

The effect of benthic nitrogen cycling on the $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ of water-column nitrate

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We used benthic chambers to determine dissolved inorganic nitrogen (DIN) fluxes in continental shelf sediments in the Santa Monica Bay (SMB), and measured the nitrogen and oxygen isotope composition of nitrate obtained from chamber water. SMB sediments were a significant net sink for total nitrogen due to microbial denitrification. Denitrification rates, which were estimated using benthic flux stoichiometry, ranged between 0.9 and 2.5 mmol N m⁻² d⁻¹. 46 to 100% of the total denitrification was fueled by nitrate from nitrification.

We demonstrate how nitrate $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ can effectively be used to de-convolve simultaneously occurring N-cycling reactions and, therefore, to yield an improved understanding of the nitrogen pathways during microbial organic matter decomposition. In general, and independent of the denitrification rate and the denitrification efficiency, nitrate $^{15}\text{N}/^{14}\text{N}$ and $^{18}\text{O}/^{16}\text{O}$ ratios did not change significantly with progressive nitrate depletion in the chambers. A lack of change in nitrate $\delta^{15}\text{N}$ could either be due to the lack of an N-isotope effect associated with sedimentary denitrification, or due to the effective balancing of such an isotope effect by isotopically light nitrate from nitrification. However, the combined measurement of nitrate $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ indicated that no gross efflux of ^{15}N -depleted nitrate from nitrification occurred in the SMB sediments, leading to the conclusion that nitrification was closely coupled to denitrification and that the apparent N and O fractionation associated with sedimentary denitrification was, in fact, negligible. We predict that in most environments, sedimentary denitrification is not a significant direct source of ^{15}N -enriched nitrate with respect to the nitrate pool in overlying water. Yet, nitrification and denitrification can still combine to produce a flux of total DIN out of the sediments, which is enriched in ^{15}N .

Equilibrium formation of oligoglycines from glycine in aqueous hydrothermal media

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Formation of the dipeptide glycylglycine (gly₂), the anhydride ring diketopiperazine (dkp) and tripeptide glycylglycylglycine (gly₃) from aqueous glycine (gly) (40mm) and parallel decarboxylation of gly has been studied at 160, 220 and 260°C and 200 bar pressure buffered by phosphate salts (3mm, pH 6.8). Stock solutions of glycine were injected into Au cells containing buffer solutions pre-equilibrated at experimental conditions. Glycine and oligoglycines were analyzed with HPLC by UV-detection at 205nm. Free energies of individual reaction were obtained from measured reactant molality quotients following establishment of steady-state.

At 160 °C gly was found to undergo dimerization towards gly₂ and rapid cyclization towards dkp. Decarboxylation of gly was not found to occur to any significant extent over the 250 hour period of the experiment. The initial growth period of the dipeptide was followed by the establishment of an equilibrium between gly and gly₂ with an observed standard free energy of gly dimerization of 16.4 kJ·mol⁻¹ at 160°C, comparing well with predicted 14.3 kJ·mol⁻¹ at the same temperature.¹ Cyclization of gly₂ towards dkp occurred rapidly and was followed by the formation of an equilibrium between the ring and gly₂ with an observed standard free energy of cyclization of -2.8 kJ·mol⁻¹, agreeing well with a previously reported experimental value of -2.9 kJ·mol⁻¹ at the same temperature.² In a separate experiment at 220°C and 200 bar pressure the free energy of gly dimerization and gly₂ cyclization was lowered to 13.4 and -5.4 kJ·mol⁻¹, respectively. When gly was injected into the Au reactor at 260°C and 200bar, we observed a lowering of the free energy of glycine dimerization towards 3.2 kJ·mol⁻¹; furthermore, the formation of the tripeptide gly₃ with an associated free energy of gly trimerization of around -11 kJ·mol⁻¹, as well as a rise of the free energy of gly₂ cyclization towards a value of 2.3 kJ·mol⁻¹.

Results from our studies indicate a trend toward increased thermodynamic stability of the gly₂ dipeptide relative to its free amino acids with increasing temperature. Moreover, at 260°C the peptide bond formed between 2 gly to form gly₂ is endergonic by 3.2 kJ·mol⁻¹ or a factor of around 4-times more difficult than the subsequent peptide bond formed between gly and gly₂.

References

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