Oxygen isotope exchange between phosphate and water at low temperatures: inorganic versus biological fractionations

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Phosphorus is a key element in the Earth's biosphere occurring principally as a tetrahedral PO_4^{3-} complex, whether inorganic or organic. Oxygen isotope geochemistry of biological phosphates has been widely used in the study of palaeoenvironments for several decades. The empirical determination of the oxygen isotope fractionation between the metabolized phosphate and water has been successfully applied to identify temperature variations in both marine and terrestrial realms. However, the thermodynamics of such isotopic fractionations are still poorly understood. One way to better understand them is to determine the kinetics and temperature-dependent fractionations that proceed in the inorganic compartment of the phosphorus cycle.

Results

Oxygen isotope fractionations have been measured experimentally between orthophosphate ions and water from 50 to 135°C with run-times of up to 180 days. The kinetics are strongly dependent on temperature and the isotopic exchange reaction was estimated to be first-order with respect to phosphate.

$$\log(K) = 12.35 \pm 0.63 - 6.98 \pm 0.24(10^3\ T^{-1})$$
$$E_a = 133.6 \pm 4.6\ \text{kJ mole}^{-1}$$

$$1000 \ln \alpha_{PO_4-H_2O} = 18.35 \pm 0.41(10^3\ T^{-1}) - 32.29 \pm 1.09$$

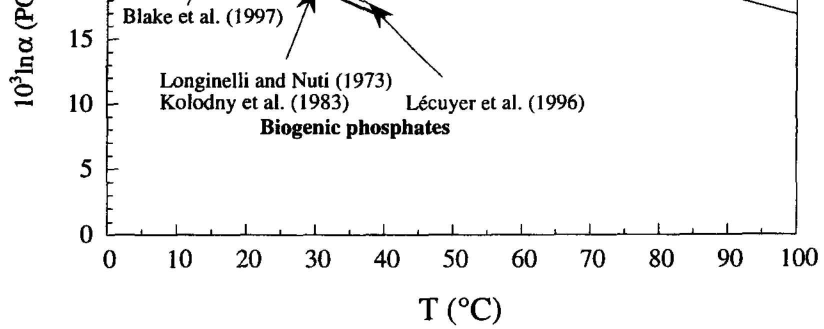

FIG. 1. Oxygen isotope fractionation curve for dissolved inorganic phosphate and water in the range 75–135°C ($[PO_4^{3-}]$ = 500 mg.l^{-1}). Comparison with empirical biogenic fractionation curves for PO_4-H_2O.

Discussion

The above fractionation equation indicates that biomineral phosphates are systematically ^{18}O-depleted by about 8‰ when compared with their inorganic counterparts over the 5–40°C surface temperature range (Fig. 1). This means that (a) dissolved $P^{16}O_4$ is preferentially metabolized by organisms during the mineralization of their hard tissues, (b) the temperature dependence of the empirical and experimental biological isotopic fractionation factors are indistinguishable from the experimental inorganic values, and (c) the empirical fractionations cannot represent equilibrium between total phosphate oxygen and free environmental waters (seawater, rivers or lakes). In a purely inorganic context, the kinetics of the homogeneous phosphate-water reaction are very slow ($k=10^{-13}$ to 10^{-11} s^{-1}) when extrapolated to surface temperatures. The experimentally determined activation energy of 134 kJmol-1 is relatively high and is the same order of magnitude as that for the sulphate-water system. Similarly to the dissolved sulphate-water system, oxygen isotope exchange between water and dissolved and mineral phosphate at oceanic and fresh water temperatures cannot significantly affect their $\delta^{18}O$ values. Application of the equilibrium fractionation equation to the oceanic system shows that the oxygen isotope composition of dissolved inorganic phosphate (DIP) is not in equilibrium with sea water at any reasonable temperature. Therefore, the oxygen isotope ratio of the dissolved phosphate pool should directly reflect source contributions. From our experimental results, we emphasize that any deviation of the isotopic composition of DIP from the isotopic composition of the inorganic sources may be attributed to biological recycling of this nutrient.

Oxygen isotope fractionations between organic or inorganic phosphate and water at low temperatures can be applied to track evidence of life activity in the geological record.

References

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