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# Mineral chemistry and petrogenesis of a HFSE(+HREE) occurrence, peripheral to carbonatites of the Bear Lodge alkaline complex, Wyoming

**ALLEN K. ANDERSEN[1,*], JAMES G. CLARK[2], PETER B. LARSON[1], AND OWEN K. NEILL[1]**

[1]School of the Environment, Washington State University, Pullman, Washington 99164-2812, U.S.A.
[2]Applied Petrographics, 4909 NE 320 Avenue, Camas, Washington 98607, U.S.A.

## ABSTRACT

Rare earth mineralization in the Bear Lodge alkaline complex (BLAC) is mainly associated with an anastomosing network of carbonatite dikes and veins, and their oxidized equivalents. Bear Lodge carbonatites are LREE-dominant, with some peripheral zones enriched in HREEs. We describe the unique chemistry and mineralogy one such peripheral zone, the Cole HFSE(+HREE) Occurrence (CHO), located ~2 km from the main carbonatite intrusions. The CHO consists of anatase, xenotime-(Y), brockite, fluorite, zircon, and K-feldspar, and contains up to 44.88% $TiO_2$, 3.12% $Nb_2O_5$, 6.52% $Y_2O_3$, 0.80% $Dy_2O_3$, 2.63% $ThO_2$, 6.0% $P_2O_5$, and 3.73% F. Electron microprobe analyses of xenotime-(Y) overgrowths on zircon show that oscillatory zoning is a result of variable Th and Ca content. Cheralite-type substitution, whereby Th and Ca are incorporated at the expense of REEs, is predominant over the more commonly observed thorite-type substitution in xenotime-(Y). Th/Ca-rich domains are highly beam sensitive and accompanied by high-F concentrations and low-microprobe oxide totals, suggesting cheralite-type substitution is more easily accommodated in fluorinated and hydrated/hydroxylated xenotime-(Y). Analyses of xenotime-(Y) and brockite show evidence of $VO_4^{3-}$ substitution for $PO_4^{3-}$ with patches of an undefined Ca-Th-Y-Ln phosphovanadate solid-solution composition within brockite clusters. Fluorite from the CHO is HREE-enriched with an average Y/Ho ratio of 33.2, while other generations of fluorite throughout the BLAC are LREE-enriched with Y/Ho ratios of 58.6–102.5.

HFSE(+HREE) mineralization occurs at the interface between alkaline silicate intrusions and the first outward occurrence of calcareous Paleozoic sedimentary rocks, which may be local sources of P, Ti, V, Zr, and Y. U-Pb zircon ages determined by LA-ICP-MS reveal two definitive $^{207}Pb/^{206}Pb$ populations at 2.60–2.75 and 1.83–1.88 Ga, consistent with derivation from adjacent sandstones and Archean granite. Therefore, Zr and Hf are concentrated by a physical process independent of the Ti/Nb-enriched fluid composition responsible for anatase crystallization. The CHO exemplifies the extreme fluid compositions possible after protracted LREE-rich crystal fractionation and subsequent fluid exsolution in carbonatite-fluid systems. We suggest that the anatase+xenotime-(Y)+brockite+fluorite assemblage precipitated from highly fractionated, low-temperature (<200 °C), F-rich fluids temporally related to carbonatite emplacement, but after significant fractionation of ancylite and Ca-REE fluorocarbonates. Low-temperature aqueous conditions are supported by the presence of fine-grained anatase as the sole Ti-oxide mineral, concentrically banded botryoidal fluorite textures, and presumed hydration of phosphate minerals. Fluid interaction with Ca-rich lithologies is known to initiate fluorite crystallization which may cause destabilization of (HREE,Ti,Nb)-fluoride complexes and precipitation of REE+Th phosphates and Nb-anatase, a model valuable to the exploration for economic concentrations of HREEs, Ti, and Nb.

**Keywords:** Xenotime, brockite, anatase, carbonatite, rare earth elements, HREE, fractionation, thorium