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Determination of clumped isotopes in carbonate using isotope ratio mass spectrometry: Toward a systematic evaluation of a sample extraction method using a static Porapak^{TM} Q absorbent trap

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ABSTRACT

In this study, we performed a detailed comparison of stable and clumped isotopic data for an extraction method passing CO_2 through a Porapak Q absorbent trap (PQT) driven by liquid nitrogen (LN method), an extraction method passing CO_2 through a PQT driven by liquid nitrogen and high vacuum pumping (LN + HV method) and an extraction method without a PQT (NAT method), to examine the effectiveness and reliability of these methods. Changes in raw Δ_{47} values along with collection times were used to constrain the optimum collection time (OCT) for each method. The OCT for the LN method shortened considerably when the PQT was warmer, i.e., from ~35 min to ~30 min when the PQT temperature changed from −15 °C to −12.5 °C. In contrast, the OCT for the LN + HV method displayed little change with the PQT temperature and was reduced to 25 min for both −15 °C and −25 °C. The contaminant removal efficiency of these methods was evaluated by Δ_{48} values, revealing that the LN method (with a −12.5 °C to −25 °C PQT) and the LN + HV method (at −25 °C) could effectively remove contaminants compared with the NAT method. Therefore, the LN + HV method (at −25.0 °C) may serve as a promising sample preparation method for routine measurement because it can save time without compromising sample cleaning efficiency. Nevertheless, the LN + HV method yielded Δ_{47} values 0.04–0.05‰ higher than the LN method at the same temperature, possibly because of different absorption–desorption states of the PQT in these methods. These findings provide useful clues for optimizing CO_2 extraction methods for clumped isotope analysis.

1. Introduction

Clumped isotopes are multiply substituted isotopologues (molecules containing two or more rare isotopes) and are a relatively new research direction in geochemistry. Recently, clumped isotope compositions of carbonate (expressed as Δ_{47}; quantifying the excess abundance of CO_2 with mass 47 ($^{13}C^{18}O^{16}O$) in carbonate) have been developed as a useful thermometer [1]. Clumped isotope thermometry has an advantage over conventional oxygen isotope thermometry in cases where the isotope composition of the water is unknown. Therefore, the clumped isotope thermometer enables a more precise reconstruction of paleotemperature than the oxygen isotope thermometer. This technique has been recently applied to determine the body temperatures of some extinct vertebrates and dinosaurs [2,3], to reconstruct changes in environmental temperatures during the geological past [4–6], to constrain diagenetic alteration [7] and to elucidate the uplift history of high mountains or plateaus [8].

Although clumped isotope thermometry has such broad applications, a large discrepancy still exists when comparing data from different laboratories. For example, the maximum difference in Δ_{47} values generated by various laboratories for the same carbonate substances in a recent inter-lab calibration reached up to 0.07‰ (Stefano Bernasconi, personal communication), corresponding to a temperature difference of approximately 15 °C or greater. The reasons for this large discrepancy may be manifold. Previous studies have shown that instrumental tuning parameters [9] and pressure imbalances between reference and sample CO_2 gases in dual-inlet mode [10] can affect the accuracy and precision of clumped isotope analysis. Other than effects from the mass spectrometer itself, the sample extraction method may be an important aspect to consider, especially when laboratories employ different processes for

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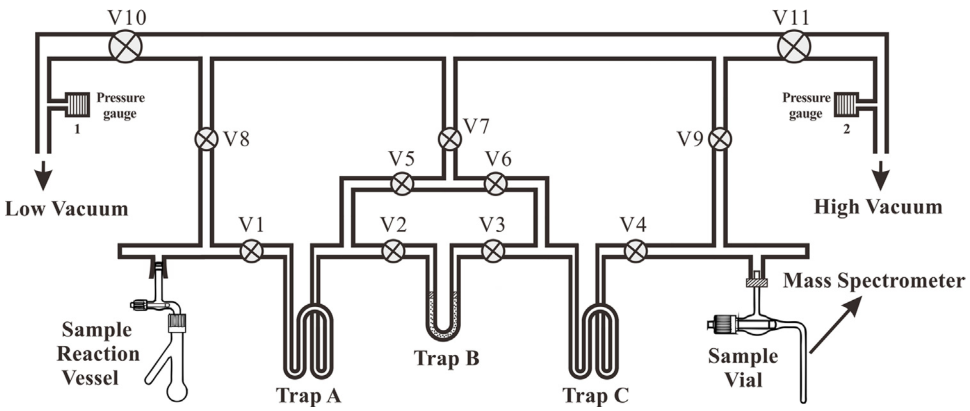

Fig. 1. Schematic map showing the collection and purification apparatus of the CO_2 produced from the phosphoric acid digestion of carbonate. Product CO_2 is cryogenically purified from water and other trace gases by passing through Trap A and Trap C, which are sequentially immersed in liquid nitrogen and a liquid nitrogen/acetone slurry. Trap B, the Porapak Q absorbent trap usually maintained at −15 °C (by immersion in a liquid nitrogen/ethylene glycol slurry), could be optionally used for the purification of hydrocarbons in this study. The CO_2 passes through Trap B if valves V2 and V3 are open and valves V5 and V6 are closed. Otherwise, the CO_2 will circumvent Trap B if valves V2, V3, and V7 are closed while valves V5 and V6 are open. Pressure gauge locations are marked as 1 and 2.

CO_2 extraction from carbonates. For example, Wacker et al. [11] studied reaction mechanisms of two different acid digestion techniques – a conventional sealed vessel method (at 25 °C) and a common acid bath method (at 90 °C), and a sample size effect on Δ_{47} values was observed for carbonates digested using the conventional sealed vessel method. To remove isobaric interferences from contaminant gases, i.e., hydrocarbons and halocarbons [12], CO_2 liberated from carbonate has been subsequently purified using two different methods: the CO_2 is entrained in a He stream flowing through a gas chromatography capillary column packed with a porous divinyl benzene polymer at −10 °C or −20 °C [1,13,14], or the CO_2 is passively passed through an absorbent trap filled with Porapak Q^{TM} (divinyl benzene polymer, 80–100 mesh) at −10 °C to −35 °C [7,15,16]. However, the extraction method using a Porapak Q absorbent trap has not yet been systematically evaluated, although it is routinely employed in Δ_{47} analysis in some laboratories.

In this study, we performed a series of contrasting experiments to examine the effectiveness of the Porapak Q absorbent trap (PQT) extraction method for CO_2 purification. The differences in measured Δ_{47} values for CO_2 extracted from pure carbonates were determined using two different methods: passing through the absorbent trap and circumventing the absorbent trap. This may provide useful future guidance to optimize sample extraction for clumped isotope analysis. To the best of our knowledge, no systematic research has been published on this issue.

2. Experimental

2.1. CO_2 extraction method

A Chinese national stable isotope standard (GBW04406) and three laboratory working standards (IVA, NB4 and P1) were analyzed for clumped isotopes. GBW04406 (calcite, supplied by the National Bureau of Standards of China) is a pure chemical reagent powder with certified $\delta^{13}C = -10.85‰$ (VPDB) and $\delta^{18}O = -12.40‰$ (VPDB). IVA (calcite, supplied by IVA Corporation, Germany) is a fine-grained chemical reagent with measured $\delta^{13}C = +2.21‰$ (VPDB) and $\delta^{18}O = -1.90‰$ (VPDB). NB4 (calcite, from Beijing Geological Museum, China) is coarse-grained white marble, which was crushed to a fine powder and homogenized using a mortar and pestle. P1 is a fine-powdered coral material, collected in Thailand. Our prior work indicated that these samples span a range of isotopic compositions and formation temperatures. We extracted CO_2 from carbonates by reaction with anhydrous phosphoric acid, generally following the method of Ghosh et al. [1]. Briefly, approximately 15 mg of sample was reacted with ~103% phosphoric acid (density 1.90 g/ml) under vacuum at 25 °C for ~16 h (overnight). The phosphoric acid was made by mixing an originally crystallized phosphoric acid (≥99%, Sigma–Aldrich) with phosphorus pentoxide powder (99%, Sigma–Aldrich). The CO_2 product was cryogenically purified by passing sequentially through different traps.

To examine the differences in measured Δ_{47} values for CO_2 purified using different extraction methods, we designed a glass extraction line with an optional pass through the Porapak Q absorbent trap (Fig. 1). The PQT used in this study was a glass U-tube trap densely packed with $Porapak^{TM}$ Q (divinyl benzene polymer, 80–100 mesh) with packed material of 8 cm in length and ~8 mm in diameter.

We adopted two different collection processes for purification extraction using the PQT: one with the CO_2 passing through the absorbent trap cryogenically drawn by liquid nitrogen (LN method), and the second with the CO_2 passing through the absorbent trap driven by liquid nitrogen and a high vacuum pump (LN + HV method). The LN method consists of the following procedures. (1) The CO_2 was first frozen in a U-shaped trap (Trap A) at the temperature of liquid nitrogen, and the trap was subsequently changed to a liquid nitrogen/acetone slurry trap at −80 °C to release the CO_2 while the water was still frozen. (2) The evolved CO_2 passed through the PQT (Trap B) immersed in a liquid nitrogen/ethylene glycol slurry (around −15 °C) and was then collected in another U-shaped trap (Trap C) at the temperature of liquid nitrogen with an optimal collection time determined during the study. (3) Once a given collection time was reached, the trap (Trap C) was subsequently changed to a liquid nitrogen/acetone slurry trap at −80 °C to freeze any trace amount of water, and the released CO_2 from Trap C was then collected in a small glass sample vessel using liquid nitrogen for clumped isotope determination. The LN + HV method generally follows the above LN method procedures except for the second step, which is described as below: the evolved CO_2 was drawn through the PQT (Trap B) immersed in a liquid nitrogen/ethylene glycol slurry (around −15 °C) with V2 and V3 simultaneously opened and collected in Trap C using liquid nitrogen. It was then continuously pumped on by a high vacuum pump downstream of Trap C through opening V4, V9 and V11. In contrast, the extraction method without purifying through a PQT (NAT method) only involved the removal of water from the CO_2 by two water traps (Trap A and Trap C) immersed in liquid nitrogen/acetone slurries (−80 °C). Prior to extraction of next sample, the PQT was heated at approximate 100 °C for 15 min and evacuated using HV pump during the same time. After one day's pretreatment, the PQT was heated and evacuated for about 2 h to ensure a complete removal of potential contaminants. During the pretreatment process, the temperatures of both the Porapak Q absorbent trap and the water traps were carefully measured to ensure that the experiments were conducted under equivalent conditions.

2.2. Clumped isotope measurements

All analyses were carried out on a Thermo Finnigan MAT253 isotope ratio mass spectrometer (IRMS), which was configured to simultaneously collect ion beams of $m/z = 44$, 45 and 46 (read through $3 \times 10^8\ \Omega$, $3 \times 10^{10}\ \Omega$ and $1 \times 10^{11}\ \Omega$ resistors), as well as 47, 48 and 49 (read through $1 \times 10^{12}\ \Omega$ resistors). The IRMS was operated with an electron energy of 84 V, an acceleration potential of ~9.5 kV, and a closed 'sulfur window'. On this IRMS, we replaced the stainless steel capillary tubes with electroformed nickel (EFNi) capillaries, which largely minimized isotope redistribution reactions [13]. The extraction potential was set at 90%, which can largely stabilize the linearity effect (as proposed by Huntington et al. [17]) of our mass spectrometer over the long term [9]. The clumped isotope measurements were made in dual-inlet mode, with an average beam intensity of 16 V on mass 44. The analysis for one sample consisted of 8 acquisitions. Each acquisition involved 8 cycles of sample–standard comparison, and each cycle involved 26 s of integration of the sample and standard ion beams. A total of 64 cycles was performed on a given sample, taking two and a half hours. Analyses were standardized via comparison with an intra-laboratory reference gas whose bulk isotopic composition had been previously calibrated against CO_2 produced by the phosphoric acid digestion of NBS-19.

In this study, we report the excess abundance of mass 47 using the Δ_{47} notation [12], which relates the measured isotopic ratios R^{47} of the sample to the ratio R^{47^*} of the same sample assuming it had a stochastic isotope distribution. Δ_{47} is calculated by the following equation:

$$\Delta_{47} = [(R^{47}/R^{47*} - 1) - (R^{46}/R^{46*} - 1) - (R^{45}/R^{45*} - 1)] \times 1000 \tag{1}$$

where R^{47}, R^{46}, and R^{45} are the abundance ratios of masses 47, 46, and 45, respectively, relative to mass 44 (e.g., 47/44). R^{47^*}, R^{46^*} and R^{45^*} are the corresponding ratios that would occur in a sample with stochastic distribution. Theoretically, Δ_{47} for CO_2 is approximately 0‰ at 1000 °C, which means a stochastic distribution is achieved. In practice, three or more heated CO_2 gases of different isotopic compositions with a large range of δ47 values relative to the reference gas were carefully measured to construct a heated CO_2 gas

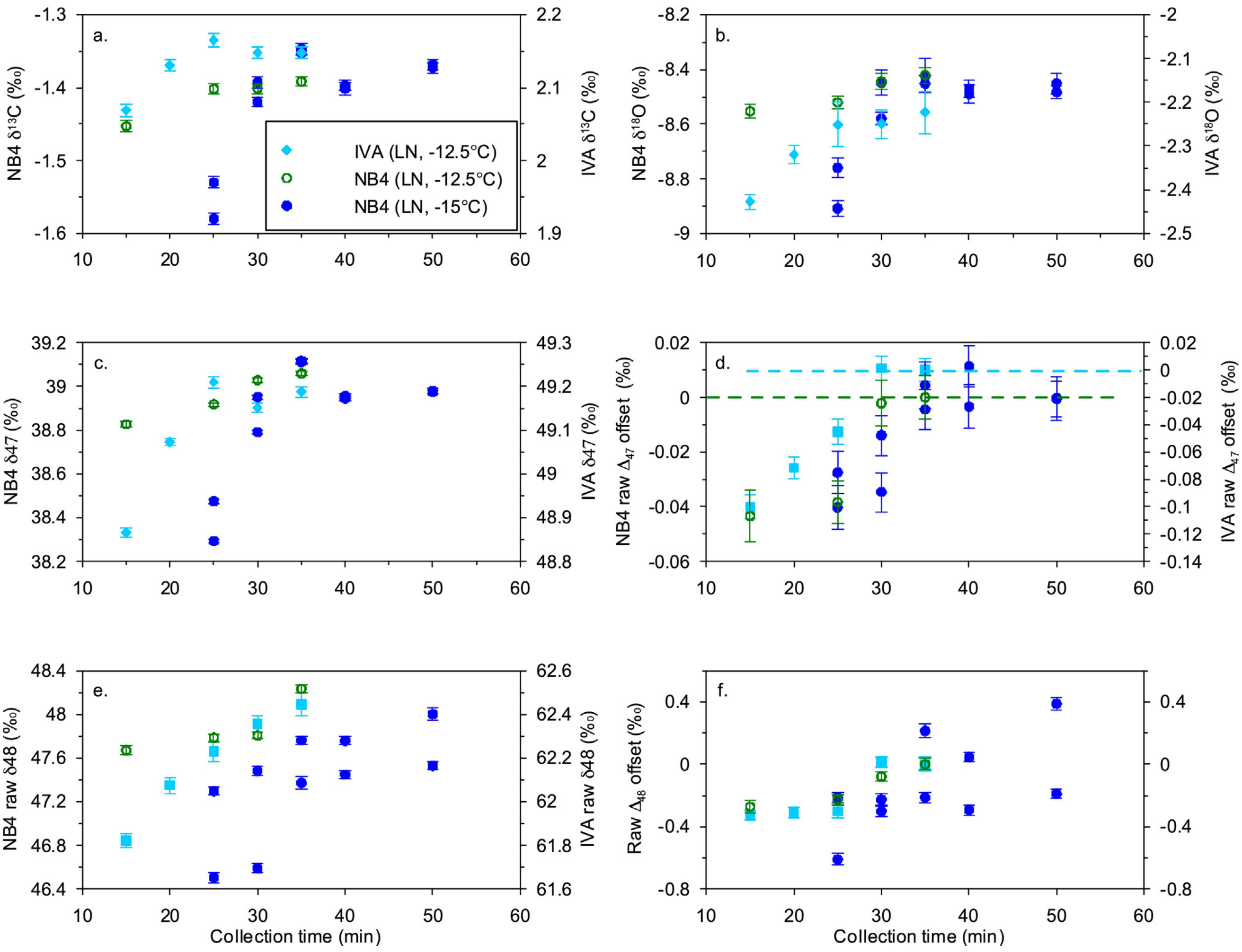

Fig. 2. Plots showing changes in $\delta^{13}C$, $\delta^{18}O$, δ47, raw Δ_{47} offset, δ48 and raw Δ_{48} offset (relative to raw Δ_{48} values determined with a 35 min collection time) values of two carbonate samples (IVA and NB4) along with collection time using the LN method at different PQT temperatures. A time of 35 min is sufficient to obtain a stable Δ_{47} value for both samples. Each point represents one extraction and individual measurement. Error bars denote internal precision for each measurement (i.e., SD for $\delta^{13}C$ and $\delta^{18}O$, SE for other values).

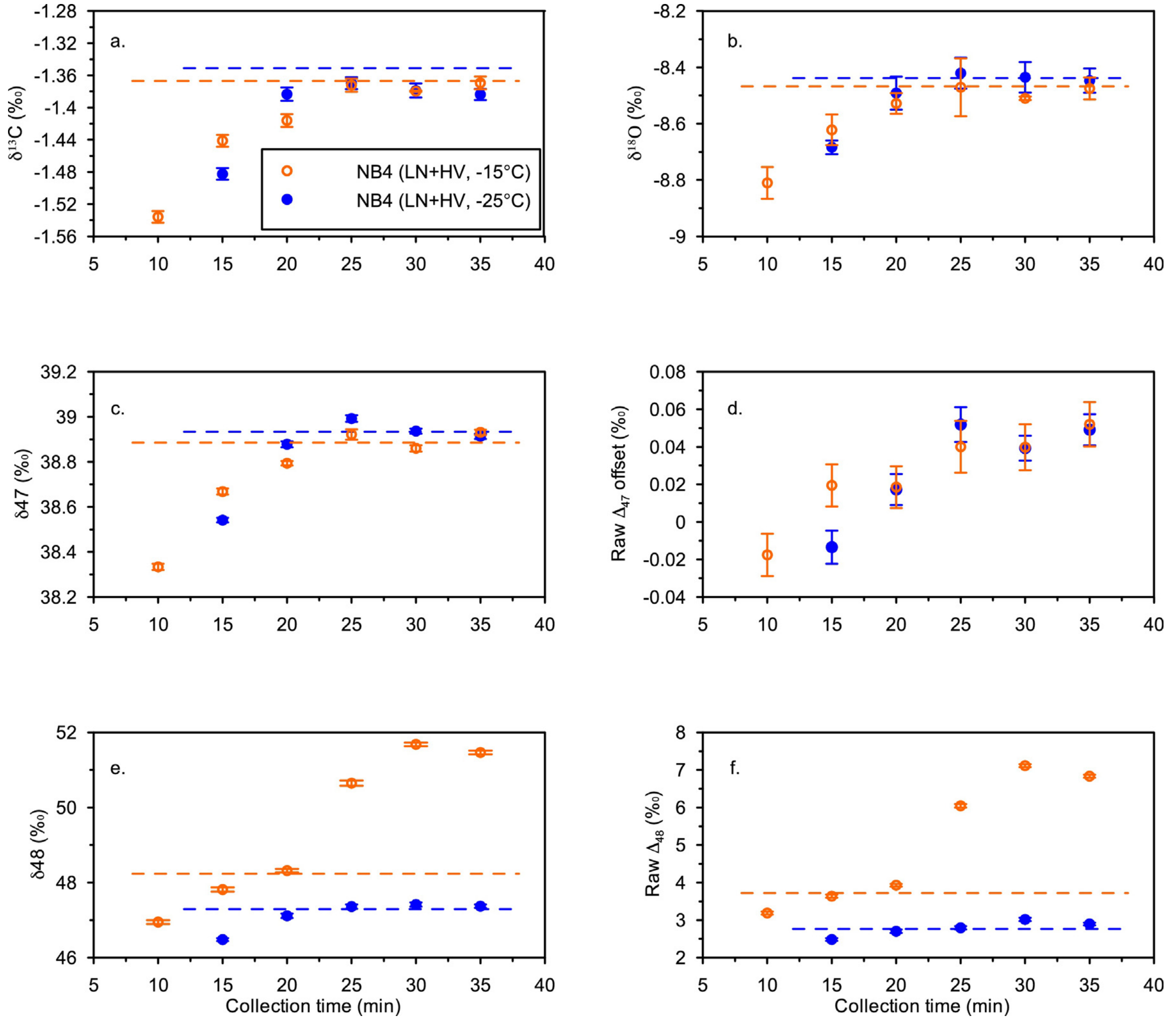

Fig. 3. Changes in δ^{13}C, δ^{18}O, δ47, raw Δ_{47} offset, δ48 and raw Δ_{48} values of NB4 along with collection time using the LN + HV method at different PQT temperatures. Each point represents one extraction and individual measurement. Error bars denote internal precision for each measurement (i.e., SD for δ^{13}C and δ^{18}O, SE for other values). The horizontal orange and blue dashed lines are the mean values measured using the LN methods at PQT temperatures of −15 °C and −25 °C, respectively, during the same day as those determined using the LN + HV method. A time of 25 min is sufficient to obtain a stable Δ_{47} value for the sample.

line (HG line, i.e., a δ47 vs. Δ_{47} plot), which was used to correct for the non-linearity effects of mass spectrometry and to obtain the real Δ_{47} value [17]. The raw Δ_{47} value of a sample was calculated using Eq. (1), but it is necessary to correct for linearity effects in the IRMS, which were determined by the measurement of heated gases of different isotopic compositions (i.e., HG line). The correction was performed following the procedures described by Schmid and Bernasconi [15].

2.3. HG line construction

In this study, carbonates with different isotopic compositions were used to construct the HG line. These carbonates are GBW04405 ($\delta^{13}C_{VPDB}$: +0.57‰; $\delta^{18}O_{VPDB}$: −8.49‰), GBW04406 ($\delta^{13}C_{VPDB}$: −10.85‰; $\delta^{18}O_{VPDB}$: −12.40‰), GBW04417 ($\delta^{13}C_{VPDB}$: −6.06‰; $\delta^{18}O_{VPDB}$: −24.12‰), LEVIG-CO-1 ($\delta^{13}C_{VPDB}$: −46.81‰; $\delta^{18}O_{VPDB}$: −13.47‰) and NBS-19 ($\delta^{13}C_{VPDB}$: +1.95‰; $\delta^{18}O_{VPDB}$: −2.20‰). The ranges for the δ^{13}C and δ^{18}O values of the above chosen carbonates normally cover those of natural carbonate samples that we have routinely measured. CO_2 gases were produced via phosphoric acid digestion of these carbonates, sealed in quartz-glass tubes, heated to 1060 °C in a muffle furnace for 3 h, and rapidly quenched in tap water at room temperature. The heated gases were purified using cryogenic procedures in a manner identical to the preparation of samples before being transferred to the IRMS.

3. Results and discussion

3.1. Optimizing the collection time for CO_2 passing through the absorbent trap driven by liquid nitrogen (LN method)

To determine the optimal collection time for CO_2 passed through the PQT, we tested different lengths of time (15–50 min) to collect the CO_2 in a downstream trap (Trap C in Fig. 1) using liquid nitrogen (LN method). Two carbonate samples (IVA and NB4) were used to generate CO_2 for this test and two different temperatures for the absorbent trap were examined. The collected CO_2 was subsequently repurified to remove trace water using a liquid nitrogen/acetone slurry and then transferred to a MAT253 IRMS (Thermo Finnigan) for clumped isotope analyses. Mass spectrometer behavior may shift over time (as documented by HG lines [17]) and the clumped isotopic composition of a working gas may also be subject to change, which prohibits direct comparison of raw Δ_{47} values (i.e., the Δ_{47} of the sample relative to the working gas). In this case, we daily measured raw Δ_{47} values for IVA or NB4 with a collection time of 35 min, as well as other collection times, in each batch of tests to monitor the working condition of our mass

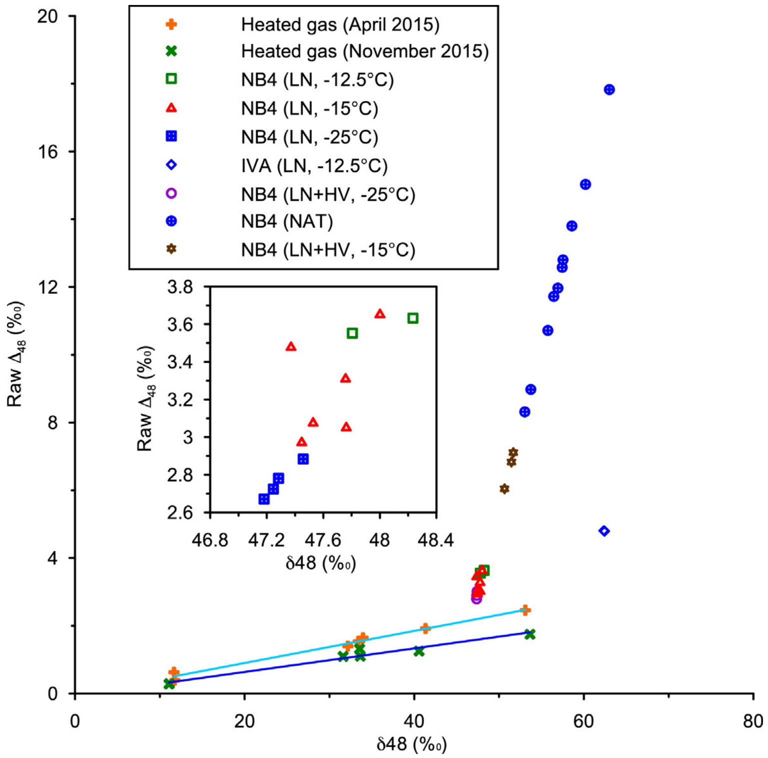

Fig. 4. A plot of $\delta48$ vs. Δ_{48} values for NB4 and IVA samples determined using the LN, LN + HV and NAT methods, compared with those of the heated gases measured during the same time.

spectrometer. Moreover, samples for the same batch collection-time test were run very proximally in time (i.e., within one day or over several consecutive days). We then calculated raw Δ_{47} offsets for each sample with different collection times using the raw Δ_{47} value of the 35 min collection time as a reference. The changes in the $\delta^{13}C$, $\delta^{18}O$, $\delta47$, raw Δ_{47} offset, $\delta48$ and raw Δ_{48} offset (relative to raw Δ_{48} values determined with a 35 min collection time) values of these two carbonate samples along with collection times are shown in Fig. 2. The raw Δ_{47} offset values for both IVA and NB4 increase with the collection time. For the absorbent trap temperature of −12.5 °C, the raw Δ_{47} offset values of both IVA and NB4 exhibit little variation when the collection time is greater than 30 min. In contrast, the raw Δ_{47} offset values of NB4 treated at a −15.0 °C trap temperature reach a plateau after 35 min (Fig. 2d).

Similarly, at a −12.5 °C trap temperature, the $\delta^{13}C$, $\delta^{18}O$ and $\delta47$ values of both IVA and NB4 generally show little change when the collection time is longer than 30 min (Fig. 2a–c). Comparatively, the $\delta^{13}C$, $\delta^{18}O$ and $\delta47$ values of NB4 when treated at a −15.0 °C trap temperature tend to be stable after 35 min. Therefore, the optimal collection time depends on the temperature of the PQT, i.e., the warmer the PQT, the shorter the collection time. In this study, we determined 35 min to be the optimum length of time to collect CO_2 passing through the absorbent trap at −15.0 °C for clumped isotope analysis.

At the same time, the $\delta48$ and raw Δ_{48} offset values exhibited an overall increasing trend with increasing collection time (Fig. 2e and f). At a −12.5 °C trap temperature, the raw Δ_{48} offset of the two carbonate standards displayed little variation after 30 min although the $\delta48$ values still increased. In comparison, both the $\delta48$ and raw Δ_{48} offset of NB4 treated at a −15.0 °C trap temperature continuously increased but the increase becomes less steep after 35 min. Moreover, the raw $\delta48$ values of NB4 treated at a −12.5 °C trap temperature were systematically higher than those at −15.0 °C for the same collection time. Taking these data together, we conclude that $^{12}C^{18}O^{18}O$ (mass 48) passes through the absorbent trap more slowly than $^{13}C^{16}O^{16}O$ (mass 45), $^{12}C^{18}O^{16}O$ (mass 46) and $^{13}C^{18}O^{16}O$ (mass 47). In this case, a relatively warm absorbent trap may cause easier passage. If Δ_{48} is used as a geothermometer because of future technical improvements of IRMS, a sample extraction method using a relatively warm PQT (i.e., near −10 °C) may be more suitable to shorten collection time. However, one risk of using warmer PQT temperatures is that contaminants will not be fully removed, requiring a balance between these competing demands.

3.2. *Δ_{47} values of CO_2 passing through the absorbent trap driven by liquid nitrogen and a high vacuum pump (LN + HV method)*

Attempting to examine whether the LN + HV method would shorten collection time, we tested different CO_2 collection periods (10–35 min) to obtain the optimum collection time for this extraction method. To eliminate the effect from varying conditions of the IRMS and possible changes in the clumped isotopic composition of the working CO_2 gas, we daily measured the raw Δ_{47} values of NB4 treated using the LN method for 35 min along with this test and calculated the raw Δ_{47} offset (relative to the above raw Δ_{47} values of NB4 using the LN method) for NB4 treated using the LN + HV method. The PQT temperature was maintained at −15.0 °C and −25.0 °C, respectively. Fig. 3 illustrates the changes in $\delta^{13}C$, $\delta^{18}O$, $\delta47$, raw Δ_{47} offset, $\delta48$ and raw Δ_{48} values of NB4 along with collection times. Clearly, for the two PQT temperatures, the raw Δ_{47} offset values generally stabilized with collection times longer than 25 min (Fig. 3d). Meanwhile, the $\delta^{13}C$, $\delta^{18}O$ and $\delta47$ values also reached a plateau after 25 min (Fig. 3a–c). These data indicate an optimum collection time of 25 min using the LN + HV method at −15.0 °C and −25.0 °C. Therefore, the LN + HV method can notably shorten the overall time of the extraction process compared with the LN method.

However, two key issues must be addressed before confirming the usefulness of the LN + HV method in routine measurement. First, the high vacuum pump may draw away some CO_2 gas, which would fractionate Δ_{47} values. To avoid this possibility, we used a doubly folded U-trap which has a total length of about 70 cm immersed in liquid nitrogen and we only opened a narrow slit for the valve (V4, Fig. 1) that attaches to the HV pump. Moreover, the occurrence of fractionation could be judged from the measured isotopic compositions. The δ^{18}O and δ47 values determined from NB4 treated using the LN + HV method (after 25 min) are almost the same within the range of error as those measured using the LN method with a collection time of 35 min (orange and blue dashed lines in Fig. 3b and c). Nevertheless, the δ^{13}C values determined using LN + HV are slightly lower by 0.02–0.03‰ than those measured using the LN method, for unknown reasons. This could rule out the possibility of fractionation caused by the HV pump. Otherwise, the δ^{13}C obtained using the LN + HV method should be higher. Second, there is a possibility that the HV pump would pull CO_2 through the PQT too quickly to efficiently remove contaminants. This may be examined by comparing the raw Δ_{48} of samples using the LN + HV method with those using the LN method. Both the δ48 values and raw Δ_{48} of NB4 from the LN + HV method show increases along with increasing collection time (Fig. 3e and f), indicating a similar pattern to that observed for the LN method (Fig. 2e and f). The δ48 values plateau after 25 min for the LN + HV method at −25.0 °C, whereas the raw Δ_{48} values continue to increase even after 25 min. The raw Δ_{48} value obtained using the LN + HV method at −25.0 °C for 25 min is very close to the mean Δ_{48} values of NB4 treated with the LN method for 35 min (blue dashed line in Fig. 3f). Although the Δ_{48} values do not stabilize, the raw Δ_{48} values for the LN + HV method at −25.0 °C (with 30 and 35 min collection times) are only approximately 0.2–0.3‰ higher than those for the LN method (at −25.0 °C for 35 min). This suggests that the LN + HV method at −25.0 °C removes contaminants as efficiently as the LN method. By contrast, both the δ48 and Δ_{48} values were obtained for the LN + HV method at −15.0 °C plateau after 30 min (orange circles in Fig. 3e and f). However, the stabilized δ48 and Δ_{48} values are clearly higher than those obtained using the LN method (at −15.0 °C for 35 min). This indicates that the LN + HV method at −15.0 °C may not sufficiently remove contaminants, although these contaminants had little influence on the measured Δ_{47} values. Further evaluation of the contaminant removal efficiency of these two methods will be discussed in the next section.

The Δ_{47} values of NB4 treated using the LN + HV method for 25 min are approximately 0.04–0.05‰ higher than those using the LN method with 35 min collection (Fig. 3d). This may be attributed to different states of absorption and desorption for the PQTs in the two methods, which may be the focus of future study.

3.3. *An evaluation of contaminant removal of the LN and LN + HV methods*

Mass-48 and mass-49 signals have previously been found to be sensitive indicators of the presence of hydrocarbons, chlorocarbons or sulfur-bearing contaminants in CO_2 [12,18]. Subsequently, a method for determining whether a sample has 'normal' Δ_{48} or is contaminated has been proposed, via comparing the raw Δ_{48} of samples to heated gases run at the same time on a plot of δ48 vs. Δ_{48} [17]. To examine whether the LN and LN + HV are actually cleaning the samples, we put the raw Δ_{48} values of IVA or NB4 treated using the LN, LN + HV and NAT methods on a plot of δ48 vs. Δ_{48} for heated gases (Fig. 4). Clearly, the raw Δ_{48} values for samples treated using the PQT are largely reduced, compared with samples not passing through the PQT (NAT method). Moreover, the raw Δ_{48} values observed using the NAT method apparently deviate from the HG line of δ48 vs. Δ_{48}, and both the δ48 and raw Δ_{48} values vary over a relatively large range. In contrast, the raw Δ_{48} values determined using the LN method (at all temperatures) and the LN + HV method (at −25.0 °C) are much closer to the HG line of δ48 vs. Δ_{48} and clustered within a very narrow range. This confirms the cleanness of the sample CO_2 gases after using these methods. The LN + HV method (at −15.0 °C) has δ48 and Δ_{48} values closer to those of the NAT method, suggesting it cannot fully remove the contaminants. However, it should be noted that all of the raw Δ_{48} values of samples lie above the HG line of δ48 vs. Δ_{48}. This is because the CO_2 gases used to construct the HG line passed through the PQT twice, i.e., both before and after heating in the furnace, while the samples were only cleaned once. In addition, the raw Δ_{48} values for the LN method show a decreasing trend as the PQT temperatures lower. This may be explained by the following two reasons: one, as previously mentioned, the mass-48 CO_2 molecule ($^{12}C^{18}O^{18}O$) passes through the cold PQT more slowly; two, the cold PQT may remove contaminants more effectively. Further elucidation of these effects awaits future research.

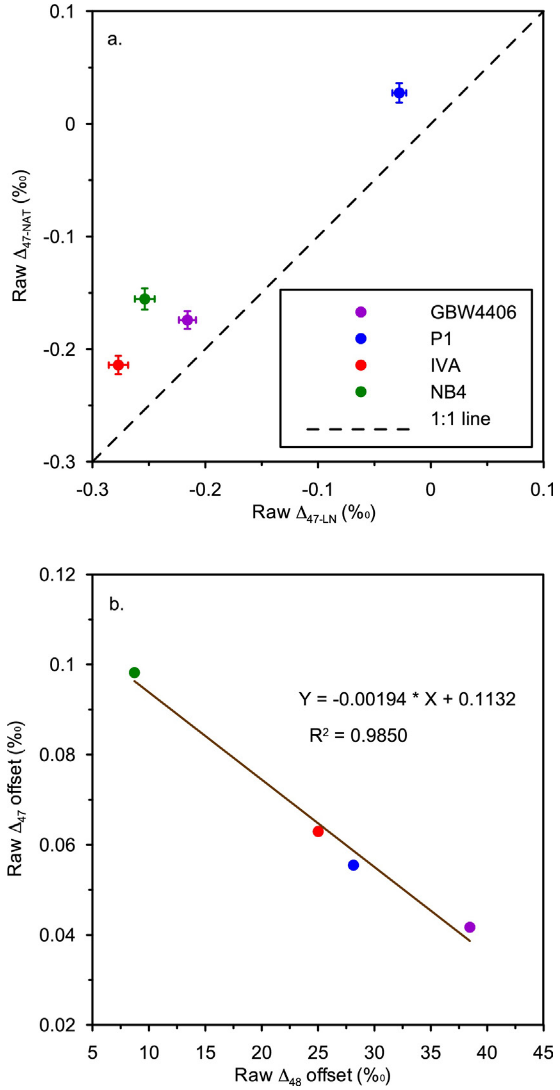

Fig. 5. (a) Comparison of the raw Δ_{47} values of four carbonate samples pretreated using the LN method with those of the same samples pretreated using the NAT method; (b) a negative correlation of the Δ_{47} offset values with the Δ_{48} offset values between the two methods. Each point represents one extraction and individual measurement. Error bars denote standard error (SE) for each measurement.

3.4. *Differences in Δ_{47} values between the LN and NAT methods*

To examine the effect of contaminants such as hydrocarbons and halocarbons on Δ_{47} values, we compared the raw Δ_{47} values determined using the NAT method ($\Delta_{47\text{-NAT}}$) with those measured using the LN method ($\Delta_{47\text{-LN}}$). This comparison was made on two pure calcium carbonate reagents (IVA and GBW4406), one naturally formed calcite (NB4) and one biogenic carbonate (P1). The collection time was 35 min for the LN method. Both the $\Delta_{47\text{-NAT}}$ and $\Delta_{47\text{-LN}}$ values for each sample were determined within the same day. Our results show that the $\Delta_{47\text{-NAT}}$ was systematically higher than the $\Delta_{47\text{-LN}}$ for all samples (Fig. 5a). This is in accordance with the pattern observed in prior work [17]. The offsets between the $\Delta_{47\text{-NAT}}$ and the $\Delta_{47\text{-LN}}$ values ranged from 0.042‰ to 0.098‰. Moreover, the $\Delta_{47\text{-NAT}}-\Delta_{47\text{-LN}}$ offsets exhibited a highly negative correlation with $\Delta_{48\text{-NAT}}-\Delta_{48\text{-LN}}$ offsets (Fig. 5b). In other words, the $\Delta_{47\text{-LN}}$ is closer to the $\Delta_{47\text{-NAT}}$ when the $\Delta_{48\text{-NAT}}$ is relatively high. Because high Δ_{48} values indicate a high level of contaminants [12,18], the above phenomena may suggest that our PQT did not sufficiently remove the interference for samples containing high levels of hydrocarbons or halocarbons. However, raw $\Delta_{48\text{-LN}}$ values for these samples only varied within a range of 2.2–3.2‰, which was largely reduced compared with $\Delta_{48\text{-NAT}}$ values (range: 11.4–40.7‰). It is still a challenge to set an appropriate Δ_{48} cutoff point to judge whether the contaminants are completely removed or not.

4. Summary

We systematically evaluated a sample extraction method involving CO_2 clean-up using a static ~8-cm-long Porapak^{TM} Q absorbent trap (PQT) for clumped isotope analysis. Comparisons of stable and clumped isotopic data were made for the following three procedures: (1) CO_2 passing through the PQT and collected using liquid nitrogen (LN method); (2) CO_2 passing through the PQT and collected using liquid nitrogen and a high vacuum pump as an extra driving force (LN + HV method); (3) CO_2 collected without passing through the PQT (NAT method). For the LN and LN + HV methods, the stable and clumped isotopes initially increased along with increasing collection time and then stabilized after a certain point, which was deemed the optimum collection time. The optimum collection time for the LN method shortened considerably when the PQT became warmer, i.e., from ~35 min to ~30 min when the PQT temperature changed from −15 °C to −12.5 °C. In comparison, the optimum collection time for the LN + HV method was reduced to 25 min at both −15 °C and −25 °C, displaying little change with the PQT temperature. Δ_{48} values were used to examine the efficiency of contaminant (i.e., hydrocarbons and chlorocarbons) removal. The raw Δ_{48} values determined when using the LN method (with PQT temperatures at −12.5 to −25 °C) and the LN + HV method (with the PQT temperature at −25 °C) were largely reduced compared with those for the NAT method and were much closer to the HG line of $\delta 48$ vs. Δ_{48}, confirming the cleanness of the CO_2 sample gases after treatment using these methods. By contrast, the LN + HV method (at a PQT temperature of −15.0 °C) exhibited $\delta 48$ and Δ_{48} values closer to those of the NAT method, suggesting it cannot fully remove the contaminants. Moreover, the raw Δ_{48} values for the LN method increased slightly with the PQT temperature, which may indicate two possibilities: first, the real Δ_{48} value for sample was not obtained within 35 min collection time at a lower PQT temperature; second, a warm PQT may not fully remove the contaminants. If the latter is correct, then a cold PQT can enhance the efficiency of contaminant removal. Nevertheless, increasing sample cleanness in this fashion would outweigh the efficiency of the sample preparation process. To summarize, the LN + HV method (at a PQT temperature of −25.0 °C) may serve as a promising sample preparation method in routine measurement of clumped isotopes because of its cost-saving abilities without compromising sample cleaning efficiency. Comparison of Δ_{47} values shows that the Δ_{47} values of four carbonate samples determined using the NAT method were 0.042–0.098‰ higher than those measured using the LN method, indicating that the removal of contaminants would lower Δ_{47} values. In contrast, the Δ_{47} values of NB4 treated using the LN + HV method are 0.04–0.05‰ higher than those using the LN method possibly because of different absorption and desorption states of the PQTs in the two methods. To the best of our knowledge, our study provides the first detailed examination of the effectiveness and reliability of the Porapak Q absorbent trap method.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.ijms.2016.03.008.

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