochlore, ferrocolumbite, manganocolumbite, fergusonite, euxenite, aeschynite, many REE-silicates (allanite-(Ce), chevkinite-(Ce), cerite-(Ce), zircon, with accessory thorite and thorogummite), many phosphates (monazite, cheralite-(Ce), cheralite-monazite-huttonite terms), some halides and tellurides, in the first mineralization stages. In the Belcina area, the rare element minerals, different than the Jolotca ones, are concentrated in the surrounding rocks of the massif and they are represented mainly by Th silicates (thorite, thorogummite) and Y phosphates (xenotime-(Y), Th-apatite, with minor Nb rutile, zircon, ferrocolumbite, monazite-(Nd), monazite-(Ce), brabantite, smirnovkite (?) and less uraninite, thorianite, baddeleyite, native mercury, formed by late stage hydrothermal activity. Some sulphides, less than in Jolotca area, are present as accessory minerals. The HgS (cinnabar), associated with native Hg were determined only in Belcina area. The Belcina complex mineralization could be the last stage, lower temperature carbonatites. The late stage Th-Y mineralization, late stage calcite veins, large development of Fe oxides/hydroxides, minor sulphides of Fe, Pb, Zn, Mo, all are the carbonatites features, evident in many carbonatites world-wide. Also, the big development of many carbonates of different generations as gangue minerals is specific to some mineralisations generated by carbothermal/hydrothermal carbonatite fluids. The isotopic studies are needed in order to establish whether silica under saturated/oversaturated rocks of Ditrau alkaline intrusive massif is originated in differentiation of primitive mantle magmas/or to be derived from crustal contamination of mantle derived silica undersaturated alkaline magmas.

## CONCLUSIONS

The Belcina thorite, thorogummite, xenotime mineralization with high content of Th and Y is unique among other occurrences of the Ditrau alkaline intrusive massif, being very different from the last ones. The Belcina thorite, thorogummite and xenotime-(Y) closely associated paragenetically, occur mainly as primary constituents. The other rare element minerals, such as Th-apatite, monazite-(Nd), monazite-(Ce), brabantite, smirnovkite, niobian rutile, zircon, ferrocolumbite, are present as secondary components and the others such as baddeleyite, uraninite, thorianite and native mercury, were determined only by microprobe analyses. The gangue/common minerals show large development as many common carbonates (calcite, dolomite, siderite, iron rich dolomite), quartz, calcedonie, feldspars, apatite, often are found with goethite, hematite, lepidocrocite. The thorite/thorogummite are the most common thorium minerals. Thorium is a highly radioactive element and could be used as a replacement for uranium in nuclear power generation. It is estimated to be three times as common as uranium, and all the thorium in the Earth's crust could have more potential energy than both uranium and the fossil fuel reserves combined (Encyclopedia Britannica, 2009). Uranium and thorium are considered to be the primary sources of the internal heat of the Earth through their radioactive decay. Although thorite is the most common thorium mineral, it is not the primary ore of thorium. The phosphate mineral monazite has an average of about 6% thorium in its composition that includes several rare earth elements and also, the brockite, brabantite and cheralite contain much more Th than monazite. Enough monazite is mined to supply most of the current thorite demand (Encyclopaedia Britannica, 2009). If monazite deposits become scarce or the demand for thorium increases, then thorite and to lesser extents other thorium bearing minerals such as thorianite, thorogummite, huttonite, brockite  $[(CaThCe)PO_4 \cdot H_2O]$  and thorutite  $[(ThUCa)Ti_2(O,OH)]$  will gain greatly in importance. Now uranothorite, a thorite variety, is currently an important ore of uranium. So, the Belcina thorite and thorogummite, also Th-monazite, brabantite occurrence could be an important Th source in the future, and the xenotime-(Y) could be an important Y source.

## ACKNOWLEDGEMENTS

Many thanks to the Roumanian Academy for material support, i.e. the grants No 133/2007-2008 and No 134/2007-2008, allowing us to work in the modern laboratories of Exeter University, Camborne School of Mines, Cornwall, UK. We are very grateful to Prof. Gheorghe Udubasa, from Bucharest University, for his careful reviews and valuable suggestions.

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