Kinetics of oxygen isotope exchange between dissolved phosphate and water catalyzed by inorganic pyrophosphatase from 3-26 °C

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In natural aqueous systems, reactions involving orthophosphate (represented here by PO₄ to encompass the range of protonation states and ion pairs) are primarily carried out by microorganisms and catalyzed by enzymes. The O-isotope composition (δ¹⁸O) of PO₄ is a widely used (paleo)thermometer [1], biomarker [2] and useful tracers of P biogeochemical cycling [e.g., 3] and intracellular reactions [4]. Recent evidence points to inorganic pyrophosphatase (PPase) as the key enzyme responsible for both the equilibrium and temperature dependence of dissolved PO₄-H₂O O-isotope exchange [5]. Calibration of equilibrium O-isotope fractionations between PO₄ and H₂O, catalyzed by PPase, was experimentally determined from 3 to 37 °C [6].

Here, we present experimentally-determined kinetics of O-isotope exchange between dissolved PO₄ and H₂O, catalyzed by PPase, from 3-26 °C. O-isotope exchange reactions were conducted using ¹⁸O-labeled PO₄ and waters in the presence of PPase (0.16 units/µmole PO₄) for a week in buffered solution at pH 7.4. The data are well described by first order reaction kinetics (rate constant k = 9E-05 to 2E-04 sec⁻¹; t₁/₂ = 64 to 696 min). The temperature dependence of the exchange reaction is well fit by the Arrhenius equation, and the activation energy is ca. 65-70 kJ/mole. The rate of PPase-catalyzed reaction is ca. 8 orders of magnitude faster than the rate of abiotic reaction (pH 5) at 20 °C calculated by extrapolation of high temperature rate data [7]. Results from this study may be used to improve interpretation of measured δ¹⁸O values of dissolved PO₄ in nature and cellular reactions (e.g., distinction between microbial overall, PPase-catalyzed or other enzymatic rates of evolution of δ¹⁸O values).