The absolute δ 18 O value for SLAP with respect to VSMOW reveals a much lower value.

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Abstract

RATIONALE: SLAP is one of the two calibration materials for the isotopic water scale. By consensus the established $\delta\,^{18}O$ value is -55.5indications that $\delta\,^{18}O_{SLAP}$ is significantly more negative. The real $\delta\,^{18}O_{SLAP}$ value as such does not influence the isotopic water scale, however knowledge of the size of isotopic scale contraction in stable isotope measurements is vital for second order isotopes. In this study quantification of $\delta\,^{18}O_{SLAP}$ with respect to $\delta\,^{18}O_{VSMOW}$ is described. **METHODS:** SLAP-like water was quantitatively mixed with highly ^{18}O enriched water to mimic VSMOW. The ^{18}O concentration was determined using an electron ionization quadrupole mass spectrometer. The isotopic composition of the SLAP-like and VSMOW-like waters were measured with an optical spectrometer, alongside real VSMOW and SLAP. **RESULTS:** This study resulted in a much more depleted $\delta\,^{18}O$ value for SLAP than expected. The averaged outcome of 7 independent experiments is $\delta\,^{18}O_{SLAP}$ -56.33 ± 0.03between the actual isotopic measurements of even the most carefully operating groups and the true $\delta\,^{18}O$ value. **CONCLUSIONS:** Although this finding as such does not influence the use of the VSMOW-SLAP scale, it raises the intriguing question what we actually measure with our instruments, and why even a fully corrected measurement can be so far off. Our result has consequences for issues like the transfer of $\delta\,^{18}O$ from and to the VPDB scale, various fractionation factors, and the $\Delta\,^{17}O$. The absolute ^{18}O abundance for SLAP was determined at 1.88798 (43) x 10^{-3} based on the absolute ^{18}O abundance of VSMOW and the presented $\delta\,^{18}O_{SLAP}$ in this paper.

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RESULTS: This study resulted in a much more depletedδ ^{18}O value for SLAP than expected. The averaged outcome of 7 independent experiments isδ $^{18}O_{SLAP}$ -56.33 $\pm$ 0.03large discrepancy between the actual isotopic measurements of even the most carefully operating groups and the trueδ ^{18}O value.

CONCLUSIONS: Although this finding as such does not influence the use of the VSMOW-SLAP scale, it raises the intriguing question what we actually measure with our instruments, and why even a fully corrected measurement can be so far off. Our result has consequences for issues like the transfer ofδ ^{18}O from and to the VPDB scale, various fractionation factors, and theΔ ^{17}O. The absolute ^{18}O abundance for SLAP was determined at 1.88798 (43) x 10^{-3} based on the absolute ^{18}O abundance of VSMOW and the presentedδ $^{18}O_{SLAP}$ in this paper.

Key Words

Water isotopic scale, SLAP, VSMOW, δ ^{18}O, calibration, IRMS, optical spectroscopy, electron ionization quadrupole mass spectrometer (EI-QMS), ^{18}O abundance, VSMOW-CO_2, VPDB-CO_2

1. INTRODUCTION

The stable isotope scale of water has been successfully established and maintained by the two primary reference waters: VSMOW and SLAP. In principle, only one reference material per isotope and per medium would be needed to define the isotopic scale, but two-point calibration leads to a dramatic improvement in inter-laboratory comparisons, due to various and variable scale contraction processes occurring in each measurement process.

In 1976 during a consultants' meeting on stable isotopes at the IAEA in Vienna, δ ^{18}O measurements of SLAP from 45 laboratories were evaluated. The data showed a rather large spread with measurements ranging between was from -54.53averagedδ ^{18}O value for SLAP was -55.49the standard deviation was 0.55outliers (-49.2 and -53.92thatδ ^{18}O SLAP would be established at the consensus value of -55.5

For deuterium, the other stable isotope of water, it is possible to (re)produce the primary reference waters based on gravimetric mixtures of isotopically pure waters. In this way, the absolute deuterium abundances of VSMOW and SLAP has been precisely determined by several authors (Hagemann[4], De Wit[5], Tse[6]).

A similar experiment for oxygen is much harder, as pure^{18}O and ^{16}O waters are not available. Only (Baertschi[7]) has performed a very extensive experiment, resulting in the absolute ^{18}O abundance of VSMOW, with a relative precision of 0.2

In this study, we take the next step, namely determination of theδ ^{18}O of SLAP with respect to VSMOW. Instead of determining the absolute abundance of SLAP, we focus on the relative difference in δ ^{18}O between VSMOW and SLAP, which we aim to achieve with much higher precision ([?] 0.05way, we achieve a more accurate S.I. traceable result for the VSMOW-SLAP scale.

We quantify the difference in δ ^{18}O between VSMOW and SLAP by gravimetrical mixing of a SLAP-like water with highly^{18}O enriched water to mimic VSMOW and compare this with real VSMOW.

Although the real δ $^{18}O_{SLAP}$value as such, does not influence the use of the VSMOW-SLAP scale, the various measurements from Gonfiantini[3] from -54.53 to -56.5Verkouteren and Klinedinst[1], Barkan and Luz[8], pointed out by Kaiser[9], from -55.11 to -56.18is. This real value can play an important role in understanding IRMS issues, such as scale contraction caused by memory effects. Understanding such IRMS side-effects is essential to work with a well-maintained instrument and for correcting measurements accordingly. Ideally, isotopic measurements from mass spectrometers and optical spectroscopic instruments, should be very close to their actual values. This is especially important if the isotopic values for different materials have to be compared, for example δ ^{18}O in carbonates, or in atmospheric CO_2, in relation to that of water. Furthermore, recent years have seen more complex, 'second order' isotope work, like exploiting the very small differences in behavior between ^{17}O and ^{18}O (expressed as ^{17}O excess, Δ^{17}O) (Hofmann[10], Landais[11]) and the deviation from stochastic distribution of the rare isotopes in molecules ('clumped isotopes') (Eiler[12], Bernasconi[13]). Also in these fields, understanding (and correcting for) instrument-related isotope effects is crucial.

2. EXPERIMENTAL SETUP AND METHOD

Our experiments were aimed at quantifying the difference in$\delta\,^{18}$O between VSMOW and SLAP by producing a surrogate VSMOW by gravimetrical mixing of a SLAP-like water with highly^{18}O enriched water, and compare this surrogate with real VSMOW. To this end, several instruments and waters and procedures were used, which are described in the next section.

2.1 Water portions.

For these experiments, a large batch (20 liter) of Antarctic water was made available to us by the isotope hydrology laboratory of the IAEA in Vienna. Its $\delta\,^{18}$O value was even slightly more negative than that of SLAP. Portions of 1 liter of this batch were mixed with demineralized Groningen tap water to mimic SLAP. Such large amounts of water were needed to reach the accuracy goal of [?] 0.05result for SLAP, because of gravimetric/weighing and sample handling precision limitations. Obviously, such quantities of the real SLAP were out of the question.

The reference waters SLAP and VSMOW (ampoules with 1 mL), for the isotopic measurements, were provided by the IAEA Terrestrial Environment Laboratory in Seibersdorf. In order to avoid additional uncertainty contributions, the IAEA provided us with the real VSMOW and SLAP and not their replacements VSMOW2 and SLAP2. The real VSMOW and SLAP were used for isotopic comparison measurements with the SLAP-like and VSMOW-like waters that were produced in the experiments.

For this study 6 highly ^{18}O enriched water portions were obtained from two manufacturers: three from Cortec (CortecNet, Voisins le Bretonneux, France, specification $^{18}O > 99\%$) and three from Rotem (Rotem industries Ltd., Arava, Israel, specification $^{18}O > 98\%$). All six water portions were from different production batches.

Furthermore, one virtually pure $^{2}H_2O$ water (10 times 1 mL ampoules) was obtained from Sigma-Aldrich^{2}H [?] 99.96% (certificate of analysis specified 99.978%, determined via NMR analysis).

The SLAP-like product of mixing Antarctic water and Groningen demineralized tap water, with the same $\delta\,^{18}$O as SLAP, will be referred to as SLAP-replicate-Oxygen henceforth in the manuscript, and in short SLAP-rep-O. $\delta^{18}O_{\text{SLAP-rep-O}}$ is [?] -55.5the VSMOW-SLAP scale. Similarly, VSMOW-rep-O refers to a VSMOW-like water in^{18}O, $\delta^{18}O_{\text{VSMOW-rep-O}}$ is [?] 0other produced replicates are VSMOW-rep-D ($\delta^{2}H_{\text{VSMOW-rep-D}}$ [?] 0VSMOW-rep-OD ($\delta\,^{2}H_{\text{VSMOW-rep-OD}}$ [?] 0So, the last replicate matches VSMOW in both water isotopes.

2.2 Instruments.

Accurate determination of the ^{18}O concentration of the highly enriched water was key to our efforts: to achieve an accuracy of [?] 0.05the^{18}O concentration of the highly enriched $H_2{}^{18}O$ water had to be determined at [?] $\pm$ 0.1%. We were able to reach this precision and accuracy by performing detailed mass scans using a quadrupole mass spectrometer (QMS) equipped with an electron ionization (EI) ion source (Extorr XT100, Extorr Inc., USA), in combination with a bespoke spectral fitting program. The measurements were carried out at an electron energy of 70 eV. For the uncertainty in our signal we use the standard deviation of the instrument's background signal-to-noise at m/z 5, as no peak is expected at m/z 5, which was around 2 x 10^{-9} Pa. The total integrated signal of m/z 1 to 41 was approximately 2 x 10^{-4} Pa. The base peak signal at m/z 20, $[H_2{}^{18}O]^+$, was almost 1.3 x 10^{-4} Pa.

All water samples were analyzed using a LGR Liquid Water Isotope Analyzer (LGR LWIA 912-0050), which is an off-axis integrated cavity output spectrometer, to determine the triple-stable isotope composition:$\delta\,^{18}$O, $\delta\,^{17}$O and$\delta\,^{2}$H. Typically sample measurements are bracketed with local references as well as international references, details of which has been presented later in the manuscript.

The portion of $H_2{}^{18}O$ water (approximately 125 mg) was weighed on a Sartorius BP210 D (210 g, readability 0.01 mg) analytical balance. The SLAP-like water used for mixing (approximately 1000 g) was weighed on a precision balance from Kern 572 (4210 g, readability 0.01 g).

To verify the NMR specification of the supplier of$^{2}H_2O$ (and check in general that sample handling of such highly enriched waters had a negligible influence on the abundances), the ^{1}H abundance of$^{2}H_2O$ was analyzed using a NMR (Bruker Avance NEO 600 MHz).

2.3 Procedure

2.3.1 Approach 1

All the steps taken to prepare the various water-replicate samples leading to the precise determination ofδ $^{18}O_{SLAP}$ with respect toδ $^{18}O_{VSMOW}$ is illustrated in Figure 1. The flow diagram illustrates the mixing steps from Antarctic water via a SLAP-replicate to the two VSMOW-replicates created by adding well-characterized $H_2{}^{18}O$ (left-hand side), and with an extra step in which also the^{2}H-side is modified (right-hand side). The most critical part of the process entails the characterization of the highly enriched ^{18}O-water that is added. Important other, but more standard determinations, are the initial creation of the SLAP-rep-O water, as well as several additional determinations (such as the determination of the ^{17}O and ^{2}H content of the ^{18}O-water, and the optical measurements of the isotopic differences between the created SLAP-rep-O and SLAP, and between the VSMOW-rep-O (or VSMOW-rep-OD) and VSMOW. The steps indicated on the right-hand side of Figure 1 is further described in 2.3.2.

<Figure 1>

Φιγυρε 1. Φλοω διαγραμ ανδ δεσϛριπτιον οφ τηε υσεδ αββρειατιονς ιν τηε προϛεσς οφ χυαντιφιϛατιον οφ τηε $\delta^{18}O_{\Sigma\Lambda\Pi}$ αλυε ωιτη ρεσπεϛτ το $\delta^{18}O_{\Sigma MO\Omega}$. $\delta^{2}H$ ανδ $\delta^{18}O$ ιν τηιϛ φιγυρε αρε εξπρεσσεδ ον τηε ΣMOΩ-ΣΛΑΠ σϛαλε.

For every experiment, we started with Antarctic water and made a fresh portion of SLAP-rep-O. After measuring the isotopic values of Antarctic water, we calculated how much demineralized Groningen tap water should be added, in order to mimic δ ^{18}O of SLAP. As the Antarctic water was isotopically "lighter" than SLAP, we had to add approximately 18 g of demineralized Groningen tap water ($\delta^{2}H$ = -43.5-6.5portions of SLAP-rep-O, which were individually measured on the LGR-LWIA along with aliquots of SLAP.

The next step in the flow diagram shows the mixing of SLAP-rep-O with highly enriched ^{18}O water in order to obtain VSMOW-rep-O. As said before, the most critical part of the whole process is the characterization of the highly enriched^{18}O-water that is added to the SLAP-O replicate. This^{18}O characterization is done by fitting a QMS spectrum of the enriched water. The steps we took for a careful determination are described in this section. We did our utmost to avoid memory effects from natural and highly enriched ^{18}O water in the QMS and we investigated the influence of several ionization processes in the ion source of the QMS on this ^{18}O determination. At the end, we performed a validation of our QMS method by diluting a $H_2{}^{18}O$ water portion with 1% and 2% $H_2{}^{16}O$. The results of this validation by comparing the expected abundances based on weights with the measured abundances and the influence from several ionization processes are described in the Results section.

To get rid of possible memory effects, the ion source of the QMS was pumped for more than 48 hours at high vacuum, before measuring highly enriched ^{18}O water (background pressure was 1.5 x 10^{-6} Pa). The mass spectrum with this "clean" source was considered as a background signal and was subtracted from the spectrum of the enriched water. For this background signal, it hardly made any difference if the previous injection, before the 48 hours of pumping, was a water with natural abundances or a water with enriched^{18}O.

Water is very "sticky" and adsorbs to the walls of the injector, dead volumes and the ion source of the QMS. Therefore, the analyzing QMS setup needs to be saturated with highly enriched ^{18}O water in order to reduce memory effects. Thus, more than 20 sequential identical sample injections were required to reach an equilibrium state. For every injection, 25 µl water was injected and a scan of m/z 1 to 41 was performed. The measurement pressure was at 2.5 x 10^{-3} Pa. The QMS exclusively measured highly enriched^{18}O water for several months in a row.

Water molecules in the ion source of the QMS ionize, break and recombine to produce a combination of

peaks corresponding to $[H]^+$, $[H_2]^+$, $[O]^+$, $[OH]^+$, $[H_2O]^+$, $[H_3O]^+$ and $[O_2]^+$ ions. All of these ions contain the two different H-isotopes and three different O-isotopes. In Figure 2, a typical QMS spectrum of a highly enriched^{18}O water is shown. All the main Oxygen-bearing fragments together produce ion signals from m/z 16 to 24. In the supplementary material, Table 5 shows a highly enriched^{18}O water (water portion D from Cortec) with the various isotopologues and fragments for this range of m/z values.

<Figure 2>

Figure 2. A typical QMS spectrum of a highly enriched^{18}O water from m/z 1-40. The insert plot shows the partial pressure (Pa, plotted on a logarithmic scale) with respect to m/z 14 to 24.

In the m/z range 16-24, several signals could not be used for our fitting analysis of the ^{18}O concentration, either because of the interference of other species, or because of the very low signal. Oxygen ($[^{16}O]^+$) from air interferes with oxygen ($[^{16}O]^+$) from $H_2{}^{16}O$ (m/z 16). Injecting water without air is virtually impossible, and small leakages are always present as well. The origin of this interference is air is clear from its correlation with m/z 14 ($[^{14}N]^+$ from air). Therefore m/z 16 was disregarded from the fit. This interference is small, and hence the consequential interferences on m/z 17 and m/z 18 from air due to $[^{17}O]^+$ and $[^{18}O]^+$ are orders of magnitude smaller and therefore negligible. Additionally, the very minor signals arising from the various clumped isotopocule ions on m/z 22-24 (see Table 5 in supplement) are too small to be of use.

In the spectrum of an ^{18}O enriched water (Figure 2) a very small signal from the recombined ion $[^{18}O_2]^+$ is visible at m/z 36. Approximately 1.5% of the spectrum is in the form of $[O]^+$ (all three different oxygen isotopes together), (see Table 5 in the supplement). Including the signal at m/z 36 in the spectral fit showed that about 7% of the $[^{18}O]^+$ ions, recombines to $[^{18}O_2]^+$. This signal at m/z 36 doesn't significantly influence the fitted^{18}O value and was therefore neglected in our fitting program.

At m/z 1 and 2 signals from $[^1H^+]$ and $[^2H^+]/[H_2{}^+]$ are visible in the spectrum (Figure 2). As these hydrogen fragments do not contain oxygen, they were not included in the fitting program.

Five m/z values in the range 17-21 could be used for a successful fit, yielding the ^{18}O concentration. The fitting program was written in R. The output of this R program, the fit parameters, were besides the abundance of ^{18}O, the size of the fractions $[H_2O]^+$, $[OH]^+$, $[O]^+$ and thus the size of the complementary fraction $[H_3O]^+$ as well. Next to the signals m/z 17-21, the abundances of ^{17}O and^{2}H were also input parameters for the fitting program. The abundances of ^{17}O and ^{2}H of the highly enriched ^{18}O water were separately determined to reduce the number of fitting parameters, which is necessary as^{17}O and ^{18}O in the fit are in fact quite correlated. Determination by dilution and comparison with reference waters is adequate in these two cases, as neither^{2}H nor ^{17}O abundances are very critical in the fitting process. This is due to the fact that both abundances are low anyway: ^{2}H because it is in the natural range, and ^{17}O because we deal with highly enriched ^{18}O waters. Because of that, there is only room for [?] 1% ^{17}O, and determination of the^{17}O abundance with a relative precision of 5% is already more than adequate. Such precision is well-achievable using dilution.

For determining ^{17}O, the enriched waters were diluted and measured alongside references IAEA 607, 608 and 609 (Faghihi[15] and CIO laboratory standards, using the LGR-LWIA. For determining ^{2}H concentration, the diluted enriched waters were measured alongside CIO laboratory standards using the LGR-LWIA as well. In both cases we calculated the abundances from our isotope delta-measurements using the literature values for the abundances in VSMOW (Hageman[4] for ^{2}H and Li[14] for ^{17}O). The results of the ^{18}O, ^{2}H and^{17}O abundances corresponding to all the highly enriched ^{18}O water portions are presented in Table 3 (results section), along with their uncertainties.

SLAP-rep-O was mixed with highly ^{18}O enriched water to mimic VSMOW, and referred to as VSMOW-rep-O (analogous to SLAP-rep-O, VSMOW-rep-O refers to water with an isotopic δ^{18}O value close to VSMOW). We added a known quantity of highly enriched ^{18}O water needed to shift the δ^{18}O to 0was weighed on a precision balance (readability 0.01 g) in a 1 L Duran brown glass flask. $H_2{}^{18}O$ was weighed on an analytical balance (readability 0.01 mg) in a small glass vial. This vial was submerged in the 1 L flask with SLAP-rep-O.

To ensure complete mixing, the resulting mixture, VSMOW-rep-O, was stirred for at least 48 hrs. Accurate determination of the weights of the mixing water portions is extremely critical in the whole calculation chain, therefore weights are also corrected for buoyancy effects, as the density of $H_2{}^{18}O$ water is significantly larger than that of $H_2{}^{16}O$ (1.11 g/mL instead of 1 g/mL). The weighing was performed as fast as possible to keep evaporation of water to a minimum.

Stable isotope measurements were performed using the LGR-LWIA. The replicates were measured alongside the real VSMOW and SLAP, such that scale contraction issues played no role (see below).

The mixing process started with the characterization of the individual 1 liter batches of SLAP-rep-O water, by direct comparison with SLAP. We then measured the produced VSMOW-rep-O by direct comparison with original VSMOW water. The difference between this measurement and the calculated value translates directly into a best $\delta^{18}O$ value for SLAP with respect to VSMOW. As we took care that both the $\delta^{18}O$ differences SLAP-rep-O vs SLAP and VSMOW-rep-O vs VSMOW are small, their differences could be determined precisely. As these differences between the replicates and the genuine VSMOW and SLAP are small, the $\delta^{18}O$ difference between the officially $\delta^{18}O$ values (VMSOW-SLAP scale) and the 'true' isotopic difference did not play a role. The calculation of the resulting $\delta^{18}O$ value for SLAP is straightforward, and has been performed with the help of a validated spreadsheet (Faghihi[16]).

2.3.2 Approach 2

Highly enriched ^{18}O water is not enriched in deuterium (on the contrary, compared to water with natural abundances it is depleted in deuterium). Therefore, after adding $H_2{}^{18}O$ to SLAP-rep-O, $\delta^{18}O_{\text{VSMOW-rep-O}}$ is close to $\delta^{18}O_{\text{VSMOW}}$ but $\delta^{2}H_{\text{VSMOW-rep-O}}$ is still close to$\delta\ ^{2}H_{\text{SLAP}}$. In principle, this does not matter for our experiment, as we only are interested in the^{18}O side. However, to exclude the possibility that this large difference in deuterium content between our VSMOW-rep-O and the real VSMOW would influence the absorption of the^{18}O line in the LGR-LWIA (and thus its determination of the $\delta\ ^{18}O$ difference between VSMOW-rep-O and VSMOW), in addition an extra step in the process was introduced. Before SLAP-rep-O was mixed with $H_2{}^{18}O$, pure$^{2}H_2O$ was added to mimic VSMOW in deuterium (called VSMOW-rep-D, $\delta\ ^{2}H$ [?] 0Subsequently VSMOW-rep-D and highly enriched ^{18}O water were mixed to get VSMOW-rep-OD ($\delta\ ^{2}H$ [?] 0and$\delta\ ^{18}O$ [?] 0on the righthand side of Figure 1. It rules out spectroscopic biases in the measurements, but otherwise is not different from the process described in 2.3.1.

We started with the same Antarctic water as described before and added Groningen tap water to produce SLAP-rep-O. Then we added$^{2}H_2O$ to mimic VSMOW in deuterium and therefore very precise quantification of the$^{2}H_2O$ content was key. Determination of^{2}H abundance of the enriched$^{2}H_2O$ water by QMS, however, was not as straightforward as determination of ^{18}O abundance of the enriched $H_2{}^{18}O$. This may be caused by the more complex spectrum for $^{2}H_2O$. The $^{2}H_2O$ spectrum, Figure 3, illustrates that m/z peaks 17,19 and 21 are about two orders of magnitude smaller than the adjacent m/z peaks 18 and 20. In the supplementary material, Table 6 shows a highly enriched^{2}H water with the various isotopologues and fragments for this range of m/z values.

Peak tailing and leading of the larger peaks makes it difficult to integrate the smaller peaks. These alternating small and large peaks, are not present in the ^{18}O spectrum (Figure 2, see logarithmic insert plot). Another possible explanation is the common knowledge that in high vacuum stainless steel tubes, there is always outgassing of hydrogen. If this is the case in the QMS, H-exchange will affect deuterium abundance measurements with the QMS, especially for these nearly pure $^{2}H_2O$ waters. This outgassing of hydrogen will obviously not affect the determination of oxygen isotope abundances.

Furthermore, the m/z 1 the signal was much larger than we expected from a nearly pure $^{2}H_2O$ water (m/z 1 is approximately 1% of m/z 2, see Figure 3, top insert plot), an observation that worried us initially. But after personal communication with the manufacturer of the QMS, Extorr, we learned that this was probably a source pressure related artifact. Working at higher pressures can cause scattering. If the QMS is not tuned for these low m/z values, a fraction of the scattered ions passes through the mass filter below 0.5. The actual m/z 1 is therefore not resolved well. This fact made signals m/z 1 and 2 useless for obtaining the deuterium

concentration of the almost pure ^2H_2O water. Therefore, we used a similar m/z signal range as was used for the^{18}O determination.

In conclusion, this discrepancy of measured (and fitted)^2H abundance (of about 99.7%) and real (specified)^2H abundance (99.98%) must be attributed to reasons mentioned above: the more complex spectrum and the continuous outgassing of hydrogen in vacuum stainless tubes. To verify the specification of the supplier we performed NMR analysis for accurate ^2H concentration analysis of the highly enriched deuterated water, which corroborated the specified value, and also excluded the possibility that sample handling of these highly enriched waters would lead to dilution due to admixture of water (vapour) from the surroundings.

<figure 3>

Figure 3. A typical QMS spectrum of^2H_2O m/z 1 to 40. The small inserts show the logarithmic plots of m/z 0 to 10 (top) and 14 to 24 (bottom).

In analogy to the mixing of enriched ^{18}O water and the replicate for SLAP, we added the amount of^2H_2O that was calculated to achieve a δ^2H [?] 0SLAP-rep-O.^2H_2O was weighed in a glass vial on an analytical balance (approximately 75 mg was weighed), SLAP-rep-O was weighed on a precision balance (1 L) in a 1 L brown Duran bottle. This vial was submerged in the 1 L flask with SLAP-rep-O. The resulting mixture VSMOW-rep-D was stirred for at least 48 hrs. All weights were corrected for the buoyancy effect.

In this second approach, the product VSMOW-rep-D (δ^2H [?] 0of the mixing process with highly enriched ^{18}O water.

The adding of highly enriched ^{18}O water needed to arrive at $\delta^{18}O$ [?] 0was the same as described before.

Characterization of the isotopic delta values of VSMOW-rep-D was performed by the LGR-LWIA by direct comparison with SLAP for $\delta^{18}O$ analysis and by direct comparison with VSMOW for δ^2H analysis (on the VSMOW-SLAP scale). Subsequently, the produced VSMOW-rep-OD was measured by direct comparison with original VSMOW water, for both isotopes.

For the calculation of the best $\delta^{18}O$ value for SLAP with the help of a validated spreadsheet (Faghihi[16], the ^{17}O and ^{18}O abundances of the enriched ^2H_2O water had to be characterized as well. In analogy to the determination of^2H and ^{17}O abundances in enriched^{18}O water, ^2H_2O was diluted first with demineralized Groningen tap water (1:7). Carbon dioxide with a known isotopic signature was equilibrated with this diluted ^2H_2O at 25 ^oC for 48 hours (procedure described in Meijer[17]. $CO_2$was extracted and $\delta\ ^{18}O$ was measured on a dual inlet IRMS Mass spectrometer (a VG (now Isoprime) SIRA10). IAEA607 with approximately the same $\delta\ ^{18}O$ signal as the diluted ^2H_2O water and some other local CIO references were identically treated and were used for normalization. $\delta\ ^{17}O$ was determined via a method described in Elsig and Leuenberger[18]. The$\delta\ ^{13}C$ from the initial equilibration gas is known, and deduced from the deviation in $\delta\ ^{13}C$ of the CO_2 gas after equilibration and before equilibration with the known $\delta\ ^{13}C$,$\delta\ ^{17}O$ could be determined. IAEA607 and the same local CIO references as for $\delta\ ^{18}O$ analysis, were used for normalization. The ^{17}O and^{18}O abundances of the^2H_2O water are presented in the results section, along with their standard deviations of three repetitions.

The difference in stable isotopes measurements and the calculated stable isotope values by the validated spreadsheet (Faghini[16]) translates directly into a best$\delta\ ^{18}O$ value for SLAP with respect to VSMOW. In addition, the second approach has the beneficial side-effect that additionally a best $\delta\ ^2H$ for SLAP could be determined. $\delta\ ^2H_{\text{VSMOW-rep-D}}$ was initially calculated from the actually added (buoyancy-corrected) weight and isotopic abundances of the ^2H_2O water and the weight and isotopic delta values of SLAP-rep-O (on the VSMOW-SLAP scale). Subsequently$\delta\ ^2H_{\text{VSMOW-rep-D}}$ was measured alongside VSMOW. The difference between this measurement and the calculated value translates directly into a best$\delta\ ^2H$ value for SLAP with respect to VSMOW.

We took care that the differences between the replicates and the genuine VSMOW and SLAP were small, so the $\delta^{18}O$ and δ^2H difference between the officially $\delta^{18}O$ and $\delta\ ^2H$ values (VMSOW-SLAP scale) and the

'true' isotopic difference, or in other words, possible scale contractions, did not play a role.

2.4 Final uncertainty calculation.

To calculate the combined uncertainty for each single experiment, a Monte Carlo simulation was performed for the full experimental process. For all different sources in the total process, from weighing waters, to ^{18}O abundance measurements by QMS, until isotopic measurements with the LGR-LWIA, the uncertainties were determined or estimated.

To ascertain the contribution of uncertainties in the weighing process, a flask was weighed multiple times in order to determine the reproducibility of weighing. This procedure revealed that the spread in the weighing of the same flask multiple times, was within 5 times the uncertainty specified by the manufacturers, and thus multiplied by a factor of 5. So, for weights measured on the precision balance the accuracy was estimated at $\pm$ 0.05 g and for the analytical balance the accuracy was estimated at $\pm$ 0.05 mg. As a part of the quality control measures we have adopted in our laboratory, all balances, including the ones used in this work, are frequently calibrated.

As a cautious estimate, the uncertainties for the QMS^{18}O abundances of the enriched ^{18}O waters were chosen to be the standard deviations of the repetitional measurements. In Table 3 this is displayed for every enriched^{18}O water. The ^{2}H and^{17}O abundances are determined via dilution. The isotopic measurements of the diluted ^{18}O waters were performed on two different measurement days, and performed nine times per measurement day. From the weighted average of the total number of analyses and twice the standard error of the mean, the^{2}H and ^{17}O abundances were deduced with their 2σ uncertainty.

The isotopic measurements for SLAP, VSMOW and their replicates were measured on the LGR-LWIA. Per measurement day every replicate was injected 60 times, and VSMOW and SLAP were injected 90 times. The difference in $\delta^{18}O$ ($\Delta\ \delta^{18}O$) between the replicate and its "parent" (so SLAP for SLAP-replicate, and VSMOW for VSMOW-replicate) was averaged per measurement day. The error in the mean in the parent-replicate $\Delta\ \delta^{18}O$ was calculated (typically better than 0.03calculating the weighted average for every $\Delta\ \delta^{18}O$ parent-replicate on multiple (typically 3) measurement days.

For the Monte Carlo simulation, a calculation was programmed in R. All calculations steps were performed 10,000 times with all the parameters and their uncertainties (assumed to belong to a normal distribution) as described above. This Monte Carlo simulation gives the uncertainty for product VSMOW-rep-O. A quadratic sum from the Monte Carlo uncertainty and the standard error in the mean of the isotopic measurements for product VSMOW-rep-O yielded the combined uncertainty per experiment. The Monte Carlo simulation was performed for the full calculation process for each experiment. The combined uncertainties per experiment are shown in the supplementary material, Table 4, and in the graph, Figure 6.

The three main uncertainty components in this combined uncertainty are the weight and ^{18}O concentration determination of the enriched ^{18}O water and the$\delta\ ^{18}O$ measurement of SLAP-rep-O.

Despite one extra step in the second approach, the uncertainty in the final result is the same. In the first approach the $\Delta\delta\ ^{18}O$ between SLAP-rep-O and SLAP and VSMOW-rep-O and VSMOW leads to a best $\delta\ ^{18}O$ value for SLAP with respect to VSMOW. In the second approach $\Delta\delta\ ^{18}O$ between VSMOW-rep-D and SLAP and VSMOW-rep-OD and VSMOW leads to a best $\delta\ ^{18}O$ value for SLAP with respect to VSMOW.

All uncertainty sources are considered to be random errors, only causing variability in the end result. In addition, there are two sources of systematic error. The first would be a biased QMS ^{18}O measurement method. It is unlikely, but still possible, that we systematically measure an ^{18}O abundance that is too low. If this would be the case, the final end result for $\delta\ ^{18}O$ value for SLAP would be more negative. In the next section, we describe a number of tests we performed to scrutinize our QMS-based abundance measurements.

The other source of systematic uncertainty is the ^{18}R value for (V)SMOW and its uncertainty as reported by Baertschi[7]: $^{18}R = (2005.20 \pm 0.45) \times 10^{-6}$. Changing this value by one standard deviation up would lead to a 0.013

As the total number of experiments is rather small (seven), the standard error in the mean of the averaged results forδ ^{18}O value for SLAP for seven experiments, is increased by multiplying with a Student's T-distribution factor.

3. RESULTS

The ^{18}O characterization of our 6 different highly enriched ^{18}O waters were carried out by measuring QMS spectra and fitting those spectra. As described in section 2.3.1, m/z signals 17-21 from the QMS spectra were used for this spectral fitting method. In Figure 4 an integrated true measured QMS signal from m/z 17-21 and the fitted signal from the bespoke program are compared, their very small residuals (in the order of 10 ppm) are shown on top panel of the figure. These residuals show that the fitted signals are in excellent agreement with the measured signals. The displayed error bars are the standard deviations of 14 measurements.

<Figure 4>

Figure 4. Relative abundance of m/z 17-21, together with the results from the fit from one injection with ^{18}O water. On this scale, the small error bars (around 10^{-4}) are not visible. On top, residuals from the true signal with respect to the fitted signal of QMS (m/z 17-21) are shown. The error bars are the standard deviations from 14 separate injections.

As a proof-of-method the enriched $H_2{}^{18}O$ water was diluted with (approximately) 1 and 2% water with ^{18}O at natural abundance. The expected differences in ^{18}O abundances between these dilutions and the not diluted enriched water based on weights, are shown in Table 1. The measured (fitted)^{18}O abundances and the expected ^{18}O abundances are within 0.03% of each other. We concluded that real (small) differences in abundances are correctly measured.

<Table 1>

Table 1. QMS measurements of ^{18}O abundances of highly enriched $H_2{}^{18}O$ and 1 and 2% diluted $H_2{}^{18}O$ with water with natural^{18}O abundance.

** The expected ^{18}O abundance of the diluted mixtures is based on the exact weights of the highly enriched water and with water with natural ^{18}O abundance.*

Further investigations into the reliability of our QMS-based abundance determination involved the possibility that ionization processes in the QMS source such as ion yield, and ion distribution might be dependent on the specific oxygen isotope. Water samples in the ion source of the QMS mainly ionize to $[H]^+$, $[O]^+$, $[OH]^+$, $[H_2O]^+$ and $[H_3O]^+$ ions. The distribution of the oxygen-bearing fragmentation ions in natural water and in highly enriched ^{18}O water has therefore been compared. The observations are shown in Table 2, and notable differences in fragmentation pattern between enriched and natural water are visible, especially for the fragmentation ion $[O]^+$: it is more preferred in natural ^{16}O water than in^{18}O water, the difference is more than 60% (relative) / 1% (absolute). In the fitting program, described in section 2.3, these differences are taken into account.

<Table 2>

Table 2. Comparison of the distribution of 4 main Oxygen-bearing fragmentation ions in QMS source for natural water and^{18}O enriched water (water portion A, Rotem). The total concentration of those 4 ions is considered as 1 (so 100%). For every ion, the averaged part of this total fraction is displayed. Between brackets the standard deviation of the repetitions (n) is displayed. Cortec water is even more enriched than Rotem water and shows slightly different fragmentation, an example is in the supplementary Table 5.

Our experiments also show a small isotope effect in the ionization efficiency between water with natural abundances and water with enriched^{18}O. Although hard to determine due to the uncertainty in the amount of water injected, natural water seems to ionize [?] 6% better than the enriched ^{18}O water. As a result of this difference in ionization yield, the ^{16}O fraction of the highly enriched ^{18}O water is overrepresented.

As said, this [?] 6% difference in ionization efficiency carries a relatively large uncertainty. Alternatively, we can use the results from the previously described 1 and 2% dilution experiment. There, the best fit between expected and determined abundance differences leads to an ionization efficiency from highly enriched ^{18}O water compared to water with natural abundances of only 0.97 ± 0.03. This value would lead to a maximum deviation in the end result of $\delta^{18}O$ for SLAP of - 0.02 ± 0.02to neglect the possible slight difference in ionization yield in our fitting process.

In Table 3 the results of the ^{18}O abundances are shown for the 6 highly enriched ^{18}O water portions (A until F) from two different suppliers, Rotem and Cortec, measured with the QMS. Water portion D was measured twice, the latter being after 4 months of the first measurement set. As can be seen in Table 3, its^{18}O abundance had decreased slightly, but significantly, after puncturing the septum in the closing cap of the vial. All highly enriched ^{18}O waters matched the specification of the suppliers. Table 3 also provides^{17}O and ^{2}H abundances of these highly ^{18}O enriched water portions, as determined via dilution.

<Table 3>

Table 3. ^{18}O, ^{2}H and^{17}O abundances of 6 highly enriched^{18}O water portions from Rotem (specified as > 98%) and Cortec (> 99%).^{18}O abundances are measured by QMS, between brackets the standard deviation of the repetitions (n) is displayed.^{2}H and ^{17}O abundances are determined via dilution, and measured with our LGR-LWIA, on two different measurement days, and with 9 repetitions per measurement day.

** ^{2}H and ^{17}O abundances of water portion D' was not remeasured .*

Following the determination of the ^{18}O content of the enriched waters, mixing the enriched water with the SLAP replicate to produce SLAP-rep-O was performed. The first approach (only mixing with $H_2{}^{18}O$) was independently performed 4 times, so with 4 different ^{18}O water portions (two from Rotem and two from Cortec, ^{18}O water portion A until D). The second approach (mixing first with$^{2}H_2{}^{16}O$ and subsequently with $H_2{}^{18}O$) was performed once with the same ^{18}O water as used in experiment 4 (^{18}O water portion D). As this portion was opened 4 months before using it the second time, the ^{18}O concentration was re-measured by QMS (now D'). The second approach was independently performed with the two remaining ^{18}O waters as well (1 from Rotem and 1 from Cortec, ^{18}O water portions E and F).

An illustration, presented in Figure 5, shows the step-by-step procedure adapted, as described in the sections before, to establish the best $\delta^{18}O$ value for SLAP using measurements performed on the LGR-LWIA.

<Figure 5>

Φιγυρε 5. Α φυλλ ςαλςυλατιον σςηεμε σηοωινγ τηε στεπς ινολεδ ιν ονε οφ τηε σεεν ινδεπενδεντ δετερμινατιον οφ τηε $\delta^{18}O$ οφ ΣΛΑΠ.

For the second approach (also mixing with$^{2}H_2O$) it was necessary to verify the^{2}H concentration specification of the supplier. The determination of the ^{2}H abundance of$^{2}H_2O$ water by QMS was not as straightforward as the determination of ^{18}O by QMS appeared to be, which has been explained in section 2.3.2. The result of the QMS fitted ^{2}H measurement was nearly 0.3% lower than the specification of the supplier. Therefore, we analyzed this sample using NMR and the results matched the supplier's specified value. The specified ^{2}H abundance of the almost pure$^{2}H_2O$ water is 0.99978, the measured (via dilution and CO_2 equilibration) and calculated^{17}O and ^{18}O abundances are 0.000808 (3), 0.005928 (6) respectively.

Between brackets the standard deviation of the three repetitions for^{17}O and ^{18}O abundances are shown.

With enriched water portions A until D the first approach is used (only mixing with enriched ^{18}O water). The $\delta^{18}O_{SLAP}$ results with the combined uncertainties as described before are shown in Figure 6 (black solid circles).

The δ $^{18}O_{SLAP}$ results with the combined uncertainties using the second approach are shown in Figure 6 as well (black open squares). The $\delta^{18}O_{SLAP}$ results are also presented in the supplementary material, Table 4. Significant difference between the two approaches was not obvious, and hence all results for $\delta^{18}O_{SLAP}$ were

averaged. The overall weighted mean of all data points is $\delta^{18}O_{SLAP}$ = -56.33 ± 0.02Taking the Student's T-factor into account, the final outcome is $\delta^{18}O_{SLAP}$ = -56.33 ± 0.03final uncertainty does not include the two systematic effects mentioned in section 2.4. These will be later discussed further in this section.

The second approach allowed determination of δ^2H for SLAP as well. The δ^2H_{SLAP} results are shown in the supplementary material, Table 4. The overall weighted mean of the three experiments is $\delta\ ^2H_{SLAP}$ = -430.3 ± 0.3

<Figure 6>

Φιγυρε 6. Ρεσυλτς οφ 7 εξπεριμεντς περφορμεδ υσινγ 6 διφφερεντ ηιγηλψ-ενριςηεδ ^{18}O ωατερ πορτιονς (A – Φ ιν ταβλε 3), φορ δετερμινινγ δ ^{18}O ΣΛΑΠ. Τηε βλαςκ σιρσλες ρεπρεσεντ τηε ρεσυλτς υσινγ τηε φιρστ απproαςη, ωηερε ΄ΣΜΟΩ ωας μιμιςκεδ ιν δ ^{18}O ονλψ. Τηε βλαςκ οπεν σχυαρες ρεπρεσεντ τηε ρεσυλτς οβταινεδ υσινγ τηε σεςονδ απproαςη ωηερε ΄ΣΜΟΩ ωας μιμιςκεδ ιν βοτη ισοτοπες. Τηε οεραλλ ωειγητεδ μεαν οφ αλλ δατα ποιντς ις -56.33 ± 0.03ςομβινεδ υνςερταιντψ ςαλςυλατεδ υσινγ α Μοντε Cαρλο απproαςη, τακινγ ιντο αςςουντ αλλ ινδιιδυαλ ερρορ σουρςες ιν τηε αβυνδανςες, ιν τηε ισοτοπις μεασυρεμεντς ανδ ιν τηε ωειγητς.

4. DISCUSSION

As explained in the introduction, the consensus values for SLAP with respect to VSMOW were established in 1976. The established δ^2H value was based on the absolute abundance measurements, however, the same for $\delta\ ^{18}O$ was lacking and thus the mean $\delta\ ^{18}O$ value, -55.5interlaboratory calibration exercise performed at that time was chosen by consensus. Among the representatives of the several participating laboratories, there was already a discussion that possible memory effects would contract the scale, so probably a more negative$\delta\ ^{18}O$ value would have been more appropriate.

In later years, thanks to improvements to both equipment and analysis procedures such as correction for cross-contamination (Meijer[19], laboratories indeed determined more negative values for SLAP. In our laboratory, we typically find values around $\delta\ ^{18}O$ = -55.85(CO_2-H_2O equilibration) and, more recently to our surprise, $\delta\ ^{18}O$ = -55.7the LGR-LWIA. We expected that by having a well-maintained IRMS and using the appropriate corrections, our results for SLAP would be close to the real values.

However, Kaiser (2009) already suggested a re-analysis of the data of an intercomparison exercise of 7 expert laboratories described in Verkouteren and Klinedinst (2004), resulting in a much more negative$\delta\ ^{18}O$ value for SLAP, i.e., -56.1 ± 0.2-55.11puzzling. The method Barkan and Luz used was also based on the isotopic exchange equilibration between H_2O and CO_2 in sealed ampoules, but followed by a fluorination of water using CoF_3 to produce O_2. Although this approach is different from the standard equilibration method, results should be identical as long as the fluorination is complete. However, their approach consistently points towards less negative values of -55.11

For a robust locking of the second anchor of the VSMOW scale we performed the work described in this paper. The reliability of our method of quantitative ^{18}O abundance determination of^{18}O water using Quadrupole Mass Spectrometry is crucial for our results. Taking various effects such as fragmentation difference of $H_2{}^{16}O$ and $H_2{}^{18}O$ into account, and by validating the method with a dilution series, and considering the excellent agreement of the fitted QMS signals and the measured ones, we are confident that the method is reliable.

A systematic deviation of our ^{18}O abundance result of 0.1% higher/lower values would lead to a more/less negative result for SLAP of 0.05to realize that, as we use very highly-enriched ^{18}O water (batches of 98% and 99% ^{18}O), in fact we do not measure this high ^{18}O abundance, but rather quantify the remaining part of ^{16}O exactly by QMS. Since there is only room for 1 to 2% ^{16}O, it is in fact this amount that has to be measured with an accuracy of [?] 0.1%, which is not a high relative accuracy. Furthermore, if we would still suffer from some systematic deviation, one can expect this deviation to be larger for the water portions with 2% ^{16}O remaining (the Rotem waters) than those with 1% (Cortec). We see no such effect in our results (Figure 6 and in the supplementary material Table 4). The portion of ^{17}O only plays a minor role in the $^{18}O/^{16}O$ ratio, and this abundance can be determined using a dilution method.

The uncertainty in $^{18}R_{VSMOW}$ leads to a systematic uncertainty in our final answer of ± 0.013to our final uncertainty.

So, the result of this study is δ ^{18}O -56.33 ± 0.03SLAP, which was an unanticipated finding.

The implication of this is that apparently complete understanding of all IRMS effects (not to mention those in optical spectroscopy) is still lacking. Measuring cross-contamination-effects (Meijer[19]) obviously is not enough for correcting the isotope measurement such that the measured delta values are very close to the real delta values.

One of the issues emerging from this lack of complete understanding of all IRMS effects, relates specifically to second order measurements such as ^{17}O excess (Δ ^{17}O) in water. For these measurements, in which the small deviation of the measured δ^{17}O from the natural relation between δ^{18}O and δ^{17}O is determined (Meijer and Li[20], Aron[21]), the question raises, how well these very small deviations (around 0.02be defined, if there are such large discrepancies between measured δ^{18}O and real δ^{18}O values. The assumption that ^{17}O and ^{18}O will fully obey mass dependent fractionation in the ion source of the IRMS may not be completely true. To put it another way: if the measured scale for δ^{18}O is already so much contracted, who can guarantee that the δ^{17}O scale contracts exactly according to the equilibrium relation between δ^{17}O and δ^{18}O.

Also clumped isotope measurements, which determine the minute deviations from stochastic distribution of the delta values for multiply substituted isotopologues, can probably not rely on the fully mass-dependent scale contraction of their machines. Also, here, full understanding of IRMS effects is key.

The oxygen isotope compositions are typically reported on the VSMOW scale, not only for water samples, but also for other types of samples, such as oxides and silicates. The VPDB scale is mostly used for reporting the stable isotope (carbon and oxygen) results of carbonate minerals and also for oxygen isotope measurements in atmospheric CO_2. These two coexisting stable isotope scales for reporting $^{18}O/^{16}O$ ratios or δ^{18}O values, can be converted into each other (Hillaire-Marcel[22]). For both scales an extra conversion step to CO_2 is necessary, because the measurand in the IRMS is CO_2. This extra reaction step is for the VSMOW-CO_2 scale, water equilibration of VSMOW with CO_2 under standard conditions (first described by Epstein and Mayeda[23], Meijer[17] and for the VPDB-CO_2 scale, acidification of IAEA-603 (formerly NBS-19) with phosphoric acid (McCrea[24], Meijer[17], Hillaire-Marcel[22]. The difference between VSMOW-CO_2 and VPDB-CO_2 on the two δ ^{18}O scales is 0.28-0.29laboratory, we have the habit to realize the two scales (water and carbonate) independently and use this scale difference as a quality check. When using two-point calibration scales, the result of a more negative δ^{18}O value for SLAP, (the second anchor of the VSMOW scale), could give potential discrepancies in the transfer ofδ ^{18}O from and to the VPDB scale. Considering the fact that the water equilibration reaction is more robust and easier to control (and therefore more reliable and accurate) than the carbonate-acid reaction, we propose the VSMOW-$CO_2\delta^{18}$O scale be defined as the primary δ^{18}O scale. The definition of the VPDB-CO_2 scale could then simply be expressed in terms of the VSMOW-CO_2 scale. Final decisions about these isotopic scales are under the auspices of the commission on isotopic abundances and atomic weights (CIAAW).

Identical treatment of sample and references, the frequent use of international reference materials and clear guidelines about how to express the results on the international scale(s) is key to provide normalized interlaboratory-comparable stable isotope measurements. This study does not affect those measurements; the VMSOW-SLAP scale can be taken as is. However, knowing the absolute ratios and/or abundances of all scale determining references would give us clear insight how large the scale contraction processes really are. In fields where VSMOW-SLAP-scaled δ^{18}O values are converted into absolute abundances and vice versa, our new δ^{18}O value for SLAP does matter. An example of such a field is energy expenditure measurements using doubly-labelled water, in which the used enriched reference waters will change their delta value (Faghihi[15]).

5. CONCLUSIONS AND RECOMMENDATIONS

With this work, the VSMOW-SLAP scale has in fact become metrologically traceable to the System Inter-

national (SI) units for both isotopes: the combination of the absolute isotope ^{18}O abundance for VSMOW (Baertschi[7] and our present result for SLAP with respect to VSMOW leads to the absolute ^{18}O abundance for SLAP of 1.88798 (43) x 10^{-3}. For ^{2}H, this traceability has long been accomplished. In this work, however, we also produce a new and probably more accurate value for $\delta^{2}H$ of SLAP with respect to VSMOW of -430.3 ± 0.3Hagemann[4], de Wit[5] and Tse[6]. However, like in the ^{18}O case, the value for ^{2}R for VSMOW influences the value we obtain for $\delta^{2}H$ of SLAP. In case we would use the$^{2}R_{VSMOW}$ value reported by de Wit (155.95 x 10^{-6}) in combination with the$^{2}R_{SLAP}$ value of Hagemann (89.02 x 10^{-6}), the difference would translate into -429.2whereas our value for SLAP would change into -429.8values" calls for a new gravimetric mixing experiment, now making use of the better and easier optical measurements of $\delta^{2}H$ of water, combined with NMR determination of the purity of the^{2}H and ^{1}H waters. We plan to perform such an experiment in the near future. When that is successful, both the $\delta^{2}H$ and $\delta^{18}O$ isotope scales would become SI-traceable. That would be a first.

Best estimates for the absolute ^{13}C abundance so far, for the VPDB-scale have been determined by Malinovsky[25] (further work is in progress). The^{18}O-side of this carbonate scale is much more complicated, due to the fractionating process that is at the basis. Furthermore, there still is no consensus on scale normalization, let alone on the absolute ^{13}C and ^{18}O abundances of such materials. For ^{18}O, coupling the^{18}O VPDB scale to VSMOW-SLAP using the CO_2 - H_2O equilibration process is probably a more fruitful route towards pinpointing this^{18}O VPDB-scale to SI units, certainly for non-carbonate materials such as atmospheric CO_2.

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Table 1

	^{18}O Abundance measured	Difference in ^{18}O measured	Expected ^{18}O abundance*	Expected difference in
^{18}O water	0.9800			
1% diluted	0.9675	0.0125	0.9678	0.0122
2% diluted	0.9580	0.0220	0.9577	0.0223

Table 2

Fragmentation ion fraction	n	$f[H_2O]^+$	$f[OH]^+$	$f[O]^+$	$f[H_3O]^+$
Natural water Average (stdev)	20	0.76050 (24)	0.19340 (19)	0.02572 (8)	0.02038 (31)
^{18}O enriched Average (stdev)	14	0.76674 (36)	0.19805 (33)	0.01505 (11)	0.02016 (50)

Table 3

Water portion	Brand ^{18}O water	^{18}O abundance (Stdev)	n	^{2}H abundance (Stdev)	^{17}O abundance (Stdev)	Rema
A	Rotem	0.9799 (7)	18	0.000017 (9)	0.0047 (2)	
B	Cortec	0.9917 (1)	8	0.000027 (6)	0.0012 (2)	
C	Rotem	0.9832 (1)	4	0.000026 (3)	0.0095 (3)	
D	Cortec	0.9939 (3)	7	0.000062 (3)	0.0011 (3)	
D'	Cortec	0.9907 (4)	5	*	*	Wate
E	Rotem	0.9818 (2)	8	0.000032 (5)	0.0074 (<1)	
F	Cortec	0.9917 (2)	8	0.000051 (2)	0.0013 (<1)	

figures/Figure-1/Figure-1-eps-converted-to.pdf