# Isotopic analysis of nitrite during abiotic reduction by bio-produced Fe(II). Potential insight into the fate of nitrite in marine environments

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Marine sediments in estuarine and coastal areas often contain terrigenous organic matter and other constituents such as iron and anthropogenic nutrients (e.g., NOx) via riverine and submarine groundwater inputs. Here, marine dissimilatory iron reducing bacteria (e.g., *Shewanella loihica*) are able to reduce Fe(III)-oxide minerals under anoxic conditions producing aqueous and mineral-associated Fe(II). Bio-produced Fe(II) can abiotically reduce nitrite ($NO_2^-$) via formation of nitrous oxide ($N_2O$). In this study, abiotic and biotic $NO_2^-$ reduction experiments were performed i) to get insight into the fate of $NO_2^-$ in marine environments and ii) to explore whether it could be possible to distinguish between abiotic and biotic (heterotrophic) $NO_2^-$ reduction by means of isotope data.

All batch experiments were prepared with synthetic seawater (pH 8.2). The abiotic $NO_2^-$ reduction was evaluated in mineral (i.e., ferrihydrite) / solution systems with bio-produced or synthetic Fe(II). The resulting isotopic fractionation values ($\varepsilon^{15}N$ and $\varepsilon^{18}O$) were compared to those observed for the biotic $NO_2^-$ reduction by *S. loihica*.

The $NO_2^-$ abiotic reduction rate for the experiments with bio-produced Fe(II) was higher than that for synthetic Fe(II) when found both dissolved and associated to minerals. The $NO_2^-$ abiotic reduction was much lower when the synthetic Fe(II) was found only dissolved or associated to minerals. However, similar $\varepsilon^{15}N/\varepsilon^{18}O$ ratios were obtained for all abiotic experiments (1.4 to 1.8). In contrast, the $\varepsilon^{15}N/\varepsilon^{18}O$ ratio was lower (0.3) for the heterotrophic denitrification of $NO_2^-$ by *S. loihica*.