The role of siderite on abiotic nitrite reduction by dissolved Fe(II)

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INTRODUCTION

Iron redox reactions affect the fate and transformation of groundwater NO_3^-. Fe(II) present in groundwater as dissolved Fe(II) or Fe(II) sorbed onto mineral surfaces is oxidised into Fe(III) (oxyhydr)oxides using NO_3^- as an electron acceptor in anoxic conditions by biotic or abiotic means (Bryce et al., 2018). N_2O is produced as an end product during abiotic nitrate-reducing Fe(II) oxidation (NRFO) (Wang et al., 2019). NO_2^-, an intermediate product during NO_3^- reduction by biotic or abiotic means, is chemically very reactive and readily reduced to N_2O by abiotic means (Wankel et al., 2017). Studies have shown that Fe(II) minerals such as iron-rich smectites, green rust and siderite are reactive and can enhance abiotic NO_2^- reduction (Grabb et al., 2017). The occurrence of abiotic NO_2^- reduction leads to the relative segregation of the lighter and heavy isotopes of N and O (kinetic isotope fractionation, ε) (Chen & MacQuarrie, 2005) providing an effective tool to quantify abiotic NO_2^- reduction processes. In the light of this, batch experiments were performed to assess the potential of micro-sized siderite to enhance abiotic NO_2^- reduction in laboratory batch experiments.

METHODOLOGY

Three series of abiotic batch experiments were performed (Sd, Fe and FeSd): Sd containing only siderite, Fe containing only dissolved Fe(II), and FeSd containing dissolved Fe(II) and siderite (Fig. 1A). In all series, a 1.0 mM NO_2^- synthetic water solution was prepared in the laboratory. In Fe and FeSd experiment, Fe(II) was added to achieve a Fe(II)/NO_2^- a ratio of 5. A fixed mass of siderite (50 mg) was employed in Sd and FeSd experiments. For each experiment, samples, each contained in 20 mL headspace vials were crimped with butyl rubber stoppers under an Ar atmosphere. Bottles of each series were sacrificed at different times and the concentration of NO_2^- and N_2O was determined from the peak amplitudes obtained in an isotope ratio mass spectrometer (IRMS). The $\delta^{15}N$ from NO_2^- was analysed following the sodium azide reduction method, while $\delta^{15}N$-N_2O from the vials headspace was analyzed using a Pre-Con (Thermo Scientific) coupled to an IRMS (Finnigan MAT 253, Thermo Scientific). Commercial N_2O used as reference gas was calibrated using the international standard USGS-51.

RESULTS AND DISCUSSION

3 % NO_2^- was removed in Sd, 56 % in Fe and 83 % in FeSd experiments (Fig. 1B) while $\delta^{15}N$-NO_2^- increased from -26.8 to -26.0 ‰ in Sd, -26.4 to -18.0 ‰ in Fe and -26.3 to -15.2 ‰ in FeSd. Similar $\varepsilon^{15}N$-NO_2^- was observed in all sets of experiments, ε = -10.8 ‰ in FeSd, ε = -13.1 ‰ in Fe and ε = -17.3 ‰ in Sd (Fig. 1C). $\delta^{18}O$ of NO_2^- is not reported due to the equilibration of $\delta^{18}O$-NO_2^- with water. Site preference (SP) of +22.5±0.5 ‰ and +23.5±0.7 ‰

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were obtained in Fe and FeSd respectively. In Sd N_2O was rarely accumulated in the headspace of the vials. Previous studies have also reported a lack of reactivity of only siderite with NO_2^- in abiotic experiments (Margalef-Martí et al., 2020). 23 % and 19 % of NO_2^- removed in Fe and FeSd was accumulated as N_2O in the headspace at the end of the experiment. $\delta^{15}N$ of the generated N_2O increased from -57.1 to -38.6 ‰ in Fe and from -52.6 to -36.6 ‰ in FeSd. The sum of the residual NO_2^- in solution and the N_2O produced in the headspace of each vial (N_t) was not always equal to the initial NO_2^- in Fe and FeSd. N_t decreased with reaction time, decreasing from 93 % at the beginning of the Fe to 57 % at the end of Fe and 95 % to 57 % in FeSd. In Sd, Nt was almost equal to the initial NO_2^- in all vials. The difference between the initial NO_2^- and N_t could be attributed to the dissolution N_2O in the synthetic water or the production of NO in the process.

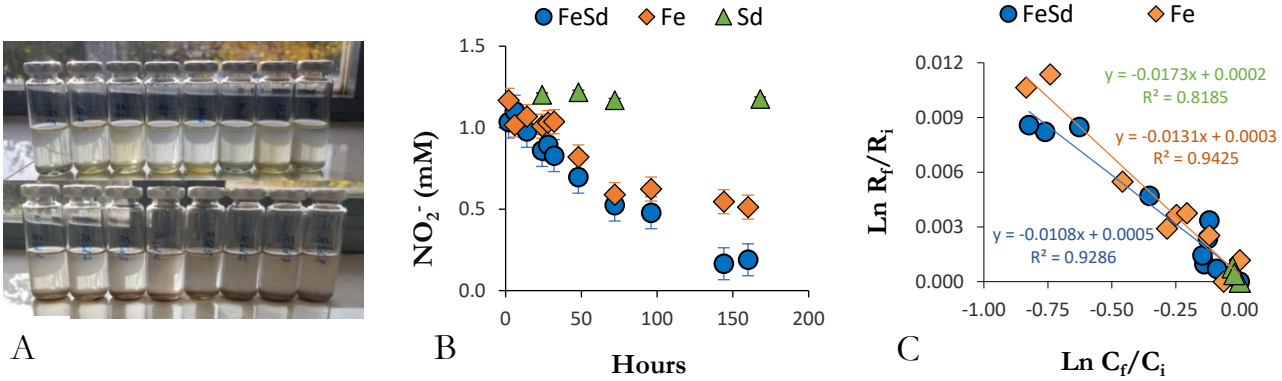

Fig 1. *(A) Scheme of the experimental setup. (B) Evolution of NO_2^- concentration in experiments containing dissolved Fe(II) and siderite (FeSd), only dissolved Fe(II) (Fe) and only siderite (Sd). (C) A plot of the natural logarithm of $\delta^{15}N$ fraction against substrate fraction in the residual NO_2^- pool depicting the isotopic fractionation observed in FeSd, Fe and Sd experiments.*

CONCLUSIONS

In laboratory batch experiments, dissolved Fe(II) at Fe(II)/NO_2^- ratio of 5 induced abiotic nitrite reduction. The Fe(II) in equilibrium with siderite in Sd experiments is too small that little or no reactivity is observed. In FeSd, Fe(II) is sorbed onto the mineral surface leaving Fe(II) in both aqueous and solid-bound forms enhancing abiotic nitrite reduction. N_2O produced in FeSd was mainly dissolved in the synthetic water.

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