In 2015 Barkan et al performed high-precision measurements of the \( \delta^{17}O \) and \( 17O_{\text{excess}} \) 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 \( 17O_{\text{excess}} \), 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 \( 17O_{\text{excess}} \) as:

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

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 a working reference gas that was previously calibrated using NBS19. The average \( \delta^{18}O \) value of IAEA-603 was \(-2.35 \pm 0.03\)% versus VPDB, which is within analytical error from the IAEA certified value (\(-2.37 \pm 0.04\)%).\(^2\) The small difference of 0.02\(\‰\) introduces only a negligible error in the calculation of CO\(_2\) \( 17O_{\text{excess}} \) values, and thus we normalized our \( \delta^{18}O \) data to the nominal value.

Data of \( 17O_{\text{excess}} \) are given in Table 1. As can be seen, \( 17O_{\text{excess}} \) 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 \( 17O_{\text{excess}} \). The resulting mean value of \( 17O_{\text{excess}} \) of CO\(_2\) extracted from IAEA-603 at 25°C is \(-194 \pm 6\) per meg.

Whereas \( 17O_{\text{excess}} \) 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 \( 17O_{\text{excess}} \) 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\(_2\) \( 17O_{\text{excess}} \) values, and thus we used the IAEA nominal values in our calculations.
The obtained $^{17}$Oexcess values were $-178 \pm 4$ per meg for NBS19 and $-162 \pm 5$ 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 $^{17}$Oexcess values within the analytical precision.

The simplest possible explanation for the difference between the two data sets is heterogeneity of $^{17}$Oexcess values among bottles of these standards. This may be due to inter-bottle differences within a batch of standards, differences between old (older than $\sim 30$ 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.
Instead, we measured $^{17}$O$_{\text{excess}}$ 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 δ$^{17}$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$_{\text{excess}}$ values. The expected $^{17}$O$_{\text{excess}}$ values for these CO$_2$ samples were calculated from the δ$^{17}$O and δ$^{18}$O values of the waters using CO$_2$–H$_2$O equilibrium fractionation factors. The waters were our in-house water standards, which were well calibrated on the VSMOW–SLAP scale and cover a wide range of δ$^{18}$O values (from −4‰ to −58‰ versus VSMOW). We also used water mixtures that were prepared such that the δ$^{18}$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$_{\text{excess}}$ values (within 5 per meg) in these CO$_2$ samples serves to support the accuracy of our carbonate $^{17}$O$_{\text{excess}}$ values.

Farquhar et al. measured a δ$^{17}$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$_{\text{excess}}$ 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$_{\text{excess}}$ value to a scale based on a different reference slope, and makes a direct comparison impractical. Liang et al. 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. The resulting $^{17}$O$_{\text{excess}}$ value is 90 per meg relative to a reference slope of 0.516. Assuming the nominal IAEA δ$^{18}$O value for NBS18 (17.522‰), we can estimate an $^{17}$O$_{\text{excess}}$ 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 δ$^{18}$O and δ$^{17}$O values, it is difficult to assess the accuracy of this value.

The first high-precision measurements of $^{17}$O$_{\text{excess}}$ values in NBS18 and NBS19 were performed by Passey et al. 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$_{\text{excess}}$ in CO$_2$ extracted from carbonates, Passey et al report $^{17}$O$_{\text{excess}}$ 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 18O, but not for 17O, and the 18O/17O ratio may vary from time to time, resulting in different $^{17}$O$_{\text{excess}}$ values in the CO$_2$ evolved in the two laboratories. As such, it should not be expected that the absolute $^{17}$O$_{\text{excess}}$ 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

| Sample | Date             | δ$^{17}$O | δ$^{18}$O | δ$^{17}$O$_{\text{excess}}$ |
|--------|------------------|-----------|-----------|----------------------------|
| 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    | −166                       |
|         | 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            | δ$^{17}$O = 9.049 ± 0.005; δ$^{18}$O = 17.522; δ$^{17}$O$_{\text{excess}}$ = −163 ± 5 |

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. 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$_2$. 

|          | Present work | Passey et al$^a$ |
|----------|--------------|-----------------|
| 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. 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$_2$. 

TABLE 3 δ$^{17}$O, δ$^{18}$O and $^{17}$O$_{\text{excess}}$ values of CO$_2$ extracted from NBS18 at 25°C. All values are versus VSMOW; δ$^{17}$O and δ$^{18}$O in ‰, $^{17}$O$_{\text{excess}}$ in per meg. Errors of the mean correspond to the 95% confidence limit (standard error of the mean multiplied by Student’s t-factor)
analytical precision (19 per meg). Furthermore, the consistency of measured and expected $^{17}\text{O}_{\text{excess}}$ 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 $^{17}\text{O}_{\text{excess}}$ 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., 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$_2$. 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 $^{17}\text{O}_{\text{excess}}$ 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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