

## Precise laboratory calibration of equilibrium fractionations between dissolved phosphate and water at low temperature, 3-37 °C

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Geochemical reactions involving organic and inorganic phosphates ( $\text{PO}_4$ ) in aquatic environments are primarily carried out by microorganisms and catalyzed by enzymes. The stable O isotope composition of  $\text{PO}_4$  ( $\delta^{18}\text{O}$ ) is a useful tracer of P cycling and (paleo)temperature and was first developed as an isotope thermometer based on empirical analyses of bioapatites with the assumption of equilibrium O-isotope exchange between  $\text{PO}_4$  and water [after 1]. However, dissolved  $\text{PO}_4$  may not only have different isotopic behavior than apatite, but there may also be differences in the behavior of biological phosphates subject to enzymatic reactions and sedimentary phosphates. Furthermore, empirically-determined fractionations may include unrecognized non-equilibrium components.

Recent evidence points to inorganic pyrophosphatase (PPase) as the key enzyme responsible for both the equilibrium and temperature dependence of dissolved  $\text{PO}_4$ -water O-isotope exchange in cells [2]. In this study, we present an expanded range of experimentally-determined calibrations of equilibrium O-isotope exchange between dissolved  $\text{PO}_4$  and water catalyzed by PPase - first determined by [2] - from 3 °C to 37 °C. PPase-catalyzed O-isotope exchange reactions were conducted using  $^{18}\text{O}$ -labeled  $\text{PO}_4$  and  $^{18}\text{O}$ -labeled waters to obtain rigorous equilibrium fractionation factors. Our results indicate that “true” equilibrium O-isotope fractionations between dissolved  $\text{PO}_4$  and water closely match recent empirical fractionations determined from biogenic apatites [3] analyzed by CF-IRMS-TCEA methods using  $\text{Ag}_3\text{PO}_4$ , but differ from previous determinations [1] based on fluorination of  $\text{BiPO}_4$ . Our results also suggest that no apparent fractionation exists between bioapatites and dissolved  $\text{PO}_4$  equilibrated by the intracellular enzyme PPase; in contrast to ca. +1 ‰ fractionation observed between sedimentary apatites and dissolved  $\text{PO}_4$  [4, 5].

[1] Longinelli & Nuti (1973) *EPSL* **19**, 373-376 [2] Blake *et al* (2005) *Am. J. Sci.* **305**, 596-620 [3] Pucéat *et al* (2010) *EPSL* **298**, 135-142 [4] Zheng (1996) *Chem. Geol.* **127**, 177-187 [5] Liang & Blake (2007) *Chem. Geol.* **238**, 121-133