Isotopologue effects in the generation and consumption of nitrous oxide

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Nitrous oxide in air and natural waters is produced and consumed by chemical and biochemical reactions that fractionate isotopes by a variety of equilibrium and kinetic mechanisms. Previous measurements of $\delta^{15}N$, $\delta^{17}O$, $\delta^{18}O$, and position-specific ^{15}N incorporation ('site preference') have identified characteristic fractionations for many of these processes. In particular, site preference measurements have successfully distinguished between N_2O produced by bacterial nitrification and denitrification. But there remain too few constraints to fully characterize the sources and sinks of pools of N_2O in complex natural settings, and no existing isotopic tools distinguish among some biological sources, e.g., archaeal and bacterial nitrification. It is possible additional progress could be made by adding new constraints from the study of the multiply substituted isotopologues of N_2O [1].

We use high resolution multi-collector gas source mass spectrometry to measure the relative proportions of six singly and doubly substituted isotopologues of nitrous oxide, including $^{14}N^{15}N^{16}O$, $^{15}N^{14}N^{16}O$, $^{14}N^{15}N^{18}O$, $^{15}N^{14}N^{18}O$, $^{14}N_2{}^{17}O$, and $^{14}N_2{}^{18}O$ [2]. Each of these species has unique chemical and physical properties that potentially lead to distinctive isotope fractionations. Here, we describe the measurement of N_2O produced by diffusion through a pinhole, which produces an isotope effect dependent only on molecular mass. This tests our ability to accurately determine the 6-dimensional isotopic 'fingerprint' of a given fractionation. For the mass 47 species, $^{14}N^{15}N^{18}O$ and $^{15}N^{14}N^{18}O$, our measured result are within 0.1‰ of the expected value. In addition, we have analyzed N_2O produced by pure cultures of a denitrifying bacterium that lacks a N_2O reductase enzyme. It has a site preference consistent with the expectation for denitrifiers [3]. Measurements of site preference and of multiply-substituted isotopologues are both consistent with a kinetic isotope effect produced at the catalytic center of the nitric oxide reductase enzyme and distinct from the predicted equilibrium fractionation [4].

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Coupling fluid residence times, erosion rates and weathering fluxes to evaluate the operation of a hydrologic thermostat

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The Earth's thermostat is thought to be a negative feedback between atmospheric CO_2 levels and chemical weathering of silicate rocks that keeps temperatures relatively moderate over geologic time scales. To evaluate the operation of this thermostat, we relate the weathering flux per area of continent to the cooperation between runoff and tectonic processes. The two are linked here by the balance between the time that water spends in the weathering zone (which depends on runoff, hydraulic conductivity and the length of the flow path) and the kinetics of mineral weathering (which depend on composition, temperature and erosion rate). We use two types of equations: (1) a reactive transport equation that quantifies weathering-derived solute as a function the fluid residence time; and (2) an equation that relates erosion to the abundance of fresh minerals in the soil. We calculate the weathering-derived solute concentration (C) as a function of the Damköhler number (Da), which is modified to account for the effect of erosion on the supply of fresh minerals. This approach requires that as fluid residence time becomes shorter than the equilibrium time, solute concentrations decrease and solute fluxes plateau. This relationship is observed in modern rivers draining tectonically inactive areas wheres solute fluxes are smaller and Damköhler numbers lower, because reduced supply of fresh lengthens the equilibrium time. In contrast, in active mountain ranges, high relief and rapid supply of fresh minerals result in long fluid residence times and short equilibration times such that solute concentrations and fluxes are high. This approach allows weathering rates to increase asymmetrically between tectonically active and inactive areas in response to changes in climate, to create a bimodal hydrologic thermostat. However, to fully evaluate this model for weathering fluxes requires improved understanding of the reactive flow paths in large catchments and how they are moderated by physical/chemical erosion, the underlying causes for variations in concentration-discharge relationships and the biogeochemical factors that influence the equilibrium time.

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