UNIVERSITY of WASHINGTON

WEST ANTARCTIC ICE SHEET DIVIDE ICE CORE
CLIMATE, ICE SHEET HISTORY, CRYOBIOLOGY

Reduced size limits for nitrate $\delta^{15}N$, $\Delta^{17}O$ and sulfate $\Delta^{17}O$ isotope measurements and first results from the WAIS Divide core

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Abstract

We present two methods used in our laboratory for 1) simultaneous measurement of sulfate $\Delta^{17}O$ and nitrate $\Delta^{17}O$ by silver salt pyrolysis, and 2) simultaneous measurement of nitrate $\delta^{15}N$ and $\Delta^{17}O$ by nitrous oxide pyrolysis from ice cores. These two methods require an order of magnitude less sample than previously published methods (200 nmol vs 2 μmol) with similar analytical uncertainty as our previous method. Below we present the first results of simultaneous measurement of nitrate $\delta^{15}N$ and $\Delta^{17}O$ from the WAIS Divide core at 100 – 600 m depth, and compare with similar measurements at other Antarctic locations.

Silver Salt Pyrolysis

200 nmol (and greater) O_2, $\Delta^{17}O$ ±1.0 ‰ precision, +0.4 ‰ accuracy

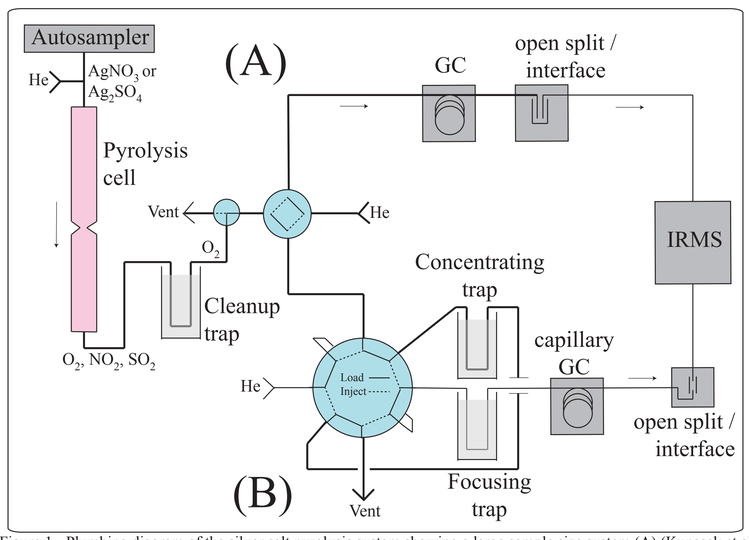

Figure 1 - Plumbing diagram of the silver salt pyrolysis system showing a large sample size system (A) (Kunasek et al. 2008) and a small sample size system (B), featured here. Silver nitrate or silver sulfate samples are dropped into a modified quartz column held at 550 ºC or 1100 ºC, respectively. Pyrolysis of the salt yields O_2 that is purified away from other products and cryofocused using a molecular sieve trap held at liquid nitrogen temperature. Sample O_2 is then passed through a capillary GC and into an IRMS for 32, 33, 34 mass / charge measurement.

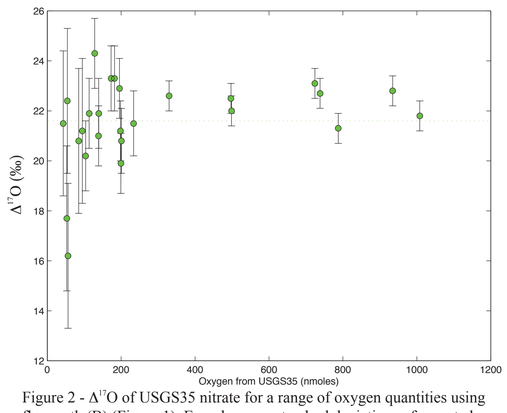

Figure 2 - $\Delta^{17}O$ of USGS35 nitrate for a range of oxygen quantities using flow path (B) (Figure 1). Error bars are standard deviations of repeated analysis at respective size classes. The dotted line indicates the accepted value for USGS35 (21.6 ‰).

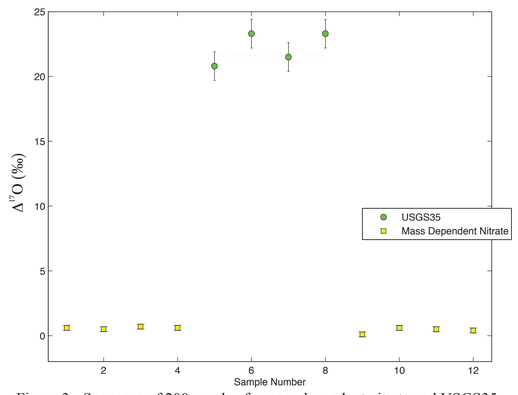

Figure 3 - Sequence of 200 nmols of a mass dependent nitrate and USGS35 nitrate using flow path (B) (Figure 1) showing no sample to sample influence on $\Delta^{17}O$. Error bars show standard deviation for 200 nmol samples. The dotted line indicates the accepted value for USGS35 (21.6 ‰).

Nitrous Oxide Pyrolysis

200 nmol (and greater) O_2, $\Delta^{17}O$ ±0.6 ‰ precision, -0.1 ‰ accuracy
$\delta^{15}N$ ±0.3 ‰ precision, +0.03 ‰ accuracy

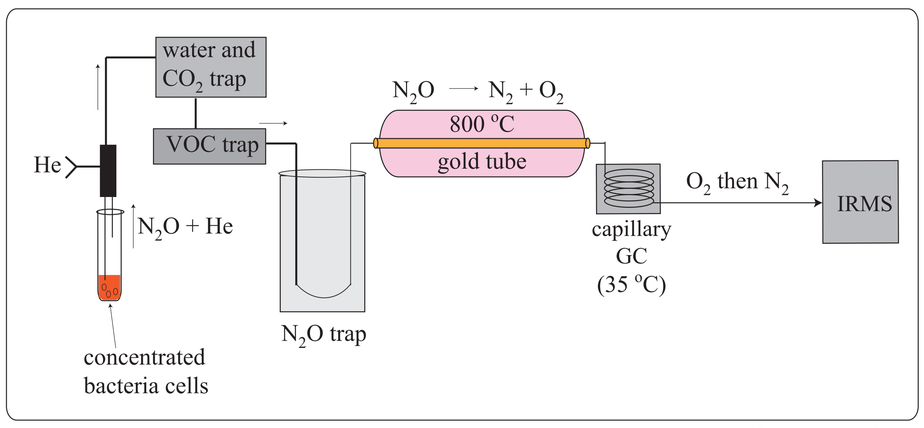

Figure 4 - Plumbing diagram of the nitrous oxide pyrolysis system. N_2O generated from nitrate via bacterial denitrification is purged from head space vials, purified, cryofocused and then passed through a gold tube held at 800 °C. Pyrolysis products, O_2 and N_2, are separated in a capillary GC and then into an isotope ratio mass spectrometer for 32, 33, 34 and then 28, 29 mass / charge measurement (adapted from Kaiser et al., 2007).

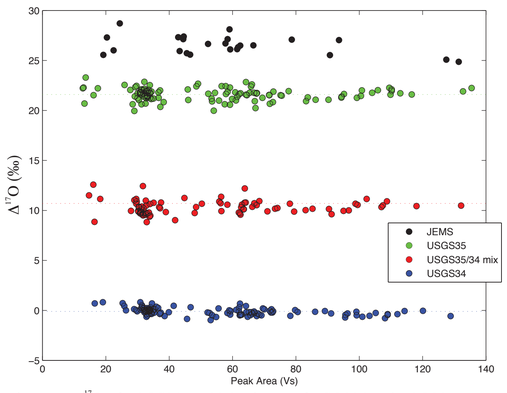

Figure 5 - $\Delta^{17}O$ of USGS34, a 50/50 mixture of USGS34 and USGS35, USGS35, and bulk Greenland Ice (~80 m depth) (JEMS) for a range of oxygen quantities. Dotted lines are the accepted values (USGS34 -0.1 ‰, USGS35 +21.6 ‰, USGS34 / USGS35 mixture +10.7 ‰). Data have been corrected to USGS34 and USGS35.

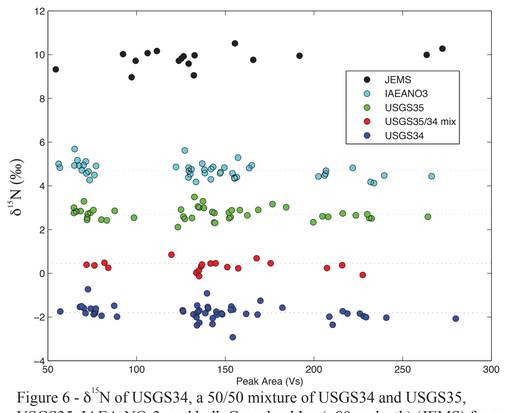

Figure 6 - $\delta^{15}N$ of USGS34, a 50/50 mixture of USGS34 and USGS35, USGS35, IAEA-NO-3, and bulk Greenland Ice (~80 m depth) (JEMS) for a range of nitrogen quantities. Dotted lines are the accepted values (USGS34 -1.8 ‰, USGS34 / USGS35 mixture +0.45 ‰, USGS35 +2.7 ‰, IAEANO3 +4.7 ‰). Data have been corrected to USGS34 and IAEA-NO-3.

WAIS Divide Preliminary Results

Recently acquired data, QA/QC ongoing, absolute values in expected range compared with similar Antarctic measurements

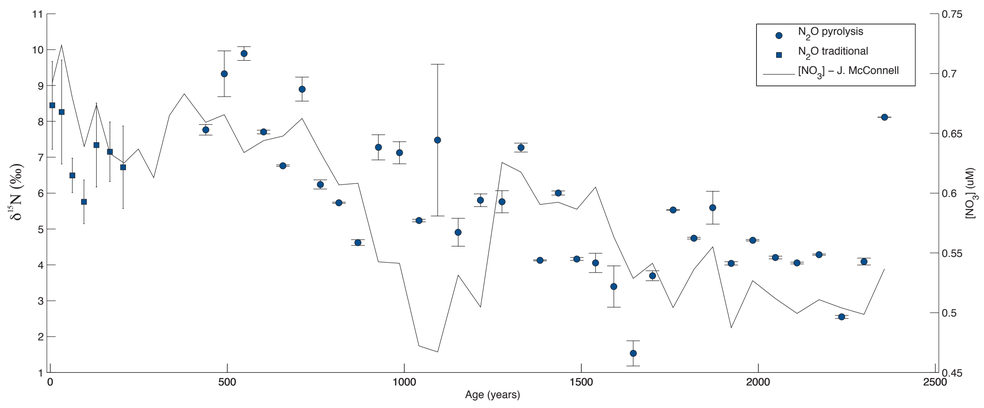

Figure 7 - $\delta^{15}N$ from 1 L subsample of 10 m section triplicate means (error bars are standard deviations) of the WAIS Divide 06A core by nitrous oxide pyrolysis (●), from 10 m means (error bars are standard errors) of 1 m sections of the WAIS Divide 05A core by traditional nitrous oxide analysis (■), and 10 m section means of $[NO_3]$ from J. McConnell high resolution data.

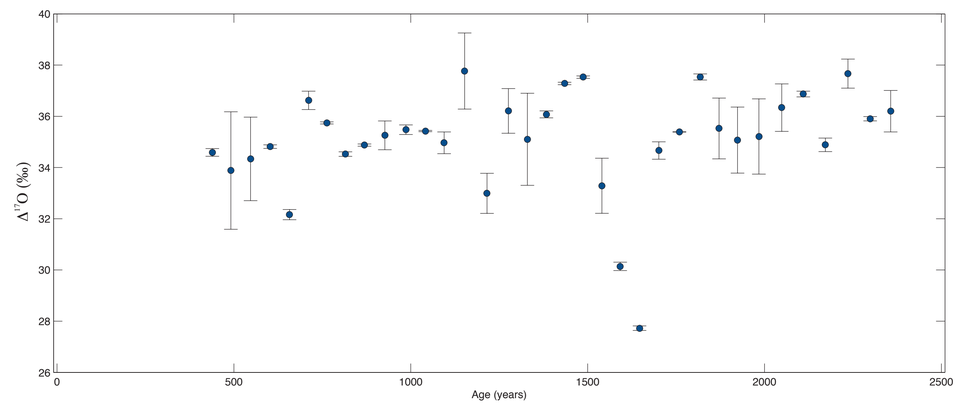

Figure 8 - $\Delta^{17}O$ from 1 L subsample of 10 m sections of the WAIS Divide 06A core measured by nitrous oxide pyrolysis (Figure 4). Values and errors bars are means and standard deviations, respectively, of triplicates.

Summary

The silver salt pyrolysis and the nitrous oxide pyrolysis methods are of particular interest because of the small quantities of ice needed for each analysis. The silver salt pyrolysis approach presented here provides an order of magnitude improvement of sample size for nitrate $\Delta^{17}O$ analysis compared to our previously published method (Kunasek et al. 2008). This reduces the amount of ice needed for $\Delta^{17}O$ analysis and increases temporal resolution of ice core analysis.

Both methods are in good agreement when nitrate from an internal standard (bulk Greenland Ice from ~80 m depth = "JEMS") is used for comparison. Silver salt pyrolysis yields $\Delta^{17}O$ 25.2 ± 1.1 ‰ (at 200 nmoles) and the nitrous oxide pyrolysis yields $\Delta^{17}O$ 26.4 ± 0.9 ‰ (at 200 nmoles and greater).

Silver salt pyrolysis of sulfate method developement is ongoing. Initial results are similar to nitrate with respect to sample size dependency and memory effect.

WAIS Divide $\Delta^{17}O$ of nitrate is generally higher than modern DDU measurements (31.6 ‰ from Savarino et al. 2007), as expected due to higher latitude and within the range predicted by a global chemical transport model (up to 41 ‰ annual mean (Alexander et al 2009)).

$\delta^{15}N$ of nitrate at WAIS Divide (20 cm/year accum.) is lower than other Antarctic sites that have lower accumulation rates, but similar to Summit, Greenland, which has a comparable annual accumulation rate (25 cm/year). Dome C has $\delta^{15}N$ ~200 ‰ near the surface and an accumulation rate of 2 cm/year (Blunier et al. 2005); the SPRESSO core from South Pole has $\delta^{15}N$ ~75 ‰ in recent pre-industrial ice and an accumulation rate of 8 cm/year (Jarvis 2008); Summit, Greenland has a $\delta^{15}N$ of ~12 ‰ in recent pre-industrial ice (Hastings et al. 2009).

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Acknowledgements

We appreciate the efforts of Rebecca Teel and Dan Gleason for laboratory support. These projects were funded in part by NSF-OPP 0538049 and the Royalty Research Fund.