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## Phosphoric acid fractionation factors for smithsonite and cerussite between 25 and 72°C

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**Abstract**—The intramolecular kinetic oxygen isotope fractionation between CO<sub>2</sub> and CO<sub>3</sub><sup>2-</sup> during reaction of phosphoric acid with natural smithsonite (ZnCO<sub>3</sub>) and cerussite (PbCO<sub>3</sub>) has been determined between 25 and 72°C. While cerussite decomposes in phosphoric acid within a few hours at 25°C, smithsonite reacts very slowly with the acid at 25°C providing yields of CO<sub>2</sub> < 25% after 2 weeks. The low yields result in a low precision for oxygen isotope measurements of the acid-liberated CO<sub>2</sub> (±1.65‰, 1σ, n = 9). The yield and reproducibility of oxygen isotope values of the acid-liberated CO<sub>2</sub> from smithsonite can be improved, the latter to ~±0.15‰, by increasing the reaction temperature to 50°C for 12 h or to 72°C for 1 h. Our new phosphoric acid fractionation factor for natural cerussite at 25°C deviates significantly from a previously published value on synthetic material. The temperature dependence of the oxygen isotope fractionation factor, α between acid-liberated CO<sub>2</sub> and carbonate at 25 to 72°C is given by the following equations

$$1000\ln\alpha_{\text{CO}_2\text{-cerussite}}^{\text{phos}} = 5.13 (\pm 0.15) + 4.79 (\pm 0.15) \times 10^5/T^2$$

$$1000\ln\alpha_{\text{CO}_2\text{-smithsonite}}^{\text{phos}} = 3.96 (\pm 0.21) + 6.69 (\pm 0.22) \times 10^5/T^2$$

with temperature *T* in kelvin. A comparison with published equations of the form  $1000\ln\alpha_{\text{CO}_2\text{-carbonate}}^{\text{phos}} = A + B \times 10^5/T^2$  for other divalent metal carbonates shows that the factors *B* of slowly-reacting carbonates from the rhombohedral calcite group (magnesite, siderite, smithsonite and rhodochrosite) are very similar (6.7 ± 0.2) and distinct from those of fast-reacting minerals witherite, cerussite, and strontianite of the orthorhombic aragonite group (4.5 ± 0.3) and calcite (5.6 ± 0.1). These differences indicate a crystallographic control on the temperature dependence of the kinetic oxygen isotope fractionation between phosphoric acid liberated CO<sub>2</sub> and carbonate. Copyright © 2003 Elsevier Ltd

## 1. INTRODUCTION

Stable isotope compositions of carbonate minerals typically occurring in oxidation zones of sulfide ore deposits, such as azurite, malachite, cerussite, or smithsonite, may yield valuable information on the conditions of oxidation, especially on temperatures and types of fluids (e.g., Melchiorre et al., 1999, 2000, 2001; Boni et al., 2003). They are thus not only useful for research on ore genesis but also for paleoclimatic studies, recording conditions during weathering. Because of the recently increasing interest in the genesis of oxidized Zn-Pb-deposits, new studies related to stable isotope compositions of smithsonite (ZnCO<sub>3</sub>) and cerussite (PbCO<sub>3</sub>) are highly desirable (e.g., Melchiorre et al., 2001; Boni et al., 2003).

A prerequisite for the application of stable isotope geochemistry to interpretations of this type, however, is (1) knowledge of the isotope fractionation factors between minerals and water as a function of temperature and (2) accurate determination of the isotopic composition of the carbonate. Significant progress has been made in recent years with respect to the first problem with new experimental (Melchiorre et al., 1999, 2000, 2001) and semitheoretical calibrations (Zheng, 1999) of oxygen isotope fractionation between carbonate minerals and water. The second problem is less obvious, but becomes important when

relating oxygen isotope analyses of carbonates to those of water, silicates or oxides. The carbon dioxide used for mass spectrometric analysis is usually generated by reaction of carbonate minerals with anhydrous phosphoric acid (McCrea, 1950). This reaction involves a significant intramolecular kinetic oxygen isotope fractionation, of ~10‰ at 25°C, between the acid-liberated carbon dioxide and the carbonate mineral. The phosphoric acid fractionation factor defined as

$$\alpha_{\text{CO}_2\text{-carbonate}}^{\text{phos}} = \frac{(1000 + \delta^{18}\text{O}_{\text{phosphoric acid-liberated CO}_2})}{(1000 + \delta^{18}\text{O}_{\text{carbonate}})} \quad (1)$$

varies mainly as a function of cation composition of the carbonate (Sharma and Clayton, 1965; Rosenbaum and Sheppard, 1986) and reaction temperature (e.g., Sharma and Sharma, 1969a). Several studies have indicated that values of  $1000\ln\alpha_{\text{CO}_2\text{-carbonate}}^{\text{phos}}$  show a linear dependence with  $1/T^2$ , the slopes being different for various minerals (Sharma and Sharma, 1969a; Rosenbaum and Sheppard, 1986; Swart et al., 1991; Böttcher, 1996; Das Sharma et al., 2002). Thus, the temperature dependence of phosphoric acid fractionation factors has to be determined for every mineral individually (Böttcher, 1996).

Sharma and Clayton (1965) determined the phosphoric acid fractionation factors for a variety of divalent metal carbonates at 25°C including smithsonite and cerussite. The  $1000\ln\alpha$  values corrected later by R.N. Clayton (in Friedman and O'Neil,

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Table 1. Results of total oxygen isotope analyses of smithsonite SMG and cerussite CET including thermal decarbonatization (step I) and subsequent fluorination of the residues (step II). The runs SMG-L and CET-L include laser fluorination of the residue (average of 2 to 4 analyses).

Run	Step I (CO <sub>2</sub> )			Step II (O <sub>2</sub> )		Total	
	Yield ( $\mu\text{mol}/\text{mg}$ )	$\delta^{18}\text{O}_{\text{VSMOW}}$ (‰)	$\delta^{13}\text{C}_{\text{VPDB}}$ (‰)	Yield ( $\mu\text{mol}/\text{mg}$ )	$\delta^{18}\text{O}_{\text{VSMOW}}$ (‰)	Yield ( $\mu\text{mol}/\text{mg}$ )	$\delta^{18}\text{O}_{\text{VSMOW}}$ (‰)
<b>Smithsonite</b>							
SMG							
SMG-1	7.73	32.19	-1.94	3.88	13.72	11.61	26.02
SMG-2*	7.74	31.58	-2.12	3.43	15.42	11.17	26.62
SMG-3*	8.12	32.09	-1.86	3.15	14.33	11.27	27.13
SMG-4*	7.70	31.61	-2.08	2.65	15.44	10.35	27.47
SMG-L	8.15	27.18	-2.04	4.43	23.87	12.58	26.01
<b>SMG avg.* (n = 2)</b>			<b>-1.99</b>				<b>26.01</b>
<b>Cerussite CET</b>							
CET-1	3.26	23.52	-19.98	1.80	2.43	5.77	16.03
CET-2	3.25	22.70	-19.97	1.65	2.52	5.58	15.97
CET-L	4.09	18.82	-20.27	1.44	10.08	5.53	15.91
<b>CET avg. (n = 3)</b>			<b>-20.07 <math>\pm</math> 0.17</b>				<b>15.97 <math>\pm</math> 0.06</b>

avg. = average value, standard deviation  $\pm 1\sigma$ . avg.\* = average value excluding samples marked with \*. The theoretical CO<sub>2</sub> yields for smithsonite are 7.97  $\mu\text{mol}/\text{mg}$  (step I), 3.99  $\mu\text{mol}/\text{mg}$  (step II), and 11.96  $\mu\text{mol}/\text{mg}$  (total), and for cerussite 3.74  $\mu\text{mol}/\text{mg}$  (step I), 1.87  $\mu\text{mol}/\text{mg}$  (step II), and 5.61  $\mu\text{mol}/\text{mg}$  (total).

1977) are 11.24 for a smithsonite of unknown origin and 10.08 for a synthetic cerussite ("laboratory reagent"). We note that Kim and O'Neil (1997) detected differences in the phosphoric acid fractionation factor of  $> 2\text{‰}$  between commercial and laboratory synthesized otavite (CdCO<sub>3</sub>). Their new determinations of  $\alpha^{\text{phos}}$  for calcite, aragonite and witherite showed significant deviations from the values reported by Sharma and Clayton (1965). No data have been reported so far for the phosphoric acid fractionation of smithsonite and cerussite at temperatures  $> 25^\circ\text{C}$ . High reaction temperatures of 50 to 150°C are usually required for complete decarbonatization of some rhombohedral carbonates, such as magnesite, siderite, rhodochrosite, and smithsonite, that react slowly with phosphoric acid. At these elevated temperatures shorter reaction periods are required and they are also often employed in automated systems for isotope analysis of carbonates. Our preliminary investigations (Gilg et al., 2001) indicated that the acid decarbonatization reaction of natural smithsonite is very sluggish at 25°C and incomplete reaction yields result in a low precision of measured oxygen isotope compositions.

We, therefore, determined the temperature dependence of the phosphoric acid fractionation factors for natural smithsonite and cerussite between 25 and 72°C. Both a conventional off-line preparation system (McCrea, 1950) in combination with a dual-inlet mass spectrometer, as well as a new automated on-line system with a mass spectrometer operating in the continuous flow mode were used in this study.

## 2. SAMPLES AND EXPERIMENTAL METHODS

The smithsonite SMG was sampled from a 3-cm-thick and 10  $\times$  30 cm colloform crust of grayish white smithsonite on limestone from Minas de Gabilan, Asturias, Spain. The cerussite CET is a 2 cm large clear colorless crystal from the Tsumeb mine, Namibia. Both mineral specimens were provided by Dr. G. Grundmann from the mineral collection at Technische Universität München. The samples were crushed with an agate mortar to a grain size of  $< 200 \mu\text{m}$ . No phases other than smithsonite or cerussite, respectively, were detected in our samples using X-ray diffraction analysis. The chemical composition of SMG based on ICP-AES analyses (ISA- Jobin Yvon JY 38) indicates

almost pure smithsonite (Zn<sub>0.96</sub>Fe<sub>0.03</sub>Ca<sub>0.04</sub>Mg<sub>0.03</sub>CO<sub>3</sub>) with minor amounts ( $< 5 \text{ mol.}\%$ ) of siderite, calcite, and magnesite components in solid solution. We detected traces of Ba (540 ppm), Sr (290 ppm), Pb (55 ppm) and Mn (40 ppm) in smithsonite SMG. The cerussite CET is high purity PbCO<sub>3</sub> with only traces of Sr (20 ppm), Ba (10 ppm), Ca (6 ppm) and Fe (6 ppm).

Total oxygen isotope compositions of carbonates were determined using a conventional silicate extraction line at the University of Tübingen, according to a technique similar to that first described by Sharma and Clayton (1965). After a preheating of the Ni reaction vessels under vacuum at 550°C, 15 to 20 mg of the sample were loaded into the reaction vessels at room temperature and subsequently evacuated at 150°C for several hours. The samples were then heated with a resistance furnace to 550°C in isolated vessels and the thermally liberated CO<sub>2</sub> was collected after 12 h of reaction. Reaction yields and isotopic composition of CO<sub>2</sub> were measured (step I). The residues of the thermal decarbonatization reaction (mostly ZnO or PbO) left in the vessels were then reacted with BrF<sub>5</sub> at 550°C overnight to produce O<sub>2</sub>, which was converted to CO<sub>2</sub> by reaction with graphite, heated by a Pt-coil (step II). After measurement of the oxygen yield, the isotopic composition was measured with a Finnigan MAT 252 mass spectrometer. Because of poor reproducibility for the total oxygen isotope composition of smithsonite and a correlation between low oxygen yield, particularly for the fluorination step of ZnO, and  $\delta^{18}\text{O}$  value (Table 1), an alternative method, adapted after Rosenbaum and Shepard (1986), was also used. The same method was also used for cerussite. For this method, a weighed amount of carbonate was placed in a molybdenum foil capsule within a silica glass tube and evacuated for 12 h at 100°C. Thereafter, the smithsonite was slowly heated to 750°C while collecting the CO<sub>2</sub> in a liquid-nitrogen cooled U-trap. For smithsonite, most of the CO<sub>2</sub> was released at temperatures between 350 and 450°C, while for cerussite, the CO<sub>2</sub> release was between 250 and 400°C and the sample was heated to a maximum of 550°C as visible Pb condensed on the glass reaction tube when the sample was heated to temperatures  $> 550^\circ\text{C}$ . After CO<sub>2</sub> extraction, the residual oxide sample was weighed and the weight-loss used to determine the yield of CO<sub>2</sub>. The residual oxide was subsequently analyzed using a laser fluorination line with fluorine gas as reagent and a Pt sample tray (e.g., Sharp, 1990; Kasemann et al., 2001).

The conventional off-line preparation system for carbonates at Technische Universität München and Universität Tübingen involved reaction of  $\sim 10 \text{ mg}$  of the sample with 10 mL anhydrous phosphoric acid in an evacuated Y-shaped reaction vessel similar to that first described by McCrea (1950), or following the sealed vessel method of Swart et al. (1991). The reaction temperatures were controlled in a temperature

Table 2. Results from decarbonatization reactions of cerussite CET using phosphoric acid.

Extr. no.	Temp. (°C)	Time (h)	Yield (μmol/mg)	<i>n</i>	δ <sup>13</sup> C <sub>V-PDB</sub> (‰)	δ <sup>18</sup> O <sub>V-SMOW</sub> (‰)	α	1000lnα
TUM-3287	25	15	4.4	1	-19.98	26.86	1.01072	10.66
TUM-3288	25	15	5.1	1	-20.15	26.59	1.01045	10.40
TUM-3289	25	15	3.4	1	-20.05	26.69	1.01055	10.49
TUM-3290	25	15	3.4	1	-20.01	26.79	1.01065	10.60
TUM-3291	25	15	4.7	1	-20.00	26.79	1.01065	10.59
TUM-3292	25	15	3.4	1	-20.08	26.80	1.01066	10.60
TUM-3293	25	15	4.5	1	-20.03	26.73	1.01059	10.53
TUM-3294	25	15	3.3	1	-20.12	26.69	1.01055	10.49
TUM-3295	25	15	3.3	1	-20.05	26.72	1.01058	10.52
TUM-3296	25	15	3.5	1	-19.99	26.83	1.01068	10.63
TUM-CET	25	15	3.7	1	-19.95	26.83	1.01069	10.63
<b>Average</b>	<b>25</b>			<b>11</b>	<b>-20.04</b>	<b>26.75</b>	<b>1.01061</b>	<b>10.56</b>
<b>Std. dev.</b>	<b>25</b>			<b>11</b>	<b>±0.06</b>	<b>±0.08</b>	<b>±0.00008</b>	<b>±0.08</b>
TÜB-CETa	50	5	4.0	1	-19.92	25.98	1.00985	9.81
TÜB-CETb	50	5	3.9	1	-19.92	25.81	1.00968	9.64
TÜB-CETc	50	5	4.0	1	-19.92	25.89	1.00976	9.72
<b>Average</b>	<b>50</b>			<b>3</b>	<b>-19.91</b>	<b>25.89</b>	<b>1.00977</b>	<b>9.72</b>
<b>Std. dev.</b>	<b>50</b>			<b>3</b>	<b>±0.00</b>	<b>±0.09</b>	<b>±0.00009</b>	<b>±0.08</b>
<b>TÜB-CETd</b>	<b>70</b>	<b>2</b>	<b>4.2</b>	<b>1</b>	<b>-19.91</b>	<b>25.47</b>	<b>1.00935</b>	<b>9.31</b>
U-CET-1	72	1.5		1	-19.93	25.23	1.00912	9.08
U-CET-2	72	1.5		1	-19.97	25.13	1.00902	8.98
U-CET-3	72	1.5		1	-20.05	25.09	1.00898	8.94
U-CET-4	72	1.5		1	-19.88	25.34	1.00922	9.18
U-CET-5	72	1.5		1	-20.01	25.26	1.00915	9.11
U-CET-6	72	1.5		1	-19.93	25.28	1.00916	9.12
<b>Average</b>	<b>72</b>			<b>6</b>	<b>-19.96</b>	<b>25.22</b>	<b>1.00911</b>	<b>9.12</b>
<b>Std. dev.</b>	<b>72</b>			<b>6</b>	<b>±0.06</b>	<b>±0.09</b>	<b>±0.00009</b>	<b>±0.09</b>

controlled water bath at 25 or 50°C (±1°C). Reaction times varied from overnight to 2 weeks. Acid-liberated CO<sub>2</sub> was purified using an ethanol-liquid nitrogen mixture (-100°C) and a liquid nitrogen trap (-196°C). Following manometric measurement of the CO<sub>2</sub> yield, the gas was isolated into 6-mm (o.d.) glass tubes and transferred to the Finnigan MAT 251 (München) or MAT 252 (Tübingen) dual-inlet mass spectrometer for isotopic measurements calibrated using the international standards NBS-18 and NBS-19, and V-SMOW.

Stable isotope analyses at the isotope laboratory of the Bayerische Staatssammlung für Paläontologie were performed with an automated Thermo/Finnigan online preparation device "Gas Bench II" connected to a Thermo/Finnigan Delta plus IRMS using a continuous flow mode (Révész and Landwehr, 2002). Samples (~100 μg) were treated with a few milliliters of anhydrous phosphoric acid in a helium (>99.996 vol.%) atmosphere in individual reaction tubes sealed with a septum. The reaction temperature was kept constant at 72°C. Reaction times varied between 90 and 210 min.

The isotopic compositions are reported as δ-values in per mil relative to V-SMOW for oxygen and V-PDB for carbon.

### 3. RESULTS

#### 3.1. Cerussite

Total oxygen isotope determinations of cerussite CET using the conventional oxygen isotope line and the laser-based extraction system yielded consistent results with a δ<sup>18</sup>O<sub>total</sub> of 15.97 ± 0.06‰ (1σ, *n* = 3) (Table 1). The decarbonatization reaction of cerussite with phosphoric acid at 25°C was complete after few hours. The acid-liberated CO<sub>2</sub> of natural cerussite CET gave a δ<sup>18</sup>O value of 26.75 ± 0.08‰ (1σ, *n* = 11) at 25°C (Table 2). A 1000lnα<sup>phos</sup> value of 10.56 was calculated for cerussite at 25°C. Our new value is higher than that determined by Sharma and Clayton (1965) on laboratory reagent PbCO<sub>3</sub> (10.08). Decarbonatization experiments using phospho-

ric acid performed at 50 and 72°C yielded 1000lnα<sup>phos</sup> values of 9.72 and 9.12, respectively (Table 2). A single determination at 70°C gave a 1000lnα<sup>phos</sup> value of 9.31. The errors of the 1000lnα<sup>phos</sup> values are estimated at ±0.2. Previous studies (Rosenbaum and Sheppard, 1986; Böttcher, 1996; Das Sharma et al., 2002) suggested that 1000lnα<sup>phos</sup> values of carbonates vary linearly as a function of 1/*T*<sup>2</sup>:

$$1000\ln\alpha_{\text{CO}_2\text{-carbonate}}^{\text{phos}} = A + B \times 10^5/T^2. \quad (2)$$

Fitting 21 individual 1000lnα<sup>phos</sup> values for cerussite that were calculated from each experiment given in Table 2 to such a function, the following equation is obtained for the temperature range between 25 and 72°C with temperature *T* in Kelvin:

$$1000\ln\alpha_{\text{CO}_2\text{-cerussite}}^{\text{phos}} = 5.13 (\pm 0.15) + 4.79 (\pm 0.15) \times 10^5/T^2. \quad (3)$$

#### 3.2. Smithsonite

The results of four total oxygen isotope determinations of SMG using the conventional oxygen extraction line are given in Table 1. The data display significant scatter in both total carbon dioxide yields (10.35–11.61 μmol/mg) and total δ<sup>18</sup>O values (26.02–27.47‰). The theoretical total CO<sub>2</sub> yield for smithsonite is 11.96 μmol/mg. There is an inverse correlation (*r* = -0.85) between total CO<sub>2</sub> yields and total delta values in our data suggesting that either incomplete reaction or variable contamination with an oxygen-poor phase is responsible for the high δ<sup>18</sup>O values. The following observations have to be considered. No phases other than smithsonite were detected in the

Table 3. Results from decarbonatization reactions of smithsonite SMG using phosphoric acid.

Extr. no.	Temp. (°C)	Time (h)	Yield ( $\mu\text{mol}/\text{mg}$ )	<i>n</i>	$\delta^{13}\text{C}_{\text{VPDB}}$ (‰)	$\delta^{18}\text{O}_{\text{VSMOW}}$ (‰)	$\alpha$	1000ln $\alpha$
TUM-3111a <sup>a</sup>	25	15	0.3	1	-2.47 <sup>a</sup>	34.52 <sup>a</sup>		
TUM-3112 <sup>a</sup>	25	120	2.0	1	-2.57 <sup>a</sup>	36.15 <sup>a</sup>		
TUM-3237	25	120	1.6	1	-2.08	37.88	1.01157	11.50
TUM-3238	25	120	1.5	1	-2.08	37.98	1.01167	11.60
TUM-3239	25	120	1.6	1	-2.07	37.71	1.01140	11.34
TUM-3240	25	120	1.5	1	-2.17	37.83	1.01152	11.45
TUM-3113	25	120	1.8	1	-2.25	37.50	1.01120	11.14
TUM-3111b	25	120	1.5	1	-2.19	37.87	1.01156	11.49
TUM-3160 <sup>a</sup>	25	330	2.0	1	-3.26 <sup>a</sup>	33.63 <sup>a</sup>		
<b>Average</b>	<b>25</b>			<b>9</b>	<b>-2.35</b>	<b>36.79</b>		
<b>Std. dev.</b>	<b>25</b>			<b>9</b>	<b>±0.38</b>	<b>±1.65</b>		
<b>Average<sup>a</sup></b>	<b>25</b>			<b>6</b>	<b>-2.14</b>	<b>37.80</b>	<b>1.01149</b>	<b>11.42</b>
<b>Std. dev.<sup>a</sup></b>	<b>25</b>			<b>6</b>	<b>±0.07</b>	<b>±0.17</b>	<b>±0.00016</b>	<b>±0.16</b>
TÜB-SMGa	50	5	6.0	1	-2.11	36.71	1.01043	10.37
TÜB-SMGb	50	5	6.2	1	-2.13	36.91	1.01062	10.57
TUM-3104	50	15	3.0	1	-2.12	36.80	1.01052	10.46
TUM-3105	50	15	2.3	1	-2.21	36.84	1.01056	10.50
TUM-3106	50	15	3.1	1	-2.11	36.77	1.01049	10.43
TUM-3108	50	15	2.9	1	-2.18	36.71	1.01043	10.37
TUM-3120	50	120	6.9	1	-2.03	36.55	1.01027	10.22
TUM-3121	50	120	6.1	1	-2.14	36.99	1.01070	10.64
TUM-3122	50	120	6.9	1	-2.12	36.91	1.01062	10.57
<b>Average</b>	<b>50</b>			<b>9</b>	<b>-2.13</b>	<b>36.80</b>	<b>1.01052</b>	<b>10.46</b>
<b>Std. dev.</b>	<b>50</b>			<b>9</b>	<b>±0.05</b>	<b>±0.13</b>	<b>±0.00013</b>	<b>±0.13</b>
U-SMG-1a	72	1.5		1	-2.43	35.90	1.00964	9.59
U-SMG-1b	72	1.5		1	-2.13	35.99	1.00973	9.68
U-SMG-1c	72	1.5		1	-2.14	35.85	1.00959	9.54
U-SMG-1d	72	1.5		1	-2.16	35.82	1.00956	9.52
U-SMG-1e	72	1.5		1	-2.33	35.75	1.00949	9.45
U-SMG-1f	72	1.5		1	-2.16	35.72	1.00946	9.42
U-SMG-2a	72	1.5		1	-2.08	35.85	1.00959	9.54
U-SMG-2b	72	1.5		1	-2.01	35.94	1.00968	9.63
U-SMG-2c	72	1.5		1	-2.34	35.97	1.00971	9.66
U-SMG-3a	72	2.5		1	-2.14	35.92	1.00966	9.61
U-SMG-3b	72	2.5		1	-2.34	35.81	1.00955	9.51
U-SMG-3c	72	2.5		1	-2.50	35.74	1.00948	9.44
U-SMG-4a	72	3.5		1	-2.13	35.72	1.00946	9.42
U-SMG-4b	72	3.5		1	-2.11	35.84	1.00958	9.54
U-SMG-4c	72	3.5		1	-2.29	35.81	1.00955	9.51
<b>Average</b>	<b>72</b>			<b>15</b>	<b>-2.22</b>	<b>35.84</b>	<b>1.00958</b>	<b>9.54</b>
<b>Std. dev.</b>	<b>72</b>			<b>15</b>	<b>±0.14</b>	<b>±0.09</b>	<b>±0.00009</b>	<b>±0.09</b>

<sup>a</sup> Values excluded as outliers; average values and standard deviations (std. dev.) excluding marked outliers.

sample by XRD analysis. The CO<sub>2</sub> yields from the thermal decarbonatization step I (7.70–8.12  $\mu\text{mol}/\text{mg}$ ) are consistent with the theoretical decarbonatization yield of 7.97  $\mu\text{mol}/\text{mg}$  for smithsonite and both  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values of CO<sub>2</sub> from step I have only relatively minor scatter ( $\pm 0.3\%$ ). In contrast,  $\delta^{18}\text{O}$  values of the fluorination step II are highly variable ( $\pm 0.85\%$ ) and low oxygen yields are indicated for experiments with high  $\delta^{18}\text{O}$  values. Johnson et al. (1990) reported sluggish reaction of natural zincite (ZnO) with BrF<sub>5</sub> even at 650°C. However, in their samples they did not detect a correlation between oxygen isotope composition and yield, suggesting that no significant isotope fractionation took place as a result of partial reactions. Nonetheless, we suspect that incomplete fluorination of the thermal decarbonatization residues (step II) is responsible for the high total  $\delta^{18}\text{O}$  values relative to the runs with higher yields. The oxygen isotope determination using the laser extraction system (SMG-L) gave a much better reproducibility of  $\delta^{18}\text{O}$  values of the decarbonatization residue ZnO ( $\pm 0.26\%$ ,  $n = 4$ ) than with the conventional extraction system

( $\pm 0.85\%$ ,  $n = 4$ ). We are aware of the high oxygen yields measured for ZnO using the former method. However, as the yields were consistent for four replicates, the amounts of samples used very small (1.5–1.8 mg) and the balance used for the samples not accurate to better than 0.2 mg with long stabilization times for such small masses, we believe that these high yields are a function of the lack of accuracy for the calibration used for yield measurements in that system. The total  $\delta^{18}\text{O}$  value of SMG-L (26.01‰) is very similar to the experiment with the highest yield using the conventional extraction line (SMG-1). Hence, we use the average total oxygen isotope value of the two experiments SMG-L and SMG-1 ( $\delta^{18}\text{O}_{\text{smithsonite SMG}} = 26.01\%$ ) with an estimated error of  $\pm 0.2\%$  for calculation of  $\alpha^{\text{phos}}$  values.

Decarbonatization reactions of smithsonite using anhydrous phosphoric acid have been conducted at temperatures between 25 and 72°C with reaction times ranging from 1.5 h to 2 weeks (Table 3). The reaction of natural smithsonite and acid is very sluggish at 25°C. Even after 2 weeks reaction yields do not

Table 4. Equations for temperature dependence of phosphoric acid fractionation factors for various carbonate minerals. The cation radius and mass (Golyshev et al., 1981) are shown for comparison.

Mineral	Cation radius	Cation mass	Phosphoric acid fractionation factor	Temperature range (°C)	Reference
<i>Calcite group (rhombohedral)</i>					
Magnesite (MgCO <sub>3</sub> )	0.65	24	$1000\ln\alpha^{\text{phos}} = 4.23 + 6.84 \times 10^5/T^2$	50–100	Das Sharma et al. (2002)
Smithsonite (ZnCO <sub>3</sub> )	0.70	65	$1000\ln\alpha^{\text{phos}} = 3.96 + 6.69 \times 10^5/T^2$	25–72	<i>This study</i>
Siderite (FeCO <sub>3</sub> )	0.79	56	$1000\ln\alpha^{\text{phos}} = 3.85 + 6.84 \times 10^5/T^2$	25–150	Rosenbaum and Sheppard (1986)
Rhodochrosite (MnCO <sub>3</sub> )	0.80	55	$1000\ln\alpha^{\text{phos}} = 2.29 + 6.91 \times 10^5/T^2$	20–90	Böttcher (1996)
Calcite (CaCO <sub>3</sub> )	1.02	40	$1000\ln\alpha^{\text{phos}} = 4.55 + 5.04 \times 10^5/T^2$	25–62	Sharma and Sharma (1969a)
			$1000\ln\alpha^{\text{phos}} = 3.95 + 5.53 \times 10^5/T^2$	25–90	Swart et al. (1991) recalculated
			$1000\ln\alpha^{\text{phos}} = 3.77 + 5.72 \times 10^5/T^2$	25–90	Böttcher (1996)
			$1000\ln\alpha^{\text{phos}} = 3.89 + 5.61 \times 10^5/T^2$	25–95	Das Sharma et al. (2002)
<i>Aragonite group (orthorhombic)</i>					
Strontianite (SrCO <sub>3</sub> )	1.35	88	$1000\ln\alpha^{\text{phos}} = 5.30 + 4.59 \times 10^5/T^2$	25–62	Sharma and Sharma (1969a)
Cerussite (PbCO <sub>3</sub> )	1.41	207	$1000\ln\alpha^{\text{phos}} = 5.13 + 4.79 \times 10^5/T^2$	25–72	<i>This study</i>
Witherite (BaCO <sub>3</sub> )	1.55	137	$1000\ln\alpha^{\text{phos}} = 5.76 + 4.58 \times 10^5/T^2$	20–90	Böttcher (1996)
			$1000\ln\alpha^{\text{phos}} = 6.26 + 4.12 \times 10^5/T^2$	25–62	Sharma and Sharma (1969a)

exceed 25% of the theoretical CO<sub>2</sub> yield for smithsonite (7.97 μmol/mg). We find, however, considerable scatter in the oxygen isotope values of acid-liberated CO<sub>2</sub> (±1.65‰, 1σ; n = 9) and, to a lesser degree, in the δ<sup>13</sup>C values (±0.38‰, 1σ; n = 9). Much of the scatter is related to three extractions after 15, 120 and 330 h of reaction (TUM-3111a, TUM-3112, TUM-3160) with δ<sup>13</sup>C values showing large deviations (>0.3‰) from the average δ<sup>13</sup>C value of SMG obtained from thermal decarbonatization and higher temperature reactions with the acid (−2.15 ± 0.15‰). Similar effects of low reaction yields on isotopic compositions of acid-liberated CO<sub>2</sub> from various carbonates have been described by Fritz and Fontes (1966), Walters et al. (1972), and Rosenbaum and Sheppard (1986). Thus, excluding the three outliers (TUM-3111a, TUM-3112, TUM-3160), we derive an average δ<sup>18</sup>O value of acid-liberated CO<sub>2</sub> from smithsonite SMG at 25°C of 37.80 ± 0.17‰ and an average δ<sup>13</sup>C value of −2.14 ± 0.07‰. Combining this average value with the total oxygen determination, a phosphoric acid fractionation expressed as 1000lnα<sup>phos</sup> of 11.42 is obtained for smithsonite. This value is in close agreement with the result of 11.24 from Sharma and Clayton (1965).

Reaction times with phosphoric acid at 50°C were varied between 5 h and 3 d. The CO<sub>2</sub> yields ranged from ~30 to 90% and both δ<sup>13</sup>C (−2.13 ± 0.05‰) and δ<sup>18</sup>O values (36.80 ± 0.13‰) reproduce well, irrespective of reaction time and yield. The 1000lnα<sup>phos</sup> value at 50°C is calculated as 10.46. Similarly, the phosphoric acid reaction at 72°C using the on-line preparation system was rapid and reproducibilities of isotopic compositions were better than ±0.15‰. Variation of reaction time from 1.5 to 3.5 h had no significant influence on measured isotopic compositions. The 1000lnα<sup>phos</sup> value at 72°C is 9.54. The standard deviation of repeated measurements of δ<sup>18</sup>O values of CO<sub>2</sub> from phosphoric acid extractions at 50 and 72°C (<±0.15‰) is slightly smaller than the estimated error of the total oxygen isotope determinations (±0.2‰). Therefore, uncertainties in our phosphoric acid fractionation factors of smithsonite are estimated at ±0.3‰.

The temperature dependence of phosphoric acid fractionation factors of smithsonite between 25 and 72°C can be described as

$$1000\ln\alpha^{\text{phos}}_{\text{CO}_2\text{-smithsonite}} = 3.96 (\pm 0.21) + 6.69 (\pm 0.22) \times 10^5/T^2 \quad (4)$$

with temperature  $T$  in Kelvin. The slope, intercept and standard errors of the linear regression are based on 30 1000lnα<sup>phos</sup> values calculated from each experiment given in Table 3.

#### 4. COMPARISON WITH OTHER STUDIES

In Table 4 we compare our new equations for the temperature dependence of the phosphoric acid fractionation for smithsonite and cerussite with those calculated for other carbonate minerals of the calcite group including siderite (Rosenbaum and Sheppard, 1986; Carothers et al., 1988), magnesite (Das Sharma et al., 2002), rhodochrosite (Böttcher, 1996), and calcite (Sharma and Sharma, 1969a; Swart et al., 1991; Böttcher, 1996; Das Sharma et al., 2002), as well as those of the aragonite group, such as witherite (Sharma and Sharma, 1969a; Böttcher, 1996) and strontianite (Sharma and Sharma, 1969a). We note that the equations presented by Sharma and Sharma (1969a), Swart et al. (1991) and Böttcher (1996) were based on the phosphoric acid fractionation factors at 25°C of Sharma and Clayton (1965). Somewhat different phosphoric acid fractionation factors have been suggested for magnesite (Perry and Tan, 1972; Cornides and Kusakabe, 1977) and strontianite (Böttcher, 1996), but these were generally based on a smaller set of analyses compared to those given in Table 4. The data for the calcite group minerals are summarized in Figure 1. The 1000lnα<sup>phos</sup> values for smithsonite are significantly distinct from those of calcite, i.e., they differ by > 1‰ between 25 and 72°C, emphasizing the importance of our new determinations. The acid fractionation factors of smithsonite are almost identical to those of siderite.

The temperature dependence of 1000lnα<sup>phos</sup> values, and thus slope  $B$  in Eqn. 2, is very similar for slowly reacting carbonates of the rhombohedral calcite group, i.e., magnesite, siderite, rhodochrosite, and smithsonite, while the intercepts  $A$  in Eqn. 2, are distinct for the minerals. There is no simple relationship between the  $A$  value of the various carbonates and cationic mass as suggested by Sharma and Sharma (1969b), nor cationic radius.

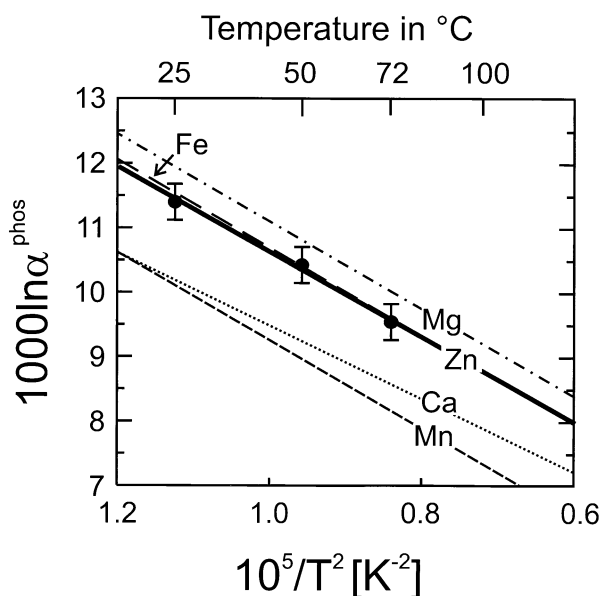


Fig. 1. Plot of  $1000\ln\alpha^{\text{phos}}$  values vs.  $10^5/T^2$  for different carbonate minerals of the calcite group. Mg = magnesite (Das Sharma et al., 2002), Fe = siderite (Rosenbaum and Sheppard, 1986), Zn = smithsonite (this study), Mn = rhodochrosite (Böttcher, 1996), Ca = calcite (Swart et al., 1991).

Minerals of the orthorhombic aragonite group that react fast with phosphoric acid at 25°C (cerussite, strontianite, and witherite) also have similar slopes  $B$  in Eqn. 2, ( $\sim 4.5 \pm 0.3$ ) that contrast with those of the slowly reacting calcite group minerals ( $\sim 6.7 \pm 0.2$ ). The factor  $B$  for calcite, which reacts rapidly with phosphoric acid at 25°C, is intermediate to these ( $\sim 5.6 \pm 0.1$ ; Swart et al., 1991; Böttcher, 1996; Das Sharma et al., 2002). The  $A$  values (intercepts) of the aragonite group minerals witherite, cerussite and strontianite, however, are similar considering the uncertainty in the  $1000\ln\alpha^{\text{phos}}$  value for witherite at 25°C (Kim and O'Neil, 1997). Whereas a single determination of  $1000\ln\alpha^{\text{phos}}$  witherite at 25°C by Sharma and Clayton (1965) gave a value of 10.91 that was used by Sharma and Sharma (1969a) and Böttcher (1996) to derive their equations (Table 4), Kim and O'Neil (1997) determined an average value of  $10.57 \pm 0.16$  ( $1\sigma$ ) from six experiments. Our new  $1000\ln\alpha^{\text{phos}}$  value at 25°C for cerussite (10.58) is within an estimated error of  $\pm 0.2$  identical to that of strontianite (10.43; Sharma and Clayton, 1965) and witherite ( $10.57 \pm 0.16$ ,  $n = 6$ ; Kim and O'Neil, 1997). The published  $1000\ln\alpha^{\text{phos}}$  value at 25°C for aragonite varies between 10.29 (Sharma and Clayton, 1965) and 11.01 (Kim and O'Neil, 1997), but could be very similar to that of the other aragonite group minerals and calcite ( $10.44 \pm 0.10$ ,  $n = 8$ ; Kim and O'Neil, 1997). Thus, as suspected by O'Neil (1986, pp. 17–18), carbonate minerals that react quickly with phosphoric acid at 25°C seem to have a similar phosphoric acid fractionation factor  $1000\ln\alpha^{\text{phos}}$  of  $\sim 10.5 \pm 0.1$ . We note, however, that the  $B$  factor, or slope in Eqn. 2, is variable and related to both crystallographic structure and reaction rate.

## 5. CONCLUSIONS

1. The reaction of natural smithsonite with anhydrous phosphoric acid at 25°C is very slow and reaction yields as low as 25% even after 2 weeks of reaction result in an unacceptably low precision for oxygen ( $\pm 1.65\%$ ,  $1\sigma$ ,  $n = 9$ ) and carbon ( $\pm 0.38\%$ ,  $1\sigma$ ,  $n = 9$ ) isotope measurements. The precision of measurements of the isotopic compositions of acid-liberated  $\text{CO}_2$  from smithsonite can be improved to  $\pm 0.15\%$  by raising the reaction temperature to 50°C with a reaction time of at least 12 h, or to 72°C with a reaction time of 1.5 h. In contrast, natural cerussite reacts rapidly with phosphoric acid at 25°C and reproducibility of oxygen and carbon isotope values is better than 0.1%.
2. Our best estimate for the intramolecular kinetic oxygen isotope fractionation factor between phosphoric acid liberated  $\text{CO}_2$  and smithsonite ( $\alpha^{\text{phos}}$ ) at 25°C is 1.01149 in agreement with a previous determination by Sharma and Clayton (1965). The  $\alpha^{\text{phos}}$  values at 50 and 72°C are 1.01052 and 1.00958, respectively. The determination of  $\alpha^{\text{phos}}$  for cerussite is 1.01061 at 25°C, 1.00977 at 50°C and 1.00911 at 72°C. Our value of  $\alpha^{\text{phos}}$  for cerussite at 25°C is notably distinct from the value for calcite (1.01024) that was used by Melchiorre et al. (2001) to calibrate their cerussite oxygen isotope thermometer.
3. The phosphoric acid fractionations show a linear dependence in a plot of  $1000\ln\alpha^{\text{phos}}$  vs.  $10^5/T^2$ , with similar slopes ( $6.7 \pm 0.2$ ) for slowly reacting carbonates of the rhombohedral calcite group (magnesite, siderite, smithsonite and rhodochrosite). The slopes for fast reacting carbonates of the orthorhombic aragonite group (witherite, strontianite, cerussite) are significantly smaller ( $4.5 \pm 0.3$ ) than those of the calcite group, but distinct from the slope of fast reacting calcite ( $5.6 \pm 0.1$ ), indicating a crystallographic control on the temperature dependent acid-liberated  $\text{CO}_2$ -carbonate fractionation.

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