



Stable isotope fractionations during reactive transport of phosphate in packed-bed sediment columns

Deb P. Jaisi *

Department of Plant and Soil Sciences, University of Delaware, Newark, DE 19716, United States

ARTICLE INFO

Article history:

Received 30 March 2013

Received in revised form 5 August 2013

Accepted 8 August 2013

Available online 28 August 2013

Keywords:

Phosphorus

Transport

Phosphate oxygen isotope ratios

$\delta^{18}\text{O}_p$

Isotope fractionation

Cape Cod

ABSTRACT

Characterizing reactivity and fate of contaminants in subsurface environments that are isolated from direct visualization is a major challenge. Stable isotopes coupled with concentration could be used as a potential tool to quantitatively analyze the chemical variability of the contaminant during reactive transport processes in the subsurface environment. This study was aimed at determining whether abiotic reactions of phosphate during its transport involve fractionation of oxygen isotopes in phosphate ($\delta^{18}\text{O}_p$). It included the effects of solution chemistry and hydrodynamics on $\delta^{18}\text{O}_p$ values during phosphate transport through a packed-bed column prepared by using natural sediment collected from the Cape Cod aquifer in Massachusetts. Results show that the isotopic fractionation between effluent and influent phosphate at early stage of transport could be $\sim 1.3\%$ at higher flow rates with isotopically-light phosphate (P^{16}O_4) preferentially retained in the sediment column. This fractionation, however, decreased and became insignificant as more phosphate passed through the column. Mobilization of phosphate initially sorbed onto sediments caused a large kinetic isotopic fractionation with isotopically-light phosphate preferentially remobilized from the sediment column, but over longer time periods, this fractionation decreased and became insignificant as well. These results collectively suggest that abiotic reactive transport processes exert minimal influence on the $\delta^{18}\text{O}_p$ composition of subsurface systems. Alternatively, fluctuation in flow rate and subsequent remobilization of phosphate could be detectable through transient changes in $\delta^{18}\text{O}_p$ values. These findings extend the burgeoning application of $\delta^{18}\text{O}_p$ to identify the different sources and geochemical processes of phosphate in the subsurface environments.

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1. Introduction

Phosphorus (P) is one of the most important nutrients for all life forms irrespective of physiological uptake mechanism or metabolic pathway. Because of the low stoichiometric need of P among other major nutrients (ca. 106C: 16N: 1P; Redfield, 1958), small amounts of P addition could cause severe impacts on water quality in the receiving catchments or groundwater aquifers and could promote eutrophication (Wetzel, 1983). Understanding the sources, cycling and transformation of P is not straightforward for phosphate, compared to many other nutrients, particularly because: a) the amount of dissolved phosphate is several orders of magnitude smaller than the pool

of rapidly cycling phosphate in soil and sediments (Frossard et al., 1995); and b) both biotic and abiotic reactions occur side by side to dissolve and precipitate phosphate at time scales varying from a few seconds to several years, and with redistribution of phosphate from one phase/pool to another (Bünemann and Condron, 2007; Jaisi et al., 2011). This complexity demands an appropriate tracer that can better constrain the pathways and mechanisms of P cycling between biotic and abiotic environments, and from one phase to another.

Under Earth's surface conditions, P occurs primarily as orthophosphate (PO_4^{3-}) and is cycled through the biosphere and geosphere primarily by biologically-mediated reactions. This leads to the use of oxygen isotope ratios in phosphate ($\delta^{18}\text{O}_p$) as a potential tracer of P in the environment where P is involved and cycled (Blake et al., 1997, 2005; Paytan et al., 2002). Fundamental properties of $\delta^{18}\text{O}_p$ values are: a) in

* Tel.: +1 302 831 1376; fax: +1 302 831 0605.

E-mail address: jaisi@udel.edu.

abiotic systems, there is negligible O-isotope exchange between phosphate and water (or other oxyanions) at low temperatures (<80 °C) and near-neutral pH values such as in modern geochemical processes on/near earth surfaces (Lecuyer et al., 1999); and b) in biological systems, O-isotope exchange is rapid between dissolved phosphate and water and follows temperature-dependent equilibrium O-isotope fractionation (Blake et al., 1998) similar to mineral phosphate (e.g. bioapatite; Longinelli and Nuti, 1973) with fractionation factor as:

$$\delta^{18}\text{O}_p - \delta^{18}\text{O}_w = (1/4.3)(111.4 - t) \quad (1)$$

where $\delta^{18}\text{O}_p$ and $\delta^{18}\text{O}_w$ are the oxygen isotopic composition of phosphate and water, respectively, in equilibrium with environmental temperature t (°C). Using this equation, the fractionation factor at 0 °C, for example, is 25.91‰. Furthermore, unlike oxyanions of bioelements such as S and C (i.e., $\delta^{18}\text{O}_{\text{SO}_4}$ and $\delta^{18}\text{O}_{\text{CO}_3}$) that are characterized by complicated kinetic fractionations (e.g., Turchyn et al., 2010), microbial metabolism of P compounds is characterized by overall equilibrium O-isotope fractionations between phosphate and water (Blake et al., 1998, 2005).

Development of phosphate oxygen isotope ratios as a geochemical tracer requires a systematic analysis on the isotope effects of relevant physico-chemical and biological processes in a wide variety of natural environments. Several aspects of O isotope systematics in microbial metabolism and water column processes have already been characterized (Blake et al., 1997, 2005; Colman et al., 2005; Goldhammer et al., 2011; McLaughlin et al., 2006; Paytan et al., 2002). Other studies have identified the isotope effects associated with sorption, desorption, and mineral transformation (Jaisi et al., 2010), partial dissolution and precipitation of new mineral phases (Jaisi et al., 2010), and biological uptake and recycling of P at the mineral–water interface (Jaisi et al., 2011). Isotopic signatures in specific P pools in aerosol, soil, and sediment have been used to identify sources of P in air and soil, as well as during soil evolution (Angert et al., 2012; Gross et al., 2013; Jaisi and Blake, 2010; Tamburini et al., 2012; Zohar et al., 2010), and biological activities in the early Earth (Blake et al., 2010). These studies have increased the realm of possibilities of applying $\delta^{18}\text{O}_p$ values as a tool to understand P dynamics in soils and sediments.

Phosphate primarily forms inner sphere sorption complex on iron oxide minerals (Sigg and Stumm, 1981). A previous study focused on the isotope effect during abiotic interactions between dissolved phosphate and iron oxides had identified the nature of kinetic fractionation during early phase of sorption (Jaisi et al., 2010). The kinetic fractionation between sorbed and aqueous phosphate was found to be high at the early phase of sorption with isotopically-light phosphate (P^{16}O_4) preferentially incorporated into sorbed phases. This fractionation showed negligible temperature-dependence and gradually decreased as a result of efficient 'ion exchange' between sorbed and aqueous phase phosphate, to become insignificant at greater than ~100 h of reaction. The equilibrium fractionation factor at the end of the reaction was about <0.5‰.

Column experiments designed to understand isotope effect during transport of oxyanions are quite limited. Few studies that include $\delta^{18}\text{O}$ of water (e.g., Koeniger et al., 2010; Raymundo-Raymundo et al., 2012), $\delta^{15}\text{N}$ of nitrate (e.g., Hinkle

et al., 2008), and $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ of sulfate (e.g., Kumar et al., 2013) have helped better understand how these oxyanions transport in subsurface environment. However, isotope effects during phosphate transport in soils and sediments have not studied at all. This gap in knowledge has limited our ability to better interpret $\delta^{18}\text{O}_p$ values measured from subsurface soils and porewater. As a result, identification of P source, degree of mixing of different sources, and internal P cycling in natural environments using $\delta^{18}\text{O}_p$ values could not be precisely identified. Therefore constraining factors that control the magnitude of isotopic fractionation and differentiating biotic and abiotic pathways is the first step for rigorous interpretation of local and temporal variability of measured $\delta^{18}\text{O}_p$ values. In this research, laboratory-scale saturated flow column transport experiments were performed by using sediment obtained from the Cape Cod aquifer in Massachusetts under a wide range of aqueous solution chemistries including site specific flow conditions. The objectives of this research were to quantify the effects of solution chemistry and hydrodynamics on the $\delta^{18}\text{O}_p$ values of phosphate and to provide insights into the mechanisms controlling the isotope compositions during transport and remobilization of phosphate. Results obtained from these studies indicate that the flow rate is an important variable for kinetic isotope fractionation, but this fractionation is expected to be insignificant in natural environments because of sustained flow of P plumes. Overall, these findings provide fresh perspectives and opportunities to understand the sources of P in subsurface environments and to apply appropriate action in any remediation efforts.

2. Materials and methods

2.1. Sediment collection from the Cape Cod aquifer

Aquifer sediment was collected at the U.S. Geological Survey Toxic Substances Hydrology Research Site (LeBlanc, 2006), near Falmouth, Cape Cod, Massachusetts, U.S.A. (Fig. 1). This site is located in the path of a contaminant plume created by about 60 years of land disposal of treated wastewater to the sand and gravel, glacial outwash aquifer (LeBlanc, 1984; Repert et al., 2006). It was retrieved with a wireline-piston core barrel and plastic core liners (Zapico et al., 1987) from the elevation of 6.61–6.97 m above the sea-level at the USGS site FSW575 (USGS core designation F575-C2A). This region was located below the water table in the waste-water plume in the aquifer. Retrieved sediment cores were frozen within 4 h in ice, and shipped in dry ice and stored frozen (−80 °C) until analysis. Sediment was freeze dried and sieved to remove coarse grained sediments >2 mm.

The grain size distribution of sediments was determined by dry sieving and porosity of the ≤2 mm size fraction was measured by using a standard pycnometer. The surface area was measured by using multipoint BET (Brunauer–Emmett–Teller) method with a Micromeritics Tristar analyzer. It utilizes adsorbed volume of liquid nitrogen to calculate surface area. The BET calculation assumes cylindrical and open-ended pore geometry without any interconnected network and utilizes the Kelvin equation to correlate the relative pressure of nitrogen in equilibrium with the porous solid with the size of the pores where capillary condensation takes place. The pore size distributions within sediment aggregates were calculated

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