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Aerts-Bijma, Anita Th; Buuren, Albert C. van; Paul, Dipayan; Meijer, Harro A. J.

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RESEARCH ARTICLE

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The absolute $\delta^{18}O$ value for SLAP with respect to VSMOW reveals a much lower value than previously established

Anita Th. Aerts-Bijma | Albert C. van Buuren | Dipayan Paul | Harro A. J. Meijer

Centre for Isotope Research (CIO), Energy and Sustainability Research Institute Groningen, University of Groningen, Groningen, The Netherlands

Correspondence
A. Aerts-Bijma, Centre for Isotope Research (CIO), Energy and Sustainability Research Institute Groningen, University of Groningen, Groningen, The Netherlands.
Email: a.t.aerts-bijma@rug.nl

Rationale: SLAP is one of the two calibration materials for the isotopic water scale. By consensus the established $\delta^{18}O$ value is −55.5‰, although several expert laboratories measure significantly more negative $\delta^{18}O_{SLAP}$ values. 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. This study describes the quantification of $\delta^{18}O_{SLAP}$ with respect to $\delta^{18}O_{VSMOW}$.

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 was measured using an optical spectrometer, alongside original VSMOW and SLAP.

Results: This study resulted in a much more negative $\delta^{18}O$ value for SLAP than expected. The averaged outcome of seven independent experiments is $\delta^{18}O_{SLAP} = -56.33 \pm 0.03$‰. There is a large discrepancy between the actual isotopic measurements of even the most carefully operating isotope laboratories 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 of 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 $\Delta^{17}O$. The absolute ^{18}O abundance for SLAP was calculated as $(1887.98 \pm 0.43) \times 10^{-6}$ based on the absolute ^{18}O abundance of VSMOW and the presented $\delta^{18}O_{SLAP}$ in this paper.

1 | INTRODUCTION

The stable isotope scale of water has been successfully established and maintained by the two primary reference waters: VSMOW and SLAP. From 2009 VSMOW2 and SLAP2 replaced the almost-exhausted supply of VSMOW and SLAP, but all stable isotope measurements from water will continue to be reported with respect to VSMOW/SLAP scale (so the materials to realize the scale have been replaced, but not the scale itself). 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 interlaboratory 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 International Atomic Energy Agency (IAEA) in Vienna, $\delta^{18}O$ and $\delta^{2}H$ measurements of SLAP from 45 laboratories were evaluated. The $\delta^{18}O$ data showed a rather large spread, with measurements ranging between −54.53‰ and −56.5‰. The averaged $\delta^{18}O$ value for SLAP was −55.49‰, and the standard deviation (SD) was 0.55‰ (two data points were considered as outliers [−49.2‰ and −53.92‰]). During this meeting, the $\delta^{18}O$ SLAP was established at the consensus value of −55.5‰ (Gonfiantini[1,2]).

The $\delta^{2}H$ data also showed a large spread, with measurements ranging from −418‰ to −452‰. The recommended $\delta^{2}H$ SLAP was established at −428‰ (Gonfiantini[1,2]).

For hydrogen, 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 determined by several authors (Hageman et al,[3] de Wit et al,[4] and Tse et al[5]).

A similar experiment for oxygen is more complicated, as pure ^{18}O and ^{16}O waters are not available. Only Baertschi[6] has determined the absolute ^{18}O abundance of VSMOW with a relative precision of 0.2‰ in a very extensive experiment.

In this study, we take the next step, namely determination of the $\delta^{18}O$ of SLAP with respect to VSMOW. The accuracy of a $\delta^{18}O$ difference determination between VSMOW and SLAP is much higher than that of the determination of the absolute ^{18}O abundance of SLAP. Direct measurement of this absolute ^{18}O abundance of SLAP would be extremely complicated, and to achieve the required uncertainty would be highly unlikely. Therefore, we focus on the relative difference in $\delta^{18}O$ between VSMOW and SLAP, which we aim to achieve with a high precision (≤0.05‰). In this way, we achieve a more accurate SI (System International) traceable result for the VSMOW–SLAP scale. To avoid additional uncertainty contributions, the IAEA provided us with the original VSMOW and SLAP, and thus their replacements VSMOW2 and SLAP2 were not used in this work.

We quantify the difference in $\delta^{18}O$ 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 original VSMOW.

The various measurements from Gonfiantini[2] from −54.53‰ to −56.5‰, and from Verkouteren and Klinedinst[7] and Barkan and Luz,[8] pointed out by Kaiser,[9] for $\delta^{18}O_{SLAP}$ from −55.11 to −56.18‰, raise the intriguing question of what the actual value is. This real value can play an important role in understanding isotope ratio mass spectrometry (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, $\delta^{18}O$ 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, $\Delta^{17}O$) (Hofmann et al[10] and Landais et al[11]) and the deviation from stochastic distribution of the rare isotopes in molecules ("clumped isotopes") (Eiler[12] and Bernasconi et al[13]). Also in these fields, understanding (and correcting for) instrument-related isotope effects is crucial.

Although a new $\delta^{18}O_{SLAP}$ value would not change the use of the $\delta^{18}O$ VSMOW–SLAP scale realization, it would influence the calculation of absolute ^{18}O abundances from $\delta^{18}O$ values, which is common practice in fields using isotope dilution or in doubly labeled water studies.

2 | EXPERIMENTAL SETUP AND METHODS

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 comparing this surrogate with real VSMOW. 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 L) 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 L 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 ≤0.05‰ in the final result for SLAP, because of gravimetric/weighing and sample handling precision limitations. Obviously, using such quantities of the original SLAP was 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. To avoid additional uncertainty contributions, as discussed earlier, the IAEA provided us with the original VSMOW and SLAP and not their replacements VSMOW2 and SLAP2. VSMOW and SLAP were used for isotopic comparison measurements with the SLAP-like and VSMOW-like waters that were produced in the experiments. Ruling out the possibility of dividing the original SLAP from a 20 mL ampoule into smaller ampoules of 1 mL would have changed the isotopic composition; isotopic measurements were performed on SLAP and SLAP2 in the same measurement batch, resulting in indistinguishable $\delta^{18}O$ values within the measurement uncertainty. For our study we used portions of four different SLAP ampoules, namely 1791, 1792, 1786, and 1661.

For this study six 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.

To differentiate the different portions, they were named A–F. ^{18}O waters from Rotem were designated A, C, and E. Cortec waters were designated B, D, and F.

Furthermore, one virtually pure $^{2}H_2O$ water (10 times 1 mL ampoules) was obtained from Sigma-Aldrich (Merck, Massachusetts, USA) ^{2}H ≥99.96% (certificate of analysis specified 99.978%, determined via nuclear magnetic resonance [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 (SLAP-rep-O). $\delta^{18}O_{SLAP\text{-}rep\text{-}O}$ is ≈−55.5‰ on the VSMOW–SLAP scale. Similarly, VSMOW-rep-O refers to a VSMOW-like water in ^{18}O; $\delta^{18}O_{VSMOW\text{-}rep\text{-}O}$ is ≈0‰. The other produced replicates are VSMOW-rep-D ($\delta^{2}H_{VSMOW\text{-}rep\text{-}D} \approx 0‰$) and VSMOW-rep-OD ($\delta^{2}H_{VSMOW\text{-}rep\text{-}OD} \approx 0‰$, $\delta^{18}O_{VSMOW\text{-}rep\text{-}OD} \approx 0‰$). Therefore, 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 ≤0.05‰ in the $\delta^{18}O$ value for SLAP, the ^{18}O concentration of the highly enriched $H_2{}^{18}O$ water had to be determined at ≤±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 source (Extorr XT100, Extorr Inc., Pennsylvania, 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 SD of the instrument's background signal to noise at m/z 5, as no peak is expected at m/z 5, which was $\sim 2 \times 10^{-9}$ Pa. The total integrated signal of m/z 1–41 was $\sim 2 \times 10^{-4}$ Pa. The base peak signal at m/z 20, $[H_2{}^{18}O]^+$, was almost 1.3×10^{-4} Pa.

All water samples were analyzed using an LGR Liquid Water Isotope Analyzer (LGR-LWIA 912-0050, Los Gatos Research, California, USA), 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 will be presented later.

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

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 NMR (Bruker Avance NEO 600 MHz, Bruker Corporation, Massachusetts, USA).

2.3 | Procedure

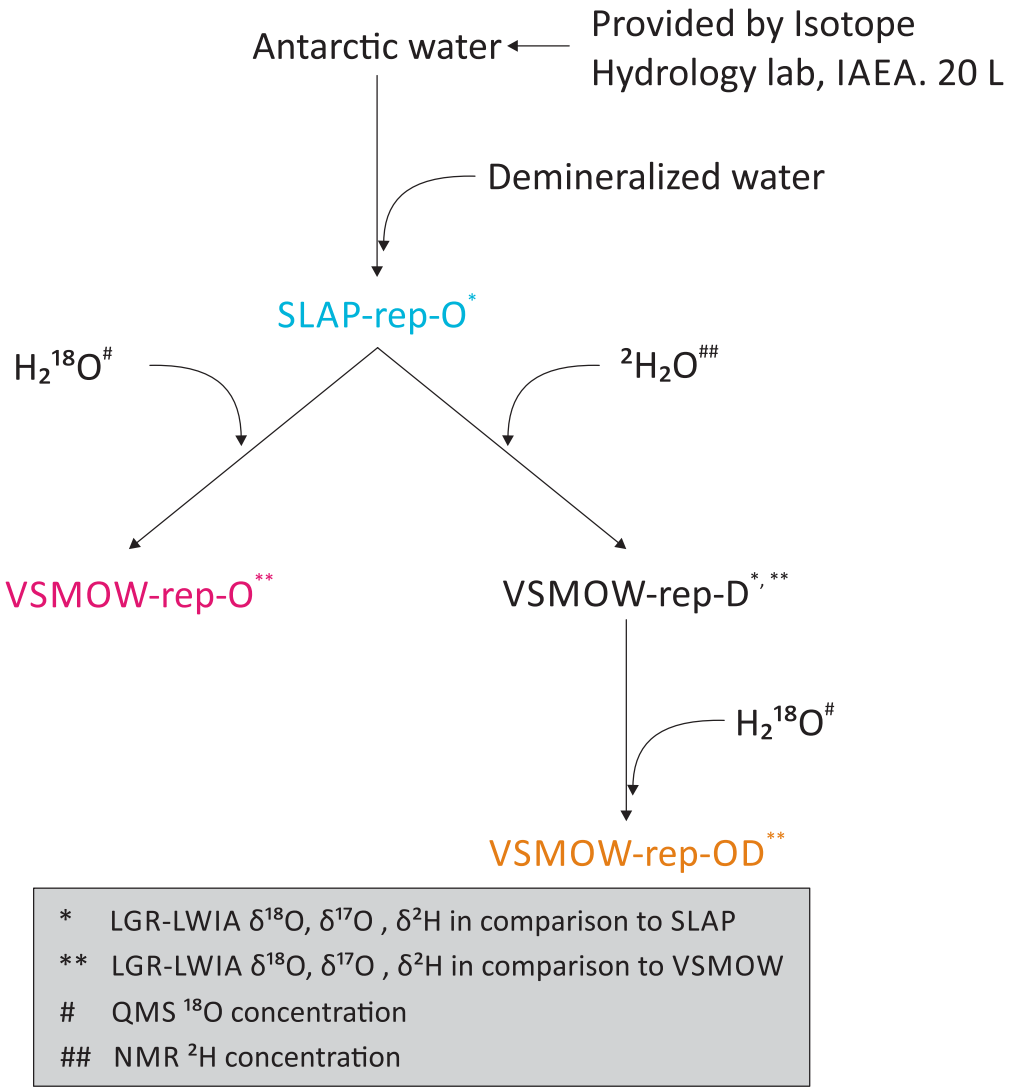
2.3.1 | Approach 1

All the steps taken to prepare the various water-replicate samples leading to the precise determination of $\delta^{18}O_{SLAP}$ with respect to $\delta^{18}O_{VSMOW}$ are shown in Figure 1. The flow diagram illustrates the mixing steps from Antarctic water through 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 (e.g., 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 are further described in Section 2.3.2.

For every experiment, we started with Antarctic water and made a fresh portion of SLAP-rep-O. Working with a fresh portion every time avoided a systematic bias. After measuring the isotopic values of Antarctic water, we calculated how much demineralized Groningen tap water should be added, to mimic $\delta^{18}O$ of SLAP. As the Antarctic water was isotopically "lighter" than SLAP, we had to add ∼18 g of demineralized Groningen tap water ($\delta^{2}H = -43.5‰$, $\delta^{18}O = -6.5‰$) to 1 L of this Antarctic water. In total, we produced seven portions 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 to obtain VSMOW-rep-O. As mentioned earlier, 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 quadrupole mass 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 validated our quadrupole mass spectrometry 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 Section 3.

To remove possible memory effects, the ion source of the QMS was pumped for more than 48 h at high vacuum, before measuring highly enriched ^{18}O water (background pressure was 1.5×10^{-6} Pa). The mass spectrum using this "clean" source was considered as a background signal and was subtracted from the spectrum of the enriched water. The height of the background signal was only



Abbreviated names	Explanation	$\delta^{2}H$ (‰)	$\delta^{18}O$ (‰)
SLAP-rep-O	SLAP replicate in ^{18}O	≈ -428	≈ -55.5
VSMOW-rep-O	VSMOW replicate in ^{18}O	≈ -428	≈ 0
VSMOW-rep-D	VSMOW replicate in ^{2}H	≈ 0	≈ -55.5
VSMOW-rep-OD	VSMOW replicate in ^{18}O and ^{2}H	≈ 0	≈ 0

FIGURE 1 Flow diagram and description of the used abbreviations in the process of quantification of the $\delta^{18}O_{SLAP}$ value with respect to $\delta^{18}O_{VSMOW}$. $\delta^{2}H$ and $\delta^{18}O$ in this figure are expressed on the VSMOW–SLAP scale. [Color figure can be viewed at wileyonlinelibrary.com]

minimally impacted by the last injection, which occurred before 48 h of pumping, irrespective of the isotopic character of that water (with either natural abundances or a water with enriched ^{18}O).

Water is very "sticky" and adheres on to the walls of the injector, dead volumes, and the ion source of the QMS. Therefore, the QMS setup needs to be saturated with highly enriched ^{18}O water to reduce memory effects. Thus, more than 20 sequential injections of identical samples were required to reach an equilibrium state. For every injection, 25 µL of water was injected, and a scan of m/z 1–41 was performed. The measurement pressure was at 2.5×10^{-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 these ions contain the two different H-isotopes and three different O-isotopes. In Figure 2, a typical quadrupole mass 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. Table S2 (supporting information) presents a highly enriched ^{18}O water (water portion D from Cortec) with the various isotopologues and fragments for this range of *m/z* values.

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 in 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 therefore, 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 resulting from the various clumped isotopocule ions on *m/z* 22–24 (see Table S2 [supporting information]) 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 S2 [supporting information]). Including the signal at *m/z* 36 in the spectral fit showed that about 7% of the $[^{18}O]^+$ ions recombines to $[^{18}O_2]^+$. Neglecting this small effect leads to a smaller apparent size of the—already-small—$[O]^+$ fraction, which is also a fit parameter, with no further consequence for the fitted result for the ^{18}O abundance.

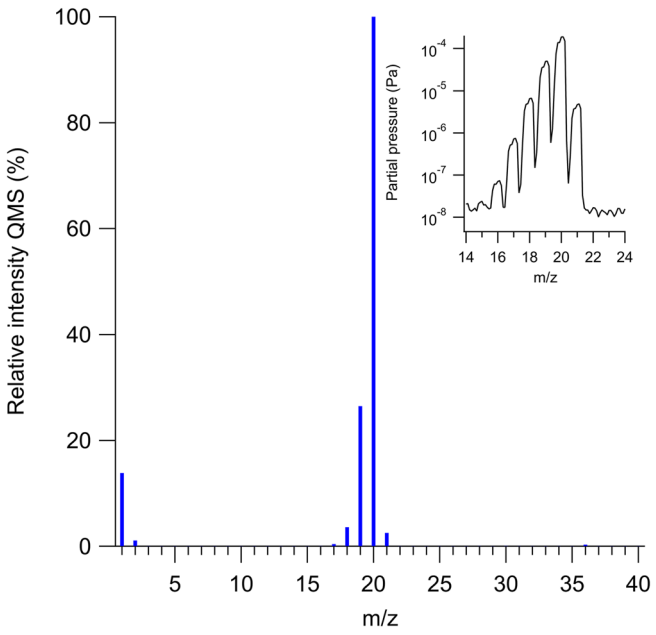


FIGURE 2 A typical quadrupole mass spectrum of a highly enriched ^{18}O water from *m/z* 1 to 40. The insert plot shows the partial pressure (Pa, plotted on a logarithmic scale) with respect to *m/z* 14–24. [Color figure can be viewed at wileyonlinelibrary.com]

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. Furthermore, the *m/z* 1 signal of the QMS does not truly represent $[^1H^+]$ (see later).

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 $[H_2O]^+$, $[OH]^+$, and $[O]^+$; and thus the size of the complementary fraction $[H_3O]^+$. Next to the signals *m/z* 17–21, the abundances of ^{17}O and ^2H were also input parameters for the fitting program. The abundances of ^{17}O and ^2H 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 ^2H nor ^{17}O abundance is very critical in the fitting process. This is because both abundances are low anyway: ^2H because it is in the natural range and ^{17}O because we deal with highly enriched ^{18}O waters. Therefore, there is room for only ≤1% ^{17}O, and the 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 et al[14]) and CIO (Centre for Isotope Research) laboratory standards, using the LGR-LWIA. For determining the ^2H 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 et al[3] for ^2H and Li[14] for ^{17}O). The results of the ^{18}O, ^2H, and ^{17}O abundances corresponding to all the highly enriched ^{18}O water portions are presented in Table 3 (Section 3), 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 $\delta^{18}O$ value close to VSMOW). We added a known quantity of highly enriched ^{18}O water needed to shift the $\delta^{18}O$ to 0‰ when measured against VSMOW. SLAP-rep-O was 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 h. 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 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 original VSMOW and SLAP, such that scale contraction issues played no role (see later).

The mixing process started with the characterization of the individual 1 L 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 precise $\delta^{18}O$ value for SLAP with respect to VSMOW. As we ensured that both the $\delta^{18}O$ differences SLAP-rep-O versus SLAP and VSMOW-rep-O versus 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 normalized $\delta^{18}O$ values (on the VSMOW–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 using a validated spreadsheet (Faghihi et al[15]).

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, $\delta^{18}O_{VSMOW\text{-}rep\text{-}O}$ is close to $\delta^{18}O_{VSMOW}$, but $\delta^{2}H_{VSMOW\text{-}rep\text{-}O}$ is still close to $\delta^{2}H_{SLAP}$. In principle, this does not matter for our experiment, as we are interested only in the ^{18}O side. However, excluding the possibility of this large difference in deuterium content between our VSMOW-rep-O and 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 ^2H_2O was added to mimic VSMOW in deuterium (called VSMOW-rep-D, $\delta^{2}H \approx 0‰$). Subsequently VSMOW-rep-D and highly enriched ^{18}O water were mixed to obtain VSMOW-rep-OD ($\delta^{2}H \approx 0‰$ and $\delta^{18}O \approx 0‰$). This second approach is shown on the right-hand side of Figure 1. It rules out spectroscopic biases in the measurements but otherwise is not different from the process described in Section 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 ^2H_2O to mimic VSMOW in deuterium, and therefore, very precise quantification of the ^2H_2O content was key. Determination of ^2H abundance of the enriched ^2H_2O water using quadrupole mass spectrometry, however, was not as straightforward as the determination of ^{18}O abundance of the enriched $H_2{}^{18}O$. This may be caused by the more complex spectrum for ^2H_2O. The ^2H_2O spectrum (Figure 3) shows that m/z peaks 17, 19, and 21 are about two orders of magnitude smaller than the adjacent m/z peaks 18 and 20. Table S3 (supporting information) presents a highly enriched ^2H water with the various isotopologues and fragments for this range of m/z values.

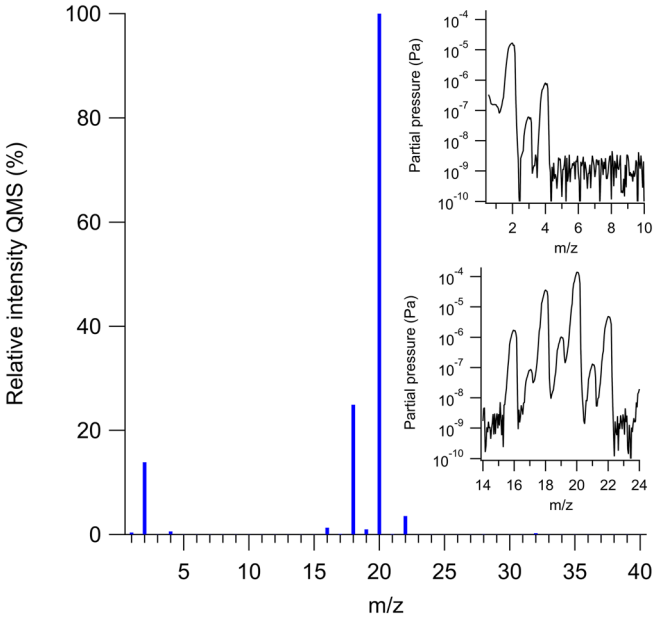


FIGURE 3 A typical quadrupole mass spectrum of ^2H_2O m/z 1–40. The small inserts show the logarithmic plots of m/z 0–10 (top) and 14–24 (bottom). [Color figure can be viewed at wileyonlinelibrary.com]

Peak tailing and leading of the larger peaks make 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 using the QMS, especially for these nearly pure ^2H_2O waters. This outgassing of hydrogen will obviously not affect the determination of oxygen isotope abundances.

Furthermore, the m/z 1 signal was much larger than we expected from a nearly pure ^2H_2O water (m/z 1 is ~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 that used for ^{18}O determination.

In conclusion, this discrepancy of measured (and fitted) ^2H abundance (of ~99.7%) and real (specified) ^2H abundance (99.98%) must be attributed to aforementioned reasons: 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 (vapor) from the surroundings.

In analogy to the mixing of enriched ^{18}O water and the replicate for SLAP, we added the amount of $^{2}H_2O$ that was calculated to achieve a $\delta^2H \approx 0‰$ to SLAP-rep-O. $^{2}H_2O$ was weighed in a glass vial on an analytical balance (~75 mg was weighed), and 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 h. All weights were corrected for the buoyancy effect.

In this second approach, the product VSMOW-rep-D ($\delta^2H \approx 0‰$, $\delta^{18}O$, still SLAP-like, $\approx -55.5‰$) was the basis of the mixing process with highly enriched ^{18}O water.

The adding of highly enriched ^{18}O water needed to obtain $\delta^{18}O \approx 0‰$ and the mixing of those two fluids were the same as described before.

The isotopic delta values of VSMOW-rep-D were characterized using 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, $\delta^{18}O$ and δ^2H of the produced VSMOW-rep-OD were measured by direct comparison with original VSMOW water.

As for the enriched ^{18}O water, the ^{17}O and ^{18}O abundances of the enriched $^{2}H_2O$ water had to be characterized as well. $^{2}H_2O$ was diluted first with demineralized Groningen tap water (1:7). Carbon dioxide with a known isotopic signature was then equilibrated with this diluted $^{2}H_2O$ at 25°C for 48 h (procedure described in Meijer[16]). CO_2 was extracted, and its $\delta^{13}C$ and $\delta^{18}O$ were measured using a dual-inlet IRMS mass spectrometer (a VG [now Isoprime] SIRA10). IAEA607 with approximately the same $\delta^{18}O$ signal as the diluted $^{2}H_2O$ water and some other local CIO references were identically treated and were used for normalization. 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; $\delta^{17}O$ could be determined via a method described in Elsig and Leuenberger.[17] 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 $^{2}H_2O$ water are presented in Section 3, along with their SD of three repetitions.

The difference between the stable isotope measurements and the calculated stable isotope values using the validated spreadsheet (Faghihi[15]) translates directly into a corresponding $\delta^{18}O$ value for SLAP with respect to VSMOW. In addition, the second approach has the beneficial side effect that additionally a δ^2H for SLAP could be determined. $\delta^2H_{VSMOW\text{-}rep\text{-}D}$ was initially calculated from the actually added (buoyancy-corrected) weight and isotopic abundances of the $^{2}H_2O$ water and the weight and isotopic delta values of SLAP-rep-O (on the VSMOW–SLAP scale). Subsequently $\delta^2H_{VSMOW\text{-}rep\text{-}D}$ was measured alongside VSMOW. The difference between this measurement and the calculated value translates directly into a δ^2H value for SLAP with respect to VSMOW.

As for approach 1, we ensured 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 normalized $\delta^{18}O$ and δ^2H values (on the VSMOW–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, like weighing waters, ^{18}O abundance measurements using a QMS and isotopic measurements using the LGR-LWIA, the uncertainties were determined or estimated.

To determine the contribution of uncertainties in the weighing process, a flask was weighed multiple times to determine the reproducibility of weighing. This procedure revealed that the spread in the weighing of the same flask multiple times was within five times the uncertainty specified by the manufacturers. Therefore, for weights measured using the precision balance, the accuracy was estimated at ±0.05 g, and for the analytical balance the accuracy was estimated at ±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 SD of the repetitional measurements. Table 3 presents this for all 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, the ^{2}H and ^{17}O abundances were deduced, and twice their standard error in the mean was used as 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 0.03‰) and was the basis for the weights for calculating the weighted average for every $\Delta\ \delta^{18}O$ parent replicate on multiple (typically three) measurement days.

The Monte Carlo simulation was programmed in R. All calculations were performed 10 000 times, with all the parameters and their uncertainties (assumed to belong to a normal distribution) as described earlier. The uncertainties in the absolute ^{17}O and ^{18}O ratios of VSMOW (Baertschi[6] and Li et al[18]) are also taken into account in the Monte Carlo simulation. This simulation gives the uncertainty for product VSMOW-rep-O (approach 1) or VSMOW-rep-OD (approach 2). 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 presented in Table S1 (supporting information) and in the graph in Figure 6. The supporting information further explains the final uncertainty calculation.

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 the pairs SLAP-rep-O, SLAP and VSMOW-rep-O, VSMOW leads to a precise $\delta^{18}O$ value for SLAP with respect to VSMOW. In the second approach those pairs are VSMOW-rep-D, SLAP and VSMOW-rep-OD, VSMOW.

All uncertainty sources are considered to be random errors, causing variability only 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 Results, 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[6]: $^{18}R = (2005.20 \pm 0.45) \times 10^{-6}$. Changing this value by one SD up would lead to a 0.013‰ less negative delta value for SLAP.

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

The reported final uncertainties in $\delta^{18}O_{SLAP}$ and in the absolute ^{18}O abundance for SLAP are one sigma combined uncertainties (SD). In the repository (https://doi.org/10.34894/1WXJSN), the uncertainty budget for all the components that contribute to the final combined uncertainty is provided.

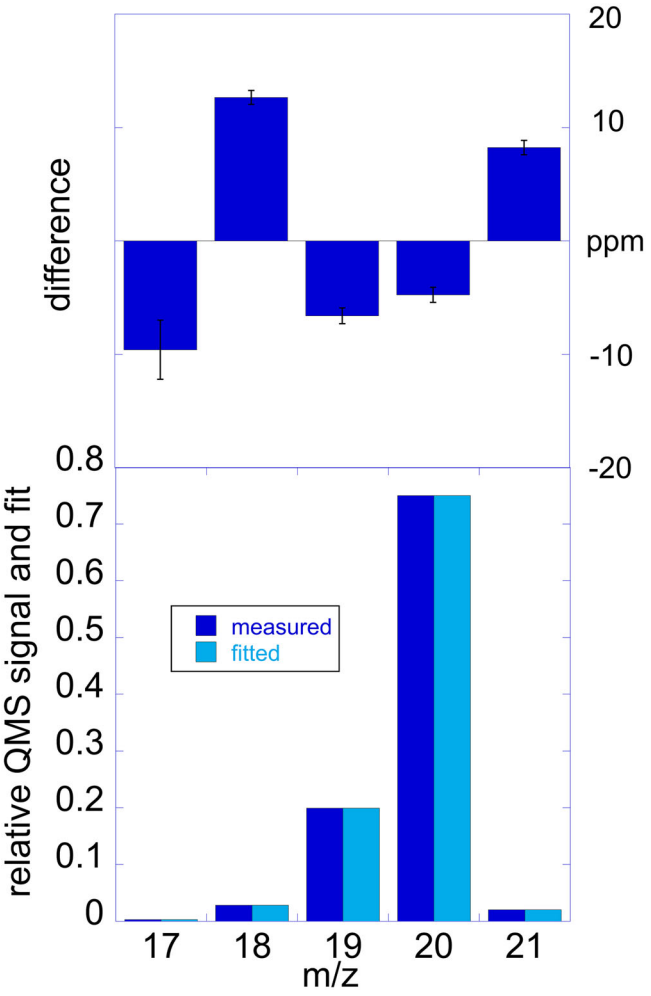


FIGURE 4 Relative abundance of *m/z* 17–21, together with the results from the fit from one injection with ^{18}O water. On this scale, the small error bars ($\sim 10^{-4}$) are not visible. On top, residuals from the true signal with respect to the fitted signal of QMS (quadrupole mass spectrometer) (*m/z* 17–21) are shown. The error bars are the SDs from 14 separate injections. [Color figure can be viewed at wileyonlinelibrary.com]

3 | RESULTS

The ^{18}O characterization of our six different highly enriched ^{18}O waters was 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 to 21 and the fitted signal from the bespoke program are compared; their very small residuals (in the order of 10 ppm) are shown on the 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 SDs of 14 measurements.

As a proof of method the enriched $H_2{}^{18}O$ water was diluted with ~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 presented in Table 1. The measured (fitted) ^{18}O abundances and the expected ^{18}O abundances are within 0.03% of each other. We conclude that real (small) differences in abundances are correctly measured.

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 presented 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

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

	^{18}O abundance measured	Difference in ^{18}O measured	Expected ^{18}O abundance[a]	Expected difference in ^{18}O[a]
^{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

[a]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.
Abbreviation: QMS, quadrupole mass spectrometer.

TABLE 2 Comparison of the distribution of four main oxygen-bearing fragmentation ions in QMS source for natural water and ^{18}O-enriched water (water portion A, Rotem).

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

Notes: The total concentration of those four ions is considered as 1 (so 100%). For every ion, the averaged part of this total fraction is displayed. SD of the repetitions (n) is shown in parentheses. Cortec water is even more enriched than Rotem water and shows slightly different fragmentation; an example is in Table S3 (supporting information).
Abbreviations: QMS, quadrupole mass spectrometer; SD, standard deviation.

TABLE 3 ^{18}O, ^{2}H, and ^{17}O abundances of six highly enriched ^{18}O water portions from Rotem (specified as >98%) and Cortec (>99%).

Water portion	Brand ^{18}O water	^{18}O abundance (SD)	n	^{2}H abundance (SD)	^{17}O abundance (SD)	Remarks
A	Rotem	0.9799 (6)	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	–[a]	–[a]	Water portion D, 4 months after opening
E	Rotem	0.9818 (2)	8	0.000032 (5)	0.0074 (<1)	
F	Cortec	0.9917 (2)	8	0.000051 (2)	0.0013 (<1)	

Notes: ^{18}O abundances are measured using a QMS. SD of the repetitions (n) is shown in parentheses. ^{2}H and ^{17}O abundances are determined via dilution, and measured using our LGR-LWIA, on two different measurement days and with nine repetitions per measurement day.
[a]^{2}H and ^{17}O abundances of water portion D′ were not remeasured.
Abbreviations: QMS, quadrupole mass spectrometer; SD, standard deviation.

in ^{18}O water, and the difference is more than 60% (relative)/1% (absolute). In the fitting program, described in Section 2.3, these differences are taken into account.

Our experiments also indicate a small isotope effect in the overall ionization efficiency between water with natural abundances and water with enriched ^{18}O: the enriched ^{18}O water seems to ionize about 6% less effectively than natural water. However, this value is very uncertain due to the uncertainty in the amount of water injected.

Alternatively, we can use the results from the previously described 1% and 2% dilution experiment to estimate this effect. There, the best fit between the expected and determined abundance differences leads to a 3 ± 3% lower ionization efficiency from highly enriched ^{18}O water compared to water with natural abundances. This effect would lead to a maximum deviation in the end result of $\delta^{18}O$ for SLAP of −0.02 ± 0.02‰. Therefore, we decided to neglect the possible slight difference in ionization yield in our fitting process.

Table 3 presents the results of the ^{18}O abundances for the six highly enriched ^{18}O water portions (A–F) from two different suppliers, Rotem and Cortec, measured using the QMS. Water portion D was measured twice, the latter being after 4 months of the first measurement set. Table 3 indicates that 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.

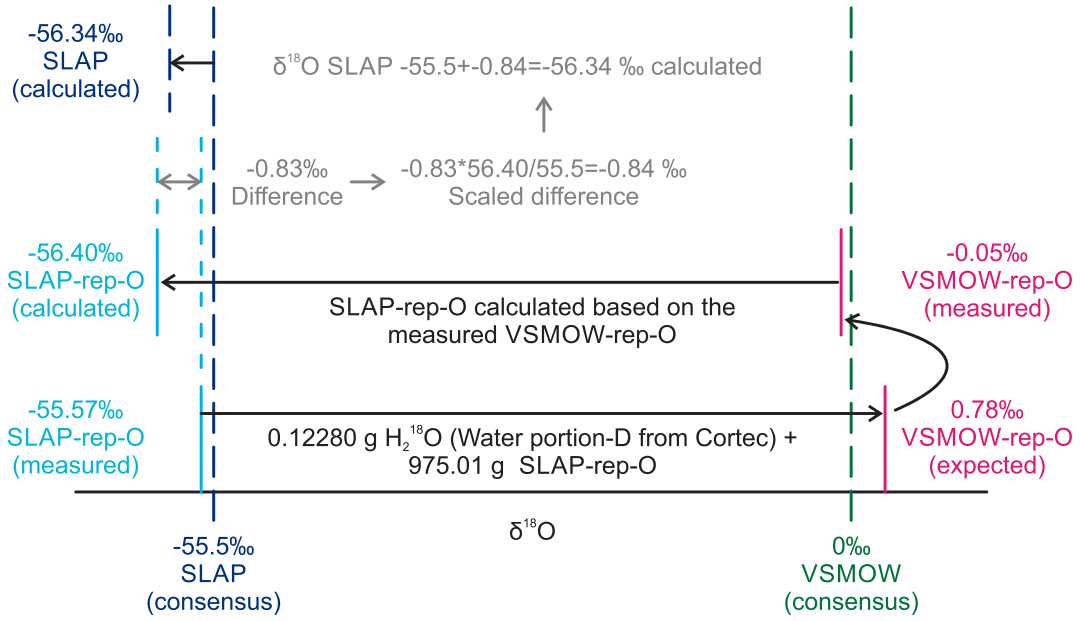


FIGURE 5 A full calculation scheme showing the steps involved in one of the seven independent determinations of the $\delta^{18}O$ of SLAP. [Color figure can be viewed at wileyonlinelibrary.com]

Following the determination of the ^{18}O content of the enriched waters, the enriched water was mixed with the SLAP replicate to produce SLAP-rep-O. The first approach (mixing only with $H_2{}^{18}O$) was independently performed four times, with four different ^{18}O water portions (two from Rotem and two from Cortec, ^{18}O water portion A–D). The second approach (mixing first with $^2H_2{}^{16}O$ and then 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 remeasured using a QMS (now D′). The second approach was independently performed with the two remaining ^{18}O waters as well (one from Rotem and one from Cortec, ^{18}O water portions E and F).

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

For the second approach (also mixing with ^2H_2O) it was necessary to verify the ^2H concentration specification of the supplier. The determination of the ^2H abundance of ^2H_2O water using a QMS was not as direct as the determination of ^{18}O using a QMS appeared to be, which has been explained in Section 2.3.2. The result of the QMS-fitted ^2H 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 ^2H abundance of the almost-pure ^2H_2O water is 0.99978, and the measured (via dilution and CO_2 equilibration) and calculated ^{17}O and ^{18}O abundances are 0.000808 (0.000003) and 0.005928 (0.000006), respectively.

The numbers in parentheses are the SDs of the three repetitions performed.

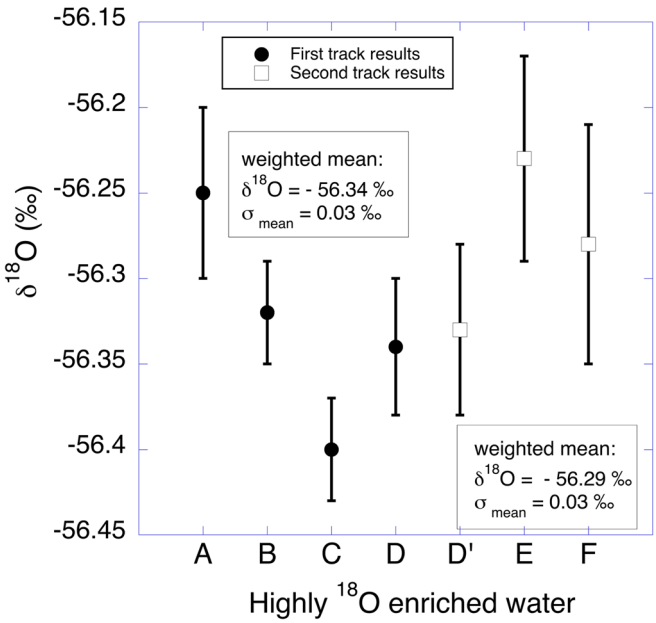


FIGURE 6 Results of seven experiments performed using six different highly enriched ^{18}O water portions (A–F in Table 3) for determining $\delta^{18}O$ SLAP. The black circles represent the results using the first approach, where VSMOW was mimicked in $\delta^{18}O$ only. The black open squares represent the results obtained using the second approach where VSMOW was mimicked in both isotopes. The overall weighted mean of all data points is −56.33 ± 0.03‰ (including the Student's *t*-factor). The error bars reflect the combined uncertainty calculated using a Monte Carlo approach, taking into account all individual error sources in the abundances, in the isotopic measurements and in the weights. [Color figure can be viewed at wileyonlinelibrary.com]

With enriched water portions A–D the first approach is used (mixing only 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 $\delta^{18}O_{SLAP}$ 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 Table S1 (supporting information). There were no significant differences between the two approaches, and therefore, all results for $\delta^{18}O_{SLAP}$ were averaged. The overall weighted mean of all data points is $\delta^{18}O_{SLAP} = -56.33 \pm 0.02‰$. Taking the Student's *t*-factor into account, the final outcome is $\delta^{18}O_{SLAP} = -56.33 \pm 0.03‰$. This final uncertainty does not include the two systematic effects mentioned in Section 2.4. These will be discussed later in this section.

The second approach allowed the determination of $\delta^{2}H$ for SLAP as well. The $\delta^{2}H_{SLAP}$ results are presented in Table S2 (supporting information). The overall weighted mean of the three experiments is $\delta^{2}H_{SLAP} = -430.3 \pm 0.3‰$ (again including the Student's *t*-factor).

4 | DISCUSSION

As explained in Section 1, the consensus values for SLAP with respect to VSMOW were established in 1976. The established $\delta^{2}H$ 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, −55.5‰, of an interlaboratory 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 et al[19]), laboratories indeed determined more negative values for SLAP. In our laboratory, we typically find values around $\delta^{18}O = -55.8‰$ using IRMS (CO_2-H_2O equilibration) and, more recently with the very different measurement technique of laser absorption spectroscopy, we found similar values around $\delta^{18}O = -55.7‰$. We expected that by having well-maintained machines and using the appropriate corrections, our results for SLAP would be close to the real values.

However, Kaiser[9] already suggested a reanalysis of the data of an intercomparison exercise of seven expert laboratories described in Verkouteren and Klinedinst,[7] resulting in a much more negative $\delta^{18}O$ value for SLAP, that is, −56.1 ± 0.2‰. On the contrary, the $\delta^{18}O$ value of −55.11‰ for SLAP measured by Barkan and Luz[8] is confusing. 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 toward this less-negative value of −55.11‰ (Hillaire-Marcel et al[20]).

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, 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 0.05‰. However, such a deviation is highly unlikely: it is good to 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 using a QMS. Because there is room for only 1%–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; Table S1 [supporting information]). The portion of ^{17}O plays only a minor role in the $^{18}O/^{16}O$ ratio, and this abundance can be determined using a dilution method.

The calculation of $\delta^{18}O_{SLAP}$ is based on the absolute ^{18}O determination of VSMOW by Baertschi.[6] The uncertainty in $^{18}R_{VSMOW}$ leads to a systematic uncertainty in our final answer of ±0.013‰, small compared to our final uncertainty. However, the large difference between the consensus value and our value for $\delta^{18}O$ of SLAP could also be caused by a bias in the determination of the absolute ^{18}O abundance of VSMOW. A deviation of 0.83‰ for $\delta^{18}O_{SLAP}$ would require a very large shift in the original published $^{18}O/^{16}O$ ratio from $(2005.2 \pm 0.45) \times 10^{-6}$ toward 2035.1×10^{-6}, a shift by 1.5%, 66 sigma away from Baertschi's value). The work by Baertschi cannot be checked in detail anymore, but such a large bias, considering the detailed description of the process, and the small uncertainty are highly unlikely. In addition, the older determination of the $^{18}O/^{16}O$ ratio (Craig[21]) was $(1993.4 \pm 2.5) \times 10^{-6}$ (lower than Baertschi's result), which supports Baertschi's value, and makes a bias toward a much higher value unlikely. It would imply a huge systematic error that has been overlooked. A somewhat less negative $\delta^{18}O_{SLAP}$ value of −55.8‰ would require a smaller bias of 0.5% of the absolute $^{18}O/^{16}O$ ratio of VSMOW, but this is still more than 20 sigma away from Baertschi's value and therefore also improbable.

Therefore, the result of this study is $\delta^{18}O = -56.33 \pm 0.03‰$ (SD), thus a very negative $\delta^{18}O$ value for SLAP, which was an unanticipated finding. The implication of the much more negative delta value for $\delta^{18}O_{SLAP}$ is that apparently a complete understanding of all IRMS effects (not to mention those in optical spectroscopy) is still lacking. Measuring cross-contamination effects (Meijer et al[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 ($\Delta^{17}O$) in water. For these measurements, in which the small deviation of the measured $\delta^{17}O$ from the natural relation between $\delta^{18}O$ and $\delta^{17}O$ is determined (Meijer and Li,[22] Aron et al,[23] Barkan and Lutz[8]), the question is how well these very small deviations (~0.02‰ or less) can be defined, if there are such large discrepancies between measured $\delta^{18}O$ and real $\delta^{18}O$ 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. In other words, if the measured scale for $\delta^{18}O$ is already so much contracted, who can guarantee that the $\delta^{17}O$ scale contracts exactly according to the equilibrium relation between $\delta^{17}O$ and $\delta^{18}O$?

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–SLAP 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 $\delta^{18}O$ values can be interconverted (Hillaire-Marcel et al[20]). 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[24]; see also Meijer[16]), and for the VPDB-CO_2 scale, acidification of IAEA-603 (formerly NBS-19) with phosphoric acid (McCrea,[25] Meijer,[16] and Hillaire-Marcel et al.[20] The difference between VSMOW-CO_2 and VPDB-CO_2 on the two $\delta^{18}O$ scales is 0.28‰–0.29‰ (Hillaire-Marcel et al[20]). In our laboratory, we 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 $\delta^{18}O$ value for SLAP (the second anchor of the VSMOW scale) could give potential discrepancies in the transfer of $\delta^{18}O$ 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 $\delta^{18}O$ 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.

Identical treatment of samples and references, the frequent use of international reference materials, and clear guidelines on how to express the results on the international scale(s) are key to provide normalized interlaboratory-comparable stable isotope measurements. This study does not affect those measurements; the VSMOW–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 into how large the scale contraction processes really are.

Finally, in fields where VSMOW–SLAP-scaled $\delta^{18}O$ values are converted into absolute abundances and vice versa, our new $\delta^{18}O$ value for SLAP does matter. An example of such a field is energy expenditure measurements using doubly labeled water, in which the used enriched reference waters will change their delta value (Guidotti et al,[26] Wang et al,[27] and Faghihi et al[14]).

5 | CONCLUSIONS AND RECOMMENDATIONS

The presented primary result of this paper is $\delta^{18}O_{SLAP}$ is −56.33 ± 0.03‰ (SD). With this work, the VSMOW–SLAP scale has in fact become metrologically traceable to the SI units for both isotopes: the combination of the absolute isotope ^{18}O abundance for VSMOW by Baertschi[6] and our present result for SLAP with respect to VSMOW leads to the calculated absolute ^{18}O abundance for SLAP of (1887.98 ± 0.43) × 10^{-6} (SD). As this result is directly dependent on Baertschi's value for the absolute ^{18}O abundance of VSMOW, redetermining this absolute ^{18}O composition of VSMOW is strongly recommended.

For ^{2}H, the 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 ± 0.3‰ (SD). This value is significantly lower than the values by Hageman et al,[3] de Wit et al,[4] and Tse et al.[5] 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 × 10^{-6}) in combination with the $^{2}R_{SLAP}$ value of Hageman (89.02 × 10^{-6}), the difference would translate into −429.2‰, whereas our value for SLAP would change into −429.8‰. This "friction of values" 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 water. For the purity of ^{1}H water, probably optical measurements are most suited. 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 et al[28] (further work is in progress). The ^{18}O-side of this carbonate scale is much more complicated, due to the fractionating process on which it is based. Furthermore, there still is no consensus on scale normalization, not to mention 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 toward pinpointing this ^{18}O VPDB scale to SI units, certainly for noncarbonate materials such as atmospheric CO_2.

AUTHOR CONTRIBUTIONS

Anita Th. Aerts-Bijma: Conceptualization; data curation; formal analysis; visualization; writing—original draft; methodology; investigation; project administration; writing—review and editing; software; validation; resources. **Albert C. van Buuren:** Investigation. **Dipayan Paul:** Visualization; methodology; supervision; writing—review and editing; validation. **Harro A.J. Meijer:** Conceptualization; methodology; supervision; writing—review and editing; software; validation; resources.

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DATA AVAILABILITY STATEMENT

The data that support the findings of this study are openly available in DataVerseNL at https://doi.org/10.34894/1WXJSN.

ORCID

Anita Th. Aerts-Bijma https://orcid.org/0000-0002-7227-791X

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SUPPORTING INFORMATION

Additional supporting information can be found online in the Supporting Information section at the end of this article.

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