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Thermodynamic basis for evolution of apatite in calcified tissues

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Abstract

Bone remodeling and tooth enamel maturation are biological processes that alter the physico-chemical features of biominerals with time. However, although the ubiquity of bone remodeling is clear, why is well-crystallized bone mineral systematically replaced by immature nanocrystalline inorganic material? In enamel, a clear evolution is also seen from the first mineral formed during the secretory stage and its mature well-crystalline form, which then changes little in the adult tooth. This contribution provides the thermodynamic basis underlying these biological phenomena. We determined, for the first time, the energetics of biomimetic apatites corresponding to an increasing degree of maturation. Our data point out the progressive evolution of the enthalpy (ΔH_f°) and free energy (ΔG_f°) of formation toward more negative values upon maturation. Entropy contributions to ΔG_f° values remained small compared to enthalpy contributions. ΔH_f° varied from $-12\,058.9 \pm 12.2$ to $-12\,771.0 \pm 21.4$ kJ/mol for maturation times increasing from 20 min to 3 weeks, approaching the value for stoichiometric hydroxyapatite, $-13\,431.0 \pm 22.7$ kJ/mol. Apatite thermodynamic stability increased as its composition moved toward stoichiometry. These findings imply diminishing aqueous solubility of calcium and phosphate ions as well as decreased surface reactivity. Such thermodynamically driven maturation is favorable for enamel maturation since this biomineral is intended to resist external aggressions such as contact with acids. In contrast, maintaining a metastable highly reactive and soluble form of apatite is essential to the effective participation of bone as a source of calcium and phosphate for homeostasis. Therefore our data strongly suggest that, far from being trivial, the intrinsic thermodynamic properties of apatite mineral represent a critical driving force for continuous bone remodeling, in contrast to current views favoring a purely biologically driven cycle. These thermodynamic data may prove helpful in other domains relating, for example, to apatite-based biomaterials development or in the field of (geo)microbiology.

Keywords: Nanocrystalline apatite, hydroxyapatite, bone remodeling, enamel maturation, calorimetry, thermodynamics, metastability, biomimetic