

Oxygen, carbon and calcium site-specific isotopic fractionation in apatite

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Apatite ($\text{Ca}_5(\text{PO}_4)_3\text{X}$, $\text{X} = \text{OH}, \text{F}, \text{Cl}$) is the most common phosphate mineral. It frequently displays minor amounts of carbonate, occurring naturally in substitution of phosphates (B site) and channel anions (A site) in the crystal structure. Stable isotope composition of biogenic apatite, and in particular the composition ($\delta^{13}\text{C}$, $\delta^{18}\text{O}$) of structural carbonate groups, is an important geochemical marker that records environmental parameters and is widely used to infer past climates, biomineralization processes, dietary preferences and habitat of vertebrates.

The interpretation of isotopic measurements relies on the knowledge of equilibrium isotopic fractionation laws usually determined experimentally. However, out-of-equilibrium fractionation during crystal growth, slow isotope exchange rates and above all the variability of apatite crystal-chemistry are sources of uncertainties in isotopic fractionation laws established experimentally. Alternatively, equilibrium fractionation factors can be determined theoretically from the computation of vibrational properties. In this contribution, theoretical equilibrium isotopic fractionation of oxygen, carbon and calcium in hydroxyapatite and carbonate-bearing hydroxyapatite is investigated using first-principles methods based on density-functional theory. Our results revealed peculiar differences in O, C and Ca isotopic fractionation behaviour depending on the substitution site for carbonate group in apatite. Significant enrichment in heavy isotopes (^{18}O , ^{13}C) is observed in A-type carbonates relative to B-type carbonate groups in apatite (typically 7‰ for O and C fractionation at 37°C). Theoretical oxygen fractionation between B-type carbonate and phosphate ($1000 \ln \alpha(\text{CO}_3^{2-}-\text{PO}_4^{3-}) = 8.5\text{‰}$ at 37°C) is in agreement with experimental values obtained on modern and well-preserved fossil biopapatites. In light of these theoretical results, measurements of site-specific isotopic fractionation properties would improve our understanding of isotopic records in apatites.