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Improved Estimates of the Isotopic Correction Constants for the Triple Point of Water

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Abstract In 2006, the CIPM clarified the definition of the kelvin by specifying the isotopic composition of the water to be used in the realization of the triple point. At the same time, the Consultative Committee for Thermometry gave recommended values for the isotopic correction constants to be used for water departing from the specified composition. However, the uncertainties in the values for the correction constants were undesirably large due to unresolved differences between the data sets from which the values were determined. This paper derives improved values of the constants by considering additional data from isotopic fractionation measurements and the heats of fusion and freezing points of the relevant water isotopologues. Values of the corrections determined from the expanded data are $A_{\mathrm{D}} = 671(10)\ \mu\mathrm{K}$, $A_{^{18}\mathrm{O}} = 603(3)\ \mu\mathrm{K}$, and $A_{^{17}\mathrm{O}} = 60(1)\ \mu\mathrm{K}$. A typical correction made with these values lies just within the expanded uncertainty ($k = 2$) of the corrections made with the older values, but has about half the uncertainty.

Keywords Correction · Isotope · Temperature · Triple point · Water

1 Introduction

In 2006, the *Comité International des Poids et Mesures* (CIPM) clarified the definition of the kelvin by specifying the isotopic composition of the water used in the

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realization of the triple point of water to be that of Vienna Standard Mean Ocean Water (V-SMOW) [1]. V-SMOW is a standard reference material distributed by the International Atomic Energy Agency for the calibration of mass spectrometers used in hydrogen and oxygen isotope analysis. The clarification in the definition of the kelvin followed research demonstrating the magnitude of isotopic effects on the water triple-point temperature [2] and an international comparison of triple-point-of-water cells in which the larger than expected dispersion of results could be attributed, in part, to unaccounted variations in the isotopic composition of the water [3]. The CIPM's Consultative Committee for Thermometry (CCT) accompanied the CIPM's clarified definition with a set of recommended values for the isotopic correction constants to be used for water departing from the specified composition [4]. The values of the correction constants were based largely on the cryoscopic measurements of Kiyosawa [5], with supporting evidence from White et al. [2] and the historical measurements of LaMer and Baker [6]. Unfortunately, the estimation of the uncertainties in the correction constants was difficult. First, there were neither estimates of the uncertainties in Kiyosawa's cryoscopic measurements, nor were there measured values for the relative isotopic abundances of the D_2O and $H_2{}^{18}O$ in the waters used in the measurements, other than the supplier's specification. This situation was further complicated by more recent work of Kiyosawa [7] suggesting that Kiyosawa's water samples might have been contaminated by other isotopologues [8]. Second, the waters used by White et al. [2] did not span a sufficient range of both D and ^{18}O relative isotopic abundances to enable correction constants to be determined with a low uncertainty. Finally, the much earlier measurements of LaMer and Baker were conducted at a time when estimates of uncertainties were not routinely reported. The CCT task group investigating the isotopic influences on the triple point concluded that Kiyosawa's measurements were the most precise and assigned the values derived from Kiyosawa's data to the correction constants. The recommended correction equation is

$$\Delta T_{\mathrm{iso}} = -A_{\mathrm{D}}\delta \mathrm{D} - A_{^{18}\mathrm{O}}\delta^{18}\mathrm{O} - A_{^{17}\mathrm{O}}\delta^{17}\mathrm{O}, \tag{1}$$

where δD, δ^{18}O, and δ^{17}O are the measured isotopic departures from V-SMOW expressed as delta values, $\delta = R_{\mathrm{sample}}/R_{\mathrm{V\text{-}SMOW}} - 1$, where R is the isotope abundance ratios, and $A_{\mathrm{D}} = (628 \pm 20)\,\mu\mathrm{K}$, $A^{18}\mathrm{O} = (641 \pm 50)\,\mu\mathrm{K}$, and $A^{17}\mathrm{O} = (57 \pm 5)\,\mu\mathrm{K}$ [4]. The assigned standard uncertainties are Type B assessments based on the degree of consistency among the various reported values, tempered with knowledge that some systematic effects had not been investigated.

The clarification of the definition and the application of corrections to water triple-point measurements have contributed to significant improvements in the reproducibility of water triple-point cells. The CCT-K7 comparison, which commenced before the clarification, included cells that realized temperatures spanning about 250 μK, with most of the variation caused by impurities, and between 70 μK and 110 μK of the variation probably due to isotopic effects. More recently, informal comparisons of cells from different manufacturers indicate that the reproducibility among new cells corrected for isotopic composition is approximately 30 μK, with the uncertainty in the isotopic corrections probably contributing less than 5 μK to the uncertainty [9]. Although the clarification and the corrections have reduced the uncertainty to practically negligible levels, there remains a need for improved confidence, preferably accompanied by reduced uncertainty, in the values assigned to the correction constants.

This paper infers values of the isotopic correction constants using additional information from the values of the solid–liquid isotopic fractionation factors as measured by Lehmann and Siegenthaler [10], with supporting data from the known thermophysical properties of the water isotopologues. Section 2 explains and applies the relationship between the freezing-point elevation and isotopic fractionation, as given by Van't Hoff's relation. Section 3 then discusses the results and compares the inferred values with the historical data.

2 Van't Hoff's Relation and the Inferred Values for the Isotopic Corrections

The isotopic influence on the triple-point temperature arises from quantum-mechanical effects [11]. Because the electronic structure of atoms is the same for all isotopes of a particular element, heavier atoms form bonds with lower vibrational frequencies; hence, they occupy slightly lower energy states. This leads to a higher freezing-point temperature for the heavier isotopologues, and a weak solid–liquid fractionation effect favoring the heavy isotopes in the solid phase. By treating the dilute isotope as a dilute impurity, these two effects can be related by Van't Hoff's relation [12]:

$$\Delta T = \frac{RT_\mathrm{f}^2}{\Delta H_\mathrm{f}} X_\mathrm{i} \left(\alpha_\mathrm{S-L} - 1\right) \tag{2}$$

where ΔT is the rise in the freezing-point temperature due to the mole fraction, X_i, of the dilute heavy isotopologue, $\alpha_\mathrm{S-L}$ is the solid–liquid fractionation factor for the isotope, T_f is the freezing-point temperature, R is the universal gas constant, and ΔH_f is the enthalpy of fusion. For the triple point of water, the cryoscopic constant $RT_\mathrm{f}^2/\Delta H_\mathrm{f}$ is 103.28 K.

The definition of the kelvin requires the water to have the composition of V-SMOW with isotopic abundance ratios $R_\mathrm{D} = 0.000\,155\,76$ mol ^{2}H per mol ^{1}H, $R_{^{17}\mathrm{O}} = 0.000\,379\,9$ mol ^{17}O per mol ^{16}O, and $R_{^{18}\mathrm{O}} = 0.002\,005\,2$ mol ^{18}O per mol ^{16}O. This corresponds to mole fractions, $X_\mathrm{D} = 0.000\,155\,74$, $X_{^{17}\mathrm{O}} = 0.000\,379\,00$, and $X_{^{18}\mathrm{O}} = 0.002\,000\,43$.

The isotopic correction constant for ^{18}O is, from Eqs. 1 and 2,

$$A_{^{18}\mathrm{O}} = \frac{RT_\mathrm{f}^2}{\Delta H_\mathrm{f}} X_{^{18}\mathrm{O,VSMOW}} \left[\alpha_\mathrm{S-L}\left({}^{18}\mathrm{O}/{}^{16}\mathrm{O}\right) - 1\right]. \tag{3}$$

The isotopic correction constant for the deuterium requires an additional factor of two to account for the fact that almost all of the deuterium is distributed in the water as HDO rather than D_2O; that is $X_\mathrm{HDO} = 2 \times X_\mathrm{D}$, and hence

$$A_\mathrm{D} = \frac{RT_\mathrm{f}^2}{\Delta H_\mathrm{f}} 2X_\mathrm{D,VSMOW} \left[\alpha_\mathrm{S-L}(\mathrm{D/H}) - 1\right]. \tag{4}$$

The isotopic correction constant for ^{17}O is inferred from the value of the ^{18}O constant by assuming that the fractionation factor scales according to the masses of the isotopes [11], i.e., proportional to $(M_2 - M_1)/(M_1 M_2)$, where M_1 and M_2 are the molecular masses of the isotopologues:

$$A_{^{17}\mathrm{O}} = \frac{RT_\mathrm{f}^2}{\Delta H_\mathrm{f}} X_{^{17}\mathrm{O,VSMOW}} \left[\alpha_{\mathrm{S-L}}^{0.526} \left({}^{18}\mathrm{O}/{}^{16}\mathrm{O}\right) - 1\right]. \tag{5}$$

Because ^{17}O occurs in very low concentrations, and ^{17}O fractionation is very weak, the value and uncertainty for $A_{^{17}\mathrm{O}}$ have little effect on the isotopic correction for typical triple-point-of-water cells.

The most recent values of the solid–liquid fractionation factors are those reported by Lehmann and Siegenthaler [10]: $\alpha_{\mathrm{S-L}}(^{18}\mathrm{O}/^{16}\mathrm{O}) = 1.002\,91(3)$ and $\alpha_{\mathrm{S-L}}(\mathrm{D/H}) = 1.021\,2(4)$. The measurements were made by slowly freezing water at 0 °C, measuring the fractionation as a function of the velocity of the freezing interface, and then extrapolating to zero interface velocity. The reported uncertainties are the Type A uncertainties in the parameter values determined from the least-squares fit. There are additional uncertainties associated with the isotope measurements, but only Type A uncertainties characterizing the precision of the measurements are given: 0.03 ‰ for $^{18}\mathrm{O}/^{16}\mathrm{O}$ and 0.5 ‰ for D/H. Although no indication of the total uncertainty is given, such measurements are usually made by interpolating the isotopic measurements between those for standard reference materials SLAP (standard light Antarctic precipitation) and V-SMOW, so that the absolute accuracy is comparable to the precision. The precision given is also very similar to the uncertainties offered by other stable-isotope laboratories. When the reported Type A uncertainties are used to calculate the correction constants using Eqs. 3, 4, and 5, the values $A_\mathrm{D} = 682(13)\ \mu\mathrm{K}$, $A_{^{18}\mathrm{O}} = 601(7)\ \mu\mathrm{K}$, and $A_{^{17}\mathrm{O}} = 60(1)\ \mu\mathrm{K}$ are obtained.

3 Comparison with Historical Measurements

This section compares the values inferred from the fractionation factors with a variety of other historical measurements.

3.1 Kiyosawa

Kiyosawa [5] measured the freezing point of water as a function of the fraction of the heavy isotopologues, $D_2{}^{16}O$ and $H_2{}^{18}O$. The correction constants determined from his data are $A_\mathrm{D} = 628.1(2.7)\ \mu\mathrm{K}$ and $A_{^{18}\mathrm{O}} = 641.1(0.8)\ \mu\mathrm{K}$, where the uncertainties are the Type A values determined from a least-squares fit of the temperature to the fraction of the heavy isotope. As already noted, Kiyosawa reported only the manufacturer's specification for the composition of the water used in the measurements. Later measurements on $H_2{}^{17}O$ by Kiyosawa [7], following a similar procedure, seemed to show the effects of contamination by other heavy isotopologues [8]. If similar contamination occurred in the earlier measurements with $D_2{}^{16}O$ and $H_2{}^{18}O$ or if the compositions were not exactly as specified by the manufacturer, then there may be significant systematic errors.

3.2 White et al.

White et al. [2] measured the triple-point temperature realized by a total of five triple-point cells containing water of different isotopic compositions. However, the spread of compositions was limited because four cells were close to the natural composition and only one was significantly different. The latter was almost depleted of deuterium and approximately 35 % depleted of ^{18}O. Therefore, these measurements placed a tight constraint on a combination of A_{D} and $A_{^{18}\mathrm{O}}$ values but not on the individual values. The fit to the data yielded $A_{\mathrm{D}} = 725(42)$ μK and $A_{^{18}\mathrm{O}} = 507(68)$ μK. If the $A_{^{18}\mathrm{O}}$ was assigned a value of 602 μK (inferred from linear interpolation between the freezing points), then the data indicated a value of $A_{\mathrm{D}} = 668(12)$ μK.

3.3 La Mer and Baker

La Mer and Baker [6] carried out measurements on D_2O and H_2O to test the equations produced by Seltz [13] for the composition of an ideal binary solution in solid and liquid phases. Their measurements of the temperature elevation of the freezing point versus mole fraction of deuterium oxide yielded data that is well fitted by

$$\Delta T = 4.212(9)X_{\mathrm{D}} - 0.408(12)X_{\mathrm{D}}^2, \tag{6}$$

so that the isotopic sensitivity, $\mathrm{d}T/\mathrm{d}X_{\mathrm{D}}$, at very low concentrations is 4.212(9) K, and the freezing point of pure D_2O ($X_{\mathrm{D}} = 1$) is 3.804(4) degrees higher than for V-SMOW. LaMer and Baker concluded that the $\{D_2O + H_2O\}$ mixture showed significant departures from an ideal binary solution. (The reasons are discussed in the next subsection.) Nevertheless, the $\mathrm{d}T/\mathrm{d}X_{\mathrm{D}}$ value at $X_{\mathrm{D}} = 0$ yields a useful estimate of $A_{\mathrm{D}} = 656(2)$ μK.

3.4 Thermophysical Data

In an ideal binary solution, the two components are miscible, no heat is absorbed or liberated when the components are mixed, and the chemical potentials of the two components are the same. In a two-phase system (solid, S, and liquid, L) composed of components A and B, the two components are distributed in the two phases so as to satisfy [12]

$$\ln\left(\frac{X_{\mathrm{A}}^{\mathrm{L}}}{X_{\mathrm{A}}^{\mathrm{S}}}\right) = \frac{\Delta H_{\mathrm{f,A}}}{R}\left(\frac{1}{T_{\mathrm{A}}} - \frac{1}{T}\right), \tag{7}$$

and

$$\ln\left(\frac{X_B^L}{X_B^S}\right) = \frac{\Delta H_{f,B}}{R}\left(\frac{1}{T_B} - \frac{1}{T}\right). \tag{8}$$

These two equations are valid for all concentrations of A and B in an ideal solution. Van't Hoff's relation, Eq. 2, follows from Eq. 7 with the additional assumptions that B is dilute and $T - T_A$ is very small. Equation 2 is useful because it is observed that all binary solutions at sufficient dilution behave as ideal solutions [12]. Equations 7 and 8, when combined with the constraints $X_A^S + X_B^S = 1$ and $X_A^L + X_B^L = 1$, yield Seltz's equations for the solidus and liquidus [13]. The slope of the liquidus near $X_B = 0$ and $T = T_A$ (i.e., B dilute), gives the isotopic sensitivity coefficient,

$$\left.\frac{\mathrm{d}T}{\mathrm{d}X_B^L}\right|_{X_B^L=0} = \frac{T_A^2 R}{\Delta H_{f,A}}\left[\exp\left(\frac{\Delta H_{f,B}}{R}\left(\frac{1}{T_A} - \frac{1}{T_B}\right)\right) - 1\right]. \tag{9}$$

This is Van't Hoff's relation for dilute isotopes again (Eq. 2); however, it now includes the functional form for the fractionation factor. That is, if the mixture of A and B is an ideal solution at high concentrations, the fractionation factor α_{S-L} at low concentrations can be determined from the freezing-point temperature and enthalpy of fusion of the dilute isotopologue as

$$\alpha_{S-L}\,(B/A) = \exp\left(\frac{\Delta H_{f,B}}{R}\left(\frac{1}{T_A} - \frac{1}{T_B}\right)\right). \tag{10}$$

Table 1 summarizes the triple-point temperatures and enthalpies of fusion for the relevant water isotopologues.

When the fractionation factor is small, which is the case for all of the isotopes considered here, the liquidus (Eq. 9) is nearly linear and the slope at low concentrations is approximated by

$$\left.\frac{\mathrm{d}T}{\mathrm{d}X_B^L}\right|_{X_B^L=0} = (T_B - T_A)\frac{T_A}{T_B}\frac{\Delta H_{f,B}}{\Delta H_{f,A}}. \tag{11}$$

Table 1 Literature values for the triple-point temperatures, enthalpies of fusion, relative temperature shifts, and predicted solid–liquid fractionation factors for water isotopologues

Isotopologue	T_f (K)	ΔH_f (kJ · mol^{-1})	$\Delta T_f/T_f$	α_{S-L}
$H_2{}^{16}O$	273.1587 [2]	6.007(4) [14]	–	–
$H_2{}^{18}O$	273.46(1) [15]	6.029(4) [15]	0.00110	1.0029(7)
$D_2{}^{16}O$	276.97(2) [16]	6.315(11) [17]	0.01395	1.040(1)
$HD^{16}O$	275.19(5) [18]	6.227(13)[a] [18]	0.00744	1.0206(5)

[a] Majoube [18] inferred values for the heat of vaporization at 0 °C from liquid-phase HDO data (0 °C to 100 °C) and similarly for the heat of sublimation from the sublimation data (−30 °C to 0 °C) of [19]. The values were corrected to $T_f = 2.04$ °C and subtracted to obtain ΔH_f for HDO at the triple point

Hence, the relative uncertainty in the liquidus slope depends on the relative uncertainties in the temperature difference, the freezing-point temperatures, and the heats of fusion. Because the heat of fusion for ordinary water is well known [14] and its triple-point temperature is defined, the uncertainty is dominated by the uncertainties in the properties of the dilute isotopologue. For example,

$$\frac{u^2\left(A_{\mathrm{D}}\right)}{A_{\mathrm{D}}^2} \approx \frac{u^2\left(T_{\mathrm{f,HDO}}\right)}{\left(T_{\mathrm{f,HDO}} - T_{\mathrm{f,H_2O}}\right)^2} + \frac{u^2\left(\Delta H_{\mathrm{f,HDO}}\right)}{\Delta H_{\mathrm{f,HDO}}^2}, \tag{12}$$

and similarly for $A_{^{18}\mathrm{O}}$.

First consider the case for $\mathrm{H_2}^{18}\mathrm{O}$, which is the simpler of the two calculations. Equation 10 is used directly with $\mathrm{A} = \mathrm{H_2}^{16}\mathrm{O}$ and $\mathrm{B} = \mathrm{H_2}^{18}\mathrm{O}$, the calculated fractionation coefficient is 1.00291(11), and the corresponding value of $A_{^{18}\mathrm{O}}$ is 606(20). These values are very close to those determined from the Lehmann and Siegenthaler fractionation data, but have a higher uncertainty. Note the high linearity of the $\mathrm{H_2}^{18}\mathrm{O}$ liquidus too: the difference between the value calculated via Eq. 9 and the value obtained by linear interpolation (i.e., $T_{\mathrm{B}} - T_{\mathrm{A}}$) is less than 0.5 %. This supports the use of linear interpolation by White et al. to constrain the value of $A_{^{18}\mathrm{O}}$. Table 2 summarizes the various estimates of the correction constant, $A_{^{18}\mathrm{O}}$.

For the case with $\mathrm{D_2}^{16}\mathrm{O}$ as a dilute impurity, the situation is more complicated. As noted above, the data of LaMer and Baker do not follow the equation for an ideal binary solution. This is because the $\mathrm{D_2O}$ isotopologue dissociates according to

$$\mathrm{H_2O} + \mathrm{D_2O} \leftrightarrow 2\mathrm{HDO}, \tag{13}$$

so the mixture has three components and not two. At very low concentrations of $\mathrm{D_2O}$, nearly all of the deuterium is present as HDO, and Eq. 10 must be applied with $\mathrm{A} = \mathrm{H_2O}$ and $\mathrm{B} = \mathrm{HDO}$. At high concentrations, nearly all of the deuterium is present as $\mathrm{D_2O}$, so that Eq. 10 must be applied with $\mathrm{A} = \mathrm{D_2O}$ and $\mathrm{B} = \mathrm{HDO}$. The difference in the two cases explains the difference in the liquidus slope at the two extremes of Eq. 6, i.e., at $X_{\mathrm{D}} = 0$ and $X_{\mathrm{D}} = 1$, and the unexpectedly strong quadratic term in Eq. 6. To employ Eq. 10 to calculate the fractionation factor for HDO, we require the enthalpy of fusion and triple-point temperature for HDO. Because the HDO can never be isolated as a pure substance, both of these quantities are conceptual. The value for the triple-point temperature of HDO of 275.19 K, given in Table 1, is taken from Majoube [18] which is calculated from his data on fractionation in dilute (e.g., natural) water

Table 2 Summary of analysis for $A_{^{18}\mathrm{O}}$

Source of data	$A_{^{18}\mathrm{O}}$ (μK)	Comments
Lehman and Siegenthaler [10]	601(7)	Type A only
Kiyosawa [5]	641.1(0.8)	Type A only, with probable systematic effects
White et al. [2]	507(68)	Type A only
Calculated from Table 1	606(20)	Similar to linear interpolation (603)

Table 3 Summary of analysis for A_D

Source of data	A_D (μK)	Comments
Lehman and Siegenthaler [10]	682(13)	Type A only
Kiyosawa [5]	628.1(2.7)	Type A only, with probable systematic effects
White et al. [2]	725(42)	Type A only
	668(12)	Type A only, assumes 602 μK for A_{18O}
LaMer and Baker [6]	656(2)	Type A uncertainties only
Calculated from Table 1 data	662(16)	Uncertainties from Majoube [18]

solutions and other similar data for ice solutions. The Majoube data can likewise be used to derive a value for the HDO enthalpy of fusion. When combined according to Eq. 10, these data give a fractionation factor of 1.0206(5), and a correction constant of 662(16) only 2.8 % less than the value inferred from the Lehmann and Siegenthaler fractionation data. Table 3 summarizes the various estimates of the isotopic correction constant A_D.

4 Discussion and Conclusions

The above analysis considers a broader collection of archival data and theory for the freezing of water isotopologue solutions than was previously included in the evaluation of isotopic correction factors by the CCT task group. One of the most reassuring aspects of the analysis is the degree of consistency between the results derived from measurements based on different physical principles. In particular, results determined from the isotopic fractionation factors, the thermophysical data, and the direct temperature-difference measurements using isotopically dilute (e.g., ∼ natural) waters are very similar. As a result of this reanalysis, we recommend values for the isotopic correction constants for the triple point of water of $A_D = 671(10)$ μK, $A_{18O} = 603(3)$ μK, and $A_{17O} = 60(1)$ μK. The recommended uncertainties are based on the un-weighted mean of values derived from experiments employing different physical principles. The unweighted mean was used because there is insufficient information available on the total uncertainties to enable the use of a weighted mean.

The data for the influence of the $H_2{}^{18}O$ isotopologue are the simplest to address because the mixture is an ideal binary solution. The close agreement between the result from fractionation data of Lehman and Siegenthaler and that from theory and the thermophysical data, within a few microkelvins, is very reassuring. The mean of the two results is 603 μK, which is also the value obtained by linear interpolation between the freezing points. As explained above, the data from White et al. is too uncertain for $H_2{}^{18}O$ to usefully contribute to the determination. The comparatively large difference between the Kiyosawa result and the other two suggests that Kiyosawa's might be subject to a systematic error. For example, contamination from as little as 0.3 % D_2O would explain the deviation. The uncertainty, based on the consistency of the two selected values, is 3 μK.

Table 4 Comparison of isotope corrections and uncertainties for a water triple-point cell manufactured by the Measurement Standards Laboratory of New Zealand

	Term	$\delta\mathrm{D} = -96.1\,‰$	$\delta^{18}\mathrm{O} = -14.7\,‰$	$\delta^{17}\mathrm{O} = -7.8\,‰$	Total correction
CCT values	ΔT	60.35	9.42	0.44	70.2(2.1)
	$u(\Delta T)$	1.92	0.74	0.04	
This work	ΔT	64.48	8.86	0.47	73.8(1.0)
	$u(\Delta T)$	0.96	0.04	0.01	

The uncertainties exclude the uncertainty associated with the isotopic analysis. All temperature values are in microkelvin

The data for the influence of D_2O are more complicated because the isotopologue dissociates forming a ternary solution. At the low concentrations typical of natural waters, the effects of D_2O can be modeled by a binary solution with HDO as the dilute solute. In this case, the agreement between Lehman and Siegenthaler result and the result based on thermophysical data is within 2.8 % in A_D. Additionally, the data from White et al. also are in good agreement with these A_D values providing that the linearly interpolated $A_{18\mathrm{O}}$ value is added in as a constraint. The simple mean of these three values for A_D is 671 μK. The Kiyosawa result lies about 6.5 % below this value, for reasons unknown.

It is instructive to compare the isotope correction and uncertainty for a triple-point-of-water cell using the two sets of values (Table 4). The values of δD, δ^{18}O, and δ^{17}O given in the table are for a cell with a moderately large isotopic correction. There are several points to note. First, the increase in the value of the correction is just within the expanded total uncertainty determined using the CCT values, so the new correction is not significantly different from that calculated with the CCT values. Second, the uncertainties associated with the corrections for the oxygen isotopes are now negligible. Finally, the uncertainty in the deuterium correction, now the dominant term, is now half of the previous value, so that the total uncertainty is also halved.

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