

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, Nb₂O₅ ≈ 50% and Ta₂O₅ ≈ 2–10%. **Ytropyrochlore-(Y)** contains beside dominant Y (≈ 15–20 wt% Y₂O₃) in A site some oxides of Ce, Nd, Dy, Gd, Yb (≈ 10 wt%). The Nb₂O₅ content varies between 40–50 and Ta₂O₅ between 1–2 wt%. It always contains some UO₂ and ThO₂, thus metamictisation being very common. In addition, ytropyrochlore-(Y) has some SiO₂ 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, Nb₂O₅ = 46.5 and Ta₂O₅ = 18.5 wt%. **Uranpyrochlore** has UO₂ dominance in A site (= 13–25%) with some Ln₂O₃ ≈ 4, Ca + Ba ≈ 10, Y₂O₃ = 1.5–6 and ThO₂ = 2 wt%. Its Nb₂O₅ content varies between 30–50 and Ta₂O₅ 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 ZrO₂ (≈ 2 wt%), being associated with cyrtolite. Like ytropyrochlore, it has high SiO₂ content (7–10 wt%). The GM **thoriopyrochlore** is Th dominant with some Y, and Fe in A site. The ThO₂ 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_B ≥ Nb_B, Nb + Ta > 2Ti) comprise the **uranmicrolite**, with Nb₂O₅ ≈ 30, Ta₂O₅ ≈ 48.5, UO₂ ≈ 14.6 wt%, **thormicrolite** with Nb₂O₅ ≈ 19, Ta₂O₅ ≈ 25, ThO₂ ≈ 48 wt%, and **yttromicrolite** with

Nb₂O₅ ≈ 22, Ta₂O₅ ≈ 25 wt%, having U, Th, respectively Y in A site > 20%. **C. Betafite subgroup**, B = 2Ti_B ≥ (Nb + Ta)_B, 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: TiO₂ = 27–30, Y₂O₃ = 15–22, Nb₂O₅ = 22–27, Ta₂O₅ = 7–19, ThO₂ = 5–10, UO₂ = 4–6 wt%. Some yttrobetafite-(Y) grains have a very Ta-rich composition: Ta₂O₅ = 31.2, Y₂O₃ = 28.8, TiO₂ = 36.0 wt% and they do not contain Nb₂O₅. 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 Nb₂O₅ = 45–58, Y₂O₃ = 25–35, Yb₂O₃ + Gd₂O₃ + Dy₂O₃ ≈ 4.5 wt% and very little Ta₂O₅, with maximum 5 wt% UO₂ and ThO₂ content. The grains of fergusonite-(Y) are zoned with **formanite-(Y)**, which has Y₂O₃ = 34.6, Ta₂O₅ = 48.2 wt% and little CaO, FeO and ThO₂. Another grain has Y₂O₃ = 36.15, Ta₂O₅ = 45.72, Ce₂O₃ = 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, Nb₂O₅ = 72.8, Ta₂O₅ = 4.2, TiO₂ = 3.5 wt% and **manganocolumbite** has Nb₂O₅ = 76.28, MnO = 10.93, FeO = 0.44, TiO₂ = 0.8 wt%. Some grains have high UO₂ content of up to 8.4 wt%. The composition of some grains are (Y₂O₃ + FeO + MnO) > 20 wt%, high Nb₂O₅ (> 65 wt%) some Ta₂O₅ and no TiO₂ which could belong to **yttrocolumbite**. **4. "Ilmenorutile"** has: TiO₂ = 49.5–52.5, Nb₂O₅ = 21.8–26.5, Ta₂O₅ = 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 ZrO₂ with some ThO₂ and very little HfO₂. **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 UO₂ = 49.1, ThO₂ = 48.0 wt%. Separately, uraninite has composition: UO₂ ≈ 96.6 wt% with little ThO₂, Y₂O₃, PbO, FeO, and thorianite has ThO₂ = 96.3, PbO = 3.27, FeO = 0.23, SiO₂ = 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.