RARE EARTH MINERALS IN DITRĂU ALKALINE CARBONATITE COMPLEX, EASTERN CARPATHIANS, ROMANIA

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Abstract. The Ditrău alkaline carbonatite complex (DACC) hosts a rich and diverse mineralization of REE, Nb, Ta, Ti, Th, Zr, Te, and U, mostly highly concentrated in two areas: Jolotca and Belcina. In the Jolotca area, many REE minerals were concentrated belonging to the **halides, oxides, carbonates, silicates and phosphates classes**. Between them, large development have carbonates such bastnäsite-(Ce), bastnäsite-(La), parisite-(Ce), hydroxylbastnäsite-(Ce); many terms of pyrochlores, fergusonites, euxenites, aeschynites; REE-silicates allanite-(Ce), chevkinite-(Ce); many phosphates (monazite-(Ce), cheralite-(Ce), cheralite-monazite-huttonite terms, and REE-fluorites of halide class. In the Belcina area, the REE minerals, different than the Jolotca ones, are concentrated in the surrounding rocks of the massif and they are represented mainly by **Y mineralization**, especially xenotime-(Y), which is closely associated with thorite. The Belcina complex mineralization could be the last stage, of lower temperature carbonatites. The late stage Y-Th mineralization, late stage carbonate veins, large development of Fe oxides/hydroxides, minor sulphides of Fe, Pb, Zn, Mo, are all characteristic of carbonatites features. The Belcina mineralization is similar with many other late carbonatites in world-wide. The development of many carbonates and apatites, of different generations, as gangue minerals in both areas, is specific to mineralizations generated by carbothermal /hydrothermal fluids.

Keywords: Ditrău alkaline carbonatite complex (DACC), REE oxides: pyrochlores, aeshynites, fergusonites; REE-carbonates: bastnäsite-(Ce), parisite-(Ce), synchysite-(Ce); REE phosphates: monazite-(Ce), xenotime-(Y); REE silicates: allanite-(Ce), cevkinite-(Ce); compositional zoning oscillatory; hydrothermal/carbothermal genesis.

Résumé. Le complexe carbonatitique alcalin de Ditrău (DACC) renferme une minéralisation riche et diversifiée en éléments des terres rares (ETR), Nb, Ta, Ti, Th, Zr, Te et U, principalement concentrée dans deux zones: Jolotca et Belcina. Dans la zone de Jolotca, de nombreux minéraux de terres rares appartenant aux classes des halogénures, oxydes, carbonates, silicates et phosphates sont concentrés. Parmi ceux-ci, les carbonates tels que la bastnäsite-(Ce), la bastnäsite-(La), la parisite-(Ce) et l'hydroxylbastnäsite-(Ce) sont particulièrement développés; on y trouve également de nombreuses variétés de pyrochlores, de fergusonites, d'euxénites et d'aeschynites; des silicates de terres rares comme l'allanite-(Ce) et la chevkinite-(Ce); de nombreux phosphates (monazite-(Ce), cheralite-(Ce), termes intermédiaires cheralite-monazite-huttonite), ainsi que des fluorites à terres rares appartenant à la classe des halogénures. Dans la zone de Belcina, les minéraux de terres rares, différents de ceux de Jolotca, sont concentrés dans les roches encaissantes du massif et sont principalement représentés par une minéralisation en yttrium, notamment la xénotime-(Y), étroitement associée à la thorite. La minéralisation du complexe de Belcina pourrait représenter le dernier stade de formation des carbonatites, à plus basse température. La minéralisation tardive en Y-Th, les veines carbonatées de stade final, le fort développement d'oxydes et d'hydroxydes de fer, ainsi que la présence mineure de sulfures de Fe, Pb, Zn et Mo sont autant de caractéristiques typiques des carbonatites. La minéralisation de Belcina est comparable à celle de nombreuses carbonatites tardives dans le monde.

Mots-clés: Complexe carbonatitique alcalin de Ditrău (DACC); oxydes à ETR : pyrochlores, aeschynites, fergusonites ; carbonates à ETR: bastnäsite-(Ce), parisite-(Ce), synchysite-(Ce); phosphates à ETR: monazite-(Ce), xénotime-(Y); silicates à ETR: allanite-(Ce), chevkinite-(Ce); zonage compositionnel oscillatoire; genèse hydrothermale/carbothermale.

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I. INTRODUCTION

The rare earth elements (REE) comprise the Group IIIA elements of the Periodic Table: scandium (atomic number 21), yttrium (39), lanthanum (57), and the lanthanides, which are the 14 elements from cerium (58) to lutetium (71). Levinson (1966) defined rare earth minerals as those minerals containing rare earth elements (REE) as essential constituents. The REE are conveniently grouped into two groups for crystal chemical purposes: the „Ce group", (the light REE), composed of lanthanides from La to Eu, and the „Y group" (the heavy REE), composed of Y and lanthanides from Gd to Lu. According to the distribution of rare earths, rare earth minerals can be classified into three types: (1) with a predominance of the smaller Y-group rare earths; (2) rich in the larger Ce-group rare earths; (3) in which the crystal structures accept both Y-group and Ce-group rare earths (Miyawaki and Nakai, 1996). Clark (1984) defined three groups of minerals according to their REE content: (1) minerals with very low amounts of REE; (2) minerals containing minor but not essential amounts of REE and (3) minerals with major concentrations of REE. In this group Clark also included some minerals belonging to the two previous ones but presenting unusually high REE contents.

Minerals with larger cation sites, such as zircon, garnet, apatite, epidote, titanite, readily accept many of the rare earth ions such that they can become a minor component of the composition (Henderson, 1996). The rare earth elements (REE) are widely distributed as trace elements in mantle rocks and mantle-derived magmas, and in crustal rocks. They are often found in abundance in many carbonatites, and in some granites and syenites. Carbonatites are host rock for the REE deposits. Carbonatites are amongst the lowest temperature terrestrial magmas known. If crystallized at shallow depths in the upper crust, primary bastnäsite group minerals could form at temperature as low as ~550° (Wyllie *et al.*, 1996).

II. OCCURRENCE

The Ditrău alkaline carbonatite complex (DACC) is situated within the crystalline rocks of Tulgheș Series in the inner part of the East Carpathians, in the Gurghiu Mts (Jakab, 1998). It has a distinct ring structure and a succession of magmatic events ranging from ultramafic, gabbroic, and dioritic magma to syenitic and various postmagmatic events. All these events developed between a Triassic extensional stage and a Jurassic rifting stage (Kräutner and Bindea, 1995). The succession of magmatic events in Ditrău could have been completed with a carbonatite intrusion that followed after the alkaline intrusion and used the same pathways as the previous alkaline silicate melt (Hîrtopanu, 2019). It is known that the peralkaline rocks are commonly characterized by extreme enrichment in alkali metals (Na, K) and high field strength elements (HFSE), such as REE, Y, Zr, Ti, Nb, and Ta. The optical and electron microprobe study established the mineralogical and genetical evolution of the Ditrău REE(Y) minerals and their associated minerals. The Ditrău complex mineralization is polygenetic, being formed in at least 5 important genetical stages, from oldest to youngest. The multistage mineralizing process is supported by textural relationships, where replacement of earlier minerals by later ones is common. Over more than 30 mineral species of REE have been determined in the complex mineralization of the DACC (Hîrtopanu, 2019). They belong to the following classes: halides, oxides and hydroxides, carbonates, silicates, and phosphates.

II.1. HALIDE CLASS

The fluorite is not itself a REE mineral but trace or minor amounts of them are frequently present.

The two varieties of Ditrău fluorites, fluorite rich in Y, $(Y,Ca)F_2$, and cerian fluorite, $(Ce,Ca)F_2$, belong to the group (2) of minerals which contain minor but not essential contents of REE (Clark, 1984). They contain trace and minor amounts of REE and can impart different colourations of the crystals (Bill, 1969). Blue and yellowish colour of fluorite is due to Eu^{3+} (Fig. 1, left). The yttrium Y^{3+} is responsible for the pink violet colour of fluorite, in Fig. 1 centre, and the yellowish-pink fluorite owe its colour to yttrium associated with cerium, in Fig. 1 right. The low refringence, the perfect octahedral cleavages**,** and the isotropy are the characteristics of fluorite in transmitted light. The fluorite belongs to the low temperature hydrothermal stage. The presence of fluorite, such Y-rich and Ce-rich varieties in the Jolotca vein mineralization, is a good evidence for a high fluorine content of the mineralizing fluids, which were also enriched in Y, Ce and trace of Eu.

The fluorite, associated with phlogopite, aegirine, Na amphiboles, pectolite, pyrochlore, natrolite is a mineral constituent in alkali syenites and mineralizations from Hereba, Aurora, Lăzarea, Jolotca, and Belcina areas. The presence of fluorite is evidence for a high fluorine content of the mineralizing fluids, which are also enriched either in REE, Y, Th or U. It is a late hydrothermal / carbothermal product resulting probably from fractionation of carbonatite and/or alkaline magma.

Figure 1. Blue fluorite, enclosed in pink large phlogopite crystal (left); pink-violet fluorite in green phlogopite small crystals (centre); large blue-yellowish fluorite crystal in analcime (right), TL, NII, x20, Jolotca area.

II.2. REE-OXIDES AND HYDROXIDES

The REE-oxides and hydroxides are associated in their chemical compositions with Ti and/or Nb-Ta**.** Uranium and Thorium also can be present leading to metamictization. The REE(Y) oxide minerals determinated in DACC belong to the following groups: **1. Pyrochlore group; 2. Aeschynite group; 3. Fergussonite group** (Hîrtopanu, 2010).

1. **Pyrochlore group** The pyrochlore group is a suite of diverse chemistry with general formula $A_{2m}B_2X_{6-w}Y_{1-n}\cdot pH_2O$, where A=Na, Ca, Mn, Fe^{2+}, Sr, Sb, Cs, Ba, REE, Pb, Bi, Th, U; B=Nb, Ta, Ti, Al, Fe^{3+}, Zr, Sn, W; X=O, OH; Y=O, OH, F. Three major subgroups were defined by Hogarth (1977) on the basis of the major B-site cations: pyrochlore ($Nb+Ta \geq 2Ti$ with $Nb>Ta$); microlite ($Nb+Ta \geq 2Ti$ with $Ta>Nb$); betafite ($2Ti \geq Nb+Ta$). Within each group, individual species are defined by the cations residing on the A-site. The cubic structure of the pyrochlore group minerals is extremely accommodating to cations of diverse ionic radii and valences. The metamictization is widespread in Ditrău pyrochlore group minerals because of subordinate to substantial U and Th contents. The REE-pyrochlore group minerals found in DACC are: ceriopyrochlore-(Ce), $(Ce,Ca,Y)_2(Nb,Ta)_2O_6(OH,F)$, yttropyrochlore-(Y), $(Y,Na,Ca,U)_{1-2}(Nb,Ta,Ti)_2(O,OH)_7$, and yttrobetafite-(Y), $(Y,U,Ce)_2(Ti,Nb,Ta)_2O_6(OH)$.

The other pyrochlore terms, such as proper pyrochlore, uranpyrochlore, kaliopyrochlore, bariopyrochlore, and plumbopyrochlore also occur frequently as accessory minerals (Hîrtopanu, 2019). The pyrochlore group belongs to low temperature hydrothermal stage. They occur in association with the new monazite-(Ce), new allanite-(Ce), LREE-carbonates in calcite carbonatite, and seems to be later than their associated minerals. They also occur in the alkaline rocks, where are later than the feldspatoids, usually being associated with natrolite or cancrinite. The pyrochlores were concentrated and then precipitated in small veinlets from residual carbothermal/hydrothermal fluids. This indicates that Nb and Ta have been concentrated in the residual fluids, and precipitated from it.

Figure 2. Zoned crystal: yellow ceriopyrochlore-(Ce) in centre, and brown yttropyrochlore on the rim in cancrinite, sample DT453 (left); Zoned crystal: red-orange uranpyrochlore on the rim and yellow ceriopyrochlore-(Ce) in centre, sample DT597B (centre); Zoned crystal: red-brownish yttropyrochlore-(Y) in centre and yellow ceriopyrochlore-(Ce) in the rim, in natrolite (white greenish) (right). TL, NII, x20.

The minerals of pyrochlore group occurs as small euhedral crystals with variable size and colour. The size varies from 0.1 to 3mm, and the colour depends on the chemical composition. In transmitted light they occur frequently zoned. In Fig. 2 left, the pyrochlore-(Ce) is in centre of the crystal and has a rim of yttropyrochlore-(Y). In Fig. 2 right, it is the other way around, yttropyrocchlore-(Y) is in centre and ceriopyrochlore-(Ce) on the rim. The zoned crystal in Fig 2 centre has ceriopyrochlore-(Ce) in the centre and uranpyrochlore on the rim. The zoned grain is interpreted as the result of a more or less continuous precipitation of pyrochlore with a composition in equilibrium with a fluid increasing concentration of the complexing ligands during the intrusion of carbonatites (Knudsen, 1989). These minerals occur as accessory phases in nepheline syenite and carbonatite of Ditrău, being concentrated in the Jolotca mineralized area.

2. **Aeschynite group** minerals have an ideal formula AMM'O_6, with A=Y, Ce; M=Nb,Ta; and M'=Ti. The substitution of Ca+(Nb,Ta) for (Y,REE)+Ti is common and it leads to the composition of vigezzite and rynersonite with a columbite-like stoichiometry and cation population close to AB_2O_6 (Černý and Ercit, 1989). The REE content of aeschynite minerals is commonly dominated by the cerium group, but the proportion of HREE increases in the Y-rich aeschynites (priorite). These Y-rich phases also commonly show enrichment in Dy (Gorzhevskaya *et al.*, 1974). Aeschynites crystalize orthorhombic. The aeschynite-(Ce) is dimorphous with lucasite-(Ce) and forms series with nioboaeschynite-(Ce) and with aeschynite-(Y). Laboratory synthesis confirmed continuous substitution of Ce and Y (Komkov and Belopolskyi, 1960). The aeschynite-(Y) has yttrium as the dominant REE. In the DACC were determined the aeschynite-(Ce), $(Ce,Ca)(Ti,Nb)_2O_6$, aeschynite-(Nd), $(Nd,Ce,Ca)(Ti,Nb)_2O_6$, and aeschynite-(Y), $(Y,Ca)(Ti,Nb)_2O_6$, as accessory minerals in Jolotca area. The Ditrău aeschynite minerals are dominated by the cerium group (LREE). These LREE-rich phases could be dominated by the neodymium, that also belongs to the cerium group. The Ditrău aeschynites have a tabular**,** prismatic, and equigranular crystals, from several mm to 1 cm, and could have radiating clusters (Fig. 3 right). In transmitted light, the tabular aeschynite-(Ce) has a yellowish red, yellow, reddish orange colour (Fig. 3 left) with weak to distinct pleochroism. The red large prismatic aeschynite-(Nd) has a perfect micaceous cleavage (Fig. 3 right and 5 right). It is biaxial with $2V \approx 80^\circ$. The birefringences of the two minerals are different, the aeschynite-(Ce) being much more brighter coloured than the aeschynite-(Ce). The crystal from the Fig. 4 has compositional variations / oscillatory composition in NII: the red zones are rich in Nd, corresponding to aeschynite-(Nd) and the yellow zones are rich in Ce, corresponding to the aeschynite-(Ce). Its birefringence in N+ also shows a zoned birefringence (Fig. 4 right). This very fine-scale oscillatory zoning of aeshynites reflect the fluctuations in the composition of the metasomatic/ hydrothermal fluid during the crystallization, apart from changes in T or P, which are constant during their formation. The aeschynites are closely associated with large niobian rutile crystals, occurring as later veinlets on its cracks and microfractures. The metamictic state is common in both type of aeschynites due their richness in Th or/and U in their compositions.

In the DACC the aeschynites are typical accessory minerals. Generally, the Ditrău aeschynites are Nb and Nd rich. The simplified electron diffractogram spectrum of aeschynite-(Nd) of sample DT39/8 can be seen in Fig. 6. It shows rich Nd and low Y and Ca contents.

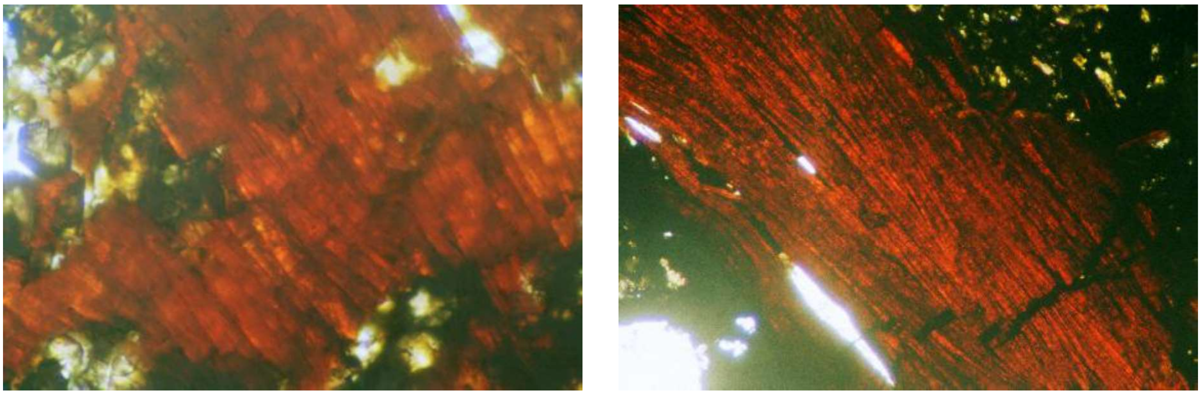

Figure 3. Aeschynite-(Ce), large red-yellowish crystal with perfect cleavage, TL, NII, x30, sample DT39/1 (left); aeschynite-(Nd), large red crystal, perfect micaceous cleavages, sample DT39/2, (right).

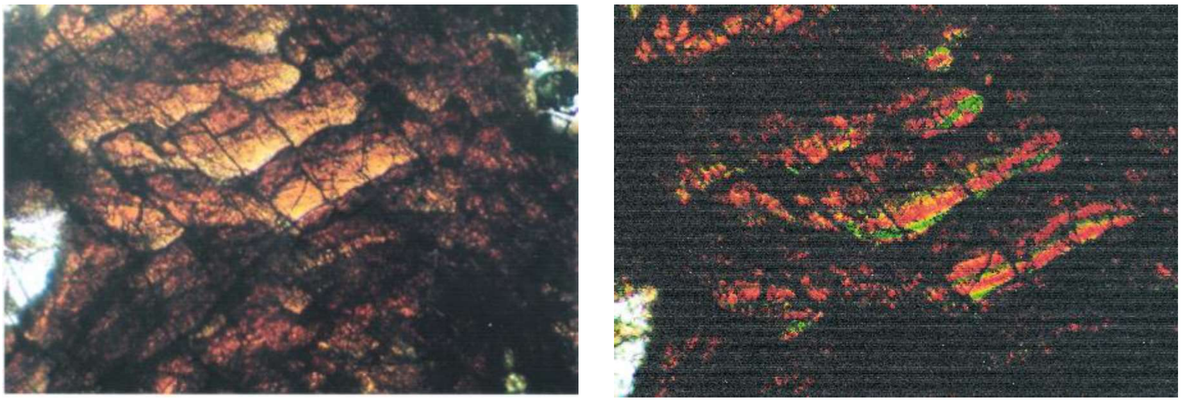

Figure 4. Aeschynite crystal with oscillatory composition: more Nd (red), more Ce (yellow), Tl, NII (left) and N+ (right), x20, sample DT39B.

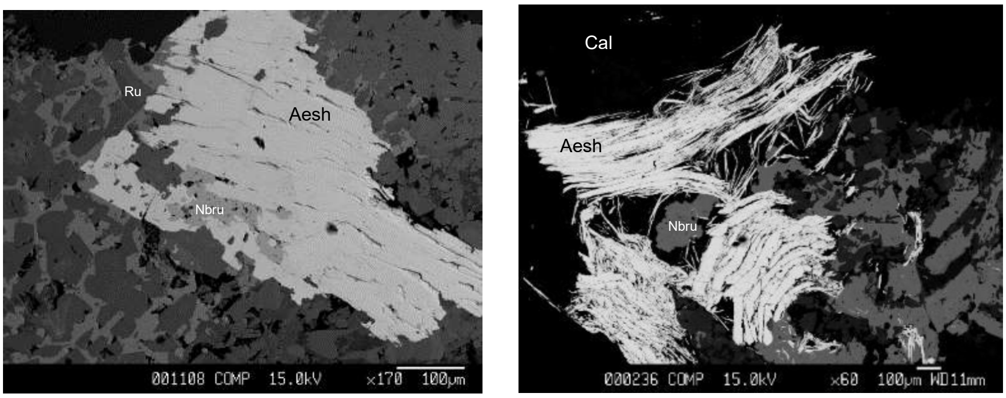

Figure 5. Backscattered electron image of aeshynite-(Ce) (Aesh, white grain with good cleavage), Nb-rutile (Nbru, light grey), and rutile (Ru, dark grey, short prisms), sample DT39 (left); Backscattered electron image of aeschynite-(Nd) (Aesh, white, perfect cleavage), Nb-rutile (Nbru, grey), and calcite (Cal, black), sample DT39A, (right).

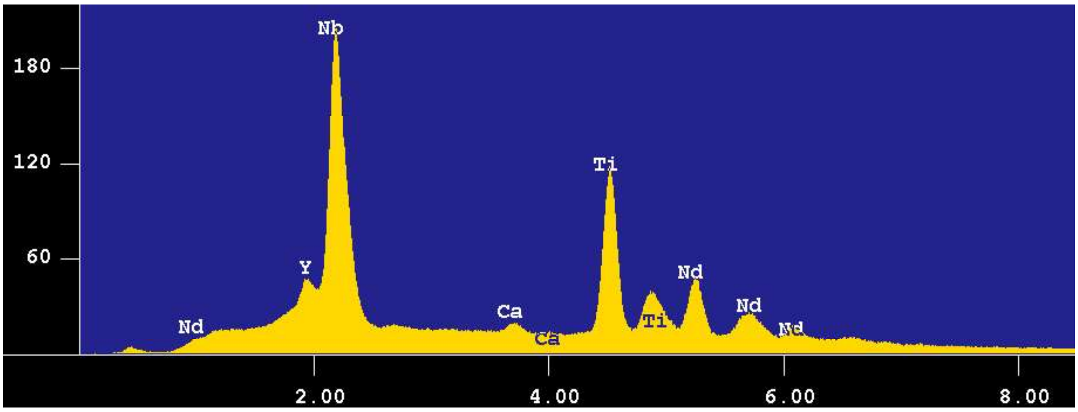

Figure 6. Electron diffractogram spectrum of aeschynite-(Nd)
of the crystal from the Fig. 5 right, sample DT39/8.

3. Fergusonite Group. Minerals of the fergusonite group are tetragonal, with the scheelite-type structure and simple formula, AMO_4, but have a variable chemical composition (Černý and Ercit, 1989). The members of the fergusonite-formanite series are chemically the least complex among the rare earth niobate-tantalates. The essential elements are Nb, Y, and low Ta. The fergusonite-(Y) has very low Ce, La, and Nd contents. However, the Gd, Dy, and Yb, which belong to Yttrium group/HREE have slightly higher contents.

The fergusonite-(Y), $YNbO_4$, is a few mm in size and has prismatic dipyramidal crystals. In transmitted light it has a light yellow-red, light brown to dark brown colour, with very high refringence and birefringence (Fig. 4). Optically it is uniaxially positive. The earlier fergusonite-(Y) is substituted on the rims by new yttropyrochlore-(Y), forming a concentrically zoned texture. It could also be substituted irregularly by new yttropyrochlore-(Y) forming a patched texture (Fig. 9). In transmitted light the fergusonite-(Y) has a reddish-yellow colour, high refringence, and it is anisotropic, but becomes isotropic when metamict. The fergusonite-(Y) is the typical accessory mineral~~s~~ for the carbonatite rocks.

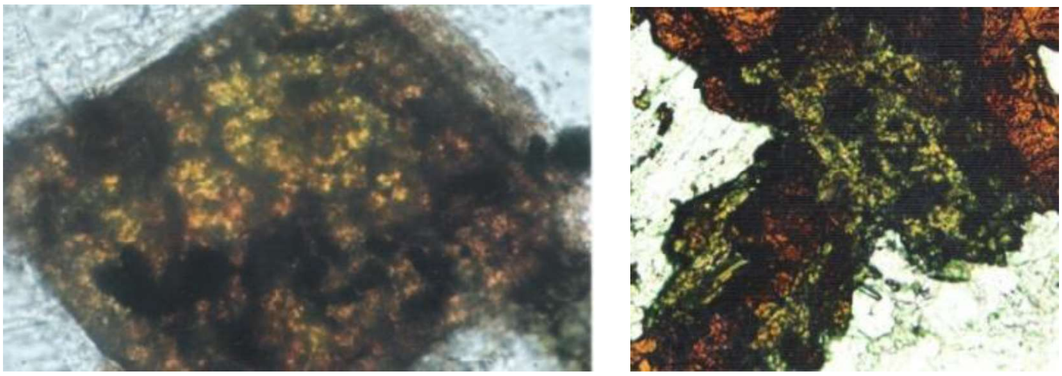

Figure 7. Fergusonite-(Y) (yellow-red) with thorianite inclusions (black) on microvein in apatite (grey), TL, NII, x35, sample Dt2/2, see its EDS in Fig. 8 (left); Fergusonite-(Y) metamictic (yellow greenish) associated with sphalerite (red) in natrolite (white), TL, NII, x30; sample Dt6 (right).

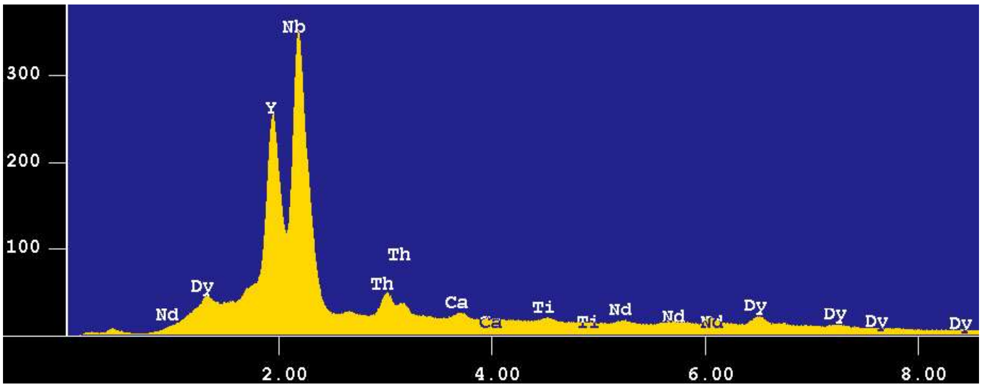

Figure 8. Electron diffractogram spectrum of fergusonite-(Y) rich in Th and low Dy from Fig. 7, sample DT2/2.

The fergusonite structure can accommodate the whole range of REE cations and in this respect the composition seems to be a function of the geochemistry of the parent environment, rather than of crystal chemical constraints (Gorzhevskaya *et al.*, 1974). The composition of fergusonite-(Y) in the electron diffractogram spectrum in Fig. 8 shows beside classic Y+HREE, the presence of another HREE, dysprosium Dy, and the presence of neodymium (Nd) which is light REE, and thorium. The fergusonite-(Ce), $(Ce,La,Nd)NbO_4$, without Ca, Ti, and Dy contents, were determined by electron diffractogram spectrum in sample DT37/1, closely associated to niobium rutile, as secondary microveins and small nests.

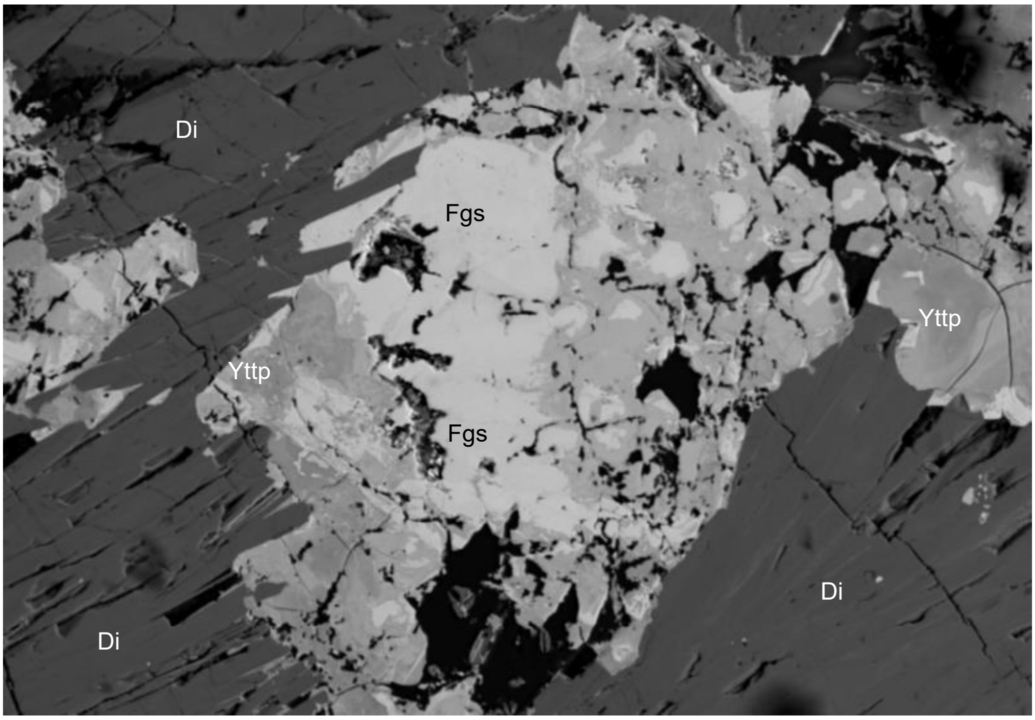

Figure 9. Backscattered electron image of fergusonite-(Y) (Fgs, white grey) substituted by yttropyrochlore (Yttp, light grey) in diopside (Di, dark grey), sample DT 8, Jolotca area, x200.

The fergusonite minerals were formed in the low temperature hydrothermal stage, as were formed aeschynite-Ce, aeschynite-(Nd), columbites, pyrochlore group (all its terms), betafite subgroup of the pyrochlore group, and many sulfides.

II.3. REE-CARBONATES

The primary LREE fluocarbonates are hosted by calcite, dolomite and siderite carbonatite rocks, all being late carbonatites. The primary LREE-carbonates were crystallized from the fluids enriched in LREE linked with the carbonatite magmas and their associated alkaline rocks, fluids which contain complex agents, such as PO_4^{3-}, CO_3^{2-} and F^-. The majority of primary REE fluocarbonates, which were determined in the DACC have in their compositions the light rare earth elements (LREE) group or Ce group.

Bastnäsite-(Ce), $(Ce,La)CO_3F$ (Fig. 10 left) sometimes is zoned with parisite-(Ce) and synchysite-(Ce). The rare bastnäsite-(La) occurs intergrown with calcite and rutile and has bastnäsite-(Ce) around it. Because of the absence of Ce layers in its structure, bastnäsite-(Ce) has the highest REE content of any of the fluocarbonate species. The allanitisation of bastnäsite-(Ce) around and inside the grains is widespread (Fig. 10 left and right).

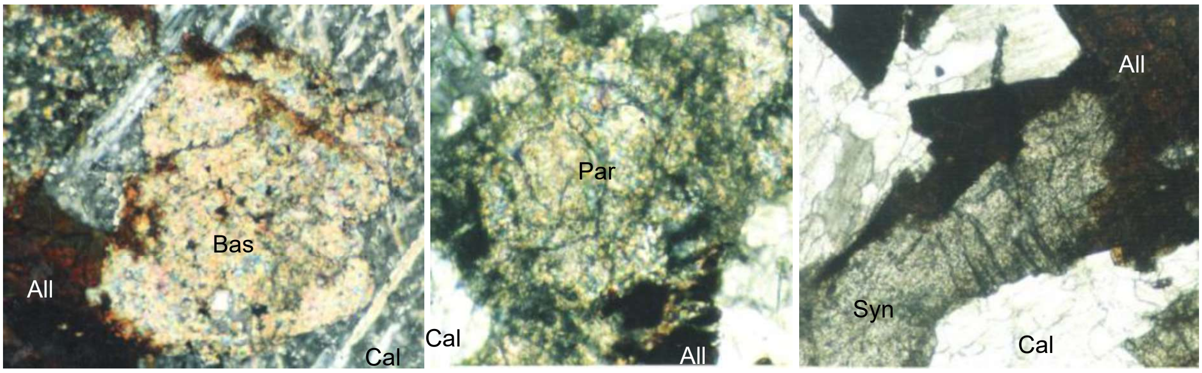

Figure 10. Bastnäsite-(Ce) (Bas, high birefringence) and allanite-(Ce) (All, brown black) in calcite (Cal, grey), TL, N+, x25 (left); Parisite-(Ce) (Par, concentrically zoned) and allanite-(Ce) (All, brown black) in calcite (Cal, white/grey), TL, N+,x25 (centre); Synchysite-(Ce) (Syn, grey, no cleavage) allanitized (All, brown black) in calcite (white grey), TL, NII, x25 (right). Jolotca area.

Bastnäsite-(Ce) could alter to hydroxylbastnäsite-(Ce) which has $(OH)^- > F^-$, and with which has a continuous series. Relics of bastnäsite-(Ce) occur in hydroxylbastnäsite-(Ce). The primary **parisite-(Ce),** $Ca(Ce,La)_2(CO_3)F_2$, forms prisms with perfect cleavage. It frequently appears zoned/with concentric texture (Fig. 10 centre). The primary synchysite-(Ce), $Ca(Ce, La)(CO_3)_2F$, forms short prismatic crystals, which have no cleavage (Fig. 10 right). Often it has an oscillatory zoned composition. The allanitisation process of synchysite-(Ce) began on the edges of grains or on the fractures, changing the shape of the grains, which became rounded, and sometimes remaining as relics in allanite-(Ce). **Synchysite-**(Y), $Ca(Ce,Y)(CO_3)_2F$, occurs more frequently in Belcina area.

A distinct aspect of the Ditrău LREE-carbonates is the anomalously high LREE content. Among them, the bastnäsite-(Ce) is the most abundant. It contains up to 70 wt% LREE or even more. The Nd_2O_3 and La_2O_3 contents have a high percentage, sometimes of the same level as that of Ce_2O_3, but the latter is usually the dominant LREE. The additional natural mixed-layer compounds with compositions between bastnäsite-(Ce) and synchysite-(Ce) and between bastnäsite-(Ce) and parisite-(Ce) have been determined in the Ditrău REE-fluocarbonates by electron microprobe.

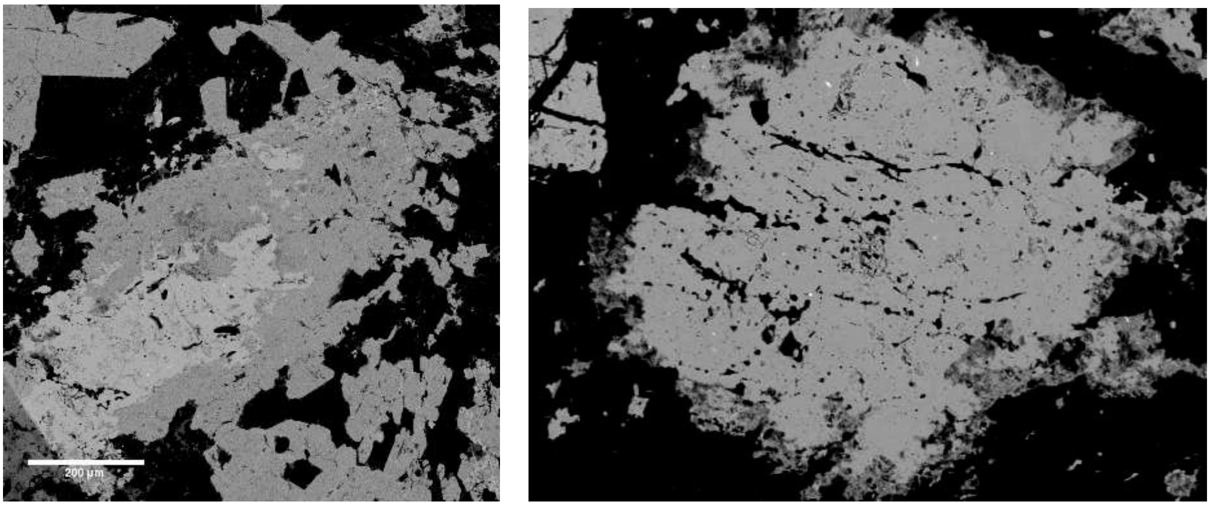

Figure 11. Backscattered electron image of zoned LREE carbonates: bastnäsite-(Ce) (white greyish, centre) zoned with synchisite-(Ce) (grey, rim) (left); Zoned grain: parisite-(Ce) (grey, centre) zoned with narrow area of synchisite-(Ce) (dark grey, at the rim) (right). Jolotca area.

The electron diffractogram spectrum of bastnäsite-Ce) of sample Dt53 in Fig. 12 shows a rich Nd and less La term. The electron diffractogram spectrum of parisite-(Ce) of sample Dt37 in Fig. 13 shows a rich La and Nd, and less Ca term, and that of synchysite-(Ce) of sample Dt216 in Fig. 4 shows a Ca and Y rich term.

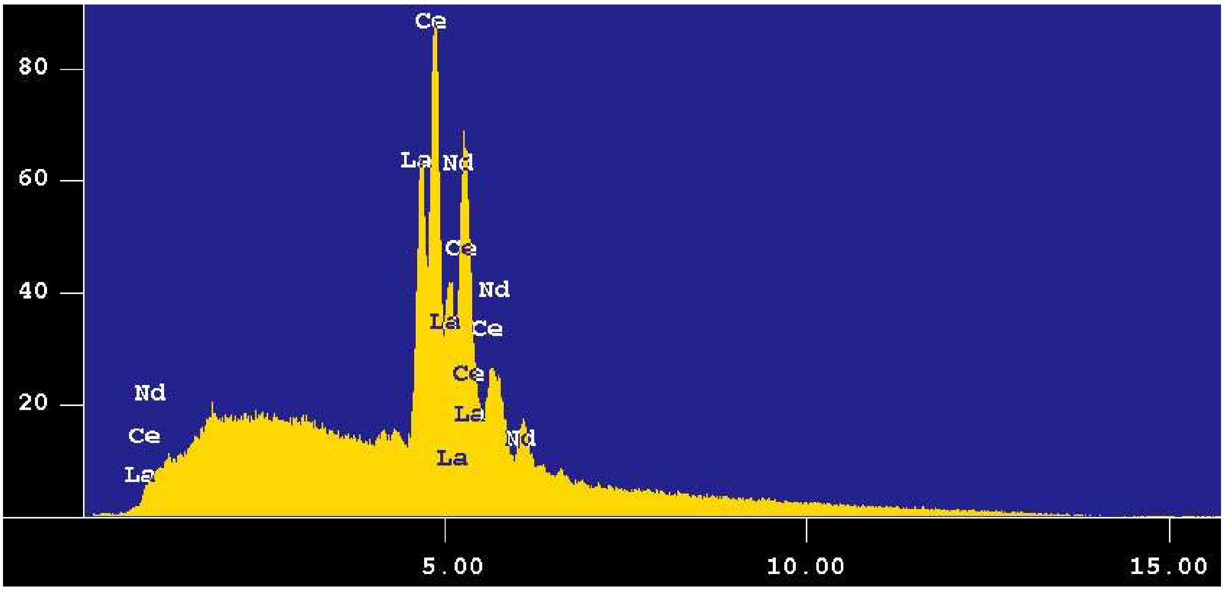

Figure 12. Simplified electron diffractogram spectrum of bastnäsite-(Ce), sample Dt53.

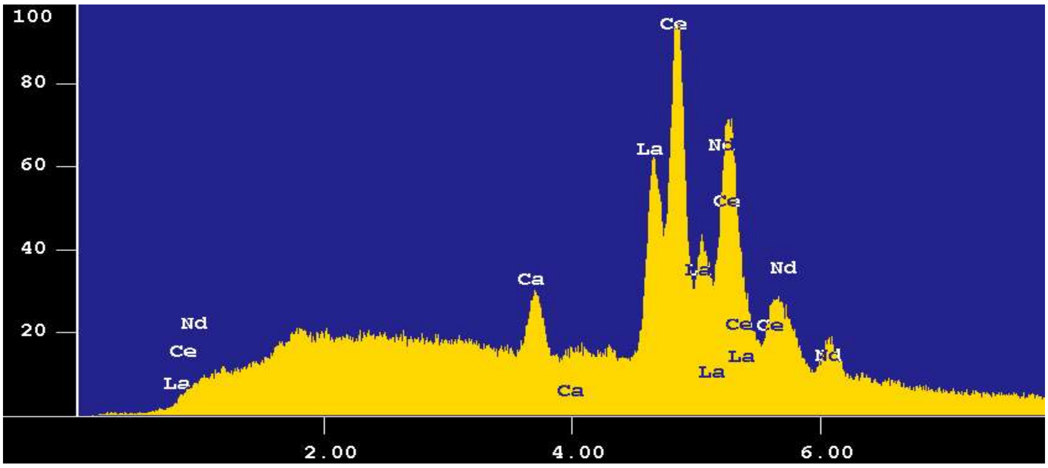

Figure 13. Simplified electron diffractogram spectrum of Nd rich parisite-(Ce), sample Dt37.

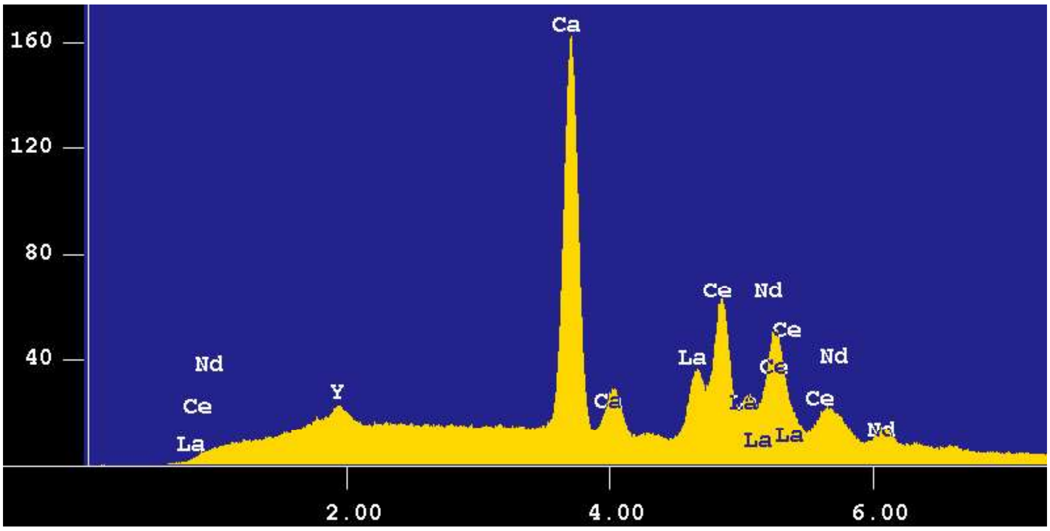

Figure 14. Simplified electron diffractogram spectrum of synchysite-(Ce), sample Dt216.

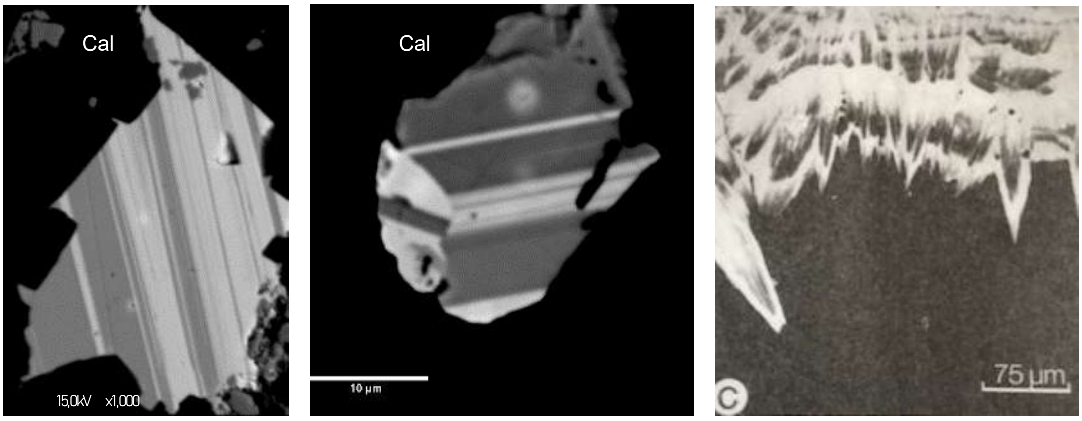

Figure 15. Backscattered electron image of zoned LREE carbonates: bastnäsite-(Ce) (white) zoned with synchisite-(Ce) (grey), calcite (black), sample Dt216, x1,100 (left); Bastnäsite-(Ce) (white) zoned with parisite-(Ce) (dark grey) in calcite (black) (centre); Bastnäsite-(Ce) (white) intergrowth with parasite-(Ce) (dark grey) from Langersunjdfjord (Larsen and Williams, 1992) (right).

The Ditrău REE carbonates exhibit a pronounced zoning, which is usually seen in backscattered electron images (Fig. 15). In Fig 15 left the bastnäsite-(Ce) is zoned with synchysite-(Ce) and in Fig. 15 centre the bastnäsite-(Ce) is zoned with parisite-(Ce). In the Fig.15 right the bastnäsite-(Ce) is intergrown with parisite-(Ce) from Langersunjdfjord, Oslo region, Norway (Larsen and Williams, 1992). This, the last fine-scale intergrowth of bastnäsite-(Ce) and parisite-(Ce) revealed by backscattered electron images, occurs similarly frequently in the Ditrău REE-carbonates.

The very fine scale oscillatory zonings reflect fluctuations in the composition of the carbothermal/hydrothermal fluid, while the T and P are constant during their formation. Sometimes fine scale oscillatory zoning is superimposed on the sector zoning. This complex zoning results mainly from variations in LREE and Ca. The electron microanalyses have shown these differences in mineral composition within individual crystals. The secondary REE-carbonates were formed by the action of late hydrothermal solutions rich in CO_2 and F on some pre-existent REE-phosphates such as monazite-(Ce), REE rich apatite, on some preexistent and diverse REE-silicates, and even on some primary REE-carbonates. The alterations (transformations) among different terms of REE-fluorcarbonates (belonging to the same group) were observed in the Ditrău REE-carbonates: some of the parisites occurring in hydrothermal mineralization were formed by alteration of primary synchysites, and the röntgenites were formed by the alteration of primary parisites. These transformations among fluocarbonates very likely result from variations in either Ca^{2+} or CO_3^{-2} activities in the fluid. The presence of fluorite as secondary mineral, associated to REE-fluocarbonates is an evidence for a high fluorine content of the mineralizing fluid. They are a late hydrothermal/carbothermal product probably resulting from the fractionation of carbonatite and/or alkaline magmas. Because of this abundance of LREE-carbonates and their associations (calcite, dolomite, ferrodolomite, and ankerite) in this carbothermal /hydrothermal stage, as well as the presence of connections with ultrabasic/basic rocks, the CO_2 source of LREE-fluocarbonates could be related to carbonatite magmas and most probably less to alkaline magmas.

Besides the bastnäsite-(Ce), bastnäsite-(La), hydroxylbastnäsite-(Ce), parisite-(Ce), parisite-(Nd), synchysite-(Ce), synchysite-(Nd), synchysite-(Y), another rare REE-carbonates, such as eisenkalkancylite (carbonate of REE, Fe and Ca), röentgenite-(Ce), and sahamalite-(Ce) also occur infrequently in DACC (Hîrtopanu, 2019).

The primary LREE-fluocarbonates were formed in the carbothermal stage. They follow the primary monazite-(Ce), or could be interfered with it. The primary REE-fluocarbonates cut through the old magnetite-apatite association being younger than the latter, belonging to a new genetical process. Frequently, primary REE-carbonates mantle old monazite-(Ce), and monazite-(Ce) mantles the old apatite.

II.4. REE-SILICATES

Generally, the silicates can accept REE in their structure, but the concentrations do not usually exceed several hundred ppm. Common silicates, such epidote, garnet, titanite, and zircon can have larger amounts exceeding 1 wt% RE_2O_3. Allanite-(Ce) has the higher REE content.

The Ditrău allanite-(Ce) forms coarse brown to good size black crystals of a few cm in size, growing tabular, prismatic to acicular in shape. It may also be granular or massive~~.~~ (Fig. 16). In thin sections it has a brown, red, and green colour with strong pleochroism (Fig.17 left). The bastnäsitisation of allanite and the reverse processes, the allanitisation of bastnäsite-(Ce), occurs frequently.

Figure 16. Banded allanite-(Ce) (grey black) with monazite-(Ce) (red), and pyrite (yellow) vein in calcite (white), 10x5x3 cm (left); Allanite-(Ce) (black prisms) and monazite-(Ce) (red) vein in dolomite (grey), Jolotca area, 2x2x1cm (right). Photo: Ana Tudor.

Allanite-(Ce) occurs as a constituent mineral in Jolotca area and as an accessory in the Belcina area. It occurs in many generations, with specifically the continuous decreasing of REE contents from the old to the new as shown by their microprobe analyses. Oscillatory zoning of allanite-(Ce) can be seen in many backscattered electron images. The allanite-(Ce) can form on monazite-(Ce) and this transformation process is reversible. The allanite-(Ce) and monazite-(Ce) as main constituents of the ore minerals in the Jolotca vein mineralization belong to the high temperature hydrothermal process.

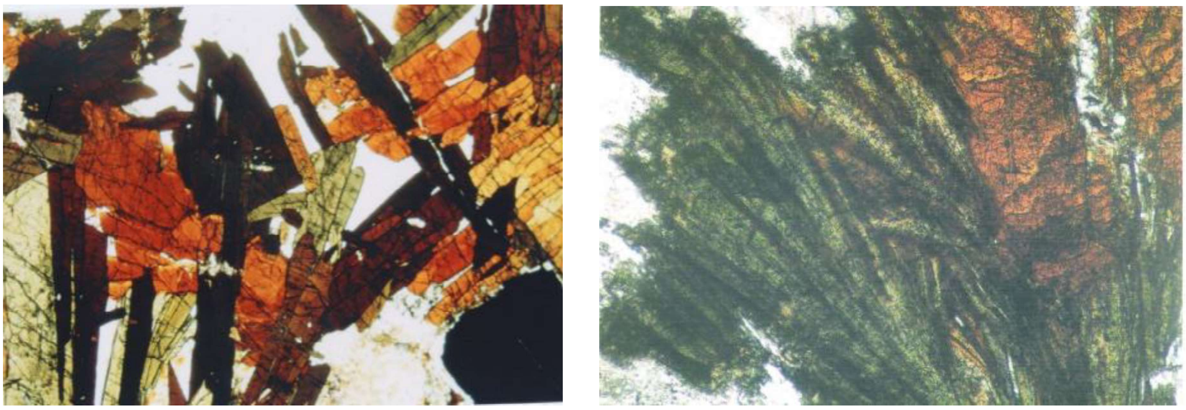

Figure 17. Pleochroism in allanite-(Ce) from yellow, green, orange, red to black, and calcite (white), TL, NII, x20, sample DT18, Jolotca area (left); Hydrothermal large red allanite-(Ce) crystals cut by green cevkinite-(Ce), TL, NII, x30, Jolotca area (right).

The microprobe analyses of allanite-(Ce) revealed the contents: SiO_2=30.00, CaO=8.107, Al_2O_3= 7.931, MgO=0.53, P_2O_5=0.064, FeO=9.338, UO_2= 0.008, ThO_2=0.089, La_2O_3=3.317, Ce_2O_3= 13.244, Nd_2O_3 =2.616, Gd_2O_3=0.86, Dy_2O_3=0.116, Yb_2O_3=0.014, MnO=2.288, F=0.289, OH=1.433 (Hîrtopanu, 2019). Some points of microprobe analyses of Ditrău allanite-(Ce) samples gave Pr_2O_3, SrO_2 (up to 1 %wt), Sm_2O_3, BaO, and ThO_2 in very small contents. The chemical composition of allanite-(Ce) has a high Fe_2O_3 content showing oxidizing conditions for its genesis. The effect of changing redox conditions could be one possible cause for the neoformation of allanite-(Ce) on the other REE silicates or phosphates.

Secondary allanite-(Ce) and many secondary REE-carbonates, REE rich epidote, REE low phyllosilicates, and REE low chlorites could be formed through replacement of old monazite-(Ce). Other REE silicates determined in DACC are: törnebohmite-(Ce), cerite-(Ce), stillwellite-(Ce), tritomite-(Ce), dollaseite-(Ce), and dissakisite-(Ce) (Hîrtopanu, 2019). The zirconium silicates are represented by hydrothermal idiomorphic and zoned zircon, different from the old magmatic zircon which has corrosion rims and no zonations. Some hydrothermal zircon has a high Th-content, becoming a thorian zircon variety. The chevkinite-(Ce) and its dimorph perrierite-(Ce) are found associated to allanite-(Ce), in a Ti-rich environment of the Jolotca mineralized area (Fig. 17 right) (Hîrtopanu *et al.*, 2013a).

II.5. REE-PHOSPHATES

The phosphates include two major REE minerals: **monazite-(Ce)** and **xenotime**-(Y).

Monazite-(Ce), $(Ce,La,Nd,Th)PO_4$, crystals are large, red brown, prismatic and are of a few cm in size (Fig.18). They are colourless, light yellow or light brown in transmitted light and have a weak pleochroism. The refringence and birefringence are high and increase with the ThO_2 content (more exactly, with the Th silicate component huttonite) in the monazite structure. The twinning of hydrothermal monazite-(Ce) is common. The (100) twins could be thick or thin. All grains/crystals are free of inclusions at high magnification, differing from old magmatic monazite-(Ce) which has many and diverse inclusions. The chemical composition of hydrothermal monazite-(Ce) determined by microprobe has the following variations of its main REE-oxides (wt%): Ce_2O_3=34.00-35.00, La_2O_3=19.00-20.00, Nd_2O_3=10.00-11.00, and F=0.826. Some contents of ThO_2, Y_2O_3, Pr_2O_3, Yb_2O_3, Dy_2O_3, Er_2O_3, Gd_2O_3, Sm_2O_3, ZrO_2, and PbO were also determined (Hîrtopanu *et al.*, 2017). The hydrothermal REE-fluorapatite has large crystals, grown radially, without inclusions, thus looking different from the old magmatic bearing REE-fluorapatite.

Other the REE(Y) phosphates predominantly in Belcina mineralization area are: REE-apatite, Th-apatite, REE-carbonate fluorapatite, brabantite-huttonite series, huttonite-monazite series, cheralite, and karnasurtite-(Ce) (Hîrtopanu, 2019). In the magmatic-metasomatic stage the most common substitution in the old apatite is the exchange $Ca^{2+}+P^{5+}\leftarrow REE^{3+}+Si^{4+}$. The incorporation mechanism of tetravalent elements (Th^{4+}) in the structure of monazite-(Ce) is described by means of coupled substitution $Th^{4+}Si^{4+}$ with $Ce^{3+}P^{5+}$. The substitution involves a coupled intervalence replacement which leads to the formation of the cheralite family $(Ca,Ce,Th)(P,Si)O_4$.

Figure 18. Monazite-(Ce) (red), pyrite (yellow) vein in dolomite (grey), 7x7x5cm (left); Monazite-(Ce) and pyrite (yellow) vein in calcite 4x4x3cm (right). Photo: Ana Tudor

The Ditrău monazite-(Ce) has been formed under a variety of conditions. The rare accessory old monazite-(Ce) has crystallized in the magmatic phase, and it has tabular irregular grains (Fig. 19 left). Also, it has many diverse inclusions. The large hydrothermal monazite-(Ce) is predominant in Ditrău, and has a spectacular appearance (Fig. 19 right). It has no inclusions. It constitutes an important economic resource. The youngest secondary monazite-(Ce) has been formed by alteration of allanite-(Ce) and REE carbonates in supergene environments.

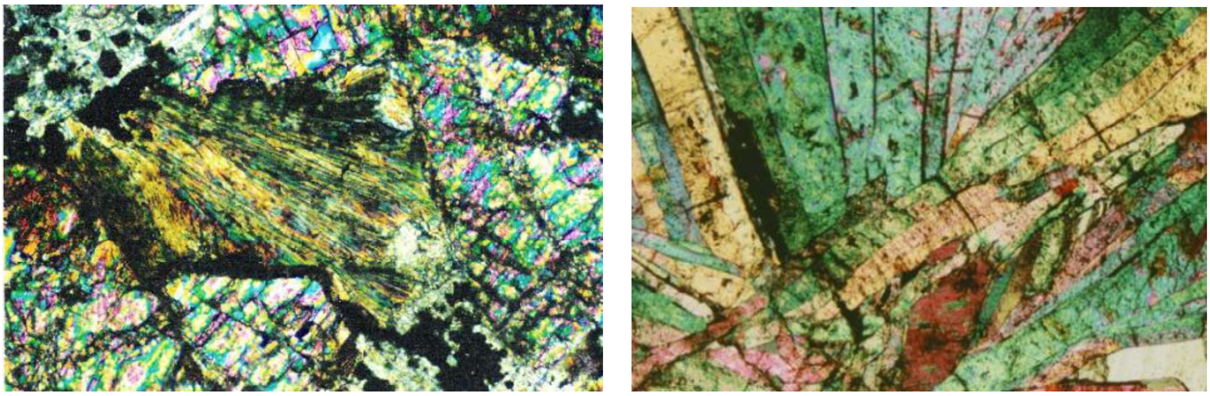

Figure 19. Old monazite-(Ce) (high refringence and birefringence) substituted by undetermined acicular mineral, TL, N+, x25, sample DT24 (left); Large prismatic hydrothermal monazite-(Ce) crystals, TL, N+, x30, sample DT5, (right)

The Ditrău hydrothermal monazite-(Ce) occurs in Jolotca hydrothermal/carbothermal veins accompanied by bastnäsite-(Ce), bastnäsite-(La), parisite-(Ce), synchysite-(Ce), allanite-(Ce), apatite, magnetite, many sulphides (predominantly pyrite) and fluorite. Among these all rare earth minerals, the monazite-(Ce) aggregates seem to be the oldest, because they are cut by sulphides and are substituted by allanite-(Ce) and REE-carbonates. Low temperature hydrothermal solutions may cause the breakdown of monazite-(Ce), thus releasing REE to form secondary REE minerals. Secondary allanite-(Ce), many secondary REE-carbonates, REE rich epidote, REE rich phyllosilicates and chlorites could be formed in this way through monazite-(Ce) replacing.

Xenotime-(Y), YPO_4, crystalizes tetragonal. The crystal structure of xenotime-(Y) shows close relationships to that of monazite-(Ce). The arrangements of the PO_4 tetrahedra, which are connected by RE atoms in both structures, are distinct, due to the differences in volumes and shapes of the RE polyhedra (Ueda, 1967). The crystal structure of xenotime-(Y) is isostructural with that of zircon. The Belcina xenotime-(Y) forms isometric, short to long prismatic crystals sometimes in radial or rosete-like aggregates. In transmitted light is colorless to very pale yellow, yellowish green, yellow or yellow-brown with weak pleochroism and (100) good cleavage (Fig. 20). It has high refringence and birefringence and is uniaxial (+). The xenotime-(Y) in some samples from Belcina (BEL12B, BEL12, BEL9) was investigated with microprobe and their determined chemical compositions showed only and P_2O_5 =40,00 %wt and Y_2 (sample BEL9) (Hîrtopanu, 2019).

Xenotime-(Y) occurs in the Y, Th, Zr, U Belcina mineralization like a constituent mineral (Hîrtopanu *et al.*, 2013b). It is closely associated with thorite (Fig 20). Other associated minerals to xenotime-(Y) in Belcina area are: zircon, baddeleyite, REE-apatite, Fe-hydroxides, chlorite, siderite, calcite. In the Jolotca area, when predominant is the Nb and REE-element mineralizations, xenotime-(Y) occurs as accessory mineral, associated with REE-carbonates, allanite, monazite, niobian rutile, ilmenite in calcite, dolomite and siderite carbonatites.

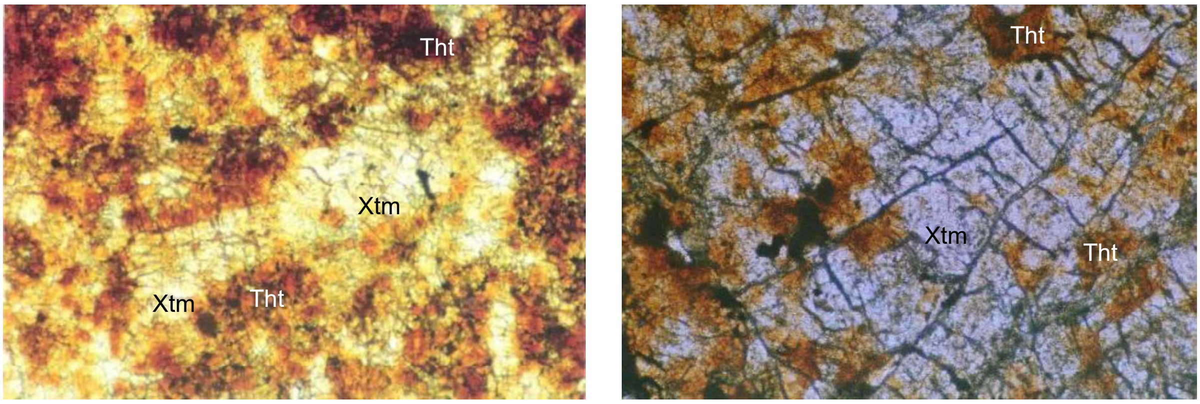

Figure 20. Xenotime-(Y) (Xtm, large grain, white-yellow) intergrown with thorite (Tht, red brown), TL, NII, x30 (left); Xenotime-(Y) (Xtm, grey, large grain) with thorite (Tht, red brown) around it (right); TL, NII, x30, Belcina area.

The **Belcina** vein type mineralization belongs to the same low-hydrothermal process, but at its late stage of very low T. It is situated outside the Ditrău massif, in the surrounding metamorphite rocks of the Tulgheș Group. The Belcina occurrence (Hîrtopanu, 2019) comprises a complex mineralization, different from those previously reported in Jolotca. The large thorite closely associated with the large xenotime-(Y) represent the characteristic paragenesis of the Belcina type mineralization. The late stage calcite, siderite, ferrodolomite, ankerite, new apatite veins, the development of the Fe-oxides and hydroxides (colomorph hematite, goethite, and lepidocrocite), and the minor sulfides of Fe, Pb, Zn, Mo and Hg, are all the carbonatites mineralization features. Also, the development of many apatites (new Th-rich apatite and Y-bearing apatite) and carbonates of different generations as gangue minerals is specific to some mineralizations generated by carbothermal/hydrothermal carbonatite fluids.

III. CONCLUSIONS

The REE minerals which were determined in DACC belong to the following classes: Halides, Oxides, Carbonates, Phosphates, and Silicates.

In the DACC, mainy Light REE/Cerium group minerals: LREE-carbonates, monazite-(Ce), allanite-(Ce), are concentrated in Jolotca area, while mainly heavy REE/Yttrium group minerals represented by xenotime-(Y), closely associated with Th silicates (thorite, thorogummite), are concentrated in the Belcina area. The magmatic/metasomatic/hydrothermal differentiation processes are responsible for the in-situ concentration of many varieties of these rare earth element minerals in the DACC. 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, and the very complicated compositions of some minerals, due to the sudden variation of hydrothermal mineralization solutions. The mineralizing process was multi-staged, having at least 5 stages. Monazite-(Ce) and allanite-(Ce) belong to the high temperature hydrothermal process. Follow the primary REE-carbonates which belong to a new genetic process, the carbothermal one, hosted by calcite, dolomite, siderite carbonate rocks. The Belcina Y-Th complex mineralization, with large xenotime-(Y) and thorite association, could be the last stage, low-temperature carbothermal stage often found with hematite, baryte, Y-fluorite, many apatites, new zircon, and sulfides.

Worldwide the vast majority of RRE-(Y) mineral resources are associated with three minerals: monazite-(Ce), bastnäsite-(Ce), and xenotime-(Y). Bastnäsite-(Ce) and monazite-(Ce) are the primary source of LREE, mainly Ce, La and Nd. Xenotime-(Y) is a primary source for HREE, including Y, Dy, Er, Gd, Yb and Ho. The Ditrău mineralized area comprises both types of mineralizations with separate localization in space and time: Jolotca, enriched in LREE minerals, and Belcina, enriched in HREE/Y.

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