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Thermochemistry of apatite compounds of relevance to biomineralization and mineralogy: experimental and modeling via the *ThermAP* approach

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Apatite minerals are a major class of ionic compounds of interest to many disciplines including medical sciences, geology, anthropology, cosmology, environmental and nuclear sciences. Nonetheless, these compounds have received only limited attention from a thermodynamic viewpoint, especially regarding solid solutions or nonstoichiometric compositions. An extensive literature overview of available experimental-based data on phosphate apatites $M_{10}(PO_4)_6X_2$ end-members with M = Ca, Ba, Sr, Mg, Cd, Pb, Cu, Zn and X = OH, F, Cl or Br has thus been made [1], in terms of standard formation enthalpy $D_fH°$, Gibbs free energy $D_fG°$ and entropy $S°$ (at 298 K). In some cases, typically for nonstoichiometric bone-like apatites or for lanthanide-substituted hydroxyapatites of practical relevance to several fields, for which no experimental data was available in the literature, drop solution oxide melt calorimetry was carried out [2,3]. Using this set of experimental-based data as reference, the thermodynamic effects of each constituting ion in the apatitic structure was examined, and a predictive thermodynamic "additive" method denoted *ThermAP* (Applied Predictive Thermodynamics) was developed [4] to estimate these properties for any solid solutions or nonstoichiometric phosphate apatites of interest incorporating the above-cited ions, at 298 K. This model allows obtaining estimates of $D_fH°$, $D_fG°$ and $S°$ based on their chemical composition, generally within 0.5 % of relative error. The use of these data may for example allow a better understanding of the formation and evolution of apatite specimens relevant to biomineralization and (Terrestrial or Martian) mineralogy. This model may also prove helpful for estimating, in a first approximation, the thermodynamic data of rare, expensive, metastable or hypothetical apatite compositions prior to getting experimental validation, if possible.

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