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Nitrogen isotope fractionation during archaeal ammonia oxidation: Coupled estimates from isotopic measurements of ammonium and nitrite

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Ammonia-oxidizing archaea (AOA) are ubiquitous in marine and terrestrial environments and knowledge about the nitrogen (N) isotope effect associated with their ammonia oxidation activity will allow a better understanding of natural abundance isotope ratios, and therefore N transformation processes, in the environment. Here we examine the kinetic isotope effect for ammonia oxidation in a pure soil AOA culture (Ca. *Nitrososphaera viennensis*) and a marine AOA enrichment culture. We estimated the isotope effect from both isotopic signatures of ammonium and nitrite over the course of ammonia oxidation. Estimates of the isotope effect based on the change in the isotopic signature of ammonium give valuable insight, because these estimates are not subject to the same concerns (e.g., accumulation of an intermediate) as estimates based on isotopic measurements of nitrite.

Our results show that both the pure soil AOA culture and a marine AOA enrichment culture have similar but substantial isotope effect during ammonia consumption (31–34 per mill; based on ammonium) and nitrite production (43–45 per mill; based on nitrite). The ^{15}N fractionation factors of both cultures tested fell in the upper range of the reported isotope effects for archaeal and bacterial ammonia oxidation (10–41 per mill) or were even higher than those. The isotope fractionation for nitrite production was significantly larger than for ammonium consumption, indicating that (1) some intermediate (e.g., hydroxylamine) of ammonia oxidation accumulates, allowing for a second ^{15}N fractionation step to be expressed, (2) a fraction of ammonia oxidized is lost via gaseous N forms (e.g., NO or N_2O), which is ^{15}N-enriched or (3) a fraction of ammonium is assimilated into AOA biomass, biomass becoming ^{15}N-enriched. The significance of these mechanisms will be explored in more detail for the soil AOA culture, based on isotope modeling and isotopic measurements of biomass and N_2O.