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Sites-specific oxygen isotope fractionation of biological apatite.

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Sites-specific oxygen isotope fractionation of biological apatite

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Apatite is the principal inorganic component of biological hard tissues such as bone and teeth and, thus, is essential to the existence of vertebrate life [1].Because of carbonate species and chloride ions are ubiquitous in the fluids of vertebrate life forms, and these species are known to compete with phosphatespecies, it is critical to understand the influence of these anions on the nucleation and composition of biological apatite. The site-specific O isotope fractionation between carbonates and phosphates are quantified using the first-principles density functional theory in this study.

Based on the six different apatite structures we built, the $D^{18/16}O_{carbonate\text{-}phosphate}$ ranges from 5.55‰ to 10.99‰ indicates site-specific O isotope fractionation is sufficient to distinguish the effect of different ions doping. From the calculated isotherms for site-specific equilibrium isotopic fractionation of all structures, only Cl^- and CO_3^{2-} doping in PO_4^{3-} site ($Ca_{10}(PO_4)_5(CO_3Cl)(OH)_2$) with an isotherm equation of $10^3 lna = -0.4413 ´ 10^6/T^2 + 4.4298$ well fitted theexperiment data for the body temperature of mammals of 310 K. Besides, the infrared (IR) spectrum also shows the $Ca_{10}(PO_4)_5(CO_3Cl)(OH)_2$ has the most closed to experimental vibration frequency of CO_3 groups ($v_2(CO_3) = 827cm^{-1}$, $v_3(CO_3) = 1412cm^{-1}$ *and* $1476cm^{-1}$). The above-mentioned results show that $Ca_{10}(PO_4)_5(CO_3Cl)(OH)_2$ is the most likely type of biological apatite. This is also supported by the much lower E_{surf} of (001) surface for $Ca_{10}(PO_4)_5(CO_3Cl)(OH)_2$ (0.36 J/m^2) compared to that of the hydroxyapatite (HA) (001) surface (1.08 J/m^2). Based on the temperature dependent oxygen isotope fractionation between the phosphate and hydroxyl sites of apatite as described by $10^3 lna_{phosphate\text{-}site – hydroxy\text{-}site} = 3.2825 ´ 10^6/T^2 + 0.6929$, we propose a geological thermometer that could be used to reconstruct paleo-temperatures using $d^{18}O$ in two specific O atom sites of HA.

[1] Pucéat, E., Joachimski, M.M., Bouilloux, A., Monna, F., Bonin, A., Motreuil, S., Morinière, P., Hénard, S., Mourin, J., Dera, G. and Quesne, D. (2010). Earth and Planetary Science Letters, 298(1–2): 135-142.