

Nitrate N and O natural abundance stable isotope ratios

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Measured by J. Granger and D. Sigman

These data are annexed to Calvin Mordy's original bottle file.

The $^{15}\text{N}/^{14}\text{N}$ and $^{18}\text{O}/^{16}\text{O}$ of nitrate were determined following the denitrifier method (Casciotti et al. 2002; Sigman et al. 2001). This method involves the quantitative conversion of nitrate (and nitrite) in a sample to nitrous oxide (N_2O) gas by denitrifying bacteria that lack the N_2O reductase enzyme and thus do not dismutate N_2O to di-nitrogen gas. The N and O isotopic composition of the N_2O gas analyte is then measured on a gas chromatograph-isotope ratio mass

spectrometer. Isotope ratios are reported using the delta (δ) notation in units of per mil (‰):

$$\delta^{15}\text{N}_{\text{sample}} = ((^{15}\text{N}/^{14}\text{N})_{\text{sample}} / (^{15}\text{N}/^{14}\text{N})_{\text{reference}} - 1) \times 1000 \quad (1)$$

$$\delta^{18}\text{O}_{\text{sample}} = ((^{18}\text{O}/^{16}\text{O})_{\text{sample}} / (^{18}\text{O}/^{16}\text{O})_{\text{reference}} - 1) \times 1000 \quad (2)$$

The $^{15}\text{N}/^{14}\text{N}$ reference is N_2 in air, and the $^{18}\text{O}/^{16}\text{O}$ reference is Vienna standard mean ocean water (VSMOW). Individual analyses were referenced to injections of N_2O from a pure gas cylinder and then standardized through comparison to the international potassium nitrate reference materials IAEA-N3 with an assigned $\delta^{15}\text{N}$ of +4.7 versus atmospheric N_2 (Gonfiantini et al. 1995) and most recently reported $\delta^{18}\text{O}$ of 25.6‰ versus VSMOW (Böhlke et al. 2003). The size of the culture blank was determined by running a prepared vial to which no sample was added. An O isotope correction is also required for exchange of the oxygen atoms with water during reduction of nitrate to N_2O (Casciotti et al. 2002). Exchange was calculated by comparing the observed and reported $\delta^{18}\text{O}$ difference between IAEA-N3 and the nitrate isotopic reference material USGS-34 ($\delta^{18}\text{O} = -27.9\text{‰}$; (Böhlke et al. 2003)). Measurement error consists of the standard deviation of 2 to 5 replicate measurements of a given nitrate sample.

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