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Assessment of carbonate-phosphoric acid analytical technique performed using GasBench II in continuous flow isotope ratio mass spectrometry

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Abstract

The commonly used online automated analytical method (in particular Thermo GasBench II) to determine stable carbon and oxygen isotope ratio composition of calcium carbonate in continuous flow isotope ratio mass spectrometry is evaluated. We have analyzed the isotopic composition of three in-house calcium carbonate standards as unknown samples for assessment of speed, accuracy and precision of isotopic measurements. Isotopic analyses of CO_2 extracted from carbonate-phosphoric acid reaction were performed, where temperature of reaction and the time allowed for the reaction was varied in the range 25–90 °C and 3–101 min (and 12 h), respectively. Our results suggest that for isotopic analyses, carbonate-acid reaction may be conducted at any temperature in the range 50–90 °C for an hour; 50–70 °C seems to be a more restricted range. The results are reproduced accurately if the raw isotopic values are normalized against international standards also analyzed under the same experimental conditions as that of the samples. For isotopically homogeneous calcium carbonate samples, isotopic analyses may also be performed after 15 min of carbonate-acid reaction at 70 °C, which is significantly less time than what is routinely used. Care must be taken to ensure complete dissolution of carbonate sample as incomplete reaction or partial dissolution of isotopically heterogeneous grains would result in respective isotopic variability of CO_2 gas produced during carbonate-acid reaction.

Keywords: Stable isotope; Carbonate; GasBench; Continuous flow; Phosphoric acid

1. Introduction

The stable carbon ($\delta^{13}C$) and oxygen ($\delta^{18}O$) isotopic composition of calcium carbonate ($CaCO_3$) has a broad range of applications such as process-identification related to their formation in a wide variety of environments and paleoclimate reconstruction both in terms of absolute and relative temperature variations during the formation of carbonates. In paleoclimate research, temperature dependency of oxygen isotope fractionation between water and carbonate has been utilized to develop paleotemperature scales [1,2]. In order to determine the isotopic composition of carbonate in stable isotope ratio mass spectrometer (IRMS), all analyses are performed on CO_2 gas released by reacting carbonate with phosphoric acid (H_3PO_4). The dissolution of $CaCO_3$ proceeds as follows:

$$CaCO_3 + H_3PO_4 = CO_2 + H_2O + CaHPO_4 \quad (1)$$

According to the reaction, since all the carbon present in the carbonate is stoichiometrically converted into CO_2 gas, the $\delta^{13}C$ signature of carbonate is retained in the extracted CO_2. On the other hand, only two-third of the total oxygen in the carbonate is converted to CO_2, which leads to fractionation of oxygen isotopes between carbonate and CO_2. The fractionation factor (α) for oxygen between carbonate and CO_2 is defined as:

$$\alpha_{CO_2\text{-carbonate}} = \frac{(^{18}O/^{16}O)_{CO_2}}{(^{18}O/^{16}O)_{carbonate}} \quad (2)$$

Since α is relatively well known for a range of temperatures from experiments (e.g., at 25 °C, $\alpha = 1.01025$ [3–5]), it can be used along with the oxygen isotopic composition of CO_2 to compute the true oxygen isotopic composition of carbonates.

The carbonate-phosphoric acid reaction method was first developed by McCrea [1] for offline chemistry and extraction of isotopically representative CO_2 from carbonate. In this method, a few mg of carbonate sample is reacted with a few mL of 100% H_3PO_4 (specific gravity in the range of 1.90–1.92 g/cm^3) under vacuum in a closed vessel at 25 °C for 24 h. The extracted CO_2

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remains in contact with the acid and is not removed until the reaction is complete. A similar analytical method was also proposed, where CO_2 prepared by an offline technique is analyzed in dual-inlet IRMS [6]. With the advent of continuous flow IRMS, this analytical step is recently performed online with the help of automated-peripheral devices, such as the Thermo GasBench II (or Kiel device), GV MultiFlow, or VG Isocarb, etc. The online technique modified the original method by increasing the reaction temperature and using a much smaller amount sample ($\leq$400 μg). Revesz and Landwehr [7] used ~400 μg samples (at 26 °C, 24–54 h reaction time) to perform online chemistry and isotope ratio analyses by coupling the GasBench device to the IRMS. Other methods utilized ~200–300 μg of carbonate that is reacted with ~100–400 μL of 100% H_3PO_4 in a helium atmosphere for 1–2 h at 72 °C [7–9]. Swart et al. [5] reported three common types of techniques (sealed vessel, common acid bath, and drip method) that are widely used in different laboratories through out the world. The drip method, which allows a small volume of acid to be dropped onto the sample, is similar to the online GasBench method. However, Swart et al. [5] did not report any data for this technique. The sealed vessel (SV) method they described is a modified version of McCrea [1] in which ~0.5–1 mg samples were reacted with 1 mL of H_3PO_4 at different temperatures (varying from 25 to 90 °C) and for different times (from 10 to 240 min). Ball et al. [10] carried out experiments similar to the conventional SV method and concluded that this technique does not reproduce accurate isotopic composition of carbonate samples weighing less than 0.5 mg. In order to achieve a high degree of accuracy and precision of isotopic analyses, they proposed a modified online technique in which small samples (30–150 μg) and acid (30 μL) are placed in a tube in a horizontal position until a reaction is initiated. In their [10] method, calcite is reacted with phosphoric acid at 70 °C for 16 h. Furthermore, the recommended (by instrument manufacturers) temperature of reaction for carbonates using the GasBench is 72 °C whereas that for the GV Multiflow is 90 °C.

It is apparent that various laboratories use different techniques where both the reaction times and temperatures vary in the range 1–24 h and 25–90 °C, respectively. This leads to two obvious questions: what is the optimum (or range) temperature at which calcite may be reacted with phosphoric acid and how long should the reaction be allowed to continue in order to reproduce isotopic analyses with accuracy and precision? The current generation of isotope ratio mass spectrometers produces extremely precise results (1σ internal error $\approx$ 0.02‰), but the accuracy of analyses depend largely on both the analytical technique used and the conversion procedure of raw isotopic data into the true isotopic composition. A proper calibration of the GasBench method will vastly improve the speed and accuracy of carbonate analyses in continuous flow IRMS.

Since the rate of a chemical reaction has an Arrhenius relation with temperature, increasing the temperature speeds up the reaction, and therefore, the reaction of carbonate with acid at higher temperatures requires less reaction time compared to that recommended for offline preparation (25 °C and 24 h). For the above reason, the fractionation of oxygen isotopes between carbonate and CO_2 is also dependent on temperature; the $\delta^{18}O$ composition of CO_2 extracted at various temperatures will be different. Therefore, accurate value of fractionation factor for a particular temperature must be known in order to compute the true $\delta^{18}O$ of carbonate. The reaction should also be allowed to continue for a given time to ascertain that all the carbon in the carbonate is released in the form of CO_2 in order to avoid analyzing isotopically variable sample CO_2 gasses produced during carbonate-acid reaction [10,11]. This factor is important for carbonate samples that contain small-scale isotopic heterogeneity and/or that consist of variable amounts of dolomite and other inorganic carbonate phases [11].

In addition, there are several other factors that may affect the accuracy and precision of carbonate isotopic analyses: acid strength and composition [12], surface areas of reacting particles and grain size distributions [11], the exchange of oxygen isotopes between water and CO_2 gas [4,5,12], and CO_2 leakage across porous seals or atmospheric contamination, and partial adsorption of sample gas by H_3PO_4 [10]. Based on experiments with H_3PO_4 heavily labeled with ^{18}O, McCrea [1] reported no fractionation of oxygen between phosphoric acid and CO_2. However, Wachter and Hayes [12] studied the fractionation of oxygen isotopes (at 25 °C) between CO_2 (enriched in ^{18}O) and different concentrated solutions of H_3PO_4 and preferred 105% H_3PO_4 that minimizes the fractionation effect; their results suggest negligible exchange of oxygen isotopes when 100% H_3PO_4 is allowed to equilibrate with CO_2 at 75 °C for a period of ~1 h.

Fractionation of oxygen isotopes between CO_2 and water at 25 °C is generally well known [3–6,12]. Because of this effect, $\delta^{18}O$ of CO_2 becomes about 40‰ heavier than the liquid phase H_2O at 25 °C [4]. Therefore, presence of water in the system (depending on the isotopic composition of water relative to sample CO_2) may affect the accuracy of $\delta^{18}O$ (not the $\delta^{13}C$) of carbonates. During the carbonate-acid reaction, water is produced from two sources: (1) equal number of moles of water and CO_2 are produced during the dissolution of $CaCO_3$ and (2) water produced due to polymerization of ortho-phosphoric acid units even in acid solutions that are nominally 100% H_3PO_4 [5,12]. Therefore, analytical techniques should be tested for the least amount of H_3PO_4 to be used during the reaction and the time that the sample CO_2 remains in contact with the water produced during the reaction should be minimized.

The continuous flow IRMS operates on the basis of identical treatment (IT) principle. In theory, "identical treatment" of international reference standards and samples during carbonate-acid reaction at a constant temperature should produce similar fractionation effect for samples and standards [13]. Therefore, an accurate and precise δ-value of carbonate samples can be obtained (without fractionation correction) by normalizing raw delta values into the VPDB scale by using a two-point calibration of international standards as proposed by Coplen et al. [14]. Such normalization procedures would facilitate meaningful interlaboratory comparison of isotopic results. The IT principle is applicable as long as both the nature and isotopic composition of unknown samples are similar to that of the reference international standards.

Table 1
Stable carbon and oxygen isotopic composition of carbonates used in this study

Samples	Type	# of analyses	‰ $\delta^{13}C_{VPDB}$	‰ $\delta^{18}O_{VPDB}$
NBS 18	Carbonatite		−5.00 [14]	−23.01*
NBS 19	Limestone		1.95*	2.20*
KH	Limestone	30	1.98 (0.07)	−2.91 (0.14)
NR	Calcite	30	−4.80 (0.07)	−14.50 (0.08)
MERCK	Artificial $CaCO_3$	41	−35.68 (0.08)	−15.99 (0.08)

$\delta^{13}C$ of NBS18 is taken from Coplen et al. [14], whereas $\delta^{13}C$ and $\delta^{18}O$ of NBS 19 and $\delta^{18}O$ of NBS 18 (the starred values) are taken from the NIST Special Publication 260–149 (2004). 1σ deviations given in brackets are computed from analyses performed over a period of 3 months. Values obtained for KH and NR agree with long-term measurements performed at the Laboratory of Isotope Geology and Geoecology, University of Wroclaw, Poland, using an offline chemical preparation method and subsequent analyses in dual-inlet IRMS.

The purpose of this research is to compare both the accuracy and precision of $\delta^{13}C$ and $\delta^{18}O$ of calcium carbonates analyses, where carbonates react with 100% H_3PO_4 at different reaction times and temperatures. Our aim is to evaluate the carbonate-acid reaction for speed, accuracy, and precision of isotopic analyses. Isotopic analyses were performed at the Laboratory for Stable Isotope Geochemistry, University of Texas at San Antonio (UTSA). The systems used consist of a Thermo Finnigan GasBench II peripheral device interfaced to a Thermo Finnigan Delta^{Plus} XP Isotope Ratio Mass Spectrometer in continuous flow mode.

2. Analytical methods

Stable carbon and oxygen isotopic ratios were determined by using the GasBench II technique in continuous flow IRMS. About 200–300 μg of carbonate samples were weighed into 10 mL Na-glass vials (Labco Limited High Wycombe, Houston, TX, USA) and sealed with butyl rubber septa. The vials were flushed for 700 s with high purity He (99.9999%) utilizing a PAL double-hole needle (ThermoElectron, part #1137020) in order to remove air contained in the vials. About 0.06 mL of 100% ortho-phosphoric acid (MERCK, Darmstadt, Germany, cat. #1.00565) was injected into the vials to extract sample CO_2 gases (carbonate-acid reaction) into the exetainer headspace. The headspace CO_2 was analyzed for $\delta^{13}C$ and $\delta^{18}O$ composition. Details of this procedure are described elsewhere [9].

All carbon and oxygen isotopic composition of samples in this study are reported in the standard δ-notation. For example, δ is defined as the relative difference, in parts per thousand (‰), between the isotope ratio of the sample (R_{sample}) and the reference carbonate standard ($R_{standard}$) as per the following equation:

$$\delta\ (\text{sample}) = \left(\frac{R_{sample}}{R_{standard}} - 1\right) \times 10^3\ ‰ \qquad (3)$$

where R is $^{13}C/^{12}C$ for carbon and $^{18}O/^{16}O$ for oxygen. The raw $\delta^{13}C$, $\delta^{18}O$ values (relative to the reference CO_2 tank) of samples were converted into the VPDB scale after normalizing (two-point calibration suggested by Coplen et al. [14]) against NBS 18 and NBS 19 international carbonate standards (distributed by the International Atomic Energy Agency, IAEA, Vienna), which were analyzed (as supplied) simultaneously with unknown samples. Three in-house laboratory carbonate standards (MERCK, NR, KH) were analyzed as unknown samples in fine powder form: NR (powdered pure calcite crystals from an ultramafic rock vein in Gogolow-Jordanow Massif, SW Poland), KH (fine to medium grained limstone from Poland), and MERCK (99.95% artificial $CaCO_3$, MERCK & Co. Whitehouse Station, NJ USA, cat. # 2059). The isotopic compositions of all carbonates used for this study are given in Table 1 and treated as true representative values for respective samples.

All the experiments were carried out according to the following set up to assess the influence of reaction temperature and time on the accuracy and reproducibility (1σ precision) of $\delta^{13}C$ and $\delta^{18}O$ analyses of carbonates. A third experiment was carried out to mimic incomplete or partial sample-acid reaction.

2.1. Influence of reaction temperature

In this experiment, sample-phosphoric acid reactions were carried out at different temperatures in the range 25–90 °C. Isotopic analyses were performed on the extracted CO_2 gas after a constant reaction time of 58 min. A set of NR, KH, and MERCK samples along with two each of international standard NBS 18 and NBS 19 were reacted with phosphoric acid at a particular temperature and subsequently analyzed for $\delta^{13}C$ and $\delta^{18}O$ isotope composition. This was repeated for different reaction temperatures. In total 78 analyses were performed. An experiment at 72 °C was conducted because this temperature is specifically recommended by ThermoFinnigan Operating Manual [15] for the GasBench II. The raw $\delta^{13}C$, $\delta^{18}O$ values of samples were converted into the VPDB scale by using the linear correlation between the measured and true δ_{VPDB}-values of NBS18 and NBS19 that were analyzed simultaneously with the unknown samples.

2.2. Influence of reaction time

In this set up, NR, KH, and MERCK samples were reacted with 0.06 mL of H_3PO_4 at a constant temperature of 70 °C, but reaction times varied in the range 3–101 min. All the raw data were converted into the VPDB scale by normalizing against NBS 18 and NBS 19 (international standards were analyzed for

Table 2
$\delta^{13}C_{VPDB}$ and $\delta^{18}O_{VPDB}$ of carbonates analyzed at different temperatures

T (°C)	NR		KH		MERCK	
	‰ $\delta^{13}C_{VPDB}$	‰ $\delta^{18}O_{VPDB}$	‰ $\delta^{13}C_{VPDB}$	‰ $\delta^{18}O_{VPDB}$	‰ $\delta^{13}C_{VPDB}$	‰ $\delta^{18}O_{VPDB}$
25	−4.98 (0.04)	−14.50 (0.02)	1.74 (0.02)	−2.81 (0.03)	–	–
50	−4.80 (0.03)	−14.51 (0.04)	1.98 (0.10)	−2.88 (0.03)	−35.65 (0.07)	−16.04 (0.02)
60	−4.69 (0.07)	−14.58 (0.02)	2.03 (0.04)	−3.07 (0.06)	−35.68 (0.03)	−16.08 (0.02)
70	−4.71 (0.04)	−14.58 (0.05)	1.99 (0.01)	−3.07 (0.05)	−35.69 (0.03)	−16.16 (0.01)
72	−4.78 (0.01)	−14.48 (0.05)	1.98 (0.02)	−3.07 (0.03)	−35.67 (0.06)	−16.01 (0.03)
80	−4.63 (0.06)	−14.33 (0.03)	2.09 (0.03)	−2.86 (0.04)	−35.59 (0.04)	−15.97 (0.05)
90	−4.64 (0.04)	−14.45 (0.06)	2.05 (0.04)	−2.94 (0.12)	−35.60 (0.04)	−16.03 (0.02)
Average 50–90	−4.71 (0.07)	−14.49 (0.09)	2.02 (0.04)	−2.98 (0.10)	−35.65 (0.04)	−16.05 (0.06)

Each δ-value represents the average (1σ in parenthesis) of 4 repetitive analyses of the same sample. These results are also shown in Fig. 1. MERCK analyses at 25 °C were abandoned because of recrystallization of H_3PO_4 that clogged the capillaries in the acid pump.

a 58 min reaction time). In total, 30 (24 unknown and 6 NBS standards) analyses were performed.

In addition, we analyzed three each of NR, KH, and MERCK samples, and two-NBS 18 and NBS 19 after 15 min, 30 min, and 12 h. In this case, the raw values were calibrated against NBS 18 and NBS 19, where the reaction time for international standards was the same as the unknown samples.

2.3. *Incomplete or partial reaction*

About 1mg each of NR, KH, and MERCK samples were reacted with phosphoric acid (∼10 μL) for 58 min at 70 °C, followed by subsequent isotope analyses. This experiment was designed to mimic an incomplete or partial reaction, where only part of the sample comes in contact with the acid and reacts and the rest of the sample remains isolated. This is important for samples that are characterized either with small-scale isotopic heterogeneity or uneven grain-size distribution.

3. Results and discussion

3.1. *Influence of reaction temperature*

The stable carbon ($\delta^{13}C_{VPDB}$) and ($\delta^{18}O_{VPDB}$) oxygen isotopic composition of NR, KH, and MERCK samples analyzed for a range of reaction temperature (25–90 °C) are presented in Table 2 and shown in Fig. 1. All isotopic compositions are reported in the VPDB scale. In general, the internal reproducibility (1σ deviation of repetitive analyses of the same sample) for both $\delta^{13}C$ and $\delta^{18}O$ are better than 0.05‰. Based on the multiple analyses of international standards NBS 18 and NBS 19 run in separate sequences and on different days, we assign an overall 1σ external reproducibility of 0.1‰ for both $\delta^{13}C$ and $\delta^{18}O$.

It is evident from Fig. 1 that when the reaction temperature is in the range 50–90 °C, both $\delta^{13}C$ and $\delta^{18}O$ of carbonate samples are accurately reproducible considering the 1σ external error of

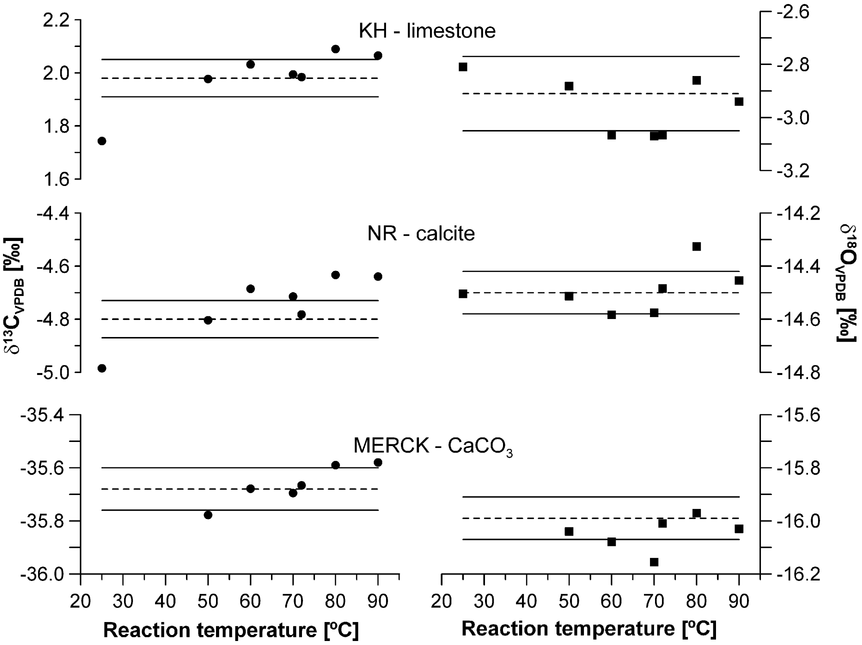

Fig. 1. Accuracy and reproducibility of $\delta^{13}C_{VPDB}$ and $\delta^{18}O_{VPDB}$ analyses (results from Table 2) performed after $CaCO_3$–H_3PO_4 reaction at various temperatures. The dashed lines represent respective true values (averages) and the solid lines represent 1σ variation associated with the averages (Table 1).

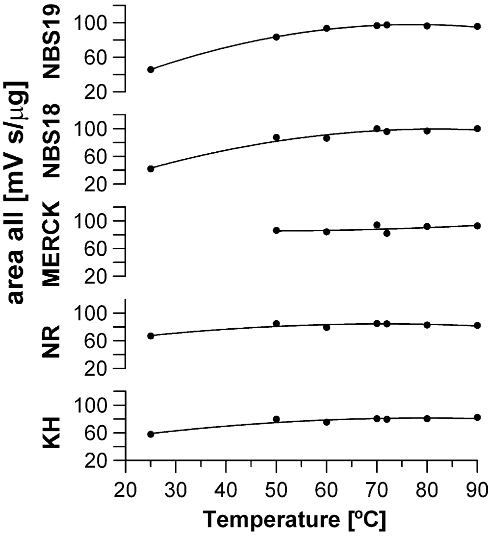

Fig. 2. Area of all peaks in mV s per μg of sample (sum of areas of *m/z* 44 + 45 + 46 peaks). Data shown represent values for the first of the 10 multiple injection peaks during a single GasBench analysis. Each dot represents an average of four analyses of the same sample.

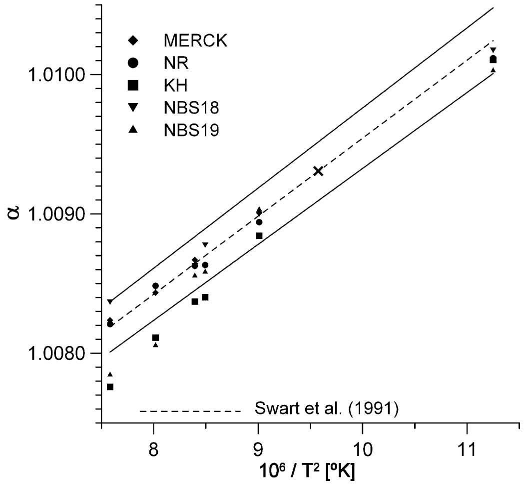

Fig. 3. Oxygen isotope fractionation factor (α) computed from raw δ-values (relative to CO_2 reference tank) at different reaction temperatures. The dotted line represents the linear relationship given by Eq. (4) and the solid lines show the range of possible values by taking into account errors on the slope and intercept (Swart et al. [5]). By using this equation we computed α_{50} (shown by 'X' mark), which is assumed to be same for all samples. See text for explanation.

true δ-values (average) presented in Table 1. This is true if the raw values are normalized against international standards also analyzed for the same reaction temperature. However, unlike the $\delta^{18}O$, the $\delta^{13}C$ of carbonates for the reaction time 25 °C could not be reproduced accurately, although individual precision was ∼0.03‰. For example, $\Delta^{13}C_{\text{true-25°}}$ (the difference between the true and 25 °C) is ≥0.18‰ for both NR and KH. We were unable to analyze MERCK at 25 °C because of recrystallization of H_3PO_4 that clogged the capillary of the acid delivery needle and tubing of the acid pump. Fig. 2 shows significant differences in a area of all peaks in mV s per μg of sample (sum of areas of *m/z* 44 + 45 + 46 peaks of the first of the 10 multiple injection peaks) for the reaction temperature 25 °C compared with that generated for the temperature range 50–90 °C (a similar trend is also observed for *m/z* = 44 intensity). Assuming that all of the CO_2 in the carbonate was released by 58 min at 90 °C, we estimate CO_2 yield (% of reaction completed, which is calculated from the areas) of ∼70% at 25 °C for KH and NR, whereas the reaction was only ∼40% complete for NBS 18 and 19. This is not surprising because the two international standards were analyzed as grains (the rate of dissolution is a function of particle diameter). In addition, the relatively high viscosity of concentrated H_3PO_4 at 25 °C compared with that at higher temperatures might be an important reason for lower CO_2 yields at 25 °C [10]. Based on our results, we conclude that at 25 °C, the reaction time of 58 min is not sufficient to reproduce results with accuracy.

We estimated the magnitude of oxygen isotope fractionation as a function of temperature for all the samples. While no temperature dependent fractionation of carbon isotopes over the range of temperature was observed, that for the oxygen isotopes is apparent. To estimate the oxygen isotope fractionation factor at any temperature (α_T), we adopted an approach similar to Swart et al. [5]. First, we computed the fractionation factor at 50 °C (α_{50}) from the equation given by Swart et al. [5]:

$$\alpha_T = [5.6(\pm 0.15) \times 10^2]T^{-2} + 1.003943(\pm 0.000067) \qquad (4)$$

where T is in Kelvin. Our estimated α_{50} is 1.009306, which is assumed to be constant for all the samples. Then we computed α at a given temperature by using the equation:

$$\alpha_T = \frac{\delta^{18}O_{CO_2(T)} + 1000}{\delta^{18}O_{CO_2(50)} + 1000} \times \alpha_{50} \qquad (5)$$

where $\delta^{18}O_{CO_2}$ is the raw value of the CO_2 gas relative to the reference CO_2 tank value. A comparison of fractionation factors computed at different temperatures for different samples is shown in Fig. 3. It is evident that the extent of fractionation for the unknown samples and the NBS standards are similar at a given temperature, although at higher temperatures (>80 °C) fractionation for KH and NBS 19 differs slightly from other samples. The fractionation for NR and MERCK fall on the line given by Eq. (4), which is reflected in higher accuracy and better reproducibility of these samples (Fig. 1) compared with KH (e.g., 1σ for KH at 90 °C is 0.12‰, the worst amongst all the analyses). Despite a relatively large scatter in α amongst the samples at higher temperature (which are mostly bounded by α-values of NBS 18 and NBS 19), accurate and precise true $\delta^{18}O$ values of samples are obtained after normalizing (2-point calibration [14]) against NBS 18 and NBS 19. Furthermore, the experimentally derived values of α [3–5,12] have an relative uncertainty of $\sim 1\sigma = 0.05$‰ at 25 °C (or at any given temperature) for pure calcite. Therefore, to estimate the true isotopic composition of calcite samples, it is necessary to apply a correction procedure that relies on the identical Treatment principle. We conclude that for isotopic analyses, carbonate-acid reaction may be conducted at any temperature in the range 50–90 °C. However, due to the similar extent of fractionation, 50–70 °C seems to be a more appropriate range.

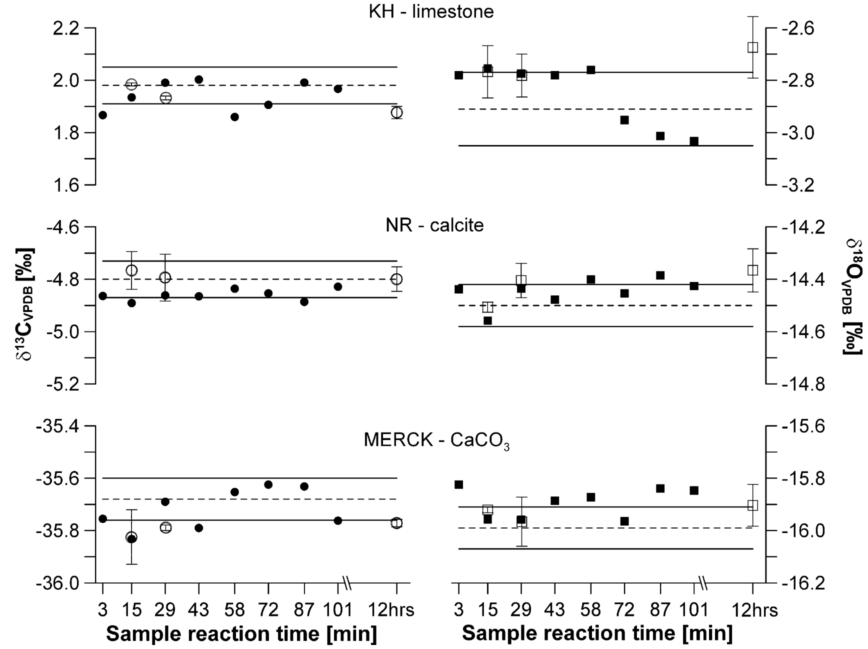

Fig. 4. Accuracy and reproducibility of $\delta^{13}C_{VPDB}$ and $\delta^{18}O_{VPDB}$ analyses vs. duration of carbonate-acid reaction. The dotted lines represent respective true values (averages) and the solid lines represent 1σ variation associated with the averages (Table 1). Each solid dot represents a single analysis, whereas each open dot represents an average of three runs each for 15 and 30 min, and 12 h. 1σ error bars are shown where applicable.

3.2. Influence of reaction time

In general, no significant differences in $\delta^{13}C_{VPDB}$ and $\delta^{18}O_{VPDB}$ are observed for samples analyzed for different reaction times in the range 3–101 min at a constant reaction temperature of 70 °C (Fig. 4). The reproducibility of $\delta^{13}C$ is slightly better than $\delta^{18}O$. A slight variation in $\delta^{18}O$ is observed for KH samples reacted longer than 58 min compared with those reacted for less than 58 min: $\delta^{18}O_{KH \leq 58min} = -2.77 \pm 0.01‰$ ($n = 5$) and $\delta^{18}O_{KH > 58min} = -3.00 \pm 0.04$ ‰ ($n = 3$). Although the $\delta^{18}O_{KH}$ for reaction times ≤58 min are isotopically heavier by 0.2‰ compared to that for reaction times ≥58 min, no systematic variation is observed for other samples. We suspect isotopic heterogeneity in KH to be the cause of such variation.

The true isotopic composition of samples analyzed separately after 15 and 29 min reaction times are also reproduced, where the raw data are normalized against NBS standards analyzed over the same reaction time. Similarly, the isotopic composition of samples analyzed after a 12 h reaction (normalized against NBS 18 and NBS 19 analyses after 12 h reaction) is close to the true isotopic composition of the respective samples. These results are also shown in Fig. 4. There is no significant difference in isotopic composition analyzed for a range of reaction times varying from 3 min to 12 h. The $\delta^{18}O_{KH}$ for the 12 h experiment does not indicate any systematic variation in oxygen isotopes with time but rather confirms our earlier observation that this sample is isotopically heterogeneous, which is also reflected by the poor external precision of this sample given in Table 1. Assuming that the reaction is complete after 12 h and that all of the CO_2 in the carbonate is released to the headspace, we computed the percentage of CO_2 yield with time by normalizing the areaall/µg of the first CO_2 peak for each reaction time against the value for the respective 12 h measurement. The results indicate that the CO_2 yield in all the samples is 90–94% after 3–15 min and ~100% by 30 min. Therefore, we conclude that although isotopic analyses may be performed after 15 min of carbonate-acid reaction for carbonate samples that are isotopically homogeneous, the ideal choice is to wait at least 30 min at 70 °C.

Furthermore, we analyzed $\delta^{18}O_{VPDB}$ of ortho-phosphoric acid (analyzed in liquid form) used in this study. An average value of $\delta^{18}O_{VPDB} = -14.18‰$ ($1\sigma = 0.30‰$, $n = 12$) is obtained from analyses performed by high temperature pyrolytic conversion of O_2 to CO analyte gas in an Elemental Analyzer (TC/EA) coupled with IRMS in continuous flow mode. The true $\delta^{18}O$ values of both NR and MERCK are close to $\delta^{18}O$ of acid (difference < 2‰), whereas $\delta^{18}O_{KH}$ is about 11‰ heavier than that of the acid. Therefore, the effect of oxygen fractionation between CO_2 and water produced due to polymerization of acid (assuming that $\delta^{18}O$ of water is same as that of acid) may shift the $\delta^{18}O_{KH}$ towards lighter δ-values with time. However, there is no systematic trend when all the $\delta^{18}O_{KH}$ (including the 12 h result) are compared. Therefore, the possibility of isotopic exchange between CO_2− and water produced during the reaction remains inconclusive. Despite such possibilities, the resulting effect is negligible when raw data are normalized against the NBS standards.

3.3. Incomplete reaction

To compute δ_{VPDB}-values for incomplete reaction experiment, we did not include the first three peaks (out of 10 peaks in a single GasBench analysis) as the signal (and area) of these peaks was too high compared with the CO_2 reference tank peak. However, even for peaks 4 through 10, signals were ~4× higher than that of the reference CO_2 peaks. Significant differences in isotopic composition (higher for $\delta^{18}O$ than $\delta^{13}C$) compared with the true-values are observed. The differences between the true $\delta^{13}C_{VPDB}$ and the average ($n = 4$) of respective samples analyzed during this experiment are: 0.05‰ for KH, 0.14‰ for NR, and 0.17‰ for MERCK. Similarly, for oxygen the values are: 0.81‰ for KH, 0.64‰ for NR and 0.80‰ for MERCK. Inaccuracy and poor precision (as high as 0.19‰ for carbon and 0.37‰ for oxygen isotopic composition of KH) of these analyses may have resulted due to analyses performed on isotopically variable sample CO_2 gasses released during partial dissolution of isotopically heterogeneous grains. Walters et al. [11] also reported such an effect.

4. Conclusions

In this work, we have evaluated the online carbonate-phosphoric acid analytical technique using the GasBench II peripheral device coupled with a $\text{Delta}^{\text{Plus}}$ XP IRMS. We have evaluated both the accuracy and reproducibility of carbon and oxygen isotopic analyses of carbonates for a range of carbonate-phosphoric acid reaction temperatures and reaction times.

Our data suggest that when carbonate-phosphoric acid reaction is carried out at 25 °C for an hour, the carbon isotopic composition of carbonates are not reproduced accurately even though the precision of multiple analyses is better than 0.04‰. Whereas the isotopic composition of carbonates are accurately reproducible for any temperature in the range 50–90 °C (1 h reaction time) provided the raw δ-values are normalized (as suggested by Coplen et al. [14]) against at least two international carbonate standards, analyzed at the same temperature and for same reaction time as the samples. Results also suggest that isotopic analyses of calcium carbonates can be performed much sooner than that adopted by most current techniques. For isotopically homogeneous samples, no significant difference in isotopic analyses is observed between that obtained for a range of carbonate-acid reaction time varying from 3 to 101 min and a 12 h reaction. However, based on the estimates of CO_2 yield with time, we conclude that isotopic analyses may be performed after 30 min of carbonate-acid reaction at 70 °C. This is a significant improvement on sample throughput considering that most commonly used continuous flow techniques require a reaction time of at least an hour. Furthermore, care should be taken to ensure that the entire sample is reacted completely with the acid. This is important for isotopically heterogeneous sample/grains in order to obtain a representative average δ-value of the whole powder sample prepared for reaction.

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