



The rate of oxygen isotope exchange between nitrate and water

Masanori Kaneko*, Simon R. Poulson

Department of Geological Sciences and Engineering MS-172, University of Nevada–Reno, 1664 N. Virginia Street, Reno, NV 89557-0138, USA

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Abstract

The oxygen isotope exchange rate between nitrate and water was measured at a temperature of 50–80 °C and pH –0.6 to 1.1. Oxygen isotope exchange is a first-order reaction, with the exchange rate being strongly affected by both reaction temperature and pH, with increased rates of isotope exchange at higher temperatures and lower pH values. The rate of oxygen isotope exchange under natural conditions is extremely slow, with an estimated half-life for isotope exchange of 5.5×10^9 years at 25 °C and pH 7. The extremely slow rate of oxygen isotope exchange between nitrate and water under typical environmental conditions illustrates that nitrate- $\delta^{18}\text{O}$ signatures (and also nitrate $\delta^{17}\text{O}$ and $\Delta^{17}\text{O}$ signatures) associated with various nitrate sources, as well as isotope compositions produced by biogeochemical processes, will be preserved. Hence, it is valid to use the value of nitrate- $\delta^{18}\text{O}$ to investigate the sources and biogeochemical behavior of nitrate, in a similar manner to the use of sulfate- $\delta^{18}\text{O}$ signatures to study the sources and biogeochemical behavior of sulfate.

Equilibrium oxygen isotope fractionation factors have been determined, although quantification of the nitrate–water equilibrium fractionation factor is not possible due to the presence of nitrate as both protonated (i.e. HNO_3) and unprotonated forms (i.e. NO_3^-) under the experimental conditions, and the difficulty in accurately calculating nitrate speciation in low pH, high ionic strength solutions.

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1. INTRODUCTION

Identification and quantification of the sources, sinks, and biogeochemical processes that affect nitrate are critical components necessary for understanding the nitrogen cycle in various ecosystems and aquatic environments, which can be difficult due to the possibility of multiple sources of nitrate, and the likelihood of multiple biogeochemical processes operating concurrently to affect nitrate behavior. In conjunction with measurement of the temporal and spatial variation of nitrate concentrations, stable isotope analysis of nitrate can provide valuable additional discriminants to help deconvolute these sources and processes, particularly when analyses of both $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ are employed (e.g.

Böttcher et al., 1990; Kendall, 1998; Burns and Kendall, 2002; Burns et al., 2009; Pellerin et al., 2009; Kaushal et al., 2011). In addition, application of the analysis of nitrate $\delta^{17}\text{O}$ and $\Delta^{17}\text{O}$ compositions is increasingly proving to be yet another useful technique to investigate nitrate behavior, particular when nitrate derived from atmospheric deposition is a significant component of the system under study (e.g. Michalski et al., 2003; Jackson et al., 2010; Costa et al., 2011; Tsunogai et al., 2011).

In order to successfully apply the oxygen isotopic composition of nitrate as a geochemical signature of sources and/or processes, the rate of oxygen isotope exchange between nitrate and water needs to be sufficiently slow under environmental conditions such that the measured $\delta^{18}\text{O}$ value of nitrate represents a $\delta^{18}\text{O}$ signature associated with the original nitrate source and/or the biogeochemical processes that have acted upon the nitrate, rather than simply reflecting a $\delta^{18}\text{O}$ value that is in equilibrium, or partly equilibrated, with the $\delta^{18}\text{O}$ composition of water. Experimental determination of the rate of oxygen isotope

* Corresponding author. Current address: Institute of Biogeosciences, Japan Agency for Marine–Earth Science and Technology (JAMSTEC), 2-15 Natsushima, Yokosuka 237-0061, Japan. Tel.: +81 46 867 9812; fax: +81 46 867 9775.

E-mail address: m_kaneko@jamstec.go.jp (M. Kaneko).

exchange between water and other oxyanions, such as sulfate (e.g. Lloyd, 1968; Seal et al., 2000) and selenate (e.g. Okumura and Okazaki, 1973; Kaneko and Poulson, 2012), demonstrate that the oxygen isotope exchange rate for these species is only fast enough to measure directly in experiments at low pH and/or elevated temperatures, and that the exchange rate at low temperatures and circum-neutral pH conditions is very slow, and hence facilitates the use of sulfate- $\delta^{18}\text{O}$ and selenate- $\delta^{18}\text{O}$ to investigate the sources and behavior of sulfate and selenate. However, the rate of oxygen isotope exchange between nitrate and water has not been quantitatively determined, and studies using the oxygen isotopic composition of nitrate have been conducted on the assumption that the oxygen isotope exchange rate between nitrate and water is sufficiently slow so that nitrate $\delta^{18}\text{O}$ compositions preserve useful and usable geochemical information. A number of previous studies qualitatively indicate that this is indeed the case, and demonstrate that detectable isotope exchange only takes place under very low pH conditions. Hall and Alexander (1940) measured little or no oxygen isotope exchange between nitrate and water under a wide (but undefined) range of pH conditions. Bunton et al. (1952) performed isotope exchange experiments with extremely high concentrations of HNO_3 (40.3–61.7 mol% HNO_3), and found that isotope exchange rates were faster at higher HNO_3 concentrations, but with the analytical techniques used in their study, the exchange rate was essentially close to zero for HNO_3 concentrations less than 40 mol%. Böhlke et al. (2003) performed experiments at 22 and 100 °C, with approximate HNO_3 concentrations of 1, 4 and 10 N, and quantified the nitrate–water oxygen isotope fractionation factor under these conditions, and also performed a limited number of isotope exchange rate experiments at 22 °C and approx. 4 N HNO_3 . However, Böhlke et al. (2003) did not perform isotope exchange rate experiments over a range of pH values, which prevents any estimation of the rate of isotope exchange at circum-neutral values of pH. In the case of nitrate-bearing ground waters with long residence times (e.g. ground waters impacted by agricultural irrigation with chlorofluorocarbon ages up to 38 years; Brown et al., 2011), the absence of the relevant exchange rate data results in uncertainty concerning the isotopic fidelity and potential utility of nitrate $\delta^{18}\text{O}$ signatures.

In apparent contrast to these studies, nitrate–water isotope exchange studies in the presence of non-sterilized soil material performed by Kool et al. (2011) suggest that the rate of oxygen isotope exchange between nitrate and water is fast (significant oxygen isotope exchange in 24 h). The pH values of the soil solutions were not measured, but it seems likely that the solutions had values of pH which were either circum-neutral or mildly acidic. Hence, there is significant uncertainty as to the rate of oxygen isotope exchange between nitrate and water, which has major implications as to the feasibility of the application of $\delta^{18}\text{O}$ nitrate analyses to study the sources and/or biogeochemical processes that affect nitrate.

This study quantified the abiological rate of oxygen isotope exchange between nitrate and water for a range of temperature and pH conditions, and subsequently esti-

mated the rate of exchange under example natural conditions (25 °C, pH 7). This study also measured the oxygen isotope equilibrium fractionation factors between nitrate and water at the same temperature and pH conditions.

2. METHODS

2.1. Oxygen isotope exchange experiments between nitrate and water

Oxygen isotope exchange experiments were performed in polypropylene bottles, with 100 ml of distilled, deionized water, with the addition of NaNO_3 (Certified ACS reagent grade, Fisher Scientific) to produce 0.1 N nitrate solutions. After pH adjustment by HCl, values of pH were measured at room temperature (pHTestr 30, Oakton), and the solutions were rapidly heated to experimental temperature (50, 65 or 80 °C). The pH at each experimental temperature was calculated using Visual MINTEQ (Allison et al., 1991). No pH buffers were used in the experiments, as many pH buffers contain oxygen, and possible oxygen isotope exchange between the pH buffer and water could confound interpretation of the experimental results. In addition, as HNO_3 has $\text{p}K_a = -1.3$ (WHO, 2003), some pH buffering due to the presence of nitrate and HNO_3 was expected at the pH conditions of the experiments. Each experiment was periodically sampled (1 ml), followed by an increase of the sample solution pH to pH 5–7 by the addition of NaOH solution, in order to quench the isotope exchange reaction (e.g. Böhlke et al., 2003; Kaneko and Poulson, 2012). The sample solution was freeze-dried to remove water and produce a NaNO_3 salt for oxygen isotope analysis.

2.2. Oxygen isotope analysis

Oxygen isotope analyses were performed using a Eurovector elemental analyzer interfaced to a Micromass IsoPrime stable isotope ratio mass spectrometer. NaNO_3 samples were loaded into silver capsules with a small amount of nickelized graphite to promote complete conversion of nitrate to CO, and then analyzed at 1300 °C in a glassy carbon reactor packed with glassy carbon chips and nickelized graphite (modified after Kornexl et al., 1999). The CO gas produced was separated from a trace N_2 component by gas chromatography before isotope analysis, with a helium carrier gas flow of 100 ml/min. Oxygen isotopic compositions were analyzed by comparison against a working CO reference gas using MassLynx software, and $\delta^{18}\text{O}$ values are reported in the usual δ notation vs. VSMOW. International Atomic Energy Agency standards NBS-127 (BaSO_4 , $\delta^{18}\text{O} = +8.6\text{‰}$; Brand et al., 2009) and IAEA-N3 (KNO_3 , $\delta^{18}\text{O} = +25.6\text{‰}$; Böhlke et al., 2003) were used for data calibration and correction. The analytical precision (1σ) based on replicate analysis of the standards and samples are $\pm 0.2\text{‰}$ and $\leq 0.8\text{‰}$, respectively. Preliminary experiments verified that there was no oxygen isotope fractionation during freeze-drying of dissolved nitrate to produce NaNO_3 salt ($\pm 0.4\text{‰}$, $n = 5$).

The water used for each experiment was analyzed for $\delta^{18}\text{O}$ using the CO_2 – H_2O equilibration method of Epstein

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