Isotopic tracers of non-classical crystallization mechanisms in hydroxyapatite

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The growth of calcium phosphate phases has long been thought to proceed via a non-classical cluster aggregation mechanism similar to oriented attachment. However, the size, composition, and surface exchange kinetics of the hypothesized growth units are poorly constrained. Growth and dissolution of phosphate minerals regulates the availability of nutrient inorganic P and the mobility of metals and metalloids in soil systems. Inorganic P is a critical non-renewable resource, so understanding the relationship between growth mechanisms and the composition and stability of the bulk material could facilitate improved understanding of and control over P fluxes in soil systems.

Calcium isotope signatures of carbonate minerals have been used to deduce the mineral-aqueous interfacial processes directing growth. Early measurements of the Ca isotope budget in vertebrates suggested a characteristic $\Delta^{44/40}$Ca on order -1.5‰ arising from the formation of skeletal material [1]. This fractionation signature is consistent with the magnitude of kinetic isotope fractionation arising during ion-by-ion driven carbonate mineralization. Carbonate-substituted hydroxyapatite (HA) is the main inorganic constituent of bone, which suggests that Ca isotopes may be used to infer HA mineralization mechanisms similar to carbonates.

Oriented attachment is a cluster-mediated mechanism somewhat analogous to the formation of amorphous calcium carbonate (ACC), which is characterized by a unique $\Delta^{44/40}$Ca signature. However, cluster attachment in HAP occurs along steps at the mineral surface, similar to ion-by-ion driven growth. A series of HA precipitation experiments were performed under varied aqueous supersaturation and Ca:P conditions to investigate the relationship between solution composition, HA precipitation kinetics, and $\Delta^{44/40}$Ca. Seeded growth experiments were conducted under continuous flow, and the Ca isotopic composition of the solid and aqueous phases were measured periodically during growth. Results of these experiments yield novel insights into aqueous cluster formation and composition, facilitating the development of a quantitative model for cluster-driven HA precipitation kinetics.

[1] Skulan & DePaolo (1999) *Proc. Nat. Acad. Sci.* **96**, 13709-13713.