Energetics of lanthanide-doped calcium phosphate apatite

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ABSTRACT
Lanthanides “Ln” (rare earths) are critical elements found in natural minerals such as calcium phosphate apatite, 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 Ln3+ ion. After estimating standard entropies, Gibbs free energies of formation and equilibrium constants for Ca2+/Ln3+ 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

INTRODUCTION
Apatites, corresponding to the general chemical formula M10(TO4)6X2, represent a large family of minerals commonly found in nature as both geological materials and biominerals in calcified tissues. In this versatile structure, M is often a divalent cation (e.g., Ca2+, Sr2+, and Pb2+), TO4 is an anionic group (e.g., PO4, SiO4, and VO4), and X is usually a monovalent anion (e.g., F−, OH−, and Cl−), although ions exhibiting other valences (e.g., CO3, HPO4, O2, Na+) may also be incorporated (Elliott 1994).

Calcium phosphate hydroxyapatite [Ca10(PO4)6(OH)2], HA, is one of the most common apatite end-members. It is produced, with varying degrees of stoichiometry, by vertebrates for ensuring physico-chemical as well as mechanical functions of hard tissues (Gomez-Morales et al. 2013) and is also encountered in many other contexts including in the geochemistry, anthropology, and biomaterials fields (Kohn et al. 2003; Bohner et al. 2008; Grunerwald et al. 2014; Prabakaran et al. 2005; Rabadjieva et al. 2010; Rodriguez-Lorenzo and Gross 2003; Verron et al. 2010). Apatite with substantial fluorine substitution for hydroxyl (fluorapatite) occurs in both sedimentary and igneous settings, sometimes as massive deposits, which are mined as a source of phosphate for fertilizer, but that are also potential sources of the lanthanides (aka rare earths), which are considered critical elements for technology (Nagasawa 1970; Reynard et al. 1999; Spear and Pyle 2002). In the paleoanthropology domain, the analysis of skeletal remains has also pointed out the occurrence of lanthanides associated to the apatitic phase during bone/teeth diagenesis (Tutken et al. 2011; Kocsis et al. 2010; Trueman and Tuross 2002). The study of Ln incorporation in apatites can also help modeling the incorporation of radioactive actinide elements, which are more complex to handle (Martin et al. 1999). Since it is compositionally and structurally close to the inorganic component of bones and teeth, hydroxyapatite is both biocompatible and bioactive, especially in nanocrystalline and nonstoichiometric form (Drouet et al. 2005; Eichert et al. 2005; Elliott 1994; Rey et al. 2007a, 2007b; Verron et al. 2010). Calcium phosphate apatite-based systems have therefore captivated the attention of biotechnology engineers for decades, and its use is now widespread in bone filling, prosthesis coating, and related applications (Cardoso et al. 2012; Rey et al. 2011). The last decades have produced numerous biomaterials based on apatite, sometimes associated with drugs or biologically active ions (Al-Kattan et al. 2010b; Barroug and Glémcher 2002; Benaziz et al. 2001; Bohner et al. 2008; Drouet et al. 2008, 2012; Iafisco et al. 2012; Weber et al. 2013). Biomimetic apatite-based hybrid...