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Clumped isotope analysis of calcite and dolomite mixtures using selective acid extraction

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Keywords:	Mixed carbonate samples, Selective acid extraction, Acid fractionation

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	correction, clumped isotope, bulk isotope

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1 Clumped isotope analysis of calcite and dolomite mixtures 2 using selective acid extraction

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12 **Abstract:** Acid extraction methods have been used in the last half century to selectively
13 extract the CO₂ produced from different carbonate minerals in mixed samples. However,
14 these methods are often time-consuming and labor intensive. Their application to
15 clumped isotope (Δ_{47}) analysis has not been demonstrated. We propose here an acid
16 extraction method with phosphoric acid for bulk stable and clumped isotope analysis
17 that treats mixtures of calcite and dolomite the same regardless of the proportional
18 composition. CO₂ evolved from calcite is extracted by allowing a reaction with
19 phosphoric acid to proceed for 10 min at 50 °C. We then extract CO₂ evolved from
20 dolomite by rapid ramping the acid temperature from 50 to 90 °C and allowing the
21 reaction to complete. The experimental results show that our method yields accurate
22 calcite and dolomite Δ_{47} values from mixed samples under different proportional
23 compositions. Our method also displays equal or higher accuracy for calcite $\delta^{13}\text{C}$ and
24 dolomite $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values from mixtures when compared to previous studies. Our
25 approach exhibits higher sample throughput than previous methods, is adequate for

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4 1 clumped isotopic analysis and simplifies the reaction progression from over 24 hours
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6 2 to less than 2 hours, while maintaining relatively high isotopic obtaining accuracy. It
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8 3 yet poorly resolves calcite $\delta^{18}\text{O}$ values, as found with previous methods.
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11 4 **Keywords:** Mixed carbonate samples; Selective acid extraction; Acid fractionation
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13 5 correction; clumped isotope; bulk isotope
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15 16 6 **Introduction**

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20 7 Coexistence of carbonate minerals such as calcite, dolomite, ankerite, siderite and
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22 8 magnesite are commonly observed in sedimentary rocks, hydrothermal deposits and
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24 9 carbonatites (Ray and Ramesh, 1998; Baudrand et al., 2012). The carbon ($\delta^{13}\text{C}$) and
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26 10 oxygen ($\delta^{18}\text{O}$) isotopic composition in these carbonates provides clues on the salinity
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28 11 and temperature of aqueous fluids involved during carbonate growth and later
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30 12 diagenesis (Leng and Marshall, 2004; Luzon et al., 2009; Dean et al., 2015) and helps
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32 13 determining the genesis of ore deposits (Maglambayan et al., 2001; Yang et al., 2009).
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34 14 However, measuring the isotopic composition of distinct carbonate phases occurring in
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36 15 natural mixtures is not straightforward because the different phases cannot be
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38 16 physically separated in most cases (Baudrand et al., 2012). The differential reactivity
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40 17 of CaCO_3 (calcite and aragonite) and $\text{CaMg}(\text{CO}_3)_2$ (dolomite) with phosphoric acid is
41
42 18 commonly used to selectively extract the CO_2 released by the two phases and track the
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44 19 evolution of its isotopic composition; it has thus been widely adopted in the last half
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46 20 century for carbonate phase extraction methods (Epstein et al., 1964; Clayton and Jones,
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48 21 1968; Aloisi et al., 2013; Chen et al., 2016; Bustillo et al., 2017).
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51 22 The selective acid extraction method with phosphoric acid has been refined through
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53 23 time as researchers discovered that reaction rate and isotopic composition are
54
55 24 significantly affected by grain size, reaction temperature, and dolomite stoichiometry
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57 25 (Walters et al., 1972; Wada and Suzuki, 1983; Al-aasm et al., 1990; Ray and Ramesh,
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59 26 1998; Kyser et al., 2002; Baudrand et al., 2012; Liu et al., 2018). A three-step extraction
60
27 procedure was gradually developed, with varying experimental parameters (Table 1).

1 First, the mixture reacts with phosphoric acid for 20 min to 2 h at 25 °C, and the CO₂
 2 evolved from this reaction is considered to carry the isotopic signature of calcite. Then,
 3 the acid digestion is continued for up to 24 h, discarding the produced CO₂ because it
 4 is considered a mixture of calcite and dolomite. Finally, the remaining carbonate is
 5 further reacted with acid for a long period (up to 24 h) and sometimes at higher
 6 temperature (50 °C), and the produced CO₂ in this step is considered to carry the isotopic
 7 signature of dolomite.

8 Table 1. A summary of previously published selective acid extraction procedures.

References	Grain Size	Reaction Temperature	Strength of H ₃ PO ₄	Recommendations
Epstein et al. (1964)	< 75µm	25°C	100%	0-1 h: Calcite-CO ₂ 1-4 h: Mixed-CO ₂ * 4-72 h: Dolomite-CO ₂
Walters et al. (1972)	(1) 5-44µm (2) 0.5-5µm	25°C	100%	(1) 0-1 h: Calcite-CO ₂ 1-3 h: Mixed-CO ₂ * 3 h-completion: Dolomite-CO ₂ (2) 0-7 min: Calcite-CO ₂ 7-20 min: Mixed-CO ₂ * 20 min-completion: Dolomite-CO ₂
Wada and Suzuki (1983)	< 75µm	25°C	(1) 90% (2) 100%	Calcite is preconcentrated to >50% (1) 0-1 h: Calcite-CO ₂ (2) 0-4 h: Mixed-CO ₂ * 4-72 h: Dolomite-CO ₂
Al-aasm et al. (1990)	< 75µm	25°C and 50°C	100%	25°C: 0-2 h: Calcite-CO ₂ 25°C: 2-24 h: Mixed-CO ₂ * 50°C: 24-28 h: Dolomite-CO ₂
Ray and Ramesh (1998)	37- 45µm	25°C	100%	Calcite >50%, 0-0.5 h: Calcite-CO ₂ 0.5-10 h: Mixed-CO ₂ * 10-72 h: Dolomite-CO ₂ Calcite <50%, 0-0.25 h: Calcite-CO ₂ 0.25-10 h: Mixed-CO ₂ * 10-72 h: Dolomite-CO ₂
Kyser et al. (2002)	Not specified	25°C and 50°C	100%	0-4 h: Calcite-CO ₂ 4-24h: Mixed-CO ₂ * 24-48 h: Dolomite-CO ₂
Liu et al. (2018)	75- 80µm	25°C and 50°C	100%	Calcite >50%, 50°C, 0-0.25 h: Calcite-CO ₂ Calcite: 30%-50%, 50°C, 0-0.1 h: Calcite-CO ₂ Calcite <50%, 25°C, 0-0.75 h: Calcite-CO ₂

9 * discarded

10 However, this 3-step procedure is labor intensive and time-consuming (Liu et al., 2018)

1 and is sometimes considered as only suitable for samples containing 1:1 calcite-
2 dolomite pairs (Ray and Ramesh, 1998). The suggested grain-size (i.e., 5-44 μ m and
3 0.5-5 μ m) or additional preparation steps (i.e., pre-concentration of calcite to >50%) in
4 various versions of the procedure add complexity to the process (Table 1). X-ray
5 diffractometry (XRD) analysis of samples is required for optimizing experimental
6 parameters such as reaction temperature and time (Ray and Ramesh, 1998; Liu et al.,
7 2018). Changes of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values for calcite and dolomite with varying duration
8 of the different steps are recurrently documented in previous works (Al-Aasm et al.,
9 1990; Yui and Gong, 2003; Baudrand et al., 2012; Liu et al., 2018), indicating kinetic
10 isotope effects induced by an only partial reaction of calcite during steps 1 and 2.

11 In addition to these experimental limitations, the effect of selective phosphoric acid
12 method on “clumped isotope” (i.e., Δ_{47}) analysis remains to be addressed. Carbonate
13 clumped isotope provide an independent proxy for carbonate growth temperature,
14 which completes the conventional isotopic toolkit (Eiler, 2011, 2014). Combined with
15 carbonate $\delta^{18}\text{O}$ values and thermometry equations, carbonate clumped isotope
16 thermometry can be used for paleoclimate reconstruction (Affek, 2012; VanDeVelde
17 et al., 2013; Frantz et al., 2014), paleoaltimetry (Lechler et al., 2013; Huntington and
18 Lechler, 2015), and the study of burial diagenetic processes and fluids (Bristow et al.,
19 2011; Dale et al., 2014). In recent years, the impact of solid-state diffusion on Δ_{47} values
20 (Lloyd et al., 2017), temperature-time paths (Mangenot et al., 2018; Staudigel et al.,
21 2018; Cong et al., 2021), kinetic and other disequilibrium effects (Guo, 2020) have been
22 explored. Understanding the effect and uncertainty of selective phosphoric acid
23 methods on clumped isotope values is necessary to acquire different clumped isotope
24 data from samples with more than one phase of carbonate.

25 These limitations call for further optimization of the acid extraction procedure. In this
26 study, we propose a new selective acid extraction method that is valid for both clumped
27 and bulk isotope analysis of carbonates. We evaluate the uncertainty and accuracy of
28 clumped and bulk isotopic analysis for calcite and dolomite phases by optimizing the

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4 1 procedure with a series of artificial carbonate mixtures with different calcite: dolomite
5 2 ratios.
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9 3 **Materials and Methods**

10 4 **Sample preparation**

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16 5 Pure calcite and dolomite crystals were used to prepare calcite-dolomite mixtures
17 6 (Table 2). The calcite end-member is from a 100% pure calcium carbonate (i.e., C64 -
18 7 Certified ACS, Calcium Carbonate, Lot 775662, Fisher Scientific, Schauer et al., 2016).
19 8 The dolomite end-member is from a 100% pure dolostone (as assessed through detailed
20 9 microscopic observation) obtained from the minerals collection of the Department of
21 10 Earth and Space Sciences, University of Washington. Both samples were crushed and
22 11 ground to powder, and were sieved to save the fraction between 75 μm and 84 μm . Such
23 12 uniform fine-grained powder was used to enhance the reaction rate and reduce the grain
24 13 size effect on the reaction (Liu et al., 2018). The $\delta^{13}\text{C}$, $\delta^{18}\text{O}$ and Δ_{47} data of pure calcite
25 14 and dolomite at different reaction temperatures are listed in Table 2 as “expected values”
26 15 throughout the paper. We chose two weighted proportions of the two carbonate powders
27 16 to represent the possible range of calcite-dolomite ratios: 70% calcite: 30% dolomite
28 17 (Mix-7v3), 30% calcite: 70% dolomite (Mix-3v7). The powders were weighed
29 18 respectively according to the above proportions, put into 5×9 mm silver capsules, and
30 19 stirred with a utensil.
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46 20 Table 2. Calcite and dolomite endmembers used in the present study. The isotopic
47 21 values at different reaction temperatures are referred to as “expected values” throughout
48 22 the text. The dolomite 50-90 treatment indicates ramping the reaction temperature from
49 23 50 °C to 90 °C rapidly, which is described below.
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End-member	Composition	Grain size (μm)	Reaction Temperature ($^{\circ}\text{C}$)	$\delta^{13}\text{C}$ (‰VPDB)	$\delta^{18}\text{O}$ (‰VSMOW)	Δ_{47} (‰CDES)
Calcite	100% CaCO_3	75-84	50	-2.11 ± 0.03	24.15 ± 0.03	0.64 ± 0.01
			90	-2.04 ± 0.02	23.21 ± 0.03	0.59 ± 0.01
Dolomite	100% $[\text{Ca}, \text{Mg}(\text{CO}_3)_2]$	75-84	50-90	-1.29 ± 0.01	31.14 ± 0.03	0.45 ± 0.02
			90	-1.33 ± 0.01	30.81 ± 0.03	0.47 ± 0.01

1

2 **CO₂ production/purification**

3 The CO₂ produced from individual minerals of mixtures was collected and purified
 4 using a carbonate digestion/CO₂ purification vacuum line in IsoLab described
 5 previously (Burgener et al., 2016). To separately extract CO₂ from calcite and dolomite,
 6 we modified the routine sample preparation procedure by optimizing the reaction
 7 parameters rather than discarding the mixed products. Our procedure is divided into
 8 two-steps:

9 Step 1: Extraction of calcite CO₂. We set the acid temperature at 50 $^{\circ}\text{C}$ and wait for 10
 10 minutes reaction time for the calcite-only reaction (duration of the reaction time tested
 11 in Test 2 below), and then extract the CO₂.

12 Step 2: Extraction of dolomite CO₂. After the extraction of the CO₂ in step 1, we isolate
 13 the acid bath and ramp its temperature to 90 $^{\circ}\text{C}$. We then let the sample reacting at 90 $^{\circ}\text{C}$
 14 for ~55 minutes. This approximate time roughly corresponds to the time needed for (1)
 15 the purification of the evolved CO₂ extracted in step 1 in our purification vacuum line
 16 (method described in Burgener et al., 2016: pure CO₂ is cryogenically separated from
 17 water on an automated stainless steel vacuum line using an ethanol-dry ice slush trap,
 18 isolated in a liquid N₂ trap, passed through a Porapaq Q trap, and finally sealed in a
 19 Pyrex break seal); and (2) the automated cleaning of the vacuum line. We then open the
 20 outlet valve of the acid bath and wait for an additional 10 minutes. The total dolomite
 21 reaction time in step 2 is ~65 min. The CO₂ extracted from step 2 is then purified as
 22 done during step 1.

23 We made a series of tests to optimize the procedure that are synthesized in Table 3.

1 Test 1: this test is on pure calcite and pure dolomite samples only. For pure calcite, we
 2 tested the impact of reaction temperature (50°C and 90°C) for a given reaction time (10
 3 min). For pure dolomite, we investigated the adequate reaction time (10, 20, and 30
 4 minutes) at 90 °C to completely digest the sample, and tested the effect of different acid
 5 temperature ramp times (13.5 and 6 minutes).

6 Test 2: The purpose of test 2 is to study the impact of varying reaction times (6 and 10
 7 minutes) for the calcite-only reaction (step 1). This test was only done with dolomite-
 8 rich mixtures (Mix-3v7).

9 Test 3: The purpose of test 3 is to study the influence of the acid bath ramp temperature
 10 pace in step 2. We tested two paces for the ramp: 13.5 min and 6 min. Once 90°C is
 11 reached, the reaction time at 90 °C for slow ramp (13.5 min) is ~51.5 min and rapid
 12 ramp (6 min) is ~59 min, to keep a total reaction time of ca. 65 min for step 2.

13 Table 3. Experimental tests

Test Number	Step 1 Reaction Temperature (°C)	Step 1 Reaction Time (min)	Step 2 Reaction Temperature (°C)	Step 2 Ramp Time (min)	Step 2 Total Reaction Time (min)
1	50/90	10	90		10/20/30
	50	10	50-90	6/13.5	ca. 65
2	50	6/10	50-90	13.5	ca. 65
3	50	10	50-90	6/13.5	ca. 65

15 Isotopic analyses

16 Carbon, oxygen and clumped isotopic composition of the collected CO₂ were measured
 17 in IsoLab, University of Washington as described in [Schauer et al. \(2016\)](#). Δ_{47} values
 18 were calculated according to [Petersen et al. \(2019\)](#). A series of carbonate reference
 19 materials were used to place all $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ on the VPDB and VSMOW scales,
 20 respectively, and a suite of reference frame gases were used to place Δ_{47} values on the
 21 CDES scale ([Schauer et al., 2016](#)).

Individual measurements are summarized in Table 4. In order to compare whether there are significant differences in isotopic composition between CO₂ produced from different mixtures, we calculated 2-sample t-tests at 95% confidence using IBM SPSS® software version 19.0 for calculation.

Table 4. Bulk and clumped isotopic compositions of pure carbonate samples and artificial mixtures under different analytical conditions. N indicates number of replicates, SE = Standard Error, SR = slow ramp, RR = rapid ramp.

Test	Sample Type	Reaction Time (min)	Reaction Temperature (°C)	$\delta^{13}\text{C}$ (‰VPDB)	±SE	$\delta^{18}\text{O}$ (‰VSMOW)	±SE	Δ_{47} (‰CDES)	±SE	N
Test 1	Pure Calcite	10	50	-2.11	0.027	24.15	0.027	0.64	0.013	5
	Pure Calcite	10	90	-2.04	0.015	23.21	0.030	0.59	0.010	4
	Pure Dolomite	10	90	-1.33	0.013	30.81	0.031	0.47	0.009	5
	Pure Dolomite	20	90	-1.34	0.006	30.83	0.035	0.46	0.012	3
	Pure Dolomite	30	90	-1.30	0.017	30.91	0.035	0.48	0.006	3
	Pure Dolomite	~65	50-90 (SR)	-1.26	0.012	31.94	0.023	0.49	0.006	3
	Pure Dolomite	~65	50-90 (RR)	-1.29	0.006	31.14	0.029	0.45	0.023	3
Test 2	Mix-3v7-Cal	6	50	-2.16	0.011	25.25	0.028	0.64	0.004	7
	Mix-3v7-Dol	~65	50-90 (SR)	-1.28	0.004	32.07	0.030	0.51	0.019	7
	Mix-3v7-Cal	10	50	-2.17	0.029	25.57	0.075	0.64	0.012	3
	Mix-3v7-Dol	~65	50-90 (SR)	-1.25	0.006	31.75	0.029	0.47	0.012	3
Test 3	Mix-3v7-Cal	10	50	-2.06	0.012	25.62	0.035	0.62	0.017	3
	Mix-3v7-Dol	~65	50-90 (RR)	-1.28	0.006	30.99	0.023	0.47	0.017	3
	Mix-7v3-Cal	10	50	-2.15	0.012	24.51	0.017	0.62	0.012	3
	Mix-7v3-Dol	~65	50-90 (SR)	-1.18	0.006	31.59	0.017	0.50	0.012	3
	Mix-7v3-Cal	10	50	-2.16	0.017	24.55	0.023	0.64	0.017	3
	Mix-7v3-Dol	~65	50-90 (RR)	-1.23	0.012	31.16	0.029	0.50	0.017	3

Results and discussion

Test 1: Impact of reaction time and heating strategy on the isotopic composition of pure calcite and pure dolomite

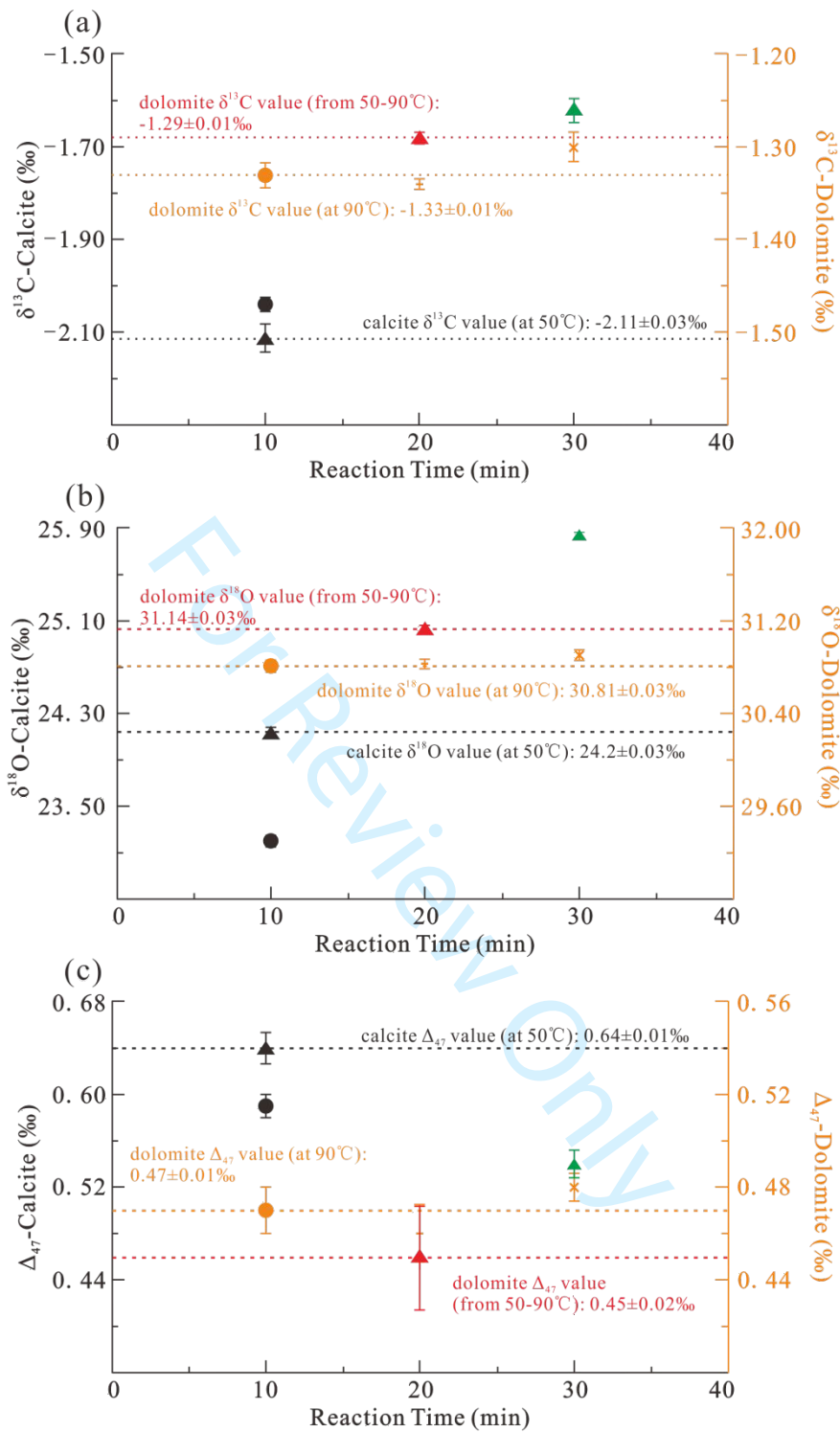
According to Liu et al. (2018), pure dolomite at 75-80 μm grain-size yields only ~8% CO₂ after 45 min at 50 °C, while pure calcite reaches 100% yield in 5 min. Pure dolomite at 90 °C reacts much faster, and reaction times of 10, 20 and 30 minutes yield similar

1 results in our experiments. $\delta^{13}\text{C}$, $\delta^{18}\text{O}$ and Δ_{47} values of pure dolomite reacted for these
2 different reaction times are statistically indistinguishable (Figure 1). An independent
3 sample t-test on the isotopic values obtained through 10- and 20-minute reaction times
4 yields p-values of 0.569 for $\delta^{13}\text{C}$, of 0.696 for $\delta^{18}\text{O}$, and of 0.665 for Δ_{47} . Besides, the
5 CO_2 % yield of individual replicates obtained with a 10-minute reaction (99.2%, 98.8%,
6 91.2%, 71.3%, 68.8%), 20-minute reaction (100%, 99.4%, 84.9%) and 30-minute
7 reaction (100%, 99.7%, 91.0%) are all close to 100%. Our >50 min reaction time at
8 90°C for step 2 ensures the complete digestion of dolomite in mixed samples. These
9 tests show that shorter reaction times (down to 10 minutes) are also adequate.

10 Our test also shows that short temperature ramp times for step 2 increase the accuracy
11 of the isotopic results for the dolomite phase. The $\delta^{13}\text{C}$, $\delta^{18}\text{O}$ and Δ_{47} values of CO_2
12 produced from pure dolomite is closer to their expected values at 90 °C for the short
13 ramp time (6 min) than for the long ramp time (13.5 min; Figure 1).

14 The $\delta^{13}\text{C}$ value obtained from pure calcite at 50 °C and pure dolomite at 90°C with short
15 temperature ramp time are statistically indistinguishable from their expected value,
16 obtained at 90 °C, with a 0.093 p-value for calcite and 0.085 for dolomite. In contrast,
17 the $\delta^{18}\text{O}$ value from pure calcite at 50 °C and pure dolomite are statistically different
18 from their expected values (Figure 1b). These results emphasize that changing reaction
19 temperatures has little impact on carbon isotopic values but significantly impact oxygen
20 isotopic values. The calcite oxygen isotope difference between phosphoric acid reaction
21 temperature at 50 °C and that at 90 °C is 0.94‰ in our data (Figure 1b). The difference
22 of dolomite $\delta^{18}\text{O}$ values between short ramping and the expected value at 90 °C is
23 1.13‰, and 0.33‰ for rapid ramping (Figure 1b).

24 Similar to oxygen isotopes, changing reaction temperature introduces a fractionation in
25 Δ_{47} that must be accounted for prior to the calculation of carbonate growth temperature
26 (Defliese et al., 2015). Previous work has already quantified the phosphoric acid
27 correction factors relative to reaction at 25 °C for calcite, aragonite, and dolomite across
28 a temperature range from 25 to 90 °C (Wacker et al., 2013; Henkes et al., 2013; Defliese



1

2 Figure 1. Pure calcite or pure dolomite isotopic values under different experimental
 3 conditions. Error bars stand for standard errors, SR = slow ramp, RR = rapid ramp.

1 et al., 2015; Peterson et al., 2019; Bernasconi et al., 2021). In the most recent
2 quantification effort, Petersen et al. (2019) calculated a phosphoric acid correction
3 compared to digestion at 25 °C of 0.066‰ at 70 °C, 0.088‰ at 90 °C reactions,
4 respectively. Our data support these results, with an average difference between
5 reactions at 50 °C and 90 °C of 0.046‰ for calcite (Figure 1c). The difference of Δ_{47}
6 value with and without temperature ramping is 0.020‰ (long ramp), and 0.016‰ (short
7 ramp; Figure 1c), but these values cannot be compared with acid temperature correction
8 factors, as most of the step 2 reaction subsequent to the temperature ramp is achieved
9 at 90°C.

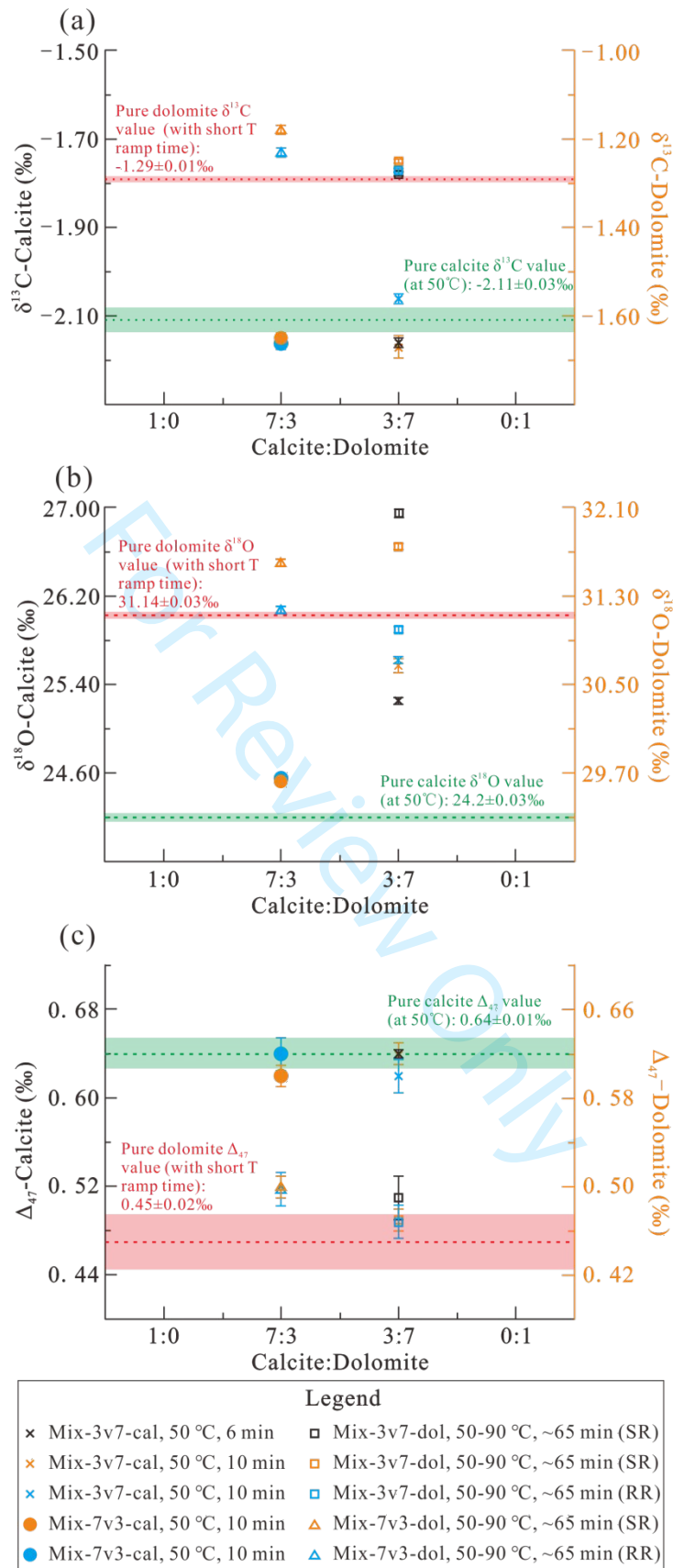
10 **Bulk and clumped isotopic composition of calcite and dolomite from mixtures**

11 *Results of test 2*

12 This test was performed on the dolomite-dominated mixture (Mix-3v7). The calcite
13 $\delta^{13}\text{C}$ and Δ_{47} values with 6- and 10-minute reaction time for step 1 are statistically
14 indistinguishable from their expected values (p-value = 0.168 and 0.906 respectively;
15 Figure 2), while the calcite $\delta^{18}\text{O}$ value is different and offset from its expected value
16 regardless of reaction time. The dolomite $\delta^{13}\text{C}$ is also statistically indistinguishable
17 from its expected value (p-value = 0.157) regardless of reaction time; while the Δ_{47}
18 value is statistically indistinguishable from its expected value for the long (10 min)
19 reaction time only (p-value = 0.091), while the dolomite $\delta^{18}\text{O}$ value is different and
20 offset regardless of reaction time. These results highlight that the long reaction time (10
21 minutes) is best to acquire accurate $\delta^{13}\text{C}$ and Δ_{47} values but does not allow a great
22 accuracy for $\delta^{18}\text{O}$ values. The accuracy in $\delta^{18}\text{O}$ values decreases with increasing
23 dolomite content (Figure 2b), as observed in previous studies (see next subsection).

24 *Results of test 3*

25 Unsurprisingly, changing ramp time has no impact on step 1 results but significant
26 impact on step 2. Dolomite $\delta^{13}\text{C}$ and Δ_{47} values are gradually offset from their expected



1

2 Figure 2. Bulk and clumped isotopic composition of calcite and dolomite from mixtures
 3 with different reaction tests. Results from pure calcite at 50°C (in green shade, 1 S.E.)

1 and pure dolomite at 90°C (with short 50 to 90°C temperature ramp time; in red shade,
2 1 S.E.) are also displayed. Samples in black have varying reaction time for step 1 (6/10
3 min) and slow ramp time for step 2 (13.5 min); samples in orange have 10 min reaction
4 time for step 1 and slow ramp time for step 2 (13.5 min); samples in blue have 10 min
5 reaction time for step 1 and rapid ramp time for step 2 (6 min). Error bars are 1 S.E.;
6 SR = slow ramp, RR = rapid ramp.

7 values with decreasing dolomite content in the mixture (Figure 2c), but this offset is
8 minimized while using the rapid (6 minutes) ramp time. For dolomite-dominated
9 mixtures with the rapid ramp time, $\delta^{13}\text{C}$ (p-value = 0.360), $\delta^{18}\text{O}$ (p-value = 0.100), and
10 Δ_{47} values (p-value = 0.067) are all statistically indistinguishable from expected values.
11 For calcite-dominated mixtures with the rapid ramp time, $\delta^{13}\text{C}$ (p-value = 0.073) and
12 $\delta^{18}\text{O}$ (p-value = 0.887) values are statistically indistinguishable from their expected
13 values, but the accuracy decreases for the Δ_{47} value (p-value = 0.012). The long (13.5
14 minutes) ramp time yield greater deviations from the expected value, especially for
15 $\delta^{18}\text{O}$ and Δ_{47} values (Figure 2).

16 *Summary*

17 We conclude from the above tests that accurate calcite and dolomite $\delta^{13}\text{C}$ and Δ_{47} values
18 in different mixtures can be acquired with the proposed parameters for step 1 (10
19 minutes of reaction time at 50°C) and fast ramp time for step 2 (6 minutes). Using the
20 fast ramp time helps acquire more accurate dolomite Δ_{47} and $\delta^{18}\text{O}$ values; the accuracy
21 of $\delta^{18}\text{O}$ values for the calcite phase significantly decreases with increasing dolomite
22 content, and accurate $\delta^{18}\text{O}$ values are difficult to obtain for step 1.

23 **Comparison with previous studies**

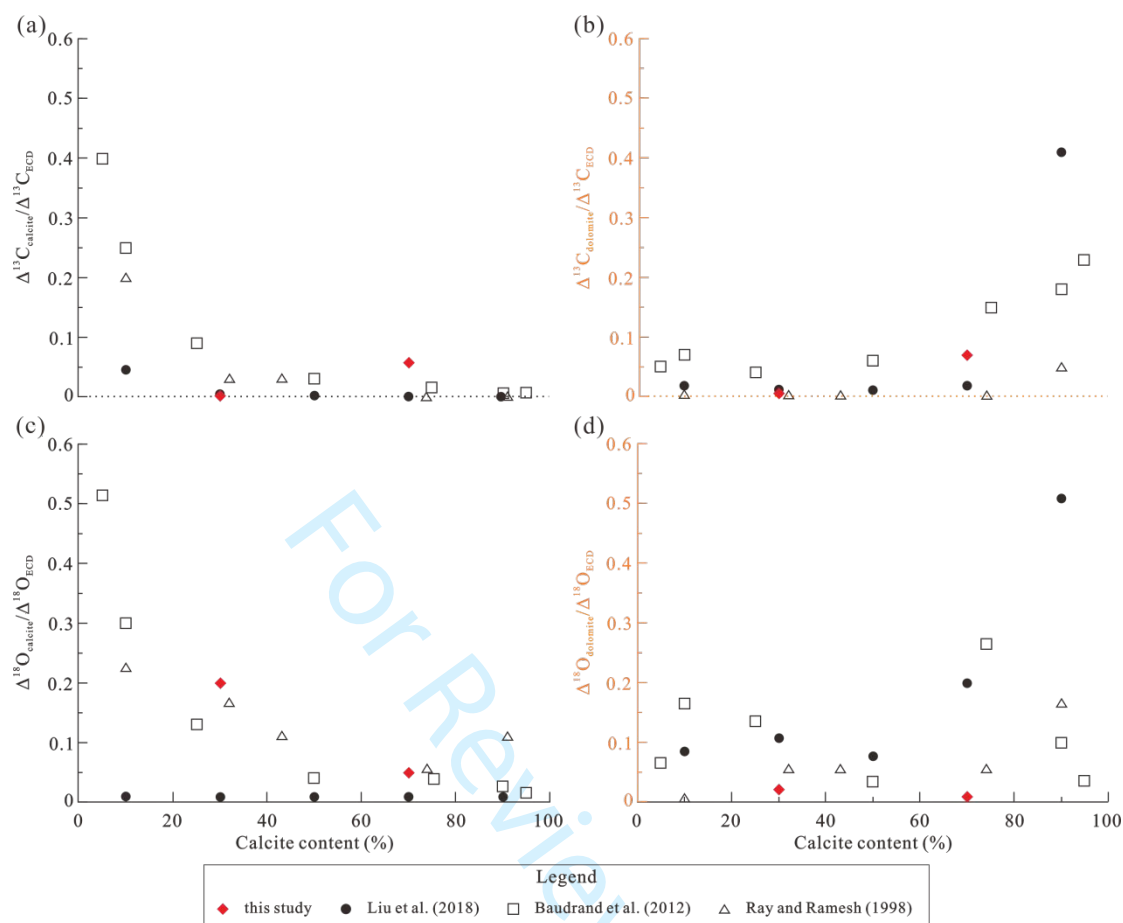
24 We compare the accuracy of our $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values for the calcite and dolomite
25 components in Table 5 with the accuracy of previous methods (Ray and Ramesh, 1998;
26 Baudrand et al., 2012; Liu et al., 2018). The $\delta^{18}\text{O}$ values in VSMOW scale are converted

1 to the VPDB reference frame through the following equation: $\delta^{18}\text{O}_{\text{VPDB}} =$
2 $0.97001 \cdot \delta^{18}\text{O}_{\text{VSMOW}} - 29.99\text{‰}$ (Brand et al., 2014).

3 To estimate gains in accuracy, previous studies (Baudrand et al., 2012; Liu et al., 2018)
4 only compared the difference between the measured and expected $\delta^{13}\text{C}$ ($\Delta^{13}\text{C} =$
5 $\delta^{13}\text{C}_{\text{expected}} - \delta^{13}\text{C}_{\text{measured}}$) and $\delta^{18}\text{O}$ values ($\Delta^{18}\text{O} = \delta^{18}\text{O}_{\text{expected}} - \delta^{18}\text{O}_{\text{measured}}$) for calcite
6 and dolomite from different mixtures. However, the amplitude of $\Delta^{13}\text{C}$ and $\Delta^{18}\text{O}$ should
7 significantly change depending on how wide is the difference between the isotopic
8 composition of pure calcite and pure dolomite in these studies. Instead, we compare the
9 $\Delta^{13}\text{C}/\Delta^{13}\text{C}_{\text{ECD}}$, where $\Delta^{13}\text{C}_{\text{ECD}}$ is the difference between the expected $\delta^{13}\text{C}$ of calcite
10 and the expected $\delta^{13}\text{C}$ of dolomite in different studies (same for $\delta^{18}\text{O}$): $\Delta^{13}\text{C}_{\text{ECD}} =$
11 $\delta^{13}\text{C}_{\text{expected for calcite}} - \delta^{13}\text{C}_{\text{expected for dolomite}}$ (Figure 3).

1 Table 5. Carbon and oxygen isotopic values from different mixtures obtained by previous studies and this study. $\Delta^{13}\text{C}_{\text{ECD}}$ and $\Delta^{18}\text{O}_{\text{ECD}}$ are the
 2 absolute difference between the expected $\delta^{13}\text{C}$ (or $\delta^{18}\text{O}$) of pure calcite and the expected $\delta^{13}\text{C}$ (or $\delta^{18}\text{O}$) of pure dolomite. The results are in VPDB
 3 scale.

References	$\delta^{13}\text{C}/\delta^{18}\text{O}$	Calcite Content											
		0	10%	20%	30%	40%	50%	60%	70%	80%	90%	100%	
Ray and Ramesh (1998)	$\delta^{13}\text{C}_{\text{calcite}}$		-2.1		-2.7	-2.7				-2.8	-2.8	-2.8 ± 0.1	
	$\delta^{18}\text{O}_{\text{calcite}}$		-10.5		-10.6	-10.7				-10.8	-10.7	-10.9 ± 0.2	
	$\delta^{13}\text{C}_{\text{dolomite}}$	0.6 ± 0.1	0.6		0.6	0.6				0.6	0.4		
	$\delta^{18}\text{O}_{\text{dolomite}}$	-9.1 ± 0.2	-9.1		-9.1	-9.2				-9.2	-9.4		
			$\Delta^{13}\text{C}_{\text{ECD}} = 3.4$		$\Delta^{18}\text{O}_{\text{ECD}} = 1.8$								
Baudrand et al. (2012)	$\delta^{13}\text{C}_{\text{calcite}}$	-2.03	-0.50		1.11			1.71		1.85	1.95	1.95	2.0 ± 0.1
	$\delta^{18}\text{O}_{\text{calcite}}$	-3.35	-2.71		-2.19			-1.93		-1.92	-1.88	-1.84	-1.8 ± 0.1
	$\delta^{13}\text{C}_{\text{dolomite}}$	-7.9 ± 0.1	-7.4 ± 0.2	-7.2 ± 0.2	-7.5 ± 0.4			-7.3 ± 0.5		-6.4 ± 0.8	-6.1 ± 1.6	-5.6 ± 3.1	
	$\delta^{18}\text{O}_{\text{dolomite}}$	-4.8 ± 0.1	-4.6 ± 0.1	-4.3 ± 0.1	-4.4 ± 0.2			-4.7 ± 0.3		-4.0 ± 0.6	-4.5 ± 1.4	-4.7 ± 3.0	
			$\Delta^{13}\text{C}_{\text{ECD}} = 9.9$		$\Delta^{18}\text{O}_{\text{ECD}} = 3.0$								
Liu et al. (2018)	$\delta^{13}\text{C}_{\text{calcite}}$		2.03 ± 0.07		2.16 ± 0.06		2.26 ± 0.04		2.28 ± 0.04		2.28 ± 0.06	2.29 ± 0.06	
	$\delta^{18}\text{O}_{\text{calcite}}$		-14.11 ± 0.12		-14.05 ± 0.10		-14.06 ± 0.06		-14.05 ± 0.07		-14.07 ± 0.10	-14.03 ± 0.08	
	$\delta^{13}\text{C}_{\text{dolomite}}$	-3.60 ± 0.06	-3.68 ± 0.13		-3.55 ± 0.23		-3.54 ± 0.31		-3.50 ± 0.34		-1.18 ± 1.74		
	$\delta^{18}\text{O}_{\text{dolomite}}$	-23.70 ± 0.1	-22.86 ± 0.95		-22.66 ± 0.68		-22.95 ± 0.64		-21.76 ± 0.74		-18.76 ± 2.48		
			$\Delta^{13}\text{C}_{\text{ECD}} = 5.89$		$\Delta^{18}\text{O}_{\text{ECD}} = 9.67$								
This study (2021)	$\delta^{13}\text{C}_{\text{calcite}}$				-2.16 ± 0.01				-2.15 ± 0.01			-2.11 ± 0.03	
	$\delta^{18}\text{O}_{\text{calcite}}$				-5.19 ± 0.08				-6.22 ± 0.02			-6.56 ± 0.03	
	$\delta^{13}\text{C}_{\text{dolomite}}$	-1.29 ± 0.01			-1.28 ± 0.01				-1.23 ± 0.01				
	$\delta^{18}\text{O}_{\text{dolomite}}$	0.22 ± 0.02			0.07 ± 0.02				0.24 ± 0.03				
			$\Delta^{13}\text{C}_{\text{ECD}} = 0.82$		$\Delta^{18}\text{O}_{\text{ECD}} = 6.78$								



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Figure 3. Accuracy of isotopic analysis for calcite and dolomite from various mixtures in this and previous studies. $\Delta^{13}\text{C}_{\text{calcite}}$ and $\Delta^{13}\text{C}_{\text{dolomite}}$ are the absolute difference between the measured calcite (or dolomite) $\delta^{13}\text{C}$ from different mixtures and expected pure calcite (or dolomite) $\delta^{13}\text{C}$ values (same for $\Delta^{18}\text{O}_{\text{calcite}}$ and $\Delta^{18}\text{O}_{\text{dolomite}}$). $\Delta^{13}\text{C}_{\text{ECD}}$ and $\Delta^{18}\text{O}_{\text{ECD}}$ are the absolute difference between the expected $\delta^{13}\text{C}$ (or $\delta^{18}\text{O}$) of pure calcite and the expected $\delta^{13}\text{C}$ (or $\delta^{18}\text{O}$) of pure dolomite.

9 We observed an overall increase in accuracy for calcite $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values with increasing calcite content (Figure 3a, 3c). Calcite $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ measurement accuracy for the method of Liu et al. (2018) is the highest regardless of the calcite: dolomite ratio; the accuracy of this method for calcite $\delta^{18}\text{O}$ results is yet among the lowest. The accuracy for calcite $\delta^{13}\text{C}$ measurements reached by our approach falls within the range of previous studies.

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4 1 Overall, the accuracy of dolomite $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values gradually decrease from their
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6 2 expected values with increasing calcite content. The accuracy for dolomite isotopic
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8 3 measurements reached by our approach is better than most previous studies, particularly
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10 4 for $\delta^{18}\text{O}$ values (Figure 3d). Our method performs thus as well, if not better than
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12 5 previous acid extraction methods.

13 14 15 6 **Conclusion**

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18 7 We developed a new method for the selective extraction of CO_2 from of calcite and
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20 8 dolomite mixtures that we subsequently tested with artificial calcite: dolomite mixtures.
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22 9 Our method reduces the previous three-step procedure to only two steps and thus greatly
23
24 10 decreases the experimental time from over 24 hours to less than 2 hours. Our tests show
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26 11 that our method provides a similar accuracy for bulk stable isotope measurement than
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28 12 previous methods; we also show that our method is accurate for clumped isotopic
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30 13 analysis. The new method, like previous methods, fails providing accurate $\delta^{18}\text{O}$ values
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32 14 when one carbonate phase overwhelms the other; the method is thus best designed for
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34 15 high throughput analyses that do not require high accuracy results for stable oxygen
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36 16 isotopic data.

37 38 39 40 17 **Acknowledgements**

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44
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47 20 and 42076220), and the Shandong Postdoctoral Innovation Research Project.

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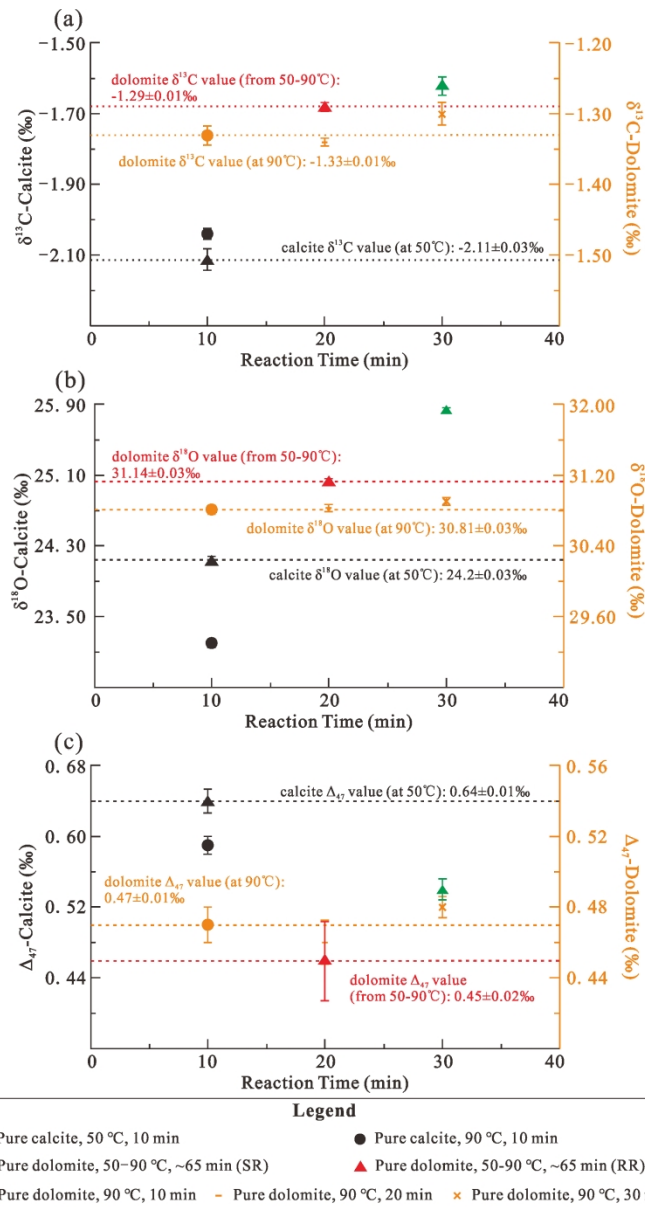


Figure 1. Pure calcite or pure dolomite isotopic values under different experimental conditions. Error bars stand for standard errors, SR = slow ramp, RR = rapid ramp.

481x812mm (118 x 118 DPI)

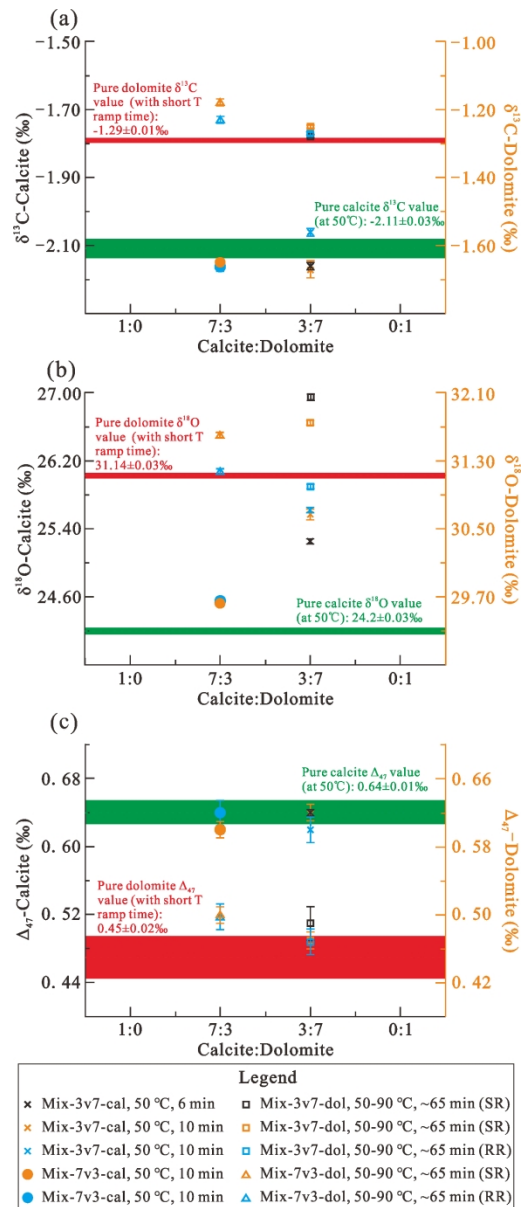


Figure 2. Bulk and clumped isotopic composition of calcite and dolomite from mixtures with different reaction tests. Results from pure calcite at 50°C (in green shade, 1 S.E.) and pure dolomite at 90°C (with short 50 to 90°C temperature ramp time; in red shade, 1 S.E.) are also displayed. Samples in black have varying reaction time for step 1 (6/10 min) and slow ramp time for step 2 (13.5 min); samples in orange have 10 min reaction time for step 1 and slow ramp time for step 2 (13.5 min); samples in blue have 10 min reaction time for step 1 and rapid ramp time for step 2 (6 min). Error bars are 1 S.E.; SR = slow ramp, RR = rapid ramp.

358x845mm (118 x 118 DPI)

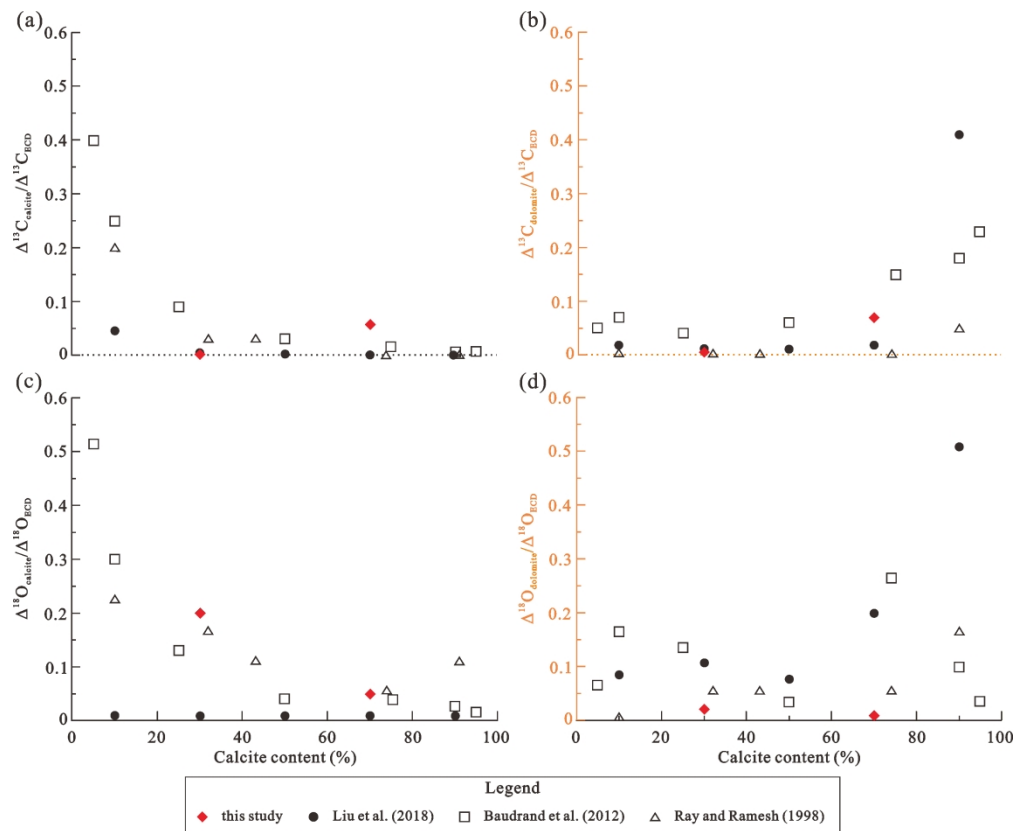


Figure 3. Accuracy of isotopic analysis for calcite and dolomite from various mixtures in this and previous studies. $\Delta^{13}\text{C}_{\text{calcite}}$ and $\Delta^{13}\text{C}_{\text{dolomite}}$ are the absolute difference between the measured calcite (or dolomite) $\delta^{13}\text{C}$ from different mixtures and expected pure calcite (or dolomite) $\delta^{13}\text{C}$ values (same for $\Delta^{18}\text{O}_{\text{calcite}}$ and $\Delta^{18}\text{O}_{\text{dolomite}}$). $\Delta^{13}\text{C}_{\text{ECD}}$ and $\Delta^{18}\text{O}_{\text{ECD}}$ are the absolute difference between the expected $\delta^{13}\text{C}$ (or $\delta^{18}\text{O}$) of pure calcite and the expected $\delta^{13}\text{C}$ (or $\delta^{18}\text{O}$) of pure dolomite.

746x613mm (118 x 118 DPI)

References	Grain Size	Reaction Temperature	Strength of H ₃ PO ₄	Recommendations
Epstein et al. (1964)	< 75µm	25°C	100%	0-1 h: Calcite-CO ₂ 1-4 h: Mixed-CO ₂ * 4-72 h: Dolomite-CO ₂
Walters et al. (1972)	(1) 5-44µm	25°C	100%	(1) 0-1 h: Calcite-CO ₂ 1-3 h: Mixed-CO ₂ * 3 h-completion: Dolomite-CO ₂
	(2) 0.5-5µm			(2) 0-7 min: Calcite-CO ₂ 7-20 min: Mixed-CO ₂ * 20 min-completion: Dolomite-CO ₂
Wada and Suzuki (1983)	< 75µm	25°C	(1) 90%	Calcite is preconcentrated to >50%
			(2) 100%	(1) 0-1 h: Calcite-CO ₂ (2) 0-4 h: Mixed-CO ₂ * 4-72 h: Dolomite-CO ₂
Al-aasm et al. (1990)	< 75µm	25°C and 50°C	100%	25°C: 0-2 h: Calcite-CO ₂ 25°C: 2-24 h: Mixed-CO ₂ * 50°C: 24-28 h: Dolomite-CO ₂
Ray and Ramesh (1998)	37- 45µm	25°C	100%	Calcite >50%, 0-0.5 h: Calcite-CO ₂ 0.5-10 h: Mixed-CO ₂ * 10-72 h: Dolomite-CO ₂ Calcite <50%, 0-0.25 h: Calcite-CO ₂ 0.25-10 h: Mixed-CO ₂ * 10-72 h: Dolomite-CO ₂
Kyser et al. (2002)	Not specified	25°C and 50°C	100%	0-4 h: Calcite-CO ₂ 4-24h: Mixed-CO ₂ * 24-48 h: Dolomite-CO ₂
Liu et al. (2018)	75- 80µm	25°C and 50°C	100%	Calcite >50%, 50°C, 0-0.25 h: Calcite-CO ₂ Calcite: 30%-50%, 50°C, 0-0.1 h: Calcite-CO ₂ Calcite <50%, 25°C, 0-0.75 h: Calcite-CO ₂

* discarded

Table 1. A summary of previously published selective acid extraction procedures.

907x939mm (118 x 118 DPI)

End-member	Composition	Grain size (μm)	Reaction Temperature ($^{\circ}\text{C}$)	$\delta^{13}\text{C}$ (‰VPDB)	$\delta^{18}\text{O}$ (‰VSMOW)	Δ_{47} (‰CDES)
Calcite	100% CaCO_3	75-84	50	-2.11 ± 0.03	24.15 ± 0.03	0.64 ± 0.01
			90	-2.04 ± 0.02	23.21 ± 0.03	0.59 ± 0.01
Dolomite	100% $[\text{Ca}, \text{Mg}(\text{CO}_3)_2]$	75-84	50-90	-1.29 ± 0.01	31.14 ± 0.03	0.45 ± 0.02
			90	-1.33 ± 0.01	30.81 ± 0.03	0.47 ± 0.01

Table 2. Calcite and dolomite endmembers used in the present study. The isotopic values at different reaction temperatures are referred to as "expected values" throughout the text. The dolomite 50-90 treatment indicates ramping the reaction temperature from 50 $^{\circ}\text{C}$ to 90 $^{\circ}\text{C}$ rapidly, which is described below.

826x207mm (118 x 118 DPI)

Test Number	Step 1 Reaction Tem- perature (°C)	Step 1 Reaction Time (min)	Step 2 Reaction Tem- perature (°C)	Step 2 Ramp Time (min)	Step 2 Total Reaction Time (min)
1	50/90	10	90		10/20/30
	50	10	50-90	6/13.5	ca. 65
2	50	6/10	50-90	13.5	ca. 65
3	50	10	50-90	6/13.5	ca. 65

Table 3. Experimental tests

626x203mm (118 x 118 DPI)

Test	Sample Type	Reaction Time (min)	Reaction Temperature (°C)	$\delta^{13}\text{C}$ (‰VPDB)	±SE	$\delta^{18}\text{O}$ (‰VSMOW)	±SE	Δ_{47} (‰CDES)	±SE	N
Test 1	Pure Calcite	10	50	-2.11	0.027	24.15	0.027	0.64	0.013	5
	Pure Calcite	10	90	-2.04	0.015	23.21	0.030	0.59	0.010	4
	Pure Dolomite	10	90	-1.33	0.013	30.81	0.031	0.47	0.009	5
	Pure Dolomite	20	90	-1.34	0.006	30.83	0.035	0.46	0.012	3
	Pure Dolomite	30	90	-1.30	0.017	30.91	0.035	0.48	0.006	3
	Pure Dolomite	~65	50-90 (SR)	-1.26	0.012	31.94	0.023	0.49	0.006	3
	Pure Dolomite	~65	50-90 (RR)	-1.29	0.006	31.14	0.029	0.45	0.023	3
Test 2	Mix-3v7-Cal	6	50	-2.16	0.011	25.25	0.028	0.64	0.004	7
	Mix-3v7-Dol	~65	50-90 (SR)	-1.28	0.004	32.07	0.030	0.51	0.019	7
	Mix-3v7-Cal	10	50	-2.17	0.029	25.57	0.075	0.64	0.012	3
	Mix-3v7-Dol	~65	50-90 (SR)	-1.25	0.006	31.75	0.029	0.47	0.012	3
Test 3	Mix-3v7-Cal	10	50	-2.06	0.012	25.62	0.035	0.62	0.017	3
	Mix-3v7-Dol	~65	50-90 (RR)	-1.28	0.006	30.99	0.023	0.47	0.017	3
	Mix-7v3-Cal	10	50	-2.15	0.012	24.51	0.017	0.62	0.012	3
	Mix-7v3-Dol	~65	50-90 (SR)	-1.18	0.006	31.59	0.017	0.50	0.012	3
	Mix-7v3-Cal	10	50	-2.16	0.017	24.55	0.023	0.64	0.017	3
	Mix-7v3-Dol	~65	50-90 (RR)	-1.23	0.012	31.16	0.029	0.50	0.017	3

Table 4. Bulk and clumped isotopic compositions of pure carbonate samples and artificial mixtures under different analytical conditions. N indicates number of replicates, SE = Standard Error, SR = slow ramp, RR = rapid ramp.

918x636mm (118 x 118 DPI)

References	$\delta^{13}\text{C}/\delta^{18}\text{O}$	Calcite Content										
		0	10%	20%	30%	40%	50%	60%	70%	80%	90%	100%
Ray and Ramesh (1998)	$\delta^{13}\text{C}_{\text{calcite}}$		-2.1		-2.7	-2.7			-2.8	-2.8	-2.8 ± 0.1	
	$\delta^{18}\text{O}_{\text{calcite}}$		-10.5		-10.6	-10.7			-10.8	-10.7	-10.9 ± 0.2	
	$\delta^{13}\text{C}_{\text{dolomite}}$	0.6 ± 0.1	0.6		0.6	0.6			0.6	0.4		
	$\delta^{18}\text{O}_{\text{dolomite}}$	-9.1 ± 0.2	-9.1		-9.1	-9.2			-9.2	-9.4		
		$\Delta^{13}\text{C}_{\text{ECD}} = 3.4$		$\Delta^{18}\text{O}_{\text{ECD}} = 1.8$								
Baudrand et al. (2012)	$\delta^{13}\text{C}_{\text{calcite}}$		-2.03 -0.50		1.11		1.71		1.85	1.95	1.95	2.0 ± 0.1
	$\delta^{18}\text{O}_{\text{calcite}}$		-3.35 -2.71		-2.19		-1.93		-1.92	-1.88	-1.84	-1.8 ± 0.1
	$\delta^{13}\text{C}_{\text{dolomite}}$	-7.9 ± 0.1	-7.4 ± 0.2		-7.2 ± 0.2		-7.5 ± 0.4		-7.3 ± 0.5	-6.4 ± 0.8	-6.1 ± 1.6	-5.6 ± 3.1
	$\delta^{18}\text{O}_{\text{dolomite}}$	-4.8 ± 0.1	-4.6 ± 0.1		-4.3 ± 0.1		-4.4 ± 0.2		-4.7 ± 0.3	-4.0 ± 0.6	-4.5 ± 1.4	-4.7 ± 3.0
		$\Delta^{13}\text{C}_{\text{ECD}} = 9.9$		$\Delta^{18}\text{O}_{\text{ECD}} = 3.0$								
Liu et al. (2018)	$\delta^{13}\text{C}_{\text{calcite}}$		2.03 ± 0.07		2.16 ± 0.06		2.26 ± 0.04		2.28 ± 0.04	2.28 ± 0.06	2.29 ± 0.06	
	$\delta^{18}\text{O}_{\text{calcite}}$		-14.11 ± 0.12		-14.05 ± 0.10		-14.06 ± 0.06		-14.05 ± 0.07	-14.07 ± 0.10	-14.03 ± 0.08	
	$\delta^{13}\text{C}_{\text{dolomite}}$	-3.60 ± 0.06	-3.68 ± 0.13		-3.55 ± 0.23		-3.54 ± 0.31		-3.50 ± 0.34	-1.18 ± 1.74		
	$\delta^{18}\text{O}_{\text{dolomite}}$	-23.70 ± 0.1	-22.86 ± 0.95		-22.66 ± 0.68		-22.95 ± 0.64		-21.76 ± 0.74	-18.76 ± 2.48		
		$\Delta^{13}\text{C}_{\text{ECD}} = 5.89$		$\Delta^{18}\text{O}_{\text{ECD}} = 9.67$								
This study (2021)	$\delta^{13}\text{C}_{\text{calcite}}$				-2.16 ± 0.01				-2.15 ± 0.01			-2.11 ± 0.03
	$\delta^{18}\text{O}_{\text{calcite}}$				-5.19 ± 0.08				-6.22 ± 0.02			-6.56 ± 0.03
	$\delta^{13}\text{C}_{\text{dolomite}}$	-1.29 ± 0.01			-1.28 ± 0.01				-1.23 ± 0.01			
	$\delta^{18}\text{O}_{\text{dolomite}}$	0.22 ± 0.02			0.07 ± 0.02				0.24 ± 0.03			
		$\Delta^{13}\text{C}_{\text{ECD}} = 0.82$		$\Delta^{18}\text{O}_{\text{ECD}} = 6.78$								

Table 5. Carbon and oxygen isotopic values from different mixtures obtained by previous studies and this study. $\Delta^{13}\text{CECD}$ and $\Delta^{18}\text{OECD}$ are the absolute difference between the expected $\delta^{13}\text{C}$ (or $\delta^{18}\text{O}$) of pure calcite and the expected $\delta^{13}\text{C}$ (or $\delta^{18}\text{O}$) of pure dolomite. The results are in VPDB scale.

1198x795mm (118 x 118 DPI)