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Nitrite reduction by Fe(II) associated with kaolinite

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Abstract Interactions of iron (Fe) with the nitrogen (N) cycle have emerged and contain elements of abiotic and biological reactions. One such abiotic reaction which has received little study is the reactivity of NO₂⁻ and Fe(II) associated with a major clay mineral, kaolinite. The main objective of this study was to evaluate the reactivity of NO₂⁻ with Fe(II) added to kaolinite under anoxic conditions. Stirred batch reactivity experiments were carried out with 10 g L⁻¹ kaolinite spiked with 25 and 100 μ M Fe(II) at pH 6.45 in an anaerobic chamber. Approximately 500 μ M NO₂⁻ was added to initiate the reaction with Fe(II)-loaded kaolinite. The rate of nitrite removal from solution was 2.4-fold slower in the high Fe(II) treatment when compared with the low Fe(II) treatment. A large portion of the NO₂⁻ removed from solution was confirmed to be reduced to $N_2O_{(g)}$ in the Fe(II)-kaolinite slurries. However, NO₂⁻ reduction was also noticed in the presence of kaolinite-alone and to somewhat lesser extent in the presence of dithionite-citrate-bicarbonate (DCB)-treated kaolinite. Chemical extractions coupled with infrared spectroscopy suggest that Fe(III) oxide mineral impurities and structural Fe(III) in kaolinite may participate in NO₂⁻ removal from solution. Furthermore, a magnetite mineral was identified based on X-ray diffraction analysis of

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untreated kaolinite and DCB-treated kaolinite. Our findings reveal a novel pathway of NO_2^- transformation in the environment in the presence of Fe(II) associated (sorbed and impurity) with kaolinite.

Keywords Nitrite reduction · Anaerobic · Abiotic XRD · SEM

Introduction

Nitrite (NO₂⁻) is a soil anion that occurs as an intermediate in biological denitrification and nitrification. Incomplete NO₃⁻ reduction can cause NO₂⁻ accumulation in soils, sediments, and groundwater (Vaclavkova et al. 2015; Matocha et al. 2012). The presence of NO_2^- can impact dissolved organic nitrogen production, uranium bioremediation, pyrite oxidation, and Fe(III) reduction (Obuekwe et al. 1981; Senko et al. 2002; Davidson et al. 2003; Picardal 2012, Yan et al. 2015). Regarding the latter process, several Fe(III)reducing bacteria can simultaneously reduce NO₃⁻ and Fe(III) (DiChristina 1992; Krause and Nealson 1997). The biologically produced Fe(II) and NO₂⁻ can react chemically, producing Fe(III) and N₂O (Moraghan and Buresh 1977). This chemical process has been invoked to explain the apparent inhibition of Fe(III) reduction in the presence of NO_3^- in pure cultures (Obuekwe et al. 1981) and anoxic soil slurries (Komatsu et al. 1978; Matocha and Coyne 2007). Cleemput and Baert (1983) showed that this reaction was more rapid as pH decreased. This may be attributed to the greater proportion of protonated nitrite species (HNO_2) . Protonation promotes N–O bond breaking; thus, HNO₂ is a stronger oxidant than NO_2^- (Shriver et al. 1994).

The production of nitrous oxide (N_2O) in the Don Juan Pond in Antarctica was attributed to abiotic processes



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involving oxidation of mineral-derived Fe(II) coupled to NO_2^- reduction (Samarkin et al. 2010). In fact, many researchers previously studied and reported abiotic reduction of NO_2^- by Fe(II) species such as Fe(II) minerals and sorbed Fe(II) on the mineral surfaces in laboratory studies (Sorensen and Thorling 1991; Hansen et al. 1994; Rakshit et al. 2008; Tai and Dempsey 2009; Dhakal et al. 2013). Solid Fe(II) minerals and sorbed Fe(II) species are more effective reductants than dissolved, hexaquo-Fe(II) (Fe(H₂O)₆²⁺) species (Wehrli 1990; Stumm and Sulzberger 1992; Luther et al. 1992; Neumann et al. 2009; Klueglein et al. 2015).

Reductive dissolution of Fe(III) (hydr)oxides by dissimilatory iron-reducing bacteria is an important process in biogeochemical iron cycling (Liu et al. 2001). Most of the Fe(II) produced during microbial Fe(III) reduction exists in precipitated or sorbed forms (Frederickson et al. 1998; Zachara et al. 2002). Regarding the latter, surface oxo- and hydroxo- ligands bonded to Fe(II) increase, the electron density at the Fe(II) center (Millero 1985; Stumm and Morgan 1996) thereby enhancing the potential of Fe(II) as a reductant of NO₂⁻. Sorensen and Thorling (1991) found that Fe(II) adsorbed to lepidocrocite (γ -FeOOH) reduced NO_2^- at a faster rate than dissolved Fe(II). However, there is very little information available about the reactivity of NO₂⁻ with Fe(II) sorbed to soil clay minerals such as kaolinite. Kaolinite has edge sites containing >Al-OH (aluminol) and >Si-OH (silanol) groups that can demonstrate pH-dependent surface charge and can adsorb metal cations such as Fe(II). In fact, Kukkadapu et al. (2001) reported that in Fe(III) oxide-rich subsoils with mixed mineralogy, dissolved biogenic Fe(II) adsorbed strongly to kaolinite. Other researchers also found there is close association between kaolinite and Fe(III) minerals in certain soil types (Jefferson et al. 1975; Golden and Dixon 1985).

Most studies evaluating the reactivity of adsorbed Fe(II)-kaolinite complexes use reference kaolinite minerals to mimic soil kaolinite. Georgia kaolinite (KGa-1b) is one of the most common reference kaolinite minerals used in research studies (Zachara et al. 1998; Foster et al. 1998). Accordingly, the objective of this study was to evaluate the reactivity of Fe(II) associated with kaolinite with NO_2^{-} .

Materials and methods

Materials

Georgia kaolinite (KGa-1b, Clay Minerals Repository, University of Missouri) was purchased and used in this study. The kaolinite was sieved to less than 45 μ m fraction size. Freshly prepared, acidified 0.1 M FeCl₂, 4H₂O stock solutions were used for preparing sorbed Fe(II)-kaolinite



complexes. The source of NO₂⁻ was derived from NaNO₂ salt, and NO₂⁻ reactivity studies were performed in an Ar/ H₂ purged anaerobic chamber (Coy Laboratory Products, Grass Lake, Michigan) (Klausen et al. 1995). The organic buffer MES [2-(N-morpholino) ethane sulfonic acid] with concentration of 0.3 M was added to control the pH (Alowitz and Scherer 2002). The MES buffer was titrated either with 1 M NaOH or with 1 M HCl to attain desired initial pH values for the NO₂⁻ reactivity studies (pH 6.45 MES). The ferrozine [3-(2-pyridyl)-5, 6 bis(4-phenylsulfonic acid)-1, 2, 4-triazine, monosodium salt] reagent was used to complex the dissolved Fe(II) present in the aliquots (Stookey 1970). All the solutions were made anoxic by purging with Ar for 2.5 h and stored in an anaerobic glove box.

Preparation of mineral suspensions

All the studies, until otherwise specified, were conducted in an anaerobic glove box (Coy Laboratory Products, Grass Lake, MI). For each experiment, 10 g L^{-1} KGa-1b was preequilibrated for 24 h with MES buffer at the desired pH. Mineral suspensions were made by adding calculated amounts of 0.1 M FeCl₂ stock into 10 g L⁻¹ KGa-1b, and the suspension was mixed with a rotator stirrer for 72 h. Suspensions were removed and filtered with 0.2-µm membrane filter paper (Fisher Scientific, Hampton, NH), and the aliquots were complexed with ferrozine reagent to measure the Fe(II) concentrations colorimetrically with a UV-VIS-NIR scanning spectrophotometer (Shimadzu, UV-3101 PC, Columbia, MD) at 562 nm wavelength. The initial added Fe(II) concentrations were 25 and 100 µM. These concentrations were chosen to mimic real environmental conditions. These Fe(II) levels were referred to as high Fe and low Fe, respectively. Kinetic experiments showed that almost all of added Fe(II) (approximately >98 %) was removed from solution by kaolinite within 72 h of reaction time (Fig. 1).

A portion of KGa-1b was chemically treated to remove well and poorly crystalline Fe(III) (hydr)oxides using the DCB (dithionite-citrate-bicarbonate) extraction method (Mehra and Jackson 1960). Untreated and DCB-treated kaolinite samples were characterized by X-ray diffraction. Additional extractions were conducted using 0.5 and 6 M HCl to determine Fe(II) and Fe(III). Approximately 30 mg of untreated kaolinite was homogenized with 300 mg of spectroscopic grade KBr and analyzed using a Nicolet 6700 Fourier Transform Infrared (FTIR) spectrometer equipped with a Thermo Fisher Smart Collector Diffuse Reflectance accessory. The FTIR spectra were collected over a range of 4000-600 cm⁻¹ with continuous nitrogen purge. Two hundred scans were co-added together at a spectral resolution of 4 cm^{-1} . Baseline corrections and further spectra processing were performed using GRAMS/32.



Fig. 1 Fe(II) sorption kinetics on 10 g L^{-1} KGa-1b. High Fe and low Fe represent 100 and 25 μ M initial spiked Fe(II). Fe(II) Ads in Y-axis is indicating the amount of sorbed Fe(II) on KGa-1b surface

Nitrite reactivity experiments

Nitrite reactivity experiments were carried out using both untreated and DCB-treated kaolinite at a suspension density of 10 g L^{-1} . Stirred batch reactivity experiments were conducted with duplicate 30-mL glass vials at a pH value of 6.45 in the high-Fe and low-Fe treatments by addition of 500 μ M NO₂⁻. To identify the effect of Fe impurities in KGa-1b, experiments were included where Fe(II) was not added (control) and where NO2⁻ was added to KGa-1b and reacted outside the glove box (labeled oxic). DCB-treated kaolinite was reacted with NO2⁻ under anaerobic conditions without added Fe(II) (labeled DCB) to identify the effect of Fe impurities on NO₂⁻ reduction. A blank experiment with no kaolinite (labeled blank) was included. The suspensions were filtered at predetermined time intervals using 0.2-µm filter paper and the filtrate was measured for NO₂⁻ concentration with a Metrohm 792 Basic ion chromatograph (Herisau, Switzerland). In separate experiments, N₂O_(g) was measured in the head space of capped 30-mL glass vials using a Varian 3700 gas chromatograph with 2 M packed column, porapak Q, with TCD detector and 20 mL min⁻¹ He carrier gas. The portion of N₂O (g) dissolved in solution was accounted for using Henry's Law constant.

Results and discussion

NO₂⁻ reduction by Fe(II) associated with kaolinite

The rates of nitrite removal from solution in the various treatments are shown in Fig. 2. Negligible removal of nitrite occurred in blank experiments in which no kaolinite was added (nitrite-alone). The rate of nitrite removal, based on the initial linear fit of concentration versus time curves, was ~ 2.4 times slower for the high Fe(II) treatment when compared with the low Fe(II) treatment (Fig. 2). These results differed from the findings of other researchers who studied reactivity of sorbed Fe(II) with contaminants, where



Fig. 2 Nitrite reduction with Fe(II) associated with Georgia kaolinite. Kaolinite-alone and oxic represent reaction of NO₂⁻ with KGa-1b under anoxic and oxic conditions, respectively, without any sorbed Fe on KGa-1b. DCB indicates reaction of NO₂⁻ with DCB-treated KGa-1b. Low Fe and high Fe represent reaction of 25 and 100 μ M sorbed Fe(II) on KGa-1b with NO₂⁻. Nitrite-alone indicates change of NO₂⁻ in solution in absence of any solid phase. All the conditions are buffered by MES at pH = 6.45, and at a KGa-1b concentration of 10 g L⁻¹

increased Fe(II) loading resulted in greater contaminant reduction rates (Klausen et al. 1995; Amonette et al. 2000). One possible reason for this phenomena could be surface oxidation of sorbed Fe(II) at the high Fe(II) treatment when preparing mineral suspensions. Recent studies by Soltermann et al. (2014) indicate that sorbed Fe(II) on edge sites of montmorillonite can be readily oxidized to secondary Fe(III) oxide minerals. Our kaolinite slurries would supply ample edge sites which might sorb and subsequently oxidize added Fe(II). If oxidized Fe(III) precipitates are forming on kaolinite, they might serve to passivate the surface, decreasing the rate of nitrite removal in the high Fe(II) treatment when compared with the low Fe(II) counterpart.

Nitrite removal from solution by kaolinite and Fe(II)treated kaolinite slurries can involve both sorption and electron transfer processes. Nitrous oxide $(N_2O_{(g)})$ was identified as a two-electron reduction product and accounted for approximately 20–80 % of the NO₂⁻ removed from solution in the Fe(II)-reacted kaolinite treatments (Fig. 3). Ammonium (NH₄⁺) was below detection limits. Thus, the production of NO_(g), N_{2(g)}, and/or sorbed nitrite might account for unrecovered N.

The addition of Fe(II) was not necessary for nitrite removal to occur based on disappearance of nitrite in control slurries (kaolinite-alone) (Fig. 2). The pattern of nitrite disappearance in the control was complex; nitrite levels resembled high Fe(II) treatments at early time points and low Fe(II) treatments at longer times (>24 h). It is possible that Fe impurities in kaolinite were responsible for NO_2^- removal from solution.





Fig. 3 Amount of N_2O (g) production in the reaction of NO_2^- with sorbed Fe(II) on KGa-1b at pH 6.45 in MES. Low Fe and high Fe represent 25 and 100 µM sorbed Fe(II) on KGa-1b

Role of impurities in kaolinite

Chemical extractions were performed on kaolinite anoxic slurries in order to identify the nature of potential impurities which might be removing nitrite from solution without added Fe(II). The 0.5 and 6 M HCl extractions conducted under anoxic conditions indicated that Fe(II) and Fe(III) were present in kaolinite (Table 1). There was a notable decrease in 6 M HCl-extractable Fe(III) after DCB extraction. Furthermore, both mineral acid extractions showed that Fe(II) was present in greater amounts than Fe(III). It is possible that discrete Fe(III) (hydr)oxide mineral impurities are present in close association with kaolinite.

Some of the Fe(III) associated with kaolinite might also exist as structural Fe(III) which has substituted for Al^{3+} . An infrared spectrum in the OH-stretching region of untreated kaolinite show the OH-stretching bands at 3695, 3667, 3651, and 3618 cm⁻¹, diagnostic of well-crystalline kaolinite (Fig. 4). In addition, there is a weak shoulder near 3590 cm⁻¹ which has been assigned by Beauvais and Bertaux (2002) as Fe^{3+} substituted for Al^{3+} in KGa-1b. Past studies have shown that trace impurities in this particular reference kaolinite (KGa-1b) can alter electron transfer and sorption behavior of inorganic contaminants. For example, it was shown that TiO₂(s) impurities in reference kaolinite participated in As(III) oxidation to As(V) (Foster et al. 1998). In addition, Zachara et al. (1998) found that a DCB extraction affected the ability of this reference kaolinite to sorb chromate (CrO_4^{2-}) .

To verify that Fe(II) associated with kaolinite was responsible for NO₂⁻ removal from solution, additional

experiments were performed by adding 500 μ M NO₂⁻ to KGa-1b under oxic conditions and after treatment with DCB under anoxic conditions at pH 6.45. It was found that DCB-treated KGa-1b reduced NO₂⁻ at a slower rate and lower amount than that of the control (kaolinite-alone) (Fig. 2). Moreover, untreated KGa-1b did not react with NO₂⁻ under oxic conditions, outside the glove box (Fig. 2). These data provide further support that Fe(II) impurities in kaolinite were responsible for NO₂⁻ removal from solution. Further experiments characterizing nitrous oxide in control slurries would be useful to evaluate whether the nitrite removed from solution is sorbing or undergoing electron transfer to form products.

The stoichiometric equivalence of Fe(II) available to NO₂⁻ reduced could not be obtained even after these experiments. The Fe(II) values in kaolinite, as determined from 0.5 to 6 M HCl extractions, were not high enough to explain the amount of NO₂⁻ reduced. From Table 1, one can find that 6 M HCl extraction of KGa-1b resulted in about 2 µmol of Fe(II) per g of KGa-1b. Converting that amount to a value relevant to the experimental conditions used here yields 20 µM Fe(II). The added 25 µM Fe(II) can add to this value to make it 45 µM Fe(II). It is evident that, if a 2:1 molar ratio of Fe(II) to NO_2^- is considered, this amount along with the added amount cannot explain the amount of NO2⁻ lost in the case of low Fe treatment (368 μ M NO₂⁻ lost). For DCB extracted and KGa-1banoxic treatments, the amounts of NO₂⁻ lost were 137 and 276 μ M, respectively, and the amount of extractable total Fe available to react were ~ 32 and 20 μ M, respectively.

One reason for the unaccounted molar equivalence of NO_2^- to Fe(II) may be that unextractable Fe (by 0.5 and 6 M HCl acid extractions) is present in KGa-1b. Researchers found that only 1-2.5 % of the Fe present in haematite (Fe₂O₃) and magnetite (Fe₃O₄) can be recovered by 0.5 M HCl extraction (Kennedy et al. 1998). They indicated one needs to use hot 12 M HCl extraction to account for the Fe-fraction containing Fe_3O_4 . It is possible that even the 6 M HCl extraction could not recover all Fe from KGa-1b. In fact, the X-ray diffraction data showed weak peaks that correspond to magnetite, a mixed Fe(II)/ Fe(III) mineral with a chemical formula of Fe_3O_4 (Fig. 5a, b). Hence, the unextractable Fe fraction coming from Fe₃O₄ may participate in NO₂⁻ reduction, particularly if surface Fe(II) is associated with magnetite (Dhakal et al. 2013). In

Table 1 Chemical extractions (0.5 and 6 M HCl) of untreated and DCB-treated KGa-1b	Untreated KGa-1b				DCB-treated KGa-1b		
	Fe-extraction	Total Fe	Fe(II)	Fe(III)	Total Fe	Fe(II)	Fe(III)
	$\mu mol \ g^{-1}$						
	0.5 M	0.76 ± 0.14	0.67 ± 0.08	0.09 ± 0.007	0.57 ± 0.03	0.47 ± 0.01	0.11 ± 0.04
	6 M	3.21 ± 0.2	2 ± 0.09	1.2 ± 0.3	1.99 ± 0.4	1.78 ± 0.6	0.21 ± 0.08





Fig. 4 Fourier transform infrared spectrum of untreated kaolinite in the OH-stretching region



Fig. 5 X-ray diffraction patterns of **a** untreated KGa-1b and **b** DCB-treated KGa-1b. K represents kaolinite, M represents magnetite, and S represents sodium chloride

addition, the finding that DCB-treated KGa-1b actually reacted with NO_2^- , although at a slower rate (Fig. 2), suggests an unextractable Fe fraction may be present and participate in NO_2^- reduction.

Environmental implications

Although the reactivity study of sorbed Fe(II) on KGa-1b with NO_2^- was confounded by the presence of Fe

impurities in KGa-1b, this phenomenon can mimic the real environmental scenarios where complex mineral assemblages are present. This kind of environmental conditions is speculated by many researchers in the light of contaminant sorption processes (Bertsch and Seaman 1999). These authors identified the need of considering surface modifications of soil clay minerals by Fe- and Al- oxides. It has been well demonstrated that contaminant sorption process was largely changed by these surface modifiers (Bertsch and Seaman 1999). Our work demonstrates that the redox behavior of soil clay mineral can largely be affected by surface modifications as well. Therefore, our work can be very relevant to the environments where kaolinite and Fe associations may occur. In fact, there are numerous reports of Fe(II) and Fe(III) association with kaolinite (Kukkadapu et al. 2001; Jefferson et al. 1975; Golden and Dixon 1985). This process may be limited to subsurface environments where Fe(III)-reducing conditions prevail and oxygen is absent. In addition to the real environmental applications, our work is important because KGa-1b is one of the most common reference kaolinite minerals used by researchers.

Conclusion

Our laboratory experiments indicate for the first time that kaolinite supplemented with Fe(II) can remove nitrite from solution. In the Fe(II)-kaolinite experiments, about 80 % of the NO_2^- was reduced to N_2O as a product. Production of N_2 (g), NO (g), or sorbed NO₂⁻ may account for unrecovered N. Our findings are confounded by the fact that impurities, especially Fe(II) associated with KGa-1b, participated in NO_2^- reduction as well without added Fe(II). Chemical extractions reveal the presence of Fe(II) and Fe(III) in association with kaolinite which might occur as free Fe(III) oxide minerals and/or structural Fe(III) substituted in kaolinite. Evidence for the latter is supported by infrared spectra which show an absorption band near 3590 cm^{-1} . X-ray diffraction results from pristine and DCB-treated KGa-1b revealed the presence of mineral phases such as magnetite, which in turn could account for greater amount of NO₂⁻ reduced than can be expected from theoretical stoichiometric equivalence of Fe(II) added plus extracted. Our findings not only mimic scenarios where Fe(II) kaolinite association could occur, but also provide insights into research findings that use KGa-1b as a reference kaolinite mineral.

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