

## Crystal-chemistry of fossil bioapatite: spectroscopic observations and theoretical modelling

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Carbonate-bearing apatite is of importance in many scientific fields, including earth science, biology, and medicine. Carbonate-bearing fluorapatite is a major phosphorous ore mineral, whereas carbonate-bearing hydroxyapatite is the main inorganic constituent of vertebrates' bones and teeth. The isotopic composition ( $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$ ) of fossil bones and teeth thus potentially provides key information for paleo-environmental reconstructions. Such approach however requires the preservation of carbonate isotopic composition during fossilization (e.g., Roche et al. 2010). Fossil apatites generally exhibit an overall decrease in carbonate content, an enrichment in fluorine, accompanied with incorporation of trace elements and an increase in crystallinity as inferred from empirical parameters. Detailed investigations of the carbonate incorporation mechanism in apatite are thus potentially crucial in better understanding apatite transformations induced by fossilization.

There is general agreement that two types of carbonate substitution occur in apatite: carbonate may replace monovalent anions in structural channels (A-type substitution) or may substitute for a tetrahedral phosphate (B-type substitution). In contrast, charge-balancing mechanisms, as well as atomic-scale models for carbonate substitution in the apatite structure are still debated. In the present study, we have investigated a series of modern and fossil mammalian teeth enamel from Mio-Pliocene hominid-bearing deposits of the Kenyan rift (Roche et al. 2010), using low-temperature Fourier-Transform Infrared spectroscopy and solid-state Nuclear Magnetic Resonance spectroscopy. Experimental results were interpreted under the light of first-principles quantum mechanical simulations (e.g., Balan et al. 2011). Such combination of experimental observations with theoretical modelling makes it possible to unravel the atomic-scale mechanisms of carbonate incorporation in fossil apatite. Our results imply that the transformation of fossil teeth may occur through dissolution and recrystallization mechanisms, which has important implications for using fossil apatite as paleo-environmental markers.

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### Literature:

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