

# Phosphoric acid fractionation factors for calcite and aragonite between 25 and 75 °C: Revisited

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## Abstract

This paper reports the results of an investigation to re-determine the phosphoric acid fractionation factor for calcite and aragonite in order to improve the accuracy and limit the uncertainty of this very important quantity. The <sup>18</sup>O/<sup>16</sup>O ratio of 100% of the oxygen in calcite and aragonite was determined directly by combining data from a two-step procedure involving thermal decomposition of the carbonate, followed by fluorination of the residual CaO using BrF<sub>5</sub>.

The oxygen isotope composition of the CO<sub>2</sub> released upon the thermal decarbonation of calcite and aragonite is enriched in <sup>18</sup>O relative to that of the remaining CaO. Reproducibility of the oxygen isotope composition of the CO<sub>2</sub> derived from each of the decarbonation and fluorination steps was 0.55‰ (1σ). Nevertheless, statistically reliable acid fractionation factors for calcite (*s<sub>e</sub>* = 0.07) and aragonite (*s<sub>e</sub>* = 0.10) were determined on the basis of a large set of combined data from conventional phosphoric acid reactions at three different temperatures, plus the decarbonation/fluorination procedure. The acid fractionation factors ( $\alpha_{\text{CO}_2(\text{ACID})\text{-carbonate}}$ ) determined in this study for calcite ( $\alpha_{\text{CO}_2(\text{ACID})\text{-Calcite}} = 1.01030$ ) and aragonite ( $\alpha_{\text{CO}_2(\text{ACID})\text{-Aragonite}} = 1.01063$ ) at 25 °C, differ slightly from previously published values.

On the basis of our new determinations at 25, 50, and 75 °C, revised expressions for the temperature dependence of the acid fractionation factors for calcite and aragonite are proposed for the temperature range of 25–75 °C:

$$1000\ln\alpha_{\text{CO}_2(\text{ACID})\text{-Calcite}} = 3.59(10^3/T) - 1.79$$

$$1000\ln\alpha_{\text{CO}_2(\text{ACID})\text{-Aragonite}} = 3.39(10^3/T) - 0.83$$

where  $\alpha_{\text{CO}_2(\text{ACID})\text{-carbonate}}$  is the phosphoric acid fractionation factor, and *T* is temperature in kelvin.

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**Keywords:** Oxygen isotope; Acid fractionation factor; Phosphoric acid; Carbonate; Calcite; Aragonite

## 1. Introduction

The calcium carbonate (CaCO<sub>3</sub>) minerals calcite and aragonite are, by far, the most widely used proxy materials of past environmental changes based on their

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Table 1

Experimental details and the corresponding acid fractionation factors for various carbonates determined at 25 °C in previous studies

Mineral	Origin	Method	Temp. (°C)	1000ln $\alpha_{(\text{CO}_2(\text{ACID})-\text{carbonate})}$ @ 25 °C	# of analyses	Anal. Error	Reference
Ankerite (Ca <sub>2</sub> MgFe(CO <sub>3</sub> ) <sub>4</sub> )	Natural	a	25, 50, 100	11.70	3	0.09	Rosenbaum and Sheppard (1986)
Aragonite (CaCO <sub>3</sub> )	Laboratory reagent	b	25	10.29	2	0.06	Sharma and Clayton (1965) <sup>a</sup>
	Synthetic	a	25	11.01	2	0.01	Kim and O'Neil (1997)
Calcite (CaCO <sub>3</sub> )	Natural	a	25, 95	10.10	1	–	Das Sharma et al. (2002)
	Natural	b	25	10.20	4	0.05	Sharma and Clayton (1965) <sup>a</sup>
	Synthetic	a	25	10.44(ave.)	8	0.10	Kim and O'Neil (1997)
	NBS 20	a	25	10.52	6	N/A	Land (1980)
Cerussite (PbCO <sub>3</sub> )	Laboratory reagent	a	25	10.08	3	0.10	Sharma and Clayton (1965) <sup>a</sup>
	Natural	a	25, 50, 72	10.56	3	0.06	Gilg et al. (2003)
Dolomite (CaMg(CO <sub>3</sub> ) <sub>2</sub> )	Natural	a & c	25	11.03	7 & 10	1 (0.06) & 3 (0.10)	Sharma and Clayton (1965) <sup>a</sup>
	Pleistocene 64.0	a	25	11.36	2	N/A	Land (1980)
	Cretaceous, RL-38	a	25	11.51	4	N/A	Land (1980)
	Mississippian	a	25	11.52	5	N/A	Land (1980)
	Pleistocene B-11a	a	25	11.54	6	N/A	Land (1980)
	Natural-1	a	25, 50, 100	11.71	1	–	Rosenbaum and Sheppard (1986)
	Pleistocene 54.7	a	25	11.72	3	N/A	Land (1980)
	Cretaceous, RL-46	a	25	11.73	6	N/A	Land (1980)
	Natural-2	a	25, 50, 100	11.79	2	0.55	Rosenbaum and Sheppard (1986)
	Devonian	a	25	11.86	4	N/A	Land (1980)
	Holocene B	a	25	12.41	4	N/A	Land (1980)
	Holocene A	a	25	12.58	5	N/A	Land (1980)
Magnesite (MgCO <sub>3</sub> )	Natural	a	50	10.79	3	0.11	Das Sharma et al. (2002)
Otavite (CdCO <sub>3</sub> )	Laboratory reagent	a	25	11.20	2	0.04	Kim and O'Neil (1997)
	Laboratory reagent	a & c	25	11.39	3 & 3	1 (0.04) & 3 (0.03)	Sharma and Clayton (1965) <sup>a</sup>
	Synthetic	a	25	12.25(ave.)	11	0.78	Kim and O'Neil (1997)
Protodolomite	Holocene	a	25	12.57	2	N/A	Land (1980)
Rhodochrosite (MnCO <sub>3</sub> )	Synthetic	a	25	10.07	3	0.19	Sharma and Clayton (1965) <sup>a</sup>
Siderite (FeCO <sub>3</sub> )	Natural	a	100, 150	8.77	5	0.08	Rosenbaum and Sheppard (1986)
	Natural	a	25, 50	11.58	4	0.02	Carothers et al. (1988)
	Synthetic	a	25, 50	11.68	3	0.08	Carothers et al. (1988)
Smithsonite (ZnCO <sub>3</sub> )	Unknown	a & c	25	11.24	3 & 3	1 (0.07) & 3 (0.04)	Sharma and Clayton (1965) <sup>a</sup>
	Natural	a	25, 50, 72	11.42	2	0.01	Gilg et al. (2003)
	Laboratory reagent	b	25	10.43	4	0.09	Sharma and Clayton (1965) <sup>a</sup>
Witherite (BaCO <sub>3</sub> )	Synthetic	a	25	10.57(ave.)	6	0.16	Kim and O'Neil (1997)
	Laboratory reagent	b	25	10.91	4	0.04	Sharma and Clayton (1965) <sup>a</sup>

Temp. = Temperatures at which acid fractionation factor is available.

# of analysis = Number of total oxygen isotope analysis.

Anal. Error = Analytical error as reported in, or inferred from, the original paper (e.g., mean deviation or standard deviation).

ave. = average from samples of same mineralogy, but different preparations.

a = Thermal decomposition and subsequent fluorination method.

b = Low temperature fluorination method.

c = High temperature fluorination method.

<sup>a</sup> The results of Sharma and Clayton (1965) were later corrected. Amended values were taken from Friedman and O'Neil (1977).

chemical and isotopic compositions (e.g., Klein et al., 1996). The variation of ocean temperature is but one prominent example of their application (e.g., Emiliani and Shackleton, 1974). Currently, with the development of modern technology, the carbon and oxygen isotope compositions of a large number (i.e., >20) of very small (e.g., 10 µg) calcium carbonate samples can be analyzed automatically in a single day. Nevertheless, the basic phosphoric acid reaction protocol, first developed more than 50 years ago by McCrea (1950) to analyze the isotopic composition of carbonate minerals, is still in use today with minor modifications where required by instrumentation. The protocols in use today all require that the reaction be performed at a controlled temperature to extract and isolate the evolved CO<sub>2</sub> before it is introduced into the mass spectrometer. Conventionally, the off-line manual extraction protocol (after McCrea, 1950) is carried out overnight at 25 °C but, in most modern automated systems, a higher reaction temperature (i.e., 75 or 90 °C) is used to promote a faster reaction (e.g., Wachter and Hayes, 1985).

As the CO<sub>2</sub> liberated by the acid reaction accounts for only 2/3 of the oxygen in the solid, an isotopic fractionation ensues whereby the acid-liberated CO<sub>2</sub> at 25 °C is nearly 10 per mil (‰) heavier than the original carbonate. This discrepancy will vary by a few per mil depending on the mineralogy of the carbonate mineral and the temperature of the reaction. Consequently, to calculate the isotopic composition of the carbonate solid, an acid fractionation factor ( $\alpha_{\text{CO}_2(\text{ACID})\text{-carbonate}}$ ) appropriate for the temperature of reaction and for a specific carbonate mineral must be applied as follows:

$$\begin{aligned} \alpha_{\text{CO}_2(\text{ACID})\text{-carbonate}} &= (\text{O}^{18}/\text{O}^{16})_{\text{CO}_2(\text{ACID})} / (\text{O}^{18}/\text{O}^{16})_{\text{carbonate}} \\ &= (\delta^{18}\text{O}_{\text{CO}_2(\text{ACID})} + 1000) / (\delta^{18}\text{O}_{\text{carbonate}} + 1000) \end{aligned} \quad (1)$$

where CO<sub>2</sub>(ACID) denotes phosphoric acid-liberated CO<sub>2</sub>.

With today's modern, high-precision mass spectrometers and carefully-controlled extraction acid techniques, and a general desire to acquire isotopic data of the highest quality, it is of utmost importance to establish the most accurate and precise acid fractionation factors possible. Only by independently determining the oxygen isotope composition of all the oxygen in a carbonate mineral, can the acid fractionation factor be confirmed or determined. As a case in point, the most widely used acid fractionation factors for calcite and aragonite were determined 40 years ago from a limited number of analyses (i.e., 4 and 2 for calcite and aragonite, respectively;

Sharma and Clayton, 1965; Table 1). These values are critical in relating the oxygen isotope composition of these carbonates to those of water, silicates, and oxides, for comparison of data from different laboratories, and for compiling different datasets. The present study was conducted to provide a more statistically reliable set of acid fractionation factors for calcite and aragonite by determining their complete isotopic compositions using a slightly refined two-step method of analysis, comprising both thermal decarbonation and fluorination, plus an acid reaction. In addition, the temperature dependence of the acid fractionation factors for both minerals was determined between 25 and 75 °C.

## 2. Previous studies

The oxygen isotope fractionations for various carbonate minerals for use with the phosphoric acid technique are reported from the literature in Table 1, and briefly reviewed below to emphasize the various techniques employed. Sharma and Clayton (1965) first measured the <sup>18</sup>O/<sup>16</sup>O ratios of the total oxygen content of alkaline earth and transition metal carbonates and concluded that differences in acid fractionation factors were due to the chemical composition of the carbonates. In order to obtain the total oxygen isotope composition ( $\delta^{18}\text{O}_{\Sigma\text{O}_2}$ ) of the carbonates, three different methods were employed to quantitatively extract oxygen from the carbonate: (1) thermal decomposition of the carbonate, followed by a BrF<sub>5</sub> reaction with the remaining oxide; (2) low temperature (~100 °C) BrF<sub>5</sub> reaction with the carbonate; and (3) high temperature (700 °C) BrF<sub>5</sub> reaction with the carbonate. In the first method, the CO<sub>2</sub> released during thermal decarbonation and the CO<sub>2</sub> derived from conversion of O<sub>2</sub> produced from the fluorination step, were each collected and analyzed separately for their isotopic compositions. In the second method, the CO<sub>2</sub> and O<sub>2</sub> generated simultaneously from the low temperature reaction with BrF<sub>5</sub> were mixed after conversion of the O<sub>2</sub> to CO<sub>2</sub> over hot graphite. In the third method, the high temperature reaction with BrF<sub>5</sub> yielded only O<sub>2</sub>, which was subsequently converted to CO<sub>2</sub>. Sharma and Clayton (1965) chose a low temperature BrF<sub>5</sub> reaction to release all the oxygen in calcium carbonate (i.e., calcite and aragonite), and amended (Friedman and O'Neil, 1977) results of their analyses yielded per mil isotopic acid fractionations ( $1000\ln\alpha_{\text{CO}_2(\text{ACID})\text{-carbonate}}$ ) for calcite and aragonite at 25 °C of 10.20 and 10.29, respectively. Almost a decade later, Land (1980) re-determined the acid fractionation factors for a single calcite and for a set of dolomites of various origins using the first method

(i.e., two-step method) of Sharma and Clayton (1965). The newly determined per mil acid fractionation (i.e.,  $1000\ln\alpha_{\text{CO}_2(\text{ACID})\text{-carbonate}}$ ) at 25 °C for calcite was 10.52, whereas for the different dolomites, it varied from 11.36 to 12.58. Land (1980) stated that he discarded almost 70% of the data based on the criteria that the total CO<sub>2</sub> yield (i.e., the sum of the CO<sub>2</sub> aliquots from each step) had to exceed 98% of the theoretical value and/or the volume of CO<sub>2</sub> collected from a decarbonation step was within 1.5% of the expected value. Rosenbaum and Sheppard (1986) determined the phosphoric acid fractionation factors of siderite, dolomite, and ankerite via the two-step method (i.e., the first method) described by Sharma and Clayton (1965). Instead of using a conventional nickel tube, as did Sharma and Clayton (1965), Rosenbaum and Sheppard (1986) placed the carbonate in a molybdenum capsule within a quartz reaction tube, and then heated it up to 800 °C until complete thermal decomposition. The remaining metal oxide was weighed in an argon atmosphere before being transferred to a nickel tube for the fluorination step at 680 °C. Their results are compiled in Table 1. Carothers et al. (1988) determined acid fractionation factors for natural as well as synthetic siderite. They also used the two-step method but, unlike previous studies, the iron oxide resulting from the thermal decomposition at 500–600 °C was reacted with ClF<sub>3</sub> instead of BrF<sub>5</sub>. In addition, they characterized the decarbonation products by X-ray diffraction analysis and identified them as elemental iron and magnetite (Fe<sub>3</sub>O<sub>4</sub>). More recently, Kim and O'Neil (1997) repeated the two-step method of Sharma and Clayton (1965), but used ClF<sub>3</sub> instead of BrF<sub>5</sub> in the fluorination step, and reported new acid fractionation factors at 25 °C for synthetic calcite, aragonite, otavite, and witherite. Depending on the mineral, these new values differ to various degrees from those published by Sharma and Clayton (1965). Gilg et al. (2003) adopted Rosenbaum and Sheppard (1986)'s protocol, described above, for the thermal decomposition of smithsonite (ZnCO<sub>3</sub>) and cerussite (PbCO<sub>3</sub>). The remaining oxides were analyzed by laser-assisted fluorination using fluorine gas (F<sub>2</sub>) as reagent. This alternative fluorination method yielded a better reproducibility ( $\pm 0.26\%$ ,  $n=4$ ) for the  $\delta^{18}\text{O}$  values of the ZnO than the conventional silicate line extraction method ( $\pm 0.85\%$ ,  $n=4$ ).

Our study focused on calcite and aragonite, for which the range of currently available per mil acid fractionations is 10.10 to 10.52 and 10.29 to 11.01, respectively, at 25 °C (Table 1). In addition to the fractionation factors at 25 °C, the temperature dependence of the  $\delta^{18}\text{O}_{\text{CO}_2(\text{ACID})}$  and carbonate mineral fractionation over the range 25–75 °C was determined.

### 3. Samples and experimental methods

#### 3.1. Calcium carbonate samples

Natural calcite and aragonite specimens, designated as Calcite H and Ara–Nat–ST–1, were used as internal standards during this study. Calcite H was purified from several samples collected in 1976 by B. Taylor from the Fenn carbonatite complex, Norway, an outcrop adjacent to the one sampled for material used to prepare the IAEA carbonatite standard RM 8543 (NBS 18). Ara–Nat–ST–1 was purchased from Ward's (Rochester, New York) and originated from Compton Martin, Somerset, England. Both specimens were reduced to powder during this study using an agate mortar and pestle, and stored for later isotopic analysis. The purity of Calcite H and Ara–Nat–ST–1 was confirmed by optical and X-ray diffraction methods: no other phases were identified. Results of the XRF analyses of the Calcite H and Ara–Nat–ST–1 solids are presented in Table 2.

#### 3.2. Release of total oxygen from carbonates

A refined version of the two-step method described by Sharma and Clayton (1965) was employed to determine the total oxygen isotope composition of calcite and aragonite. First, the carbonate samples were dried a minimum of 1 h (typically overnight) at 100 °C to remove adsorbed moisture and obtain a constant weight ( $\pm 0.01$  mg). Thereafter, the carbonate samples were transferred to a conventional silicate extraction line and loaded into nickel reaction vessels fitted with special caps designed for contamination-free loading (e.g., Taylor, 2004). Samples were degassed under vacuum for 1 or 2 h at room temperature, then sealed and heated (i.e., decarbonated) at 600 °C overnight. A non-condensable gas was occasionally present with the CO<sub>2</sub> following decarbonation. Upon its identification as O<sub>2</sub> by the color of Tesla coil-induced spark discharge, it was converted to CO<sub>2</sub> in the presence of hot graphite, and mixed with the originally liberated CO<sub>2</sub>. The production of O<sub>2</sub> during decarbonation was uncontrollable and unpredictable, and may have originated from reaction of the sample with F<sub>2</sub> released from the nickel fluoride coating on the inner walls of the reaction vessels upon heating. The nickel tubes were, in all cases, thoroughly degassed of any residual BrF<sub>5</sub> from previous runs. It is noteworthy that, at the early stage of development of our two-step method, an unknown gas, yellowish in color when frozen, was occasionally collected with CO<sub>2</sub> when the alcohol slush trap (T-3, Fig. 20.1 in Taylor, 2004) was not cold enough (i.e., above –90 °C). This yellowish gas was not

Table 2  
Results of XRF analyses of the Calcite H and Ara–Nat–ST–I solids

	SiO <sub>2</sub>	SO <sub>3</sub>	TiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Cr <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3(Total)</sub>	MnO	MgO	CaO	Na <sub>2</sub> O	K <sub>2</sub> O	P <sub>2</sub> O <sub>5</sub>	Cl	Ba	Nb	Rb	Sr	Zr	LOI	TOTAL
Calcite H	0	N/A	0	0	0	0.3	0.21	0.77	54.97	0	0	0.01	N/A	54.7 <sup>a</sup>	0 <sup>a</sup>	0 <sup>a</sup>	7490 <sup>a</sup>	0 <sup>a</sup>	41	98.1
Detection limit (wt.%)	0.4	N/A	0.05	0.2	0.02	0.1	0.02	0.1	0.1	0.1	0.05	0.02	N/A	30 <sup>a</sup>	20 <sup>a</sup>	20 <sup>a</sup>	20 <sup>a</sup>	20 <sup>a</sup>	N/A	N/A
Ara–Nat–ST–I	0.25	0.24	N/A	0.06	N/A	N/A	N/A	0.34	N/A	0.15	0.03	N/A	0.26	N/A	N/A	N/A	0.18	N/A	N/A	N/A
Detection limit (wt.%)	0.01	0.01	N/A	0.01	N/A	N/A	N/A	0.01	N/A	0.01	0.01	N/A	0.01	N/A	N/A	N/A	0.01	N/A	N/A	N/A

The results are expressed as weight percent.

<sup>a</sup>Denotes a value reported in ppm.

observed when the temperature of the slush trap was maintained between –90 and –100 °C. All the data reported in this study were collected under the latter conditions when only CO<sub>2</sub> gas passed through the T-3 trap. The second step, extraction of the remaining oxygen from the residual CaO, was carried out by fluorination using a standardized aliquot of BrF<sub>5</sub> and reaction temperature of 650 °C overnight. The O<sub>2</sub> released by the reaction was converted to CO<sub>2</sub> as described above, and its volume was measured.

The isotopic compositions of the CO<sub>2</sub> components were measured in a Finnigan MAT 252 isotope ratio mass spectrometer at the Geological Survey of Canada, Ottawa. The external precision of the mass spectrometer for oxygen and carbon isotope composition of (> 100 bar μL) CO<sub>2</sub> is typically ca. 0.04‰ and 0.02‰, respectively. Oxygen isotope compositions of carbonates are reported in the familiar δ<sup>18</sup>O notation relative to the V-SMOW standard. The total oxygen isotope composition (δ<sup>18</sup>O<sub>ΣO<sub>2</sub></sub>) of each calcium carbonate sample was obtained from a weighted average of the isotopic compositions of the O<sub>2</sub> bearing gases (i.e., CO<sub>2</sub> or O<sub>2</sub>) recovered from each of the two oxygen extraction steps as follows:

$$\delta^{18}\text{O}_{\Sigma\text{O}_2} = \delta^{18}\text{O}(\text{Dec.}) \times \left( \frac{\mu\text{molCO}_2(\text{Dec.})}{\mu\text{molCO}_2(\text{Dec.}) + \mu\text{molCO}_2(\text{Flu.})} \right) + \delta^{18}\text{O}(\text{Flu.}) \times \left( \frac{\mu\text{molCO}_2(\text{Flu.})}{\mu\text{molCO}_2(\text{Dec.}) + \mu\text{molCO}_2(\text{Flu.})} \right) \quad (2)$$

where Dec. and Flu. denote the decarbonation and fluorination steps, respectively.

The percentage of the total theoretical oxygen yield (% T.Y.) attained (Tables 3 and 4) was calculated from the ratio of the total CO<sub>2</sub> (in μmol, incl. any converted O<sub>2</sub>) collected from both steps (i.e., decarbonation and fluorination) to the corresponding maximum theoretical yield (i.e., 9.99 or 5.00 μmol CO<sub>2</sub>/mg of CaCO<sub>3</sub> from the decarbonation or fluorination steps, respectively), multiplied by 100 to express it as a percentage.

### 3.3. Reaction of carbonates with phosphoric acid at 25, 50, and 75 °C

The isotopic composition of the CO<sub>2</sub> liberated by the reaction of calcium carbonates with phosphoric acid was determined using the classical procedure of McCrea (1950). Five to six mg of carbonate and ~6 mL of 100% phosphoric acid were loaded into separate arms of a

Table 3

Oxygen isotope compositions and experimental data for total oxygen isotope analyses of calcite (Calcite H)

ID	Sample	Weight (mg)	Decarbonation step				Fluorination step				Total	
			$\mu\text{mol CO}_2$	% T.Y.	O <sub>2</sub> produced	$\delta^{18}\text{O}_{(\text{Dec.})}$	$\mu\text{mol CO}_2$	% T.Y.	$\delta^{18}\text{O}_{(\text{Flu.})}$	% T.Y.	$\delta^{18}\text{O}_{\Sigma\text{O}_2}$	
FVIII-78-1	Calcite H	12.48	128.1	102.7	No	12.80	62.1	99.5	-7.40	101.7	6.20	
FVIII-78-2	Calcite H	12.51	125.5	100.4	No	12.50	68.4	109.4	-5.25	103.4	6.24	
FVIII-78-3	Calcite H	12.53	125.4	100.2	No	13.35	64.6	103.1	-6.95	101.2	6.45	
FVIII-78-4	Calcite H	12.52	125.6	100.4	No	14.53	59.1	94.5	-8.46	98.4	7.17	
FVIII-78-5	Calcite H	12.49	126.2	101.1	No	12.25	64.1	102.7	-4.08	101.6	6.75	
FVIII-78-6	Calcite H	12.54	130.6	104.3	Yes	14.15	60.6	96.7	-7.28	101.7	7.36	
FVIII-78-7	Calcite H	12.55	129.2	103.1	Yes	14.27	61.4	97.8	-8.94	101.3	6.79	
FVIII-78-8	Calcite H	12.54	129.4	103.3	Yes	14.01	N/A	N/A	N/A	N/A	N/A	
FVIII-78-9	Calcite H	12.55	126.9	101.2	No	N/A	67.1	106.9	-4.75	103.1	N/A	
FVIII-78-10	Calcite H	12.49	128.8	103.2	Yes	13.55	58.9	94.3	-7.48	100.3	6.95	
FVIII-78-11	Calcite H	12.53	131.3	104.9	No	13.13	59.6	95.1	N/A	101.6	N/A	
FVIII-78-12	Calcite H	12.48	128.5	103.0	Yes	13.26	61.2	98.1	-6.89	101.4	6.76	
FVIII-85-1	Calcite H	12.48	129.7	104.0	No	12.74	61.8	99.1	-6.09	102.4	6.66	
FVIII-85-2	Calcite H	12.61	130.6	103.7	Yes	13.49	62.6	99.3	-7.03	102.2	6.84	
FVIII-85-3	Calcite H	12.55	127.7	101.9	No	13.78	67.6	107.8	-7.48	103.8	6.42	
FVIII-85-4	Calcite H	12.60	128.8	102.3	Yes	14.10	57.2	90.9	-7.34	98.5	7.51	
FVIII-85-5	Calcite H	12.58	121.4	96.6	No	14.23	64.2	102.1	-6.82	98.4	6.95	
FVIII-85-6	Calcite H	12.55	126.7	101.1	Yes	13.75	62.4	99.5	-7.26	100.5	6.82	
FVIII-85-7	Calcite H	12.53	128.1	102.4	No	13.40	65.0	103.8	-7.17	102.8	6.48	
FVIII-85-8	Calcite H	12.53	121.1	96.7	No	12.96	67.0	107.0	-4.50	100.1	6.74	
FVIII-85-9	Calcite H	12.54	124.9	99.7	No	12.54	65.1	103.8	-5.12	101.1	6.49	
FVIII-85-10	Calcite H	12.53	134.4	107.4	No	11.47	57.1	91.2	-5.03	102.0	6.55	
FVIII-85-11	Calcite H	12.56	133.3	106.3	No	11.02	56.5	89.9	-3.42	100.8	6.72	
FVIII-85-12	Calcite H	12.56	132.6	105.7	No	11.88	58.9	93.8	-4.86	101.7	6.73	
FVIII-86-1	Calcite H	3.09	30.4	98.5	No	13.61	15.8	102.3	-6.50	99.7	6.73	
FVIII-86-2	Calcite H	3.04	23.1	76.1	No	13.50	27.9	183.5	0.08	111.9	6.16	
FVIII-86-3	Calcite H	5.04	50.9	101.1	No	13.62	27.7	109.8	-5.51	104.0	6.88	
FVIII-86-4	Calcite H	5.05	49.5	98.2	No	15.11	32.7	129.4	-8.60	108.6	5.68	
FVIII-86-5	Calcite H	7.02	70.8	101.0	No	14.33	36.2	103.2	-8.17	101.7	6.72	
FVIII-86-6	Calcite H	7.14	70.7	99.1	No	13.95	38.9	108.9	-7.59	102.4	6.30	
FVIII-86-7	Calcite H	9.03	91.6	101.5	No	13.94	45.1	99.8	-8.35	101.0	6.59	
FVIII-86-8	Calcite H	9.12	89.9	98.6	No	13.79	48.8	107.1	-6.60	101.5	6.62	
FVIII-86-9	Calcite H	11.05	113.4	102.7	No	13.39	55.9	101.1	-7.22	102.2	6.58	
FVIII-86-10	Calcite H	11.08	117.3	106.0	No	11.57	51.3	92.5	-4.74	101.5	6.61	
FVIII-86-11	Calcite H	12.59	134.2	106.7	No	11.76	57.9	92.0	-5.35	101.8	6.60	
FVIII-86-12	Calcite H	12.61	132.7	105.4	No	12.58	59.5	94.3	-6.57	101.7	6.65	
FVIII-87-1	Calcite H	3.11	28.0	90.3	No	11.94	19.0	121.9	-3.12	100.8	5.85	
FVIII-87-2	Calcite H	3.08	12.5	40.6	No	9.47	32.3	209.7	2.34	97.0	4.33	
FVIII-87-3	Calcite H	3.24	32.0	99.0	No	12.57	15.5	96.0	-5.53	97.8	6.66	
FVIII-87-4	Calcite H	7.07	66.1	93.5	No	15.20	37.3	105.5	-8.41	97.6	6.68	
FVIII-87-5	Calcite H	7.03	69.6	99.2	No	13.86	35.1	100.0	-7.16	99.4	6.81	
FVIII-87-6	Calcite H	7.12	71.2	100.1	No	12.85	35.6	99.9	-5.60	100.1	6.70	
FVIII-87-7	Calcite H	3.09	30.0	97.1	No	12.81	17.1	110.8	-4.03	101.7	6.70	
FVIII-87-8	Calcite H	3.10	18.5	59.7	No	12.15	25.7	165.7	0.29	95.1	5.25	
FVIII-87-9	Calcite H	3.05	26.1	85.7	No	13.14	18.7	122.6	-3.55	98.0	6.17	
FVIII-88-1	Calcite H	3.20	32.4	101.2	No	13.25	16.2	101.1	-2.64	101.3	7.95	
FVIII-88-2	Calcite H	3.03	27.6	91.1	No	13.48	18.9	124.8	-3.75	102.4	6.48	
FVIII-88-3	Calcite H	3.03	30.9	102.0	No	13.47	14.7	96.7	-6.98	100.4	6.88	
FVIII-88-4	Calcite H	3.06	25.5	83.5	No	14.11	19.5	127.4	-3.18	98.1	6.62	
FVIII-88-5	Calcite H	3.08	30.0	97.5	No	15.05	15.5	100.9	-7.01	98.6	7.54	
FVIII-88-6	Calcite H	3.03	30.6	101.2	No	13.43	16.1	106.4	-5.73	102.8	6.82	
FVIII-88-7	Calcite H	5.28	53.8	102.1	No	13.47	27.6	104.4	-5.49	102.8	7.04	
FVIII-88-8	Calcite H	5.02	45.6	91.0	No	13.39	30.0	119.5	-3.68	100.5	6.62	
FVIII-88-9	Calcite H	5.16	51.3	99.4	No	14.19	26.9	104.4	-7.47	101.1	6.74	
FVIII-88-10	Calcite H	5.11	55.1	108.0	No	12.24	23.6	92.3	-5.98	102.7	6.78	
FVIII-88-11	Calcite H	5.04	56.9	113.1	No	11.71	20.4	81.1	-7.03	102.3	6.76	

Table 3 (continued)

ID	Sample	Weight (mg)	Decarbonation step				Fluorination step			Total	
			$\mu\text{mol CO}_2$	% T.Y.	O <sub>2</sub> produced	$\delta^{18}\text{O}_{(\text{Dec.})}$	$\mu\text{mol CO}_2$	% T.Y.	$\delta^{18}\text{O}_{(\text{Flu.})}$	% T.Y.	$\delta^{18}\text{O}_{\Sigma\text{O}_2}$
FVIII-88-12	Calcite H	5.06	56.7	112.2	No	12.31	20.5	81.0	-7.30	101.8	7.10
FVIII-95-4	Calcite H	7.18	65.8	91.7	No	15.37	35.6	99.0	-7.14	94.2	7.47
FVIII-95-5	Calcite H	7.20	69.6	96.7	No	14.34	35.1	97.5	-7.98	97.0	6.86
FVIII-95-6	Calcite H	7.03	71.6	101.9	Yes	14.82	26.9	76.7	-10.94	93.5	7.79
FVIII-97-10	Calcite H	7.08	72.3	102.2	No	12.79	31.1	87.8	-5.08	97.4	7.42
FVIII-97-11	Calcite H	7.21	73.4	101.9	No	12.57	32.4	89.7	-5.06	97.9	7.17
FVIII-97-12	Calcite H	7.02	73.3	104.5	No	12.14	34.8	99.2	-6.62	102.7	6.10

% T.Y. = % theoretical yield.

standard reaction vessel with acid side arm, degassed under vacuum for a minimum of 1.5 h, and thermostated in a water bath at 25, 50, or 75 °C ± 0.1 °C for 1 h prior to reaction. The reaction was allowed to proceed for a

minimum of 15 h at 25 and 50 °C, and for 1 h at 75 °C. Subsequently, the amount of CO<sub>2</sub> gas evolved was measured manometrically, cryogenically purified, and then flame-sealed in a 6 mm O.D. Pyrex<sup>®</sup> tube.

Table 4

Oxygen isotope compositions and experimental data for total oxygen isotope analyses of aragonite (Ara-Nat-ST-1)

ID	Sample	Weight (mg)	Decarbonation step				Fluorination step			Total	
			$\mu\text{mol CO}_2$	% T.Y.	O <sub>2</sub> produced	$\delta^{18}\text{O}_{(\text{Dec.})}$	$\mu\text{mol CO}_2$	% T.Y.	$\delta^{18}\text{O}_{(\text{Flu.})}$	% T.Y.	$\delta^{18}\text{O}_{\Sigma\text{O}_2}$
FVIII-89-1	Ara-Nat-ST-1	2.98	30.5	102.3	No	33.54	14.5	97.3	4.40	100.7	24.15
FVIII-89-2	Ara-Nat-ST-1	3.13	32.1	102.8	No	32.00	18.1	115.8	9.10	107.0	23.74
FVIII-89-3	Ara-Nat-ST-1	3.00	31.3	104.4	No	31.61	14.5	96.6	8.99	101.8	24.45
FVIII-89-4	Ara-Nat-ST-1	3.20	31.7	99.1	No	33.19	16.4	102.7	N/A	100.3	N/A
FVIII-89-5	Ara-Nat-ST-1	5.07	51.0	100.8	No	31.43	25.8	101.7	11.27	101.1	24.66
FVIII-89-6	Ara-Nat-ST-1	5.11	52.2	102.3	No	32.28	26.6	104.0	9.52	102.9	24.60
FVIII-89-7	Ara-Nat-ST-1	5.14	52.8	102.8	No	31.38	26.2	102.0	10.64	102.5	24.50
FVIII-89-8	Ara-Nat-ST-1	5.05	52.0	103.1	No	31.31	25.6	101.5	11.48	102.5	24.77
FVIII-89-9	Ara-Nat-ST-1	7.17	74.4	103.8	No	31.00	36.0	100.5	11.77	102.7	24.73
FVIII-89-10	Ara-Nat-ST-1	7.07	81.9	116.0	No	28.64	27.1	76.7	12.97	102.9	24.74
FVIII-89-11	Ara-Nat-ST-1	7.01	79.2	113.1	No	29.30	29.9	85.3	12.86	103.8	24.79
FVIII-89-12	Ara-Nat-ST-1	7.13	79.5	116.1	No	29.50	29.7	83.4	12.39	102.2	24.85
FVIII-91-1	Ara-Nat-ST-1	7.26	77.9	107.5	No	31.66	34.5	94.9	8.37	103.3	24.51
FVIII-91-2	Ara-Nat-ST-1	7.23	22.4	31.0	Yes	N/A	10.5	28.9	5.50	30.4	N/A
FVIII-91-3	Ara-Nat-ST-1	7.19	77.6	108.1	Yes	N/A	33.9	94.2	5.60	103.5	N/A
FVIII-91-4	Ara-Nat-ST-1	7.23	76.6	106.1	Yes	35.72	29.9	82.7	1.14	98.3	26.01
FVIII-91-5	Ara-Nat-ST-1	5.00	53.8	107.7	Yes	34.88	20.6	82.4	2.32	99.3	25.86
FVIII-91-6	Ara-Nat-ST-1	5.01	55.3	110.5	Yes	35.67	20.4	81.6	-0.95	100.8	25.80
FVIII-91-7	Ara-Nat-ST-1	5.01	54.0	107.9	Yes	34.25	20.9	83.4	2.32	99.7	25.34
FVIII-91-8	Ara-Nat-ST-1	4.96	50.8	102.5	No	N/A	22.3	89.8	8.79	98.3	N/A
FVIII-91-9	Ara-Nat-ST-1	5.12	54.0	105.6	Yes	33.76	22.9	89.4	5.73	100.2	25.41
FVIII-91-10	Ara-Nat-ST-1	5.15	59.7	116.0	No	28.39	20.4	79.3	11.29	103.8	24.03
FVIII-91-11	Ara-Nat-ST-1	4.96	54.8	110.7	No	29.96	20.3	81.7	10.48	101.0	24.69
FVIII-91-12	Ara-Nat-ST-1	4.95	58.7	118.6	No	29.44	19.3	78.1	9.83	105.1	24.59
FVIII-95-1	Ara-Nat-ST-1	7.35	76.3	103.9	No	31.30	34.7	94.3	8.34	100.7	24.12
FVIII-95-2	Ara-Nat-ST-1	7.00	72.4	103.5	Yes	34.71	29.9	85.4	1.85	97.5	25.11
FVIII-95-3	Ara-Nat-ST-1	7.38	74.4	100.9	No	31.57	35.0	94.9	9.95	98.9	24.65
FVIII-97-7	Ara-Nat-ST-1	7.33	73.7	100.6	No	32.34	35.6	97.0	7.77	99.5	24.34
FVIII-97-8	Ara-Nat-ST-1	7.32	75.5	103.3	Yes	31.95	30.8	84.2	9.94	96.9	25.57
FVIII-97-9	Ara-Nat-ST-1	7.22	75.6	104.8	Yes	34.32	32.4	89.6	3.94	99.8	25.21
FVIII-122-1	Ara-Nat-ST-1	7.08	73.0	103.1	No	32.43	33.0	93.3	7.26	99.9	24.59
FVIII-122-2	Ara-Nat-ST-1	7.28	75.2	103.4	No	32.70	37.0	101.6	10.27	102.8	25.30
FVIII-122-3	Ara-Nat-ST-1	7.20	73.7	102.4	No	31.93	38.7	107.5	11.33	104.1	24.84

% T.Y. = % theoretical yield.

#### 4. Results and discussion

The results of 60 calcite and 29 aragonite analyses derived from the two-step analytical protocol used in this study are reported in Tables 3 and 4. The analytical uncertainties for each step of the total oxygen isotope analysis are propagated through the calculations of new acid-fractionation factors and their temperature dependence. Given that the random experimental errors associated with Sharma and Clayton (1965) and Kim and O'Neil (1997)'s analytical protocols are likely similar to those of this study, the uncertainties of the newly determined acid fractionation factors for calcite and aragonite are reduced by a factor of 5.5 and 3.8, respectively, relative to the previously reported values, on the basis of the number of analyses performed (Harris, 2003). Furthermore, when the sample size exceeds a value between 20 and 30, empirical research has shown that the sampling distribution of a sample mean can be approximated by a normal distribution and has a mean equal to the mean of the population from which the sample was selected, irrespective of the shape of the population distribution (Chapter 7 in Sincich et al., 2002). Based upon this *central limit theorem*, a population mean can be estimated with more statistical confidence from the large number of analyses (e.g., 29 new measurements for aragonite as opposed to the commonly-used average of two measurements).

##### 4.1. Oxygen isotope compositions of the O<sub>2</sub>-bearing gases

Data in Figs. 1 and 2 reveal that the oxygen isotope composition of the CO<sub>2</sub> (or sometimes CO<sub>2</sub>+O<sub>2</sub>; Tables 3

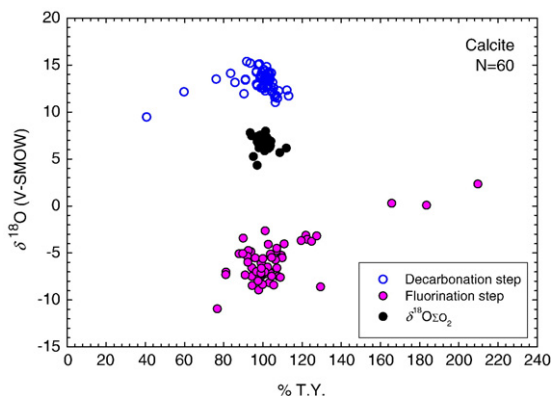


Fig. 1. Plot of  $\delta^{18}\text{O}_{\text{V-SMOW}}$  vs. percent theoretical oxygen yield (% T.Y.) for calcite, including analytical data for each of the two components of a two-step analytical process. Sixty analyses of total oxygen isotope composition of Calcite H are plotted.

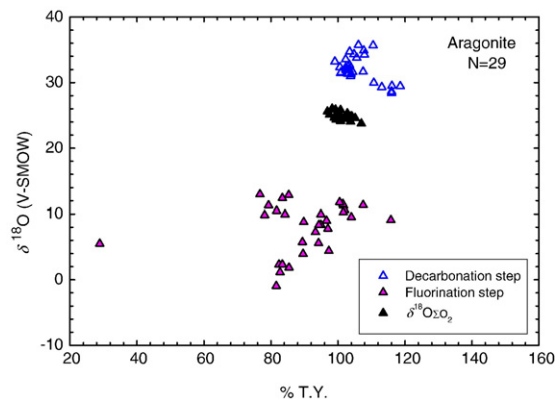


Fig. 2. Plot of  $\delta^{18}\text{O}_{\text{V-SMOW}}$  vs. percent theoretical oxygen yield (% T.Y.) for aragonite, including analytical data for each of the two components of a two-step analytical process. Twenty nine analyses of total oxygen isotope composition of Ara-Nat-ST-1 were carried out.

and 4) released from the decarbonation step is always isotopically heavier than the total oxygen isotope composition ( $\delta^{18}\text{O}_{\Sigma\text{O}_2}$ ) of the original carbonate mineral, regardless of the % T.Y. In contrast, the  $\delta^{18}\text{O}$  value of the O<sub>2</sub> extracted from the fluorination step is always lower than the total oxygen isotope composition of the carbonate solid. It has been reported that when the decarbonation process is not carried out in vacuum, but under a He pressure of 3 bar for much shorter heating times and higher temperatures (e.g., Sharp et al., 2003), the  $\delta^{18}\text{O}$  value of the released CO<sub>2</sub> is identical to value of  $\delta^{18}\text{O}_{\Sigma\text{O}_2}$  (i.e., no fractionation).

##### 4.2. Total oxygen isotope compositions and analytical precision of the two-step method

The oxygen isotope compositions of the O<sub>2</sub>-bearing gases obtained from calcite or aragonite during each step (i.e., thermal decarbonation and fluorination) are not, individually, very reproducible (Figs. 1 and 2). The average  $\delta^{18}\text{O}$  values of the O<sub>2</sub>-bearing gases released from calcite upon decarbonation and fluorination are 13.23‰ ( $\pm 1.08\%$ ) and  $-5.88\%$  ( $\pm 2.26\%$ ), respectively (Table 3), whereas they are 32.07‰ ( $\pm 1.94\%$ ) and 8.01‰ ( $\pm 3.70\%$ ), respectively, for aragonite (Table 4). The poor reproducibility of the individual decarbonation and fluorination steps, also noted by McCrea (1950), prevented him from developing a decarbonation process as a routine protocol to determine the isotopic composition of carbonate minerals. Sharma and Clayton (1965) later commented that the poor reproducibility of McCrea (1950)'s experimental protocol might have resulted from variations of the temperature of decarbonation, and reported the temperature dependence of the oxygen isotope compositions of the CO<sub>2</sub> released



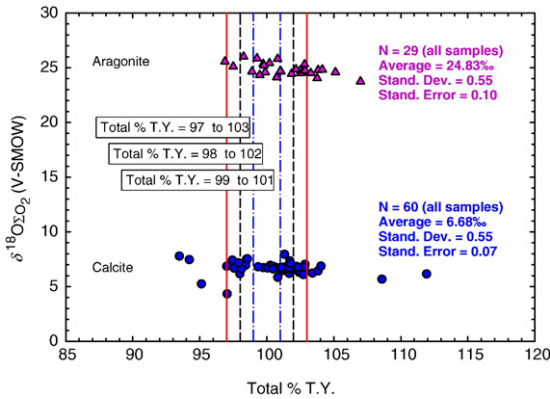


Fig. 3. A diagram showing the effect of applying a data selection criterion to the value of  $\delta^{18}\text{O}_{\Sigma\text{O}_2}$  for both the Calcite H and Ara–Nat–ST–1 samples. The best achievable analytical precision ( $1\sigma$ ) for the two-step method carried out in a conventional silicate extraction line in this study is  $\pm 0.55\%$ .

from the decarbonation of dolomite with a mean deviation of less than  $\pm 0.09\%$ . The oxygen isotope data reported in this study were all obtained from decarbonation at a constant temperature of 600 °C ( $\pm 10$  °C, monitored by a thermocouple positioned at the hot spot on the outside wall of the reactor) and, yet relatively large analytical standard deviations were found ( $\pm 1.08\%$ , calcite;  $\pm 1.94\%$ , aragonite). Nonetheless, when  $\delta^{18}\text{O}_{\Sigma\text{O}_2}$  values of the carbonates are calculated using the weighted averaging method (Eq. (2); see above), the final results are far more reproducible.

Fig. 3 and Table 5 show how the application of a data selection criterion based on % T.Y. reduces the number of data considered, the average value of  $\delta^{18}\text{O}_{\Sigma\text{O}_2}$ , the associated standard deviation ( $\sigma$ ), and the standard error ( $s_e = \sigma/\sqrt{n}$ ). For calcite, the smaller the % T.Y. range, the smaller the standard deviation, whereas the average value of  $\delta^{18}\text{O}_{\Sigma\text{O}_2}$  does not change significantly as the

data selection criterion is narrowed. In the case of aragonite, the best analytical precision (i.e., the second smallest standard deviation and the smallest standard error) is obtained when all the data are included. Based on all of the data in this study, the average values of  $\delta^{18}\text{O}_{\Sigma\text{O}_2}$  for calcite and aragonite are, respectively, 6.68‰ ( $\sigma = 0.55\%$  and  $s_e = 0.07\%$ ) and 24.83‰ ( $\sigma = 0.55\%$  and  $s_e = 0.10\%$ ).

The carbon isotope composition of the  $\text{CO}_2$  released from the decarbonation step ( $\delta^{13}\text{C}_{(\text{Dec.})}$ ) should, ideally, be the same as the  $\delta^{13}\text{C}$  value of the acid liberated  $\text{CO}_2$  of the same carbonate. In contrast, a significant variability (i.e.,  $< 1\%$ ) of the  $\delta^{13}\text{C}_{(\text{Dec.})}$  from the expected value was observed, but a screening test revealed that its variability did not affect, within the uncertainty of our measurements, the average value of  $\delta^{18}\text{O}_{\Sigma\text{O}_2}$  for either calcite or aragonite.

#### 4.3. Temperature dependence of the oxygen isotope composition of acid liberated $\text{CO}_2$

The oxygen and carbon isotope compositions of the  $\text{CO}_2$  evolved from the reaction of calcite or aragonite with phosphoric acid at three temperatures (i.e., 25, 50, and 75 °C) are presented in Table 6. Given that the carbon isotope composition of  $\text{CO}_2$  from the phosphoric acid reaction is independent of the temperature of reaction (e.g., Swart et al., 1991; Böttcher, 1996) and a typical analytical precision for its mass spectrometric measurement is 0.02‰, several analyses for which the  $\delta^{13}\text{C}$  (marked with superscripted “a” in Table 6) deviated by more than  $1\sigma$  (0.06‰ for calcite and 0.08‰ for aragonite) from the average values ( $-4.62\%$  for calcite and  $-12.88\%$  for aragonite) were excluded from the fractionation calculations in the following sections.

The temperature dependence of  $\delta^{18}\text{O}_{\text{CO}_2(\text{ACID})}$  determined in this study is  $-0.035$  and  $-0.034\%$ /°C for

Table 5

The number of selected individual analyses, averages, the corresponding standard deviations, and standard errors of total oxygen isotope compositions for calcite and aragonite

Total % T.Y.	Calcite				Aragonite			
	Number	Average <sup>a</sup>	$\sigma$	$s_e$	Number	Average <sup>a</sup>	$\sigma$	$s_e$
All samples	60	6.68	0.55	0.07	29	24.83	0.55	0.10
97 to 103	52	6.71	0.49	0.07	22	24.90	0.52	0.11
98 to 102	35	6.78	0.38	0.06	14	24.95	0.62	0.17
99 to 101	11	6.67	0.28	0.08	10	24.95	0.62	0.20

% T.Y. = % theoretical yield.

$\sigma$  = Standard deviation.

$s_e$  = Standard error.

Both the average and standard deviations change according to the data selection criterion, as discussed in text.

<sup>a</sup> Denotes an average of  $\delta^{18}\text{O}_{\Sigma\text{O}_2}$ .

Table 6

Carbon and oxygen isotope compositions of CO<sub>2</sub> from the reaction of phosphoric acid with calcite (Calcite H) and aragonite (Ara–Nat–ST–1) at three temperatures

ID	Sample	Temperature (°C)	$\delta^{18}\text{O}_{\text{CO}_2(\text{ACID})}$	$\delta^{13}\text{C}$
<i>Calcite</i>				
CII-38-4	Calcite H	25	17.10	−4.67
CII-38-5	Calcite H	25	17.11	−4.65
CII-40-5	Calcite H	25	17.03	−4.68
CII-40-6	Calcite H	25	17.09	−4.65
CII-41-4	Calcite H	25	16.98	−4.58
CII-41-5	Calcite H	25	16.98	−4.72
CII-50-3 <sup>a</sup>	Calcite H	25	17.27	−4.52
CII-50-4 <sup>a</sup>	Calcite H	25	17.32	−4.52
CII-51-4 <sup>a</sup>	Calcite H	25	17.28	−4.54
CII-51-5 <sup>a</sup>	Calcite H	25	17.33	−4.51
CII-49-4	Calcite H	50	16.07	−4.65
CII-49-5	Calcite H	50	16.10	−4.62
CII-49-6	Calcite H	50	16.15	−4.66
CII-49-7	Calcite H	50	16.11	−4.66
CII-49-11	Calcite H	75	15.29	−4.65
CII-49-12	Calcite H	75	15.32	−4.62
CII-50-1	Calcite H	75	15.30	−4.64
CII-50-2	Calcite H	75	15.31	−4.63
CII-52-1	Calcite H	75	15.32	−4.63
CII-52-2	Calcite H	75	15.27	−4.66
<i>Aragonite</i>				
CII-38-1	Ara–Nat–ST–1	25	35.70	−12.96
CII-38-2	Ara–Nat–ST–1	25	35.74	−12.95
CII-38-3	Ara–Nat–ST–1	25	35.79	−12.96
CII-41-2	Ara–Nat–ST–1	25	35.69	−12.96
CII-41-3	Ara–Nat–ST–1	25	35.68	−12.93
CII-50-5 <sup>a</sup>	Ara–Nat–ST–1	25	35.98	−12.73
CII-50-6 <sup>a</sup>	Ara–Nat–ST–1	25	36.04	−12.74
CII-51-6 <sup>a</sup>	Ara–Nat–ST–1	25	35.91	−12.77
CII-51-7 <sup>a</sup>	Ara–Nat–ST–1	25	35.81	−12.77
CII-49-1	Ara–Nat–ST–1	50	34.72	−12.94
CII-49-2	Ara–Nat–ST–1	50	34.77	−12.91
CII-49-3	Ara–Nat–ST–1	50	34.74	−12.92
CII-49-8	Ara–Nat–ST–1	75	34.03	−12.90
CII-49-9	Ara–Nat–ST–1	75	34.00	−12.92
CII-49-10	Ara–Nat–ST–1	75	34.03	−12.88
CII-52-2	Ara–Nat–ST–1	75	34.07	−12.85

<sup>a</sup>Samples excluded as outliers.

calcite and aragonite, respectively. Our values are statistically identical to each other and lie within the range (i.e., −0.037 to −0.026) of previously published values (e.g., Sharma and Sharma, 1969; Swart et al., 1991; Böttcher, 1996; Das Sharma et al., 2002). The analytical precision of the conventional off-line extraction protocols of McCrea (1950) is typically on the order of  $\pm 0.07\%$ . Thus, this uncertainty would correspond to a  $\pm 2$  °C difference in the reaction temperature with phosphoric acid.

#### 4.4. Acid fractionation factors for calcite

The oxygen isotope compositions of the international carbonate reference materials (i.e., NBS 18 and NBS 19) have never been measured directly, but, rather, estimated based upon the widely accepted acid fractionation factor, 1.01025 (or  $1000\ln\alpha_{\text{CO}_2(\text{ACID})-\text{Calcite}} = 10.20$ ) for calcite at 25 °C (Coplen et al., 1983). The value of 10.20 was originally determined by the low temperature BrF<sub>5</sub> reaction, and a very limited number of replicate analyses (i.e., 4 and 2 for calcite and aragonite, respectively; Sharma and Clayton, 1965). Only three additional studies (Kim and O'Neil, 1997; Land, 1980; Das Sharma et al., 2002) have reported measurements of the calcite acid fractionation factor, and the results (Table 1) differ by −0.1 to +0.32‰ from the value determined for a natural calcite by Sharma and Clayton (1965). Inasmuch as the standard deviation of the oxygen isotope data obtained by the two-step method in this study ( $\sigma = 0.55\%$ ) is larger than the existing disparity of 0.43‰, the discrepancies in  $1000\ln\alpha_{\text{CO}_2(\text{ACID})-\text{carbonate}}$  between the current and previous studies (e.g., 10.25 compared to 10.10, 10.20, 10.44, and 10.52; Table 1) are not significant. Nevertheless, it should be emphasized that our new determinations of acid fractionation factors for calcite are the most robust and statistically reliable reported to date (Table 5), supporting their continued use with greater confidence.

The acid fractionation factors for calcite, determined at three temperatures in this study, are summarized in Table 7. As the temperature of the reaction increases, the per mil acid fractionation becomes smaller, decreasing from a value of  $1000\ln\alpha_{\text{CO}_2(\text{ACID})-\text{Calcite}} = 10.25$  at 25 °C to 8.52 at 75 °C. The temperature dependence of the acid fractionation factor for calcite shown in Fig. 4 can be represented over the temperature range of 25 to 75 °C by:

$$1000\ln\alpha_{\text{CO}_2(\text{ACID})-\text{Calcite}} = 3.59(10^3/T) - 1.79 \quad (3)$$

where  $\alpha_{\text{CO}_2(\text{ACID})-\text{Calcite}}$  is the phosphoric acid fractionation factor for calcite, and  $T$  is in kelvin.

#### 4.5. Acid fractionation factors for aragonite

The acid fractionation factor for aragonite at 25 °C has been reported only twice, and without temperature dependence. The  $1000\ln\alpha_{\text{CO}_2(\text{ACID})-\text{carbonate}}$  value for aragonite was initially determined by Sharma and Clayton (1965), and later revised by Friedman and O'Neil (1977) to 10.29 ( $\pm 0.06$ ;  $n=2$ ) at 25 °C. More recently, Kim and O'Neil (1997) proposed a value of 11.01 ( $\pm 0.01$ ;  $n=2$ ).

Table 7

Acid fractionation factors ( $\alpha_{\text{CO}_2(\text{ACID})\text{-carbonate}}$ ) and  $1000\ln\alpha_{\text{CO}_2(\text{ACID})\text{-carbonate}}$  values for calcite and aragonite at 25, 50, and 75 °C determined in this study, as well as the values for  $\delta^{18}\text{O}_{\text{CO}_2(\text{ACID})}$  and  $\delta^{18}\text{O}_{\Sigma\text{O}_2}$

Mineral/temperature	$\delta^{18}\text{O}_{\text{CO}_2(\text{ACID})}$	$\sigma(n)$	$s_e$	$\delta^{18}\text{O}_{\Sigma\text{O}_2}$	$\sigma(n)$	$s_e$	$\alpha_{\text{CO}_2(\text{ACID})\text{-carbonate}}$	$1000\ln\alpha$
Calcite								
25 °C	17.05	0.05 (6)	0.02	6.68	0.55 (60)	0.07	1.01030	10.25
50 °C	16.11	0.03 (4)	0.02	6.68	0.55 (60)	0.07	1.00937	9.33
75 °C	15.30	0.02 (6)	0.01	6.68	0.55 (60)	0.07	1.00856	8.52
Aragonite								
25 °C	35.72	0.04 (5)	0.02	24.83	0.55 (29)	0.10	1.01063	10.57
50 °C	34.74	0.02 (3)	0.01	24.83	0.55 (29)	0.10	1.00967	9.62
75 °C	34.03	0.02 (4)	0.01	24.83	0.55 (29)	0.10	1.00898	8.94

$\sigma$  = Standard deviation.

$n$  = Number of analysis.

$s_e$  = Standard error.

Results of this study suggest a value of  $1000\ln\alpha_{\text{CO}_2(\text{ACID})\text{-carbonate}}$  at 25 °C for aragonite of 10.57,  $\sim 0.3\%$  larger than the value proposed by Friedman and O'Neil (1977) and  $\sim 0.4\%$  smaller than the value reported by Kim and O'Neil (1997). Still, previous estimates fall within the range of uncertainty of our measurements ( $\sigma=0.55\%$ ; Tables 5 and 7). The proposed  $1000\ln\alpha_{\text{CO}_2(\text{ACID})\text{-Aragonite}}$  values (Tables 5 and 7) in this study are statistically firmer than previously reported values (e.g., standard error ( $s_e$ ) of  $0.10\%$  for  $\delta^{18}\text{O}_{\Sigma\text{O}_2}$  analysis) and provide confidence in their use.

The acid fractionation factors for aragonite at 25, 50, and 75 °C, obtained from numerous total oxygen isotope analyses of a single aragonite specimen in this study, are presented in Table 7. Like that for calcite, the acid fractionation for aragonite becomes smaller as the reaction temperature increases. For example, from a

$1000\ln\alpha_{\text{CO}_2(\text{ACID})\text{-Aragonite}}$  value of 10.57 at 25 °C, it decreases to 9.62 at 50 °C and, further, to 8.94 at 75 °C.

Based on our determinations at three temperatures, the temperature dependence of the acid fractionation for aragonite between 25 and 75 °C can be expressed as:

$$1000\ln\alpha_{\text{CO}_2(\text{ACID})\text{-Aragonite}} = 3.39(10^3/T) - 0.83 \quad (4)$$

Fig. 4 shows that the slope of the temperature dependence equation for aragonite ( $3.39\pm 0.17$ ) is practically identical to that for calcite ( $3.59\pm 0.03$ ), but the intercepts of the newly proposed equations for calcite and aragonite are significantly different.

In most stable isotope laboratories equipped with an automated carbonate analysis system (e.g., Finnigan™ Kiel device, or GV instruments MultiCarb™ system), aragonite samples are reacted with phosphoric acid at higher temperatures (e.g., 75 or 90 °C) to facilitate processing efficiency. However, until now, acid fractionation factors for aragonite were not available for these higher temperatures (e.g., 50 or 75 °C), and the oxygen isotope data were, irrespective of the sample mineralogy, ultimately normalized to the isotope ratios of two international calcite reference materials (i.e., NBS 18 and NBS 19), either directly by joint processing, or indirectly via laboratory standards. This practice might be inconsequential in the resolution of certain geochemical problems, but the error introduced by this substitution becomes significant in the matter of standards, absolute isotopic ratios, and relating oxygen isotope analyses of carbonates to those of water, silicates and oxides, or in comparing various data sets (e.g., by different laboratories) acquired using different reaction temperatures, or other (e.g., manual) extraction methods. Consequently, it is recommended that an acid fractionation factor for aragonite at the temperature of reaction be applied to the

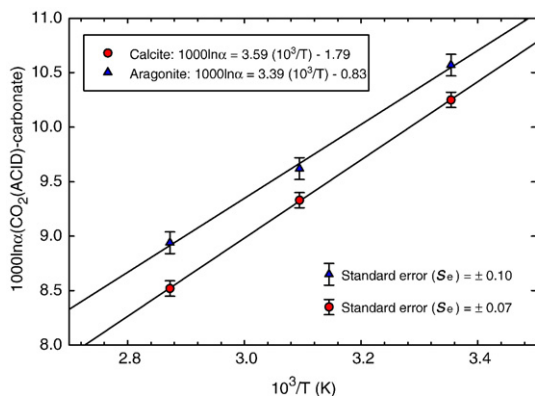


Fig. 4. Relation between  $1000\ln\alpha_{\text{CO}_2(\text{ACID})\text{-carbonate}}$  for calcite and aragonite and temperature. Two new equations for the temperature dependence of the acid fractionation factor for calcite and aragonite are also presented.

calculation of the oxygen isotope composition of the CO<sub>2</sub> evolved from the reaction of aragonite with phosphoric acid in order to ensure accurate reporting of the oxygen isotope compositions of the aragonite samples.

## 5. Conclusions

Statistically reliable mineral-specific acid fractionation factors and their temperature dependence are required in order to determine the accurate oxygen isotope composition of a carbonate mineral. In spite of its fundamental importance to stable isotope geochemistry, very few studies have been conducted to determine the acid fractionation factors for CaCO<sub>3</sub>. Because available published values differ significantly, new determinations of the acid fractionation factors for calcite and aragonite were carried out by combining results from thermal decarbonation and the reaction of residual CaO with BrF<sub>5</sub>. Based upon this two-step method and the phosphoric acid reactions carried out at three temperatures, two new equations for the temperature dependence of the acid fractionation factor for calcite and aragonite between 25 and 75 °C are proposed:

$$1000\ln\alpha_{\text{CO}_2(\text{ACID})-\text{Calcite}} = 3.59(10^3/T) - 1.79$$

$$1000\ln\alpha_{\text{CO}_2(\text{ACID})-\text{Aragonite}} = 3.39(10^3/T) - 0.83$$

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## References

- Böttcher, M.E., 1996. <sup>18</sup>O/<sup>16</sup>O and <sup>13</sup>C/<sup>12</sup>C fractionation during the reaction of carbonates with phosphoric acid: effects of cationic substitution and reaction temperature. *Isot. Environ. Health Stud.* 32 (2–3), 299–305.
- Carothers, W.W., Adami, L.H., Rosenbauer, R.J., 1988. Experimental oxygen isotope fractionation between siderite–water and phosphoric acid liberated CO<sub>2</sub>–siderite. *Geochim. Cosmochim. Acta* 52 (10), 2445–2450.
- Coplen, T.B., Kendall, C., Hopple, J., 1983. Comparison of stable isotope reference samples. *Nature* 302 (5905), 236–238.
- Das Sharma, S., Patil, D.T., Gopalan, K., 2002. Temperature dependence of oxygen isotope fractionation of CO<sub>2</sub> from magnesite–phosphoric acid reaction. *Geochim. Cosmochim. Acta* 66 (4), 589–593.
- Emiliani, C., Shackleton, N.J., 1974. The Brunhes epoch: isotopic paleotemperatures and geochronology. *Science* 183 (4124), 511–514.
- Friedman, I., O'Neil, J.R., 1977. Compilation of stable isotope fractionation factors of geochemical interest. In: Fleischer, M. (Ed.), *Data of Geochemistry Sixth Edition*. U.S. Government Printing Office, Washington. U.S. Government Printing Office, Washington.
- Gilg, H.A., Struck, U., Vennemann, T., Boni, M., 2003. Phosphoric acid fractionation factors for smithsonite and cerussite between 25 and 72 °C. *Geochim. Cosmochim. Acta* 67 (21), 4049–4055.
- Harris, D.C., 2003. *Quantitative chemical analysis*. W.H. Freeman and Co., New York. 744 pp.
- Kim, S.-T., O'Neil, J.R., 1997. Equilibrium and nonequilibrium oxygen isotope effects in synthetic carbonates. *Geochim. Cosmochim. Acta* 61 (16), 3461–3475.
- Klein, R.T., Lohmann, K.C., Thayer, C.W., 1996. Bivalve skeletons record sea-surface temperature and δ<sup>18</sup>O via Mg/Ca and <sup>18</sup>O/<sup>16</sup>O ratios. *Geology* 24 (5), 415–418.
- Land, L.S., 1980. The isotopic and trace element geochemistry of dolomite: the state of the art. In: Zenger, D.H., B., D.J., L., E.R. (Eds.), *SEPM special publication*, pp. 87–110.
- McCrea, J.M., 1950. On the isotopic chemistry of carbonates and a paleotemperature scale. *J. Chem. Phys.* 18, 849–853.
- Rosenbaum, J., Sheppard, S.M.F., 1986. An isotopic study of siderites, dolomites and ankerites at high temperatures. *Geochim. Cosmochim. Acta* 50 (6), 1147–1150.
- Sharma, T., Clayton, R.N., 1965. Measurement of O<sup>18</sup>/O<sup>16</sup> ratios of total oxygen of carbonates. *Geochim. Cosmochim. Acta* 29 (12), 1347–1353.
- Sharma, S.K., Sharma, T., 1969. Oxygen isotope fractionation factor between CO<sub>2</sub> and CO<sub>3</sub><sup>2-</sup>. *Int. J. Mass Spectrom. Ion Phys.* 2, 367–371.
- Sharp, Z.D., Papike, J.J., Durakiewicz, T., 2003. The effect of thermal decarbonation on stable isotope compositions of carbonates. *Am. Mineral.* 88 (1), 87–92.
- Sincich, T., Levine, D.M., Stephan, D., 2002. *Practical statistics by example using Microsoft Excel and MINITAB*. Prentice Hall, Upper Saddle River, N.J. 789 pp.
- Swart, P.K., Burns, S.J., Leder, J.J., 1991. Fractionation of the stable isotopes of oxygen and carbon in carbon-dioxide during the reaction of calcite with phosphoric acid as a function of temperature and technique. *Chem. Geol.* 86 (2), 89–96.
- Taylor, B.E., 2004. Fluorination methods in stable isotope analysis. In: de Groot, P.A. (Ed.), *Handbook of Stable Isotope Analytical Techniques vol. 1*, 400–472.
- Wachter, E.A., Hayes, J.M., 1985. Exchange of oxygen isotopes in carbon dioxide–phosphoric acid systems. *Chem. Geol.* 52 (3–4), 365–374.