

Interactive comment on “Impact of reactive surfaces on the abiotic reaction between nitrite and ferrous iron and associated nitrogen and oxygen isotope dynamics” by Anna-Neva Visser et al.

Anonymous Referee #1

Received and published: 12 June 2020

This study is based on laboratory experiments and aims to trace the NDFeO. The work is colossal with a large amount of data obtained. I regret that some of the data are not presented or discussed (see my comments). The paper is very well written but I am stuck on the fact that the decrease in nitrite concentrations is accompanied by (i) a depletion and then an enrichment of $\delta^{15}\text{N}$, (ii) that the $\delta^{18}\text{O}$ of the residual nitrite in the end varies very little. There is no mass balance, which makes it difficult to monitor the extent of the processes. If the nitrite is transformed into N_2O and this accumulates, it is very easy to calculate what its $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ should be compared with the measured

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values. My more detailed comments below :

L39-40: I'm surprised there are no older references to the role of iron. General experiment setup section : The conditions of the experiment are anoxia and the addition of iron and nitrogen in the form of nitrite. Under these conditions, in the environment, it is conceivable that dissimilative reduction of nitrite to ammonium may occur. Of course under perfect abiotic conditions DNRA should not occur. Did the authors measure ammonium concentrations throughout the experiment to ensure that no other processes than the one under study were taking place?

L120-121 : How long does it take from incubation to the measurement of concentrations and isotopes? Light is a factor that can generate abiotic reactions, which in turn can generate isotope fractionation. What about it?

L179-180 : Two nitrite isotope standards have been used. What are the values of these standards? Do these values include those of the samples measured in this study? What is the analytical precision of the method (preparation + intrinsic analysis) for the determination of the isotopic composition of nitrite (^{15}N and ^{18}O)?

L285-291 : Rayleigh conditions allow the isotope fractionation factor to be easily determined by looking at the slope of the line on a representation $\ln C/C_0$ as a function of $d^{15}\text{N}$, but not C (with C the concentration at time t and C_0 the initial concentration). This paragraph is not clear to me. Moreover, doesn't the fact that there is first a decrease of ^{15}N , i.e. an inverse isotopic fractionation, with a decrease of the amount of heavy isotope in the residual substrate, and then an enrichment, mean that several processes could take place and that process 1 takes place at the beginning of the experiment with a higher rate than the second process which either starts at the beginning of the experiment or when process 1 is completed? Very concretely, the trend line is calculated on the points starting from the lowest $d^{15}\text{N}$ values? I think it would be necessary to clarify this part.

L296-302: Is it not possible to envisage that the variations in ^{18}O are due solely to an

exchange between the oxygen of the nitrite and the oxygen of the water? By the way, what is the isotopic composition of water? Is it constant during the experiment?

L309-313: The authors have done a significant analytical work. Why not show the variations in N₂O concentration as a function of nitrite concentrations. Before any interpretation with isotopes or isotopologists, it seems to me useful and necessary to work on the concentrations and in particular to make mass balances.

L314-315: The authors do not discuss the very negative SP value, which is very distinct from the other points. Is this an analytical problem?

L326 : There is no figure S6. But mentioned in S5 section figure 3.

L484-486 : Large variations of $\delta^{15}\text{N}$ are not associated with variations of $\delta^{18}\text{O}$. While these are measurements made on the residual substrate. The drop in ^{18}O at the beginning of the experiment is more likely due to an isotopic exchange with the oxygen in the water than evidence of a process.

L531-538 : It might be interesting to look at $\delta^{18}\text{O}$ variations of N₂O during the experiment. And see if it correlates with that of nitrite. This would also be an opportunity to confirm or deny whether there is an isotope exchange between the oxygen in the nitrite and the oxygen in the water.

L551-552: if N₂O is considered to accumulate, it can be considered to be the accumulated product in the case of a Rayleigh distillation. In this case, and taking into account the isotope fractionation associated with nitrite reduction, it is easy to calculate what the expected ^{15}N and ^{18}O of the N₂O produced. It would then be interesting to compare the measured values with the expected values.

Interactive comment on Biogeosciences Discuss., <https://doi.org/10.5194/bg-2020-73>, 2020.

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