



Constraining the role of iron in environmental nitrogen transformations: Dual stable isotope systematics of abiotic NO_2^- reduction by Fe(II) and its production of N_2O

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Abstract

Despite mounting evidence for biogeochemical interactions between iron and nitrogen, our understanding of their environmental importance remains limited. Here we present an investigation of abiotic nitrite (NO_2^-) reduction by Fe(II) or ‘chemo denitrification’, and its relevance to the production of nitrous oxide (N_2O), specifically focusing on dual (N and O) isotope systematics under a variety of environmental conditions. We observe a range of kinetic isotope effects that are regulated by reaction rates, with faster rates at higher pH (~8), higher concentrations of Fe(II) and in the presence of mineral surfaces. A clear non-linear relationship between rate constant and kinetic isotope effects of NO_2^- reduction was evident (with larger isotope effects at slower rates) and is interpreted as reflecting the dynamics of Fe(II)–N reaction intermediates. N and O isotopic composition of product N_2O also suggests a complex network of parallel and/or competing pathways. Our findings suggest that NO_2^- reduction by Fe(II) may represent an important abiotic source of environmental N_2O , especially in iron-rich environments experiencing dynamic redox variations. This study provides a multi-compound, multi-isotope framework for evaluating the environmental occurrence of abiotic NO_2^- reduction and N_2O formation, helping future studies constrain the relative roles of abiotic and biological N_2O production pathways.

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1. INTRODUCTION

Evidence is mounting for the environmental importance of interactions between iron (Fe) and nitrogen (N) in biogeochemistry. For example, the reduction of Fe(III) coupled to the oxidation of ammonium (‘feammox’) has been recently demonstrated in soils (Shrestha et al., 2009; Yang et al., 2012; Li et al., 2015), while the reduction of nitrate or nitrite coupled to the oxidation of Fe(II) – or chemodenitrification – has been demonstrated across studies of both soils and bacterial cultures and/or enrichments

(Straub et al., 1996; Weber et al., 2006; Klueglein and Kappler, 2012; Picardal, 2012b; Kopf et al., 2013; Melton et al., 2014). Despite the potential importance of these processes in the fate of nitrogen, our understanding of their significance remains limited. In particular, a number of these reactions may be catalyzed both chemically and biologically and the resulting nitrogenous products vary widely, including ammonium (NH_4^+), nitric oxide (NO), nitrous oxide (N_2O) and dinitrogen (N_2). The relative contribution of these reaction pathways, therefore, has wide implications for ecosystem function (e.g., N retention/loss) and production of potent greenhouse gases. Furthermore, distinguishing between biologically and chemically catalyzed pathways has important implications for geobiology, including an improved understanding of the evolution of

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iron and nitrogen based metabolic systems and a mechanistic understanding of biologically mediated transformations of nitrogen, iron and carbon across a host of modern and historical environments (Falkowski et al., 2001).

Natural abundance isotopes of nitrogen and oxygen have proven useful as tools for disentangling complex networks of environmental nitrogen transformations (Sigman et al., 2005; Casciotti and McIlvin, 2007; Kendall et al., 2007; Wankel et al., 2009; Rafter and Sigman, 2016). In large part, these efforts rely on information gained from environmental samples and/or from experimental cultures grown under environmentally relevant conditions aimed at carefully constraining kinetic isotope effects ($^{15}\epsilon$ and $^{18}\epsilon$ for N and O, respectively), as well as establishing the nature of coupling between isotope effects ($^{18}\epsilon:^{15}\epsilon$). Nevertheless, there remain important gaps in our understanding, in particular with respect to important isotope effects involving key nitrogen intermediates including nitrite (NO_2^-), nitric oxide (NO), nitrous oxide (N_2O), and hydroxylamine (NH_2OH). For example, although the dual isotope systematics for biologically mediated oxidative processes involving NO_2^- have been characterized (e.g., NO_2^- formation by NH_4^+ oxidation (Casciotti et al., 2010) and NO_2^- oxidation to NO_3^- (Buchwald and Casciotti, 2010)), information on the dual isotope systematics of reductive processes involving NO_2^- , whether biological or abiotic, is more limited (Bryan et al., 1983; Casciotti et al., 2002; Brunner et al., 2013; Jones et al., 2015; Martin and Casciotti, 2016).

Specifically, there has been little investigation into the kinetic isotope effects of N and O catalyzed by abiotic chemical reduction of NO_2^- by Fe(II) – or ‘chemodenitrification’ (Samarkin et al., 2010; Jones et al., 2015). These types of reactions may represent an important control on the dual NO_3^- and NO_2^- isotopic composition in reducing environments high in iron but low in organic carbon (e.g., aquifers) as well as in environments experiencing dynamic redox fluctuations (coastal sediments, estuaries, rivers). Moreover, although abiotic reactions are thought to contribute significantly to the production of the potent greenhouse gas N_2O , little is known about the controls on the N and O isotope composition of its production by these pathways, hindering their use in constraining global sources of N_2O . Thus, there is a need for a systematic investigation of N and O isotope effects catalyzed by chemical reactions with Fe before they can be used to constrain biological/abiotic interactions between N and Fe in the environment.

To this end, we investigated the stable N and O isotope dynamics of the abiotic reduction of NO_2^- by Fe(II), including characterization of the yield and isotopic composition of the product N_2O . As more studies suggest a potential for anaerobic (a)biotic nitrogen transformations coupled with iron cycling, the N and O isotope effects determined here will aid in the application of dual isotopes of nitrite and N_2O for deciphering the underlying biogeochemical mechanisms controlling the fate of N across a host of environments including aquatic systems, aquifers, soils, sediments and wastewater treatment plants.

2. MATERIALS AND METHODS

2.1. Nitrite reduction experiments

Batch experiments were conducted anaerobically under reaction conditions outlined in Fig. 1 and Table 1 with 200 μM nitrite and aqueous Fe(II) ranging from 0.5 to 8.1 mM in the presence and absence of goethite at room temperature. Experiments varied three primary parameters: Fe(II) concentration, solution pH, and the presence/absence of the iron-oxide goethite. All experiments were initiated in sterilized anoxic HEPES buffer (30 mM) adjusted to the desired pH using NaOH. 140 mL of buffer was added to 160 mL serum bottles and purged with N_2 gas for 30 min to remove any trace oxygen. Bottles were then transferred into an anaerobic glove box (5% $\text{H}_2/95\%$ N_2), where Fe(II) was added from a concentrated anoxic FeCl_2 stock solution (~ 1 M). Bottles were then pre-incubated by shaking for 3 days and any Fe precipitates were removed by filtration. In a subset of bottles, the Fe(III) oxyhydroxide goethite (FeOOH) (as synthesized and fully characterized previously – see (Ekstrom et al., 2010)) was added to a final

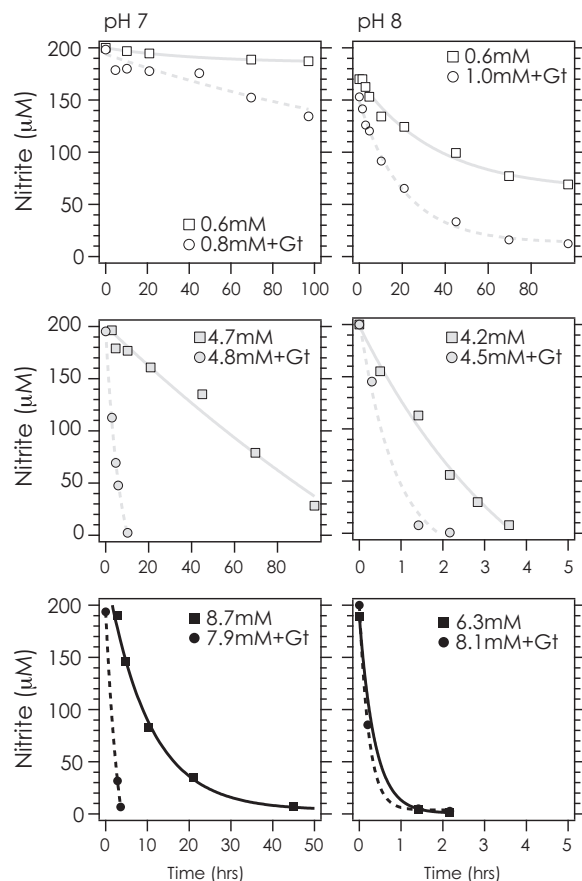


Fig. 1. Reaction of nitrite with aqueous Fe(II) as a function of time. Rates of nitrite reduction were faster at higher Fe(II) concentrations, higher pH and in the presence of exogenous goethite. Note the time scale change at higher iron and high pH.

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