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## Measurement of $\delta^{18}\text{O}$ , $\delta^{17}\text{O}$ , and $^{17}\text{O}$ -excess in Water by Off-Axis Integrated Cavity Output Spectroscopy and Isotope Ratio Mass Spectrometry

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### Abstract

Stable isotopes of water have long been used to improve understanding of the hydrological cycle, catchment hydrology, and polar climate. Recently, there has been increasing interest in measurement and use of the less-abundant  $^{17}\text{O}$  isotope in addition to  $^2\text{H}$  and  $^{18}\text{O}$ . Off-axis integrated cavity output spectroscopy (OA-ICOS) is demonstrated for accurate and precise measurements  $\delta^{18}\text{O}$ ,  $\delta^{17}\text{O}$ , and  $^{17}\text{O}$ -excess in liquid water. OA-ICOS involves no sample conversion and has a small footprint, allowing measurements to be made by researchers collecting the samples. Repeated (514) high-throughput measurements of the international isotopic reference water standard GISP demonstrate the precision and accuracy of OA-ICOS:  $\delta^{18}\text{O}_{\text{VSMOW-SLAP}} = -24.74 \pm 0.07 \text{‰}$  ( $1\sigma$ ) and  $\delta^{17}\text{O}_{\text{VSMOW-SLAP}} = -13.12 \pm 0.05 \text{‰}$  ( $1\sigma$ ). For comparison, the IAEA value for  $\delta^{18}\text{O}_{\text{VSMOW-SLAP}}$  is  $-24.76 \pm 0.09 \text{‰}$  ( $1\sigma$ ) and an average of previously reported values for  $\delta^{17}\text{O}_{\text{VSMOW-SLAP}}$  is  $-13.12 \pm 0.06 \text{‰}$  ( $1\sigma$ ). Multiple (26) high-precision measurements of GISP provide a  $^{17}\text{O}$ -excess<sub>VSMOW-SLAP</sub> of  $23 \pm 10$  per meg ( $1\sigma$ ); an average of previously reported values for  $^{17}\text{O}$ -excess<sub>VSMOW-SLAP</sub> is  $22 \pm 11$  per meg ( $1\sigma$ ). For all these OA-ICOS measurements, precision can be further enhanced by additional averaging. OA-ICOS measurements were compared with two independent isotope ratio mass spectrometry (IRMS) laboratories and shown to have comparable accuracy and precision as the current fluorination-IRMS techniques in  $\delta^{18}\text{O}$ ,  $\delta^{17}\text{O}$ , and  $^{17}\text{O}$ -excess. The ability to measure accurately  $\delta^{18}\text{O}$ ,  $\delta^{17}\text{O}$ , and  $^{17}\text{O}$ -excess in liquid water inexpensively and without sample conversion is expected to increase vastly the application of  $\delta^{17}\text{O}$  and  $^{17}\text{O}$ -excess measurements for scientific understanding of the water cycle, atmospheric convection, and climate modeling among others.

### Introduction

Stable isotopic compositions of water, particularly  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$ , have long been used to improve understanding of the hydrological cycle,<sup>1</sup> catchment hydrology,<sup>2</sup> and polar climate.<sup>e.g. 3</sup> The combination of the measurements,  $d\text{-excess} = \delta^2\text{H} - 8\delta^{18}\text{O}$ , roughly describes the degree to which  $\delta^2\text{H}$  values vary from what would be expected at low and temperate latitudes if equilibrium processes were solely responsible for the relationship

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between  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$  values. Kinetic fractionation processes, such as diffusive processes associated with evaporation, are partially responsible for the variation in *d-excess* which varies as a function of both evaporative temperature and humidity.<sup>1, 3</sup> Given its sensitivity to environmental conditions of evaporation, *d-excess* has been used extensively to characterize climate and hydrological conditions today and in the past.<sup>e.g. 3-6</sup>

Recently, there has been increasing interest in measurement and use of the less-abundant  $^{17}\text{O}$  isotope in addition to  $^2\text{H}$  and  $^{18}\text{O}$ . Similarly to *d-excess*, the deviation from an expected relationship between  $^{17}\text{O}/^{16}\text{O}$  and  $^{18}\text{O}/^{16}\text{O}$  ratios has been defined by  $^{17}\text{O-excess} = \ln(\delta^{17}\text{O} + 1) - 0.528\ln(\delta^{18}\text{O} + 1)$  and variation in  $^{17}\text{O-excess}$  in waters is dominated by kinetic fractionation effects.<sup>7</sup> However  $^{17}\text{O-excess}$  is relatively insensitive to temperature and thus can be used as a direct proxy for humidity at the region of evaporation.<sup>7, 8</sup> Combined measurements of *d-excess* and  $^{17}\text{O-excess}$  allow researchers to understand more fully the contributions of both temperature and relative humidity to water isotope fractionation, thus improving atmospheric models and understanding of climate processes.<sup>e.g. 8</sup> Recent advances using fluorination coupled to isotope ratio mass spectrometry (IRMS) have made possible the precise measurements of  $^{17}\text{O-excess}$  in waters; these measurements have been applied to ice,<sup>8, 9</sup> meteoric waters,<sup>10</sup> and African precipitation.<sup>11</sup>

The variation in  $^{17}\text{O-excess}$  in meteoric waters is generally a very small quantity (reported in per meg, parts per million) and meaningful measurements require extremely high precision. Careful studies of  $^{17}\text{O-excess}$  typically cite precisions for  $^{17}\text{O-excess}$  of less than 10 per meg,<sup>e.g. 8, 12, 13</sup> an order of magnitude smaller than the cited precisions for both  $\delta^{18}\text{O}$  and  $\delta^{17}\text{O}$ . While at first glance it seems impossible to measure a derived quantity to better precision than its constituent measurements, the improvement in precision is real and is described in detail by Landais et al.<sup>14</sup> and Luz and Barkan.<sup>10</sup> Briefly, the definition of  $^{17}\text{O-excess}$  is derived from the measured global meteoric water line (GMWL) for  $\delta^{18}\text{O}$  and  $\delta^{17}\text{O}$ , so that  $^{17}\text{O-excess}$  values indicate deviations from the GMWL. The GMWL is itself naturally created by the isotopic fractionation of water due to vapor-liquid kinetics and equilibrium and vapor diffusion in air, and thus the slope of 0.528 in the  $^{17}\text{O-excess}$  definition<sup>12, 15</sup> is extremely close to the liquid-vapor equilibrium fractionation slope of 0.529<sup>12</sup> and reasonably close to the kinetic evaporation slope of 0.518.<sup>7</sup> The consequence of this is that any measurement errors which result from mass-dependent equilibrium fractionation of a sample will cancel nearly perfectly on calculation of  $^{17}\text{O-excess}$ , provided that  $\delta^{18}\text{O}$  and  $\delta^{17}\text{O}$  are measured on the same sample. This cancellation of mass-dependent equilibrium fractionation errors can thus enable measurements of  $^{17}\text{O-excess}$  that are much more precise than the constituent measurements of  $\delta^{18}\text{O}$  and  $\delta^{17}\text{O}$ .

All of the previously published measurements of  $^{17}\text{O-excess}$  in water have utilized fluorination of water into  $\text{O}_2$  followed by IRMS (see e.g. Baker *et al.*<sup>16</sup> and Barkan and Luz<sup>12</sup> and references therein). This IRMS method requires chemical conversion using toxic reagents and measurement on sophisticated and expensive equipment with highly-skilled operators; only a handful of laboratories worldwide currently have this measurement capability. In this work we demonstrate for the first time the use of off-axis integrated cavity output spectroscopy (OA-ICOS) to directly measure  $\delta^{18}\text{O}$ ,  $\delta^{17}\text{O}$ , and  $^{17}\text{O-excess}$  in liquid water. OA-ICOS involves no sample conversion and has a small footprint, allowing measurements to be made by researchers collecting the samples. This study demonstrates by comparison with two independent IRMS laboratories that OA-ICOS measurements of  $\delta^{18}\text{O}$ ,  $\delta^{17}\text{O}$ , and  $^{17}\text{O-excess}$  in liquid water achieve accuracy and precision comparable to the fluorination and IRMS method.

## Experimental

### Off-Axis ICOS Analysis

We utilized a commercially-available, OA-ICOS laser absorption spectrometer (Los Gatos Research (LGR) Triple Isotope Water Analyzer (TIWA-45EP)) for simultaneous direct measurement of the  $^2\text{H}/^1\text{H}$ ,  $^{18}\text{O}/^{16}\text{O}$ , and  $^{17}\text{O}/^{16}\text{O}$  stable isotope ratios in liquid water. The OA-ICOS instrument employs near-infrared tunable diode laser absorption spectroscopy with the laser coupled off-axis to a high-finesse optical cavity<sup>17</sup> to provide highly accurate quantification of  $\delta^{18}\text{O}$ ,  $\delta^{17}\text{O}$ , and  $\delta^2\text{H}$  in injected water samples. The OA-ICOS instrument is very robust<sup>18</sup> and more compact<sup>19</sup> than the current IRMS configuration.  $^{17}\text{O}$ -excess was calculated from measurements of  $\delta^{18}\text{O}$  and  $\delta^{17}\text{O}$  according to the definition  $^{17}\text{O}$ -excess =  $\ln(\delta^{17}\text{O} + 1) - 0.528\ln(\delta^{18}\text{O} + 1)$ .<sup>7</sup> Water samples were introduced without sample conversion into the OA-ICOS instrument via a PAL HTC-xt autoinjector (CTC Analytics) equipped with a heated ( $\approx 85^\circ\text{C}$ ) injector block (LGR), where the water samples were evaporated for isotope analysis directly on the water vapor. Liquid water samples were injected into the injector block using a Hamilton 1.2  $\mu\text{L}$ , zero dead volume syringe (P/N: 203185/01).

Simultaneous measurements of  $\delta^{18}\text{O}$ ,  $\delta^{17}\text{O}$  and  $\delta^2\text{H}$  were completed at a speed of approximately 90 seconds per measurement of an individual injection. In the normal range of natural waters, LGR recommends injecting each sample 6 times and averaging the last four injections to produce a single, high-throughput sample measurement; in this way 128 sample measurements can be completed per day in addition to reference water standards. Because of the use of a large span of primary reference water standards and the desire to measure  $\delta^2\text{H}$ , as well as  $\delta^{18}\text{O}$  and  $\delta^{17}\text{O}$ , nine preparatory injections (injections which are not measured, designed to eliminate inter-sample memory) followed by 5 measurement injections were run for each sample in this study to overcome memory effects (see discussion below). The last four injections were averaged to produce a single, high-throughput (HT) sample measurement. Multiple HT measurements of the same sample can be averaged to improve measurement precision as described below.  $\delta^2\text{H}$  values, while measured throughout this study, are outside the scope of this manuscript and will be discussed in a future manuscript. Primary isotopic reference water standards were interleaved with samples throughout each run; data normalization is described in detail below.

### Off-Axis ICOS Data Processing

Processing of raw instrumental OA-ICOS data proceeded in the following steps. First, any injection with measured water number density outside of the manufacturer's suggested range of  $2 - 4.5 \times 10^{16} \text{H}_2\text{O}$  molecules/ $\text{cm}^3$  was discarded. Second, any injection for which the water had not fully evaporated prior to measurement of the isotope ratios was discarded. Incomplete evaporation can be caused by septum pieces, salts, or other debris inside the injector block. Incomplete evaporation was detected by examining the standard deviation of the measured water number density ( $\sigma_{\text{nmeas}}$ ) as reported by the instrument. Injections with a  $\sigma_{\text{nmeas}}$  more than three standard deviations higher than the average  $\sigma_{\text{nmeas}}$  for the analysis were discarded. Any measurement set (typically a 20 hour run sequence of interleaved samples and standards) with more than 2% of injections rejected by the preceding two filters was repeated.

Third, a mathematical injected volume correction was applied similar to that described by Lis et al.<sup>20</sup> This type of correction commonly is called a "linearity correction" in IRMS data reductions. A single isotopic reference water was measured on the analyzer at varying injected volumes between 600 and 1200 nL. The measured water number density ( $n_{\text{meas}}$ )

was then normalized,  $N = (n_{\text{meas}} - n^*)/n^*$ , where  $n^* = 3 \times 10^{16}$  molecules/cm<sup>3</sup>. For each isotope, the measured isotope ratios of the isotopic reference water,  $R(^{18}\text{O}/^{16}\text{O})$  and  $R(^{17}\text{O}/^{16}\text{O})$ , were plotted versus the normalized injected volumes and a linear least-squares fit was utilized to determine the slope of the injected volume effect. The slopes, one for each isotope, remained relatively constant over the six month analysis period. For each measurement injection, the measured water number density was normalized and then multiplied by the previously-determined slopes to establish the ratio correction. The injected volume correction was applied separately for each isotope to each injection in an analysis before further processing. After the above processing, the isotope ratios of the final four injections of each sample were averaged to produce raw isotope ratios,  $R(^{18}\text{O}/^{16}\text{O})$  and  $R(^{17}\text{O}/^{16}\text{O})$ , which were then normalized as described below. The average of the last four injections of each sample produced the final, measured value for that sample and is herein referred to as an individual high-throughput (HT) sample measurement. Multiple HT measurements can be averaged to improve measurement precision of all isotope analyses, as is described below for averages of 20 HT measurements, herein referred to as high-precision (HP) sample measurements.

### Isotope Ratio Mass Spectrometric Analysis

Isotope ratio mass spectrometric (IRMS) analyses were performed at both the Laboratoire des Sciences du Climat et l'Environnement (LSCE) and Johns Hopkins University (JHU). The analytical approaches at both laboratories are based on methods outlined by Baker et al.<sup>16</sup> and modified by Luz and Barkan.<sup>12</sup> Briefly, 2–3  $\mu\text{L}$  of water was fluorinated using  $\text{CoF}_3$  under helium flow to quantitatively produce  $\text{O}_2$ .  $\text{O}_2$  was separated from helium on a molecular sieve trap immersed in liquid nitrogen and finally trapped by liquid helium for mass spectrometric analysis. Mass Spectrometry was performed on a dual-inlet Thermo MAT 253 mass spectrometer which allows simultaneous measurements of  $m/z$  32, 33, and 34.

IRMS measurements at JHU used a modified fluorination line similar to that described by Schoenemann et al.<sup>13</sup> All JHU IRMS measurements were run against a working  $\text{O}_2$  reference gas during 7 sequences of 10 dual inlet runs. The working  $\text{O}_2$  reference was routinely calibrated by analyzing the International Atomic Energy Agency (IAEA) primary reference water standards Vienna Standard Mean Ocean Water 2 (VSMOW2) and Standard Light Arctic Precipitation 2 (SLAP2)<sup>21</sup> as part of the analytical sequence. Using this procedure, a maximum of 8 total waters (including references) can be processed and measured per day at JHU.

IRMS measurements at LSCE were run against a working  $\text{O}_2$  isotopic reference standard during 2 sequences of 16 dual inlet runs. The working  $\text{O}_2$  standard was calibrated by analyzing VSMOW2 and SLAP2. Every day, one or two isotopic reference waters, themselves also calibrated against VSMOW2 and SLAP2, were processed together with the samples. In order to avoid any memory effects, blanks were run between samples any time their  $\delta^{18}\text{O}$  differences exceed 3 ‰. Using this procedure, 4 to 5 duplicate samples were processed and measured per day at LSCE in addition to isotopic reference waters.

### Data Normalization

In order to make meaningful comparisons of isotope measurements between laboratories, a common data normalization scheme is necessary. All three laboratories involved in this comparison have utilized the primary isotopic reference water standards VSMOW2 and SLAP2 with the normalization proposed by Schoenemann et al.<sup>13</sup> Specifically, VSMOW2 values of  $\delta^{18}\text{O}_{\text{VSMOW-SLAP}} = 0 \pm 0.02$  ‰<sup>21</sup> and  $\delta^{17}\text{O}_{\text{VSMOW-SLAP}} = 0 \pm 0.02$  ‰<sup>22</sup> and SLAP2 values of  $\delta^{18}\text{O}_{\text{VSMOW-SLAP}} = -55.5 \pm 0.02$  ‰<sup>21</sup> and  $^{17}\text{O-excess}_{\text{VSMOW-SLAP}} = 0$

( $\delta^{17}\text{O}_{\text{VSMOW-SLAP}} \approx -29.6986 \text{ ‰}$ )<sup>13</sup> were used in all calculations. The  $^{17}\text{O}$ -excess<sub>VSMOW-SLAP</sub> values for both VSMOW2 and SLAP2 were taken to be defined as zero and thus considered to have no uncertainty for propagation of errors.<sup>13</sup> The uncertainty of the  $\delta^{17}\text{O}_{\text{VSMOW-SLAP}}$  of SLAP2 was calculated from the uncertainty of  $\delta^{18}\text{O}_{\text{VSMOW-SLAP}}$  and  $^{17}\text{O}$ -excess<sub>VSMOW-SLAP</sub> and determined to be 0.02 ‰. In all cases, the uncertainties of the measured  $\delta^{18}\text{O}$  and  $\delta^{17}\text{O}$  values have been convolved with the uncertainties of the reported VSMOW2 and SLAP2 values to report values on the VSMOW-SLAP scale. No convolution has been used in the case of  $^{17}\text{O}$ -excess as the standard values are taken to have zero uncertainty.

The OA-ICOS instrument outputs raw data as isotope ratios; conversion to  $\delta$ -values utilized the VSMOW isotope ratios  $R(^{18}\text{O}/^{16}\text{O}) = 2005.20 \times 10^{-6}$ <sup>23</sup> and  $R(^{17}\text{O}/^{16}\text{O}) = 379.9 \times 10^{-6}$ .<sup>24</sup> Note that while these ratios were measured on VSMOW, measurements of VSMOW and VSMOW2 show that they have indistinguishable  $\delta^{18}\text{O}$  and  $\delta^{17}\text{O}$  values,<sup>22</sup> and thus indistinguishable  $R(^{18}\text{O}/^{16}\text{O})$  and  $R(^{17}\text{O}/^{16}\text{O})$  values. Normalization was completed on ratios after which normalized ratios were converted into normalized  $\delta$ -values vs VSMOW-SLAP. Normalization in ratio space is algebraically identical to normalization in  $\delta$ -value space; the order of operations is insignificant. Dual-inlet IRMS instruments output raw data in both ratios and  $\delta$ -values relative to an internal  $\text{O}_2$  working isotopic reference standard; normalization was completed on raw  $\delta$ -values to produced normalized  $\delta$ -values vs. VSMOW-SLAP.

For OA-ICOS measurements, the primary isotopic reference water standards VSMOW2 and SLAP2 were interleaved throughout each measurement set, typically > 10 measurements of each standard in an approximately 20 hour run. In order to minimize the effects of instrumental drift, a spline calibration was used. Specifically, for each standard, a cubic spline function was used to interpolate between measurements of that standard to produce a local value of each standard for every measurement (either standard or sample). For each standard or sample measurement, the local values of SLAP2 and VSMOW2 were fitted to the accepted values for the standards using the 'traditional linear' method as described by Schoenemann et al.<sup>13</sup> This produced a local slope and intercept that were used to normalize the measurement to the VSMOW-SLAP scale. This procedure was completed separately for each measured isotope ratio.

## Results and Discussion

### Sample-to-sample memory

Many researchers have noted with laser-based measurements of water isotopes that there is a sample-to-sample memory effect between samples (e.g. <sup>20, 25-27</sup>). This memory effect is likely due to a combination of factors, including mixing of waters and carryover by the sampling syringe<sup>28</sup> as well as the tendency of water to adhere to the internal surfaces of the instrument.<sup>20</sup> Sample-to-sample memory is particularly apparent for large changes in isotope ratio and for the  $^2\text{H}$  isotope. Figure 1a illustrates the memory observed (from all causes) with the TIWA instrument for the transition from SLAP2 to VSMOW2 ( $-55.5 \text{ ‰}$  to 0 for  $\delta^{18}\text{O}$ ), which is among the largest differences encountered between natural waters. Fourteen injections of VSMOW2 were performed directly after 14 injections of SLAP2. The solid line is at 0, the known value for VSMOW2, and the dashed lines are at  $\pm 0.2 \text{ ‰}$ , approximately the  $1\sigma$  measurement uncertainty of a single injection (as noted above, four injections are generally averaged to produce a single, HT measurement with the factor of two improvement in precision). For the SLAP2 to VSMOW2 transition, for  $\delta^{18}\text{O}$  (black squares), the first four injections and for  $\delta^{17}\text{O}$  (red circles) the first two injections fall outside of the  $\pm 0.2 \text{ ‰}$  band. In contrast, for  $\delta^2\text{H}$  (see inset) the first 6 injections fall outside of the  $1\sigma$  uncertainty band for a single injection of  $1.0 \text{ ‰}$ . For smaller isotopic composition

changes in the common range of natural waters, < 25 ‰ change in  $\delta^{18}\text{O}$  and < 13 ‰ change in  $\delta^{17}\text{O}$ , two or fewer injections fall outside of the  $1\sigma$  uncertainty band for all three isotopes. Figure 1b illustrates this case on VSMOW2 measured immediately after Greenland Ice Sheet Precipitation (GISP), a transition from  $-24.76$  ‰ to  $0$  ‰ for  $\delta^{18}\text{O}$ .<sup>29</sup> Note that the scales on both panels are the same to facilitate comparison. These data suggest that for measurements of  $\delta^{18}\text{O}$ ,  $\delta^{17}\text{O}$ , and  $^{17}\text{O}$ -excess, depending on the largest isotope step encountered, memory can be addressed using 1 – 4 preparatory injections on the TIWA instrument followed by 4 measurement injections. If  $\delta^2\text{H}$  measurements are also desired, a larger number of preparatory injections may be necessary. It is also possible to utilize mathematical memory corrections (see *e.g.* <sup>25–27</sup>); these are outside the scope of this manuscript and will be discussed in a future manuscript. The accuracy and precision of the isotope measurements described herein demonstrate the suitability of this procedure to effectively handle sample-to-sample memory.

### Measurement Precision and Accuracy of $\delta^{18}\text{O}$ and $\delta^{17}\text{O}$

The international isotopic reference water standard GISP was analyzed on the OA-ICOS instrument to produce 514 HT measurements over a 6 month period. Each instrumental analysis was constructed as described above, with VSMOW2 and SLAP2 interleaved throughout the analysis. All data was processed with the injected volume correction and normalized with the spline calibration as described above. Figure 2 shows the excellent measurement precision and accuracy for these HT measurements, with an average  $\delta^{18}\text{O}_{\text{VSMOW-SLAP}} = -24.74 \pm 0.07$  ‰ ( $1\sigma$ ) and  $\delta^{17}\text{O}_{\text{VSMOW-SLAP}} = -13.12 \pm 0.05$  ‰ ( $1\sigma$ ). The best-fit normal distribution for  $\delta^{18}\text{O}_{\text{VSMOW-SLAP}}$  shows a center value of  $-24.74$  ‰ with a half width half max (HWHM) of  $0.06$  ‰. The IAEA reported value for  $\delta^{18}\text{O}_{\text{VSMOW-SLAP}}$  in GISP is  $-24.76 \pm 0.09$  ‰ ( $1\sigma$ ).<sup>29</sup> The best-fit normal distribution for  $\delta^{17}\text{O}_{\text{VSMOW-SLAP}}$  shows a center value of  $-13.12$  ‰ with a HWHM of  $0.04$  ‰. For comparison, the collected average of 5 previously reported IRMS measurements of  $\delta^{17}\text{O}_{\text{VSMOW-SLAP}}$  in GISP was  $-13.12 \pm 0.06$  ‰ ( $1\sigma$ ).<sup>13</sup> Allan deviation analyses<sup>30</sup> (not shown) for both  $\delta^{18}\text{O}$  and  $\delta^{17}\text{O}$  show that averaging improves the precision of the measurements to an instrumental noise floor of approximately  $0.02$  ‰ in  $\delta^{18}\text{O}$  and  $0.01$  ‰ in  $\delta^{17}\text{O}$ . This precision is achieved by averaging 20 HT measurements to produce a single high-precision (HP) measurement as described below. Throughout this manuscript, these values, convolved with the uncertainties of the primary isotopic reference water standards, are reported as the measurement uncertainties for high-precision measurements of  $\delta^{18}\text{O}_{\text{VSMOW-SLAP}}$  and  $\delta^{17}\text{O}_{\text{VSMOW-SLAP}}$  in any case where using the standard error of the mean would result in an error lower than these noise floors.

Instrumental accuracy was further demonstrated by measuring GISP and four commercially-available United States Geological Survey (USGS) isotopic reference waters<sup>31–34</sup> by OA-ICOS and by IRMS as described above. The data are summarized in Table 1. Figure 3 shows the measurement accuracy of measurements by OA-ICOS and IRMS for GISP and the four USGS isotopic reference waters. For  $\delta^{18}\text{O}$ , measurements are plotted as the difference between each measurement and the published  $\delta^{18}\text{O}$  value.<sup>29, 31–34</sup> Neither IAEA nor USGS publishes values for  $\delta^{17}\text{O}$  of reference waters. For this reason,  $\delta^{17}\text{O}$  values for GISP are shown as the difference between each measurement and an average of collected previously reported values.<sup>13</sup>  $\delta^{17}\text{O}$  values for the USGS isotopic reference waters are shown as the difference between each measurement and the average of the three experimental measurements inversely weighted by the uncertainty. Error bars shown represent the standard error of the mean for IRMS measurements and the measured limit of instrumental precision as described above for OA-ICOS. The correlation of measurement errors between  $\delta^{18}\text{O}$  and  $\delta^{17}\text{O}$  described in the introduction is clearly evident in Figure 3.

## Measurement Precision and Accuracy of $^{17}\text{O}$ -excess

$^{17}\text{O}$ -excess was calculated from the aforementioned OA-ICOS measurements of the international isotopic reference water standard GISP. In order to reach the extremely high precision needed for meaningful measurements of  $^{17}\text{O}$ -excess by either IRMS or OA-ICOS, averaging of multiple individual measurements is required. The precision achieved as a function of the number of averaged OA-ICOS HT measurements is shown in Figure 4(a). This Allan deviation<sup>30</sup> plot clearly demonstrates that averaging improves the measurement precision; the solid line shows the case of perfect white noise averaging, which reduces the standard deviation by the square root of the number of averaged measurements. Typical IRMS measurements average 70–100 individual dual-inlet measurements of  $\text{O}_2$  gas from a water sample to produce a single, high-precision measurement of  $^{17}\text{O}$ -excess and typically report a measurement precision of 5–10 per meg ( $1\sigma$ ).<sup>e.g. 8, 12, 13</sup> Individual HT measurements on the OA-ICOS instrument are averages of 4 injections; therefore, averaging of 20 HT OA-ICOS measurements produces a high-precision (HP) measurement which is based on 80 measured injections of the water sample, comparable to the IRMS technique. Using this procedure, 6–7 HP sample measurements in the normal range of natural waters can be completed per day in addition to standards. Figure 4(b) shows the excellent measurement precision achieved with HP OA-ICOS measurements of  $^{17}\text{O}$ -excess, with an average  $^{17}\text{O}\text{-excess}_{\text{VSMOW-SLAP}} = 23 \pm 10$  per meg ( $1\sigma$ ). The best-fit normal distribution for  $^{17}\text{O}\text{-excess}_{\text{VSMOW-SLAP}}$  of GISP shows a center value of 23 per meg with a half width half max of 9 per meg. For comparison, the collected average of 3 previously reported IRMS measurements of  $^{17}\text{O}\text{-excess}_{\text{VSMOW-SLAP}}$  in GISP was  $22 \pm 11$  per meg ( $1\sigma$ ).<sup>13</sup>

Figure 5 shows the excellent measurement agreement among  $^{17}\text{O}$ -excess measurements by OA-ICOS and IRMS for GISP and the four USGS isotopic reference waters. Error bars represent the standard error of the mean for multiple HP measurements of each sample. The line behind the GISP columns shows the collected average of 3 previously reported IRMS measurements.<sup>13</sup> These data all illustrate the utility of  $^{17}\text{O}$ -excess measurements in distinguishing among natural waters; note that USGS45 (Biscayne Aquifer Drinking Water) and USGS48 (Puerto Rico Precipitation) have essentially identical  $\delta^{18}\text{O}$  and  $\delta^{17}\text{O}$  values, but significantly different  $^{17}\text{O}$ -excess values. The exceptional precision for  $^{17}\text{O}$ -excess measurements among different laboratories and between methods makes it possible to differentiate the  $^{17}\text{O}$ -excess composition of these two waters. Table 1 summarizes all IRMS and OA-ICOS measurements of GISP and the USGS isotopic reference waters. Averages are weighted by the inverse of the listed precision of the measurements. Uncertainties listed are standard errors of the mean for IRMS measurements, weighted standard deviations for the averages of the three reported experimental measurements, the published standard deviation for GISP, and the published 95-percent confidence intervals for the USGS values.

Uncertainties for OA-ICOS are listed as the standard error of the mean for  $^{17}\text{O}$ -excess and as the measured limit of instrumental precision for  $\delta^{18}\text{O}$  and  $\delta^{17}\text{O}$  as described above.

## Conclusions

In this work we demonstrate for the first time the use of off-axis integrated cavity output spectroscopy (OA-ICOS) to measure  $\delta^{18}\text{O}$ ,  $\delta^{17}\text{O}$ , and  $^{17}\text{O}$ -excess in liquid water. OA-ICOS involves no sample conversion and has a small footprint, allowing measurements to be made by researchers collecting the samples. Repeated (514) high-throughput measurements of the international standard isotopic reference water GISP made over a 6 month period demonstrate the precision and accuracy of the OA-ICOS instrument:  $\delta^{18}\text{O}_{\text{VSMOW-SLAP}} = -24.74 \pm 0.07$  ‰ ( $1\sigma$ ) and  $\delta^{17}\text{O}_{\text{VSMOW-SLAP}} = -13.12 \pm 0.05$  ‰ ( $1\sigma$ ). For comparison, the IAEA reported value for  $\delta^{18}\text{O}_{\text{VSMOW-SLAP}}$  in GISP is  $-24.76 \pm 0.09$  ‰ ( $1\sigma$ )<sup>29</sup> and the average of 5 previously reported measurements of  $\delta^{17}\text{O}_{\text{VSMOW-SLAP}}$  in GISP is  $-13.12 \pm$

0.06 ‰ ( $1\sigma$ ).<sup>13</sup> To achieve the high precision needed for meaningful  $^{17}\text{O}$ -excess measurement, we average 20 high-throughput OA-ICOS measurements to get a single, high-precision measurement. In this way we measure the  $^{17}\text{O}$ -excess<sub>VSMOW-SLAP</sub> of GISP as  $23 \pm 10$  per meg ( $1\sigma$ ); the average of 3 previously reported measurements of  $^{17}\text{O}$ -excess<sub>VSMOW-SLAP</sub> in GISP is  $22 \pm 11$  per meg ( $1\sigma$ ).<sup>13</sup> For OA-ICOS measurements of  $\delta^{18}\text{O}$ ,  $\delta^{17}\text{O}$ , and  $^{17}\text{O}$ -excess, precision can be enhanced further by additional averaging. OA-ICOS measurements are compared with two independent IRMS measurements of commercially available GISP and USGS isotopic reference waters and shown to have comparable accuracy and precision as fluorination followed by IRMS. The ability to measure accurately  $\delta^{18}\text{O}$ ,  $\delta^{17}\text{O}$ , and  $^{17}\text{O}$ -excess in liquid water inexpensively and without sample conversion is expected to increase vastly the application of  $\delta^{17}\text{O}$  and  $^{17}\text{O}$ -excess measurements for understanding of the water cycle, atmospheric convection, and climate modeling among others.

## Acknowledgments

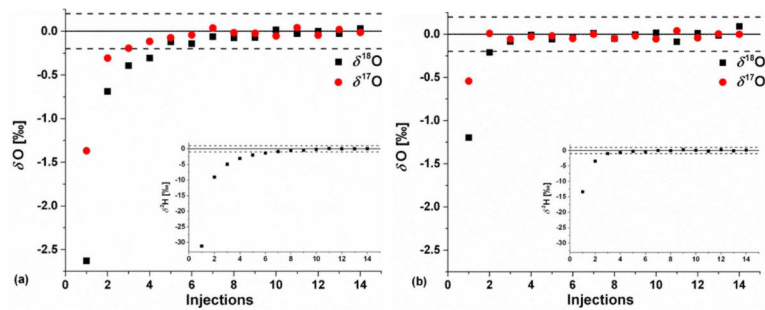
This work was supported by NIH SBIR Grant no. 1R43DK093362-01 and NASA SIBR Grant no. NNX13CA03C.  $^{17}\text{O}$ -excess measurements at LSCE were funded by the ERC Starting Grant COMBINISO n° 306045. An ACS-PRF grant (#52651-DNI2) and the Department of Earth & Planetary Sciences supported the work at JHU. A.L. would like to thank Frédéric Prié for laboratory assistance. E.B. would like to thank Spruce Schoenemann and Tyler Coplen for helpful discussion of normalization.

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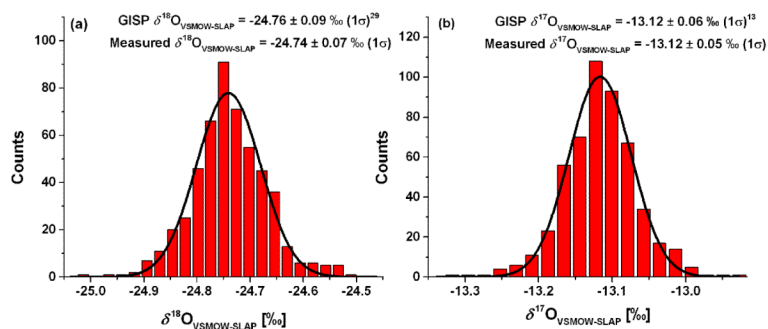


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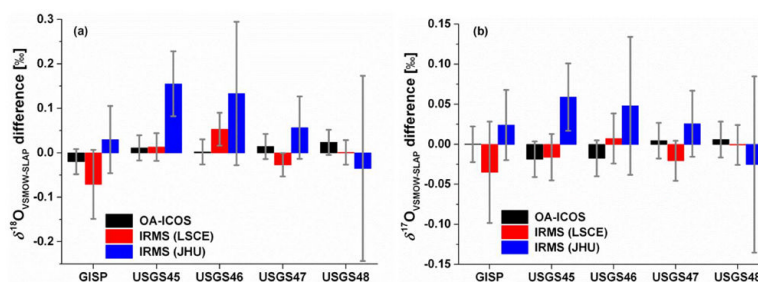


**Figure 1.**

a) Sample-to-sample memory for the transition from SLAP2 to VSMOW2 for  $\delta^{18}\text{O}$  (black squares),  $\delta^{17}\text{O}$  (red circles), and  $\delta^2\text{H}$  (inset). b) Sample-to-sample memory for the transition from GISP to VSMOW2. The solid lines show the known VSMOW2 values of 0 ‰; the dashed lines show the approximate single injection  $1\sigma$  uncertainty band for  $\delta^{18}\text{O}$  and  $\delta^{17}\text{O}$  of  $\pm 0.2$  ‰ and for  $\delta^2\text{H}$  of  $\pm 1.0$  ‰. Note that the scales on both panels are the same to facilitate comparison.

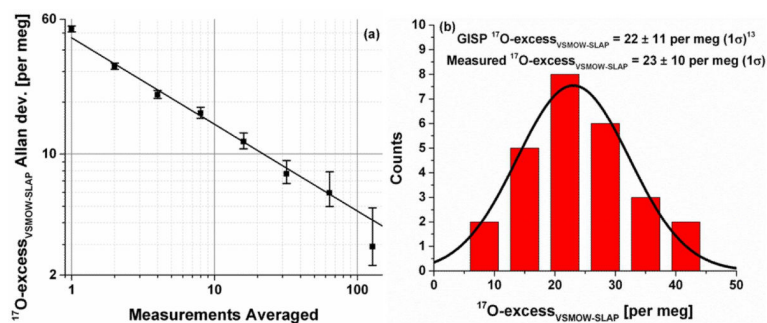


**Figure 2.** Measurement precision for 514 HT OA-ICOS measurements of GISP calibrated against VSMOW2 and SLAP2 with injected volume correction and spline calibration. Histograms with overlaid normal distribution fit for (a)  $\delta^{18}\text{O}_{\text{VSMOW-SLAP}}$  and (b)  $\delta^{17}\text{O}_{\text{VSMOW-SLAP}}$ . The average and standard deviation of the measured values are noted along with the IAEA accepted value for  $\delta^{18}\text{O}_{\text{VSMOW-SLAP}}$ <sup>29</sup> and a published average value of  $\delta^{17}\text{O}_{\text{VSMOW-SLAP}}$ <sup>13</sup> (IAEA does not list a value for  $\delta^{17}\text{O}$ ).



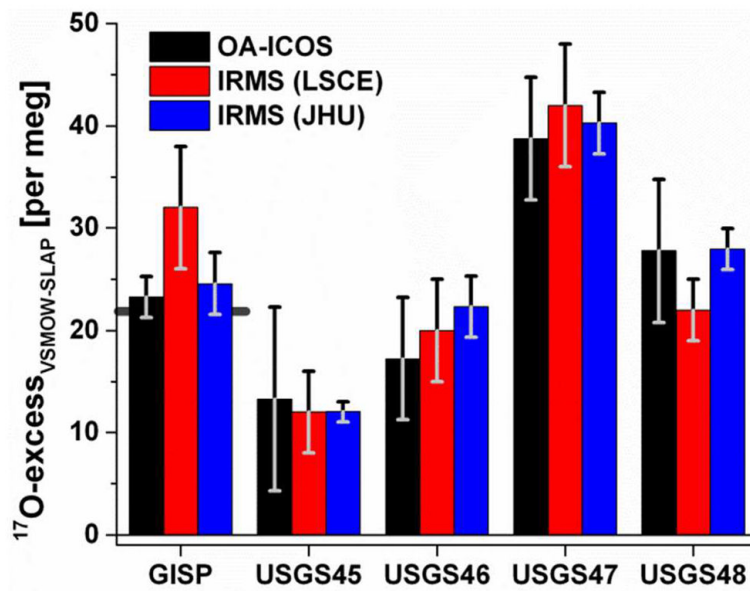
**Figure 3.**

Measurement accuracy demonstrated by measurements of GISP and four commercially-available USGS isotopic reference waters by OA-ICOS and IRMS. Measurements of  $\delta^{18}\text{O}_{\text{VSMOW-SLAP}}$  (a) are shown as differences from the values published by IAEA<sup>29</sup> and USGS<sup>32–34</sup> as appropriate. Neither IAEA nor USGS publishes values for  $\delta^{17}\text{O}$  of reference waters. Measurements of  $\delta^{17}\text{O}_{\text{VSMOW-SLAP}}$  (b) for GISP are shown as the difference between each measurement and an average of previously reported values<sup>13</sup>. Measurements of  $\delta^{17}\text{O}_{\text{VSMOW-SLAP}}$  (b) for USGS isotopic reference waters are shown as the difference between each measurement and the average of the three experimental measurements inversely weighted by the uncertainty. Error bars shown represent the standard error of the mean for IRMS measurements and the measured limit of instrumental precision for OA-ICOS.



**Figure 4.**

a) Allan deviation plot showing precision as a function of number of HT OA-ICOS measurements averaged. The solid line represents perfect averaging of white noise. b) Histogram with overlaid normal distribution fit for HP OA-ICOS measurements (averages of 20 HT measurements) of  $^{17}\text{O-excess}_{\text{VSMOW-SLAP}}$  of GISP calibrated against VSMOW2 and SLAP2 with injected volume correction and spline calibration. The average and standard deviation of the measured values are noted, along with a published average value.<sup>13</sup>



**Figure 5.** Measurement accuracy for  $^{17}\text{O-excess}_{\text{VSMOW-SLAP}}$  demonstrated by measurements of GISP and four commercially-available USGS isotopic reference waters by OA-ICOS and two independent IRMS labs. Error bars represent one standard error of the mean. The line behind the GISP columns shows the collected average of 3 previously reported IRMS measurements.<sup>13</sup>

**Table 1**

OA-ICOS and IRMS measurements of GISP and commercially available USGS isotopic reference waters. Averages are weighted by the inverse of the listed precision of the measurements. Uncertainties listed are standard errors of the mean for IRMS measurements, weighted standard deviations for the weighted averages of the three reported experimental measurements, the published standard deviation for GISP, and the published 95-percent confidence intervals for the USGS values. Uncertainties for OA-ICOS are listed as the standard error of the mean for  $^{17}\text{O}$ -excess and as the convolved measured limit of instrumental precision for  $\delta^{18}\text{O}$  and  $\delta^{17}\text{O}$ .

		# of HP measurements	$\delta^{18}\text{O}_{\text{VSMOW-SLAP}} [\text{‰}]$	$\delta^{17}\text{O}_{\text{VSMOW-SLAP}} [\text{‰}]$	$^{17}\text{O}$ -excess <sub>VSMOW-SLAP</sub> [per meg]
<b>GISP</b>	OA-ICOS	26	$-24.74 \pm 0.03$	$-13.12 \pm 0.02$	$23 \pm 2$
	IRMS (LSCE)	3	$-24.69 \pm 0.08$	$-13.08 \pm 0.06$	$32 \pm 6$
	IRMS (JHU)	9	$-24.79 \pm 0.08$	$-13.14 \pm 0.04$	$25 \pm 3$
	Wt. Average		$-24.74 \pm 0.03$	$-13.12 \pm 0.02$	$25 \pm 3$
	IAEA <sup>29</sup>		$-24.76 \pm 0.09$		
<b>USGS45</b>	OA-ICOS	4	$-2.25 \pm 0.03$	$-1.17 \pm 0.02$	$13 \pm 9$
	IRMS (LSCE)	5	$-2.25 \pm 0.03$	$-1.18 \pm 0.03$	$12 \pm 4$
	IRMS (JHU)	14	$-2.39 \pm 0.07$	$-1.25 \pm 0.04$	$12 \pm 1$
	Wt. Average		$-2.27 \pm 0.05$	$-1.19 \pm 0.03$	$12 \pm 1$
	USGS <sup>31</sup>		$-2.238 \pm 0.011$		
<b>USGS46</b>	OA-ICOS	3	$-29.80 \pm 0.03$	$-15.83 \pm 0.02$	$17 \pm 6$
	IRMS (LSCE)	3	$-29.85 \pm 0.04$	$-15.86 \pm 0.03$	$20 \pm 5$
	IRMS (JHU)	5	$-29.93 \pm 0.16$	$-15.90 \pm 0.09$	$22 \pm 3$
	Wt. Average		$-29.83 \pm 0.04$	$-15.85 \pm 0.02$	$20 \pm 2$
	USGS <sup>34</sup>		$-29.80 \pm 0.02$		
<b>USGS47</b>	OA-ICOS	3	$-19.81 \pm 0.03$	$-10.47 \pm 0.02$	$39 \pm 6$
	IRMS (LSCE)	5	$-19.77 \pm 0.03$	$-10.45 \pm 0.03$	$42 \pm 6$
	IRMS (JHU)	10	$-19.86 \pm 0.07$	$-10.49 \pm 0.04$	$40 \pm 3$
	Wt. Average		$-19.80 \pm 0.03$	$-10.47 \pm 0.02$	$40 \pm 1$
	USGS <sup>33</sup>		$-19.80 \pm 0.02$		
<b>USGS48</b>	OA-ICOS	3	$-2.25 \pm 0.03$	$-1.16 \pm 0.02$	$28 \pm 7$
	IRMS (LSCE)	3	$-2.22 \pm 0.03$	$-1.15 \pm 0.03$	$22 \pm 3$
	IRMS (JHU)	5	$-2.19 \pm 0.21$	$-1.13 \pm 0.11$	$28 \pm 2$
	Wt. Average		$-2.23 \pm 0.02$	$-1.15 \pm 0.01$	$26 \pm 3$
	USGS <sup>32</sup>		$-2.224 \pm 0.012$		