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Stoichiometry effect on stable isotope analysis of dolomite

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Abstract

Dolomite admixed with calcite in partially dolomitized limestones is often nonstoichiometric. Precise stable isotope compositions of these two minerals in such samples are difficult to determine. Differential acid extraction and weak-acid leaching are the two common methods used. In the present study, we evaluate the validity of these methods. Our results show that the reaction rate between dolomite and phosphoric acid is sensitive to not only grain size but also stoichiometry of dolomite. Nonstoichiometric calcium-rich dolomite is more liable to react with acid than stoichiometric dolomite. This stoichiometry effect increases the difficulty in adopting the differential acid extraction method to recover reliable stable isotope compositions of partially dolomitized samples. Acceptable results could be expected only if sample grain size is well confined and the sample-acid reaction time for calcite-CO_2 is properly reduced based on predetermined dolomite chemical compositions. Moreover, the data also imply that differential leaching of dolomite in the weak-acid leaching method is quite probable and may induce additional errors. Such an effect on analytical results must be taken into consideration before making meaningful interpretation on isotopic data of coexisting calcite and dolomite.

Keywords: Stoichiometry; Dolomite; Stable isotope analysis

1. Introduction

Dolomitization has been a subject of debate and has interested carbonate geologists for decades. Because a vast amount of Mg ion is needed to convert limestones to dolomites, the fluid/rock ratio during dolomitization is presumed to be very large. The source(s) of the fluid responsible for dolomitization is therefore one of the important issues to explore. Since fluids of different origins near the Earth's surface generally have characteristic stable isotope compositions (e.g., Sheppard, 1986), O- and C-isotope composition of dolomite has therefore been commonly employed to infer the source(s) of dolomitization fluid, which is supposed to have buffered the O-, or even C-isotope system during dolomitization (e.g., Land, 1980). The available data show that normal seawater, evaporated seawater, seawater mixed with freshwater, or seawater modified by diagenesis of organic matter might be the candidates responsible for dolomitization (Budd, 1997). However, in his compilations, Budd (1997) noted that O-isotope compositional data sets of dolomite in some duplicate case studies differ from each other by as large as 1 ‰, which may affect subtle arguments and lead to different conclusions. Although such differences may be real due to sampling bias in different

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studies, Budd (1997) suggested that the distinctions could also result from differences in analytical techniques separating dolomite from admixed calcite.

In partially dolomitized rocks, calcite and dolomite are difficult to physically separate for stable isotope analysis. Two chemical methods are generally used. One removes all of the more soluble calcite with weak-acid (such as acetic acid or ethylenediamine tetraacetic acid, EDTA) leaching (e.g., Glover, 1961; Humphrey, 1988; Swart and Melim, 2000) and the other makes use of differential phosphoric acid extraction time (e.g., Epstein et al., 1964; Walters et al., 1972; Al-Aasm et al., 1990; Ray and Ramesh, 1998). The uncertainty of the former method is primarily due to errors from mineralogical percentage estimation, while that of the latter mainly comes from different degrees of cross mixing of gases derived from carbonate phases. For the differential acid extraction method, it has been shown that there might be up to 1‰ and 0.8‰ difference in oxygen isotope composition between the first 10–20% evolved gas and the true value for calcite and dolomite, respectively (e.g., Walters et al., 1972; Al-Aasm et al., 1990). The difference may be up to 3‰ between the first and the last evolved gases (Walters et al., 1972). The degree of such an isotopic difference is, more or less, grain size dependent: the finer the grain size, the larger the difference. An important point is that when the differential acid extraction method has been employed, the time duration adopted for acid extraction of calcite-CO_2 or dolomite-CO_2, as well as the grain size of the sample analyzed, were sometimes different in different studies. Some (certainly not all) examples are listed in Table 1. It is clear that unless a standardized procedure for the differential acid extraction method is agreed upon or the uncertainties of different methods are evaluated, explicit comparison among data sets will remain difficult.

Table 1
Some examples of acid reaction time duration and sample grain size used for the differential acid extraction method in analyzing partially dolomitized samples

References	Grain size (μm)	Temperature (°C)	Acid reaction time
Epstein et al. (1964)	< 75	25	0–1 h: calcite-CO_2 1–4 h: mixed CO_2 4–72 h: dolomite-CO_2
Walters et al. (1972)	(1) 44–5	25	(1) 0–1 h: calcite-CO_2 1–3 h: mixed CO_2 3 h-completion: dolomite-CO_2
	(2) 5–0		(2) 0–7 min: calcite-CO_2 7–20 min: mixed CO_2 20 min-completion: dolomite-CO_2
Matsumoto and Matsuda (1987)	Not specified	25	0–0.5 h: calcite-CO_2 0.5–120 h: dolomite-CO_2
Al-Aasm et al. (1990)	< 75	25	0–2 h: calcite-CO_2 2–24 h: mixed CO_2
		50	24–28 h: dolomite-CO_2
Pleydell et al. (1990)	< 44	25	0–1 h: calcite-CO_2 1–4 h: mixed CO_2 4–240 h: dolomite-CO_2
Bottcher et al. (1998)	Not specified	23 50	0–1 h: calcite-CO_2 1–14 h: dolomite-CO_2
Ray and Ramesh (1998)	45–37	25	(1) Calcite > 50% 0–0.5 h: calcite-CO_2 0.5–10 h: mixed CO_2 10–72 h: dolomite-CO_2 (2) Dolomite > 50% 0–15 min: calcite-CO_2 15 min–10 h: mixed CO_2 10–72 h: dolomite-CO_2
Kyser et al. (2002)	Not specified	25	0–4 h: calcite-CO_2 4–24 h: mixed CO_2
		50	24–48 h: dolomite-CO_2

In addition to factors such as carbonate-acid reaction time and mineral grain size, dolomite nonstoichiometry may also play a role in causing errors for the differential acid extraction method. The composition of dolomites of Neogene carbonates may vary from calcium-rich $(Ca_{60}Mg_{40})CO_3$ to stoichiometric $(Ca_{50}Mg_{50})CO_3$ (Budd, 1997). The reason for this compositional variation is not yet clear, but it may be related to chemical composition of fluid phase and/or reaction kinetics (e.g., Morrow, 1978; Chai et al., 1995). Nonstoichiometric, calcium-rich dolomite is shown to be thermodynamically less stable than stoichiometric dolomite (Chai et al., 1995) and is therefore theoretically more liable to react with phosphoric acid. Although natural ^{18}O fractionation and ^{18}O phosphoric acid fractionation as a function of stoichiometry have been suggested by Vahrenkamp and Swart (1994) and Gill et al. (1995), the possible stoichiometry effect on dolomite reaction rate with phosphoric acid has yet been addressed by previous studies (e.g., Epstein et al., 1964; Walters et al., 1972; Al-Aasm et al., 1990; Ray and Ramesh, 1998). In this report, we will show that dolomite nonstoichiometry may cause significant errors in differential acid extraction method analyzing stable isotope compositions of partially dolomitized samples, unless the analytical conditions are strictly constrained.

2. Samples and analytical methods

A calcite sample, A (162–164 m), and two dolomite samples, B (175 m) and C (203.9 m), were selected from a borehole drilled at an atoll islet named Taiping (or Itu Aba) (N114°22′ E10°23′) in the South China Sea in the present study. For comparison, one metamorphic dolomitic marble (sample D) from Taiwan metamorphic basement was also included. All samples were ground to powder for further analyses.

Mineral identification was performed by a Rigaku D/MAX X-ray diffractometer with Cu Kα radiation, scanning 25–35° 2θ at a rate of 1° 2θ per minute. An internal standard of calcium fluoride was used. Dolomite samples were leached with EDTA at pH of 6.3 to dissolve any possible minor presence of calcite (Glover, 1961). Complete removal of calcite in these samples was further confirmed by X-ray diffraction. Dolomite stoichiometry was determined by X-ray diffraction analysis using the equation of Lumsden and Chimahusky (1980).

The four sample powders were then subjected to size separation. Each sample was divided into three size fractions, 90–63, 63–38 and 38–1 μm. Each of the carbonate fractions was reacted with 100% phosphoric acid at 25 °C under vacuum, following the standard procedure of McCrea (1950). The released carbon dioxide was sequentially collected after different lengths of reaction time in 240 min and volumetrically measured. For dolomite samples, reaction was continued for another 4 days and the released gases were collected and volumetrically measured. All gas samples, some of which were combined to get enough quantity for mass spectrometry, were then subjected to isotopic measurements with a Finnigan MAT 252 mass spectrometer. Oxygen isotopic acid fractionation factor used in data reduction is 1.01025 and 1.01109 for calcite and dolomite, respectively (Sharma and Clayton, 1965). The results were reported as per mil $\delta^{18}O$ and $\delta^{13}C$ relative to PDB.

3. Results and discussion

Chemical compositions of dolomite samples B, C and D were determined to be $(Ca_{58}Mg_{42})CO_3$, $(Ca_{52}Mg_{48})CO_3$ and $(Ca_{50}Mg_{50})CO_3$, respectively. Results of integrated CO_2 yields (%) at different carbonate-

Table 2
Integrated CO_2 yield (%) at different phosphoric acid–carbonate reaction time for three grain size fractions of each carbonate sample

Reaction time (min)	A			B		
	90–63 μm	63–38 μm	38–1 μm	90–63 μm	63–38 μm	38–1 μm
7	24.2	55.4	71.3	2.3	3.3	1.9
15	41.6	74.6	87.9	5.3	4.2	2.4
22	53.3	83.4	92.9	–	–	–
30	62.9	89.6	96.2	9.1	7.5	3.8
45	75.5	95.8	98.4	14.4	10.8	5.7
60	83.2	97.4	99.0	18.2	15.1	9.0
75	90.0	97.9	–	22.0	18.9	11.4
90	92.9	98.9	99.9	25.0	22.7	15.2
105	–	–		28.8	26.5	17.1
120	96.8	99.8		31.1	29.8	21.4
150	–			34.9	35.0	26.6
180	98.0			37.9	39.7	30.9
210				40.9	44.0	35.2
240				44.7	47.8	39.0
100 h				98.7	99.6	99.3

Reaction time (min)	C			D		
	90–63 μm	63–38 μm	38–1 μm	90–63 μm	63–38 μm	38–1 μm
7						
15			2.1			
22			–			
30		2.9	3.7			
45		–	–			
60		4.1	4.7			2.0
75		–	–			–
90		4.7	7.3		1.8	2.5
105		–	–		–	–
120	2.3	5.3	10.9		2.3	3.6
150	2.9	5.9	13.5	2.5	3.2	4.6
180	4.1	7.1	17.1	3.0	3.7	6.1
210	5.2	7.6	19.7	3.4	4.2	8.0
240	6.2	8.2	24.4	3.9	4.6	10.2
100 h	76.4	90.2	97.4	44.0	54.6	84.7

acid reaction times for each size fraction of each sample are listed in Table 2. The isotope compositions of collected gases are listed in Table 3.

As shown in Table 2, calcite sample A reacts with phosphoric acid, giving CO_2 gas very rapidly. Complete reaction is almost achieved within 180 min. As expected, the reaction rate is faster for sample powder with finer grain size due to larger surface area (Walters et al., 1972). On the other hand, dolomite sample D, which has a stoichiometric composition, reacts very

Table 3
Isotopic compositions of gas samples collected in the present study

A

90–63 μm			63–38 μm			38–1 μm		
Gas fraction (%)	δ^{18}O (‰)	δ^{13}C (‰)	Gas fraction (%)	δ^{18}O (‰)	δ^{13}C (‰)	Gas fraction (%)	δ^{18}O (‰)	δ^{13}C (‰)
24.2	−5.30	−3.72	55.4	−5.34	−3.70	71.3	−5.34	−3.74
17.4	−5.24	−3.60	19.2	−5.19	−3.64	16.6	−5.21	−3.62
11.7	−5.29	−3.67	8.8	−5.22	−3.66	8.3	−5.22	−3.65
9.6	−5.36	−3.68	6.2	−5.34	−3.75	3.7	−5.38	−3.67
12.6	−5.44	−3.70	10.2	−5.42	−3.78			
14.5	−5.48	−3.75						
8.0	−5.69	−3.84						
Total	−5.26	−3.63	Total	−5.30	−3.69	Total	−5.31	−3.71

B

90–63 μm			63–38 μm			38–1 μm		
Gas fraction (%)	δ^{18}O (‰)	δ^{13}C (‰)	Gas fraction (%)	δ^{18}O (‰)	δ^{13}C (‰)	Gas fraction (%)	δ^{18}O (‰)	δ^{13}C (‰)
9.1	+1.40	+1.60	4.2	+0.35	+0.94	5.7	+1.13	+1.09
9.1	+1.88	+1.41	6.6	+1.48	+1.29	5.7	+1.64	+1.29
6.8	+1.84	+1.38	8.1	+1.61	+1.31	10.0	+1.80	+1.30
12.9	+1.74	+1.39	7.6	+1.73	+1.35	9.5	+1.81	+1.34
6.8	+1.51	+1.39	8.5	+1.80	+1.39	8.1	+1.89	+1.38
54.0	+1.45	+1.39	4.7	+1.80	+1.40	60.3	+1.60	+1.45
			8.1	+1.81	+1.42			
			51.8	+1.78	+1.45			
Total	+1.53	+1.39	Total	+1.68	+1.38	Total	+1.63	+1.38

C

90–63 μm			63–38 μm			38–1 μm		
Gas fraction (%)	δ^{18}O (‰)	δ^{13}C (‰)	Gas fraction (%)	δ^{18}O (‰)	δ^{13}C (‰)	Gas fraction (%)	δ^{18}O (‰)	δ^{13}C (‰)
6.2	+1.70	+2.18	8.2	+2.11	+2.20	7.3	+1.88	+2.04
70.2	+2.51	+2.26	82.0	+2.47	+2.31	6.2	+2.43	+2.28
						6.2	+2.56	+2.32
						4.7	+2.50	+2.31
						73.0	+2.44	+2.24
Total[a]	+2.40	+2.23	Total[a]	+2.40	+2.23	Total[a]	+2.40	+2.23

D

90–63 μm			63–38 μm			38–1 μm		
Gas fraction (%)	δ^{18}O (‰)	δ^{13}C (‰)	Gas fraction (%)	δ^{18}O (‰)	δ^{13}C (‰)	Gas fraction (%)	δ^{18}O (‰)	δ^{13}C (‰)
3.9	−9.17	+3.86	4.6	−10.17	+3.33	10.2	−10.86	+2.84
40.1	−7.55	+4.18	50.0	−7.45	+4.20	74.5	−7.58	+4.20
Total[a]	−7.60	+4.19	Total[a]	−7.60	+4.19	Total[a]	−7.60	+4.19

[a] Compositions derived from separate 38–1 μm sample-acid reaction at 25 °C for 6 days.

slowly with phosphoric acid even for the 38–1 μm size fraction, a result similar to that previously reported (e.g., Al-Aasm et al., 1990). However, dolomite sample C shows a higher reaction rate with phosphoric acid than dolomite sample D. In 240 min, the yielded CO_2 gas (or inferred reaction rate with the acid) for dolomite sample C is almost doubled compared with that of dolomite sample D for each grain size fraction. Considering the constrained experimental conditions, this difference can only be accounted for by the nonstoichiometric nature of dolomite sample C. This stoichiometry effect on reaction rate with phosphoric acid is even more prominent for dolomite sample B, which has the lowest $MgCO_3$ content among dolomite samples in the present study. For example, ~ 30% and ~ 45% of dolomite sample B with grain size in the range of 90–63 μm reacted with phosphoric acid in 120 and 240 min, respectively. Note that in contrast with other three samples, reaction rate between dolomite sample B and phosphoric acid does not show systematic relation with grain size in the 240-min experiment. The finest grain size fraction (38–1 μm), which should have the highest reaction rate with acid, actually shows the lowest reaction yields. The 90–63 μm size fraction also has a higher reaction rate than the 63–38 μm size fraction for the first 150 min. This is certainly contradictory with what is expected based on the consideration that larger surface area (i.e., finer grain size fraction) of sample powders should yield higher rate of reaction with acid. The reasons are not clear, but probably are due to sample heterogeneity below X-ray detection limit and/or particle aggregation during carbonate-acid reaction. In any case, the fast reaction of dolomite sample B, in any size fraction, with phosphoric acid, either within 240 min or 100 h, is obvious and significant.

Fig. 1 shows the relation between integrated CO_2 yield (%) and carbonate-acid reaction time in the first 240 min for each size fraction of different samples. For size fractions of 63–38 μm (Fig. 1, middle plot) and 38–1 μm (Fig. 1, right plot), reaction yields for dolomite sample B would be the lower limit since, theoretically, these yields should be higher than those of the corresponding yields of dolomite sample B in the plot of 90–63 μm size fraction as discussed above. The latter curve is therefore included in these two plots (i.e., B′) as a reference. It is obvious from these plots that dolo-

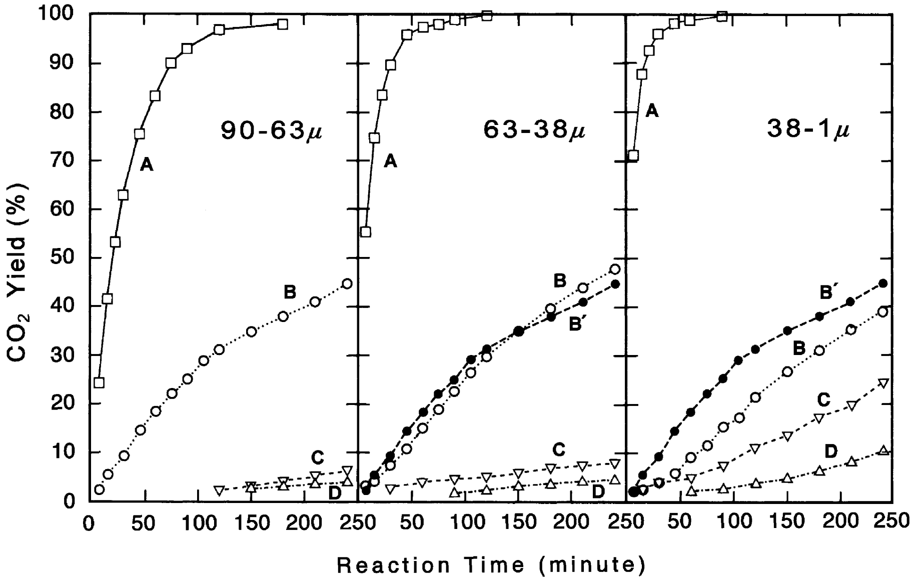

Fig. 1. Relation between integrated CO_2 yield (%) and carbonate–phosphoric acid reaction time in the first 240 min for different grain size fraction of each sample. Integrated yield of dolomite sample B with grain size in the range of 90–63 μm is also shown as curve B′ in the middle and right plots as a reference (see text).

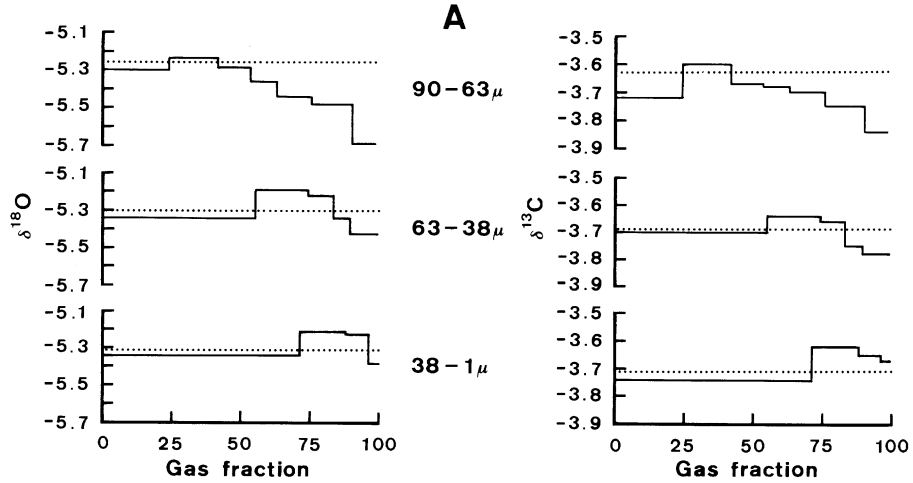

Fig. 2. Oxygen and carbon isotope compositions of gas fractions for sample A with different grain-size ranges. Dotted lines are integrated isotope compositions of gas fractions.

mite-acid reaction rate shows a correlation with calcium content of dolomite.

The isotope compositions of collected gases are graphically shown in Figs. 2–5 for samples A/B/C/D, respectively. In most cases, oxygen isotope composition of the evolved gas of a particular sample increases first and then decreases, similar to those observed by Walters et al. (1972). The largest difference between different gas fractions is 0.5 ‰ for calcite sample A (Fig. 2) and 1.5 ‰ for dolomite sample B/C (Figs. 3 and 4), but is up to 3 ‰ for dolomite sample D (Fig. 5). Carbon isotope composition shows less systematic and a smaller variation (Figs. 2–5). Note that for calcite sample A, ~ 55% of the expected gas, irrespective of the sample grain size, is enough to give accurate isotope results as suggested by Ray and Ramesh (1998) (Table 3).

Comparing the results in Fig. 1 with the various procedures of differential acid extraction method listed in Table 1, it is evident that most procedures

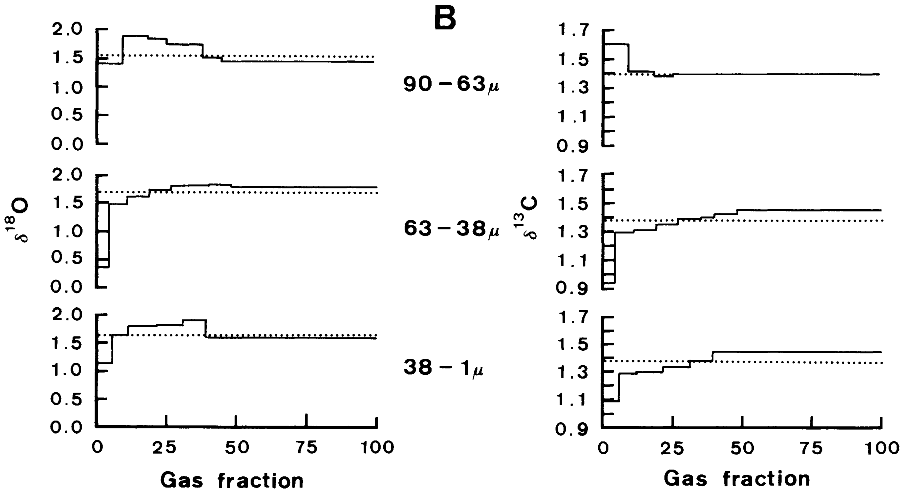

Fig. 3. Oxygen and carbon isotope compositions of gas fractions for sample B with different grain-size ranges. Dotted lines are integrated isotope compositions of gas fractions.

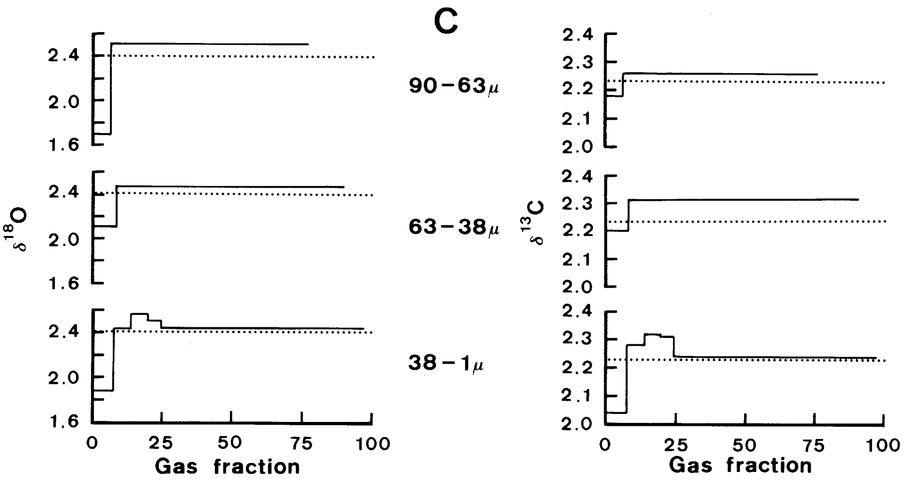

Fig. 4. Oxygen and carbon isotope compositions of gas fractions for sample C with different grain-size ranges. Dotted lines are isotope compositions derived from separate 38–1 μm sample-acid reaction at 25 °C for 6 days.

could effectively resolve the isotopic compositions of calcite and coexisting stoichiometric dolomite (such as dolomite sample D), if the grain size constraint is specifically noted. For example, with a well-confined grain-size range, reasonable isotopic compositions would be derived following the procedure proposed by Walters et al. (1972). Similarly, the procedure given by Ray and Ramesh (1998) could also lead to fair results, although the mixed CO_2 in the procedure (i.e., gas evolved up to 10 h) would contain a substantial amount of dolomite-CO_2, which may cause larger errors of dolomite analysis. On the other hand, the 1–4 h mixed gas in the procedure of Epstein et al. (1964) would contain dolomite-CO_2 from at least 10% of dolomite present with grain size less than 38 μm (Table 2). The errors in dolomite stable isotope compositions caused by such a partially confined grain size fraction (e.g., < 75 μm) is difficult to evaluate. However, considering the relatively constant oxygen and carbon isotope compositions of evolved gas after 240 min of dolomite sample D of different size fractions (see Fig. 2 and Table 3), the results might

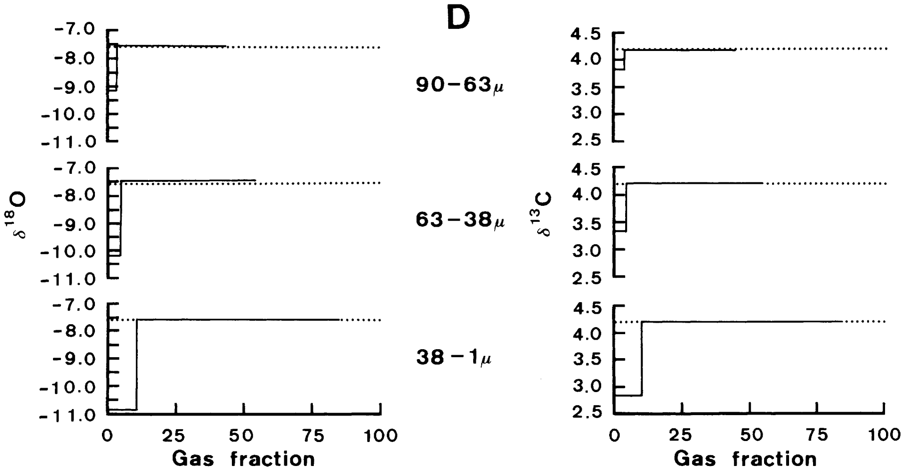

Fig. 5. Oxygen and carbon isotope compositions of gas fractions for sample D with different grain-size ranges. Dotted lines are isotope compositions derived from separate 38–1 μm sample-acid reaction at 25 °C for 6 days.

not deviate from the true value by more than 0.3‰ and 0.1‰, respectively.

On the other hand, most published procedures of differential acid extraction methods listed in Table 1 would cause serious cross-contamination if samples contain mixtures of calcite and nonstoichiometric dolomite. Reasonable results may be difficult, especially for those samples containing nonstoichiometric dolomite like dolomite sample B in the present study, which would yield substantial amount of CO_2 in the first 15–30 min reaction with phosphoric acid (Table 2). Although depending on the stable isotope composition difference between coexisting calcite and nonstoichiometric dolomite in each case, errors may not be overlooked even for samples having a well-confined grain-size range. To have acceptable results, one possible way, taking the present study as an example, is to confine the grain size in the range of 63–38 μm and to take the first 7-min gas as the calcite-CO_2. The gas between 7 and 120 min is taken as the mixed gas and the rest gas is dolomite-CO_2. Reasons for this procedure are that (1) ~ 55% of the expected CO_2 from calcite is sufficient to provide accurate isotopic composition (Table 3; Ray and Ramesh, 1998); (2) finer grain size fraction will have more dolomite-derived CO_2 mixed with "calcite-CO_2"; and (3) coarser grain size fraction would not yield enough calcite-CO_2 in the first 7 min and would take longer time to get rid of "mixed-CO_2", which will contain a higher dolomite-CO_2 component. It should be pointed out that the above suggested time duration for carbonate-acid reaction would vary in different cases depending on the stoichiometric composition of dolomite and grain size fraction employed.

Following the above-proposed procedure and the data shown in Tables 2 and 3, a hypothesized sample containing calcite sample A and dolomite sample B can be employed to estimate theoretical errors. Taking oxygen isotope compositions of calcite and dolomite to be − 5.3‰ and + 1.7‰ (Table 3), respectively, the proposed procedure would give about + 0.1‰ difference for dolomite analysis. However, the difference for calcite analysis would be up to + 1.0‰, + 0.3‰ and + 0.1‰ for samples with calcite to dolomite ratio of 1:4, 1:1 and 4:1, respectively. Similar calculations show that carbon isotope composition would also have comparable errors. The errors would be smaller (larger) for samples containing dolomite with lower (higher) calcium content. For example, samples containing equal amount of calcite sample A and dolomite sample C or D would give results with errors less than 0.1‰ for calcite analysis. As a comparison, calcite would have theoretical errors of + 0.6‰, + 1.0‰ or + 1.6‰ in oxygen isotope composition if a hypothesized sample contains comparable amount of calcite sample A and dolomite sample B and if, following the procedures in Table 1, the first 30-, 60- or 120-min evolved gas is taken as calcite-CO_2, respectively.

The present study evidently shows that, in addition to factors such as reaction time and grain size, the effect of dolomite stoichiometry on carbonate-acid reaction rate must be considered when the differential acid extraction method is adopted for dolomitization studies. However, considering the possible chemical and mineralogical variations resulting from the dolomitization process, it would be difficult, if not impossible, to develop one differential extraction procedure that could yield internally consistent accuracy even excluding samples with extreme calcite to dolomite ratios. This difficulty would introduce further uncertainties in data comparison, either within or among data sets. It should be stressed, however, that although the differential acid extraction method may have difficulties in stable isotope studies of dolomitization process as discussed above, the method is certainly applicable to metamorphic or igneous samples containing stoichiometric dolomite.

The other method to chemically separate calcite from dolomite commonly employed in dolomitization studies is the weak-acid-leaching method (e.g., Humphrey, 1988; Swart and Melim, 2000, among others). Calcite–dolomite mixtures and the corresponding weak-acid-leached, calcite-free dolomite samples are analyzed for their isotopic compositions separately. The results, combined with mineral composition estimates, are then employed to calculate isotopic compositions of calcite. The major error in this method would come from the mineral composition estimates, in addition to minor errors from isotopic analysis and the ^{18}O acid fractionation factor discussed next. Assuming mineral composition estimates would give an uncertainty not worse than ± 5%, the theoretical maximum errors in calcite oxygen or carbon isotope composition of weak-acid leaching method for the above hypothesized sample, containing calcite sample A and dolomite sample B (or C/D), could be -2.6‰ to $+1.5$‰, ± 0.8‰ and ± 0.5‰ for samples with calcite to dolomite ratio of 1:4, 1:1 and 4:1, respectively. The accuracy of the method is obviously poorer but the method has the advantage of a uniform experimental procedure. However, the present data would imply the possibility of differential leaching of dolomite with heterogeneous chemical compositions in partially dolomitized samples by the weak acid. The uncertainties caused by such an effect is difficult to evaluate, but would certainly lead to larger errors.

At last, a rough correlation between dolomite-acid reaction rate and dolomite composition can be discerned from Fig. 1 and Table 2 as previously mentioned. More calcium-rich dolomite is more liable to react with phosphoric acid. This is consistent with the thermodynamic prediction by Chai et al. (1995). Further detailed work is needed to confirm a quantitative relation. These data assuredly imply different ^{18}O acid fractionation factors for dolomites with different chemical compositions. Such a stoichiometry effect has been inferred from the correlation between oxygen isotopic composition and Mg content of dolomite (Vahrenkamp and Swart, 1994; Gill et al., 1995). Although this stoichiometry effect on ^{18}O acid fractionation factor of dolomite may not be large in the composition range considered, precise measurement of oxygen isotopic compositions of nonstoichiometric dolomite would not be possible before the effect is quantitatively determined. Note that this inferred effect also shows that the ^{18}O acid fractionation factor used in the present study in data reduction for dolomite sample B and C would not give true values. However, the relative variation of δ^{18}O values, but not true values, among gas fractions of any particular sample is of concern in this study.

4. Conclusions

Stable isotope analysis is a useful tool in deciphering dolomitization processes. However, precise stable isotope analysis for partially dolomitized samples has always been a problem, which may hamper subtle discussions in dolomitization studies. Data presented in this study clearly show that, in addition to reaction time and grain size, differences in dolomite stoichiometry may also cause significant errors in the differential acid extraction method for analyzing stable isotope compositions of coexisting calcite and dolomite. One possible way to have acceptable stable isotopic compositions, as suggested in the present study, is to strictly confine the sample grain size and, according to predetermined dolomite chemical composition, to reduce the sample-acid reaction time as short as possible, but still yielding enough gas (>55% of the expected yield), for calcite-CO_2. The present data also indicate potential larger errors caused by possible differential leaching of chemically heterogeneous dolomite for the weak-acid leaching method. One should be cautious in comparing published isotopic data of coexisting dolomite and calcite if grain size and stoichiometry of dolomite were not taken into consideration. A stoichiometry effect on ^{18}O acid fractionation factor during dolomite-phosphoric acid reaction is also inferred by the present data. Further quantitative studies in this regard are obviously needed.

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