

Gadolinium-dominant monazite and xenotime: Selective hydrothermal enrichment of middle REE during low-temperature alteration of uraninite, brannerite, and fluorapatite (the Zimná Voda REE-U-Au quartz vein, Western Carpathians, Slovakia)

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ABSTRACT

A hydrothermal quartz vein with REE-U-Au mineralization in the Zimná Voda (Gemic Unit, Western Carpathians, Slovakia) is associated with contact metamorphism between Permian granites and host phyllites and metaquartzites. It contains unique REE minerals of the monazite and xenotime groups. Monazite-(Ce), monazite-(Nd), monazite-(Sm), and Gd-dominant monazite [“monazite-(Gd)”], along with xenotime-(Y) to Gd-dominant xenotime [“xenotime-(Gd)”] and Gd-rich hingganite-(Y) show heterogeneous compositions and reflect a strong fractionation trend toward the enrichment of MREE (Sm to Dy), particularly Gd. Here, the gadolinium abundance reported in “monazite-(Gd)” (≤ 23.4 wt% Gd_2O_3) and Gd-rich xenotime-(Y) to “xenotime-(Gd)” (≤ 28.7 wt% Gd_2O_3) and accompanied by Gd-rich hingganite-(Y) (≤ 15.8 wt% Gd_2O_3), is among the highest Gd concentrations ever reported in natural minerals. The Gd-richest compositions show the following formulas: $(Gd_{0.31}Sm_{0.24}Nd_{0.15}Ce_{0.10}La_{0.05}Dy_{0.03}Y_{0.03}\dots)_{0.98}PO_4$ [“monazite-(Gd)”], $(Gd_{0.36}Y_{0.32}Dy_{0.13}Sm_{0.08}Tb_{0.05}\dots)_{0.98}(P_{0.96}As_{0.04})_{1.00}O_4$ [“xenotime-(Gd)”] and $(Y_{0.71}Gd_{0.43}Dy_{0.23}Sm_{0.22}Tb_{0.06}Er_{0.04}Nd_{0.06}\dots Ca_{0.06})_{1.96}(□_{0.87}Fe_{0.13}^{2+})_{1.00}(Be_{1.82}B_{0.18})_{2.00}(Si_{1.90}As_{0.10})_{2.00}O_8(OH_{1.70}O_{0.30})_{2.00}$ [hingganite-(Y)]. The MREE-rich monazites, xenotimes, and hingganite-(Y) precipitated in response to the alteration of primary uraninite, brannerite, and fluorapatite by low-temperature hydrothermal fluids of heterogeneous compositions on a microscale. These are responsible for the strong enrichment of individual MREE, especially Gd in the secondary minerals. This is accompanied by the advancing development of the W-type tetrad effect on REE through monazite species. The substantial incorporation of Gd into both REE-selective monazite and xenotime structures that are accompanied by LREE vs. HREE segregation indicates the possibility of differently sized REE³⁺ miscibility in REEPO₄ solid solutions, as well as the stabilization of the Gd-rich orthophosphate structure by substitution of the remaining A-site cations with smaller HREE+Y in the xenotime-type, and/ or larger LREE in the monazite-type structure.

Keywords: Monazite, xenotime, hingganite, Gd-enrichment, REE fractionation, MREE enrichment, tetrad effect, Western Carpathians