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Introduction

Stable isotope ratios of water in polar precipitation, as measured in ice cores, have been particularly useful in the interpretation of past climates. While $\delta^{18}\text{O}$ alone is used as a proxy of past temperature, the recent development of techniques to measure the $^{17}\text{O}/^{16}\text{O}$ ratio precisely (Barkan & Luz, 2005) has allowed ^{17}O -excess to be added to the ice-core isotope toolbox. The combination of $\delta^{18}\text{O}$, $\delta^{17}\text{O}$ and δD – giving the parameters ^{17}O -excess and deuterium excess – could provide valuable additional information on the evaporative conditions of the oceanic moisture sources for Antarctic precipitation. Deuterium excess has been widely used, but with mixed results due to its sensitivity to conditions both during evaporation and during precipitation; this is theoretically less problematic for ^{17}O -excess.

Definition

^{17}O -excess = $\delta^{17}\text{O} - 0.528 \times \delta^{18}\text{O}$,
where $\delta^{18}\text{O} = \ln(R_{\text{SAM}}/R_{\text{SMOW}})$ where
 $R_{\text{SAM}} = {}^x\text{O}/^{16}\text{O}$ in sample, $R_{\text{SMOW}} = {}^x\text{O}/^{16}\text{O}$
in Vienna Standard Mean Ocean Water.
 $x = 18, 17$. Note the different definition
of 'delta' from the conventional one: $\delta^x\text{O} = R_{\text{SAM}}/R_{\text{SMOW}} - 1$. (Barkan & Luz, 2005)

Materials & Methods

The analytical method for determination of the oxygen isotopic ratios is based on work by Barkan & Luz, 2005. To start, 5 μL of water are injected via syringe through a high temp (400 $^{\circ}\text{C}$) septum into a CoF_3 reaction tube, instantaneously converting H_2O to O_2 and creating HF and Co as a byproduct. The O_2 sample is cyrofocused in a liquid nitrogen (LN_2) trap, and then transferred to a cold finger in a liquid helium (LHe) dewar. O_2 samples in stainless steel cold fingers are warmed to room temperature and inserted vertically, one at a time, into the dual inlet port of the IRMS.

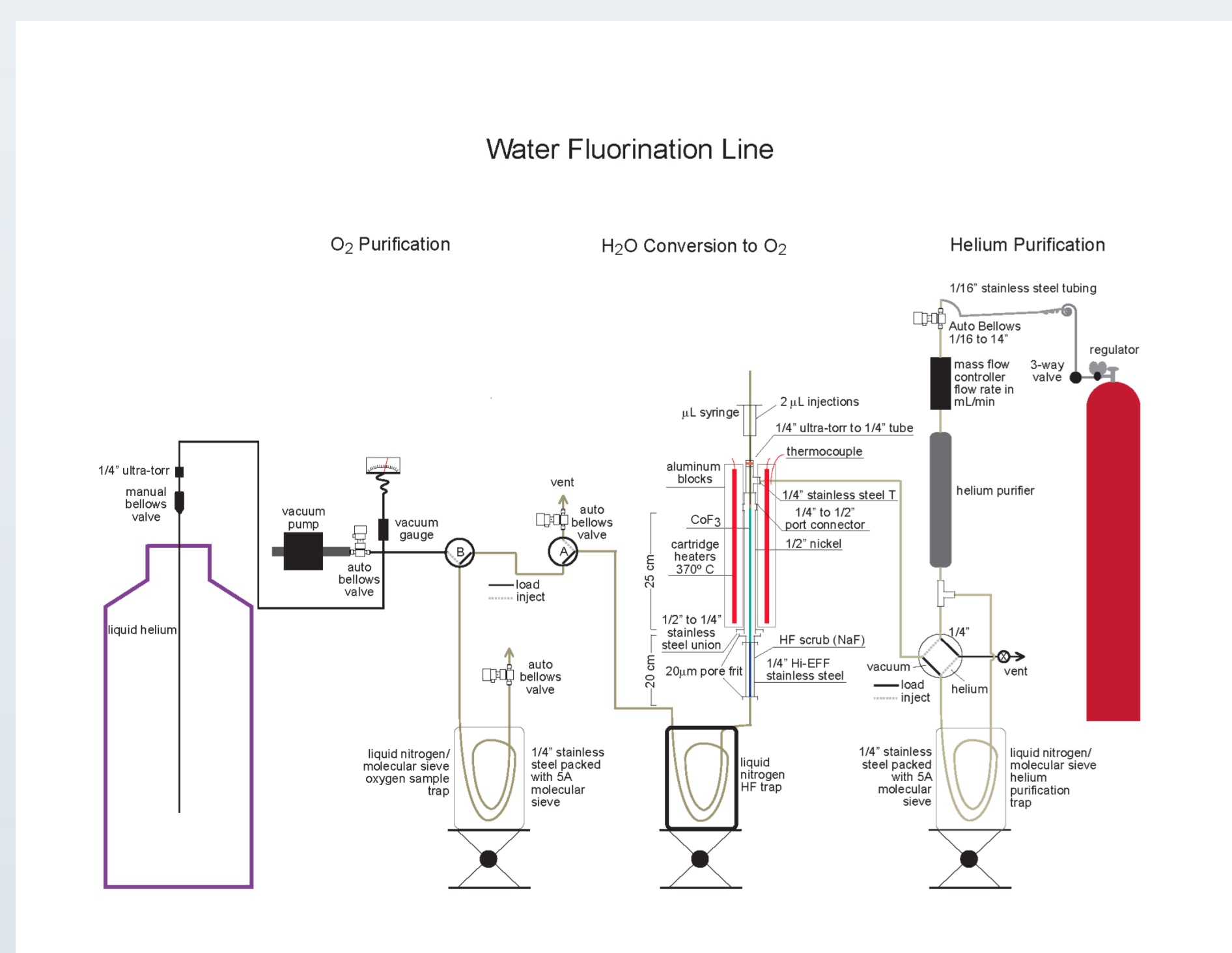


Figure 1. Plumbing schematic of ^{17}O Water Fluorination system showing He flow, injection port, CoF_3 reaction heater, LN_2 traps, and LHe dewar. Fluorination of water converts H_2O to O_2 , which is purified by NaF scrub, and cyrofocused using a molecular sieve trap held at liquid nitrogen temperature. The O_2 sample is then transferred to a cold finger in a liquid helium dewar.

The O_2 sample is then run on a ThermoFinnigan MAT 253 isotope ratio mass spectrometer (IRMS). The O_2 sample is analyzed for mass 32, 33, and 34 abundance measurements for $\delta^{18}\text{O}$ and $\delta^{17}\text{O}$ in dual-inlet mode by multicollector mass spectrometry.

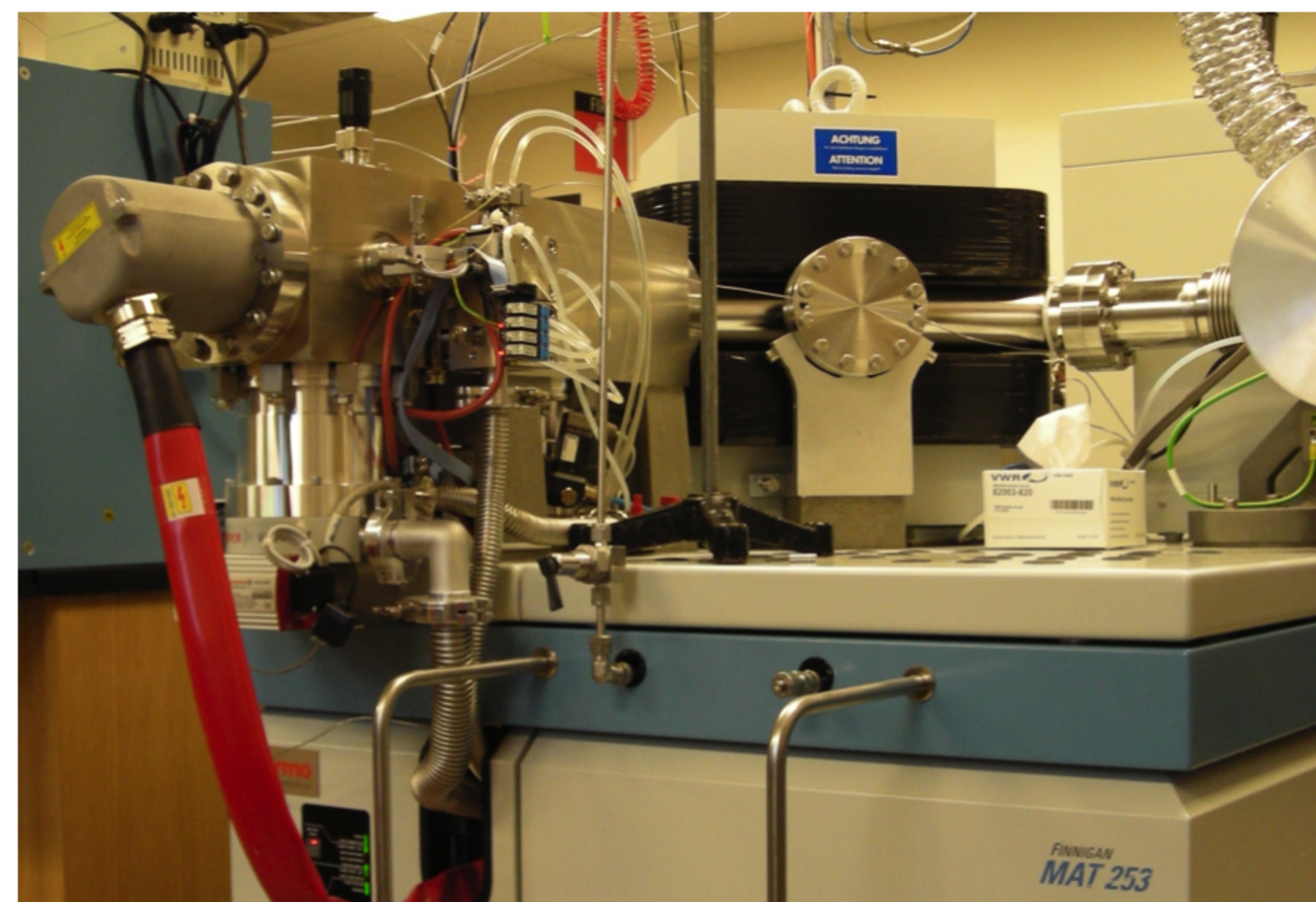


Figure 2. ThermoFinnigan MAT 253 Isotope Ratio Mass Spectrometer (IRMS) with dual inlet. O_2 sample is collected in stainless steel cold finger and then placed vertically in sample side of dual inlet.

Each mass spectrometric measurement is comprised of three separate acquisitions during which the ratio of sample to reference is determined 25 times. Each of these cycles consists of 26 seconds of integration to maximize counting statistics and 30 seconds of idle time between each cycle to eliminate any residence time (memory) effects. The pressures of the sample and reference gas are balanced before each acquisition and the reference gas is refilled before each set of three acquisitions.

Results

Refinement of mass spectrometer integration period (seconds) and intensity range (mV) has improved precision of the $\Delta^{17}\text{O}$ measurement to a standard error of 4 per meg. WAIS water standards put through the ^{17}O Water Fluorination line have been run on the IRMS, but with poor reproducibility thus far. Currently, a small (1-2 per mil) decline of isotopic values occurs during the entire length (25 cycles) of the run. The primary cause for this trend is most likely a decrease of the sample gas volume and pressure within the sample bellows.

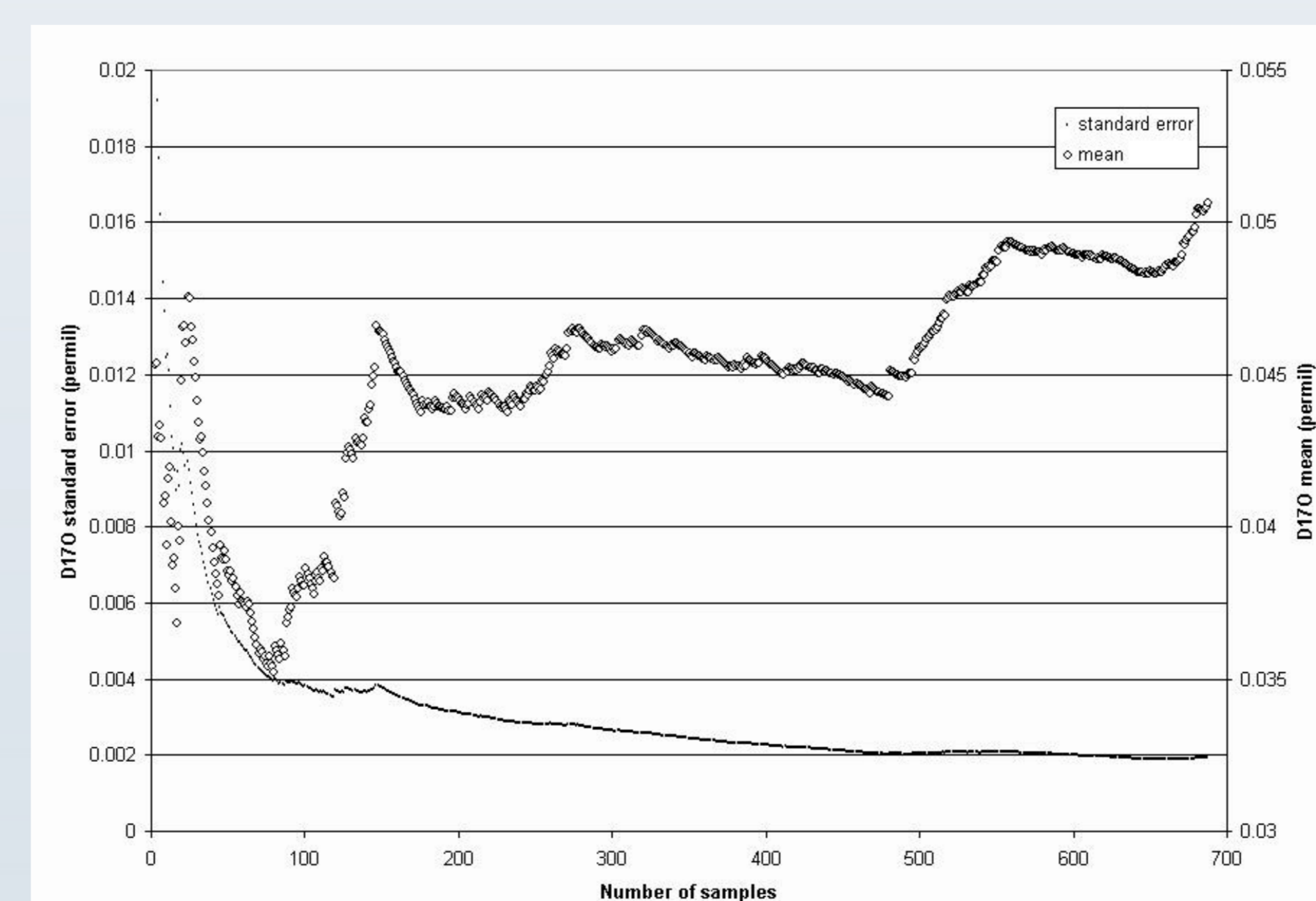


Figure 3. Standard error of $\Delta^{17}\text{O}$ approaches (2 per meg) with increasing measurement number. Mean $\Delta^{17}\text{O}$ shows possible drift after 500 samples. In this plot, each point represents one comparison of sample and standard; consisting of 26 seconds of integration and 30 seconds of idle time between each cycle.

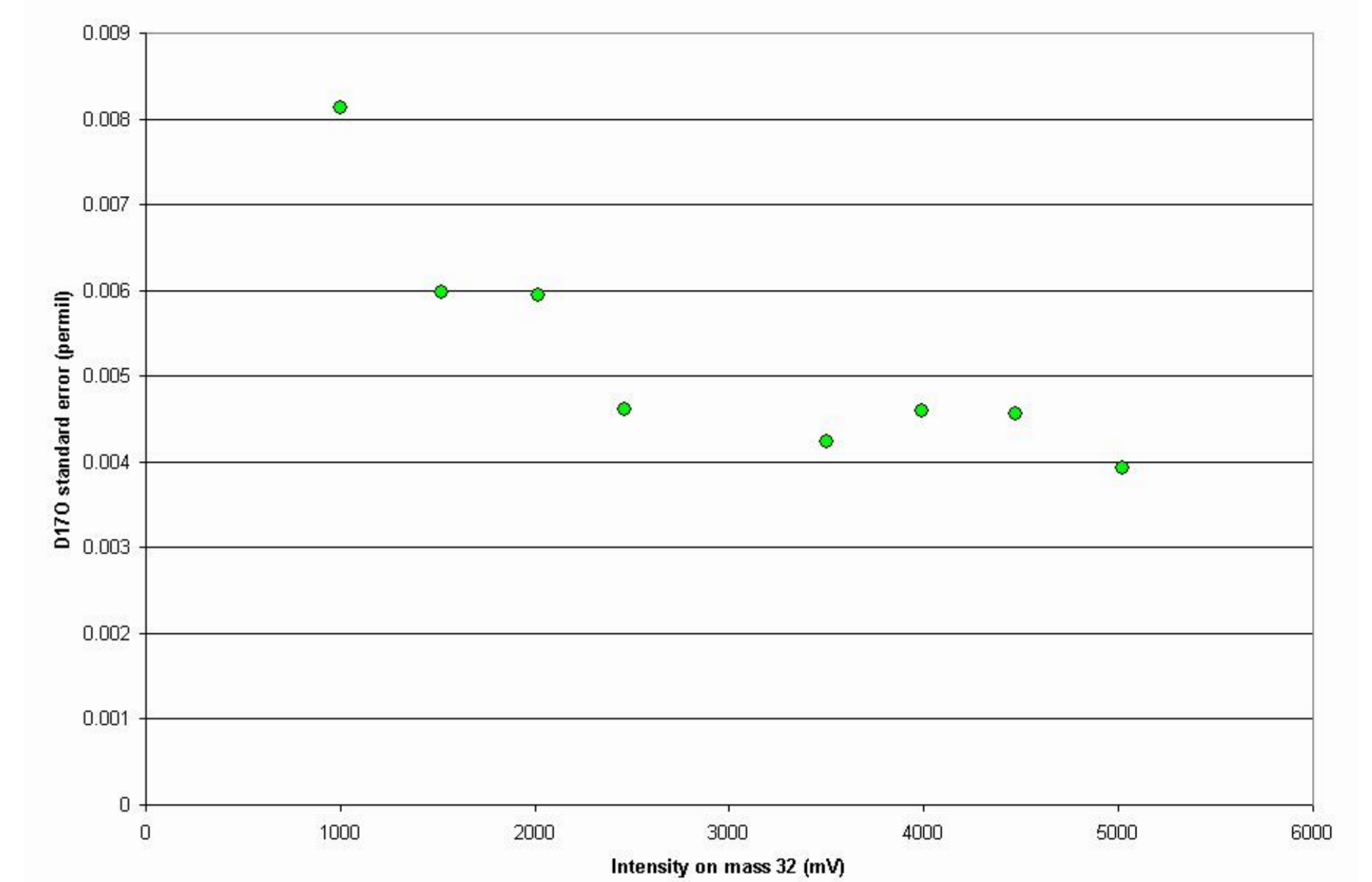


Figure 4. Standard error of $\Delta^{17}\text{O}$ from high-purity O_2 reference gas for a range of mass 32 intensities (mV) from a total of 80 acquisitions (run). The mass spectrometer error (standard error of the mean) for $\Delta^{17}\text{O}$ has reached 0.004‰, (4 per meg) for higher intensities.

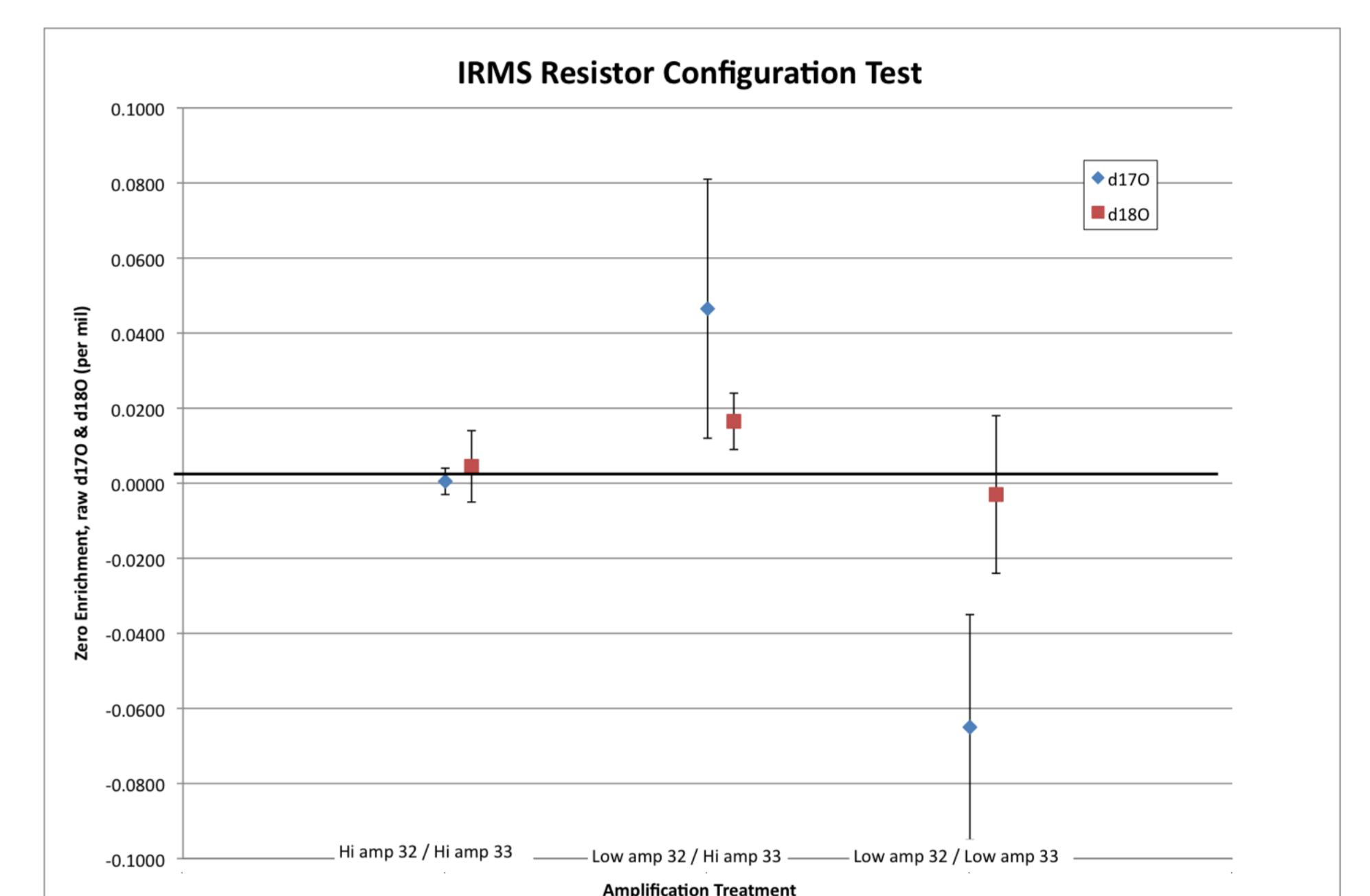


Figure 5. Test of resistor configuration. Note that high amplification treatment on both Mz 32 & 33 produces the highest precision.

Summary

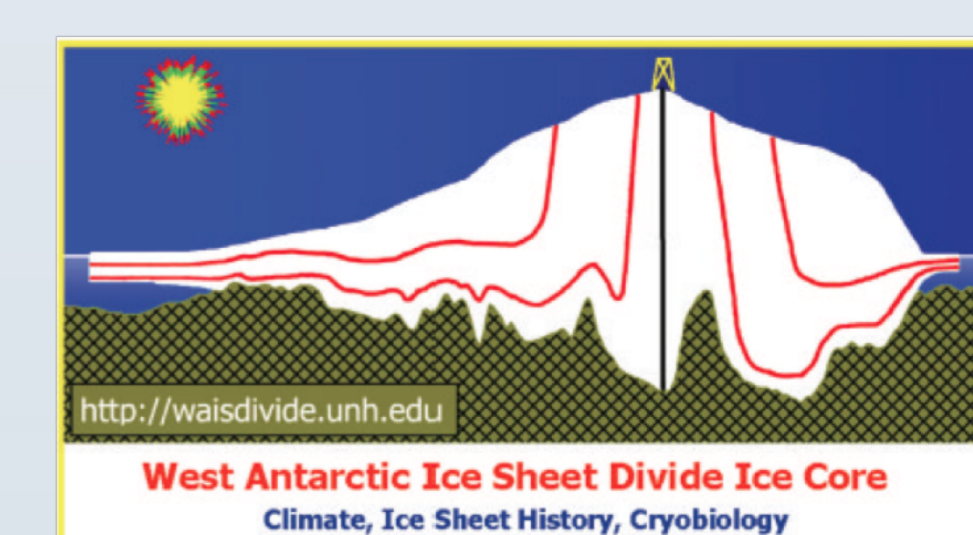
Measuring ^{17}O -excess requires exceptionally high precision (per meg) and sample reproducibility. We are continuing to pursue the shot noise limits of the mass spectrometer to achieve the best precision we can and to hone the ^{17}O Water Fluorination process for consistent reproducibility of WAIS water standards, before running actual ice-to-water samples

References

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Further Information

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<http://depts.washington.edu/isolab/>