RARE MINERALS IN GRĂDIŞTEA DE MUNTE AREA, ŞURIANU MOUNTAINS, ROMANIA

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ABSTRACT. Mineralogical features of the minerals of Gradistea de Munte, demonstrate its long multistage crystallization. The multi-staged mineralizing process is supported by textural relationships of all rare minerals constituents of ore, where replacement of earlier minerals by later ones is common. The textural relations between -Nb, -REE(Y), -Th, -U an -Zr minerals, and between the zircon and minerals of the host rock, show that zircon/cyrtolite shows many generations: the old zircon occurs as discrete grains in phlogopite and magnetite, is good crystallized, transparent, similar to igneous zircon; the zircon/cyrtolite have a texture consisting of a mixture of two microdomains, metamict and crystalline. The new zircon generations overgrown as small clean crystals, as a fringe on cyrtolite, baddeleyite, thorite, etc could be considered as resulting from hydrothermal processes. Their geochemical zoning indicates a different origin of each part of the crystal. Representative microprobe analysis of Gradistea de Munte zircon/cyrtolite show high contents of Th, Y, Yb, Ce, Hf; U and less La, Nd, Sm, Dy and Nb. The heavy rare earth elements (HREE), specially *Y*, beside *T*h and sometimes *H*f; are the predominant trace elements in OM zircon/cyrtolite, because of their similarity in ionic radius to Zr^{4+} . The baddeleyite occurrence as one of the oldest mineral, indicates that the first vein mineralizing solutions were subsaturated in silica. The absence of silica has stabilized baddeleyite and its presence has stabilized the zircon/cyrtolite.

Key words: zircon, cyrtolite, yttropyrochlore, uranpyrochlore, thorite, cassiterite, baddeleyite.

1. Geological setting

The rare element minerals occurrence on the north slope of the Şurianu Mountains, South Carpathians, is situated around Gradiştea de Munte village, in the upper course of the Orastie river. From a structural geological point of view the Gradiştea de Munte area belongs to Sebes-Lotru Seties ofthe Upper Proterozoic Getic Crystalline. It is metamorphosed under amphibolite facies and in this area is represented by micaschists with kyanite and garnets, quartz-feldspar gneisses and amphibolites.

The quartz-feldspar gneisses/" granites" represent here the most important

petrographic type, being the host of mineralization. Their mineralogical composition is: *microcline, albite, quartz, biotite* and *muscovite*. They have a pink grey color or red because of the important presence of potassium feldspar, when the rock looks like a granite, constituted only by *microcline* and *quartz*.

Sometimes, the quartz is missing, the rocks being formed only from microcline, with little albite and some accessory minerals.

The mineralization is linked with this "granite". When this gneiss/granite is mineralized it becames typical dark red or brick-colored, easy to recognize on the field.

The Gradistea de Munte rare elements mineralization comprised 4 bodies of microcline gneisses/ granites amongst them the body no. 1 was the best. It is of 3,5/0,5/0,05 km in size and was explored by mining workings and drilling. The content of Nb+Ta established with these workings was more than 1,5 % wt, the content of REE (Y) was about of 0,5% wt (the Y content was much more than Ce). Also, the Th content (about 0.5% wt) was much more than U. The zirconium has the highest content amongst all these rare elements and its silicate mineral-zircon/ cvrtolite is the most common mineral being omnipresent in high content in the ore/rock.

2. Mineralogy of Gradiştea de Munte occurrence

The gneiss/"granite", host of mineralization, contains magnetite and the zircon/cyrtolite as constituents minerals, while the other rare element minerals occur as accessory ones and sometimes even less.

The mineralogy of Grădiiștea de Munte rare element minerals is very complex. The rare Nb, Ta, REE (Y), Zr, Sn, Th and U minerals belong to the following four classes: oxides, carbonates, phosphates and silicates.

The oxides class is represented by 9 supergroup/groups: pyrochlore supergroup (with 2 groups, proper *pyrochlore* and *betafite*), *fergusonite*, *columbite*, *euxenite*, *Nb-rutile*, *cassiterite*, *baddeleyite*, *uraninite* +*thorianite*.

The carbonates, although less widespread, are diversified, being represented by 6 minerals: *bastnasite-(Ce)*, *bastnasite-(Y)*, *thorbastnasite*, *parisite-(Ce)*, *synchysite-(Y)* and *synchysite-(Ce)*.

Amongst rare earth phosphates, there are present the thorium phosphate, *brabantite*, and Y (REE) phosphates, represented by *monazite-(Ce)*, *xenotime-(Y)* and *cheralite-(Ce)*.

In the Grădiiștea de Munte occurrence

the most widespread rare element minerals are the silicates, represented by Nb, LREE, Y, Th, Zr and D, and among them the Y-silicates and Th-silicates are predominant. The LREE-silicates are represented by *allanite-(Ce)*, *yttrifer allanite-(Ce)* and *cerite-(Ce)*. The Y-silicates are largely being represented by several terms: yttrialite-(Y), th alenite-(Y), rowlandite-(Y), tombarthite-(Y).

3. Physical and optical properties of zircon/cyrtolite

Zircon often alters chemically, especially when it contains U, Th, Y, Pb and cations of valence lower than four. It is characterized by the presence of water and by a deficiency of silica. These features provide the proof for suspecting the existence of an $(OH)_n:(SiO_n)$ substitution in zircon such as that indicated for thorite. The substitution in the following manner: one OH substitutes for one O in SiO₄ tetrahedra, as Si(O,OH). The hydroxyl substitution in zircon and tho rite make them prone to metamictization. So, a small substitution of (OH) for O as Si(O,OH) tetrahedra occurs in zircon and thorite, but the total water content is not higher than 5-6%.

Kostyleva first (1946) established that the metamictic disintegration is the result of destruction of bonds in the lattice produced by alpha radiation from the radioactive elements present. The cyrtolite was first noted at Bedford, N.Y., by Luquer (1904) as being "a zircon which contains uranium, thorium and rare earth as well as the usual zircon constituents: zirconium, hafnium, silicon and oxygen". Since cyrtolite range from crystalline to amorphous, it is assumed that the originally possessed a definite crystalline structure which subsequently has been completely or partially destroyed.

Cyrtolite, is a metamict substance. It has a weakly ionic structure which would be readily susceptible to changes into state of ionization (Norton, 1957). The Grădiiștea de Munte zircon/cyrtolite forms veinlets and small nests of a few cm and bigger in the host rock. Most of the Grădiiștea de Munte zircon/cyrtolite grains/aggregates range from 2-3 mm to 1 cm in diameter and much more. The hand specimens of samples are dark reddish brown, grey, green or blackish brown color. The zircon/cyrtolite grains are irregular in shape and boundaries. A few crystals show tetragonal symmetry, typical zircon-like prisms, most of them being flattened and distorted (Fig. 1A).

The cyrtolite has microcrystalline granular to fibrous structure (Fig. 2A).

Also, there were observed cauliflower-

like aggregate of cyrtolite. Some crystals are roughly triangular or pseudohexagonal in outline. Their colours in thin sections are pale reddish, orange red, yellow, orange yellow (Fig. 2B), brown (Fig. 1B), greyish green, green to light green (Fig. 1A, 7B) and are sometimes colourless.

A long yellow brown fibrous grain aggregate of cyrtolite with rounded shape is surrounded with small light yellow brown new zircon grains with good shape (Fig IA).

In the figure 2A and 2B one can see the zonation of the fibrous cyrtolite, which develops a cross texture in the centre of the grains (2A). In the Fig. lB, big yellow brown micro granular aggregate of cyrtolite with



Fig. 1. Rounded, irregular shape of cyrtolite grain (Cy, big grain, yellow-green) with new zircon grains with good shape and high refringence around (Zr)
TL, NII, sample 015-1/4, (A); Cyrtolite brown grain aggregate (Cy) with isotropic areas and low birefringence, and new small zircon grains (Zr) around with good shape and high birefringence, TL, N+, sample 015-4/3 (B).



Fig. 2. Fibrous sectorial and marginal zoned of fibrous cyrtolite grains (Cy, green) showing a texture like ofthat of chiastolite cross, with new generation of small zircon (Zr, clean, no fibrous) grains around, TL, NII, sample 011-2 (A); Fibrous zoned marginal cyrtolite (Cy) with metamict areas (Mtc), with low birefringence TL, N+, sample OMI5-1/8 (B).



Fig. 3. Baddeleyite (Bad, big grain, centre, grayish white, clean, high refringence) with many small zircons around (Zr, grey), as a fringe, associated with phlogopite (PhI), and other new zircon grains around, NII sample 011-2-1/1 (A); Thorogummite (Th, yellow brown prismatic grain) with new small grains zircon (Zr) around, as a fringe, NII, sample 011-2/11 (B).

low birefringence, is surrounded by another small later zircon crystals with high birefringence. No optical figure could be obtained for Grădiiștea de Munte cyrtolite. The dark isotropic areas are metamict (Figs. IB, 2B).

4. Association

The Grădiiștea de Munte zircon/cyrtolite crystals are concentrated as small lens in magnetite, phlogopite/biotite and feldspars (albite and microcline), being associated with *yttropyrochlore-(Y)* (Fig. 4B),

fergusonite-(Y), uranpyrochlore (Fig. 7B), mo nazite-(C e), xenotime-(Y), many Y-silicates, thorite/thorogummite (Figs. 3B, 4A), Zr-thorite, Nb-Zr-silicates, cassiterite (Fig. 6B) and has uraninite (Fig. 5B), baddeleyite thorianite and fergusonite inclusions (Fig. 5A).

Some zoned clean zircons are associated with *yttrocolumbite* with oscillatory composition.

The oldest zircon is enclosed in *phlogopite* and *magnetite*. Small grains of cyrtolite, together with apatite (Fig. 4B) and xenotime-(Y) are enclosed in Y-silicates, the



Fig. 4. BSE image of oscillatory composition in thorite (Th): white more Th, Nb, Y, Fe and white grey with more Si and Th and less Nb, Fe and Y, many zircons (Zr) inside and around, sample GII-5/2a (A); BSE image of zircons (Zr) enclosed in yttropyrochlore-(Y) (Ytp) with oscillatory composition: more Ta and less Y (white grey) and more Nb and Y (white), sample G15BA/I (B).



Fig.5. BSE image of zircon/cyrtolite grain with baddeleyite (Bad, white grey, small) andfergussonite (Fgs, whitebright, small) inside,sample G11-2-1(A); BSE image of zircon/cyrtolitegrain with porous texture (Zr,grey),uraninite (Urn, white, enclosed in zircon), Y-carbonate(Ycb, fibrous,grey, belowuraninite), sampleGrădiiştea de MunteC/2 (B).

latter minerals being amongst the newest formed minerals in the occurrence.

Sometimes, the zircon grains grow around Y-silicates, belonging probably to another generation. Also, new grain zircons with good shape are associated with a mixture of apatite and thorium phosphate silicate (cheralite-huttonite) (sample G15BA/6).

In the associations with secondary fibrous Y-REE-Ca carbonates, the zircon grains are clean and with good prismatic shape and zoned (sample GI5BA/6), while in the associations with *thorite /thorogummite* and *uranpyrochlore* the cyrtolite is predominant.

The old *baddeleyite* is surrounded by new small zircons grains as fringes (Fig. 3A), showing that the first vein mineralization solutions were subsaturated in silica. The absence of silica has stabilized baddeleyite and its presence has stabilized zircon/ cyrtolite. The same as zoning of zircons/ cyrtolites, the substitution relations zircon-baddeleite, demonstrates the sudden change in minor and major element contents of mineralizing solutions during rapid, late stage crystallization. Also, the other Grădiiştea de Munte silicates, especially Y and Th, change their composition even in the same crystal (as seen in their backscattered



Fig. 6. BSE image of Y-silicate grain (Y-sil, prism, with oscillatory composition), with zircon (Zr) and xenotime (Xn) inside; in the corner up left thorite with zirconium (Th) with apatite (Ap) around, sample Grădiiştea de Munte31/10, (A); BSE image of zoned cassiterite (white, grey white) with enclosed zircon (prismatic, grey), sample GII-4A11, (B).

electronic images) and pass from one variety to another, because of the rapid change in composition of mineralizing solutions.

Chemistry of Grădiiştea de Munte zircon/cyrtolite

All the total percentages of microprobe analyses of Grădiiştea de Munte zircon/cyrtolite are less then 100% (Table 1). This is because the water was not determined. Also, many important trace elements are below the detection limit of this method. sites for cation substitution, a tetragonal (Si) and a triangular dodecahedral sites (Zr) (Speer, 80). The predominant substitution involves replacement of Zr in the larger triangular dodecahedral sites. Zircon type compounds display variable degrees of solid solution among end members.

Zircon/cyrtolite is isostructural with thoritel thorogummite with which it forms a complete series. The ZrO_2 content in some Grădiiștea de Munte thorite/thorogummite is around 15% wt, confirming an extent of solid solution between $ZrSiO_4$ and $ThSiO_4$. In some cyrtolites the ThO₂ have sometimes high

Sample	G15-4/64	G15BA/4b/4	G11-2-1/6/1	G11-2-1/6a/2	G40-1b/2	G40/4/2	G40/7/1	G15BA/1a/3	G15BA/4/7
SiO ₂	31.614	32.31	31.16	30.15	32.06	35.70	35.17	35.41	33.75
ZrO ₂	62.268	55.94	58.16	58.17	57.62	56.87	54.68	45.05	55.95
Y_2O_3	0	2.64	2.63	2.65	2.63	2.61	0.09	2.13	2.62
B ₂ O ₃	0	0	0	0	0	0	0.01	0.43	0
Ta ₂ O ₅	0	0.06	0.12	0.12	0.05	0.11	2.97	0.43	0.25
La ₂ O ₃	0	0	0	0	0	0	0.51	0.07	0
Nb ₂ O ₅	0	0	0	0	0	0	0	6.02	0.62
P2O5	0.124	0.58	0.05	0.04	0	0	0.07	0	0.63
Ce ₂ O ₃	0	0.06	0.04	0.07	0.04	0.03	3.05	0.79	0.10
Pr ₂ O ₃	0	0.09	0	0	0	0.01	0.20	0	0
Nd ₂ O ₃	0.024	0	0.03	0	0.03	0.01	0.79	0.28	0.07
Sm ₂ O ₃	0	0.01	0	0	0	0	0.15	0.04	0.02
Eu ₂ O ₃	0	0	0	0	0	0	0.09	0,01	0
Gd ₂ O ₃	0.022	0	0	0.04	0	0	0.18	0.04	0.04
Dy2O3	0.001	0.12	0.04	0.01	0	0	0	0.08	0.04
Yb ₂ O ₃	0.097	0.14	0.22	0.20	0.05	0.17	0.10	0.35	0.38
Tb ₂ O ₃	0	0.03	0.01	0.04	0.04	0.02	0	0	0
Ho ₂ O ₃	0	0	0	0	0	0	0	0	0
Er_2O_3	0	0	0	0	0	0	0	0	0
Tm ₂ O ₃	0	0.03	0.04	0.05	0.02	0.03	0	0	0.04
Lu ₂ O ₃	0	0.05	0.02	0.04	0	0.06	0	0.05	0
PbO	0	0.01	0.02	0	0.03	0.01	0.14	0.02	0
ThO ₂	0	0.10	0.06	0.15	0	0.01	0	0.30	0.17
UO ₂	0.010	0.05	0.11	0.34	0.23	0.18	0.01	0.51	0.46
HfO ₂	0	0.09	0.03	0.20	0.10	0.11	0.08	0.40	0.16
F	0	0.15	0.12	0	0.08	0	0.01	0	0.03
Na ₂ O	0.071	0	0	0	0	0	0	0	0
K ₂ O	0	0.02	0	0	0.01	0.01	0.06	0.02	0.01
MgO	0.160	0.03	0.03	0	0	0	0	0	0
Cr ₂ O3	0	0	0	0	0.02	0	0.02	0.02	0
Al ₂ O ₃	0.016	0.14	0	0.05	0	0	0.35	0	0.02
CaO	0.271	0.04	0	0	0	0	0.02	0.01	0.09
SrO	0	0	0	0	0	0	0	0	0
BaO	0	0	0.01	0.02	0	0	0.06	0.10	0.02
FeO	0	0.08	0.08	0.22	0.02	0.08	0.13	0.85	0.13
MnO	0.002	0.00	0.01	0.01	0	0	0.03	0.07	0.01
TiO ₂	0.098	0.37	0	0	0.01	0.01	0.22	0.19	0.04
Total	94,780	95.38	95.19	96.71	94.90	95.91	94.25	94.17	95.63

Table 1. Representative microprobe analyses of cyrtolite/zircon

The ability of zircon to incorporate and retain trace elements is largely determined by its crystal structure. The zircon structure has general formula ATO_4 , in which high field strength T-sites cations occupy isolated tetrahedral, and A-site cations occupy larger eight coordinated structural sites.

values (5% wt), and it could be named *Th-cyrtolite*, (Th,Zr)(SiO₄)(OH)₄. Because the zircon is isostructural with xenotime, the Y and P will preferential enter in its structure in the agreement with the substitution: $Zr^{4+} + Si^{4+}$. $Y^{3+} + P^{5+}$.

The zircon structure has two possible

The Grădiiștea de Munte zircon/cyrtolite has the P_2O_5 content around 0-0,63 (Table 1),

and Y_2O_3 has the highest contents, around 2,62% wt (Table 1). The Yb_2O_3 is always present, but with smaller contents than Y_2O_3 .

Another possible substitution in zircon is: $2Zr^{4+}$ * (NbTa)⁵⁺ + REE³⁺. The substitution of Zr by REE-Nb in Grădiiștea de Munte zircon occurs rarely, because the big difference between their ionic radius and the Nb-REE were finally concentrated in fergusonite.

The incorporation of U and Th into zircon is primarly governed by coupling the thorite substitution with the coffinite substitution $U^{4+} + Th^{4+} * 2Zr^{4+}$ (Mihoko et al, 2010).

The HfO₂ has a large content variation, between 0-6,50% wt. The high content of Hf, has the cyrtolite from Fig 7A, with

represent the true age of the mineral.

At least some of the U- as *uraninite* and Th- as *thorianite* from Grădiiștea de Munte cyrtolite is secondary, forming veinlets and nests inside it (Fig 5B). The ThO₂ contents of zircon/cyrtolite in Table 1, have been placed in the structure during the original crystallization of the mineral.

The variations of trace elements in zircons cause its zoning. In fig 7 A, the core of crystal is enriched in Th and U, transforming it into brown blackish cyrtolite, while the rims are transparent, devoid of visible imperfections of structure and no inclusions. Also, the zircon zoning reflects the sudden change of trace elements contents during rapid, late stage crystallization, being a geochemical zoning.

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Fig 7. Zoned crystal:cyrtolite (Cy, core, high Hf), zircon (Zr, rim, clean, no Hf), sample Grădiiştea de Munte31 (A); uranpyrochlore (Upy, yellow orange) associated with green radioactive cyrtolite variety (Cy), LT, NII, sample G15-1 (B).

representative microprobe analysis: SiO₂=28,30, FeO=0,22, ZrO₂=64,96, $HfO_2=6,50\%$ wt, that could be a new variety cyrtolite, hafnium cyrtolite of $(Hf,Zr)(SiO_4)(OH)_4$. Because the cyrtolite grains have uraninite inclusions (Fig 5B), it is difficult to established for Grădiiștea de Munte cyrtolite if its alpha emitters (Th, U and possible Sm¹⁵²) have been placed in the structure during the original crystallization of the mineral, or all the alpha emitters have been introduced secondarily. In this last case, metamictization might have occurred, but the degree of metamictisation would not

Conclusions

Zirconium, together with Nb and REE are high-field-strength elements (HFSE), i.e., their ions are relatively small and highly charged and they are considered to be among the most immobile elements in aqueous solutions. However, at least locally mobility of Zr has been reported in a variety of geological settings.

Many studies have suggested that hydrothermal transport and deposition were the primary processes in creating some zirconium ores. The Grădiiștea de Munte zircon was affected by metamict disintegration, consisting in progressive hydration and destruction of the crystalline network, due to the effect of the self-radioactive damage.

The cyrtolite is surrounded by a fringe of a new zircon generation. This new zircon generation could be considered as resulting from hydrothermal overgrowth processes.

Recognizing the hydrothermal nature of zircon is important for reconstructing ore-forming processes by U-Pb dating.

The Grădiiștea de Munte zircon/ cyrtolite, especially the old generation, is not very good crystallized, presenting an intermediary degradation degree to a metamictic state, because of the presence of the radioactive element (U and Th) contents in its composition.

Thus, frequently its structure consists of a mixture of the two microdomains: metamictic and crystalline. It was proved that the metamict zircon (with a serious degradation of crystalline structure) has a higher solubility than the zircon with a good structural network, that explains its presence in the hydrothermal later paragensis. The method of X-ray fluorescence and X-ray diffraction procedures are necessary to establish that the Grădiştea de Munte zircon/cyrtolite can be used for age determinations.

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