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## Solubility of the rhabdophane, $\text{LnPO}_4 \cdot 0.667 \text{H}_2\text{O}$ (Ln = La to Dy): implications for the long-term stability of monazite matrices.

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Minerals belonging to the monazite family,  $\text{REEPO}_4$  (REE: Y, Sc, La to Dy) could incorporate in their structure substantial amounts of Th and U [1]. Moreover, monazites maintain their crystallinity even after geological times of exposure to self-irradiation. Therefore, this phase appears as a promising candidate for the specific conditioning of transuranic elements (AnIV, AnIII). Already, many thermodynamic properties of monazite are reported in the literature [2]. However, its hydrated form namely, rhabdophane,  $\text{REEPO}_4 \cdot 0.667 \text{H}_2\text{O}$  could be stabilized at low temperatures, and thus control the concentrations of actinides in solution after the leaching of the monazite matrices [3, 4].

For the first time, a systematic study of the solubility of the rhabdophane,  $\text{LnPO}_4 \cdot 0.667 \text{H}_2\text{O}$  (Ln = La to Dy) was performed using over-saturated and under-saturated experiments at different temperatures (298 to 363 K) to demonstrate the reversibility of the solubility equilibrium [5]. The structure of the neoformed phases was carefully controlled in the entire range of temperatures in order to attribute unambiguously the solubility products and the derived thermodynamic data associated to the rhabdophane phases. The obtained results indicate that the stability domain of the rhabdophane phase is limited in temperature and depends on the ionic radius of the lanthanide. The values of the solubility constant depend also slightly on the lanthanide with  $\log K_{S,0^\circ}$  (298 K) ranging from  $-25.6 \pm 0.8$  (Pr) to  $-24.9 \pm 1.7$  (Eu) with minimum values for Pr to Sm. The values of the standard free energy of formation at 298 K varied between  $-1984 \pm 2$  and  $-2004 \pm 2$  kJ.mol<sup>-1</sup> whatever the lanthanide element considered, except for Eu-rhabdophane that presented the highest value for the Gibbs energy of formation ( $-1896 \pm 2$  kJ.mol<sup>-1</sup>).

From the solubility data obtained at various temperatures, the values of enthalpy of formation of the rhabdophanes were found between  $-2151 \pm 13$  and  $-2130 \pm 12$  kJ. mol<sup>-1</sup> excepted for Eu for which it reached  $-2057 \pm 9$  kJ.mol<sup>-1</sup>. It is worth noting that the data reported by Ushakov et al. [6] for monazites  $\text{LnPO}_4$  (Ln = La to Gd) determined by oxide melt calorimetry and recalculated by taking into account the contribution of the water molecules are in very good agreement with the data obtained for rhabdophane in this work. This result indicates that the enthalpy of formation of the rhabdophane can be simply deduced from the enthalpy of formation of the monazite by adding the contribution of 0.667 molecule of structural water.

These results could be used to estimate the thermodynamic properties of  $\text{AnIIIPO}_4 \cdot 0.667 \text{H}_2\text{O}$  (with AnIII = Am, Pu or Cm) by analogy with the lanthanides of close ionic radii. The rhabdophane structure can also incorporate AnIV by coupled substitution of LnIII by MII and AnIV. In this field,  $\text{Nd}_{0.8}\text{Ca}_{0.1}\text{Th}_{0.1}\text{PO}_4 \cdot n \text{H}_2\text{O}$  were prepared by wet chemistry route and preliminary solubility data were determined, which showed that this phase is metastable in solution at 298 K, Th and Nd being released leading to the formation of  $\text{Th}_2(\text{PO}_4)_2(\text{HPO}_4) \cdot \text{H}_2\text{O}$  (TPHPH) [7] and  $\text{NdPO}_4 \cdot 0.667 \text{H}_2\text{O}$ , respectively.

### References:

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## Summary

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