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An experimental approach to understanding REE patterns in fluorite associated with critical mineral deposits

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The geochemistry of fluorite associated with critical mineral deposits can provide valuable information on the source(s) of the ore-forming fluids. This is typically done by correlating the REE pattern in fluorite with patterns from accessory minerals in or the bulk rock composition of proximal igneous rocks. This simplified technique is controversial because the REE partitioning between fluorite and fluid has only been experimentally determined at 120 °C, leaving the effect of temperature, pH, ligands, and other physicochemical parameters largely undetermined. In this study, we synthesized fluorite from H_2O solutions with 100-500 mg/L of each REE, pH 3-11, 25-150 °C, and < 1 to 4 M NaCl, and compared the REE contents of the fluorite to the solutions. Our results show that increasing the pH of REE-bearing solutions results in a decrease in the total REE content and a depletion of HREEs of the solution. The synthesized fluorite has an identical REE distribution pattern to the fluid in every experiment. Fluorite precipitated from acidic, neutral, and basic solutions yield partition coefficients ranging 5-20, 7-24, and 0.09-18, respectively. Applying these results to fluorite from the Chinese Baiyanghe Be-U-Mo and US Gallinas Mts Ba-REE-Cu deposits indicate fluorite REE patterns must be interpreted with caution. Fluorite from both deposits yield multiple REE patterns, but only a few match the proximal igneous rocks. The dissimilar patterns could represent removal of LREEs during post-crystallization processes as other studies suggested. This study demonstrates fluorite will acquire the REE pattern of the fluid which may reflect its source.