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LETTER TO THE EDITOR

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Calibration of $\delta^{17}O$ and $^{17}O_{excess}$ values of three international standards: IAEA-603, NBS19 and NBS18

In 2015 Barkan et al performed high-precision measurements of the $\delta^{17}O$ and $^{17}O_{excess}$ values of the international carbonate standards NBS19 and NBS18.[1] In 2016 a new standard (IAEA-603) was introduced, aimed to replace NBS19 that had been exhausted, as the new international standard for $\delta^{13}C$ and $\delta^{18}O$ analyses.[2] In order to use it also as a standard for $^{17}O_{excess}$, we present here high-precision measurements of three oxygen isotopes in this standard.

The measurements were carried out by direct oxygen isotope exchange between CO_2 extracted from $CaCO_3$ and O_2 of known three oxygen isotopic composition, followed by analysis of the resulting O_2 for $\delta^{17}O$ and $\delta^{18}O$ values. These values were used to calculate $^{17}O_{excess}$ as:

$$^{17}O_{excess} = 10^6\ [\ln(10^{-3}\delta^{17}O + 1) - 0.528\ \ln(10^{-3}\delta^{18}O + 1)].$$

All methodological details, including those for CO_2 extraction from carbonates, were given previously.[1] In short, CO_2 samples were extracted from $CaCO_3$ by digestion with 1.92 g/cm^3 phosphoric acid at 25°C. The CO_2 underwent isotopic exchange with O_2 of a known isotopic composition over hot platinum. After isotope exchange, the O_2 samples were measured by dual-inlet mass spectrometry versus an O_2 working reference gas that was calibrated with respect to VSMOW. The obtained values were then normalized to the VSMOW–SLAP scale, assuming that the $^{17}O_{excess}$ value of SLAP equals zero.[3] As the ^{17}O isotopic fractionation for phosphoric acid digestion is unknown, the reported values are for the CO_2 rather than for $CaCO_3$.[4]

All measurements were performed alongside an in-house CO_2 standard that was analyzed daily to check the performance of the CO_2-O_2 isotope exchange setup and of the mass spectrometer. This standard was accurately calibrated for $^{17}O_{excess}$ using CO_2 equilibrated with waters of different three oxygen isotopic compositions, as well as CO_2 produced by quantitative conversion over hot graphite of pre-calibrated O_2 gas to CO_2 with a known three oxygen isotopic composition.[5,6] On days in which the measured $^{17}O_{excess}$ value of this in-house CO_2 standard was offset from the long-term mean, a correction was applied to the values obtained for all samples measured on that day.

Two different ampoules of IAEA-603 were analyzed for their $\delta^{17}O$ and $^{17}O_{excess}$ values. In order to minimize the effect of potential unrecognized analytical errors, replicate analyses were performed on different days and the full set of measurements was repeated 6 months apart. Each CO_2 sample was measured for its $\delta^{18}O$ value versus a working reference gas that was previously calibrated using NBS19. The average $\delta^{18}O$ value of IAEA-603 was −2.35 ± 0.03‰ versus VPDB, which is within analytical error from the IAEA certified value (−2.37± 0.04‰).[2] The small difference of 0.02‰ introduces only a negligible error in the calculation of CO_2 $^{17}O_{excess}$ values, and thus we normalized our $\delta^{18}O$ data to the nominal value.

Data of $^{17}O_{excess}$ are given in Table 1. As can be seen, $^{17}O_{excess}$ values varied by 5–6 per meg among replicates, and the two ampoules differed by only 3 per meg, less than our analytical error. This suggests that this standard is homogenous with respect to $^{17}O_{excess}$. The resulting mean value of $^{17}O_{excess}$ of CO_2 extracted from IAEA-603 at 25°C is −194 ± 6 per meg.

Whereas $^{17}O_{excess}$ values of NBS19 and NBS18 have been previously measured at high precision, there is a clear discrepancy between the values measured in our laboratory[1] and those measured by Passey et al.[8] Therefore, we re-measured the $^{17}O_{excess}$ values of NBS19 and NBS18 alongside the measurements of IAEA-603 to verify the exact relationship between the three standards. Unfortunately, the materials in the bottles of NBS19 and NBS18 used in 2015 were exhausted and, hence, the exact same materials could not be re-measured. Accordingly, measurements were performed using a new bottle (purchased in 2016) for each of the two standards.

Our CO_2 working reference gas has been calibrated for $\delta^{18}O$ using NBS19. Therefore, our average $\delta^{18}O$ value of NBS19 is the same as the IAEA certified value,[7] within our analytical precision (0.03‰). The measured $\delta^{18}O$ value for NBS18 was slightly higher than the nominal value[7] (offset by 0.07‰), although it is still within the uncertainty estimate given by the IAEA for this standard (0.22‰). As noted above, such small differences in $\delta^{18}O$ values introduce only a negligible error in the calculated CO_2 $^{17}O_{excess}$ values, and thus we used the IAEA nominal values in our calculations.

TABLE 1 δ^{17}O, δ^{18}O and ^{17}O$_{excess}$ values of CO$_2$ extracted from IAEA-603 at 25°C. All values are versus VSMOW; δ^{17}O and δ^{18}O in ‰, ^{17}O$_{excess}$ in per meg. Errors of the mean correspond to the 95% confidence limit (standard error of the mean multiplied by Student's t-factor)

Date	δ^{17}O	δ^{18}O^{a}	^{17}O$_{excess}$
Ampoule 1			
19/12/17	20.214	39.019	−198
25/12/17	20.211	39.019	−201
26/12/17	20.217	39.019	−195
02/01/18	20.228	39.019	−184
03/01/18	20.221	39.019	−191
07/01/18	20.212	39.019	−200
13/05/18	20.223	39.019	−189
15/05/18	20.213	39.019	−199
16/06/18	20.214	39.019	−198
27/06/18	20.215	39.019	−197
01/07/18	20.216	39.019	−196
Aver.	20.217	39.019	−195
± SE*t	0.005		5
Ampoule 2			
27/12/17	20.221	39.019	−191
28/12/17	20.212	39.019	−200
24/01/18	20.227	39.019	−185
25/01/18	20.222	39.019	−190
29/01/18	20.228	39.019	−184
15/05/18	20.222	39.019	−190
16/05/18	20.215	39.019	−197
25/06/18	20.221	39.019	−191
26/06/18	20.212	39.019	−200
01/07/18	20.224	39.019	−188
02/07/18	20.215	39.019	−197
Aver.	20.220	39.019	−192
± SE*t	0.006		6
Grand averages	δ^{17}O = 20.218 ± 0.005; δ^{18}O = 39.019; ^{17}O$_{excess}$ = − 194 ± 6		

[a] This value was calculated from the IAEA recommended value[2] (−2.37‰ versus VPDB) using 1.01025 as the ^{18}O fractionation factor in the acid digestion reaction of CaCO$_3$ by H$_3$PO$_4$ at 25°C[13] and using the conversion equation relating the VPDB scale to the VSMOW scale.[7] See explanation in the main text.

TABLE 2 δ^{17}O, δ^{18}O and ^{17}O$_{excess}$ values of CO$_2$ extracted from NBS19 at 25°C. All values are versus VSMOW; δ^{17}O and δ^{18}O in ‰, ^{17}O$_{excess}$ in per meg. Errors of the mean correspond to the 95% confidence limit (standard error of the mean multiplied by Student's t-factor)

Sample	Date	δ^{17}O	δ^{18}O^{a}	^{17}O$_{excess}$
Bottle 1 (IAEA)	27/12/17	20.320	39.196	−184
	28/12/17	20.331	39.196	−173
	03/01/18	20.323	39.196	−181
	04/01/18	20.323	39.196	−181
	07/01/18	20.330	39.196	−174
	07/01/18	20.321	39.196	−183
	24/01/18	20.330	39.196	−174
	25/01/18	20.325	39.196	−179
	26/01/18	20.329	39.196	−175
	28/01/18	20.331	39.196	−173
	31/01/18	20.325	39.196	−179
	03/05/18	20.332	39.196	−172
	03/05/18	20.321	39.196	−178
	06/05/18	20.324	39.196	−175
	07/06/18	20.319	39.196	−180
	08/06/18	20.323	39.196	−181
	09/06/18	20.325	39.196	−179
Aver.		20.325	39.196	−178
± SE*t		0.004		4
Bottle 2 (IAEA)	07/05/18	20.325	39.196	−179
	08/05/18	20.326	39.196	−178
	10/05/18	20.326	39.196	−178
	24/05/18	20.316	39.196	−188
	25/05/18	20.325	39.196	−179
	27/05/18	20.321	39.196	−183
	27/05/18	20.319	39.196	−185
Aver.		20.323	39.196	−181
± SE*t		0.004		4
Bottle 3 (IAEA)	12/05/18	20.316	39.196	−188
	13/05/18	20.317	39.196	−187
	21/05/18	20.311	39.196	−193
	24/06/18	20.317	39.196	−187
	25/06/18	20.317	39.196	−186
	27/06/18	20.315	39.196	−189
Aver.		20.315	39.196	−188
± SE*t		0.003		3
Bottle 4 (NIST)	09/05/18	20.312	39.196	−192
	14/05/18	20.318	39.196	−186
	16/05/18	20.312	39.196	−192
	12/06/18	20.307	39.196	−197
	14/06/18	20.317	39.196	−187
	16/06/18	20.320	39.196	−184
	21/06/18	20.326	39.196	−178
	27/06/18	20.323	39.196	−181
	28/06/18	20.315	39.196	−189
Aver.		20.317	39.196	−187
± SE*t		0.006		6
Grand averages	δ^{17}O = 20.320 ± 0.006; δ^{18}O = 39.196; ^{17}O$_{excess}$ = −182 ± 6			

[a] This value was calculated from the IUPAC recommended value[7] (−2.20‰ versus VPDB) as noted in Table 1. See explanation in the main text.

The obtained ^{17}O$_{excess}$ values were −178 ± 4 per meg for NBS19 and −162 ± 5 per meg for NBS18 (Bottle 1 in Tables 2 and 3). These results are surprising as both values differ significantly from those that we measured a few years ago[1] −227 per meg for NBS19 and 3 per meg for NBS18. At the same time, our in-house Carrara marble, which has been systematically measured over these 3 years, shows stable ^{17}O$_{excess}$ values within the analytical precision.

The simplest possible explanation for the difference between the two data sets is heterogeneity of ^{17}O$_{excess}$ values among bottles of these standards. This may be due to inter-bottle differences within a batch of standards, differences between old (older than ~30 years) and new batches of these materials, or variations between bottles prepared by IAEA and NIST. In addition, it is possible that the specific bottles that we used previously have been compromised over many years of use.

Because the specific materials analyzed previously are unavailable, it was impossible to test directly for heterogeneity between these old bottles and the current batch of standards.

TABLE 3 $\delta^{17}O$, $\delta^{18}O$ and $^{17}O_{excess}$ values of CO_2 extracted from NBS18 at 25°C. All values are versus VSMOW; $\delta^{17}O$ and $\delta^{18}O$ in ‰, $^{17}O_{excess}$ in per meg. Errors of the mean correspond to the 95% confidence limit (standard error of the mean multiplied by Student's t-factor)

Sample	Date	$\delta^{17}O$	$\delta^{18}O^a$	$^{17}O_{excess}$
Bottle 1 (IAEA)	02/01/18	9.057	17.522	−155
	03/01/18	9.048	17.522	−164
	04/01/18	9.043	17.522	−169
	04/01/18	9.054	17.522	−158
	07/01/18	9.050	17.522	−162
	29/01/18	9.052	17.522	−160
	03/05/18	9.056	17.522	−156
	06/05/18	9.045	17.522	−167
	07/05/18	9.056	17.522	−156
	08/05/18	9.046	17.522	−166
	02/06/18	9.047	17.522	−165
	03/06/18	9.049	17.522	−163
	04/06/18	9.046	17.522	−166
Aver.		9.050	17.522	−162
± SE*t		0.005		5
Bottle 2 (IAEA)	12/05/18	9.049	17.522	−163
	13/05/18	9.045	17.522	−167
	21/05/18	9.056	17.522	−156
	24/06/18	9.054	17.522	−159
	25/06/18	9.055	17.522	−158
	26/06/18	9.043	17.522	−169
Aver.		9.050	17.522	−162
± SE*t		0.005		5
Bottle 3 (NIST)	10/05/18	9.043	17.522	−169
	13/05/18	9.052	17.522	−160
	14/05/18	9.042	17.522	−170
	15/06/18	9.043	17.522	−169
	16/06/18	9.042	17.522	−171
	17/06/18	9.048	17.522	−164
Aver.		9.045	17.522	−167
± SE*t		0.004		4
Grand averages	$\delta^{17}O$ = 9.049 ± 0.005; $\delta^{18}O$ = 17.522; $^{17}O_{excess}$ = −163 ± 5			

[a]This value was calculated from the IUPAC recommended value[7] (−23.01‰ versus VPDB) as noted in Table 1. See explanation in the main text.

Instead, we measured $^{17}O_{excess}$ values in several different bottles of each standard. These bottles included materials prepared by both IAEA and NIST, with variable time of purchase. This allowed us to test for inter-bottle heterogeneity and for potential differences between the two sources of standard materials. As can be seen in Tables 2 and 3, there are no significant differences between bottles, irrespective if the materials were prepared by IAEA or NIST. It is therefore most likely that the problem was specifically with the materials that we used in 2015 that may have been slightly contaminated, resulting in an $\delta^{17}O$ offset.

It is important to note that in order to verify the accuracy of our values, in parallel to the carbonates analyses we measured CO_2 that was equilibrated with different waters of known $^{17}O_{excess}$ values. The expected $^{17}O_{excess}$ values for these CO_2 samples were calculated from the $\delta^{17}O$ and $\delta^{18}O$ values of the waters using CO_2–H_2O equilibrium fractionation factors.[9] The waters were our in-house water standards, which were well calibrated on the VSMOW–SLAP scale and cover a wide range of $\delta^{18}O$ values (from −4‰ to −58‰ versus VSMOW). We also used water mixtures that were prepared such that the $\delta^{18}O$ values of equilibrated CO_2 would be similar to that of the CO_2 extracted from NBS19 and NBS18. The agreement with the expected $^{17}O_{excess}$ values (within 5 per meg) in these CO_2 samples[5] serves to support the accuracy of our carbonate $^{17}O_{excess}$ values.

Farquhar et al[10] measured a $\delta^{17}O$ value in CO_2 extracted from NBS18 by acid digestion followed by fluorination of the CO_2 to release O_2. The reported $^{17}O_{excess}$ value was calculated with respect to a reference slope of 0.52. The precision given for these data is too low to reliably convert the $^{17}O_{excess}$ value to a scale based on a different reference slope, and makes a direct comparison impractical. Liang et al[11] reported a single measurement of CO_2 extracted from NBS18 and analyzed by CO_2–O_2 exchange, as in our case, using the setup and protocol of Mahata et al.[13] The resulting $^{17}O_{excess}$ value is 90 per meg relative to a reference slope of 0.516. Assuming the nominal IAEA $\delta^{18}O$ value for NBS18 (17.522‰), we can estimate an $^{17}O_{excess}$ value of −119 per meg relative to a reference slope of 0.528. This value is between our value and that of Passey et al. Unfortunately, because Liang et al do not provide their measured $\delta^{18}O$ and $\delta^{17}O$ values, it is difficult to assess the accuracy of this value.

The first high-precision measurements of $^{17}O_{excess}$ values in NBS18 and NBS19 were performed by Passey et al.[8] Our new values are in much better agreement with their data (Table 4) relative to our 2015 values, although some differences remain. We note that the methods used in the two laboratories are very different. Whereas we report directly $^{17}O_{excess}$ in CO_2 extracted from carbonates, Passey et al report $^{17}O_{excess}$ in O_2 derived from water that, in turn, is produced by methanation of CO_2. Furthermore, the extraction of CO_2 from $CaCO_3$ was performed by acid digestion under different conditions: 25°C in McCrea-type vessels in our laboratory versus 90°C in a common acid bath in Passey et al. The fractionation in the acid digestion reaction is known for ^{18}O, but not for ^{17}O, and the $^{18}\alpha/^{17}\alpha$ ratio may be temperature dependent, resulting in different $^{17}O_{excess}$ values in the CO_2 evolved in the two laboratories. As such, it should not be expected that the absolute $^{17}O_{excess}$ values agree. However, as the methodological differences are systematic, it is expected that the difference between two samples (namely, NBS19 and NBS18) would be consistent across methods. The observed discrepancy of 17 per meg between the two data sets (Table 4) is within the combined

TABLE 4 Comparison of the $^{17}O_{excess}$ values (per meg) of NBS19 and NBS18[a]

	Present work	Passey et al[8]
NBS19	−182	−135
NBS18	−163	−98
Difference	20	37

[a]Note that the values in the present study were obtained by acid digestion of the carbonates at 25°C and are reported for CO_2. In Passey et al[8] CO_2 was obtained by acid digestion at 90°C, and the values are reported for O_2 produced by water fluorination, which in turn was obtained by methanation of extracted CO_2.

analytical precision (19 per meg). Furthermore, the consistency of measured and expected $^{17}O_{excess}$ values in CO_2 equilibrated with isotopically known waters provides strong support for the robustness of our current values for CO_2 extracted from $CaCO_3$. We therefore suggest using the $^{17}O_{excess}$ values reported here in all three international standards for normalizing triple oxygen isotope data in carbonates, in order to enable meaningful comparisons of results among laboratories.

As noted by Mahata et al,[12] CO_2 and O_2 exchange over hot platinum is a heterogeneous reaction involving adsorption, desorption, and catalytic exchange. There may also be isotope effects associated with thermal diffusion between the cold and hot parts of the preparation lines. As a result, the empirical values of $^{17}\alpha$ and $^{18}\alpha$ are a combination of the fractionations in all the processes operating in the exchange reaction, and they therefore differ from the modeled values of equilibrium fractionations between CO_2 and O_2.[12] These empirical values should be considered as effective, or apparent, steady-state fractionations, rather than true equilibrium fractionation factors. Being empirical fractionation factors, they may vary among different experimental setups as well as depending on suppliers (or even batches) of the Pt sponge catalyst. Therefore, they may potentially vary over time and affect the resulting $^{17}O_{excess}$ values. These variations can be corrected for by routine measurements of in-house standards, calibrated using IAEA-603, NBS19 and NBS18.

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