Mineralization of rare earth elements as phosphate at room temperature

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Mineralization of rare earth elements (REEs), which are potential fission products and used as a surrogate of trivalent actinide, is one of the important processes governing the geochemical behavior of REEs in sub-surface; however, there are still uncertainties in the mineralization as phosphate at room temperature. The present study investigates the formation processes by reaction with aqueous phosphate or apatite crystals at room temperature to elucidate the physico-chemical properties of REE phosphate ($REPO_4$) and the parameters constraining the processes.

A series of $REPO_4$ were formed at room temperature by mixing 0.10 mM RE^{3+}(RE_{single}=Ln=La-Lu except Pm or RE_{all}=all Ln) and 0.10 mM PO_4^{3-} at pH 3.0 for 3 days. Selected $RE_{single}PO_4$ (RE: La, Tb, Dy, Ho, and Yb) and $RE_{all}PO_4$ were reacted for 30 days to examine the aging effect. Mineralization on hydroxyapatite (HAP, $Ca_5(PO_4)_3OH$) was performed, in which 0.20 g of HAP was added to 100 mL of 2.0 mM RE^{3+} (RE: La, Tb, Yb and all RE) and stirred at pH 5.0 for 1 hour-10 days at room temperature. Solid characterization was completed by using XRD, TG/DTA, FT-IR, and TEM. The solution was analyzed using ICP-AES.

$RE_{single}PO_4$ synthesized in contact with PO_4^{3-}(aq) was classified to three groups; $LREPO_4$ for La-Gd with rhabdophane-structure, $MREPO_4$ for Tb-Ho and $HREPO_4$ for Er-Lu exhibiting broaden 4-line and 5-line in their XRD patterns, respectively. The latter two groups contained 2.2-2.7 H_2O in the unit formula and 30-60 % of amorphous phase. The structure changed consistently with ionic radius within the same group. $RE_{all}PO_4$ consisted of 35 % of rhabdophane-structure and 65 % of $TbPO_4$-structure after 3 days, which transformed to 100 % rhabdophane-structure after 30 days. In the mineralization on HAP, the rate of $REPO_4$ formation was constrained by dissolution rate of HAP: 3.5×10^{-8} mol m^{-2} min^{-1}. When the solution with all REEs was contacted with HAP, LREEs were preferentially incorporated with apparent tetrad effects into nano-crystalline $RE_{all}PO_4$ that precipitated on HAP. Consequently, hydrated $REPO_4$ nanocrystallization is a key process for retarding RE mobility in the environment, which can constrains distribution of RE and potentially trivalent actinides in aquifer by the unique crystal-chemistry.