

Apatite Trace Element Geochemistry—A Comparison Between Regional Magmatism and the Pea Ridge IOA-REE and Boss IOCG Deposits, Southeast Missouri U.S.A.

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Apatite is a ubiquitous accessory phase in silicic magmas and an abundant mineral in iron oxide-apatite-rare earth element (IOA-REE) deposits. The low solubility of P_2O_5 in silicate melts commonly leads to early crystallization of apatite that may continue through late-stage fluid saturation and metal deposition. Apatite typically shows great resistance to weathering, making it ideal to investigate the geochemical history of complex REE-bearing magmatic-hydrothermal systems.

The Pea Ridge IOA-REE deposit is the largest IOA-type deposit, and Boss is the largest known iron oxide-copper-gold (IOCG) deposit in the Mesoproterozoic igneous terrane of the St. Francois Mountains terrane, Missouri U.S.A. Voluminous high-silica rhyolite ash and lava flows (rhyolite suite) and lesser amounts of basalt to andesite volcanic and subvolcanic rocks (mafic- to intermediate-composition suite) comprise the caldera complex. Deposition of the host rhyolite at Pea Ridge (~1473 Ma) was followed closely by faulting and emplacement of the magmatic-hydrothermal IOA ore (~1471 Ma; 210 Mt, 47–55% Fe). The Th- and REE-rich breccia pipes cut the IOA body several My later (~1465 Ma; 0.2 Mt, 12% REE oxides).

We report results from microprobe, LA-ICP-MS, and spectral-CL image analysis of apatite from the rhyolite suite, mafic- to intermediate-composition suite, Pea Ridge deposit (magnetite-zone, amphibole-zone, REE breccia pipe), and Boss IOCG deposit (magnetite-zone). We also test the new apatite trace element classification scheme of Mao et al. (2016) for its applicability to IOA/IOCG deposits.

Apatite from all samples is nearly end member fluorapatite ranging from 2.5 to 6.5 wt % F. The hydroxyl component is generally low. Most samples contain low concentrations of Cl <0.4 wt %, but can have 0.6 wt % Cl (amphibole-zone) up to 1.4 wt % Cl (magnetite-zone). Samples vary in Na (200–10,000 ppm), S (below detection to 1,500 ppm), Fe (100–30,000), Mn (100–8,000 ppm), and Mg (70–3,000 ppm), Sr (40–1,000 ppm), Pb (2–50 ppm), U (1–100 ppm), and Th (0.5–500 ppm). As expected for igneous-related apatite, all samples contain low abundances of Cs and Rb (generally below detection), however, they have remarkably high Ba (10–300 ppm) and As (10–2,000 ppm).

Spectral-CL imaging reveals no primary igneous zoning but highlights intricate dissolution/precipitation textures with distinct REE signatures in some samples. Mafic- to intermediate-composition suite samples range from 0.4 to 1.0 wt % Σ REE whereas rhyolite suite samples span to 1.9 wt %, reflecting higher mineral-melt partition coefficients with higher magmatic SiO_2 and lower temperatures. Pea Ridge deposit samples vary widely from 0.25 to 1.75 wt % Σ REE whereas Boss IOCG samples contain <0.25 wt % Σ REE. The degree of REE fractionation varies greatly ($(Ce/Yb)_{CN} \sim 0.5-20$), and Eu and Ce anomalies ($Eu/Eu^* \sim 0.05-1.0$; $Ce/Ce^* \sim 0.8-1.3$) indicate apatite crystallization over a range of moderately reduced to oxidized

conditions. Application of the Mn-oxybarometer (Miles et al., 2014) appears to contradict Eu and Ce data and is unsuitable for this system.

Our results indicate that the apatite trace element classification scheme of Mao et al. (2016) is robust for discriminating between unmineralized and mineralized samples and between IOA/IOCG ore systems and other mineral deposit types (e.g., porphyry, skarn, orogenic). We conclude that more high-quality apatite data are needed to discern IOA from IOCG deposits.