





Improved Apparatus for Phosphoric Acid Digestion of Carbonates to Determine the Carbon, Oxygen and Clumped Isotope Compositions

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ABSTRACT

The carbon, oxygen and clumped isotope compositions of carbonates are typically analyzed by carbonate-phosphoric acid digestion. Although this approach has been widely used since the 1950s, this procedure has problems in the operability. To address these issues, an improved apparatus with properly sized accessories, including an I-shaped vessel, a sample boat, a magnet, and a magnetic stir bar, has been developed for sample digestion. Similar to a long neck flask, this apparatus has a straight and axisymmetric structure, providing advantages in terms of cost and operability, and thus can be easily implemented in both open and sealed vessel digestion. To evaluate the reliability of the stable and clumped isotope compositions using this new vessel, international and interlaboratory carbonate standards were analyzed with this new apparatus and two commonly used Y-shaped and T-shaped vessels. The results using the new apparatus were consistent with those obtained by the others and in previous studies, suggesting suitability for the traditional phosphoric acid digestion of carbonates.

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Introduction

Carbonate-phosphoric acid digestion is the cornerstone of studies on carbon, oxygen and clumped isotopes in carbonates (McCrea 1950; Swart, Burns, and Leder 1991; Ghosh, Garzzone, et al. 2006; Rosenbaum and Sheppard 1986), which provide important information on paleoclimate, paleoenvironment, paleoelevation, diagenesis and ore deposits (Gilg et al. 2008; Deng et al. 2019; Ghosh, Garzzone, et al. 2006; Li et al. 2019). The traditional digestion procedure is manually carried out on an offline system, which consists of containers for powders reacting with anhydrous phosphoric acid and a glass/stainless vacuum line for removal of CO₂ (McCrea 1950; Swart, Burns, and Leder 1991; Ghosh, Garzzone, et al. 2006). Commercial carbonate devices that use sample vials as reaction containers offer automated procedures for carbonates with low sample requirements, high efficiency, and reduced labor (Groot 2009; Révész and Landwehr 2002;

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Spötl and Vennemann 2003). Hence, the automated procedures are preferentially employed for the measurements on stable isotopes in carbonates that are soluble in acid, such as calcite, aragonite and dolomite, that completely react with phosphoric acid in less than 30 mins (Dean et al. 2015; Currie et al. 2016; Deng et al. 2017; Liu, Deng, and Wei 2019). In recent years, technical improvements have been implemented on automated systems for clumped isotopes in carbonates (100-120 μg) (Schmid and Bernasconi 2010; Schmid, Radke, and Bernasconi 2012; Hu et al. 2014; Meckler et al. 2014), allowing measurements of small or high-resolution samples (Leutert et al. 2019; Meinicke et al. 2020). However, manual procedures are used when analyzing isotopic compositions of acid-resistant carbonates (such as magnesite and siderite), CO_2 selectively extracted from impure carbonates (such as coexisting calcite-dolomite pairs), and determining phosphoric acid fractionation factors in carbonate minerals (Swart, Burns, and Leder 1991; Rosenbaum and Sheppard 1986; Sharma, Patil, and Gopalan 2002; Fernandez et al. 2016; Swart et al. 2019; Al-Aasm, Taylor, and South 1990).

In the traditional procedure, a McCrea-type (Y-shaped) vessel brings the carbonate powder in contact with phosphoric acid by tilting its body when thermal equilibrium is achieved (Figure S1(A)) (McCrea 1950). The thermal equilibrium is essential to stabilize the acid fractionation factors of oxygen and clumped isotopes (McCrea 1950; Swart, Burns, and Leder 1991; Ghosh, Garzzone, et al. 2006; Kim, Coplen, and Horita 2015). Therefore, the McCrea-type vessel has been widely used since 1950 in the traditional procedure, although other containers have been developed (Figure S1) (McCrea 1950; Swart, Burns, and Leder 1991; Ghosh, Garzzone, et al. 2006; Groot 2009; Kim, Coplen, and Horita 2015). Acid digestion handled by these reaction containers includes sealed vessel (SV) and open vessel (OV) (Swart, Burns, and Leder 1991; Kim, Coplen, and Horita 2015; Groot 2009; Fernandez et al. 2016). The CO_2 produced by SV digestion is transferred into the cleaning line after completion of the acid reaction, while CO_2 produced by OV digestion is continuously collected in the cleaning line (Swart, Burns, and Leder 1991; Fernandez et al. 2016). The McCrea-type vessel may be used in either mode, but it is generally used in SV digestion because more accessories and manual operations are needed for OV digestion (Fernandez et al. 2016).

To improve the analysis of carbonate clumped isotopes, some reaction containers in OV digestion are designed for a common or an individual acid bath (CAB or IAB, respectively), in which an aliquot of acid reacts with one or several samples (Passey et al. 2010; Kluge and John 2015; Defliese, Hren, and Lohmann 2015). Consequently, memory effects or cross-contamination may occur in CAB (Swart, Burns, and Leder 1991; Passey et al. 2010). For an IAB carried out through a new reaction container with T-shaped glass tube (Figure S1(C)), its convenience involves the tipping of the McCrea-type vessel replaced with a push operation using a sample boat and magnets on the horizontal glass arm of the container (Kluge and John 2015). However, this T-shaped vessel has a limitation that samples and the boat are not heated until they are in phosphoric acid (Figure S1(C)). Hence, an unstable fractionation of oxygen and clumped isotopes theoretically exists because carbonates initially react with phosphoric acid under thermal disequilibrium (Guo, Deng, and Wei 2019; Kluge and John 2015; Groot 2009). To date, the effect of this thermal disequilibrium on the measured results has not been technically identified when a 90°C temperature is used (Guo, Deng, and Wei

2019; Kluge and John 2015). The thermal disequilibrium on acid fractionation factors is probably changed or enlarged by the boat size, the ratio of sample to acid, and the content of noncarbonate components in the samples.

The McCrea-type (Y-shaped) and Kluge-type (T-shaped) vessels (Figure S1A, S1C)) are the most common design for IABs (McCrea 1950; Swart, Burns, and Leder 1991; Groot 2009; Swart et al. 2019; Y. Guo, Deng, and Wei 2019; Kluge and John 2015), because carbonates are separated from phosphoric acid using the two glass arms in a straightforward manner. However, there are disadvantages of these vessels. First, the assembly consists of many steps requiring special care; otherwise, unexpected contact between the sample and acid will occur. Second, the vessel may tip over because of the asymmetric design; thus, the vessel should be handled with caution. The asymmetry also complicates the manufacturing process. In particular, unlike the McCrea-type vessel, the horizontal glass arm of the Kluge-type vessel is sealed using a stainless steel tube fitting (Kluge and John 2015), which increases the difficulty of assembly, the vessel asymmetry, and a possible leakage point.

Two straight-tube reaction containers generally include one large and one small glass tube for carbonate powders and phosphoric acid, respectively (Figure S1B, S1D) (Swart, Burns, and Leder 1991; Krishnamurthy, Atekwana, and Guha 1997; Fosu et al. 2019). The simple and symmetric structure of these vessels facilitates the manufacture, sample load and acid injection. Nevertheless, when using these vessels, tilting is needed to trigger the reaction between carbonates and acid. The vessel in Figure S1B is rarely used because of weak seal by the septum and potential contamination from glue to attach the acid boat (Krishnamurthy, Atekwana, and Guha 1997). The sample boat method (Figure S1D) has been used (Swart, Burns, and Leder 1991; Fosu et al. 2019; Murray, Arienzo, and Swart 2016) with valve (Swart, Burns, and Leder 1991; Murray, Arienzo, and Swart 2016) and flame (Fosu et al. 2019) methods to seal the vessel. Flame sealing makes the vessel leak-free and suitable for carbonate digestions that take longer times (Fosu et al. 2019).

In this study, an improved apparatus was designed for acid digestion that includes a simple I-shaped vessel with a magnet, a sample boat and a magnetic stir bar. The assembly, movement and sample introduction of this I-shaped vessel are more convenient than previous designs and hence allows the routine phosphoric acid digestion of carbonates to determine stable and clumped isotope compositions.

Experimental

Samples

Six carbonate samples were analyzed for intervessel and interlaboratory comparisons. Three are reference materials distributed by the International Atomic Energy Agency (IAEA): NBS18, NBS19 and IAEA-C1 (Rozanski et al. 1992; Friedman, O'Neil, and Cebula 1982). NBS18 and NBS19 are used as carbonate stable-isotope standards, and their clumped isotope compositions have also been reported (Li et al. 2019; Fosu et al. 2019; Chang et al. 2020; Wacker, Fiebig, and Schoene 2013). IAEA-C1 is a reference material for ^{14}C activity and made from a slab of Carrara marble (Rozanski et al. 1992). When analyzing carbonate clumped isotope compositions, IAEA-C1 was used as an in-

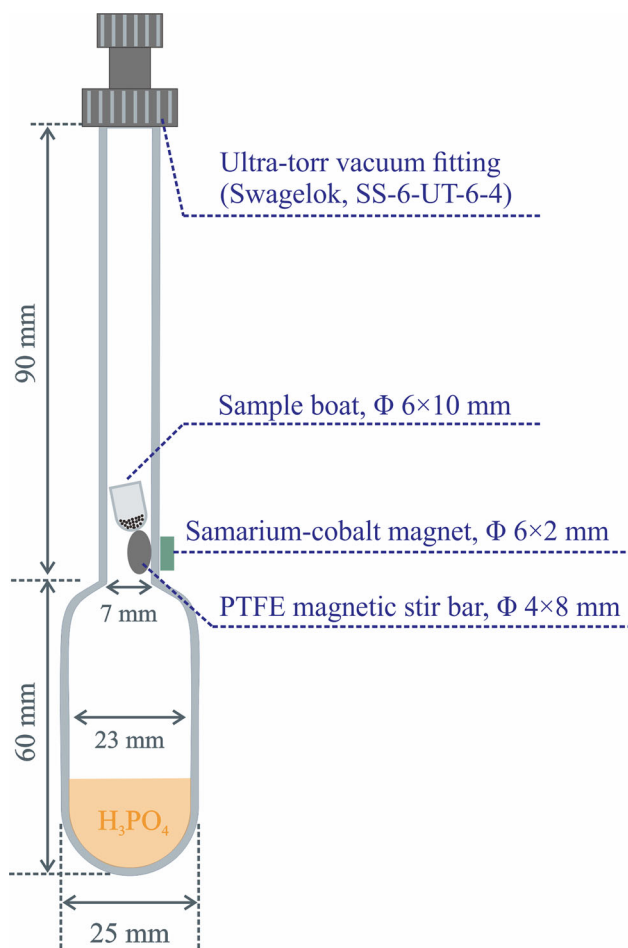


Figure 1. Schematic of the assembled I-shaped vessel.

house standard to monitor instrumental drift and make water-equilibrated or heated gases (Guo, Deng, and Wei 2019; Guo, Deng, and Wei 2019; Guo et al. 2020). BACS and ISCS are also in-house standards for carbonate clumped isotopes prepared from tropical *Porites* coral aragonite and Iceland spar calcite, respectively (Y. Guo, Deng, and Wei 2019). The interlaboratory standard, ETH-4, for carbonate clumped isotopes is a synthetic distributed by the Geological Institute of ETH Zürich (Bernasconi et al. 2018).

Vessels for the phosphoric acid digestion of carbonates

To evaluate the reliability of measurements using the I-shaped vessel (Figure 1), acid digestion was also performed on the Y-shaped and T-shaped vessels similar to Figure S1A and Figure S1C. Considering that there are possible fractionation differences in oxygen and clumped isotopes between OV and SV digestions at the popular reaction temperature of 90 °C (Swart, Burns, and Leder 1991; Fernandez et al. 2016; Swart et al. 2019), both modes of the I-shaped vessel were used to assess the differences. In all

digestions, each sample was weighed to 4–6 mg in a quartz glass sample boat (Φ 6 \times 10 mm), and \sim 104% phosphoric acid is used.

The Y-shaped vessel is used to conduct SV digestion. Different from previous studies (McCrea 1950; Swart, Burns, and Leder 1991; Fernandez et al. 2016; Ghosh, Garziona, et al. 2006; Rosenbaum and Sheppard 1986), carbonate powders were initially loaded into a sample boat and placed at the bottom of the vessel to avoid powders attaching to the vessel. Approximately 2 mL phosphoric acid was introduced into the slant arm using a plastic pipette. After assembly with a vacuum fitting and a ball valve, vessels are connected to the vacuum line and evacuated for approximately 12 h. Subsequent procedures are similar to those employed using McCrea-type vessels (McCrea 1950; Swart, Burns, and Leder 1991; Ghosh, Garziona, et al. 2006). Thermal equilibrium is achieved in a water bath at 90 °C for $>$ 0.5 h. The reaction is activated by tilting the vessel and lasts for $>$ 0.5 h. When the reaction is completed, the vessel is connected to the CO₂ cleaning line. After the cleaning line under vacuum, the CO₂ is collected by a liquid nitrogen trap. This procedure is used for the IAEA-C1 samples and labeled C1-Y-M.

The T-shaped vessel is similar to the container of Kluge and John (2015) (Figure S1C) and has also been used for OV digestion (Guo, Deng, and Wei 2019; Guo 2019). Approximately 2 mL phosphoric acid and a PTFE magnetic stir bar (Φ 4 \times 8 mm) were placed into the vertical arm of the T-shaped vessel. Caution should be exercised when the sample boat loaded with 4–6 mg sample and two magnets are assembled with the horizontal arm to prevent the powder from escaping or the boat from dropping into the vertical arm. The two arms of the T-shaped vessel were carefully sealed using a combination of vacuum fitting and glass tube so that moisture cannot be absorbed by phosphoric acid. After the connection of the assembled vessel to the vacuum line, the vertical arm is heated in a 90 °C water bath. The vessel is evacuated for $>$ 0.5 h to achieve a vacuum on the order of 10^{-3} to 10^{-2} mbar. The degassing of phosphoric acid is promoted by stirring. The reaction is activated when the sample boat is pushed into the vertical arm by the magnets. The CO₂ is continuously collected in a liquid nitrogen trap. This process was used for the BACS samples labeled as BACS-T.

The I-shaped vessel designed in this study is a long neck flask (Figure 1) with four assembly steps. First, 2 mL phosphoric acid are transferred to the vessel using a plastic pipette. Phosphoric acid is viscous, and the slender part of the vessel should be free from acid to ensure the smooth movement of the sample boat. Second, a PTFE magnetic stir bar (Φ 4 \times 8 mm) and a samarium-cobalt magnet (Φ 6 \times 2 mm) are jointly slid into the vessel \sim 1 cm from the vessel mouth. Next, the sample boat (Φ 6 \times 10 mm) is placed onto the stir bar and the outside magnet drives the stir bar and sample boat to the shoulder of the vessel (Figure 1). Third, a vacuum fitting and a sealed glass tube are used to isolate the vessel from moisture. Fourth, the magnet outside the vessel is fixed with a few turns of thread seal tape to improve the robustness of the apparatus as vessels are placed in tube rack, moved, and thermalized together in a water bath. The tape is used due to its low cost and stability at 90 °C.

OV and SV digestions were conducted using the I-shaped vessel. For the former, the operations are similar to those of the T-shaped vessel. The I-shaped vessel is connected to the vacuum line and the tape is removed from the vessel. A 90 °C water bath loaded to ensure a liquid level higher than the top of the sample boat and samarium-cobalt

magnet. Thermal equilibrium and evacuation are carried out for >0.5 h. The samarium-cobalt magnet is removed by tweezers, the sample boat falls into the acid, and the reaction is activated. The CO₂ is continuously collected by trap. Samples analyzed by this procedure are denoted with an I as C1-I.

For the SV digestion, most I-shaped vessel operations are similar to those of the McCrea-type (Y-shaped) vessel, except for the activation of the carbonate-phosphoric acid reaction. Several IAEA-C1 samples were analyzed via this process, which are labeled C1-I-M.

Isotopic analyses

After the first liquid nitrogen trap collects the CO₂, cleaning is conducted according to the procedure of Guo (2019). The CO₂ is released from the first trap by replacing the liquid nitrogen with −100 °C ethanol slush, passes through a −20 °C Porapak-Q trap), and is collected by a second trap for 25 min. Lastly, the CO₂ in the second trap is transferred into a glass tube for analysis.

The carbon, oxygen and clumped isotope compositions of CO₂ were determined by dual-inlet isotope ratio mass spectrometry (DI-IRMS) at the State Key Laboratory of Isotope Geochemistry (SKLaBIG) in the Guangzhou Institute of Geochemistry, Chinese Academy of Sciences (GIG-CAS). The Thermo Scientific 253 Plus DI-IRMS is configured with Faraday cup arrays of 3×10^8 , 3×10^{10} , 1×10^{11} and $1 \times 10^{13} \Omega$ to measure mass 44, mass 45, mass 46 and masses 47-49 (including mass 47.5), respectively. Before each acquisition, the beam intensity of mass 44 is automatically adjusted to 10 V for the sample and reference gas bellows. This signal intensity is sufficient to measure masses 47-49 on the DI-IRMS (Guo, Deng, and Wei 2019; Guo 2019). An analysis includes six acquisitions. Each acquisition consists of 10 cycles of 26 s.

The carbon, oxygen, and clumped isotope compositions are respectively expressed by:

$$\delta^{13}\text{C} = \left(\frac{R(^{13}\text{C}/^{12}\text{C})_{\text{sample}}}{R(^{13}\text{C}/^{12}\text{C})_{\text{VPDB}}} - 1 \right) \times 1000 \text{ ‰}$$

$$\delta^{18}\text{O} = \left(\frac{R(^{18}\text{O}/^{16}\text{O})_{\text{sample}}}{R(^{18}\text{O}/^{16}\text{O})_{\text{VPDB}}} - 1 \right) \times 1000 \text{ ‰}$$

$$\Delta_{47} = \left[\left(\frac{R^{47}}{R^{47*}} - 1 \right) - \left(\frac{R^{46}}{R^{46*}} - 1 \right) - \left(\frac{R^{45}}{R^{45*}} - 1 \right) \right] \times 1000 \text{ ‰}$$

where $R(^{13}\text{C}/^{12}\text{C})$ and $R(^{18}\text{O}/^{16}\text{O})$ are the abundance ratios of the heavy to light isotopes; R^{47} , R^{46} and R^{45} represent the abundance ratios of masses 47, 46 and 45 to mass 44, respectively; and R^{47*} , R^{46*} and R^{45*} are the 47/44, 46/44, and 45/44 ratios when all isotopes among isotopologues are in the stochastic distribution.

The raw Isodat data files are processed using Easotope (John and Bowen 2016) to export the carbon, oxygen and clumped isotope compositions ($\delta^{13}\text{C}$, $\delta^{18}\text{O}$ and Δ_{47}). Detailed data processing parameters used in Easotope are described in Guo, Deng, and Wei (2019). The internal precisions (1 standard error) for $\delta^{13}\text{C}$, $\delta^{18}\text{O}$ and Δ_{47} are $\sim 0.01 \text{ ‰}$. The raw Δ_{47} values are corrected for the linearity effect by the equilibrated gas lines

Table 1. Summary of the stable and clumped isotope compositions using the Y-, T- and I-shaped vessels.

Sample ID	$\delta^{13}\text{C}$ (‰)	$\delta^{18}\text{O}$ (‰)	$\Delta_{47\text{-AC}}$ (‰)	Number of samples
BACS-I	-1.88 ± 0.02	-4.51 ± 0.02	0.711 ± 0.018	17
BACS-T	-1.88 ± 0.03	-4.47 ± 0.03	0.702 ± 0.015	17
C1-I	2.44 ± 0.01	-2.37 ± 0.02	0.362 ± 0.016	20
C1-T	2.44 ± 0.01	-2.35 ± 0.02	0.369 ± 0.014	17
C1-I-M	2.41 ± 0.01	-2.39 ± 0.02	0.386 ± 0.014	7
C1-Y-M	2.39 ± 0.04	-2.40 ± 0.03	0.374 ± 0.011	11
ETH4-I	-10.20 ± 0.01	-18.90 ± 0.01	0.523 ± 0.007	6
ISCS-I	2.19 ± 0.01	-14.51 ± 0.02	0.546 ± 0.011	21
NBS18-I	-4.99 ± 0.01	-23.12 ± 0.02	0.440 ± 0.015	9
NBS19-I	1.95 ± 0.01	-2.25 ± 0.04	0.368 ± 0.007	8

(EGL, see data in Table S1) (Huntington et al. 2009; Dennis et al. 2011) and calibrated to the absolute reference frame (ARF) by the empirical transfer function (ETF) (Dennis et al. 2011). Subsequently, the $\Delta_{47\text{-ARF}}$ values are calibrated to the $\Delta_{47\text{-AC}}$ values at the reference frame with the digestion temperature 25 °C using an acid fractionation factor of 0.068‰ (Guo, Deng, and Wei 2019; Dennis et al. 2011). A factor of 0.068‰ was experimentally determined with NBS19, IAEA-C1 and BACS digestion at 25 °C and 90 °C (Guo, Deng, and Wei 2019; Guo 2019), and is close to the theoretical value of 0.069‰ from Guo et al. (2009) and the measured value of 0.070‰ from Wacker, Fiebig, and Schoene (2013).

Results and discussion

Influence of acid digestion vessel

The carbon, oxygen, and clumped isotope compositions obtained using different vessels are displayed in Table S2. These data include (Table 1): (1) $\delta^{13}\text{C}$, $\delta^{18}\text{O}$ and $\Delta_{47\text{-AC}}$ values from the I-shaped vessels (BACS-I and C-I) are consistent with those obtained from the T-shaped vessels (BACS-T and C1-T) within the error range; (2) few differences are observed for the I- and Y-shaped vessels, i.e., C1-I-M and C1-Y-M; and the (3) IAEA-C1 samples (C1-I and C1-I-M in Table 1) by OV and SV digestion in the I-shaped vessel show no significant differences in their stable and clumped isotope compositions.

The consistency between C1-I-M and C1-Y-M indicates that the I-shaped vessel is suitable replacement for the Y-shaped device for SV digestion. The I-shaped vessel may also be used in OV digestion because no significant differences were observed in its open and sealed modes (C1-I and C1-I-M in Table 1). The consistency between I- and T-shaped vessels (BACS-I, C1-I and BACS-T, C1-T) signifies that fractionation due to thermal disequilibrium between the two arms of the T-shaped vessel may be ignored when a 90 °C reaction temperature is used, as shown by Guo (2019) and Kluge and John (2015).

Overall, there are no significant differences among the $\delta^{13}\text{C}$, $\delta^{18}\text{O}$ and $\Delta_{47\text{-AC}}$ values using these vessels. This result implies that the conditions in this study are far from those factors that can induce obviously different fractionations of the $\delta^{18}\text{O}$ and $\Delta_{47\text{-AC}}$ values in different vessels through the isotope exchange reaction between CO_2 and the $\text{H}_3\text{PO}_4\text{-H}_2\text{O}$ system (Swart, Burns, and Leder 1991; Swart et al. 2019; Fernandez, Tang, and Rosenheim 2014). The short reaction time at the high temperature (90 °C) may

play an important role in restraining isotope exchange. Similarly, different acid fractionation factors may exist in OV and SV digestion (Swart, Burns, and Leder 1991; Fernandez, Tang, and Rosenheim 2014), although this phenomenon was not observed in this study. This phenomenon is important for the carbonate-phosphoric acid method by showing that the acid fractionation factors of carbonates determined by SV digestion are suitable for isotopic calculation in OV digestion (Fernandez et al. 2016; Y. Guo, Deng, and Wei 2019; Kim, Coplen, and Horita 2015). However, due to difference in the acid fractionation factor observed in OV and SV digestions conducted using diverse containers (e.g., McCrea-type vessel and vial) (Swart, Burns, and Leder 1991; Fernandez et al. 2016; Swart et al. 2019) and that the factors affecting the fractionation processes in carbonate-phosphoric acid reactions (e.g., shape, volume and airtightness of the reaction containers) cannot be uniform in all laboratories, the acid fractionation factor differences between OV and SV digestions need to be further evaluated. The designed I-shaped vessel is suitable due to easy switching between OV and SV digestion.

Intercomparisons of $\delta^{13}\text{C}$, $\delta^{18}\text{O}$ and Δ_{47-AC} among different studies

The published $\delta^{13}\text{C}$, $\delta^{18}\text{O}$ and Δ_{47-AC} values of carbonate standards (Li et al. 2019; Fosu et al. 2019; Chang et al. 2020; Wacker, Fiebig, and Schoene 2013; Guo 2019; Fan et al. 2018; Fiebig et al. 2019; Henkes et al. 2013; Müller et al. 2017; Upadhyay et al. 2020) were selected a comparison with those in this study (Figure 2).

An obvious feature is that ETH-4 from different studies is statistically consistent in Δ_{47-AC} values but inconsistent in $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values (Figure 2). Anomalies in $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values are from three studies (Chang et al. 2020; Fan et al. 2018; Fiebig et al. 2019), which probably means that ETH-4 has heterogeneous stable isotope compositions or was contaminated during distribution. Another obvious difference occurs in $\delta^{18}\text{O}$ and Δ_{47-AC} values of NBS18 from Fosu et al. (2019) and this study (Figure 2). IAEA recommended $\delta^{18}\text{O}$ value of NBS18 as -23.2 ± 0.1 ‰, and the $\delta^{18}\text{O}$ values by Fosu et al. (2019) and this study are -22.76 ± 0.15 ‰ and -23.12 ± 0.02 ‰, respectively. The $\delta^{18}\text{O}$ value of NBS18 from Fosu et al. (2019) is ~ 0.4 ‰ higher than those from IAEA and this study. The result may be attributed to small internal volume of the leak-free vessel, long reaction time and the very negative $\delta^{18}\text{O}$ value of NBS18 (Fosu et al. 2019), which may affect the rate of oxygen isotopic exchange between CO_2 and $\text{H}_3\text{PO}_4\text{-H}_2\text{O}$ system (Swart et al. 2019; Wacker, Fiebig, and Schoene 2013).

Except for ETH-4 and NBS18, $\delta^{13}\text{C}$, $\delta^{18}\text{O}$ and Δ_{47-AC} values of other standards are comparable across laboratories (Figure 2). The interlaboratory consistency of the $\delta^{18}\text{O}$ values is better than for the Δ_{47-AC} values, possibly because the calibration processes and parameters of the $\delta^{18}\text{O}$ values are simpler than for the Δ_{47-AC} values (Swart, Burns, and Leder 1991; Ghosh, Garziona, et al. 2006; Groot 2009; Swart et al. 2019; Dennis et al. 2011; Chang et al. 2020). Particular attention should be paid to the symbols in Figure 2 that distinguish samples treated with OV or SV digestion and do not show the diverse reaction containers used for these samples (more details are provided in Table S3). IAEA-C1 and NBS19 notably indicate no differences in the $\delta^{18}\text{O}$ and Δ_{47-AC} values obtained from different apparatuses by OV and SV digestion (Figure 2 and Table S3). This observation suggests that fractionations of oxygen and clumped isotopes observed

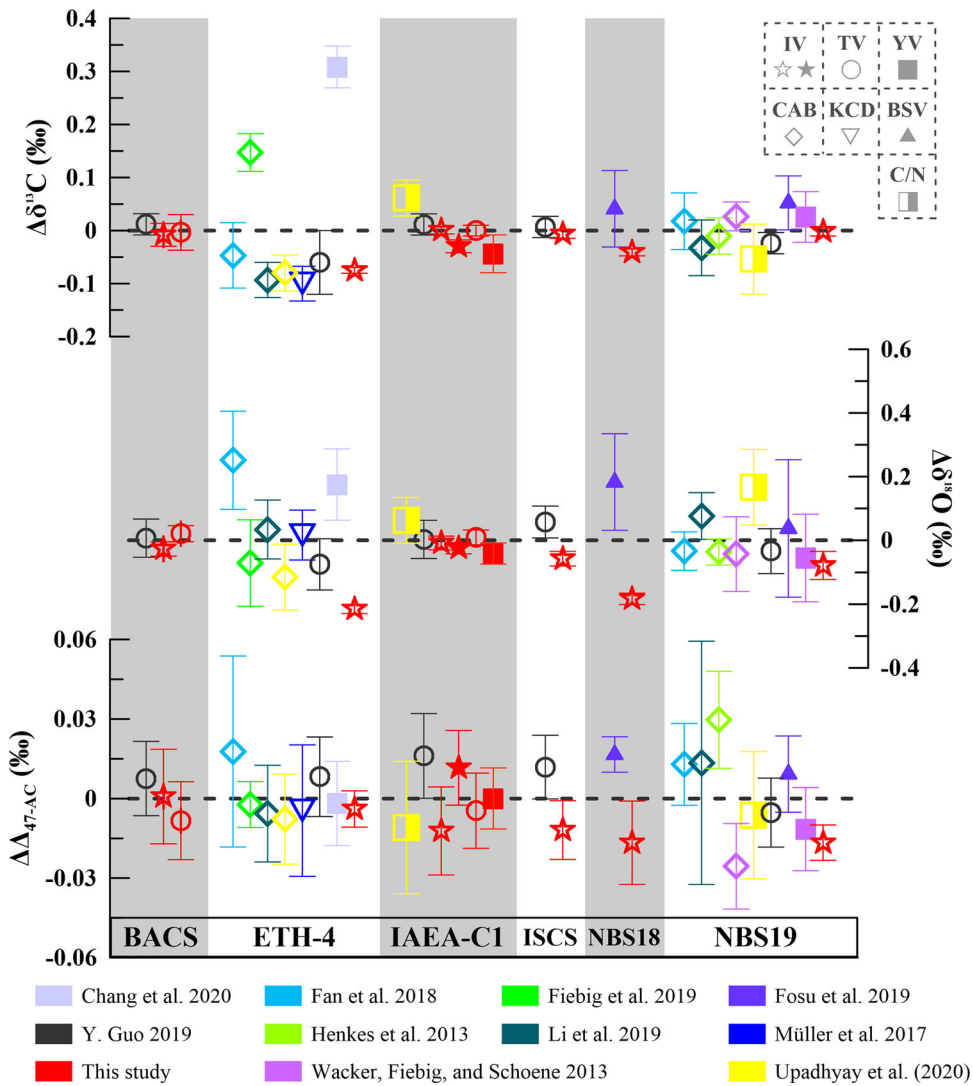


Figure 2. Intercomparisons on $\delta^{13}\text{C}$, $\delta^{18}\text{O}$ and Δ_{47-AC} of carbonate standards from different studies (Li et al. 2019; Fosu et al. 2019; Chang et al. 2020; Wacker, Fiebig, and Schoene 2013; Guo 2019; Fan et al. 2018; Fiebig et al. 2019; Henkes et al. 2013; Müller et al. 2017; Upadhyay et al. 2020). $\Delta\delta^{13}\text{C} = \delta^{13}\text{C} - \delta^{13}\text{C}_{x\text{-average}}$, where $\delta^{13}\text{C}_{x\text{-average}}$ is the $\delta^{13}\text{C}$ average of all 'x' samples (such as BACS, ETH-4 and IAEA-C1) from Table 1 and Table S3, so are the definitions of $\Delta\delta^{18}\text{O}$ and $\Delta\Delta_{47-AC}$. Detailed data are provided in Table 1 and Table S3. The symbols denote different reaction vessels; open and solid symbols represent open vessel (OV) digestion and sealed vessel (SV) digestion, respectively. IV, TV, YV, CAB, KCD, BSV, and C/N represent I-shaped vessel, T-shaped vessel, Y-shaped vessel, common acid bath, Kiel carbonate device, break seal vessel, and common acid bath or Nu carb, respectively. The error bars represent 1 standard deviation.

in extreme conditions (e.g., reaction time of hundreds of hours, low-density phosphoric acid, or samples with extreme isotope compositions) (Swart et al. 2019) cannot be discerned for natural carbonates measured in normal conditions within analytical errors and demonstrates the reliability of the I-shaped vessel for measuring stable and clumped isotope compositions of carbonates by OV and SV digestion.

Conclusions

An improved apparatus for the phosphoric acid digestion of carbonates is proposed to determine carbon, oxygen and clumped isotope compositions. This apparatus is made of simple and common parts and accessories, including I-shaped vessels, sample boats, magnets and magnetic stir bars with specifically designed sizes, shapes and architectures. The isotopic data of international and interlaboratory carbonate standards obtained from this apparatus are consistent with those generated by other devices and from other laboratories. In addition, the straight and axisymmetric structure of the I-shaped vessel has advantages in manufacturing cost, operability, and ease of switching between modes. Therefore, this improved apparatus is a substitute for other vessels in the analysis of stable and clumped isotope composition of carbonates.

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