Brief Report

Oxygen Isotope Phosphoric Acid Fractionation Factor and Uncertainty on the $\delta^{18}$O Measurements of Calcite

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Abstract: At present, the isotope ratio $^{18}$O/$^{16}$O (in the text expressed as $\delta^{18}$O) of carbonate ($\text{CO}_3^{2-}$) is usually determined by isotope ratio mass spectrometry measuring the $\text{CO}_2$ gas produced dissolving the $\text{CO}_3^{2-}$-bearing substance in concentrated $\text{H}_3\text{PO}_4$. As with any analytical data, the $\delta^{18}$O values of carbonate are also affected by uncertainty which must be considered mainly when data from different laboratories are compared. Usually, scientific papers report only repeatability and/or reproducibility of analytical results, which, have scarce significance for data comparison. With the aim of evaluating the overall uncertainty for new analytical data for low-Mg calcites, in this paper we reconsidered the $\delta^{18}$O data, which are reported in the literature. Two kinds of uncertainty must be taken into account: (1) that due to the calibration of the delta values using international standards (prediction uncertainty), (2) that due to small differences in the chemistry of low-Mg calcites. The two uncertainties must be added when comparing data produced in the same or different laboratories. We found that this overall uncertainty cannot be lower than about 0.2‰. Thus, uncertainty lower than 0.2‰, sometimes reported in the literature, is misleading.

Keywords: oxygen isotopes; low-Mg calcite; uncertainty on $\delta^{18}$O

1. Introduction

Oxygen stable isotopes of carbonate ($\text{CO}_3^{2-}$) of several minerals are largely used in geology, environmental sciences, and archaeology. For instance, changes in seawater $^{18}$O/$^{16}$O ratio and temperature are recorded by variations in the $^{18}$O/$^{16}$O ratio of Ca-carbonates of marine fossils and microfossils, thus providing the basis for global chronostratigraphy ([1] and reference therein). In archaeology, together with the oxygen isotopes of the phosphate ($\text{PO}_4^{3-}$, $\text{HPO}_4^{2-}$) of bioapatite of human and animal bone and tooth remains, oxygen isotopes of the carbonate of bioapatite may give information on the diagenetic conditions of the remains and, thus, on their ability to furnish palaeoenvironmental indications ([2,3], as pioneering works). However, as with any analytical results, the $^{18}$O/$^{16}$O ratio values are affected by uncertainties that must be taken into account when different data are compared. In most papers, however, only data for precision (repeatability and/or reproducibility) are reported, values that have scarce significance for comparison of data obtained in the same laboratory with different calibrations and in different laboratories even more. A correct evaluation of uncertainty is essential: it must include prediction uncertainty due to calibration as well as the possible effect of chemical composition/crystal lattice of the different $\text{CO}_3^{2-}$-bearing phases in analysis. The evaluation of this overall uncertainty for low-Mg calcites is the most important topic of this report.

The total oxygen of $\text{CO}_3^{2-}$ may be determined by decarbonatization/fluorination methods, as described, for instance, by Sharma and Clayton [4]. At present, this method is rarely used. Actually, starting from the fifty years of the last century [5], usually, the substances containing carbonate (e.g., carbonate minerals, $\text{CO}_3^{2-}$-bearing apatite, et cetera) are dissolved in concentrated $\text{H}_3\text{PO}_4$ with production of $\text{CO}_2$ which is analysed by isotope
ratio mass spectrometry (IRMS). During dissolution, only two oxygens of CO\textsubscript{2}\(^{-}\) form CO\textsubscript{2}. Thus, the formation of CO\textsubscript{2} generates oxygen isotope fractionation between the original carbonate CO\textsubscript{3}\(^{2-}\) and the new formed CO\textsubscript{2} gas. At a given temperature \(T\) of dissolution, this fractionation is expressed by the “oxygen isotope phosphoric acid fractionation factor”, \(\alpha_{\text{ACID}}^{T}(\theta)\), which is defined as

\[
\alpha_{\text{ACID}}^{T}(\theta) = \frac{\delta^{18}O_{\text{CO}_2(\theta)/R\text{M}} + 1}{\delta^{18}O_{\theta}/R\text{M}} + 1 \quad (1)
\]

where \(\theta\) is the generic substance containing CO\textsubscript{3}\(^{2-}\), \(\delta^{18}O_{\theta}/R\text{M}\) and \(\delta^{18}O_{\text{CO}_2(\theta)/R\text{M}}\) are the isotopic values (in the following text, the parameter delta (\(\delta\)) is defined according to IUPAC (International Union of Pure and Applied Chemistry): \(\delta^{E}_i/R\text{M} = \frac{R^{(E/\delta E)_{i/R\text{M}}}}{R^{(E/\delta E)_{0/R\text{M}}}} - 1 = 10^3\) \(\left(\frac{R^{(E/\delta E)_{i/R\text{M}}}}{R^{(E/\delta E)_{0/R\text{M}}}} - 1\right)%\), where \(R\) is the ratio between the abundances of the isotope \(E\) and of the isotope \(\delta E\) present in a chemical species of the material \(i\), \(R\text{M}\) the reference material, and \(\%\) = \(10^{-3}\). Moreover, approximately, we assume \(R^{(18O/16O)}_{\text{PDB}} = R^{(18O/16O)}_{\text{VPDB}}\), where PDB and VPDB are the original international reference material and the present-day reference, respectively. They have very similar \(R^{(18O/16O)}\) values.) for the total oxygen of CO\textsubscript{2}\(^{-}\) of the substance \(\theta\) and for CO\textsubscript{2} gas produced by dissolution of \(\theta\) in concentrated H\textsubscript{3}PO\textsubscript{4} solution (usually, \(\geq 100\%\) of the chemical component H\textsubscript{3}PO\textsubscript{4}, density \(\equiv 1.90\ \text{g cm}^{-3}\) at a given temperature \(T\), and \(R\text{M}\) is a reference material.

It is noteworthy that the international standards used for calibration in the isotope analysis of the carbonate group in different substances are low-Mg calcites (such as NBS 19, NBS 18, IAEA-CO-1, IAEA-CO-8, with MgO < 0.8% weight, [6]). For a standard (st) consisting of low-Mg calcite (CAL), we may write the ratio

\[
\frac{\delta^{18}O_{\text{CO}_2(\text{CAL})/w} + 1}{\delta^{18}O_{\text{CAL}/PDB} + 1} = B_{\text{CAL}}^{T} \quad (2)
\]

where \(\delta^{18}O_{\text{CO}_2(\text{CAL})/w}\) is the measured value for CO\textsubscript{2} gas obtained from stCAL at temperature \(T\) referred to the working standard \(w\) of the laboratory (CO\textsubscript{2} in tank) and \(\delta^{18}O_{\text{CAL}/PDB}\) is the “true” value of delta referred to the primary international standard PDB. In the case the spectrometric response is ideally linear (consider the abundance ratio \(18^\text{R} = (18O/16O)\). The instrumental response is ideally linear in case the following relation holds: \(R^{18}O_{\text{CAL}/w} = k R^{18}O_{\theta}\), where \(R^{18}O_{\theta}\) and \(R^{18}O_{\text{CAL}/w}\) are “true” value and the measured value, respectively, for the carbonate group of the substance \(\theta\), and \(k\) is a constant.)). Equation (2) may be re-written as a calibration line

\[
\delta^{18}O_{\text{CAL}/PDB} + 1 = \frac{1}{B_{\text{CAL}}^{T}} (\delta^{18}O_{\text{CO}_2(\text{CAL})/w} + 1) \quad (3)
\]

where \(\delta^{18}O_{\text{CAL}/PDB}\) is the estimated value for a generic calcite that behaves as the standard stCAL during dissolution in H\textsubscript{3}PO\textsubscript{4}, \(\delta^{18}O_{\text{CO}_2(\text{CAL})/w}\) is the measured value referred to the working standard \(w\), and \(B_{\text{CAL}}^{T}\) is a constant at temperature \(T\). To improve the calibration, usually more than one standard of low-Mg calcite is used.

If the material \(\theta\) in analysis is different from stCAL (e.g., calcite different from stCAL, dolomite, ankerite, CO\textsubscript{3}\(^{2-}\)-bearing apatite, et cetera), an apparent value

\[
\delta^{18}O_{\theta\theta/PDB} + 1 = \frac{1}{B_{\text{CAL}}^{T}} (\delta^{18}O_{\text{CO}_2(\theta)/w} + 1) \quad (4)
\]
is obtained. The value $\delta^{18}O_{\theta/VPDB}$ is an estimate of $\delta^{18}O_{\theta/VPDB}$ for the phase $\theta$ in the case it behaves as stCAL during dissolution. Thus, we may write

$$\alpha_{ACID(stCAL)}^T = \frac{\delta^{18}O_{\theta/VPDB}^{T\theta}}{\delta^{18}O_{\theta/VPDB}^{T\theta} + 1}$$  \hspace{1cm} (5)$$

By definition, is

$$\alpha_{ACID(\theta)}^T = \frac{\delta^{18}O_{\theta/VPDB}^{T\theta}}{\delta^{18}O_{\theta/VPDB}^{T\theta} + 1}$$  \hspace{1cm} (6)$$

Thus, dividing (5) by (6),

$$\frac{\alpha_{ACID(stCAL)}^T}{\alpha_{ACID(\theta)}^T} = \frac{\delta^{18}O_{\theta/VPDB}^{T\theta} + 1}{\delta^{18}O_{\theta/VPDB}^{T\theta} + 1} \rightarrow \delta^{18}O_{\theta/VPDB}^{T\theta} + 1 = \frac{\alpha_{ACID(stCAL)}^T}{\alpha_{ACID(\theta)}^T} (\delta^{18}O_{\theta/VPDB}^{T\theta} + 1)$$  \hspace{1cm} (7)$$

Equation (7) is very important for several reasons. Essentially, it tells us that (a) in the case the ratio $\frac{\alpha_{ACID(stCAL)}^T}{\alpha_{ACID(\theta)}^T}$ is independent from temperature, then also $\delta^{18}O_{\theta/VPDB}^{T\theta}$ is independent from temperature, (b) in the particular case is $\frac{\alpha_{ACID(stCAL)}^T}{\alpha_{ACID(\theta)}^T} = 1$, is $\delta^{18}O_{\theta/VPDB}^{T\theta} = \delta^{18}O_{\theta/VPDB}^{T\theta}$, (c) when the ratio $\frac{\alpha_{ACID(stCAL)}^T}{\alpha_{ACID(\theta)}^T}$ changes with temperature, also the apparent value $\delta^{18}O_{\theta/VPDB}^{T\theta}$ changes with temperature and, thus, both the values $\alpha_{ACID(stCAL)}^T$ and $\alpha_{ACID(\theta)}^T$ are necessary to obtain $\delta^{18}O_{\theta/VPDB}^{T\theta}$.

As already stated above, hereafter we consider only low-Mg calcite (CAL) from the literature: (a) we investigate the variation of its oxygen isotope phosphoric acid fractionation factor at different temperature, (b) we discuss the significance of the $\delta^{18}O_{\theta/VPDB}^{CAL}$ value obtained using international standard(s), (c), for $\delta^{18}O_{\theta/VPDB}^{CAL}$, we evaluate the uncertainty $u(\delta^{18}O_{\theta/VPDB}^{CAL})$ related to the variable behaviour of different samples of low-Mg calcite during dissolution in phosphoric acid, and (d) we estimate the overall uncertainty due to (c) and to the prediction uncertainty related to the calibration line obtained with international standards. Owing to the small amount of data at disposal, the approach is very simplified and only approximate. However, in spite of this, we think that the results obtained allow us to draw some interesting conclusions.

2. Oxygen Phosphoric Acid Fractionation Factor for Low-Mg Calcite: Data and Discussion

2.1. Selection of Data at Different Temperatures

Many important papers report data of $\alpha_{ACID(\theta)}^T$ for carbonate minerals and/or of $\delta^{18}O_{CO2(\theta)}^{T}$ at different temperatures (e.g., [4,7–16]); for a list of $\alpha_{CO2}^{298.15}$ estimated values see [17]). Among these data, we selected some values for low-Mg calcite according to the following two criteria:

1. Only data sets that include values for more than two analytical temperatures were considered and compared.
2. We considered only data obtained with the individual-acid bath method (IAB).

Unfortunately, the authors frequently do not report single data, but averages at different temperatures, which reduces the statistical information. For this reason, we were compelled to use averages instead of single data (with the exception of Calcite H$^{(1)}$ in Table 1).
Table 1. Statistical data for the regressions obtained for different samples of low-Mg calcite (CAL).

<table>
<thead>
<tr>
<th>Regression</th>
<th>Calcite Sample</th>
<th>n</th>
<th>b</th>
<th>s(b)</th>
<th>a</th>
<th>s(a)</th>
<th>p_{x=0}</th>
<th>s(yx)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crowley [16]</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
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<tr>
<td>1</td>
<td>NBS19</td>
<td>5</td>
<td>576</td>
<td>20</td>
<td>3.6 × 10^{-5}</td>
<td>5.9 × 10^{-5}</td>
<td>0.59</td>
<td>6.8 × 10^{-5}</td>
</tr>
<tr>
<td>2</td>
<td>NBS18</td>
<td>5</td>
<td>540</td>
<td>18</td>
<td>3.7 × 10^{-5}</td>
<td>5.1 × 10^{-5}</td>
<td>0.52</td>
<td>5.9 × 10^{-5}</td>
</tr>
<tr>
<td>3</td>
<td>IAEA-CO-1</td>
<td>5</td>
<td>514</td>
<td>16</td>
<td>4.4 × 10^{-5}</td>
<td>4.7 × 10^{-5}</td>
<td>0.41</td>
<td>5.3 × 10^{-5}</td>
</tr>
<tr>
<td>4</td>
<td>LIVM</td>
<td>5</td>
<td>540</td>
<td>13</td>
<td>1.4 × 10^{-5}</td>
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<td>0.74</td>
<td>4.4 × 10^{-5}</td>
</tr>
<tr>
<td>5</td>
<td>LIVF</td>
<td>5</td>
<td>541</td>
<td>30</td>
<td>8.1 × 10^{-5}</td>
<td>8.7 × 10^{-5}</td>
<td>0.42</td>
<td>9.9 × 10^{-5}</td>
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<td>PCC</td>
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<td>566</td>
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<td>2.7 × 10^{-5}</td>
</tr>
<tr>
<td>7</td>
<td>CM</td>
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<td>549</td>
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<td>IAEA-CO-8</td>
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<td>652</td>
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<td>7.8 × 10^{-5}</td>
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<tr>
<td>9</td>
<td>LIVC</td>
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<td>7.0 × 10^{-5}</td>
<td>0.59</td>
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<td>3.0 × 10^{-5}</td>
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<tr>
<td>11</td>
<td>CHALK</td>
<td>5</td>
<td>601</td>
<td>21</td>
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<td>6.2 × 10^{-5}</td>
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<td>7.1 × 10^{-5}</td>
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<tr>
<td>Kim et al. [15]</td>
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<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>Calcite H</td>
<td>3</td>
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<td>3.5</td>
<td>-0.3 × 10^{-5}</td>
<td>0.7 × 10^{-5}</td>
<td>0.77</td>
<td>0.7 × 10^{-5}</td>
</tr>
<tr>
<td>13</td>
<td>Calcite H (^{1})</td>
<td>20</td>
<td>604</td>
<td>17</td>
<td>-0.2 × 10^{-5}</td>
<td>3.0 × 10^{-5}</td>
<td>0.95</td>
<td>9.8 × 10^{-5}</td>
</tr>
<tr>
<td>Böttcher [8]</td>
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<td></td>
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<td></td>
</tr>
<tr>
<td>14</td>
<td>LMC</td>
<td>5</td>
<td>552</td>
<td>12</td>
<td>-2.8 × 10^{-5}</td>
<td>2.7 × 10^{-5}</td>
<td>0.37</td>
<td>3.7 × 10^{-5}</td>
</tr>
<tr>
<td>15</td>
<td>PSU-4</td>
<td>6</td>
<td>558</td>
<td>28</td>
<td>2.4 × 10^{-5}</td>
<td>5.8 × 10^{-5}</td>
<td>0.70</td>
<td>8.6 × 10^{-5}</td>
</tr>
</tbody>
</table>

n = number of data used in regression for each calcite sample; b = slope of the regression straight line; s(b) = standard error on the slope; a = intercept of the regression line; s(a) = standard error on the intercept; \(p_{x=0}\) = probability for \(a = 0\); s(yx) = standard error of regression. \(^{1}\) Value obtained using all the data at the different temperatures.

Some of the cited works demonstrate the low analytical repeatability of the fractionation factor determination at 25 °C (e.g., [13,15]). Kim et al. [15] report a spread of data that is larger at 25 °C than at higher temperature. These authors use the \(\delta^{13}C_{\text{CAL}}/PDB\) values for the selection of the oxygen data on low-Mg calcite. Given a defined sample, they consider the average \(\delta^{13}C_{\text{CAL}}/PDB \pm \) standard deviation = -4.62‰ ± 0.06‰ for the carbon isotopes and eliminate the corresponding \(\delta^{18}O_{\text{CO}_2(\text{CAL})/PDB}\) value in case the sample is \(10^3|\delta^{13}C_{\text{CAL}}/PDB - \bar{\delta^{13}C}_{\text{CAL}}/PDB| > 0.06\). This drastic method is very “efficient”, although not typical for the identification of aberrant values. We prefer to consider all the data for the reasons listed below.

Firstly, regarding elimination of data we follow the Burke’s golden rule [18]: “No value should be removed from a data set on statistical ground alone” (p. 20) and “Delete extreme values only when a technical reason for their aberrant behavior can be found” (p. 23). Additionally, in case this opinion is not accepted, only data with very low probability of occurrence (indicatively with probability less than 0.05 or 0.01) should be eliminated.

The carbon \(\delta^{13}C\) data reported by Kim et al. [15] have abnormal distribution (Shapiro–Wilk test: \(P_{\text{normal}} = 0.014\)). In this case, the standard deviation of the statistical sample does not express the spread of the data around the central value in the right way. In the case that the distribution is not normal, the use of simple non-parametric methods is suggested.
For instance, the box and whiskers plot [19] indicates that no one value from Kim et al.’s data [15] for calcite is an “outlier”.

2.2. Estimation of Oxygen Isotope Phosphoric Acid Fractionation Factor, $\alpha^T_{ACID(CAL)}$, at 298.15 K

Using the estimated values reported by the authors, we verified that the linear relation between the data $\alpha^T_{ACID(\theta)}$ vs $T^{-2}$ (in kelvin when not indicated otherwise) generally gave lower standard error of regression than vs $T^{-1}$. Then, we used the following regression to estimate $\alpha^T_{ACID(CAL)}$:

$$\alpha^T_{ACID(\theta)} = \frac{\delta^{18}O^T_{CO_2(\theta)/PDB} + 1}{\delta^{18}O_{\theta/PDB} + 1} = bT + \delta^T_{ACID(CAL)}$$

(8)

where the intercept $b'$ represents a weighted value of the fractionation factor at $T = 298.15$ K.

In the literature, there is disagreement about the values of $\alpha^T_{ACID(CAL)}$ at different temperatures (e.g., [4], natural calcite; [9,20,21] Islandic spar Mg-low calcite PSU-4, Pleistocene Key Largo formation Mg-low calcite LMC: 11 data items; [8] CaCO$_3$ Merck, synthetic carbonate: 3 data items; [10,15] Calcite H, natural calcite with MgO = 0.77; 20 data items). In particular, the values at 25 °C have a large span, from about 1.01008 ([4], corrected to 1.01025 by Friedman and O’Neil [20]) to 1.01050 [10]. Only Kim et al. [15] report several data at different temperatures for the same sample; using their data (averages at temperatures 25, 50, and 75 °C, 3 data items), the regression type (8) gives intercept $b = 1.01040 \pm 0.00001$ (standard error on the intercept), which represents a weighted estimate of $\alpha^T_{ACID(CAL)}$.

Some authors (e.g., [22] and references therein, [17]) suggest the value 1.01025. In particular, Kim et al. ([17] p. 276, abstract) state that they use 1.01025 because it is “the most commonly accepted value for this quantity” (see, for instance, [20,23,24]). Although this value is conventional, it is very important because it is used for defining the value of CO$_2$ gas produced through digestion of the standard NBS19 in 100% H$_3$PO$_4$ at 25 °C.

2.3. The Ratio $\alpha^T_{ACID(CAL)} / \alpha^{298.15}_{ACID(CAL)}$ vs. Temperature

Since generally the values $\delta^{18}O_{CAL/PDB}$ are not measured directly, the $\alpha^T_{ACID(CAL)}$ values cannot be evaluated. Thus, comparison between the different data sets was generally carried out using the following regression, that, theoretically, represents a straight line passing for the origin:

$$\frac{\alpha^T_{ACID(CAL)}}{\alpha^{298.15}_{ACID(CAL)}} = \frac{\delta^{18}O^T_{CO_2(CAL)/PDB} + 1}{\delta^{18}O^{298.15}_{CO_2(CAL)/PDB} + 1} = b + \frac{1}{298.15^2} \frac{\delta^{18}O_{CAL} + 1}{\delta^{18}O^{298.15}_{CAL} + 1}$$

(9)

where $\alpha^T_{ACID(CAL)}$ is defined as $\alpha^T_{ACID(CAL)} = 1$ for $T = 298.15$ K. Regression (9) could exhibit an intercept $a$ numerically different from zero, but, in any case, with very high probability for $a = 0$. We calculated a total of the 15 regressions

$$\frac{\alpha^T_{ACID(CAL)}}{\alpha^{298.15}_{ACID(CAL)}} = b_{CAL} \left( \frac{1}{T^2} - \frac{1}{298.15^2} \right) + a_{CAL}$$

(10)

for low-Mg calcites (Table 1). As expected (see Equation (9)), the probability for $a_{CAL} = 0$ is very high. Moreover, according to Zar [25], we compared the slopes, $b_{CAL}$, and the elevations, $E_{CAL}$ (vertical position on a graph), by determining the probability of the null hypothesis $H_0$: $b_{CAL,1} = b_{CAL,2} = \ldots = b_{CAL,15}$ and $H_0$: $E_{CAL,1} = E_{CAL,2} = \ldots = E_{CAL,15}$, where 1, 2, ..., 15 refer to the regressions obtained for the samples analysed by the different author (Table 1). The probability for the null hypothesis $H_0$: $b_{CAL,1} = b_{CAL,2} = \ldots = b_{CAL,15}$
and $H_0$: $E_{CAL,1} = E_{CAL,2} = \ldots = E_{CAL,15}$ is very low ($p < 0.001$), suggesting that not all the low-Mg calcites considered behave in the same way during the dissolution process at different temperatures. The reason of this behavior is not well known (see discussion in [16]), although it is evident that the cation species that are present and their concentration play an important role. Thanks to the data reported by Crowley [16], we may reasonably suppose that the decrease of Ca and increase of Sr substitution in the low-Mg calcite lattice play the most important role on the variation of the regression slope: as the weight fraction of CaCO$_3$ decreases, the $b$ value decreases, whereas it increases at increasing weight fraction of SrCO$_3$.

For each given temperature (298.15, 323.15, 348.15, 373.15 K), using each equation of Table 1, a set of $\frac{\alpha_{T,ACID(CAL)}}{\alpha_{298.15,ACID(CAL)}} - 1$ values are obtained (Figure 1, Table 2). The maximum (+) and the minimum (−) values obtained for $\frac{\alpha_{T,ACID(CAL)}}{\alpha_{298.15,ACID(CAL)}} - 1$ at different temperature T are reported in Table 2. From Figure 1, it is evident that for a given $(1/T^2 - 1/298.15^2)$, the variance of $\frac{\alpha_{T,ACID(CAL)}}{\alpha_{298.15,ACID(CAL)}} - 1$ is not the same: actually, it increases as $(1/T^2 - 1/298.15^2)$ decreases. We considered all these data to calculate an overall regression line $\frac{\alpha_{T,ACID(CAL)}}{\alpha_{298.15,ACID(CAL)}} - 1$ on $(1/T^2 - 1/298.15^2)$

Since the variance of $\frac{\alpha_{T,ACID(CAL)}}{\alpha_{298.15,ACID(CAL)}} + 1$ is not constant, WLS (weighted least square regression; see, for instance [26]) in place of OLS (ordinary least square regression) must be used. The overall WLS obtained line is

$$\frac{\alpha_{T,ACID(CAL)}}{\alpha_{298.15,ACID(CAL)}} - 1 = 575 \left( \frac{1}{T^2} - \frac{1}{298.15^2} \right) + 0.000015 \quad (11)$$

with $n = 60$ couples of data and $R^2 = 0.985$. The standard uncertainty on $Y_{298.15\,(CAL)}$ referred to the weighted regression line is easily calculated ([26]): considering $t_{0.3173, 58} = 1.009$, Student’s t value (two-tailed) for significance level 0.3173 ($\approx 0.32$) and $v = 58$ degrees of freedom, standard uncertainty is well expressed by the polynomial equation

$$u\left(\frac{\alpha_{T,ACID(CAL)}}{\alpha_{298.15,ACID(CAL)}}\right)_{10b} \approx -1.362 \times 10^{-10} T^3 + 1.348 \times 10^{-7} T^2 - 4.250 \times 10^{-5} T + 4.332 \times 10^{-3} \quad (12)$$

Figure 1. Regression $Y_{298.15\,(CAL)} - 1 = \frac{\alpha_{T,ACID(CAL)}}{\alpha_{298.15,ACID(CAL)}} - 1$ on $(1/T^2 - 1/298.15^2)$ for the values $Y_{298.15\,(CAL)}$ calculated at different temperatures for samples of low-Mg calcite (CAL) (see Table 1). The figure evidences the increasing of the data as the $(1/T^2 - 1/298.15^2)$ value increases.
Table 2. Maximum (+) and the minimum (−) values obtained for \( \frac{\alpha^T_{\text{ACID(NBS19)}}}{\alpha^T_{\text{ACID(CAL)}}} - 1 \) at different temperatures and related standard uncertainty \( u(\frac{\alpha^T_{\text{ACID(NBS19)}}}{\alpha^T_{\text{ACID(CAL)}}}) \)10b, and uncertainty \( u(\frac{\alpha^T_{\text{ACID(NBS19)}}}{\alpha^T_{\text{ACID(CAL)}}}) \)11b.

<table>
<thead>
<tr>
<th>T (K)</th>
<th>298.15</th>
<th>323.15</th>
<th>348.15</th>
<th>373.15</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \frac{1}{T^2} - \frac{1}{298.15^2} )</td>
<td>0</td>
<td>-1.6733 \times 10^{-6}</td>
<td>-2.9992 \times 10^{-6}</td>
<td>-4.0676 \times 10^{-6}</td>
</tr>
<tr>
<td>( Y^T_{298.15} (\text{CAL}) - 1 )</td>
<td>0.000081</td>
<td>-0.00082</td>
<td>-0.00150</td>
<td>-0.00205</td>
</tr>
<tr>
<td>( Y^T_{298.15} (\text{CAL}) - 1 )</td>
<td>-0.000037</td>
<td>-0.00111</td>
<td>-0.00197</td>
<td>-0.00267</td>
</tr>
<tr>
<td>( u(Y^T_{298.15} (\text{CAL})) )10b</td>
<td>0.000033</td>
<td>0.000079</td>
<td>0.000127</td>
<td>0.000166</td>
</tr>
</tbody>
</table>

For instance, at 25 °C, 50 °C, and 75 °C, uncertainty is 0.032‰, 0.077‰, and 0.125‰, respectively. This uncertainty is only related to the different behavior of the analyzed calcites during the acid dissolution.

Consider now the equation obtained for the standard NBS19:

\[
\frac{\alpha^T_{\text{ACID(NBS19)}}}{\alpha^T_{\text{ACID(CAL)}}} - 1 = 576 \left( \frac{1}{T^2} - \frac{1}{298.15^2} \right) + 0.000036 \tag{13}
\]

The prediction uncertainty for an estimate of \( \frac{\alpha^T_{\text{ACID(NBS19)}}}{\alpha^T_{\text{ACID(CAL)}}} \) (for a new value \( \frac{1}{T^2} - \frac{1}{298.15^2} \)) obtained using Equation (13) is given by the following relation ([26,27]):

\[
u \left( \frac{\alpha^T_{\text{ACID(NBS19)}}}{\alpha^T_{\text{ACID(CAL)}}} \right) \approx -7.244 \times 10^{-11} T^3 + 8.246 \times 10^{-8} T^2 - 3.061 \times 10^{-5} T + 3.914 \times 10^{-3} \tag{14}
\]

For example, at 25 °C, 50 °C, and 75 °C we obtain 0.11‰, 0.091‰, and 0.090‰, respectively.

The Equations (11) and (13) referred to NBS19 are very similar. For this reason, Equation (13) could be used to approximately evaluate \( u(\frac{\alpha^T_{\text{ACID(CAL)}}}{\alpha^T_{\text{ACID(NBS19)}}}) \) for a generic low-Mg calcite. The total uncertainty \( u(\frac{\alpha^T_{\text{ACID(CAL)}}}{\alpha^T_{\text{ACID(NBS19)}}}) \) on the evaluated value \( \frac{\alpha^T_{\text{ACID(CAL)}}}{\alpha^T_{\text{ACID(NBS19)}}} \) may be approximatively calculated, assuming that the dispersion of the regression lines reported in Figure 1 is representative of all the low-Mg calcites in nature. This, of course, is a restrictive condition that could lead to underestimation of the total uncertainty. The evaluation of the total uncertainty is given combining (12) and (14):

\[
u(\frac{\alpha^T_{\text{ACID(CAL)}}}{\alpha^T_{\text{ACID(NBS19)}}})_{\text{tot}} \approx \sqrt{u^2(\frac{\alpha^T_{\text{ACID(CAL)}}}{\alpha^T_{\text{ACID(NBS19)}}})_{10b} + u^2(\frac{\alpha^T_{\text{ACID(NBS19)}}}{\alpha^T_{\text{ACID(CAL)}}})_{11b}} \approx -2.772 \times 10^{-10} T^3 + 2.911 \times 10^{-7} T^2 - 1.003 \times 10^{-4} T + 1.148 \tag{15}
\]
For instance, at 25 °C, 50 °C and 75 °C, \( u(\delta_{\text{O}}^{18}\text{CAL/PDB}) \) is 0.11‰, 0.12‰, and 0.16‰ respectively. This total uncertainty is due both to the different behavior of calcites during the acid dissolution and to the substitution of 10a with 11a.

2.4. Approximate Standard Uncertainty on \( \alpha_{\text{ACID(CAL)}}^T \)

Considering that is
\[
\alpha_{\text{ACID(CAL)}}^{298.15} = 1 \pm u(\alpha_{\text{ACID(CAL)}}^{298.15})_{\text{tot}}, \text{ with}
\]

\[
u^2(\alpha_{\text{ACID(CAL)}}^{298.15})_{\text{tot}} = 0.11% \text{ as calculated using Equation (15)},
\]

we obtain:
\[
u^2(\alpha_{\text{ACID(CAL)}}^{298.15})_{13} \approx \frac{u(\alpha_{\text{ACID(CAL)}}^{298.15})_{\text{tot}}}{\sqrt{2}} = 0.078‰ \tag{16}
\]

Since the values of the fractionation factors are close to the unit and, thus, is
\[
u^2(\alpha_{\text{ACID(CAL)}}^{298.15})_{\text{tot}} \approx \nu^2(\alpha_{\text{ACID(CAL)}}^{298.15}) + \nu^2(\alpha_{\text{ACID(CAL)}}^T), \text{the total uncertainty } u(\alpha_{\text{ACID(CAL)}}^T) \text{ at different temperature is}
\]

\[
u(\alpha_{\text{ACID(CAL)}}^T) \approx \sqrt{\nu^2(\alpha_{\text{ACID(CAL)}}^{298.15}) + \nu^2(\alpha_{\text{ACID(CAL)}}^T)}_{\text{tot}} \approx -6.333 \times 10^{-10} T^3 + 6.431 \times 10^{-7} T^2 - 2.158 \times 10^{-4} T + 2.403 \times 10^{-2} \tag{17}
\]

For example, at 25 °C, 50 °C, and 75 °C we obtain about 0.08‰, 0.09‰, and 0.14‰, respectively.

2.5. Calibration with the Low-Mg Calcite Standard NBS19 and Standard Uncertainty on New Analytical Data \( \delta^{18}O_{\text{CAL/PDB}} \)

Now, we calculate the uncertainty on the \( \delta^{18}O_{\text{CAL/PDB}} \) value. Going back now to relation (7), the calibration line that is used to calculate \( \delta^{18}O_{\text{CAL/PDB}} \) for a new sample of low-Mg calcite. Using the standard NBS 19, we write:

\[
\delta^{18}O_{\text{CAL/PDB}} + 1 = \frac{\alpha_{\text{ACID(CAL)}}^T}{\alpha_{\text{ACID(CAL)}}^{\text{NBS19}}} (\delta^{18}O_{\text{CAL/PDB}}^\text{#T} + 1) \tag{18}
\]

Thus, considered that \( \alpha_{\text{ACID(CAL)}}^T, \alpha_{\text{ACID(CAL)}}^{\text{NBS19}}, \) and \( \delta^{18}O_{\text{CAL/PDB}}^\text{#T} + 1 \) have values close to the unit, approximately we obtain

\[
u(\delta^{18}O_{\text{CAL/PDB}}) \approx \sqrt{\nu^2(\alpha_{\text{ACID(CAL)}}^{298.15}) + \nu^2(\delta^{18}O_{\text{CAL/PDB}}^\text{#T})_{\text{tot}}} \geq \nu(\alpha_{\text{ACID(CAL)}}^{298.15})_{\text{tot}}
\]

At 25 °C, 50 °C, and 75 °C, the value \( u(\delta^{18}O_{\text{CAL/PDB}}) \) never may be lower than 0.11‰, 0.12‰, and 0.16‰. Assuming, for instance, that the uncertainty on \( \delta^{18}O_{\text{CAL/PDB}}^\text{#T} \) is about 0.2‰ (as it is the case for our laboratory), at 25 °C, 50 °C, and 75 °C we obtain \( u(\delta^{18}O_{\text{CAL/PDB}}) \) of about 0.23‰, 0.26‰, and 0.26‰, respectively.

We conclude that, because of the variable behavior of the different samples of low-Mg calcite during the acid dissolution and the uncertainty on the \( \alpha_{\text{ACID(CAL)}}^T \) value, the calibration with the standard NBS19 does not allow us to obtain results with standard uncertainty better than about 0.2‰. This result is very important in the case we want to compare data obtained for different low-Mg calcites in the same laboratory or different laboratories.
3. Conclusions

We reconsidered the oxygen isotope phosphoric acid fractionation factor $\alpha_{\mathrm{ACID(CAL)}}^T$ for low-Mg calcite at different temperatures and the overall uncertainty on the estimated value $\delta^{18}O_{\mathrm{CAL/PDB}}$ of the carbonate. The following points appeared to be of great relevance:

(a) The regressions ($\frac{\alpha_{\mathrm{ACID(CAL)}}^T}{\alpha_{\mathrm{ACID(CAL)}}^T - 1}$) obtained for several low-Mg calcites do not have the same slope and elevation. This demonstrates that the mineral behavior during dissolution in $\mathrm{H}_3\mathrm{PO}_4$ is not always the same for different low-Mg calcites; this generated analytical uncertainty. The variable behavior is probably due to little variations in the chemical composition of low-Mg calcite.

(b) To calculate the overall uncertainty of the estimated value $\delta^{18}O_{\mathrm{CAL/PDB}}$ obtained using the standard NBS19, the uncertainty at point (a) must be added to uncertainty due to the analytical calibration (prediction uncertainty): the overall value cannot be lower than 0.2‰. Uncertainties smaller than about 0.2‰ reported in the literature is unrealistic. These results must be considered when different data are compared.

Usually, the scientific papers only report repeatability or reproducibility of the data, very rarely the prediction uncertainty due to the calibration line [26,27]; this is despite the fact that only prediction uncertainty is relevant for comparison of data obtained in the same laboratory or in different laboratories.

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References


