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Temperature dependence of oxygen isotope fractionation of CO₂ from magnesite-phosphoric acid reaction

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Abstract—New experimental results are reported on oxygen isotope fractionation factors, α_T , between the $\delta^{18}\text{O}$ compositions of carbon dioxide liberated by phosphoric acid in the temperature interval of 323 to 373K and that of total oxygen from a natural magnesite (MgCO_3). These results are distinctly different from some previously published mutually inconsistent data, and can be expressed as a linear relationship: $10^3 \ln \alpha_T = [\{ (6.845 \pm 0.475) \cdot 10^5 / T^2 \} + (4.22 \pm 0.08)]$, where $10^3 \ln \alpha_T$ refers to fractionation at different temperatures T in Kelvin.

Fractionation factors have also been determined at 323 and 368K on a natural calcite. The results on calcite are in excellent agreement with previously published data and can be written as: $10^3 \ln \alpha_T = [\{ (5.608 \pm 0.151) \cdot 10^5 / T^2 \} + (3.89 \pm 0.08)]$.

The combined results on magnesite and calcite yield a computed value of $\alpha = 1.01117$ for dolomite at 298K, assuming equal proportion of 0.5 mole of magnesium and calcium in dolomite, the previously reported experimental values being 1.01109 and 1.01110. Copyright © 2002 Elsevier Science Ltd

1. INTRODUCTION

The standard procedure for determining carbon and oxygen isotope composition of carbonates involves digestion of samples in a closed reaction vessel with 100% phosphoric acid at a constant temperature of 25°C (McCrea, 1950). Since this process liberates two-thirds of the total oxygen as carbon dioxide, fractionation of oxygen isotopes takes place between the evolved carbon dioxide and remaining oxide. Sharma and Clayton (1965) performed experiments on several alkaline earth and transition metal carbonates and found that the fractionation factors between acid liberated and total oxygen [$\alpha = \{ (^{18}\text{O}/^{16}\text{O})_{\text{acid liberated at } 25^\circ\text{C}} \} / \{ (^{18}\text{O}/^{16}\text{O})_{\text{total}} \}$] vary considerably, indicating that α is dependent on the composition of the carbonate mineral. Several workers have also observed that phosphoric acid reacts sluggishly at 25°C with carbonates like siderite, ankerite, dolomite, and magnesite (Becker, 1971; Perry and Tan, 1972; Rosenbaum and Sheppard, 1986). However, the rate of reaction can be enhanced if higher temperature is employed (Rosenbaum and Sheppard, 1986; Carothers et al., 1988). Böttcher (1996) has recently estimated the oxygen isotope fractionation of calcite, rhodochrosite, kutnahorite, witherite, and strontianite during phosphoric acid reaction as a function of temperature in the range of 20 to 90°C. He found that the temperature dependence of oxygen isotope fractionation of the studied carbonates is characterized by specific slopes. It is therefore essential to estimate the fractionation factor α_T for particular carbonate mineral of interest at various reaction temperatures T (in Kelvin). While the temperature-dependent oxygen isotope fractionations of siderite, ankerite, and dolomite during acid reaction have been well established (Rosenbaum and Sheppard, 1986; Carothers et al., 1988), similar systematic determinations have not been performed for

magnesite. A careful examination of available α_T data on magnesite reveals that there exists a large discrepancy among the reported values (Table 1).

In the present study carbon dioxide has been extracted using 100% phosphoric acid from a natural magnesite sample at four different reaction temperatures in the interval of 50 to 100°C. Values of α_T have been determined from acid liberated and total oxygen isotope compositions, and these are expressed in terms of an equation between $10^3 \ln \alpha_T$ and $1/T^2$. To authenticate the data on magnesite, total oxygen has also been liberated from a natural calcite sample along with phosphoric acid reaction at 25 and 95°C to evaluate the values of α_T . These values are compared with published data reported by Friedman and O'Neil (1977), Swart et al. (1991), and Böttcher (1996).

2. SAMPLING AND EXPERIMENTAL PROCEDURE

Magnesite occurs in the form of veins, 2 to 100 cm in thickness within dunite and serpentinite at Karya deposit near Mysore, Karnataka State in southern India. The sample collected for the present study is compact, massive, snow white in color, and free from other materials. Petrographic examination shows that the sample is cryptocrystalline and homogeneous in nature. X-ray diffraction results confirm the presence of only magnesium carbonate. The chemical compositions of the sample, along with a limestone standard GSR-6, were determined on a Phillips MagiX PRO 2440 X-ray fluorescence spectrometer. CO₂ content was determined by loss-on-ignition method. The chemical analyses are presented in Table 2.

Minor modification was made in the h-shaped glass reaction vessel of McCrea (1950) so that the cone-socket grease joint was replaced by a Swagelok joint with teflon ferrules to provide vacuum sealing. About 7- to 10-mg finely crushed (~60 μm) sample powder and 100% phosphoric acid were reacted and kept for reaction for 4 to 240 h, depending on temperature (see Table 3). Constant temperature bath (Lauda) with ethylene glycol and water in the ratio of 1 : 1 was used as bath fluid

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Table 1. Reported values of oxygen isotope fractionation factor at various temperatures (α_T) for magnesite-phosphoric acid reaction.

Temperature (K)	Fractionation factor (α_T)	Reference	Remarks
298	1.0123	Perry and Tan (1972)	Measured experimentally
323	1.0116	Perry and Tan (1972)	-do-
363	1.01028	Abu-Jaber (1991)	Total oxygen not determined
368	1.008	Cornides and Kusakabe (1977)	Measured experimentally
373	1.00933	Rosenbaum and Sheppard (1986)	Estimated

during the reaction. The temperature was kept constant to within $\pm 0.1^\circ\text{C}$ of the set temperature for all the runs. Two representative runs with sample amounts of 25-mg each at 50 and 75°C were performed to establish the relationship among percentage yield and $\delta^{18}\text{O}$ as a function of reaction time (Fig. 1a,b). The $\delta^{18}\text{O}$ values of CO_2 liberated at different time intervals at a particular temperature were close to each other (within ± 0.08 and ± 0.04 at 50 and 75°C , respectively). This indicates that as far as the present sample was concerned, the oxygen isotopic composition is independent of yield. Aharon (1988) and Abu-Jaber (1991) also noted similar observations with their magnesite samples.

Total oxygen was liberated as CO_2 in two steps: (1) thermal decomposition of magnesite up to a temperature of $\sim 650^\circ\text{C}$ and (2) fluorination of magnesium oxide using bromine pentafluoride and conversion of O_2 to CO_2 (Sharma and Clayton, 1965). Yield was measured to be within $100 \pm 2\%$ of the expected value obtained based on chemical composition. A natural calcite sample was also introduced as an accompanying run for total oxygen and reacted with 100% phosphoric acid at 25 and 95°C . Replicate runs were performed for total oxygen in magnesite and all acid digested magnesite and calcite samples (Table 3). Isotopic analyses were performed on a VG 903 mass spectrometer. Oxygen isotope data are reported in standard δ notation relative to V-SMOW. During the course of this study, the NBS-28 standard gave $\delta^{18}\text{O} = 9.72 \pm 0.15\%$ as against the reported value of 9.64%.

Table 2. Major element compositions of natural magnesite and GSR-6. Recommended values of GSR-6 are after Govindaraju (1994).

Oxide	Magnesite	GSR-6 (present study)	GSR-6 (recommended)
SiO_2	1.14	15.17	15.6
TiO_2	—	0.3	0.33
Al_2O_3	0.07	5.24	5.03
Fe_2O_3	—	2.43	2.52
MnO	—	0.06	0.06
MgO	47.08	4.97	5.19
CaO	0.65	35.12	35.67
Na_2O	—	0.04	0.081
K_2O	—	0.74	0.78
P_2O_5	—	0.05	0.052
CO_2	50.52	32.97	32.44

3. RESULTS AND DISCUSSION

The $\delta^{18}\text{O}$ values of acid-liberated CO_2 at different temperatures and those from total oxygen along with fractionation factors are given in Table 3. The fractionation factors are calculated from experimentally determined $\delta^{18}\text{O}$ values using the relationship $\alpha_T = (1000 + \delta^{18}\text{O}_{\text{acid-liberated CO}_2 \text{ at } T}) / (1000 + \delta^{18}\text{O}_{\text{total oxygen}})$. Figure 2a shows the relationship between $10^3 \ln \alpha_T$ and $1/T^2$ for calcite obtained in the present study as well as those reported by Friedman and O'Neil, (1977), Swart et al. (1991), and Böttcher (1996). Although Swart et al. (1991) have reported fractionation factors using sealed-vessel and common acid bath methods, we have plotted in Figure 2a their data on the sealed-vessel method to avoid the possibility of memory effect in the latter. Within the limits of experimental error, the agreement between the results presented here and the published results are excellent. Using data points in Figure 2a, the relationship between $10^3 \ln \alpha_T$ and $1/T^2$ has been determined and can be expressed as

$$10^3 \ln \alpha_T = [(5.608 \pm 0.151) \cdot 10^5 / T^2] + (3.89 \pm 0.08) \quad (1)$$

$$r = 0.99$$

Figure 2b exhibits the temperature-dependent fractionation of oxygen isotopes in the case of magnesite. The function $10^3 \ln \alpha_T$ varies linearly against $1/T^2$ for the studied temperature interval of 50 to 100°C . The least squares fit shown by line AB can be expressed in the form of equation

$$10^3 \ln \alpha_T = [(6.845 \pm 0.475) \cdot 10^5 / T^2] + (4.22 \pm 0.08) \quad (2)$$

$$r = 0.99$$

Data of $10^3 \ln \alpha_T$ obtained at different temperatures by previous workers are also included in Figure 2b for comparison. It can be seen that the values of fractionation reported by Perry and Tan (1972), Abu-Jaber (1991), and Cornides and Kusakabe (1977) at 25, 50, 90, and 95°C plot away from line AB, and that reported by Rosenbaum and Sheppard (1986) at 100°C is close to AB. It is to be noted that Rosenbaum and Sheppard (1986) did not experimentally determine the phosphoric acid-related fractionation factor of magnesite, but their value was evaluated on the basis of mole percent composition of carbonate end-members. To evaluate the possible reasons for the large deviation between our results and those of previous workers, we have critically examined the procedures adopted in each study. Although the approach of Cornides and Kusakabe (1977) was identical to ours, two problems in their experiment need critical assessment: (1) temperature of reaction and (2) yield. First, these authors used an electric furnace in which only the lower part of the reaction vessel was kept at a set temperature. They do not mention the accuracy at which thermal equilibrium was maintained during the reaction. Second, the amount of gas liberated from the sample was not measured. They report complete dissolution after 3 h at 95°C based on a visual estimate. It is also important to note that $\alpha_{95^\circ\text{C}}$ obtained by them is equal to that of calcite at 95°C using Eqn. 1. This is in contradiction with the values obtained on dolomite, which show enrichment compared to calcite (Friedman and O'Neil, 1977). In the experiment of Abu-Jaber (1991), magnesite was reacted at 25 and 90°C . Total oxygen was not extracted for evaluating $\alpha_{90^\circ\text{C}}$. Instead, the equation $\alpha_{90^\circ\text{C}} / \alpha_{25^\circ\text{C}} = (1000 + \delta^{18}\text{O}_{90^\circ\text{C}}) / (1000 + \delta^{18}\text{O}_{25^\circ\text{C}})$, along with reported $\alpha_{25^\circ\text{C}}$ of

Table 3. Oxygen isotope compositions of phosphoric acid liberated carbon dioxide at various temperatures and total carbonates (magnesite and calcite). The fractionation factors (α_T) are determined from $\delta^{18}\text{O}$ values of acid liberated CO₂ and total carbonates. $10^3 \ln \alpha_T$ refers to fractionation.

Sample	T, K	Reaction time (hours)	$\delta^{18}\text{O}$ (‰ V-SMOW)	α_T (CO ₂ -carbonate)	$10^3 \ln \alpha_T$
Magnesite (acid liberated)	323	163–240	29.28 ± 0.07 (4)	1.010847	10.79
	348	30–48	28.39 ± 0.04 (4)	1.009976	9.93
	358	24	27.92 ± 0.04 (4)	1.009514	9.47
	373	4	27.63 ± 0.06 (3)	1.009228	9.19
Magnesite (total)			18.23 ± 0.11 (3)		
Calcite (acid liberated)	298	24	16.65 ± 0.04 (4)	1.01015	10.10
Calcite (total)	368	1	14.54 ± 0.06 (3)	1.00806	8.03
			6.43		

Perry and Tan (1972), was used to arrive at the reported value. It appears that the value obtained by Abu-Jaber (1991) was influenced by two data points of Perry and Tan (1972), as is obvious from Figure 2b ($r = 0.992$). Hence, he did not check

the validity of his result at other temperatures. As far as the data by Perry and Tan (1972) are concerned, no characterization of analyzed magnesite was made; hence, it is difficult to assign significance to these results.

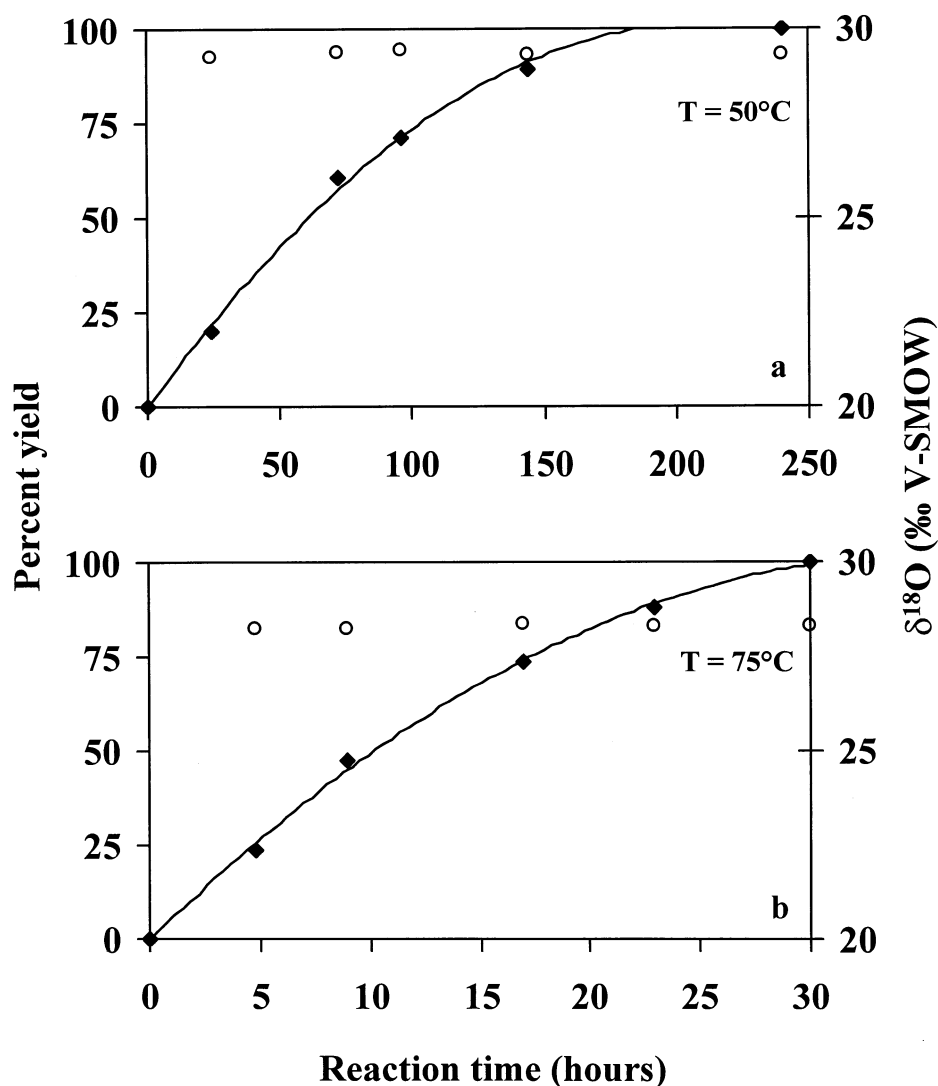


Fig. 1. Relationship among percentage yield (solid diamond) and $\delta^{18}\text{O}$ (open circle) at (a) 50°C and (b) 75°C as a function of reaction time.

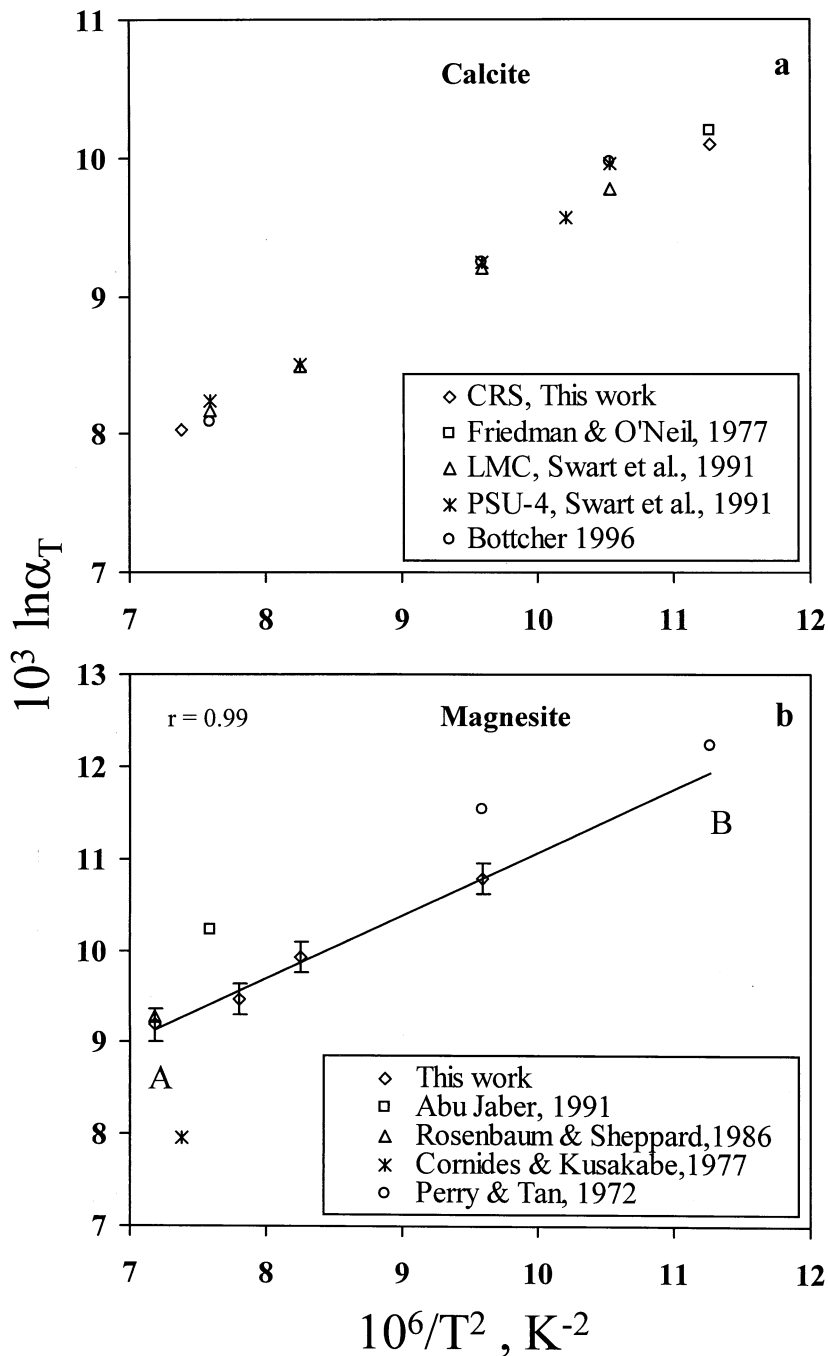


Fig. 2. Variations of experimentally determined phosphoric acid fractionations, $10^3 \ln \alpha_T$, as a function of $1/T^2$ for (a) calcite and (b) magnesite. Published data on calcite are from Friedman and O'Neil (1977), Swart et al. (1991), and Böttcher (1996). LMC, PSU-4, and CRS refer to sample numbers. Data on magnesite are from Abu-Jaber (1991), Rosenbaum and Sheppard (1986), Cornides and Kusakabe (1977), and Perry and Tan (1972). Line AB represents the least squares fit of data obtained in this study. Error bars are also shown.

Using Eqn. 1 and 2, the relationship between $10^3 \ln \alpha_T$ and $1/T^2$ for dolomite has been computed with an assumed equal mole proportion of calcium and magnesium ($X_{Ca} = X_{Mg} = 0.5$), which can be written as

$$10^3 \ln \alpha_T = [(5.858 \pm 0.189) \cdot 10^5 / T^2] + (4.51 \pm 0.06) \quad (3)$$

Becker (1971) and Friedman and O'Neil (1977) reported experimentally determined α values at 25°C (1.01110 and 1.011091, respectively) from dolomite-phosphoric acid reaction, which are close to our computed dolomite data (1.01117). However, values of 1.01169 (Land, 1980) and 1.01178 to 1.01186 (Rosenbaum and Sheppard, 1986) at 25°C are signif-

icantly different. Although the reason for this discrepancy is not known, it has been suggested that the fractionation factor for dolomite may vary due to differences in chemical compositions (Rosenbaum and Sheppard, 1986).

3.1. Importance of the Present Work

The results on magnesite presented here are significant, particularly when oxygen isotope compositions are used for estimating temperature based on coexisting mineral pairs. For example, if magnesite and dolomite equilibrate oxygen in a common reservoir at 25°C, then using this temperature and the fractionation equations for magnesite-water with $A = 3.53$ and $B = -3.58$ (Aharon, 1988; see also Fallick et al., 1991) as well as dolomite-water (Northrop and Clayton, 1966) systems [i.e., $10^3 \ln \alpha_{\text{dol}}^{\text{mag}} = (0.33 \cdot 10^6)/T^2 - 1.58$], the difference between $\delta^{18}\text{O}$ values of magnesite and dolomite ($\Delta = \delta^{18}\text{O}_{\text{magnesite}} - \delta^{18}\text{O}_{\text{dolomite}}$) can be calculated as 2.14‰. Using fractionation factors at 50°C obtained by us and by Perry and Tan (1972), the reported $\delta^{18}\text{O}$ value of magnesite with respect to V-SMOW will differ by 0.7‰. Consequently, the estimation of temperature of equilibration of the magnesite-dolomite pair will be significantly different; for example, if our fractionation factor yields a temperature of equilibration as 25°C, data of Perry and Tan (1972) will give 0.2°C. Another important observation can also be made from the work of Aharon (1988), who determined carbon and oxygen isotopic compositions of coexisting magnesite and dolomite (sample # MRL 12584 A/1 and 2; MRL 12584 B/1 and 2) from Lower Proterozoic Rum Jungle uranium field, Australia. Using the fractionation correction of Perry and Tan (1972), he reported $\delta^{18}\text{O}$ values of two magnesite samples as 11.2 and 11.6‰, which are depleted, compared to the coexisting dolomites with values of 11.7 and 12.2‰, respectively. It is to be noted that under isotopic equilibrium condition, the ^{18}O composition of magnesite should be greater than that of dolomite (Tarutani et al., 1969). The oxygen isotope data of Aharon (1988) may, therefore, indicate that magnesite and dolomite represent an isotopically disequilibrium assemblage. However, if the fractionation correction for magnesite is performed using our data, the isotopic compositions will be 11.6 and 12.0‰ (enriched by 0.4‰). These values are indistinguishable from those of the dolomites if one considers the experimental error, in which case they may not indicate disequilibrium pairs.

4. CONCLUSIONS

A new calibration of oxygen isotope fractionation factors on release of CO₂ from magnesite by reaction with phosphoric acid at different temperatures has been performed. If faster dissolution of acid-resistant carbonates like magnesite and dolomite are performed at higher temperatures, the experimental/theoretically determined fractionation corrections presented

here could be used while reporting $\delta^{18}\text{O}$ values relative to V-SMOW.

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