Supplement of Biogeosciences, 17, 4355–4374, 2020
https://doi.org/10.5194/bg-17-4355-2020-supplement

Supplement of

Impact of reactive surfaces on the abiotic reaction between nitrite and ferrous iron and associated nitrogen and oxygen isotope dynamics

Anna-Neva Visser et al.

Correspondence to: Anna-Neva Visser (a.visser@unibas.ch)

S.1. Nernst equation and values used for Pourbaix diagram calculation

Nernst equation: $Eh = Eh^{\circ} + \left(\frac{0.59V}{z_e} log \frac{a_{Ox}}{a_{Red}}\right)$ (2)

Reaction	Eh° [V]	Source
$O_2 + 4H^+ + 4\,e^- \rightarrow 2H_2O$	1.229	(Rumble et al., 2012)
$2H^+ + 2\,e^- \rightarrow H_2$	0	
$Fe^{3+} + e^- \rightarrow Fe^{2+}$	0.767	(Cornell and Schwertmann, 2003)
$Fe(OH)_{3,s} + 3H^+ + e^- \rightarrow Fe^{2+} + 3H_2O$	0.944	
$Fe(OH)_2 + e^- + H^+ \rightarrow Fe^{2+} + H_2O$	0.897	
$Fe(OH)_{3,s} + e^- + H^+ \rightarrow Fe(OH)_{2,s} + H_2O$	0.254	
$NO_3^- + 2H^+ + 2e^- \rightarrow NO_2^- + H_2O$	0.42	(Berks et al., 1995)
$NO_2^- + 2H^+ + e^- \rightarrow NO + H_2O$	0.375	
$2NO + 2H^+ + 2e^- \rightarrow N_2O + H_2O$	1.175	
$N_2O + 2H^+ + 2e^- \rightarrow N_2 + H_2O$	1.355	
$2\,NO_3^-(aq) + 4\,H^+(aq) + 2e^- \rightarrow 2\,NO_2(g) + 2H_2O(l)$	0.8	[1]

[1] http://www2.ucdsb.on.ca/tiss/stretton/database/Standard_Reduction_Potentials.htm

S.2. Fe tot concentrations (presented as % of initial)

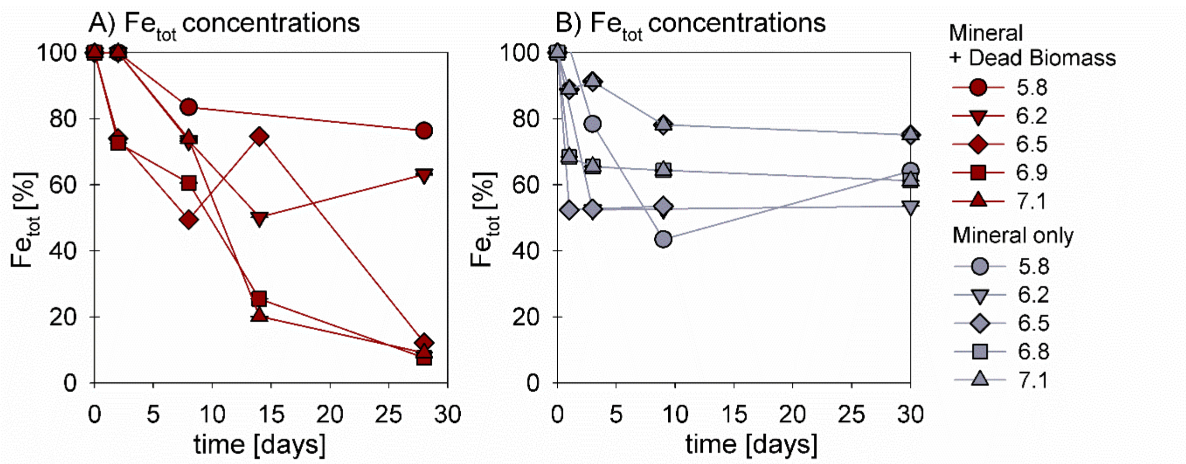

Figure 1: Fe total concentrations for the mineral + dead biomass (A) and the mineral only (B) amended experimental sets obtained from the dissolution of the spun-down pellet in 1 M HCl. Standard error is given as error bars. Fe total values decrease over time, suggesting that the classical ferrozine assay approach applied was insufficient

S.3. 2 mM NO_2^- as threshold value

Klueglein and Kappler (2013) showed that in the presence and absence of goethite, the oxidation of 8 mM Fe(II) was enhanced when ≥2 mM NO_2^- were added. This and the fact that most NDFeO bacteria tend to accumulate up to several mM NO_2^- (Muehe et al., 2009; Weber et al., 2009), which might be a crucial point in order to explain the possible abiotically driven Fe(II) oxidation in NDFeO bacteria, drove our decision to perform our experiments at a threshold of 2 mM Fe(II) and NO_2^-.

S.4. N_2O versus nitrite concentrations

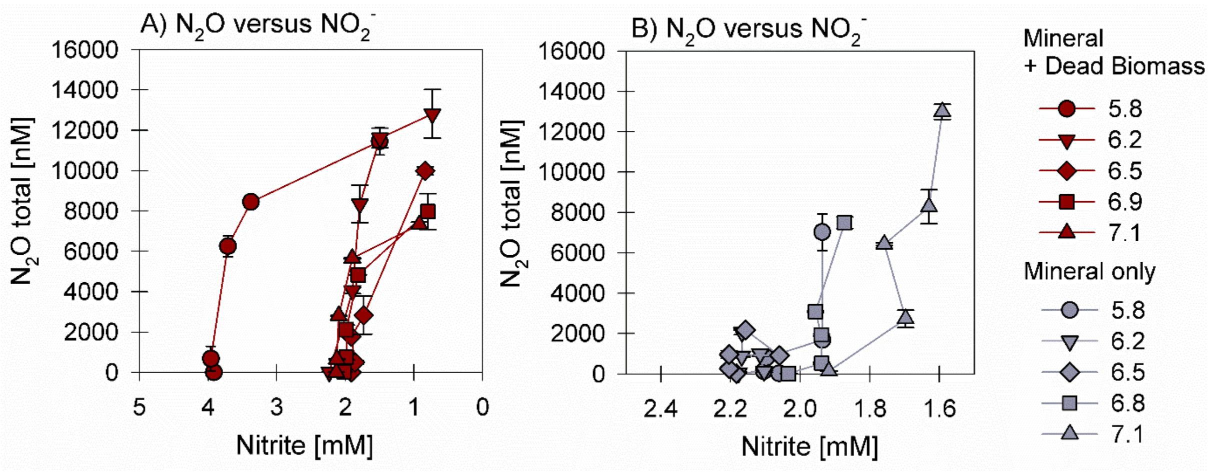

Figure 2: N_2O versus NO_2^- concentrations for the mineral + dead biomass (A) and the mineral-only (B) experiments. Standard error is represented by the error bars.

S.5. Rayleigh plots for mineral only setups

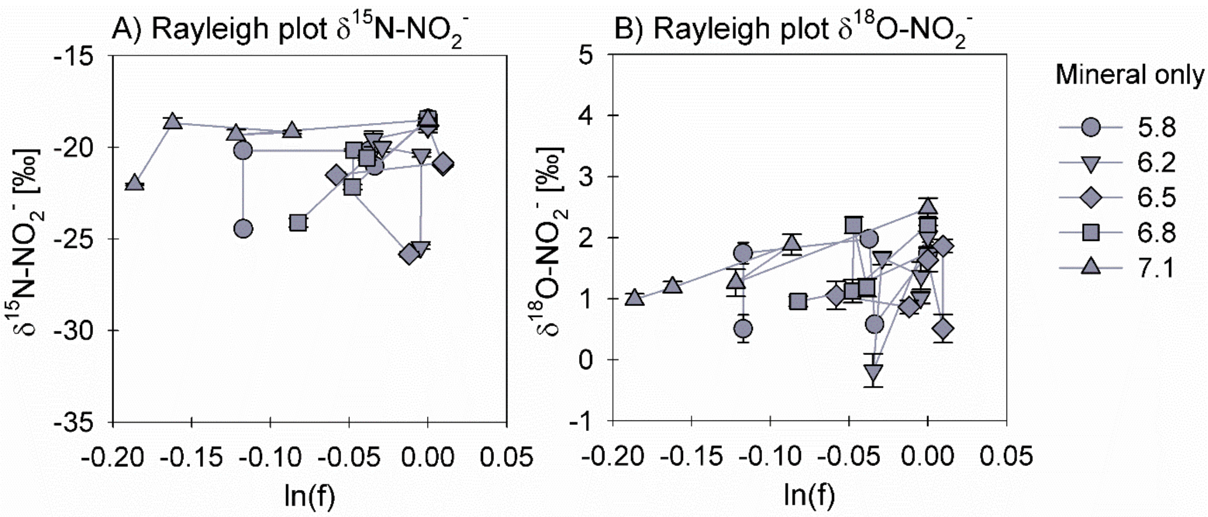

Figure 3: Rayleigh plots for $\delta^{15}N$- (A) and $\delta^{18}O$- (B) NO_2^- values obtained from the mineral-only experiments. Standard error is represented by the error bars. Results obtained do not follow classical Rayleigh fractionation patterns since the concentrations did not decrease significantly over time.

S.6. Rayleigh plots for $\delta^{15}N^{\alpha}$, $\delta^{15}N^{bulk}$ and SP of the N_2O

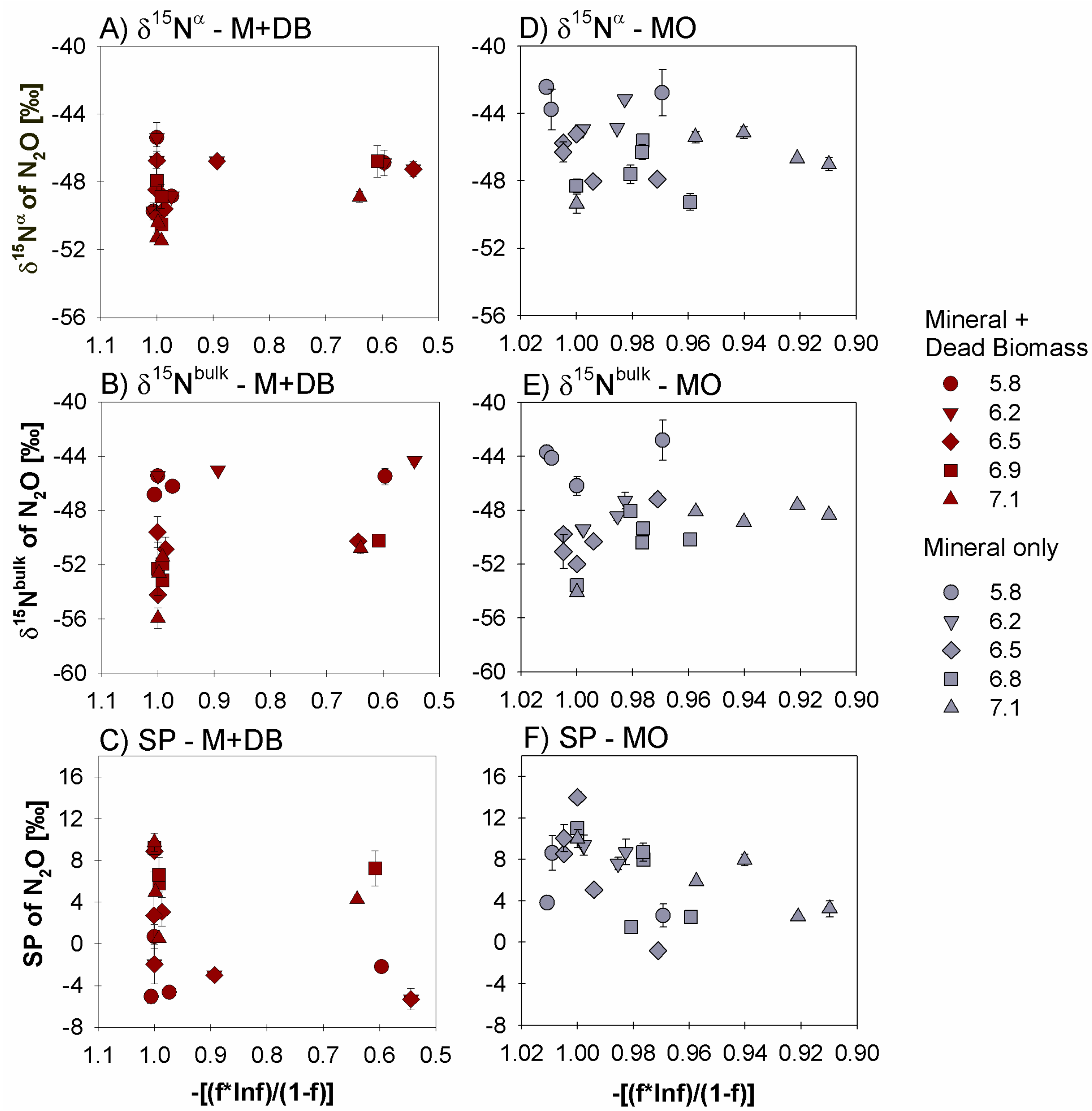

Figure 4: Rayleigh plots for N_2O $\delta^{15}N^{\alpha}$ (A, D), $\delta^{15}N^{bulk}$ (B, E) and site preference, SP (C, F) in mineral plus dead biomass (MDB, red) and mineral-only (MO, grey) experiments. Standard error calculated from biological replicates (n = 3 or 2) is represented by the error bars.

S.7. $\delta^{18}O$ vs $\delta^{15}N^{bulk}$

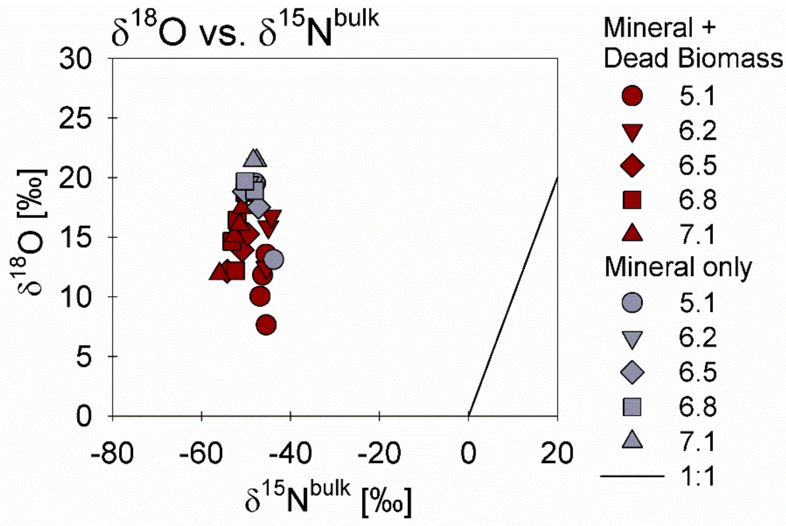

Figure 5: $\delta^{18}O$ vs $\delta^{15}N^{bulk}$ in N_2O combined plot for mineral + dead biomass amended experiments (red) and mineral only experiments (grey). Standard error is represented by the error bars.