Anaerobic activity of nitrite-oxidizing microorganisms affects the $\delta^{18}O$ of dissolved nitrate during microbial denitrification

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The stable isotopes of nitrate in water are frequently used to assess denitrification and sources of nitrate in the environment. It was previously assumed for terrestrial environments that a relative increase in $\delta^{18}O$ of nitrate compared to its $\delta^{15}N$ of 0.5 is indicative of denitrification.

We anaerobically incubated sediments with natural microbial populations from 3 different anoxic habitats and a pure culture of the nitrite oxidizing bacterium *Nitrobacter vulgaris* in strongly ^{18}O-labeled water with nitrate and adequate electron donors. A significant influence of $\delta^{18}O$ of water on the $\delta^{18}O$ of nitrate was found in all experiments. All incubations clearly expressed microbial denitrification. Given oxic conditions, the microbial populations of all incubations were also able to oxidize nitrite. We thus assume the presence of nitrite oxidizing microorganisms in all incubations. As nitrite oxidizers may catalyze the observed isotopic shift in pure cultures, they are likely also the driving parameter of the observed shift in the environmental incubations. This shift questions the stability of predicted $\Delta\delta^{18}O/\Delta\delta^{15}N$ ratios in the environment during denitrification. Such a shift in $\delta^{18}O$ of nitrate under anoxic conditions also questions the validity of nitrate source determination by 2D isotopic fingerprinting, specifically in respect to the $\delta^{18}O$ axis.

Nitrite oxidizing microorganisms possess a nitrite oxidoreductase enzyme (NXR) which is able to oxidize nitrite as well as reduce nitrate, depending on the redox conditions. Regular denitrifiers possess a nitrate reductase (Nar) which only reduces nitrate irreversibly. We hypothesize that the nitrate reduction reaction at the NXR enzyme by nitrite oxidizing microorganisms is reversible even under anoxic conditions, allowing the incorporation of oxygen-atoms from water into nitrate.

$$NO_3^- + 2H^+ \leftrightarrow NO_2^- + H_2O$$

It is likely that a variable activity of nitrite oxidizers in anoxic environments produces a variable shift of $\delta^{18}O$ of nitrate towards $\delta^{18}O$ of ambient water and thus varied ratios of $\Delta\delta^{18}O/\Delta\delta^{15}N$.

Geochemical impacts of carbon dioxide leakage into carbonate aquifer rocks

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Leakage of CO_2 during geological carbon sequestration can prevent meeting environmental and storage goals. A significant environmental concern is acidification of groundwater with a potential subsequent increase in aqueous metal concentrations due to mineral dissolution and desorption. Even though carbonate aquifers supply about 20% of drinking water worldwide, these aquifers are somewhat neglected in the CO_2 sequestration literature, because carbonate minerals are presumed to buffer pH increases. The common carbonate minerals (calcite, dolomite) are rarely found in pure form in nature, and typically contain metal impurites. Dissolution of these minerals is very sensitive to pH changes, and we hypothesized that metals could be released during carbonate dissolution. Previous studies usually point to sulfide minerals as likely sources of toxic metals. Pressurized experiments containing natural carbonate rocks at elevated CO_2 pressures resulted in elevated aqueous concentrations of Mn, Ni, As, Cr, Sr, Ba, Co, Mo and Tl, with few elements rising above U.S. regulatory limits. Geochemical modeling (constrained by our experimental results) suggest that carbonate minerals may be the dominant contributors to metal release in a carbonate aquifers, not pyrite. Consequently, models that ignore co-release of metals from carbonates may underpredict metal release. However, geochemical modeling also demonstrates that pyrite may be an important source of metals under oxidizing conditions, and that the influence of O_2 partial pressures is equally important that of CO_2.

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