Earth and Planetary Science Letters 423 (2015) 164–172

Contents lists available at ScienceDirect

Earth and Planetary Science Letters

www.elsevier.com/locate/epsl

Iron isotope fractionation in sediments of an oligotrophic freshwater lake

Kai Liu [a,b], Lingling Wu [a,b,*], Raoul-Marie Couture [a,b,c], Weiqiang Li [d,e,f], Philippe Van Cappellen [a,b]

[a] Department of Earth and Environmental Sciences, University of Waterloo, Waterloo, Ontario, Canada
[b] Water Institute, University of Waterloo, Waterloo, Ontario, Canada
[c] Norwegian Institute for Water Research – NIVA, Oslo, Norway
[d] Department of Geoscience, University of Wisconsin–Madison, Madison, WI, United States
[e] NASA Astrobiology Institute, University of Wisconsin–Madison, Madison, WI, United States
[f] State Key Laboratory for Mineral Deposits Research, School of Earth Sciences and Engineering, Nanjing University, China

ARTICLE INFO

Article history:
Received 22 October 2014
Received in revised form 31 March 2015
Accepted 5 May 2015
Available online 14 May 2015
Editor: J. Lynch-Stieglitz

Keywords:
Fe isotope fractionation
sediments
oligotrophic lake
pore water
dissimilatory iron reduction

ABSTRACT

In situ iron (Fe) isotope compositions of pore water and solid-bound Fe phases were measured in sediments of an oligotrophic, sulfate-poor freshwater lake (Lake Tantaré, Québec, Canada). Previous work has shown that dissimilatory Fe(III) reduction (DIR) is the main Fe reduction pathway in this setting. Hence, the lake sediments provide a well-characterized, natural environment in which to assess the transferability of DIR-produced Fe isotope fractionations obtained in laboratory model systems. Iron redox cycling within the sediments produces isotopically light pore water Fe(II) (average $\delta^{56}Fe = -2.1 \pm 0.6‰$) and sorbed Fe(II) (average $\delta^{56}Fe = -1.2 \pm 0.2‰$), compared to the Fe(III) oxyhydroxide (average $\delta^{56}Fe = +0.6 \pm 0.2‰$) and tightly solid-bound Fe(II) (average $\delta^{56}Fe = +0.3 \pm 0.2‰$) sediment pools. The apparent isotope fractionation factor between aqueous Fe(II) and Fe(III) oxyhydroxides of $-2.6 \pm 0.5‰$ derived for Lake Tantaré sediments falls within the range reported for experimentally determined isotopic fractionations during DIR. Our results yield the first comprehensive set of Fe isotope signatures associated with microbially driven Fe redox cycling obtained directly in sediments of an oligotrophic freshwater lake.

1. Introduction

The biogeochemical cycling of iron (Fe) plays an important role in near-surface environments, because the electron transfer processes during Fe redox transformations are closely tied to reactions with other redox-sensitive elements, including oxygen (Millero et al., 1987), carbon (Lalonde et al., 2012), nitrogen (Straub et al., 1996), sulfur (Thamdrup et al., 1994), and contaminants such as chromium (Buerge and Hug, 1999). Furthermore, sorption to Fe oxyhydroxides can significantly influence the fate of oxyanions of nutrient elements, for example phosphorus (Hongve, 1997) and silicon (Davis et al., 2002), and trace elements (Belzile et al., 2000).

Iron isotopes provide a powerful tool to unravel Fe cycling processes, in modern and ancient Earth settings (e.g., Borrok et al., 2009; Johnson et al., 2008). Both biotic and abiotic processes can fractionate Fe isotopes; the largest fractionations are associated with redox transformations between ferric and ferrous Fe (Crosby et al., 2005; Wu et al., 2012). Oxidation of aqueous Fe(II) and reduction of solid Fe(III) phases may both generate isotopically light Fe(II). In the former case, the combination of equilibrium fractionation between aqueous Fe(II) and aqueous Fe(III) and kinetic fractionation upon precipitation of Fe(III) yields an overall fractionation of -1 to $-2‰$, that is, values smaller than would be obtained under exclusively equilibrium conditions (Beard and Johnson, 2004; Wu et al., 2013). Dissimilatory Fe(III) reduction (DIR) has been shown to produce fractionations on the order of $-3‰$, both in the laboratory and in natural settings (Crosby et al., 2005, 2007; Percak-Dennett et al., 2011; Tangalos et al., 2010). Abiotic reduction of Fe(III) oxide phases, for example through reaction with H_2S produced by microbial sulfate reduction, is also likely to fractionate Fe isotopes, although the exact magnitude remains unknown. In addition, sorption of Fe(II) to Fe(III) oxyhydroxides may result in electron and Fe atom exchanges (Brantley et al., 2004). The accompanying fractionations, however, are small, generally in the range 0.2–0.9‰, where sorbed Fe(II) is enriched in heavy isotopes relative to aqueous Fe(II) (Crosby et al., 2005; Wu et al., 2009, 2010).

* Corresponding author at: Department of Earth and Environmental Sciences, University of Waterloo, Waterloo, Ontario, Canada. Tel.: +1 519 888 4567x33235.
E-mail address: lingling.wu@uwaterloo.ca (L. Wu).

http://dx.doi.org/10.1016/j.epsl.2015.05.010
0012-821X/

Iron isotopes have been applied to infer biogeochemical processes and conditions in a variety of environments, including soils (Wiederhold et al., 2007) and riverine (Bergquist and Boyle, 2006), marine (Fehr et al., 2008) and groundwater (Teutsch et al., 2005) settings. Variations in the Fe isotope compositions of Precambrian marine sedimentary rocks have played a prominent role in discussions on past Fe cycling in the earth surface environment (e.g., Johnson et al., 2008). Few studies, however, have analyzed Fe isotope compositions in lakes. The existing studies have generally been carried out in extreme lacustrine environments, such as Fe-rich meromictic lakes (Busigny et al., 2014; Teutsch et al., 2009) and have focused on water column Fe isotope signatures (Busigny et al., 2014; Malinovsky et al., 2005; Teutsch et al., 2009). The observed gradients in isotopic composition of dissolved Fe(II) across redox transitions in stratified lakes have been interpreted as resulting from either partial oxidation of Fe(II) (Busigny et al., 2014; Malinovsky et al., 2005) or DIR (Teutsch et al., 2009). A more definite characterization and interpretation of the Fe isotope signatures of Fe redox processes remain a high priority for the application of Fe isotopes to modern environments and the rock record.

In this study, in situ measured Fe isotope compositions of pore water and solid-bound Fe in sediments of Lake Tantaré, a pristine headwater lake in Québec, Canada, are used to test the transferability of stable Fe isotope fractionations obtained in laboratory studies. The sediments of Lake Tantaré were selected because (1) detailed data on pore water chemistry and solid-phase Fe geochemistry plus mineralogy are available (Couture et al., 2008, 2010b; Fortin et al., 1993), and (2) the oligotrophic, sulfate-poor conditions in the lake may provide an analog for early Precambrian aquatic environments. The existing data for Lake Tantaré sediments are consistent with an active early diagenetic redox cycling of Fe below the sediment–water interface (SWI). The quantitative interpretation of the pore water and solid-bound Fe depth profiles using reactive transport modeling further indicates that DIR is the main Fe reduction pathway, with only a minor contribution of reductive dissolution of Fe(III) oxyhydroxides by sulfide (Couture et al., 2010b). Thus, the sediments of Lake Tantaré enable the comparative analysis of the isotopic compositions of various Fe pools in a natural sedimentary environment under well-constrained biogeochemical conditions.

2. Methods

2.1. Site and sampling

Lake Tantaré (47°04′N, 71°33′W) is located along the southern fringe of the boreal forest, in a catchment dominated by ferrohumic podzols with mesic drainage conditions that developed on sandy loam till (Payette et al., 1990). The bedrock is granite and gneiss, typical of the Canadian Shield. Lake Tantaré is an acidic (pH 5.4–6.0), oligotrophic lake, separated by sills into four basins (Couture et al., 2010b). Sampling was carried out in two basins, Basin A and Basin B, at the westernmost end of the lake. The results presented here are primarily from Basin A, which has a maximum water depth of about 15 m and permanently oxic bottom waters (>3.8 mg O_2 L^{-1}) (Couture et al., 2008). Basin B has a maximum depth of 21 m and its bottom waters become anoxic (<0.01 mg O_2 L^{-1}) during late summer-early fall (Couture et al., 2008).

Three acrylic peepers were inserted by divers in the sediments at the deepest point of Basin A in July 2012 and left to equilibrate for 21 days. The chambers of the peepers were spaced equally at 1 cm intervals. In order to minimize contamination by oxygen, the peepers were prepared according to the procedure developed by Carignan et al. (1994), who carried out their method validation study in Lake Tantaré. The peepers were soaked in an acidic solution for 7 days and in ultra-pure water for another 7 days. The peeper chambers were then filled with ultra-pure water and covered with a 0.2 µm pore size membrane (Gelman HT-200 polysulfone) plus a thin plexiglass sheet with holes fitting the cell apertures. The assembled peepers were stored under N_2 for two weeks to allow for the complete removal of oxygen, and kept under N_2 until deployment.

Upon retrieval, the peepers were raised one by one and immediately sampled. Water from the peeper chambers were collected directly into vials pre-acidified with ultra-pure HCl (Seastar grade). The vials were kept at 4 °C until analysis. Sediment cores were collected in both basins by divers using butyrate tubes. The cores were immediately sectioned onshore in 0.5 cm or 1 cm depth intervals. The sediment was frozen and kept frozen until freeze-drying. The freeze-dried sediment samples were stored under humidity-free conditions prior to the chemical extractions, which were performed within 2 weeks time.

2.2. Sequential Fe extractions

Three-step sequential acid extractions were performed on the sediment samples following the method of Tangalos et al. (2010). Extractions 1 and 2 were carried out in an anaerobic chamber. All extraction solutions were deoxygenated with O_2-free N_2 gas. In extraction 1, 5 mL of 0.1 M HCl was added to 10 mg freeze-dried sediment. The mixture was left to react for 1 h, then centrifuged at 4800 rpm for 10 min. The supernatant was filtered through a 0.2 µm pore size syringe filter (extract 1). The remaining solid was mixed with 5 mL of 0.5 M HCl. After 24 h, the mixture was centrifuged (4800 rpm for 10 min) and the supernatant was filtered (0.2 µm pore size syringe filter) producing extract 2. The remaining solid was mixed with 5 mL of 7 M HCl and then placed in a 70 °C oven for 72 h. After that, the mixture solution was centrifuged and the supernatant was filtered as described before, yielding extract 3.

Based on previous work, extraction 1 removes sorbed Fe(II) and the most reactive fraction of amorphous Fe(III) oxyhydroxides (Tangalos et al., 2010); extraction 2 removes amorphous Fe(III) oxyhydroxides and residual solid-phase Fe(II) such as FeS and some silicate Fe that cannot be extracted by 0.1 M HCl (Severmann et al., 2006; Tangalos et al., 2010). We refer to the Fe(II) in extract 2 as "tightly-bound Fe(II)". Both 0.1 M and 0.5 M HCl mainly extract amorphous to poorly-crystalline Fe phases. Crystalline Fe phases, such as hematite, goethite, and magnetite, but not pyrite and Fe silicates, are extracted by 7 M HCl (extraction 3) (Severmann et al., 2006; Tangalos et al., 2010).

2.3. Iron concentrations

Iron concentrations in the pore water samples and the solutions from the sediment extractions (i.e., extracts 1, 2 and 3) were determined spectrophotometrically by the *Ferrozine* method (Stookey, 1970; Viollier et al., 2000). Prior to the analyses, the pore water samples were carefully screened for evidence that precipitates formed during storage: in all cases, the solutions were completely clear. The total Fe (Fe(tot)) concentration of a sample was determined after adding 10% hydroxylamine HCl, which reduces any soluble Fe(III) present in the sample. The concentration of Fe(III) in the sample was then calculated as the difference between the concentration of Fe(tot) and that of Fe(II) measured before adding hydroxylamine. A reagent blank was prepared by adding 10% hydroxylamine HCl to a 0.5 M HCl solution. The reagent blank was subtracted from the sample absorbance when calculating the Fe concentration from the standard curve. The detection limit of 0.5 µM was estimated based on the minimum detectable change