



## Oxygen isotopic composition of nitrate and nitrite produced by nitrifying cocultures and natural marine assemblages

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**ABSTRACT:** The  $\delta^{18}\text{O}$  value of nitrate produced during nitrification ( $\delta^{18}\text{O}_{\text{NO}_3, \text{pic}}$ ) was measured in experiments designed to mimic oceanic conditions, involving cocultures of ammonia-oxidizing bacteria or ammonia-oxidizing archaea and nitrite-oxidizing bacteria, as well as natural marine assemblages. The estimates of ranged from  $-1.5\text{‰} \pm 0.1\text{‰}$  to  $+1.3\text{‰} \pm 1.4\text{‰}$  at  $\delta^{18}\text{O}$  values of water ( $\text{H}_2\text{O}$ ) and dissolved oxygen ( $\text{O}_2$ ) of  $0\text{‰}$  and  $24.2\text{‰}$  vs. Vienna Standard Mean Ocean Water, respectively. Additions of  $^{18}\text{O}$ -enriched  $\text{H}_2\text{O}$  allowed us to evaluate the effects of oxygen ( $\text{O}$ ) isotope fractionation and exchange on . Kinetic isotope effects for the incorporation of  $\text{O}$  atoms were the most important factors for setting overall values relative to the substrates ( $\text{O}_2$  and  $\text{H}_2\text{O}$ ). These isotope effects ranged from  $+10\text{‰}$  to  $+22\text{‰}$  for ammonia oxidation ( $\text{O}_2$  plus  $\text{H}_2\text{O}$  incorporation) and from  $+1\text{‰}$  to  $+27\text{‰}$  for incorporation of  $\text{H}_2\text{O}$  during nitrite oxidation. values were also affected by the amount and duration of nitrite accumulation, which permitted abiotic  $\text{O}$  atom exchange between nitrite and  $\text{H}_2\text{O}$ . Coculture incubations where ammonia oxidation and nitrite oxidation were tightly coupled showed low levels of nitrite accumulation and exchange ( $3\% \pm 4\%$ ). These experiments had values of  $-1.5\text{‰}$  to  $+0.7\text{‰}$ . Field experiments had greater accumulation of nitrite and a higher amount of exchange (22% to 100%), yielding an average value of  $+1.9\text{‰} \pm 3.0\text{‰}$ . Low levels of biologically catalyzed exchange in coculture experiments may be representative of nitrification in much of the ocean where nitrite accumulation is low. Abiotic oxygen isotope exchange may be important where nitrite does accumulate, such as oceanic primary and secondary nitrite maxima.

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