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Triple oxygen isotope analysis of nitrate using cavity ringdown laser spectroscopy

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Triple oxygen isotopes in nitrates are a valuable tool to ascertain the pathways of nitrate formation in the atmosphere and the fate of nitrate in ecosystems. Current analytical methods for determining $^{17}O/^{16}O$, $^{18}O/^{16}O$ and derived ^{17}O anomalies ($\Delta^{17}O$) are tedious, time-consuming and sometimes involve hazardous reagents. Here we present a new method for triple oxygen isotope analysis of nitrate, based on nitrate-water isotope equilibration (IE) and subsequent isotopic analysis of water using cavity ringdown laser spectroscopy (CRDS). First, oxygen of nitrate ($O\text{-}NO_3$) is equilibrated with oxygen of water ($O\text{-}H_2O$) at low pH (0.1) and 80^oC in sealed borosilicate tubes for at least three days. After neutralizing the solution (pH$\sim$7), the isotopic composition of the equilibrated water is determined by CRDS on a Picarro L-2140i analyser. $\delta^{17}O$ and $\delta^{18}O$ of waters are scaled to V-SMOW and V-SLAP. International references USGS-34, USGS-35 and IAEA-NO_3 are used to calibrate in-house nitrate standards, that in turn are utilized for calibration of unknowns. We provide isotopic measurements of synthetic and natural nitrates with a wide range of $\Delta^{17}O$ values. In addition, we demonstrate a direct inter-lab comparison between the results of $\Delta^{17}O$ obtained by IE-CRDS and the classic method of thermal-decomposition of nitrate followed by isotope ratio mass spectrometry of O_2 (TD-IRMS) at Louisiana State University. The precision of our method improves with sample size. This is 0.8‰ for $\delta^{17}O$, 1.8‰ for $\delta^{18}O$ and 0.2‰ for $\Delta^{17}O$ when using a $O\text{-}NO_3/O\text{-}H_2O$ of 0.0112 ± 0.0001 (e.g. 1 mg of $NaNO_3$ in 50 μl of the acid solution). This reproducibility is comparable to that from other methods. IE-CRDS and TD-IRMS methods yield similar isotopic results for the analysis of both synthetic and natural nitrate samples within analytical errors of the two methods. The IE-CRDS method is cheaper, safer, and requires less tedious sample preparation and analysis than IRMS-based methods, with a relatively high sample throughput ($\sim$12 samples/day).