*American Mineralogist, Volume 99, pages 2320–2327, 2014*

# Energetics of lanthanide-doped calcium phosphate apatite

**S. Mahboobeh Hosseini[1,2], Christophe Drouet[3], Ahmed Al-Kattan[3] and Alexandra Navrotsky[1,2,*]**

[1]Peter A Rock Thermochemistry Laboratory and NEAT ORU, University of California Davis, One Shields Avenue, Davis, California 95616, U.S.A.
[2]Department of Chemical Engineering and Materials Science, University of California Davis, One Shields Avenue, Davis, California 95616, U.S.A.
[3]CIRIMAT Carnot Institute—Phosphates, Pharmacotechnics, Biomaterials Group, UMR CNRS/INPT/UPS 5085, University of Toulouse, 4 allée Emile Monso, 31030 Toulouse, France

## Abstract

Lanthanides "Ln" (rare earths) are critical elements found in natural minerals such as calcium phosphate apatites, in sedimentary and igneous settings as well as in skeletal diagenesis. From a medical point of view, nanoparticles of lanthanide-doped apatites can be produced for conferring luminescence properties of interest in cancer cells detection. However, the impact of the substitution of Ln for Ca on the stability and solubility of related apatite phases is still essentially unknown. To investigate the thermochemical effects of such lanthanide substitution for calcium in apatite, we prepared and analyzed four series of apatites with up to 10% lanthanide substitution for calcium. After thorough physicochemical characterization via complementary techniques (XRD, FTIR, TG/DSC, and IPC-AES), high-temperature oxide melt solution calorimetry in molten sodium molybdate at 973 K was performed to determine their enthalpies of formation from constituent oxides and from the elements, at 298 K. Our results indicate that although enthalpies of formation are strongly exothermic in all cases, Ln-doping has a destabilizing effect, which increases with dopant concentration and with the size of the incorporated $Ln^{3+}$ ion. After estimating standard entropies, Gibbs free energies of formation and equilibrium constants for $Ca^{2+}/Ln^{3+}$ exchange reactions in apatite were then evaluated, for the first time allowing access to quantitative thermodynamic data that may be used in various fields for stability calculations or partitioning estimates between fluids and solids.

**Keywords:** Calcium phosphate hydroxyapatite; lanthanide substitution; enthalpy of formation; calorimetry