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Nitrogen Fixation Isotope Dynamics: Nitrogenase Structure is Functionally Adapted to Metal Diversity in the Modern Oxygenated Atmosphere

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Biological nitrogen fixation (BNF) is the only natural process that can convert abundant but inert dinitrogen gas into bioavailable ammonia. It thus serves as the primary natural source of new bioavailable N, constraining primary productivity and other ecosystem functions over Earth history. BNF is catalyzed by prokaryotic metalloenzyme nitrogenase, which occurs in the environmentally dominant molybdenum (Mo)-dependent form as well as alternative forms in which vanadium (V) or iron (Fe) replace the Mo of the active site cofactor. In vitro studies show nitrogenases to be two-protein systems that use a complex sequence of ATP-driven, electron transfers to the active site cofactor to help it cleave the N_2 triple bond at ambient conditions. Environmental BNF is often assumed to rely solely on Mo-nitrogenase[1]. The contribution of and environmental controls on BNF by different nitrogenase metalloenzymes are poorly understood but are critical for constraining present and past N cycling.

I will highlight research on BNF metal-variability revealed by nitrogen (N) and carbon (C) stable isotopes. We have determined the mechanistic basis of the widely used $^{15}N/^{14}N$ isotope signature of BNF using nitrogenase structure-function and isotope modeling approaches constrained by nitrogenase N_2-reduction reaction mechanism. $^{15}N/^{14}N$-isotope dynamics indicate enzymatic N_2 diffusion limits cellular BNF by naturally-occurring Mo- and V-nitrogenases, consistent with their near perfect (high efficiency) catalysis in organisms[2]. Structurally-based diffusional limitation suggests nitrogenase structure is well-adapted to the modern oxygenated atmosphere and that BNF isotope signatures could vary with atmospheric oxygen over geologic time due to enzyme structural change. We also developed and applied quantitative $^{13}C/^{12}C$ isotope biomarkers of BNF flux by different nitrogenase metalloenzymes[3, 4]. We found terrestrial BNF by different metalloenzymes to be controlled by trace metal and N availability. Our studies reveal N-fixers have adapted nitrogenase function to geochemically variable environments through changes in enzyme structure. Our results help understand N budgets and metal-macronutrient cycle interactions in the past, present, and future.

References:

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