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Stable carbon and oxygen isotope analyses of carbonate using a continuous flow isotope ratio mass spectrometry

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Abstract Basic performance of a continuous-flow isotope ratio mass spectrometer (Thermo Scientific GasBench II and Delta V Advantage) installed in the laboratory of evolution of earth environment of Kanazawa University is examined by multiple analyses of standard reference materials (NBS19, LSVEC, etc.). Internal precision of Delta V Advantage determined by 10 consecutive analyses of online reference CO_2 gas is 0.01 ‰ for both $\delta^{13}C$ and $\delta^{18}O$ values. Internal precision of GasBench II inlet system coupled to Delta V Advantage examined by four CO_2 gas aliquots, which is evolved by a reaction of 300 μg of NBS19 and anhydrous phosphoric acid, is 0.06 ‰ and 0.08 ‰ for $\delta^{13}C$ and $\delta^{18}O$, respectively. External precision of the system determined by 20 consecutive NBS19 analyses over 16 hours within the same day represents 0.02 ‰ and 0.04 ‰ for $\delta^{13}C$ and $\delta^{18}O$, respectively. A peak area of the first sample aliquot on a chromatogram detected on Delta V Advantage significantly correlates with amount of carbonate reacted ($r = 0.99$, $p << 0.01$). This positive correlation indicates that amount of carbonate within a given sample can be estimated from the chromatogram within an error of ±30 μg, which enable us to determine carbonate content of the bulk samples in at least better than 10 % precision.

Key words: stable isotopes, carbonate, CF-IRMS, GasBench

1 Introduction

Carbon and oxygen stable isotope analyses of carbonate materials are widely applied in geoscience, especially in paleoceanography, paleoclimatology, paleontology, etc. Carbon isotopic composition potentially represents biogeochemical cycles (e.g., Hasegawa and Saito, 1993; Hasegawa, 1997; McCarren et al., 2008), and oxygen isotope composition is utilized for paleothermometry (e.g., Moriya et al., 2003, etc), ice-volume estimation

(Lisiecki and Raymo, 2005; Moriya et al., 2007; Zachos et al., 2008), as well as the other paleoclimate analyses.

Stable isotope analyses of carbonate materials have predominantly been achieved by the dual-inlet isotope ratio mass spectrometry (DI-IRMS) with cryotrap(s). Some automated inlet systems are designed for DI-IRMS, for example, Thermo Scientific Kiel IV Carbonate Device and Isoprime MultiPrep. Since the development of the continuous-flow isotope ratio mass spectrometry (CF-IRMS), it is widely and actively applied to many fields of science. CF-IRMS technique is also introduced for isotope analyses of carbonate materials (e.g. Révész and Landwehr, 2002; Paul and Skrzypec, 2006), even for analyses of ultra small amount of carbonate (Ishimura et al., 2004; Ishimura et al., 2008).

Here, we report basic performance of carbon and oxygen isotope ratio measurements on CF-IRMS in the laboratory of evolution of earth environment of Kanazawa University. Internal and external precisions are reported on the basis of multiple analyses of standard reference materials. The possible application of CF-IRMS for carbonate content estimation in bulk samples is also discussed.

2 Methodology and equipment

The isotope ratio mass spectrometer (Thermo Scientific Delta V Advantage) equipped with Thermo Scientific GasBench II inlet system including autosampler (CTC GC PAL) was installed in our laboratory on February, 2010. GasBench II is an online gas preparation and introduction system for the isotope ratio mass spectrometer using continuous flow techniques (Figure 1). This preparation system can be used for isotope ratio analyses of headspace gas samples including CO_2 evolved from carbonate and phosphoric acid reaction, CO_2 equilibrated with water, and atmospheric gases.

For carbonate analyses, 300 μg of carbonate sample is loaded on a 12 ml borosilicate vial capped with a rubber septum (A in Figure 1). The rubber septum keeps an airtight seal after being punctured with a syringe for acid dosing or a needle for gas transfer. Those vials with samples are placed on the temperature-stabilized tray and kept at 70.0 ± 0.1 °C. Prior to the acid dosing, residual air is removed from the sample vial by automated autosampler-assisted flushing with ultra-pure helium ($> 99.99995\%$ He), using a flow of 100 ml/min of He for 5 minutes. After flushing all vials, 0.1 ml of anhydrous phosphoric acid, which is pre-heated at 70 °C, is manually injected into each vial with a disposable syringe. CO_2 gas evolved in the headspace of the vial is delivered to a sample loop (D in Figure 1) by the ultra-pure He flow with automated CTC GC PAL autosampler through a water removal system (B in Figure 1) and a multi-port valve (C in Figure 1) (shown by a solid line in Figure 1). The sample loop aliquots the sample CO_2 gas into four fractions, and is repetitively emptied onto a GC column (E in Figure 1) (shown by a dashed line in Figure 1). The sample CO_2 gas is chromatographically separated from

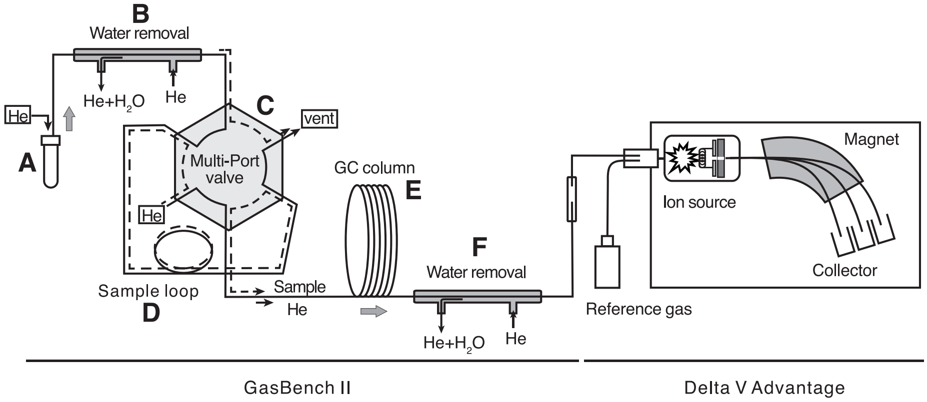

Figure 1: Schematic diagram showing GasBench II inlet system and Delta V Advantage mass spectrometer. A. Autosampler (96 vials); B. Water removal system 1; C. Loop injection system; D. 100 μl sample loop; E. Isothermal gas chromatograph; F. Water removal system 2.

other gas species, and the peak of CO_2 is delivered to the mass spectrometer through the second water removal system (F in Figure 1). Abundance of each CO_2 molecule of mass 44, 45, and 46 in each pure CO_2 aliquot is determined by the mass spectrometer (Figure 1 and 2).

In our laboratory, phosphoric acid is manually injected into all vials at the same time after the He flushing was completed. After acid injection, the sample CO_2 gas evolved is delivered to the mass spectrometer through GasBench II with CTC GC PAL autosampler. While isotopic composition of the first sample is analyzed at 60 minutes after the acid injunction, other vials are kept on the temperature-stabilized tray at 70 ℃ until analyses. Therefore, reaction time between carbonate samples and phosphoric acid is not constant, i.e., longer in the sample analyzed in the later in a batch. We analyzed NBS19 ($\delta^{13}C = +1.95$ ‰, $\delta^{18}O = -2.20$ ‰, distributed by International Atomic Energy Agency), LSVEC ($\delta^{13}C = -46.6 \pm 0.2$ ‰, $\delta^{18}O = -26.7 \pm 0.2$ ‰, distributed by International Atomic Energy Agency), W-lab-std ($\delta^{13}C = +2.16 \pm 0.05$ ‰, $\delta^{18}O = -1.76 \pm 0.05$ ‰, courtesy of Prof. Weissert), and Lab-std (pure carbonate, > 99.95 %, of $\delta^{13}C$ and $\delta^{18}O$ unknown, produced by Wako Pure Chemical Industries, Ltd.) over consecutive 16 hours within the same day for this report (see chapter 3.2 for detailed description of W-lab-std and Lab-std). All δ values are reported relative to VPDB in this report.

3 Analytical results

A set of a single sample analysis is composed of three reference gas injections and four sample gas aliquots injections (Figure 2). For ideal analyses, it is desirable that intensity

[mV] of reference gas and each sample gas aliquot would be equivalent. In the analyses on GasBench II, as shown in Figure 2, intensity of each sample aliquot decrease through retention time, so we should have known the dynamic range (and linearity) of the GasBench II system (Goto et al., 2012). Goto et al. (2012) analyzed various amount of carbonate samples and reported δ^{13}C and δ^{18}O values against an area [V·sec] of each aliquot on the chromatogram (Figure 2). On the basis of those analyses, they discussed the dynamic range of the GasBench II system in our laboratory. They concluded that both δ^{13}C and δ^{18}O are constant within the range of the area from 10 thorough 70 [V·sec] (Goto et al., 2012). All the analyses described in this report are conducted under this condition, and we report accuracy and precision of isotope ratio analyses of standard reference materials, including NBS19 and LSVEC, in this report.

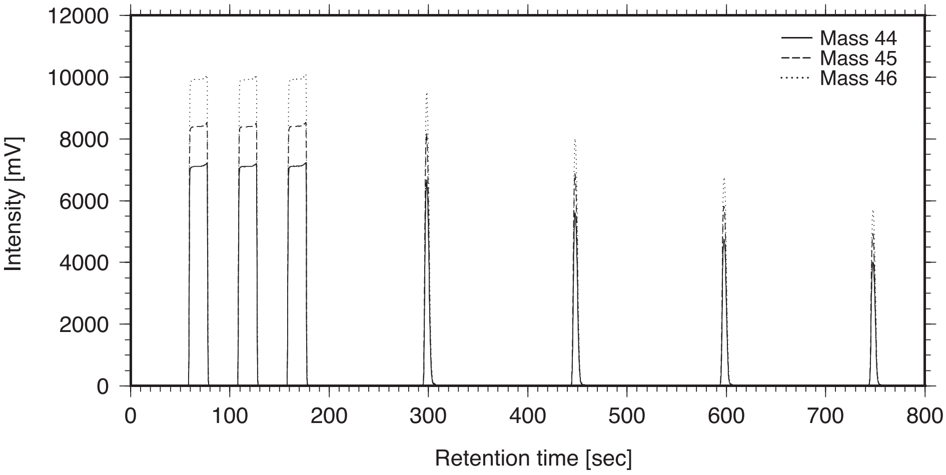

Figure 2: Typical chromatogram of CO_2 isotope ratio analysis. Three reference gas injection pulses at 70, 120, and 170 sec are followed by a set of four sample gas aliquots pulses at 300, 450, 600, and 750 sec for each sample.

3.1 Internal and external precisions of GasBench II/Delta V Advantage

Internal precision of Delta V Advantage in our laboratory

Pure CO_2 gas (>99.995 % CO_2), of which δ^{13}C and δ^{18}O are previously determined by dual inlet system with NBS19, is connected on the mass spectrometer as reference gas in our system (Figure 1). δ^{13}C and δ^{18}O of 10 pulses of reference gas introduced by continuous flow technique are shown in Figure 3. δ^{13}C and δ^{18}O of the first pulse are regarded as 0.00 ‰ in this test. Internal precision (1σ) of these 10 consecutive analyses is 0.01 ‰ for both δ^{13}C and δ^{18}O (Table 1).

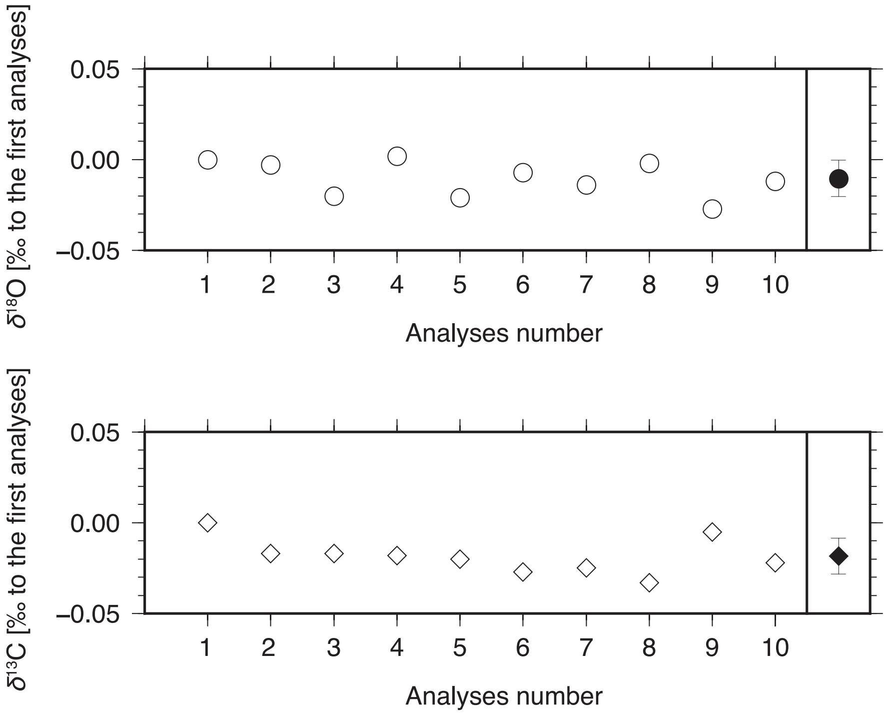

Figure 3: Carbon and oxygen isotope ratios of multiple analyses of online reference CO_2 gas showing the internal precision of Delta V Advantage in our laboratory. Open symbols show each reference gas analysis. Filled symbols and whiskers show average and standard deviation (1σ) of 10 consecutive analyses, respectively.

Internal and external precisions of GasBench II/Delta V Advantage

20 samples of approximately 300 µg each of NBS19 were analyzed over 16 consecutive hours (Figure 4). Headspace CO_2 gas in a single vial evolved from the reaction between phosphoric acid and 300 µg of NBS19 was delivered to the sample loop in GasBench II, and aliquoted into four fractions (Figure 2). Average and precision (1σ) of these four sample aliquots analyses are shown in Figure 4 (open symbols and whiskers). The precision (1σ) of these four aliquot analyses is considered as internal precision of the combination of GasBench II and Delta V Advantage (Table 1). Although minimum precision is surprisingly small, 0.01 ‰ for both $\delta^{13}C$ and $\delta^{18}O$, maximum precision of 0.06 ‰ and 0.08 ‰ for $\delta^{13}C$ and $\delta^{18}O$, respectively, is reported as the internal precision of the system in this report (Table 1).

Analyte and method	Number of analyses	Isotope	Precision (1σ)	Remarks
Reference CO_2 gas	10	$\delta^{13}C$	0.01 ‰	Internal precision of Delta V Advantage
Reference CO_2 gas	10	$\delta^{18}O$	0.01 ‰	Internal precision of Delta V Advantage
CO_2 evolved from a single reaction between phosphoric acid and 300 µg of NBS19	4	$\delta^{13}C$	0.06 ‰	Maximum internal precision of GasBench II/Delta V Advantage
CO_2 evolved from a single reaction between phosphoric acid and 300 µg of NBS19	4	$\delta^{18}O$	0.08 ‰	Maximum internal precision of GasBench II/Delta V Advantage
CO_2 evolved from multiple reactions between phosphoric acid and 300 µg of NBS19	20	$\delta^{13}C$	0.02 ‰	External precision of GasBench II/Delta V Advantage
CO_2 evolved from multiple reactions between phosphoric acid and 300 µg of NBS19	20	$\delta^{18}O$	0.04 ‰	External precision of GasBench II/Delta V Advantage

Table 1: Performance data for GasBench II/Delta V Advantage system in the laboratory of evolution of earth environment of Kanazawa University.

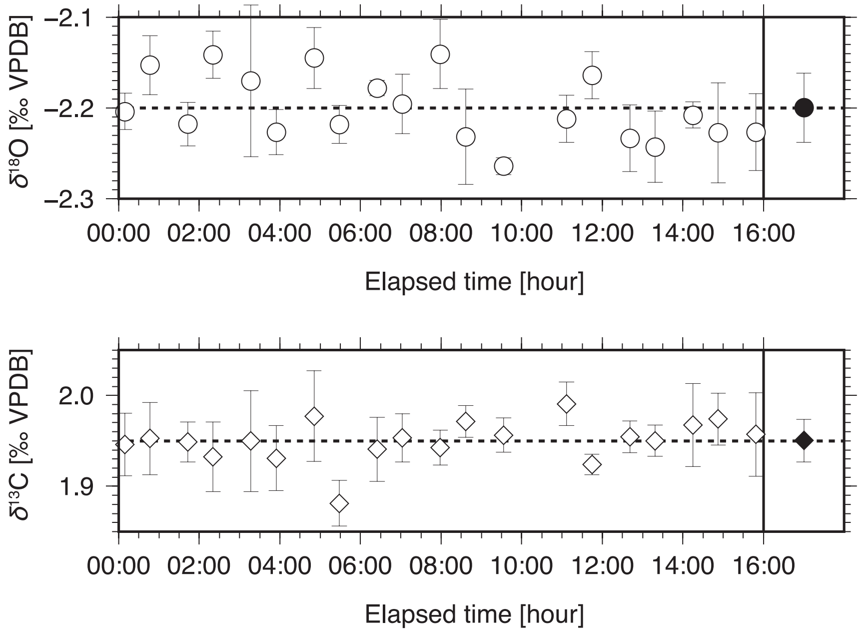

Figure 4: Time series analyses of the standard reference material (NBS19) over 16 consecutive hours. Open symbols and whiskers show average and standard deviation (1σ) of quadruplicate aliquots analyses of each sample (cf. Figure 2). Filled symbols and whiskers show average and standard deviation (1σ) of all analyses. Dashed lines represent the certified value by definition of VPDB scale (δ^{13}C $= +1.95$ ‰, δ^{18}O $= -2.20$ ‰).

External precision of 20 analyses of NBS19 over 16 consecutive hours is presented in Figure 4 as well (filled symbols and whiskers). The external precision is 0.02 ‰ and 0.04 ‰ for δ^{13}C and δ^{18}O, respectively (Table 1). Révész and Landwehr (2002) also reported external precision of δ^{13}C and δ^{18}O analyses with GasBench II coupled to Thermo Scientific Delta Plus XL mass spectrometer. As we have done in our laboratory, they manually injected 0.1 ml of phosphoric acid with a syringe, so their method is quite comparable to our method. However, acid reaction temperature in their method was 26 ℃, which is significantly lower than our methods (70 ℃). They described that higher acid reaction temperature (65 ℃) significantly deteriorated the accuracy and precision of δ^{13}C and δ^{18}O analyses. In fact, under the condition of overnight reaction at 65 ℃, they found that δ^{18}O of NBS19 showed -8 ± 1.88 ‰ deviation from the certified value (Révész and Landwehr, 2002). Instead of using the overnight acid reaction at higher temperature, they employed approximately 24 to 54 hours reaction time at 26 ℃ to improve accuracy and precision. Finally, they achieved the precision of 0.1 ‰ and 0.2 ‰ for δ^{13}C and δ^{18}O, respectively, with this reaction condition. In contrast to their struggle, both internal and external precision of our analyses are fairly acceptable even in higher acid reaction temperature. However, as mentioned above, we should be aware that reaction time is not constant in our method, which will be discussed below.

3.2 Accuracy and precision of oxygen and carbon isotope analyses of various materials

In addition to NBS19, we used W-lab-std (carrara marble), which is kindly provided by Helmut Weissert in Swiss Federal Institute of Technology Zurich (Eidgenössische Technische Hochschule Zürich) for further investigations. Reported values for δ^{13}C and δ^{18}O of W-lab-std are $+2.16 \pm 0.05$ ‰ and -1.76 ± 0.05 ‰, respectively. We analyzed 10 W-lab-stds over 16 consecutive hours (Figure 5). Average and precision (1σ) of those analyses are $+2.09 \pm 0.03$ ‰ and -1.76 ± 0.04 ‰ for δ^{13}C and δ^{18}O, respectively. As seen in NBS19 analyses, precision of those analyses is fairly small for both δ^{13}C and δ^{18}O. On the other hand, while δ^{18}O is very accurately determined by our analyses, the average of δ^{13}C shows 0.07 ‰ difference from the reported value. This result indicates that carbon isotope analyses in our laboratory might have systematic uncertainty of less than 0.1 ‰. This uncertainty is currently under reevaluation with other carbonate reference materials, such as NBS18 and IAEA-CO-8.

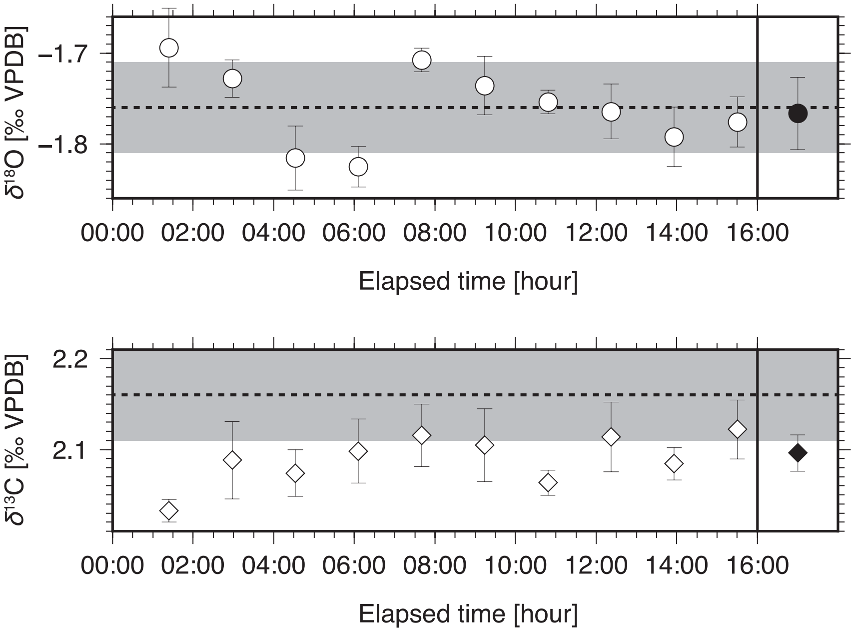

Figure 5: Time series analyses of W-lab-std (see text for detail) over 16 consecutive hours. Open symbols and whiskers show average and standard deviation (1σ) of quadruplicate aliquots analyses of each sample (cf. Figure 2). Filled symbols and whiskers show average and standard deviation (1σ) of all analyses. Dashed lines, and gray shadings represent recommended values and standard deviations (1σ) of W-lab-std (δ^{13}C = $+2.16 \pm 0.05$ ‰, δ^{18}O = -1.76 ± 0.05 ‰).

LSVEC, the other reference material composed of lithium carbonate, is also analyzed. Reported isotopic values of LSVEC are -46.6 ± 0.2 ‰ and -26.7 ± 0.2 ‰ for δ^{13}C and δ^{18}O, respectively (Stichler, 1995; Ghosh et al., 2005). Because isotopic measurement results become less accurate if unknown samples have significantly negative δ^{13}C value relative to NBS19, such as δ^{13}C in organic carbon, it is recommended using two-point calibration with NBS19 and LSVEC for δ^{13}C analyses of such samples (Coplen et al., 2006). In this report, instead of regarding the average values of δ^{13}C and δ^{18}O as anchor points, i.e., normalizing δ^{13}C and δ^{18}O analyzed to -46.6 ‰ and -26.7 ‰, δ values of LSVEC are reported by direct comparison to NBS19 (Figure 6). The δ values determined in our analyses are -46.35 ± 0.06 ‰ and -26.11 ± 0.12 ‰ for δ^{13}C and δ^{18}O, respectively. Although both δ^{13}C and δ^{18}O show systematic uncertainty from the recommended values, standard deviation (1σ) for δ^{13}C is fairly small, indicating that two-point calibration with NBS19 (Coplen et al., 2006) would provide precise results for the samples having negative δ^{13}C. On the other hand, standard deviation (1σ) for δ^{18}O is significantly larger than any other analyses (± 0.12 ‰) (see Table 1). Additionally, it is obvious that δ^{18}O values become more positive with elapsed time (Figure 6). In fact, δ^{18}O val-

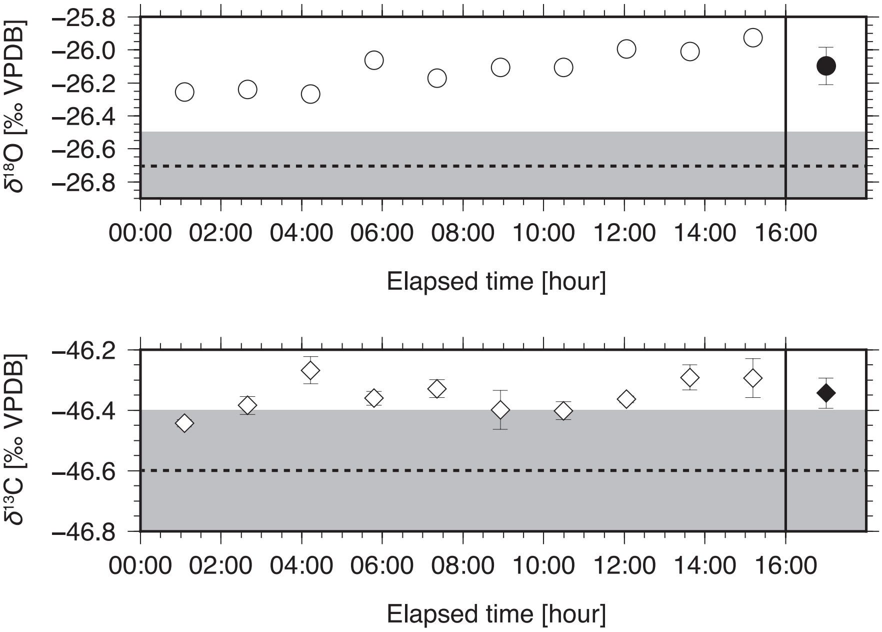

Figure 6: Time series analyses of the standard reference material (LSVEC) over 16 consecutive hours. Open symbols and whiskers show average and standard deviation (1σ) of quadruplicate aliquots analyses of each sample (cf. Figure 2). Filled symbols and whiskers show average and standard deviation (1σ) of all analyses. Dashed lines and gray shadings represent recommended values and standard deviations (1σ) of LSVEC ($\delta^{13}\mathrm{C} = -46.6 \pm 0.2$ ‰, $\delta^{18}\mathrm{O} = -26.7 \pm 0.2$ ‰). Note that *y*-axis scale is different from the other figures. Whiskers showing 1σ in each δ^{18}O analyses are small enough to be hidden beneath the symbols.

ues have the positive correlation with elapsed time ($r = 0.91$, $p << 0.01$). The positive correlation between δ^{18}O and elapsed time has also been observed in analyses of Lab-std which is pure carbonate utilized for laboratory working standard ($r = 0.88$, $p << 0.01$) (Figure 7). Average and standard deviation (1σ) of Lab-std analyses are -5.22 ± 0.03 ‰ and -19.03 ± 0.10 ‰ for δ^{13}C and δ^{18}O, respectively. As seen in LSVEC analyses, standard deviation (1σ) of δ^{18}O value is significantly larger than that of δ^{13}C.

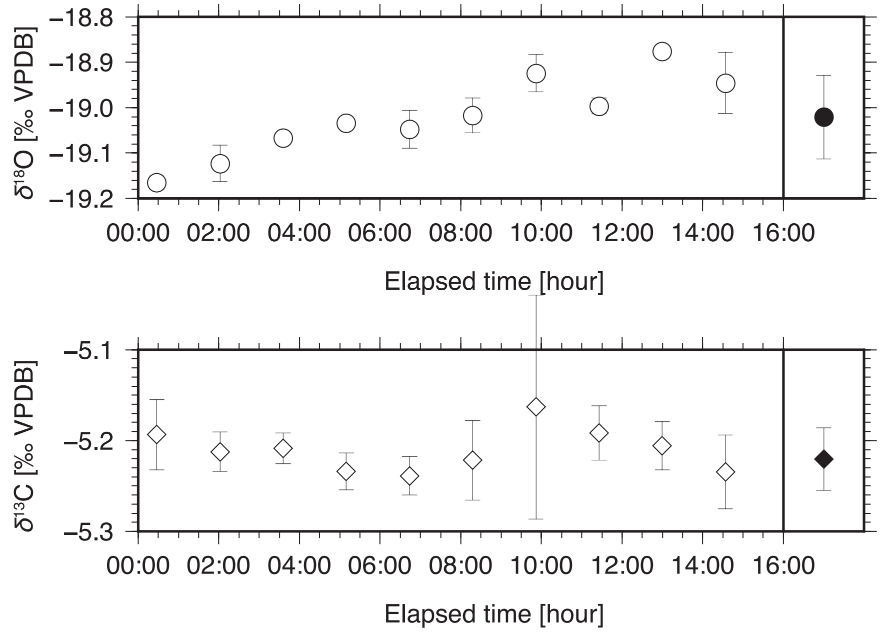

Figure 7: Time series analyses of the Lab-std (pure carbonate) over 16 consecutive hours. Open symbols and whiskers show average and standard deviation (1σ) of quadruplicate aliquots analyses of each sample (cf. Figure 2). Filled symbols and whiskers show average and standard deviation (1σ) of all analyses. Note that y-axis scale is different from the other figures.

Because all analyses reported here have been conducted within a single batch on the same day, all analyses should have exactly the same analytical condition except for the acid reaction time. Although they didn't mention the correlation and/or trend between δ^{18}O and acid reaction time, Révész and Landwehr (2002) also found significantly larger standard deviation in δ^{18}O value in longer acid reaction time. Because, as shown in our results, the acid reaction time seems to affect δ^{18}O only, Révész and Landwehr (2002) hypothesized that CO_2 evolved with phosphoric acid reaction exchanges oxygen isotopes with water vapor within a vial. Carbonate samples react with phosphoric acid following the equation of;

$$\mathrm{CaCO_3 + H_3PO_4 \quad \longrightarrow \quad CaHPO_4 + H_2O + CO_2}$$

If CO_2 stays in the headspace of a vial for substantially longer time after the reaction under high temperature, it is expected that oxygen isotope exchange reaction occurs between CO_2 and H_2O (Révész and Landwehr, 2002). The positive correlation observed between δ^{18}O and elapsed time, hence reaction time, in LSVEC and Lab-std can be explained by this isotope exchange reaction within the headspace. In theory, this isotope exchange reaction should be observed in NBS19 and W-lab-std as well. However, strong correlation has not been observed in NBS19 and W-lab-std. We suspect that δ^{18}O value of CO_2, which exchanged oxygen isotopes with water vapor, would be similar to that of original CO_2 evolved in the reaction of NBS19 and W-lab-std. If this is the case, oxygen isotope exchange reaction between CO_2 and H_2O can't be detected in these materials, indicating that δ^{13}C and δ^{18}O analyses of unknown samples, of which δ^{13}C and δ^{18}O are close to NBS19, shouldn't be affected by the oxygen isotope exchange reaction within the headspace.

4 Possible application for carbonate content estimation

The mass spectrometer produces the mass chromatogram for each analysis (Figure 2). Because the area [V·sec] of the first sample aliquot is a function of the amount of sample, these two variables should have the liner correlation (Figure 8). In fact, $CaCO_3$ [µg] shows the significant positive correlation with total area of the first aliquot peak ($r = 0.99$, $p << 0.01$). Using this correlation, $CaCO_3$ [µg] within a given bulk sediment sample will be predicted from the area of the first aliquot peak [V·sec]. Precision of the estimation of the $CaCO_3$ content within the 95 % prediction interval is better than ±30 [µg]. Révész and Landwehr (2002) also reported the correlation between $CaCO_3$ [µg] and the first aliquot peak [V·sec]. However, the correlation coefficient they found is less than 0.5. They mentioned that "however, the area of the first injection peak is not simply a linear function of the amount of sample material: the linear correlation coefficient between the amount of sample and the first peak was only 0.22, suggesting that some factor in addition to any error in weighing confounded this relationship" (Révész and Landwehr, 2002). In contrast to their results, we found very strong significant correlation. One possible reason that Révész and Landwehr (2002) haven't found significant correlation would be the clogging of capillary with phosphoric acid.When Goto et al. (2012) reported linearity of our mass spectrometer, they didn't find reasonable correlation between $CaCO_3$ [µg] and the first aliquot peak [V·sec]. Because headspace CO_2 is transported into GasBench II by He flow, phosphoric acid stuck on/around the rubber septum would also be accidentally delivered into GasBench II. Phosphoric acid contaminating the multi-port valve and capillary would block gas flow within GasBench II. As a result, the first aliquot peak [V·sec] becomes smaller than expected, and doesn't show significant correlation with $CaCO_3$ [µg] reacted. In fact, after we cleaned the multi-port valve and capillary after a series of analyses made by Goto et al. (2012), we found significant positive correlation (Figure 8).

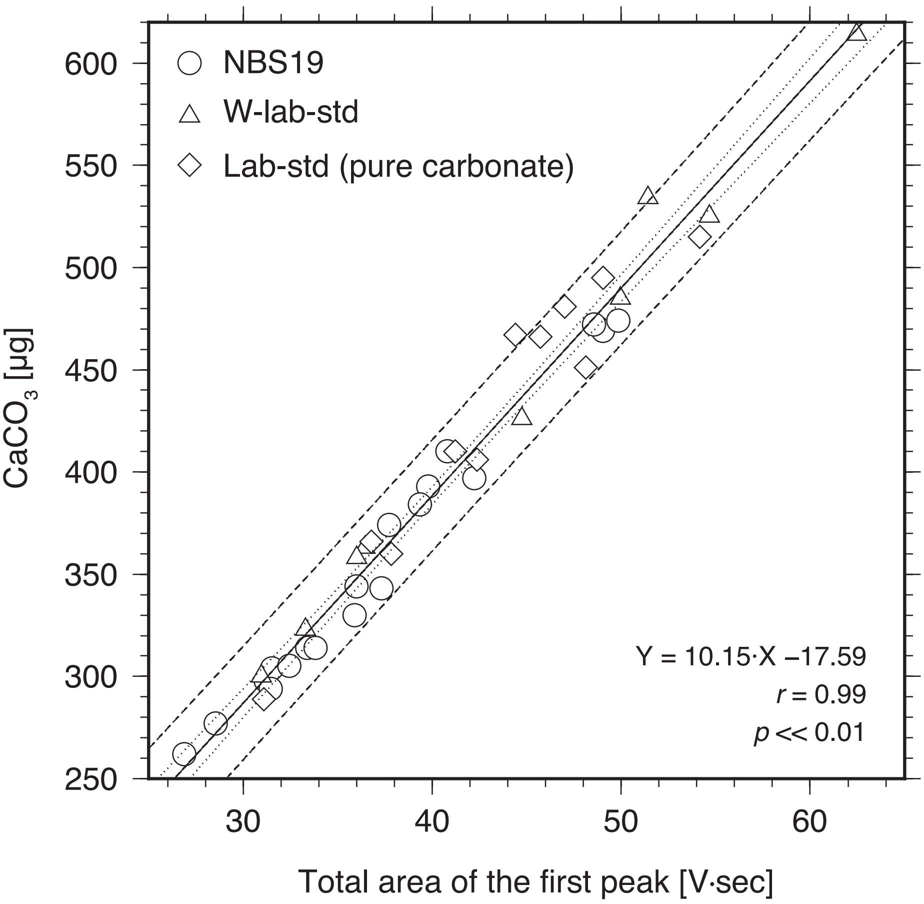

Figure 8: Scatter diagram showing $CaCO_3$ [μg] reacted with phosphoric acid and total area [V·sec] of the first sample aliquot peak (sum of areas of mass 44, 45, and 46) (cf. Figure 2). Solid, dotted, and dashed lines show the least-squares regression, 95 % confidential interval, and 95 % prediction interval for the regression, respectively.

5 Concluding remarks

On the basis of reference CO_2 gas and NBS19 analyses, we reported the internal and external precisions of $\delta^{13}C$ and $\delta^{18}O$ analyses in our system. Those values reported here are well comparable with those reported by Thermo Scientific, which ensure results produced in our system. However, analyses of LSVEC and Lab-std indicate the isotope exchange reaction between CO_2 and water vapor evolved by phosphoric acid reaction within a headspace of a vial. If CO_2 evolved is kept in the headspace of the vial for a longer time, i.e., taking a longer reaction time, the isotope exchange reaction is expected to progress more. Therefore, we recommend that acid reaction time should be consistent through the analyses. Alternatively, lower acid reaction temperature should be used as employed by Révész and Landwehr (2002).

Carbonate content within bulk sediment samples, especially for pelagic sediments, potentially represents global carbon perturbation. Although analyses of carbonate content are best achieved by coulometry, it takes considerable amount of time. While the precision is less than that of coulometry, carbonate content estimation by GasBench II/IRMS is significantly faster than coulometry. In our system, precision of carbonate content estimation is better than ±30 μg within the range from 300 through 600 μg. In addition to the quicker measuring time, a 12 ml vial allows loading large amount of sample of which carbonate content is expected to be low. Therefore, the GasBench II/Delta V Advantage system has an advantage of analyzing bulk carbonate samples.

6 Acknowledgement

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