

## Nb, Ta, Ti, REE(Y), Zr, Sn, Th, U OXIDES FROM GRADISTEA DE MUNTE RARE ELEMENT MINERALS OCCURRENCE, SEBES MTS., ROMANIA

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The Gradistea de Munte (GM) rare element minerals occurrence is situated in the north of the Sebes Mts., Southern Carpathians, in the upper course of the Orastie River. Geologically-structurally the GM area consists of the amphibolite facies rocks of the Upper Proterozoic Sebes-Lotru Series of the Getic Crystalline. The most important host rock of the mineralization is a quartz-microcline-albite gneiss/"granite". Sometimes the rocks being formed only from microcline, albite, some phlogopite/biotite and accessory rare minerals, quartz is missing. Cyrtolite/zircon and magnetite are always present as ore/mineral components of the rock. The rare earth element mineralization is represented by carbonates, oxides, silicates and phosphates, in veinlets and nests of mm to cm size grains. The REE oxides in GM belong to 7 groups: **pyrochlore**, **fergusonite**, **columbite**, **"ilmeno-struverite"**, **baddeleyite**, **cassiterite** and **thorianite-uraninite**. **1. Pyrochlore group** has 3 subgroups. **A. Pyrochlore subgroup** with the major B-site cations (Nb + Ta) > Ti and Nb > Ta, comprises **pyrochlore**, **ytropyrochlore-(Y)**, **uranpyrochlore**, **plumbopyrochlore** and **thoriopyrochlore**, defined by the cations residing in A-site. The GM **pyrochlore** has (Ca,Fe,U,Th) > 20% in A-site, Nb<sub>2</sub>O<sub>5</sub> ≈ 50% and Ta<sub>2</sub>O<sub>5</sub> ≈ 2–10%. **Ytropyrochlore-(Y)** contains beside dominant Y (≈ 15–20 wt% Y<sub>2</sub>O<sub>3</sub>) in A site some oxides of Ce, Nd, Dy, Gd, Yb (≈ 10 wt%). The Nb<sub>2</sub>O<sub>5</sub> content varies between 40–50 and Ta<sub>2</sub>O<sub>5</sub> between 1–2 wt%. It always contains some UO<sub>2</sub> and ThO<sub>2</sub>, thus metamictisation being very common. In addition, ytropyrochlore-(Y) has some SiO<sub>2</sub> content, common in metamictic and late stage hydrated pyrochlores. Ytropyrochlore-(Y) is the best widespread term of pyrochlore. **Plumbopyrochlore** has (Pb,Ca,U) > 20% in A site, Nb<sub>2</sub>O<sub>5</sub> = 46.5 and Ta<sub>2</sub>O<sub>5</sub> = 18.5 wt%. **Uranpyrochlore** has UO<sub>2</sub> dominance in A site (= 13–25%) with some Ln<sub>2</sub>O<sub>3</sub> ≈ 4, Ca + Ba ≈ 10, Y<sub>2</sub>O<sub>3</sub> = 1.5–6 and ThO<sub>2</sub> = 2 wt%. Its Nb<sub>2</sub>O<sub>5</sub> content varies between 30–50 and Ta<sub>2</sub>O<sub>5</sub> between 10–15 wt%. It is omnipresent as few mm to cm size grains in all types of rocks/ores from GM. In transmitted light it is light red, yellow orange, red. It contains some ZrO<sub>2</sub> (≈ 2 wt%), being associated with cyrtolite. Like ytropyrochlore, it has high SiO<sub>2</sub> content (7–10 wt%). The GM **thoriopyrochlore** is Th dominant with some Y, and Fe in A site. The ThO<sub>2</sub> content is very high, around 40 wt%. It contains OH and chlorine (≈ 0.6 wt%) in Y site. It is associated with thorite and thorgummite. **B. Microlite subgroup** (Ta<sub>B</sub> ≥ Nb<sub>B</sub>, Nb + Ta > 2Ti) comprise the **uranmicrolite**, with Nb<sub>2</sub>O<sub>5</sub> ≈ 30, Ta<sub>2</sub>O<sub>5</sub> ≈ 48.5, UO<sub>2</sub> ≈ 14.6 wt%, **thormicrolite** with Nb<sub>2</sub>O<sub>5</sub> ≈ 19, Ta<sub>2</sub>O<sub>5</sub> ≈ 25, ThO<sub>2</sub> ≈ 48 wt%, and **yttromicrolite** with

Nb<sub>2</sub>O<sub>5</sub> ≈ 22, Ta<sub>2</sub>O<sub>5</sub> ≈ 25 wt%, having U, Th, respectively Y in A site > 20%. **C. Betafite subgroup**, B = 2Ti<sub>B</sub> ≥ (Nb + Ta)<sub>B</sub>, in GM is represented by the occurrence of **betafite** (U > 20% in A site) and **yttrobetafite-(Y)** (Y > 20% in A site). The last one occurs as big grains of up to 1 cm. The chemical composition of yttrobetafite-(Y) varies: TiO<sub>2</sub> = 27–30, Y<sub>2</sub>O<sub>3</sub> = 15–22, Nb<sub>2</sub>O<sub>5</sub> = 22–27, Ta<sub>2</sub>O<sub>5</sub> = 7–19, ThO<sub>2</sub> = 5–10, UO<sub>2</sub> = 4–6 wt%. Some yttrobetafite-(Y) grains have a very Ta-rich composition: Ta<sub>2</sub>O<sub>5</sub> = 31.2, Y<sub>2</sub>O<sub>3</sub> = 28.8, TiO<sub>2</sub> = 36.0 wt% and they do not contain Nb<sub>2</sub>O<sub>5</sub>. Compositional zoning was visible from yttrobetafite-(Y) inside to **Ta-yttrobetafite-(Y)** outside in a grain. **2. The fergusonite group** contains the **fergusonite-(Y)** with Nb<sub>2</sub>O<sub>5</sub> = 45–58, Y<sub>2</sub>O<sub>3</sub> = 25–35, Yb<sub>2</sub>O<sub>3</sub> + Gd<sub>2</sub>O<sub>3</sub> + Dy<sub>2</sub>O<sub>3</sub> ≈ 4.5 wt% and very little Ta<sub>2</sub>O<sub>5</sub>, with maximum 5 wt% UO<sub>2</sub> and ThO<sub>2</sub> content. The grains of fergusonite-(Y) are zoned with **formanite-(Y)**, which has Y<sub>2</sub>O<sub>3</sub> = 34.6, Ta<sub>2</sub>O<sub>5</sub> = 48.2 wt% and little CaO, FeO and ThO<sub>2</sub>. Another grain has Y<sub>2</sub>O<sub>3</sub> = 36.15, Ta<sub>2</sub>O<sub>5</sub> = 45.72, Ce<sub>2</sub>O<sub>3</sub> = 5.17 and CaO = 4.43 wt% composition. The same grain could be built up from many phases, corresponding to ytropyrochlore-(Y), yttromicrolite-(Y), formanite-(Y) showing the Ta increase. **3. Ferrocolumbite** has: FeO = 16.2, MnO = 3.03, Nb<sub>2</sub>O<sub>5</sub> = 72.8, Ta<sub>2</sub>O<sub>5</sub> = 4.2, TiO<sub>2</sub> = 3.5 wt% and **manganocolumbite** has Nb<sub>2</sub>O<sub>5</sub> = 76.28, MnO = 10.93, FeO = 0.44, TiO<sub>2</sub> = 0.8 wt%. Some grains have high UO<sub>2</sub> content of up to 8.4 wt%. The composition of some grains are (Y<sub>2</sub>O<sub>3</sub> + FeO + MnO) > 20 wt%, high Nb<sub>2</sub>O<sub>5</sub> (> 65 wt%) some Ta<sub>2</sub>O<sub>5</sub> and no TiO<sub>2</sub> which could belong to **yttrocolumbite**. **4. "Ilmenorutile"** has: TiO<sub>2</sub> = 49.5–52.5, Nb<sub>2</sub>O<sub>5</sub> = 21.8–26.5, Ta<sub>2</sub>O<sub>5</sub> = 7.7–13.31, FeO = 9.4–12.03 wt%, showing a solid solution with **"struverite"**. **5. Baddeleyite** appears to be one of the oldest minerals, older than cyrtolite and its presence indicates that the first mineralized solutions were subsaturated in silica. Its composition shows only ZrO<sub>2</sub> with some ThO<sub>2</sub> and very little HfO<sub>2</sub>. **6. Cassiterite** appears as big cm grains in hydrothermal veinlets and has little U, Th and Fe in its composition. **7. Uraninite** and **thorianite**, usually form solid solutions with the composition UO<sub>2</sub> = 49.1, ThO<sub>2</sub> = 48.0 wt%. Separately, uraninite has composition: UO<sub>2</sub> ≈ 96.6 wt% with little ThO<sub>2</sub>, Y<sub>2</sub>O<sub>3</sub>, PbO, FeO, and thorianite has ThO<sub>2</sub> = 96.3, PbO = 3.27, FeO = 0.23, SiO<sub>2</sub> = 0.16 wt%. Generally, the content of Nb + Ta in all rare minerals is higher than that of Y + REE, and the Y content is much higher than Ce. Also, the Th content is much higher than U. The zirconium has the highest content.