



# Site-specific equilibrium isotopic fractionation of oxygen, carbon and calcium in apatite

Julie Aufort<sup>a,\*</sup>, Loïc Ségalen<sup>b</sup>, Christel Gervais<sup>c</sup>, Lorenzo Paulatto<sup>a</sup>,  
Marc Blanchard<sup>d</sup>, Etienne Balan<sup>a</sup>

<sup>a</sup> Sorbonne Université, UPMC Université Paris 06 – Institut de Minéralogie, de Physique des Matériaux et de Cosmochimie (IMPMC), UMR CNRS 7590, UMR IRD 206, MNHN, 4 place Jussieu, 75252 Paris cedex 05, France

<sup>b</sup> Sorbonne Université, UPMC Université Paris 06 – Institut des Sciences de la Terre de Paris (ISTEP), Biominéralisations et Environnements Sédimentaires, UMR 7193, 4 place Jussieu, 75252 Paris cedex 05, France

<sup>c</sup> Sorbonne Université, UPMC Université Paris 06 – Laboratoire de Chimie de la Matière Condensée de Paris (LCMCP), UMR 7574, Collège de France, 4 place Jussieu, 75252 Paris cedex 05, France

<sup>d</sup> Géosciences Environnement Toulouse, Observatoire Midi-Pyrénées, CNRS-Université de Toulouse, 14, avenue Edouard Belin, 31400 Toulouse, France

Received 19 December 2016; accepted in revised form 10 September 2017; Available online 19 September 2017

## Abstract

The stable isotope composition of biogenic apatite is an important geochemical marker that can record environmental parameters and is widely used to infer past climates, biomineralization processes, dietary preferences and habitat of vertebrates. In this study, 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 and compared to the theoretical isotopic fractionation properties of calcite, CO<sub>2</sub> and H<sub>2</sub>O. Considering the variability of apatite crystal-chemistry, special attention is given to specific contributions of crystal sites to isotopic fractionation. Significant internal fractionation is calculated for oxygen and carbon isotopes in CO<sub>3</sub> between the different structural sites occupied by carbonate groups in apatite (typically 7‰ for both <sup>18</sup>O/<sup>16</sup>O and <sup>13</sup>C/<sup>12</sup>C fractionation at 37 °C). Compared with calcite-water oxygen isotope fractionation, occurrence of A-type substitution in apatite structure, in addition to the main B-type substitution, could explain the larger temperature dependence of oxygen isotope fractionation measured at low temperature between carbonate in apatite and water. Theoretical internal fractionation of oxygen isotopes between carbonate and phosphate in B-type carbonated apatite (~8‰ at 37 °C) is consistent with experimental values obtained from modern and well-preserved fossil bio-apatites. Concerning calcium, theoretical results suggest a small fractionation between apatite and calcite (−0.17‰ at 37 °C). Internal fractionation reaching 0.8‰ at 37 °C occurs between the two Ca sites in hydroxyapatite. Furthermore, the Ca isotopic fractionation properties of apatite are affected by the occurrence of carbonate groups, which could contribute to the variability observed on natural samples. Owing to the complexity of apatite crystal-chemistry and in light of the theoretical results, measurements of site-specific isotopic fractionation properties could improve our understanding and the interpretation of isotopic records in apatites.

© 2017 The Authors. Published by Elsevier Ltd. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

**Keywords:** Apatite; Ab initio; Stable isotope; Isotopic fractionation; Carbonate

\* Corresponding author.

E-mail address: [julie.aufort@impmc.upmc.fr](mailto:julie.aufort@impmc.upmc.fr) (J. Aufort).

## 1. INTRODUCTION

Apatite ( $\text{Ca}_5(\text{PO}_4)_3\text{X}$ , X = OH, F, Cl) is the most common phosphate mineral (McConell, 1973). It frequently contains minor amounts of carbonate, occurring naturally in substitution of phosphate (B site) and channel ions (A site) in the crystal structure (e.g. Fleet, 2009). While sedimentary deposits of carbonated fluorapatite yield the world's major phosphorus resources (Knudsen and Gunter, 2002), carbonated hydroxyapatite is the major inorganic component of vertebrate skeletons (Elliott, 2002). Stable isotope compositions of biogenic apatites, and in particular the isotope composition ( $\delta^{13}\text{C}$ ,  $\delta^{18}\text{O}$ ) of structural carbonate groups, are widely used to reconstruct past climates, past environments and dietary preferences of vertebrates (e.g. Kohn and Cerling, 2002; Roche et al., 2010; Roche et al., 2013; Pack et al., 2013; Reynard and Balter, 2014). For example, the carbon stable isotope composition of carbonate-bearing bio-apatites reflects that of ingested food and is used to infer dietary preferences of vertebrates in a variety of paleoecological studies (Lee-Thorp and van der Merwe, 1987; Quade et al., 1992). More recently, carbonate clumped isotopes (i.e.  $\Delta_{47}$ ) have generated a great interest (e.g. Schauble et al., 2006; Stolper and Eiler, 2015; Wacker et al., 2016) for their use as a geothermometer tool revealing formation temperatures of carbonate bearing minerals and, in particular, body temperature of vertebrates. The stable oxygen isotope composition of bioapatite is linked to the body water which depends on climatic and ecophysiological factors (Longinelli, 1984; Kohn et al., 1996). Beyond  $\delta^{18}\text{O}$  measurements, high-precision triple oxygen isotope analysis (i.e.  $\Delta^{17}\text{O}$ ) of carbonate minerals and structural carbonate in bioapatites is now also used to reconstruct past water compositions and has been suggested as a possible tracer for diagenetic alteration of fossil bones and teeth (Gehler et al., 2011; Passey et al., 2014).

Beside traditional isotopes, recent analytical advances have allowed the rapid development of Ca stable isotope composition analysis on bioapatites. Skulan et al. (1997) first reported the importance of biological calcium isotopic fractionation within the global calcium geochemical cycle and the possibility of calcium isotopic composition of fossils to record information on diet and environment. Calcium isotope fractionation in carbonate minerals has been widely investigated (Lemarchand et al., 2004; Marriott et al., 2004; Gussone et al., 2005). Several studies investigated carbonated bioapatites (Skulan and DePaolo, 1999; Heuser et al., 2009, 2011; Reynard et al., 2010; Tacail et al., 2016), providing reference values for  $\delta^{44}\text{Ca}$  in biogenic apatite. Though marine carbonate sediments are the phase most commonly used for the reconstruction of calcium isotopic composition of seawater through time (Skulan et al., 1997; De La Rocha and DePaolo, 2000), the possibility of using other proxies such as foraminifera (Heuser et al., 2005) and phosphorites (Soudry et al., 2004) has been explored. Soudry et al. (2006) investigated the use of carbonated fluorapatite formed in marine sediments as a potential candidate for long term reconstructions of isotopic composition of seawater  $\text{Ca}^{2+}$ . Farkas

et al. (2007) compiled records from various biogenic carbonates and authigenic phosphates to discuss the calcium isotope budget over Phanerozoic times. Calcium isotope fractionation might however vary depending on the type of phosphate deposit, e.g. sedimentary peloidal phosphates or phosphorite crusts (Arning et al., 2009). Considering the importance of understanding the oceanic mass balance of calcium and its impact on the regulation of carbon dioxide concentration in the atmosphere, the potentiality for calcium phosphate too to be used as a proxy for investigating past changes in Ca fluxes has to be determined. Despite this growing interest, the mechanisms and magnitude of calcium isotopic fractionation are still under debate.

The oxygen isotopic composition of biogenic apatite can also provide important information on paleotemperatures, its interpretation relying on the knowledge of apatite isotopic fractionation properties. Since the pioneering empirical studies of Longinelli (1965) and Kolodny et al. (1983), several experimental oxygen isotope fractionation relations have been established between bioapatite phosphate and water (Puc at et al., 2010) and between dissolved phosphate and water (Chang and Blake, 2015). In low temperature systems the isotopic equilibrium cannot be achieved through efficient diffusion-mediated exchange between the relevant phases. In the case of phosphate, inorganic processes are not efficient enough to drive the system to equilibrium (L cuyer et al., 1999). However it has been shown that enzymatic catalysis either related to microbial activity or intracellular metabolism enhances oxygen exchange between phosphate groups and water and could account for equilibrium exchange and temperature dependence observed in bioapatites and sedimentary apatites (Blake et al., 2005; Chang and Blake, 2015). An equation for oxygen isotope fractionation between carbonate groups in carbonated hydroxyapatite and water has also been determined from controlled experiments (L cuyer et al., 2010). Uncertainties remain however, due to possible out-of-equilibrium isotope fractionation during crystal growth, slow isotope exchange rates and the variability of the apatite crystal-chemistry (Rakovan and Pasteris, 2015). Additional difficulties may also arise when non-conventional stable isotopes are investigated due to the small magnitude of isotopic fractionation factors (e.g. Blanchard et al., 2017). Experimental equilibrium fractionation laws may therefore be affected by large uncertainties at low temperatures.

Alternatively, equilibrium fractionation factors can be determined theoretically from the computation of vibrational properties. The advantages of calculating fractionation factors within first principles methods are to provide independent equilibrium fractionation laws, over a wide range of temperatures, from which comparison with experimental data may help understand deviations from equilibrium values and kinetic effects. Theoretical computation of isotopic fractionation properties can also be applied to non-conventional isotopes for which experimental measurements are difficult or lacking. A variety of isotopes and minerals have been investigated using first-principles methods based on density functional theory (DFT), such as stable isotopes O and C in carbonates (Schauble et al.,

Download English Version:

<https://daneshyari.com/en/article/5783261>

Download Persian Version:

<https://daneshyari.com/article/5783261>

[Daneshyari.com](https://daneshyari.com)