



Large iron isotope fractionation at the oxic–anoxic boundary in Lake Nyos

Nadya Teutsch^{a,b,*}, Martin Schmid^c, Beat Müller^c, Alex N. Halliday^{b,d},
Helmut Bürgmann^c, Bernhard Wehrli^{c,e}

^a Eawag, Swiss Federal Institute of Aquatic Science and Technology, 8600 Dübendorf, Switzerland

^b Institute of Isotope Geochemistry and Mineral Resources, ETH-Zürich, 8092 Zürich, Switzerland

^c Eawag, Swiss Federal Institute of Aquatic Science and Technology, 6047 Kastanienbaum, Switzerland

^d Mathematical, Physical and Life Sciences Division, 9 Parks Road, Oxford OX1 3PD, United Kingdom

^e Institute of Biogeochemistry and Pollutant Dynamics, ETH-Zürich, 8092 Zürich, Switzerland

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ABSTRACT

The degassing of volcanic Lake Nyos (Cameroon) provides the opportunity to study the strong isotopic variation of dissolved Fe(II) in a well constrained redox cycle and to identify the governing processes by reaction–transport modeling. Two depth profiles sampled in the lake in March 2004 and 2005 reveal an increase in iron concentrations and $\delta^{57}\text{Fe}$ from around 1 mg L^{-1} and -1.88% at 55 m depth up to 344 mg L^{-1} and $+0.83\%$ at the bottom of the lake, respectively. A steep increase in $\delta^{57}\text{Fe}$ was observed across the oxic–anoxic boundary. As many biological and geochemical processes are known to fractionate Fe isotopes, we used a calibrated reaction–transport model to disentangle the processes governing the Fe cycle. The model combines the isotopic signatures of dissolved Fe(II) and settling Fe(III) particles with the concentration profiles and settling fluxes of the Fe particles in the lake. We show that the strong shift in $\delta^{57}\text{Fe}$ is caused by isotopic fractionation via dissimilatory Fe reduction across the oxic–anoxic boundary of Lake Nyos. The shift towards more positive values below the oxic–anoxic interface could be attributed to vertical mixing of a heavier component from the bottom of the lake.

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1. Introduction

Over the last decade considerable effort has been expended exploring isotopic variations associated with the biogeochemical cycling of Fe (Anbar, 2004; Johnson et al., 2004b; Dauphas and Rouxel, 2006). Many low temperature environments such as marine sediments (Severmann et al., 2006; Staubwasser et al., 2006; Fehr et al., 2008), terrestrial sediments (Matthews et al., 2004), soils (Emmanuel et al., 2005; Thompson et al., 2007; Wiederhold et al., 2007a,b), lakes (Malinovsky et al., 2005), groundwater (Teutsch et al., 2005), and rivers (Bergquist and Boyle, 2006; Ingri et al., 2006) have been studied.

Oxidation–reduction processes play a particularly important role in Fe geochemistry and have a significant effect on Fe isotopes as well. The biogeochemical Fe cycle at redox fronts in lakes is governed by (1) the sedimentation of Fe-bearing particles and their reductive

dissolution, (2) vertical transport by turbulent diffusion of dissolved Fe(II), and (3) reoxidation followed by secondary precipitation at the oxic–anoxic interface (Davison, 1993). As with other transition metals with several oxidation states, the oxidized form of Fe is generally enriched in the heavy isotopes (Johnson et al., 2004a). This has been theoretically predicted (Schauble et al., 2001; Anbar et al., 2005), established under laboratory conditions (Welch et al., 2003) and also found in a field study (Bullen et al., 2001).

A particularly important process taking place in anoxic environments that strongly influences Fe(III)–Fe(II) transformations is microbial dissimilatory Fe reduction. In laboratory experiments it has been found that Fe reduction of ferrihydrite, hematite, and goethite by this process results in lighter Fe(II)_{aq} (Beard et al., 1999; Crosby et al., 2005; Crosby et al., 2007). Iron isotope variations have been postulated to be produced by microbial dissimilatory Fe reduction in several ancient (Yamaguchi et al., 2005; Archer and Vance, 2006; Johnson et al., 2008) and recent (Severmann et al., 2006; Staubwasser et al., 2006) terrestrial environments. However, little research has been published on Fe isotope compositions in lakes. In a fresh water lake, Fe isotope variations were observed at the oxic–anoxic interface, where the dissolved Fe(II) under reducing conditions was lighter compared to the coexisting and overlying oxic suspended material (Malinovsky et al., 2005). They attributed this shift to equilibrium effects during the oxidation of Fe(II) species and precipitation of Fe(III) oxides.

* Corresponding author. Present address: The Fredy and Nadine Herrmann Institute of Earth Sciences, Hebrew University of Jerusalem, 91904 Jerusalem, Israel. Tel.: +972 2 6584719; fax: +972 2 5662581.

E-mail addresses: teutsch@cc.huji.ac.il (N. Teutsch), martin.schmid@eawag.ch (M. Schmid), beat.mueller@eawag.ch (B. Müller), alex.halliday@mpls.ox.ac.uk (A.N. Halliday), helmut.buergmann@eawag.ch (H. Bürgmann), bernhard.wehrli@eawag.ch (B. Wehrli).

In this paper we report Fe isotope data for a particularly interesting volcanic lake. The meromictic Lake Nyos with its steep Fe-concentration gradient across the oxic–anoxic redox boundary is perfectly suited to study the processes of the Fe cycle. It is a volcanic crater lake in northwest Cameroon (Lockwood and Rubin, 1989), which suffered a sudden catastrophic release of CO₂ in 1986 that killed about 1700 people (Kling et al., 1987). The lake has a surface area of 1.58 km² and a maximum depth of 210 m. It is permanently stratified with an oxidized epilimnion of about 55 m thickness during overturn in the dry season. Its deep water contains high concentrations of CO_{2(aq)}, HCO₃, Ca, Mg and Fe and its composition is governed by the dissolution of local rock (Kusakabe et al., 1989; Giggenbach, 1990). It is continuously fed by a source of warm water with a high partial pressure of geogenic CO₂, which accumulates in the deep water of the lake. To avoid the recurrence of a catastrophic CO₂ outgassing, the lake is now artificially degassed by a tube that drains water from 203 m depth to the surface (Halbwachs et al., 2004; Kling et al., 2005; Schmid et al., 2006; Kusakabe et al., 2008). This system spreads deep water with high concentrations of dissolved Fe(II) in a 50 m high jet on the lake surface, thus enhancing the Fe cycle significantly. Iron oxidation occurs almost quantitatively at the surface of Lake Nyos, and therefore, fractionation effects due to oxidation can be neglected. Concentrations of dissolved Fe(II) in the oxic surface waters are negligible, while immediately below the chemocline Fe(II) concentrations sharply increase, with the highest values in the deepest layers of the lake (Kusakabe et al., 2008). Across the oxic–anoxic boundary, reduced Fe species diffuse upwards into oxic conditions where they are rapidly oxidized by oxygen to form Fe(III)(hydr)oxide particles. When these settling particles reach reducing conditions they are transformed via microbial dissimilatory Fe reduction releasing high concentrations of soluble Fe(II)_{aq} (Davison, 1993; Emmenegger et al., 1998).

Lake Nyos was chosen as an ideal natural laboratory to study the isotopic fractionation of Fe due to its stable stratification, the well constrained mixing, the geochemical input restricted to volcanic sources, and the continuous supply of Fe rich water ejected from the bottom of the lake to the surface. This study took place as part of a broader aim of monitoring Lake Nyos and examining the functioning of the degassing system. We document the gradients of dissolved Fe(II) and the Fe isotopic variations in Lake Nyos. A one-dimensional reaction-transport model is applied to identify the governing processes and the physical and geochemical parameters responsible for the strong isotopic shifts of dissolved Fe(II) in this lake.

2. Materials and methods

2.1. Field sampling and analysis

Water from various depths was collected with a Niskin bottle with a balloon attached to the open upper valve to avoid contamination from higher water layers due to the vigorous outgassing of CO₂ during retrieval. Two sediment samples from 21 and 210 m water depth were collected with a grab sampler. For a good representation of the volcanic rock underlying Lake Nyos, six samples of the Oku Volcanic field from the vicinity of Oku with Fe concentrations of 9.2 ± 0.9 wt.% were chosen (Lee, 1994). Vertical profiles of conductivity, temperature, depth, pH, and O₂ were recorded with a CTD Sea-Bird SBE-25 probe (Sea-Bird Electronics, Washington, USA). Oxygen concentrations were also determined with the Winkler method. For elemental analysis, filtered (0.45 μm cellulose acetate membrane filters, Whatman) samples were acidified with 0.4% (v/v) HNO₃ (suprapure). Iron concentrations were determined with the ferrozine photometric method (Stookey, 1970), Ca by inductively coupled plasma optical emission spectroscopy (ICP-OES; Spectro Ciros, Spectro Analytical Instruments, Germany), and Na concentrations were determined on non-acidified water samples by ion chromatography (Metrohm, IC 861). For the analysis of Fe isotopes, filtered samples were acidified with 0.4% (v/v) HCl (suprapure) and further treated as described below. A homogenized aliquot of 100 mg

solid sample (i.e., volcanic rocks and dry sediments) was totally digested in a microwave oven (lavisETHOS, MLS, Germany) in a mixture of concentrated HNO₃–HF–HCl. The digested sample was further treated like the water samples (i.e., evaporation, oxidation and purification).

2.2. Sample preparation for isotope analysis

Water samples and solid digestions containing at least 70 μg Fe were evaporated using pre-cleaned (concentrated HNO₃) PFA Teflon beakers. Due to high matrix to Fe ratios, water samples with Fe concentrations greater than 1 mg L⁻¹ could be processed for Fe isotopic analysis. The evaporated sample was oxidized with 30% H₂O₂ (HNO₃) in order to convert Fe(II) to Fe(III) and decompose the organic material. Iron was quantitatively purified on an anionic exchange resin (Bio-Rad AG1 X4, 200–400 mesh, HCl form). The matrix was eluted with 6 M HCl and Fe(III) was subsequently collected in 0.05 M HCl. Finally, the sample was dried and redissolved in 0.05 M HCl to 8 ppm for isotopic measurements. A more detailed description of water and sediment processing is given in Teutsch et al. (2005).

2.3. Iron isotope analysis

Iron isotope compositions were measured by multiple collector inductively coupled plasma mass spectrometer (MC-ICPMS; Nu-Plasma, Nu Instruments, UK) using the sample-standard bracketing approach with the international Fe isotopic reference material IRMM-014. The isotopic ratios ⁵⁷Fe/⁵⁴Fe and ⁵⁶Fe/⁵⁴Fe are expressed in the conventional delta notation in per mil (‰) units:

$$\delta^{57}\text{Fe} = \left(\frac{{}^{57}\text{Fe} / {}^{54}\text{Fe}_{\text{SAMPLE}}}{{}^{57}\text{Fe} / {}^{54}\text{Fe}_{\text{IRMM-014}}} - 1 \right) \times 10^3 \quad (1)$$

$$\delta^{56}\text{Fe} = \left(\frac{{}^{56}\text{Fe} / {}^{54}\text{Fe}_{\text{SAMPLE}}}{{}^{56}\text{Fe} / {}^{54}\text{Fe}_{\text{IRMM-014}}} - 1 \right) \times 10^3. \quad (2)$$

Here, the subscript SAMPLE denotes the ratio of the measured sample and IRMM-014 refers to the average of the standard ratios placed before and after the sample in the analytical sequence. To minimize the argide interferences (ArN, ArO, and ArOH) on the Fe masses (54, 56, and 57, respectively) a microconcentric desolvating nebulizer (MCN 6000, CETAC, US) with no nitrogen flux was used and sample and standard Fe concentrations were matched. The magnitudes of the ⁴⁰Ar¹⁶O⁺ and ⁴⁰Ar¹⁴N⁺ beams were determined at the beginning of the analytical session, and typically account to ~0.03% (mass 56) and ~0.1% (mass 54) of the sample and standard intensities. All masses were collected in Faraday cups equipped with 10¹¹ Ω resistors except for the 56 beam which was collected in a Faraday cup (H5) fitted with a 10⁹ Ω resistor. All ⁵⁷Fe/⁵⁴Fe and ⁵⁶Fe/⁵⁴Fe ratios plot on the theoretical mass fractionation line. However, the choice of resistors affected the precision of the ⁵⁶Fe/⁵⁴Fe measurement. Due to the smaller analytical errors of our ⁵⁷Fe/⁵⁴Fe ratios, all Fe isotopic compositions will be reported and discussed as δ⁵⁷Fe. The contribution of the minor ⁵⁴Cr isotope on mass 54 was monitored using mass 52 or 53, which was found to be negligible after chemical purification. All analyses were carried out only after carefully checking an internal laboratory standard of hematite or Fe-salt. At least one of these standards was also monitored throughout every analysis session. Details on our internal hematite standard are given elsewhere (Teutsch et al., 2005). The Fe-salt reproducibility (5 months covering 6 individual sets of analyses) was δ⁵⁷Fe = −1.05 ± 0.12‰ and δ⁵⁶Fe = −0.71 ± 0.18‰ (2SD, n = 98). The Fe-salt standard was measured with a Micromass Isoprobe MC-ICPMS at the Laboratory for Isotope Geology in the Swedish Museum of Natural History and the results are in excellent agreement with our measurements: δ⁵⁷Fe = −1.07 ± 0.15‰ and δ⁵⁶Fe = −0.73 ± 0.10‰ (n = 89, 2SD; Fehr et al., 2008). In addition to the tests conducted for groundwater (Teutsch et al., 2005) for evaluating

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