

On the Direction and Magnitude of Oxygen Isotope Fractionation Between Calcite and Aragonite at Thermodynamic Equilibrium

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Abstract. Oxygen isotope fractionation factors between calcium carbonates and water have been applied to ancient marine geochemistry principally for the purpose of geothermometry. The problem was encountered, however, with respect to the direction and magnitude of oxygen isotope fractionation between calcite and aragonite at thermodynamic equilibrium. This basically involves sound understanding of both thermodynamics and kinetics of oxygen isotope fractionation between inorganically precipitated carbonate and water at low temperatures. Thus the crucial issues are to acknowledge the processes of chemical reaction and isotopic exchange during precipitation of CaCO_3 minerals in solution, the kinetic mechanism of isotope equilibrium or disequilibrium, the effect of polymorphic transition from metastable aragonite to stable calcite under hydrous or anhydrous conditions, and the presence or absence of isotope salt effect on oxygen isotope exchange between carbonate and water in response to the hydrous or anhydrous conditions at thermodynamic equilibrium. Because good agreements exist in carbonate–water oxygen isotope fractionation factors between theoretical calculations and experimental determinations, it is encouraging to applying the thermodynamic and kinetic data to isotopic paleothermometry and geochemical tracing.

Key words: calcium carbonate, experimental determination, fractionation factor, kinetic mechanism, oxygen isotope, theoretical calculation, thermodynamic equilibrium

1. Introduction

Calcium carbonate is one of the most important minerals in reconstructing paleoclimate and paleoenvironment by means of oxygen isotope analysis. A large number of data has been accumulated for oxygen isotope fractionation in $\text{CaCO}_3\text{--H}_2\text{O}$ systems since the classic work of Urey (1947) that laid out the theoretical basis of isotopic fractionation in the carbonate. Since the pioneering study of McCrea (1950) to calibrate the oxygen isotope geothermometer involving calcium carbonates, a great number of laboratory experiments, empirical estimates and theoretical calculations have been

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performed in the last five decades. It has been the general consensus that the carbonates are enriched in ^{18}O relative to H_2O but depleted in ^{18}O relative to the dissolved CO_2 at thermodynamic equilibrium; oxygen isotope fractionation among crystalline carbonates is principally determined by structural and cationic effects (e.g., O'Neil et al., 1969; Tarutani et al., 1969; Zheng, 1999). New experimental data for oxygen isotope fractionations involving dolomite (Schmidt et al., 2005; Vasconcelos et al., 2005), calcite (Zhou and Zheng, 2005), aragonite (Zhou and Zheng, 2003) and cerussite (Melchiorrer et al., 2001) have not only testified the theoretical calculations of Zheng (1999), but also shed light on the assumptions used in modifying the increment method.

However, there are still discrepancies among theoretical calculations, experimental measurements, and natural observations of oxygen isotope fractionation factors between two CaCO_3 polymorphs, calcite and aragonite (e.g., Kim and O'Neil, 1997; Zhou and Zheng, 2003). In particular, the direction and magnitude of oxygen isotope fractionation involving calcium carbonates at thermodynamic equilibrium has been controversial for a long time because there are significantly unresolved conflicts between the results of theoretical calculation, experimental measurement and empirical estimate. These issues have great bearing on the confidence of paleoclimatic reconstruction by means of isotope geothermometry. Thus there is no doubt about the importance in resolving the direction and magnitude of equilibrium oxygen isotope fractionation between calcite and aragonite. In doing so, we also need to take into account both kinetic mechanism of oxygen isotope exchange and equilibrium and effect of solution chemistry in carbonate syntheses. This review attempts to address these issues by point to point.

2. Disagreements in the literature data

It is well known that there are considerable disagreements in the aragonite–calcite–water fractionations from the literature data. As shown in Figure 1 (lines 1 and 2), the slow precipitation experimental results from $\text{Ca}(\text{HCO}_3)_2$ solutions show that the oxygen isotope fractionations concerning calcite by Kim and O'Neil (1997) are very close to those concerning the aragonite and aragonite–calcite mixtures by McCrea (1950). The calcite–water fractionations determined by Tarutani et al. (1969) and Jimenez-Lopez et al. (2001) at 0°C are indistinguishable from each other (not shown in Figure 1), but slightly greater than that by McCrea (1950) concerning the aragonite and aragonite–calcite mixtures. The experimental determination of Kim and O'Neil (1997) on the calcite–water system at low temperatures is consistent with the experimental calibration of McCrea (1950) concerning the aragonite and aragonite–calcite mixtures. It remains to resolve why these coincidences

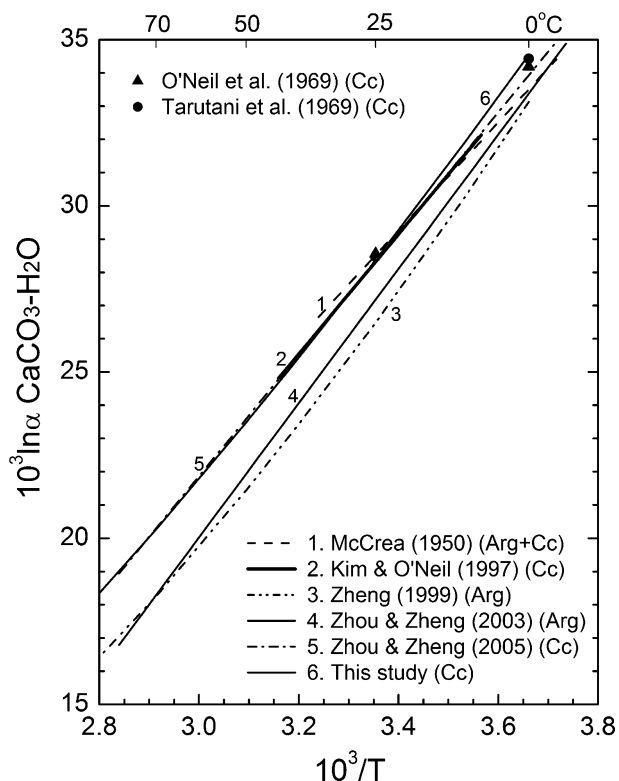


Figure 1. A comparison of oxygen isotope fractionation factors for the $\text{CaCO}_3\text{-H}_2\text{O}$ systems between experimental determination and theoretical calculation. The experimental data are after McCreath (1950) for aragonite–calcite mixture, O’Neil et al. (1969), Tarutani et al. (1969), Kim and O’Neil (1997), and Zhou and Zheng (2005) for calcite, and Zhou and Zheng (2003) for aragonite. The theoretical data are after Zheng (1999) for aragonite and this study for a revised calculation of average calcite (delete the correction for calcite/water interaction).

occur in the experimental results concerning the different polymorphs of calcium carbonate.

Kim and O’Neil (1997) assumed that calcite in their experiments is primary rather than secondary by polymorphic transition from aragonite. The cited evidence is that the larger (10–15 μm) rhombs were obtained without the coexistence of aragonite and calcite in their synthesized samples. It appears that such evidence is faint because the initial aragonite could have all been transformed by the rapid process of dissolution–reprecipitation to calcite in the final product. If aragonite would isotopically behave unlike calcite, a possible explanation is that the low-temperature runs of Kim and O’Neil (1997) could originally precipitate as aragonite that would subsequently convert to calcite by the mechanism of dissolution–reprecipitation to approach oxygen isotope reequilibration with water. In this regard, the

metastable aragonite was suspected by Zhou and Zheng (2003) to precipitate at first from aqueous solutions in the infancy of CaCO_3 crystallization, but it achieves the isotopic equilibrium with water via the mechanism of dissolution–reprecipitation at low temperatures. This is a point now has been confirmed by an experimental study of Zhou and Zheng (2005).

From their hydrothermal experiments at 500 °C and 1–20 kbar Clayton et al. (1975) did not observe measurable effect on oxygen isotope fractionation between CaCO_3 and H_2O that was expected to occur due to calcite–aragonite phase change between 11 and 13 kbar. As listed in Table 4 of Kim and O’Neil (1997) for oxygen isotope data concerning pure vaterite and vaterite–calcite mixture that were synthesized at 25 and 40 °C, negligible fractionations were observed between the pure vaterite and the vaterite–calcite mixture. Similarly, no oxygen isotope inheritance occurs during polymorph transition if the process of dissolution–reprecipitation was involved in such kinds of experiments (Zhou and Zheng, 2005).

3. Direction of calcite–aragonite fractionation

At present there are two contrasting views concerning the direction of equilibrium oxygen isotope fractionation between calcite and aragonite. On one hand, the precipitation experiments of Tarutani et al. (1969) and the natural observations of Sommer and Rye (1978) as well as Grossman and Ku (1986) suggested that calcite is depleted in ^{18}O relative to aragonite. On the other hand, the natural observations of Epstein et al. (1953), Behrens and Land (1972) as well as Horibe and Oba (1972) show that calcite is enriched in ^{18}O relative to aragonite.

The equilibrium isotope partitioning between mineral and fluid can vary with the chemical composition and bond character of the mineral. Vibrational behavior of carbonate ions is influenced by the structure of crystal lattice and the numbers of atomic coordination. The effects of isotope fractionation are principally caused by the thermodynamic (vibrational) behavior of the C–O bonds in the carbonate ion ($[\text{CO}_3]^{2-}$). The denser aragonite lattice with its $^{[9]}\text{Ca}^{[3]}\text{C}^{[4]}\text{O}_3$ coordination enhances the fractionation of oxygen isotopes compared to calcite ($^{[6]}\text{Ca}^{[3]}\text{C}^{[3]}\text{O}_3$ coordination). According to the electrostatic potentials of oxygen sites in the CaCO_3 polymorphs, Smyth (1989) predicted that calcite is enriched in ^{18}O relative to aragonite at isotopic equilibrium. This prediction is reasonably valid because the mass of divalent cation Ca^{2+} is the same for both calcite and aragonite. Following the principle of the increment method (Schuetze, 1980; Zheng, 1991, 1993a, b), the relatively denser aragonite was quantitatively predicted to be depleted in ^{18}O relative to the less dense calcite at thermodynamic equilibrium (Zheng, 1999).

The increment method calculating oxygen isotopic fractionation in solid minerals has been established as a function of statistico-mechanical and crystal structural effects. It was primarily developed by Schuetze (1980) but significantly modified by Zheng (1991, 1993a, b). It focuses on individual bonds of cation-oxygen, the relative strengths of which are given by integral ionic charges and bond-lengths determined from ionic radii. Cation mass is included in a form appropriate for diatomic molecules. Because the effects of both bond strength and cation mass on isotopic substitution have been taken into account, oxygen isotope fractionation in minerals is calculated as it moves away in increments from a reference mineral. According to the principle of the increment method, the degree of ^{18}O -enrichment in a mineral can be quantified by the oxygen isotope index ($I-^{18}\text{O}$) of the mineral relative to that of a reference mineral.

In principle, the greater the $I-^{18}\text{O}$ index of a mineral, the richer in ^{18}O the mineral. Calcium carbonates are composed of Ca, C and O ions with the same masses for both aragonite and calcite. Thus the difference in $I-^{18}\text{O}$ index between aragonite and calcite depends primarily on the relative strengths of cation-oxygen bonds. As calculated by Zheng (1999), aragonite and calcite have $I-^{18}\text{O}$ indices of 0.9296 and 1.0000, respectively. Thus aragonite is depleted in ^{18}O relative to calcite at thermodynamic equilibrium. The observed difference in Ca isotope fractionation between calcite and aragonite is also explained by different Ca–O bond strengths in the two polymorphs of calcium carbonate (Gussone et al., 2005). The Ca–O bonds are about 60% stronger in the calcite structure than in aragonite (Zheng, 1999). Therefore, calcite is predicted to enrich in ^{44}Ca relative to aragonite at thermodynamic equilibrium. This prediction matches the observation of Gussone et al. (2005) for less fractionated, isotopically heavier Ca isotopes in calcite compared to aragonite.

It merits to point out that the increment calculations also predict a considerable difference in oxygen isotope fractionation between the minerals of calcite group and aragonite group (Zheng, 1999), with the calcite group being systematically enriched in ^{18}O relative to the aragonite group at isotopic equilibrium. The same sequence of ^{18}O -enrichment was obtained from the hydrothermal experiments of O'Neil et al. (1969) for calcite, strontianite and witherite. Tarutani et al. (1969) investigated the effect of magnesium substitution on oxygen isotope fractionation between CaCO_3 and H_2O at 25 °C and found that ^{18}O concentrates in magnesium calcite. This is concordant with the theoretical prediction that magnesite is enriched in ^{18}O relative to calcite (Zheng, 1999). The effect of cation mass and radius on oxygen isotope fractionation between carbonate minerals is only valid within the same group of crystal structure.

The low-T synthesis experiments of Zhou and Zheng (2003, 2005) have provided two independent equations of oxygen isotope fractionation between aragonite, calcite and water at 0–70 °C (lines 4 and 5 in Figure 1):

$$10^3 \ln \alpha_{\text{Cc-W}} = 18.21 \times 10^3/T - 32.72 \quad (1)$$

$$10^3 \ln \alpha_{\text{Arg-W}} = 20.44 \times 10^3/T - 41.48 \quad (2)$$

A combination of Equations (1) and (2) yields a fractionation equation for the calcite–aragonite system at 0 to 70 °C:

$$10^3 \ln \alpha_{\text{Cc-Arg}} = -2.23 \times 10^3/T + 8.76 \quad (3)$$

As illustrated in Figure 2, the equilibrium calcite–aragonite fractionations are 0.60–2.26‰ at 0–70 °C and thus positive in any case. In this regard, the coexisting calcite–aragonite pairs showing negative fractionations would be simply assemblages in isotope disequilibrium.

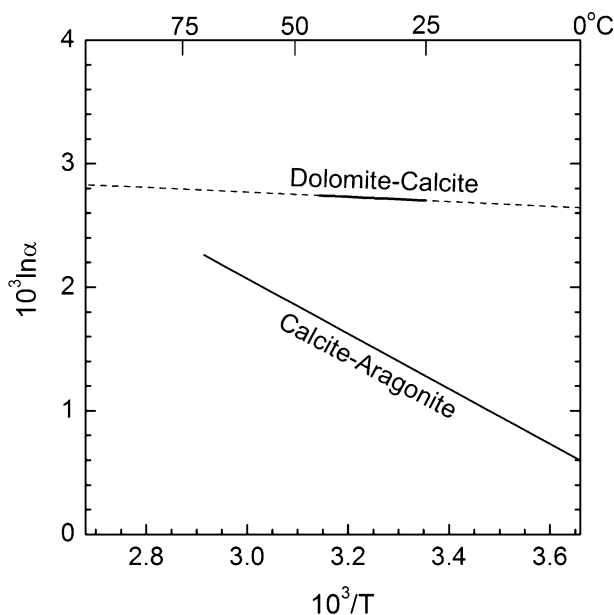


Figure 2. Experimentally determined oxygen isotope fractionation factors between calcite and aragonite and dolomite and calcite. The curve for the calcite–aragonite system is obtained by simply combining the data of Zhou and Zheng (2005) for the calcite–water system with those Zhou and Zheng (2003) for the aragonite–water system. The curve for the dolomite–calcite system is calculated by simply combining the hydrothermal data of Zhou and Zheng (2005) for the calcite–water system with the microbial data of Vasconcelos et al. (2005) for the dolomite–water system. A linear regression is used to fit the experimental data of Vasconcelos et al. (2005) into the form of $10^3 \ln \alpha = 18.02 \times 10^3/T - 29.38$.

A further example can be found in the hydrothermal experiments of O'Neil et al. (1969) on the oxygen isotope fractionation between CaCO_3 and H_2O . An extrapolated equilibrium fractionation is $18.66 \pm 0.67\text{‰}$ (1σ) at $100\text{ }^\circ\text{C}$ when a natural calcite was used as starting material¹. This value is greater than a fractionation of $16.89 \pm 0.20\text{‰}$ (1σ) at the same temperature obtained by using a reagent aragonite as starting material. This indicates that calcite was enriched in ^{18}O relative to aragonite although potentially larger errors might be associated with their exchange experiments because of low exchange percentages (26% versus 77%). Their other three sets of run with a reagent calcite as a starting material gave two fractionations of $17.98 \pm 0.56\text{‰}$ and $17.04 \pm 0.47\text{‰}$ at $103\text{ }^\circ\text{C}$, and one fractionation of $17.60 \pm 0.44\text{‰}$ at $108\text{ }^\circ\text{C}$. These are greater than, or equal to, the fractionation of $16.89 \pm 0.2\text{‰}$ derived from the aragonite reagent despite the 3–8 $^\circ\text{C}$ higher exchange temperature. It is well established that equilibrium oxygen isotope fractionations between carbonate mineral and water decrease with increasing temperature. The observation that the calcite–reagent fractionations of higher temperatures are still not lower than that with the aragonite reagent suggests that aragonite was not enriched in ^{18}O relative to calcite despite the low exchange fractions of 27–38%. Therefore, this lends support to the contention that the calcite–aragonite fractionation at thermodynamic equilibrium is positive rather than negative.

4. Magnitude of calcite–aragonite fractionation

With respect to the theoretical magnitude of oxygen isotope fractionation between calcite and aragonite at thermodynamic equilibrium, it is important to take into account the isotopic salt effect of dissolved minerals in aqueous solutions that is different between calcite and other minerals (Hu and Clayton, 2003; Cole et al., 2004). The isotope salt effect normally refers to the influence of mineral dissolution in water on isotope fractionations between mineral and water. Thermodynamically, the isotope ratios of a crystalline mineral may differ from those of its dissolved one in aqueous fluids because of the differential partition of isotopes between the two states of phase. Mineral solubility in aqueous systems is dictated by surface reactions between mineral and fluid. The presence of dissolved salts (e.g., NaCl and CaCl_2) can exert significant influences on the mineral solubility in aqueous fluids, so that the isotope salt effect of NaCl is a common example that affects the isotope fractionations between mineral and water in hydrothermal experiments of natural and artificial laboratory (e.g., Taube, 1954; O'Neil and Truesdell, 1991; Shmulovich et al., 1999; Driesner and Seward, 2000).

The size of the isotope salt effect for a mineral–water system depends on how much the mineral becomes dissolved in the aqueous fluid during the

isotope exchange between mineral and water. This is essentially determined by the quantitative difference in mineral solubility between pure water and the aqueous fluid containing the dissolved mineral. It turns out that this difference quantitatively affects the isotope fractionation between the mineral and water because of the presence of dissolved mineral in the mineral–water system. If a dissolved mineral itself has a measurable isotope salt effect, the observed isotope fractionations between the mineral and water in the mineral–solute–water system is a combination of the isotope salt effect with a real fractionation between the minerals and the pure water. The net contribution to the isotope salt effect is produced by the difference in the isotope fractionations concerning the pure water or the dissolved mineral under the same temperature and pressure. Substantially, the size of isotope salt effect depends on the degree of mineral–water interaction when dissolving the mineral in an aqueous solution (i.e. solute–water interaction). Thus both cation–oxygen bond strength and cation mass in minerals dictate the mineral solubility (solute concentration), solute species and hydration (numbers), which in turn all are a function of temperature and pressure. To a first approximation, the isotope salt effect of dissolved minerals corresponds to the mineral/water term in the modified increment method of Zheng (1993a). This term is used to quantitatively describe the effect of mineral–water interaction on oxygen isotope partitioning when calculating mineral–mineral fractionation factors by combining the fractionation factors of two mineral–water systems. Like the isotope salt effect, the mineral/water term may also be a function of temperature and pressure that remains to develop in the future.

As demonstrated by Hu and Clayton (2003) in their high-T/high-P experiments of oxygen isotope exchange, the isotope salt effect of a dissolved mineral is the main reason for the observation that the experimentally calibrated oxygen isotope fractionations between a mineral and water are systematically 1.5–2‰ more positive than the results of theoretical calculations. This effect is particularly significant on oxygen isotope fractionations concerning quartz, so that it provides an experimental confirmation for the introduction of the mineral/water term to the modified increment method of Zheng (1993a). This is illustrated in Figure 3 for the quartz–water system, the oxygen isotope fractionations derived from the calculation of Zheng (1993a) are in good agreement with those from experimental data.

However, no isotope salt effect was observed by Hu and Clayton (2003) on oxygen isotope fractionation between calcite and water although the exchanged fluid contained trace amounts of dissolved carbonate and bicarbonate species. This is confirmed by an experimental study of Zhou and Zheng (2005) on effect of polymorphic transition on oxygen isotope

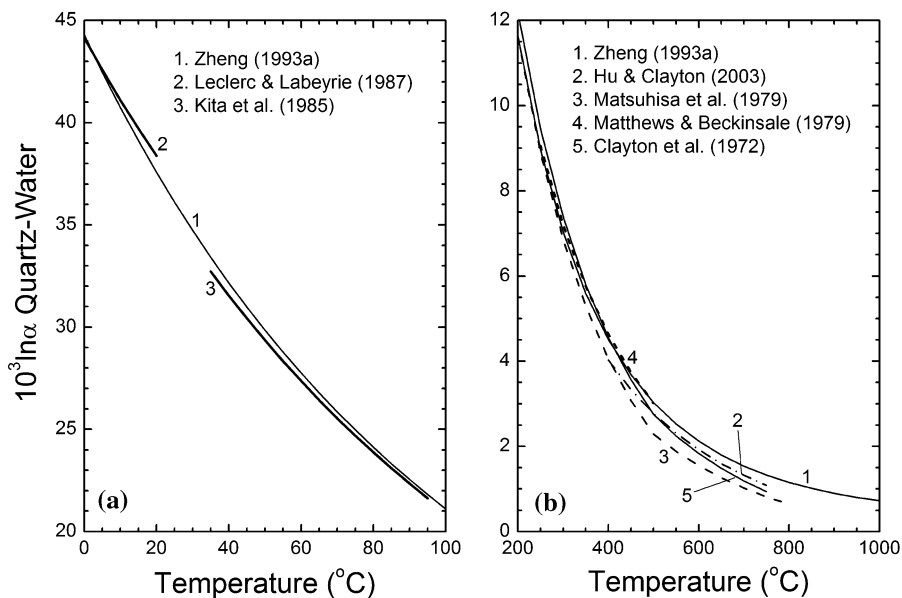


Figure 3. A comparison of oxygen isotope fractionation factors between quartz and water calculated by Zheng (1993a) with the experimental data in the literature: (a) at low temperatures (Leclerc and Labeyrie, 1987; Kita et al., 1985), and (b) at high temperatures (Hu and Clayton, 2003; Matsuhisa et al., 1979; Matthews and Beckinsale, 1979; Clayton et al., 1972). While excellent agreements are obtained between the theoretical and experimental results by the correction for quartz–water interaction at the low temperatures, discrepancies occur at the high temperatures above the supercritical point possibly due to overcorrection for mineral/water interaction in combining $10^3 \ln \beta$ values for quartz and water.

fractionation between aragonite, calcite and water at low temperatures. An important finding from this study is that once the calcium carbonates were dissolved in aqueous fluids, it is ready to achieve oxygen isotope equilibrium between precipitated calcite and water regardless of its precursor composition. For this reason, the correction for calcite–water interaction is not necessary when combining the reduced partition function ratios for oxygen isotopes in calcite ($10^3 \ln \beta_{\text{Cc}}$) as theoretically calculated by Bottinga (1968), Shiro and Sakai (1972), Kieffer (1982), and Chacko et al. (1991) with the reduced partition function ratios for oxygen isotopes in water ($10^3 \ln \beta_{\text{W}}$) by Hattori and Halas (1982).

The previous regression to the theoretical $10^3 \ln \beta$ values were algebraically presented in the form of $10^3 \ln \beta = A \times 10^6/T^2 + B \times 10^3/T + C$ over a large temperature range from 0 to 1200 $^{\circ}\text{C}$. This can bring about variable degrees of bias from the original data at low temperatures. In order to avoid the possible bias, we have linearly regressed the theoretical $10^3 \ln \beta$ values only at 0–100 $^{\circ}\text{C}$. Furthermore, by removing the correction for calcite/water

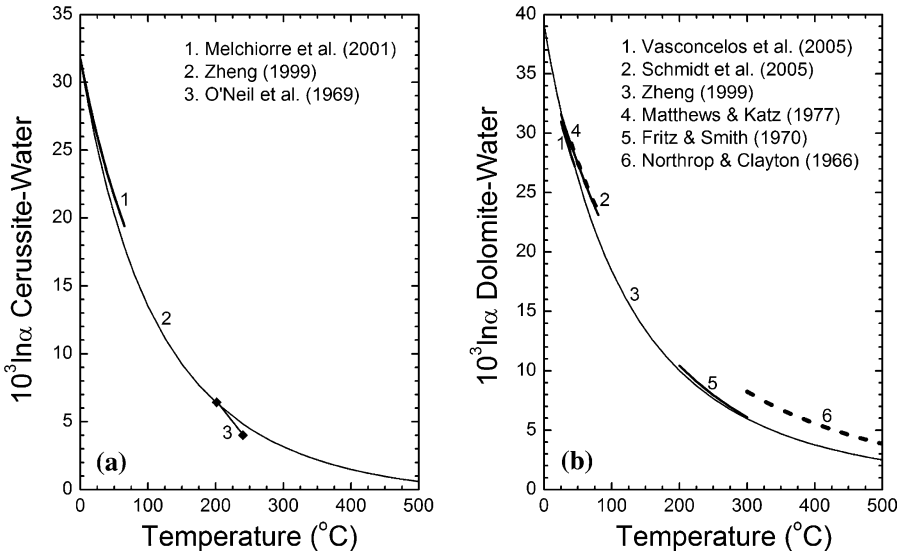


Figure 4. A comparison of oxygen isotope fractionation factors for carbonate–water systems. (a) Cerussite–water fractionations from the theoretical calculation (Zheng, 1999) with those from the experimental data of O’Neil et al. (1969) at high temperatures and Melchiorre et al. (2001) at low temperatures; (b) Dolomite–water fractionations from the theoretical calculation (Zheng, 1999) with those measured by microbial experiments at 25–45 $^{\circ}\text{C}$ (Vasconcelos et al., 2005) and chemical syntheses at 40–80 $^{\circ}\text{C}$ (Schmidt et al., 2005) as well as hydrothermal experiments at 25–300 $^{\circ}\text{C}$ (Matthews and Katz, 1977; Fritz and Smith, 1970). Note that the old data of Matthews and Katz (1977) exactly overlap the new data of Schmidt et al. (2005) when a correction of -0.8‰ is made for the phosphoric acid fractionation factor for dolomite at 25 $^{\circ}\text{C}$. Excellent agreements are brought about between the theoretical and experimental results by the correction for mineral/water interaction at both low and middle temperatures except the experimental data of Northrop and Clayton (1966) from the partial exchange technique at high temperatures. O’Neil (1986) pointed out that the dolomite–water fractionations determined by the partial exchange technique are probably greater than the equilibrium fractionations. Zheng (1999) noted that a large scatter of these experimental data is associated with their fitted curve of fractionation equation and thus is not qualified for the experimental calibration of stable isotope fractionation factors. Therefore, it would be misleading if the dolomite–water curve of Northrop and Clayton (1966) is used as the reference for the true fractionation factors between dolomite and water at thermodynamic equilibrium.

interaction that was taken into account in the previous treatment of Zhou and Zheng (2003), the theoretical equations of oxygen isotope fractionation for the calcite–water system at 0–100 $^{\circ}\text{C}$ are revised as follows:

Chacko et al. (1991):

$$10^3 \ln \alpha_{\text{Cc-w}} = 2.58 \times 10^6 / T^2 + 1.95 \times 10^3 / T - 7.45 \quad (4a)$$

Kieffer (1982):

$$10^3 \ln \alpha_{\text{Cc-w}} = 2.12 \times 10^6/T^2 + 4.91 \times 10^3/T - 12.12 \quad (4b)$$

Shiro and Sakai (1972):

$$10^3 \ln \alpha_{\text{Cc-w}} = 2.20 \times 10^6/T^2 + 4.23 \times 10^3/T - 11.71 \quad (4c)$$

Bottinga (1968):

$$10^3 \ln \alpha_{\text{Cc-w}} = 2.25 \times 10^6/T^2 + 5.16 \times 10^3/T - 12.75 \quad (4d)$$

An averaged equation of oxygen isotope fractionation for the theoretical calcite–water system at 0–100 °C can be obtained from the above four computations:

$$10^3 \ln \alpha_{\text{Cc-w}} = 2.29 \times 10^6/T^2 + 4.06 \times 10^3/T - 11.01 \quad (5)$$

As shown in Figure 1 (curve 6), the theoretical fractionation at 0 °C well match the experimental data of Tarutani et al. (1969) but is slighter greater than the other results.

Because the isotope salt effect cannot be precluded on the aragonite–water system at thermodynamic equilibrium, the mineral–water correction is necessary when combining the reduced partition function ratios for oxygen isotopes in aragonite as calculated by Zheng (1999) with the reduced partition function ratios for oxygen isotopes in water by Hattori and Halas (1982). As a result, the theoretical equation of fractionation factors for the aragonite–water system at 0–1200 °C (curve 3 in Figure 1) is as follows (Zheng, 1999):

$$10^3 \ln \alpha_{\text{Arg-w}} = 3.91 \times 10^6/T^2 - 5.79 \times 10^3/T + 1.92. \quad (6)$$

As shown in Figure 4a, the validity of such a treatment is supported from the cerussite–water system, another mineral of aragonite group, by an agreement of the theoretically calculated fractionation factors (Zheng, 1999) with those measured by both hydrothermal exchange experiment at high temperatures (O’Neil et al., 1969) and slow precipitation experiment at low temperatures (Melchiorrer et al., 2001). Likewise, necessity for the dolomite–water correction is illustrated in Figure 4b by an agreement of theoretically calculated fractionation factors (Zheng, 1999) with those measured by the newest microbial experiments at 25–45 °C (Vasconcelos et al., 2005) and chemical syntheses at 40–80 °C (Schmidt et al., 2005) as well as old hydrothermal experiments at 25–300 °C (Matthews and Katz, 1977; Fritz and Smith, 1970). In addition, the agreements between the theoretically calculated and experimentally measured fractionation factors have been shown not only for the witherite–water and siderite–water systems (Figure 5) but also for the

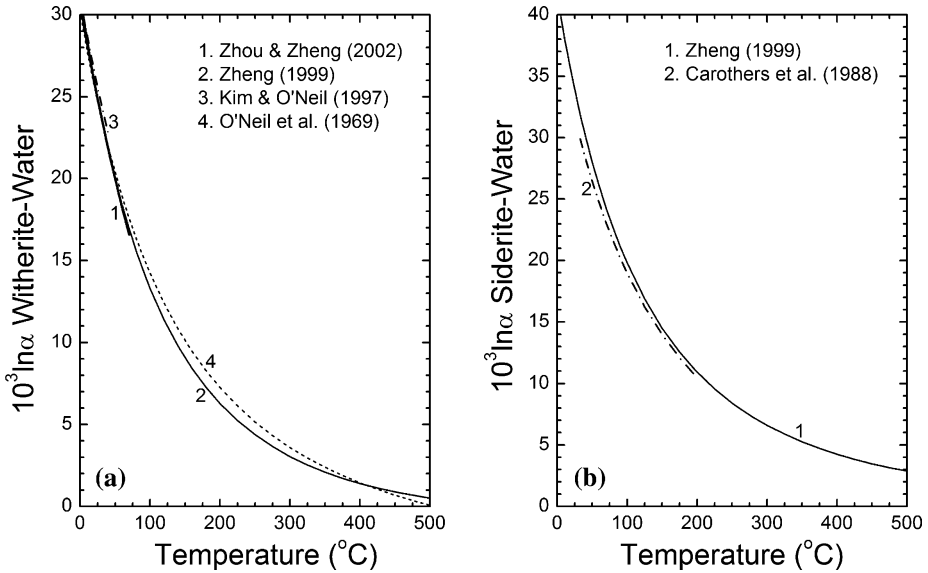


Figure 5. A comparison of oxygen isotope fractionation factors for carbonate–water systems. (a) Witherite–water fractionations from the theoretical calculation (Zheng, 1999) with those measured by the synthesis experiments of Zhou and Zheng (2002) and Kim and O’Neil (1997) at low temperatures as well as both synthesis and exchange experiments of O’Neil et al. (1969) at low and temperatures, respectively; (b) Siderite–water fractionations from the theoretical calculation (Zheng, 1999) with those measured by hydrothermal exchange experiments at 33–197 °C (Carothers et al., 1988).

aragonite–water system (lines 3 and 4 in Figure 1). These imply that the isotope salt effect of dissolved minerals is significant for these carbonates.

In the first modification of Zheng (1991) to the increment method of Schuetze (1980), two correction terms (the low-temperature term and the coupling coefficient) were introduced in order to bring the theoretical data in reasonable agreements with existing experimental and empirical data for oxygen isotope fractionation in metal oxides. Zheng (1993a) further introduced the third correction term called the miner/water interaction for the purpose of reconciling the discrepancies between the theoretical and experimental data for anhydrous silicate minerals. It is the mineral/water term that was used by Zhou and Zheng (2003) to calculate the theoretical calcite–water fractionation equations by a simple combination of the theoretical $10^3 \ln \beta$ values for calcite and water, respectively. In the all follow-up series-calculations for various minerals of geochemical interest by means of the modified increment method, the $10^3 \ln \beta$ values for quartz and calcite have been used as the reference minerals, respectively, for different categories of crystal structure and chemical composition (e.g., Zheng, 1991, 1992, 1993a, b, 1995, 1996, 1997, 1998, 1999). These reference $10^3 \ln \beta$ values were not calculated by the increment method

itself, but simply accepted from the theoretical calculations of Kieffer (1982) with the experimental corrections of Clayton et al. (1989).

The comparisons illustrated in Figures 1, 3–5 show the excellent agreements between the theoretical and experimental data. In particular, the new experimental data for cerussite (Figure 3a) and dolomite (Figure 3b) confirm the theoretical calculations of Zheng (1999). These prove that the theoretical calculations of Zheng (1999) for the carbonate minerals are reasonably valid in a thermodynamic sense. So far theoretically no other method is available to calculate a series of stable isotope fractionation factors for crystalline minerals with the reasonable accuracy for the purpose of geochemical applications. Statistico-mechanical methods and their modifications (with certain parameter adjustments) have only been applied to calculation of stable isotope fractionation factors for a few minerals, with the reasonable accuracy and thus a limited success only for few minerals including quartz and calcite (Kieffer, 1982; Chacko et al., 1991). In this regard, the increment method is a robust means for theoretical geochemistry.

Except for calcite, the isotope salt effect occurs in all the other minerals of geochemical interest, at least for the other carbonates (Figures 1, 3–5). Thus it is necessary to apply the mineral/water term to the calculations of mineral–water oxygen isotope fractionation factors when combining the calculated $10^3 \ln \beta$ values for mineral and water, respectively. In terms of the above discussion it appears that oxygen isotope fractionation between calcite and aragonite is different in the presence or absence of water. In the absence of water, on one hand, fractionation equation between calcite and aragonite can simply be calculated from the theoretical data of Zheng (1999):

$$10^3 \ln \alpha_{\text{Cc-Arg}} = 0.10 \times 10^6/T^2 + 1.14 \times 10^3/T - 0.48. \quad (7)$$

The calcite–aragonite fractionation is 4.47‰ at 25 °C under the dry conditions. In the presence of water, on the other hand, fractionation equation between calcite and aragonite is obtained from Equations (5) and (6):

$$10^3 \ln \alpha_{\text{Cc-Arg}} = -1.62 \times 10^6/T^2 + 9.85 \times 10^3/T - 12.93. \quad (8)$$

The theoretical calcite–aragonite fractionation is 1.88‰ at 25 °C under wet conditions (Figure 1). This value is greater than a value of 1.28‰ from the combined experimental determinations of Zhou and Zheng (2003, 2005) and a calcite–strontianite fractionation of 1.14‰ from the precipitation experiments of O’Neil et al. (1969), but smaller than calcite–witherite fractionations of 3.50‰ and 2.51‰ measured by O’Neil et al. (1969) and Kim and O’Neil (1997), respectively, at the same temperature.

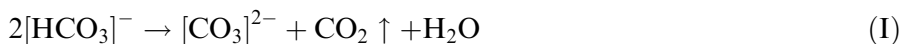
The presence or absence of water in the systems that contained calcite/aragonite can result in the significant differences in oxygen isotope fractionation between calcite/aragonite and the other minerals. As concluded

by Hu and Clayton (2003), differences in the isotope salt effects of dissolved minerals are the reason for the discrepancies between fractionations of pairs of minerals obtained by indirect hydrothermal exchange and by carbonate exchange; the oxygen isotope salt effects of dissolved minerals in experimental studies are the main reason for the discrepancy between the experimentally calibrated mineral–water fractionation and the calculated mineral–water fractionation. Furthermore, this may also be the potential reason for the systematical differences in quartz–calcite fractionation factor between the experimental data of Clayton et al. (1989) from nominally anhydrous experiments and the empirical curve of Sharp and Kirschner (1994) on the basis of observed fractionations in the natural samples from greenschist-facies marbles, veins composed of cogenetic quartz and calcite, and various low-grade metamorphic rocks.

In nature and nominally anhydrous experiments, in fact, calcite could form by the polymorphic transition from aragonite under hydrous or anhydrous conditions even with a progressive transformation between them. As experimentally demonstrated by Zhou and Zheng (2005), a solid-state polymorphic transition from aragonite to calcite without dissolution–recrystallization does not yield measurable change in oxygen isotope composition within the analytical uncertainties between precursor aragonite and the secondary calcite. On the other hand, oxygen isotope fractionations between the CaCO_3 polymorph of different phase compositions and water vary with the progress of polymorphic transition from aragonite to calcite. If a mechanism of dissolution–reprecipitation is involved during calcite crystallization from aqueous solution, thermodynamic equilibrium prevails for oxygen isotope fractionations between the final calcite and water. The hydrothermal experiments of Clayton et al. (1975) did not yield the measurable effect on oxygen isotope fractionation between CaCO_3 and H_2O at the pressures involving the calcite–aragonite transition. These would cause additional complexity when quantitatively applying the observed quartz–calcite fractionations to geothermometric work.

5. Kinetic mechanism of oxygen isotope exchange and equilibrium

One general consensus that has been universally accepted is that CaCO_3 minerals precipitated from $\text{Ca}(\text{HCO}_3)_2$ solution proceed via following two basic chemical reactions:

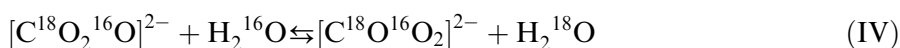
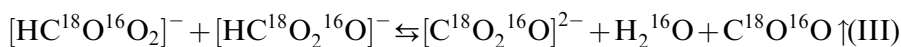


It is well known that different initial materials, for instances of CaCl_2 and Na_2CO_3 solutions, or $\text{Ca}(\text{HCO}_3)_2$ solution as initial materials, precipitate calcium carbonate following different reaction processes. For the dissociation of $\text{Ca}(\text{HCO}_3)_2$ method, the two reactions would take place. These two reaction processes determine the complexity of isotope fractionation between CaCO_3 and H_2O .

On the other hand, the crystal structure of calcium carbonates determines the stability of CaCO_3 polymorphs, which in turn dictates the difference in oxygen isotope partition between CaCO_3 polymorphs. Crystallographic investigations show that rhombohedral calcite and hexagonal vaterite have threefold symmetry axes, and their space groups are respectively $R\bar{3}c$ and $P6_3/mmc$, while orthorhombic aragonite in the space group $Pm\bar{c}n$ does not have such threefold axes. Another distinction of the aragonite structure is that the Ca^{2+} ions are nine-coordination, rather than displaying the 6-coordination in the calcite and vaterite structures. The instability of aragonite under ambient conditions ascribes to the fact that Ca^{2+} is rather small for 9-coordination. In contrast, SrCO_3 , BaCO_3 and PbCO_3 with the aragonite structure are stable owing to the larger cations (Kuether et al., 1998; Zhou et al., 2004). Metastable aragonite is easily susceptible to polymorphic transition to stable calcite by the mechanism of dissolution–reprecipitation, so that such transition is much faster in aqueous solutions than in anhydrous states (Wary and Daniels, 1957; Fyfe and Bischoff, 1965; Deleuze and Brantley, 1997; Zhou and Zheng, 2001).

The synthesis experiments of Zhou and Zheng (2001) have clearly demonstrated that the rod-like aragonite with the length of 2–6 μm easily transforms into ca. 10 μm rhombic calcite in solutions within 24 h even at 50 or 70 °C. In the 0 °C aqueous solutions, spherical vaterite transforms into rhombic calcite after aging for 10 min. To the best of our knowledge, however, no valid technique is available to corroborate the primary or secondary genesis of calcite at such low temperatures as 0 and 25 °C. It appears that these complicated the genetic identification of CaCO_3 minerals, especially calcite, which could originate from polymorphic transition of metastable aragonite or unstable vaterite by the rapid processes of dissolution–reprecipitation. Thus, the experimental calibration of oxygen isotope fractionation for the aragonite–water system can provide direct and reliable results in this aspect.

The other general consensus is that the slower the precipitation rate of mineral, the closer to equilibrium for oxygen isotope fractionation between the precipitated mineral and solution. For the CaCO_3 – H_2O system, the following processes of oxygen isotope exchange would be involved during the CaCO_3 precipitation from $\text{Ca}(\text{HCO}_3)_2$ solution:

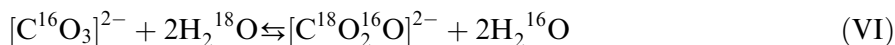


where reaction (III) denotes the oxygen isotope exchange during $[\text{HCO}_3]^-$ decomposition to $[\text{CO}_3]^{2-}$, H_2O and CO_2 gas, reaction (IV) means the oxygen isotope exchange and equilibration between the formed $[\text{CO}_3]^{2-}$ and H_2O , and reaction (V) reflects the isotope exchange during the formation of crystalline CaCO_3 , i.e., structural effect on isotope fractionation during mineral crystallization.

As shown by Zhou and Zheng (2002), the processes of oxygen isotope exchange would be involved during the CaCO_3 precipitation from $\text{Ca}(\text{HCO}_3)_2$ solution for the $\text{CaCO}_3\text{-H}_2\text{O}$ system. For the low-temperature calibration of oxygen isotope fractionation between CaCO_3 and H_2O , a special $\text{Ca}(\text{HCO}_3)_2$ solution was extensively used for the slow precipitation of CaCO_3 (e.g., McCrea, 1950; Tarutani et al., 1969; O'Neil et al., 1969; Kim and O'Neil, 1997; Zhou and Zheng, 2003). If CaCO_3 precipitation from such a solution is sufficient slow, the oxygen isotope fractionation between the precipitated CaCO_3 and H_2O should be much more close to equilibrium. This also means that the $[\text{CO}_3]^{2-}$ formed from the dissociation of $[\text{HCO}_3]^-$ can sustain in solution for a longer time, so that it can adequately exchange oxygen isotopes with H_2O to achieve thermodynamic equilibrium. In contrast, if CaCO_3 precipitation is faster, oxygen isotope fractionation between the precipitated CaCO_3 and H_2O tend to deviate from equilibrium, i.e., the formed $[\text{CO}_3]^{2-}$ has insufficient time to exchange oxygen isotopes with water. This implies that the presence or absence of isotope equilibrium between the dissolved $[\text{CO}_3]^{2-}$ and H_2O during the CaCO_3 precipitation controls the final isotope equilibrium or disequilibrium for the $\text{CaCO}_3\text{-H}_2\text{O}$ system (Zhou and Zheng, 2002).

A kinetic mechanism of oxygen isotope exchange and equilibrium between carbonates and water was proposed by Zhou and Zheng (2002) based on their experimental observations. The equilibrium oxygen isotope fractionation between the precipitated carbonate and water proceeds via the following two processes:

- (i) Oxygen isotope exchange between $[\text{CO}_3]^{2-}$ and H_2O :



- (ii) A combination of divalent metal cation M^{2+} with the $[\text{CO}_3]^{2-}$ to form carbonate:



where reactions (VI) and (VI) have similar implications to the reactions (IV) and (V). The reaction (VI) is the rate-limiting step for equilibrium oxygen isotope fractionation between carbonate and water. The mineral formation reaction (VI) bears the structural effect of carbonate crystallization on oxygen isotope fractionation during mineral precipitation. Therefore, different carbonates, either witherite or aragonite that both belong to the aragonite group crystal structure, exhibit the similar trend but different magnitudes of oxygen isotope fractionation (Zhou and Zheng, 2002).

It merits to emphasize the effects of the chemical composition of solutions used in synthesis experiments on the carbonate–water fractionations, but it is not allowed to overlook the kinetic mechanism of oxygen isotope exchange and equilibrium in carbonate–water systems. Kim and O’Neil (1997) observed that carbonates could be precipitated reproducibly in or out of oxygen isotope equilibrium with the environmental solution by varying the concentrations of bicarbonate anion and metal cation. They found that the fractionation factors between synthesis carbonates and water measured for solutions with different initial concentrations differ by as much as 2–3‰ at a given temperature. According to McConnaughey (1989), however, oxygen isotope disequilibrium between synthetic carbonates and water would occur when CO₂ underwent reactions to form [HCO₃]⁻. Furthermore, McConnaughey (1989) predicted that the slow exchange of oxygen isotopes between dissolved [CO₃]²⁻ and H₂O is the most likely step to prevent oxygen isotope equilibrium during carbonate precipitation. These highlight the critical importance in judging the achievement of oxygen isotope equilibrium between the dissolved carbonate complex anions and water prior to the precipitation of either aragonite or calcite. With respect to the carbonate precipitation and associated isotopic equilibrium, we must be clearly aware of the above two general consensuses.

6. Effects of solution chemistry

6.1. ONE-STEP AND TWO-STEP EXPERIMENTS

Precipitation experiments have been widely applied to calibration of oxygen isotope fractionation factors between calcium carbonate and water at low temperatures. Principal approaches are to synthesize calcium carbonate via either slow decomposition of Ca(HCO₃)₂ or rapid precipitation of CaCO₃ by adding CaCl₂ to NaHCO₃–Na₂CO₃ solutions (e.g., McCrea, 1950; O’Neil et al., 1969; Tarutani et al., 1969; Kim and O’Neil, 1997). All of the experiments involve a hydrolysis of carbonate to bicarbonate, carbonic acid and

dissolved CO_2 . The steps of oxygen isotope exchange take place among carbonic acid, H_2O and CO_2 and among CO_2 , bicarbonate and hydroxide. Equilibrium isotope partitioning is obtained when CaCO_3 precipitates slowly from solution; rapid precipitation fosters disequilibrium (McCrea, 1950; O'Neil et al., 1969; Romanek et al., 1992). As outlined by Usdowski et al. (1991), the strongest fractionation is caused by the isotope exchange between CO_2 and H_2O , and the smallest fractionation occurs between dissolved and gaseous CO_2 ; the fractionation between the dissolved carbonate species and H_2O is intermediate and decrease in magnitude in the order of H_2CO_3 , $[\text{HCO}_3]^-$, and $[\text{CO}_3]^{2-}$. Zeebe (1999) observed that oxygen isotope fractionation between CaCO_3 and H_2O depends not only on the temperature but also on the pH of the solution from which it is formed.

It is possible that the observed differences in experiment-derived calcite–aragonite fractionation would be caused by rapid (disequilibrium) precipitation of aragonite from either $[\text{CO}_3]^{2-}$ or $[\text{HCO}_3]^-$ dominant solutions. The experiments of Zhou and Zheng (2002) were just designed with one- and two-step approaches, respectively, corresponding to the two complex anions of dissolved carbonate prior to aragonite precipitation. The difference between the one- and two-step approaches lies in the duration of oxygen isotope exchange between dissolved carbonate and water prior to aragonite precipitation. The two-step approach has taken sufficient time to achieve oxygen isotope equilibrium between dissolved carbonate and water, whereas the one-step approach has not (Zhou and Zheng, 2002). Witherite and metastable aragonite were directly synthesized by the direct precipitation and the overgrowth techniques, respectively. The one- and two-step experiments involving witherite and aragonite have unambiguously demonstrated that the degree of oxygen isotope exchange between $[\text{CO}_3]^{2-}$ and H_2O controls the final equilibrium or disequilibrium between carbonate and water (Zhou and Zheng, 2002). The two-step experiments provided equilibrium fractionations between the precipitated carbonate and water, whereas one-step experiments did not. As clearly demonstrated by Zhou and Zheng (2002) in their two-step experiments at different periods from 20 to 60 days, the dissolved $[\text{CO}_3]^{2-}$ and H_2O have achieved an oxygen isotope equilibrium prior to the aragonite precipitation.

The results of Zhou and Zheng (2002) from the one- and two-step experiments can provide a rational evaluation to the results from $\text{Ca}(\text{HCO}_3)_2$ solution. If the initial concentration of $\text{Ca}(\text{HCO}_3)_2$ solution is high, the accumulation of $[\text{CO}_3]^{2-}$ dissociated from $[\text{HCO}_3]^-$ will quickly increase, so that the supersaturation of $[\text{CO}_3]^{2-}$ and Ca^{2+} in solution is quickly achieved to result in the rapid precipitation of CaCO_3 . In this case, the insufficient exchange of oxygen isotopes occurs between the $[\text{CO}_3]^{2-}$ and H_2O . As a consequence, the $[\text{CO}_3]^{2-}$ will partly inherit the oxygen isotope composition of $[\text{HCO}_3]^-$, and higher fractionation values will be obtained. On the other

hand, if the concentration of $\text{Ca}(\text{HCO}_3)_2$ solution is enough low, the $[\text{CO}_3]^{2-}$ dissociated from $[\text{HCO}_3]^-$ will sustain in solution for a longer time, the sufficient exchange of oxygen isotopes to approach equilibrium fractionation can occur between the dissolved $[\text{CO}_3]^{2-}$ and H_2O . Consequently, equilibrium oxygen isotope fractionations between precipitated carbonate and water will closely be approached and even finally achieved.

It could be suspected that the observed results from the two-step experiments may have bearing on the effects of high solution pH, the low $^{18}\text{O}/^{16}\text{O}$ ratio of $[\text{CO}_3]^{2-}$ and rapid precipitation. These seem reasonable because $[\text{CO}_3]^{2-}$ is depleted in ^{18}O relative to $[\text{HCO}_3]^-$ in carbonate-dissolved solutions that are in internal equilibrium (Usdowski and Hoefs, 1993; Zeebe, 1999). The quickly precipitated carbonate tends to inherit the oxygen isotope signature of dissolved carbonate complex anion in solution (McCrea, 1950). If so, the quickly precipitated witherite or aragonite should have the same oxygen isotope fractionation. However, the one-step and two-step experiments all show that witherite and aragonite have different values of fractionation relative to water (Zhou and Zheng, 2002). As shown in Figure 2 of Zhou and Zheng (2002), these fractionations for either witherite-water or aragonite-water system only depend on the duration of isotope exchange between $[\text{CO}_3]^{2-}$ and H_2O prior to the carbonate precipitation at the same temperature. A very important finding from the one-step and two-step experiments is that, for the carbonate minerals that contains the complex anion of $[\text{CO}_3]^{2-}$, the degree of approaching the equilibrium oxygen isotope fractionation between the precipitated carbonate and water depends on the degree of achieving the equilibrium between the complex anion of dissolved $[\text{CO}_3]^{2-}$ and H_2O prior to the carbonate precipitation.

Experimental temperatures also have the same effect as the initial concentration of $\text{Ca}(\text{HCO}_3)_2$. The higher the experimental temperature, the faster the precipitation of carbonate minerals. Thus, the oxygen isotope fractionations obtained at higher temperatures may represent disequilibrium even at the low concentrations of $\text{Ca}(\text{HCO}_3)_2$ solution. Our detailed SEM investigation for the synthesized minerals provides powerful proof. By means of SEM technique we investigated in detail the aragonite minerals precipitated from $\text{Ca}(\text{HCO}_3)_2$ solution at 0, 25 and 50 °C (Zhou and Zheng, 2003). The results show that the experiments of lower temperatures (0 and 25 °C) resulted in aragonite aggregates consisting of rod-like aragonite crystals, whereas dispersed and bigger rod-like aragonites were precipitated at higher temperature (50 °C). This confirms that the higher temperature leads to the rapid growth of aragonite crystals from the $\text{Ca}(\text{HCO}_3)$ solution. The SEM observations suggest that the calibration of fractionation factors at higher temperature (50 °C) by virtue of $\text{Ca}(\text{HCO}_3)_2$ solution may be unsuitable.

6.2. SLOW PRECIPITATION EXPERIMENTS

It is possible that the oxygen isotope composition of precipitated aragonite depends on the concentration of dissolved carbonate species in aqueous solutions. In the slow precipitation experiments of Zhou and Zheng (2003), 1.25 g CaCO_3 powders were used to prepare the $\text{Ca}(\text{HCO}_3)_2$ solution; only a small amount of CaCO_3 solid could be dissolved under the conditions of bubbling CO_2 gas. Thus the concentration of $\text{Ca}(\text{HCO}_3)_2$ solution is far less than 25 mM (the complete dissolution of 1.25 g CaCO_3 solid will reach a maximum concentration of 25 mM). In addition, the duration of the first appearance of initial precipitate in their experiments is longer than that in Kim and O'Neil (1997). This means that the lower concentration of $\text{Ca}(\text{HCO}_3)_2$ solutions was used in our runs of slow precipitation.

In addition, various $\text{Ca}(\text{HCO}_3)_2$ solutions with far different concentrations were used to examine whether the $\text{Ca}(\text{HCO}_3)_2$ concentrations have an effect on the oxygen isotope fractionation. As depicted in Table 3 of Zhou and Zheng (2003), the results show negligible fractionation with decreasing $\text{Ca}(\text{HCO}_3)_2$ concentration. Among the runs, two samples 97CB44 (0.2*n* mol/L) and 97CB45 (0.2*n* mol/L), where the suffix *n* denotes the initial concentration of $\text{Ca}(\text{HCO}_3)_2$ in the starting solution, were slowly precipitated at 25 °C for 90 days, but produced insufficient precipitates for XRD and isotope analyses (as described in the Section 2.2.1 CaCO_3 dissolution, Zhou and Zheng, 2003), indicating that the used $\text{Ca}(\text{HCO}_3)_2$ was very low.

Moreover, the Mg^{2+} concentrations of 0–1 M (Tables 1 to 4 of Zhou and Zheng, 2003) were used to synthesize pure aragonite, oxygen isotope fractionations between CaCO_3 and H_2O at various Mg^{2+} concentrations also show negligible effect (Tables 2, 3 and 5 of Zhou and Zheng, 2003). These demonstrate that the salt effect of Mg^{2+} concentration is negligible in the synthesis experiments of low temperatures. In addition, the equilibrium fractionation data marked by the notation ‡ in Table 5 of Zhou and Zheng (2003) were also obtained from a wide range of Mg^{2+} concentrations from 0.016 M (samples 97CB20.2 and 97CB22.2) through 0.032 M (97CB18) and 0.375 M (97CB01) to 1.0 M (samples 97CB02, 97CB03, 97CB04 and 97CB05). Again, the oxygen isotope fractionation values measured clearly demonstrated a negligible effect of Mg^{2+} concentrations on the oxygen isotope fractionations within the analytical error, indicating that no salt effect of Mg^{2+} cation occurred under our experimental conditions. Otherwise at least an observable fractionation difference would occur with the change in Mg^{2+} concentrations.

For the system of $\text{Ca}(\text{HCO}_3)_2$ solution with Mg^{2+} , furthermore, even if there existed the $[\text{MgHCO}_3]^+$ species in solution (but no evidence shows the presence of such a species) when the precipitation of carbonate occurred in this solution, this species, like $[\text{HCO}_3]^-$, must decompose into $[\text{CO}_3]^{2-}$ that

was then combined with Ca^{2+} to form the CaCO_3 precipitate. When such a process proceeds slowly, the formed mineral can approach oxygen isotope equilibrium with water. Likewise, this implies that the formed $[\text{CO}_3]^{2-}$ must be sustained in the solution for a longer time, otherwise the measured oxygen isotope fractionation between mineral and water will be far away from the equilibrium value.

7. Kinetic isotope fractionation during CaCO_3 polymorphism

In order to examine the effect of polymorphic transition on oxygen isotope fractionation between calcite and water, Zhou and Zheng (2005) sequentially precipitated aragonite–calcite mixture of different proportions by controlling transition time from 5, 30, 60, 300 to 1440 min at 50 and 70 °C, and extracted CaCO_3 minerals and water at different time intervals during the polymorphic transition from aragonite to calcite. The experiments follow the overgrowth technique by Zhou and Zheng (1998) for aragonite synthesis, but have been slightly modified for the purpose of calibrating isotope fractionation factors. The initial aragonite was prepared by the one- and two-step approaches, respectively, with different states of disequilibrium or equilibrium oxygen isotope fractionation with water (Zhou and Zheng, 2002). Relative content of calcite in aragonite–calcite mixtures was estimated by the XRD technique. For the one-step experiments at 50 °C, oxygen isotope fractionations between calcium carbonate and water almost have constant $10^3 \ln \alpha$ values of 23.89– 24.03‰ with changing transition times from 5 to 1440 min and thus corresponding percentages of transformed calcite from 0 to 100%. This implies that the rates of oxygen isotope exchange among DIC (dissolved inorganic carbon) species are much faster than the rates of polymorphic transition in aqueous solution.

For the two-step experiments, nevertheless, the oxygen isotope fractionations between CaCO_3 and H_2O progressively increase with time as the polymorphic transition from aragonite to calcite proceeds, and finally approach the fractionation values for the pure calcite. With increasing the transition time from 5 to 1440 min, they change from 21.77‰ at 100% aragonite to 23.51‰ at 100% calcite at 50 °C, and from 18.84‰ at 100% aragonite to 20.36‰ at 100% calcite at 70 °C. There is a linearly increased relationship of $10^3 \ln \alpha_{\text{CaCO}_3-\text{H}_2\text{O}}$ to the calcite content, indicating that the kinetics of oxygen isotope exchange among DIC species parallels the kinetics of polymorphic transition in aqueous solution. All of the one- and two-step approach experiments demonstrate that the degree of oxygen isotope reequilibration between secondary calcite and water heavily depends on the equilibrium state of initial aragonite and thus the reaction mechanism involved during the precipitation of initial calcium carbonates. The observed

difference may thus be caused by the difference in kinetic rate between oxygen isotope exchange among the DIC species and the aragonite–calcite polymorphic transition in aqueous solution.

It has been puzzled why there is a close similarity in oxygen isotope fractionation among the calcite of Kim and O'Neil (1997), the pure aragonite and aragonite–calcite mixtures of McCrea (1950) and the calcite, calcite–aragonite mixtures and aragonite of Zhou and Zheng (2003). The observed coincidences and discrepancies in the $\text{CaCO}_3\text{--H}_2\text{O}$ fractionation factors between the different synthesis experiments may reflect a metastable steady-state “dynamic equilibrium” during the precipitation of calcium carbonates under the each run conditions. The so-called steady-state “dynamic equilibrium” is not a true thermodynamic equilibrium but refers to a kinetically controlled transition state at non-equilibrium during the processes of isotope exchange reactions, whereas the thermodynamic equilibrium corresponds to the minimum free energy for isotope exchange reactions. As stated by Lasaga (1998), the steady-state is a crucial and important concept to much of geochemical kinetics. In mineral–water interactions under open system conditions, fluid can move in or out of the mineral–water system. The steady-state stems from the interplay between the input of fluid of a given composition, the dissolution or precipitation reaction with the fluid, and the output of fluid of a different composition. After some initial time period, the concentration of any species in the cell solution reaches a constant (steady-state) value.

The steady-state “dynamic equilibrium” may be common for oxygen isotope fractionation in biogenic carbonates. A comparison of the literature data shows that oxygen isotope fractionations determined by Xia et al. (1997) for calcite are close to those by Grossman and Ku (1986), Thorrold et al. (1997) and Boehm et al. (2000) for the aragonite–water system. However, oxygen isotope fractionations for the biogenic aragonite by Grossman and Ku (1986) and Thorrold et al. (1997) are greater than those for the biogenic calcite by Epstein et al. (1953) as well as Erez and Luz (1983). The oxygen isotope fractionations by Patterson et al. (1993) for the biogenic aragonite–water system are very close to those by Epstein et al. (1953) and Erez and Luz (1983) for the calcite–water system. It appears that there are significant disagreements among the empirical calibrations for the biogenic calcium carbonates. This suggests that the biogenic calcite may attain the steady-state equilibrium of oxygen isotope fractionations with ambient water during its precipitation. Moreover, different biological species may have different vital effects on oxygen isotope fractionations involving calcium carbonates. This is a likely cause for the variable magnitudes or directions of oxygen isotope fractionations observed in biogenic calcium carbonates.

8. Discussion

In nature and laboratory experiments, thermodynamically unstable aragonite is not always precipitated earlier than stable calcite from aqueous solutions at low temperatures. In other words, calcite can be precipitated first from the $\text{Ca}(\text{HCO}_3)_2$ solution depending on the chemistry of solution at the time of precipitation. On the other hand, the results from the literature data by the synthesis experiments for the calcite–water system do not satisfy any rigorous conditions for proof of thermodynamic equilibrium with respect to the conventional experiments by isotopic exchange from two contrary directions. Therefore, our knowledge of equilibrium oxygen isotope fractionations for the calcite–water system is incomplete and thus has to be tested for self-consistency with available data from theoretical calculations, experimental determinations and natural observations. In particular, the mechanism of calcite formation by either primary precipitation or secondary transformation is a critical issue in judging the achievement and preservation of equilibrium fractionation in this mineral.

In many low-temperature systems, furthermore, mineral precipitation often occurs through the Ostwald Step Rule, which consists of the sequence of a sequential precipitation event where metastable solid phases nucleate and are progressively replaced by more stable phases (Morse and Casey, 1988). Chemically, aragonite nucleation may be sometimes favored kinetically when precipitating CaCO_3 from aqueous fluids, compared to calcite, presumably due to low activation energy for the nucleation of the former mineral. On the other hand, trace element chemistry may sometimes be the driving force for the precipitation of aragonite and recrystallization to calcite (Wray and Daniels, 1957). Metastable aragonite may be replaced by stable calcite through a series of dissolution–precipitation reactions (Zhou and Zheng, 2001).

Experimental studies on oxygen isotope fractionation in the $\text{CaCO}_3\text{-H}_2\text{O}$ system indicate that dissolution–reprecipitation controls the rate of isotope exchange between finely dispersed calcium carbonate and aqueous solutions (Clayton, 1959; Northrop and Clayton, 1966; O’Neil et al., 1969; Zhou and Zheng, 2005). On the basis of oxygen isotope exchange kinetics and detailed microscopic examination, Anderson and Chai (1974) concluded that dissolution and reprecipitation is the mechanism by which isotope exchange occurs between calcite and water under hydrothermal conditions. They also found that the extent of fractional isotope exchange correlates with the observed extent of recrystallization. Experiments of oxygen isotope exchange in three-phase systems of calcite–silicate–fluid indicate that minerals experienced surface-controlled isotopic exchange through dissolution–recrystallization in the early stage, but diffusion-controlled isotopic exchange through transport of oxygen-bearing species in the later stage (Zheng et al., 1999,

2004). Oxygen isotope partitioning during mineral–fluid interaction was initially controlled primarily by the Ostwald ripening process, and then becomes diffusion-controlled afterwards when the systems had attained chemical equilibrium. The change in the oxygen isotope compositions of both calcite and fluid is very significant during the dissolution–recrystallization, but becomes relatively insignificant during the diffusion. The rates of oxygen isotope exchange through dissolution–recrystallization are much faster than those through diffusion.

Clayton (1959) observed that the calcium carbonate in the high temperature experiments underwent recrystallization during polymorphic transition from aragonite to calcite and hence achieved new calcite–water isotope equilibrium under the hydrothermal conditions. This implies the breaking and rebinding of the bonds not only between Ca^{2+} and carbonate complex $[\text{CO}_3]^{2-}$ but also between carbon and oxygen within the carbonate complex during the polymorphic transition and recrystallization. However, it is unclear whether the calcium carbonate in the low temperature experiments of Kim and O'Neil (1997) experienced the breaking and rebinding of the bonds not only between Ca^{2+} and $[\text{CO}_3]^{2-}$ but also between carbon and oxygen within the carbonate complex during the polymorphic transition. Further studies on synthetic products by atomic force microscopy and/or other techniques are thus required to clarify this process.

Although the positive fractionation values always occur between calcite and aragonite at thermodynamic equilibrium (Figure 2), a negative slope is yielded for the equation of oxygen isotope fractionation factors at 0–70 °C. This differs from most of other mineral-pairs that show positive slopes in the case of positive fractionations. It appears that an unusual behavior of oxygen isotope fractionation occur between the two polymorphs of calcium carbonate if they form at isotopic equilibrium from the same fluid. On the other hand, almost constant fractionation values of 2.64 to 2.83‰ occur at 0–100 °C between dolomite and calcite (Figure 2). This indicates that the dolomite–calcite fractionations are insensitive to temperature, with the nearly constant ^{18}O enrichment in dolomite relative to calcite at thermodynamic equilibrium. Dolomite formation proceeds by primary precipitation and secondary replacement, either of which takes place in the presence of water. Oxygen isotope fractionation in the course of dolomite formation is estimated to be about 2–6‰ heavier than calcite precipitated at 25 °C (Humphrey, 2000). Land (1980) concluded that equilibrium oxygen isotope fractionations between dolomite and calcite are most likely $3 \pm 1\%$ at 25 °C, a value gaining confirmation from naturally occurring dolomite–calcite mixtures of the Persian Gulf (McKenzie, 1981). These abnormal behaviors of oxygen isotope fractionations between dolomite, calcite and aragonite may bring additional complexities to

the interpretation of oxygen isotope partition in natural and experimental samples.

9. Conclusions

Oxygen isotope data for carbonate assemblages have been extensively used to understand the mode of their origin and the temperature of precipitation from seawater. It is essential that the interpretation of natural variations in oxygen isotope ratios depends on knowledge of the magnitude and temperature dependence of isotopic fractionation factors between minerals and fluids. It has been known for over a half of century that oxygen isotope fractionations between calcium carbonate and water are temperature dependent at thermodynamic equilibrium and thus can be used to determine past oceanic temperatures. Numerous thermometric calibrations involving carbonates have been made on the basis of experimental, theoretical and empirical studies. Good agreements exist in oxygen isotope fractionation factors for carbonate–water systems between theoretical calculations and experimental determinations. In particular, the new experimental data for dolomite and cerussite confirm the theoretical calculations of Zheng (1999). This has not only testified validity of the assumptions used in the increment method, but also provides physico-chemical basis for application of the thermodynamic and kinetic data to isotopic geothermometry and geochemical tracing. According to the calibrations from the different approaches, it appears that the direction of oxygen isotope fractionation between calcite and aragonite is positive rather than negative at thermodynamic equilibrium. In particular, the two-step overgrowth technique is an appropriate protocol for synthesizing calcium carbonates in oxygen isotope equilibrium with water and dissolved carbonate species. The increment method is a robust means for theoretical calculation of oxygen isotope fractionation factors for crystalline minerals of geochemical interest.

Notes

1. The oxygen isotope fractionation between two phases is a relative value and thus does not matter with which standard is used for the concerned $^{18}\text{O}/^{16}\text{O}$ ratios. However, the oxygen isotope composition of phases is an absolute value and thus their $^{18}\text{O}/^{16}\text{O}$ ratios are reported in the conventional $\delta^{18}\text{O}$ notation with reference to a given standard of either VSMOW or VPDB. In dealing with the oxygen isotope fractionations, of course, the same standard is used for the internal consistency in any case.

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References

- Anderson T. F. and Chai B. H. (1974) Oxygen isotope exchange between calcite and water under hydrothermal conditions. In: *Geochemical Transport and Kinetics* (eds. A. W. Hofmann, B. J. Giletti, H. S. Yoder Jr. and R. A. Yund), pp. 219–227. Carnegie Institution of Washington Publication.
- Behrens E. W. and Land L. S. (1972) Subtidal Holocene dolomite, Baffin Bay, Texas, *J. Sed. Petrol.* **42**, 155–161.
- Boehm F., Joachimski M. M., Dullo W.-C., Eisenhauer A., Lehnert H., Reitner J. and Woerheide G. (2000) Oxygen isotope fractionation in marine aragonite of coralline sponges, *Geochim. Cosmochim. Acta* **64**, 1695–1703.
- Bottinga Y. (1968) Calculation of fractionation factors for carbon and oxygen isotopic exchange in the system calcite–carbon dioxide–water, *J. Chem. Phys.* **72**, 800–808.
- Carothers W. W., Adami L. H. and Rosenbauer R. J. (1988) Experimental oxygen isotope fractionation between siderite–water and phosphoric acid liberated CO₂–siderite, *Geochim. Cosmochim. Acta* **52**, 2445–2450.
- Chacko T., Mayeda T. K., Clayton R. N. and Goldsmith J. R. (1991) Oxygen and carbon isotope fractionation between CO₂ and calcite, *Geochim. Cosmochim. Acta* **55**, 2867–2882.
- Clayton R. N. (1959) Oxygen isotope fractionation in the system calcium carbonate–water, *J. Chem. Phys.* **30**, 1246–1250.
- Clayton R. N., O'Neil J. R. and Mayeda T. K. (1972) Oxygen isotope exchange between quartz and water, *J. Geophys. Res.* **B77**, 3057–3067.
- Clayton R. N., Goldsmith J. R., Karel K. J., Mayeda T. K. and Newton R. C. (1975) Limits on the effect of pressure on isotopic fractionation, *Geochim. Cosmochim. Acta* **39**, 1197–1201.
- Clayton R. N., Goldsmith J. R. and Mayeda T. K. (1989) Oxygen isotope fractionation in quartz, albite, anorthite and calcite, *Geochim. Cosmochim. Acta* **53**, 725–733.
- Cole D. R., Horita J., Polyakov V. B., Valley J. W., Spicuzza M. J. and Coffey D. W. (2004) An experimental and theoretical determination of oxygen isotope fractionation in the system magnetite–H₂O from 300 to 800 °C, *Geochim. Cosmochim. Acta* **68**, 3569–3585.
- Deleuze M. and Brantley S. (1997) Inhibition of calcite crystal growth by Mg²⁺ at 100 °C and 100 bars: Influence of growth regime, *Geochim. Cosmochim. Acta* **61**, 1475–1485.
- Driesner T. and Seward T. M. (2000) Experimental and simulation study of salt effects and pressure/density effects on oxygen and hydrogen stable isotope liquid–vapor fractionation for 4–5 molar aqueous NaCl and KCl solutions to 400 °C, *Geochim. Cosmochim. Acta* **64**, 1773–1784.
- Epstein S., Buchsbaum H. A., Lowenstam H. and Urey H. C. (1953) Revised carbonate–water isotopic temperature scale, *Geol. Soc. Am. Bull.* **64**, 1315–1326.
- Erez J. and Luz B. (1983) Experimental paleotemperatures equation for planktonic foraminifera, *Geochim. Cosmochim. Acta* **47**, 1025–1031.

- Fritz P. and Smith D. G. (1970) The isotopic composition of secondary dolomites, *Geochim. Cosmochim. Acta* **34**, 1161–1173.
- Fyfe W. S. and Bischoff J. L. (1965) The calcite–aragonite problem, *Soc. Econ. Paleont. Mineral. Spec. Publ.* **13**, 3–13.
- Gussone N., Boehm F., Eisenhauer A., Dietzel M., Heuser A., Teichert B. M. A., Reitner J., Woerheide G. and Dullo W.-C. (2005) Calcium isotope fractionation in calcite and aragonite, *Geochim. Cosmochim. Acta* **69**, 4485–4494.
- Grossman E. L. and Ku T. L. (1986) Oxygen and carbon isotope fractionation in biogenic aragonite, *Temp. Effects. Chem. Geol.* **59**, 59–74.
- Hattori K. and Halas S. (1982) Calculation of oxygen isotope fractionation between uranium dioxide, uranium trioxide and water, *Geochim. Cosmochim. Acta* **46**, 1863–1868.
- Horibe Y. and Oba T. (1972) Temperature scales of aragonite–water and calcite–water systems, *Fossils (in Japanese)* **23/24**, 69–79.
- Hu G.-X. and Clayton R. N. (2003) Oxygen isotope salt effects at high pressure and high temperature, and the calibration of oxygen isotope geothermometers, *Geochim. Cosmochim. Acta* **67**, 3227–3246.
- Humphrey J. D. (2000) New geochemical support for mixing-zone dolomitization at Golden Grive, Barbados, *J. Sediment. Res.* **70**, 1160–1170.
- Jimenez-Lopez C., Caballero E., and Romanek C. S. (2001) Chemical, mineralogical and isotope behavior, and phase transformation during the precipitation of calcium carbonate minerals from intermediate ionic solution at 25 °, *Geochim. Cosmochim. Acta* **65**, 3219–3231.
- Kieffer S. W. (1982) Thermodynamics and lattice vibration of minerals: 5 Application to phase equilibria, isotopic fractionation, and high pressure thermodynamic properties, *Rev. Geophys. Space Phys.* **20**, 827–849.
- Kim S. T. and O’Neil J. R. (1997) Equilibrium and nonequilibrium oxygen isotope effects in synthetic carbonates, *Geochim. Cosmochim. Acta* **61**, 3461–3475.
- Kita I., Taguchi S. and Matsubaya O. (1985) Oxygen isotope fractionation between amorphous silica and water at 34–93 °C, *Nature* **314**, 83–84.
- Kuether J., Nelles G., Seshadri R., Schaub M., Butt H.-J. and Tremel W. (1998) Templated crystallization of calcium and strontium carbonates on centred rectangular self-assembled monolayers substrates, *Chem. Eur. J.* **4**, 1834–1842.
- Land L. S. (1980) The isotopic and trace element geochemistry of dolomite The state of the art. In *Concepts and Models of Dolomitization* (eds. D.H. Zenger, J.B. Dunham and R.L. Ethington), vol. 28, pp. 87–110. Society of Economic Paleontologists and Mineralogists Special Publication.
- Lasaga A. C. (1998) *Kinetic Theory in the Earth Sciences*. Princeton University Press, Princeton, New Jersey, 811.
- Leclerc A. J. and Labeyrie L. (1987) Temperature dependence of the oxygen isotopic fractionation between diatom silica and water, *Earth Planet. Sci. Lett.* **84**, 69–74.
- Matsuhisa Y., Goldsmith J. R. and Clayton R. N. (1979) Oxygen isotope fractionation in the system quartz–albite–anorthite–water, *Geochim. Cosmochim. Acta* **43**, 1131–1140.
- Matthews A. and Katz A. (1977) Oxygen isotope fractionation during the dolomitization of calcium carbonate, *Geochim. Cosmochim. Acta* **41**, 1431–1438.
- Matthews A. and Beckinsale R. D. (1979) Oxygen isotope equilibration systematics between quartz and water, *Am. Mineral.* **64**, 232–240.
- McCrea J. M. (1950) On the isotopic chemistry of carbonates and a paleotemperature scale, *J. Chem. Phys.* **18**, 849–857.
- McConnaughey T. (1989) ¹³C and ¹⁸O isotopic disequilibrium in biological carbonates: II. In vitro simulation of kinetic isotopic effects, *Geochim. Cosmochim. Acta* **53**, 163–171.

- McKenzie A. J. (1981) Holocene dolomitization of calcium carbonate sediments from the coastal sabkhas of Abu Dhabi, UAE A stable isotope study, *J. Geol.* **89**, 185–198.
- Melchiorrer E. B., Williams P. A. and Bevins R. E. (2001) A low temperature oxygen isotope thermometer for cerussite, with applications at Broken Hill, New South Wales, Australia, *Geochim. Cosmochim. Acta* **65**, 2527–2533.
- Morse J. W. and Casey W. H. (1988) Ostwald processes and mineral paragenesis in sediments, *Am. J. Sci.* **288**, 537–560.
- Northrop D. A. and Clayton R. N. (1966) Oxygen-isotope fractionations in systems containing dolomite, *J. Geol.* **74**, 174–195.
- O'Neil J. R., Clayton R. N. and Mayeda T. K. (1969) Oxygen isotope fractionation in divalent metal carbonates, *J. Chem. Phys.* **51**, 5547–5558.
- O'Neil J. R. (1986) Theoretical and experimental aspects of isotopic fractionation, *Rev. Mineral.* **16**, 1–40.
- O'Neil J. R. and Truesdell A. H. (1991) Truesdell, Oxygen isotope fractionation studies of solute-water interactions. In: *Stable Isotope Geochemistry: A Tribute to Samuel Epstein* (eds. H.P. Taylor, J.R. O'Neil and I.R. Kaplan), vol. 3, pp. 17–25. *Geochem. Soc. Spec. Publ.*
- Patterson W. P., Smith G. R. and Lohmann K. C. (1993) Continental paleothermometry and seasonality using the isotopic composition of aragonite otoliths of freshwater fishes. In: *Climate Change in Continental Isotopic Records* (eds. P.K. Swart, C.K. Lohmann, J. Mckenzie and S. Savin), vol. 78, pp. 191–202, Geophysical Monograph Series.
- Romanek C. S., Grossman E. L. and Morse J. W. (1992) Carbon isotopic fractionation in synthetic aragonite and calcite: Effects of temperature and precipitation rate, *Geochim. Cosmochim. Acta* **56**, 419–430.
- Schmidt M., Xeflide S., Botz R. and Mann S. (2005) Oxygen isotope fractionation during synthesis of CaMg-carbonate and implications for sedimentary dolomite formation, *Geochim. Cosmochim. Acta* **69**, 4665–4674.
- Schuetze H. (1980) Der Isotopenindex – eine Inkrementenmethode zur naeherungsweise Berechnung von Isotopenaustauschgleichgewichten zwischen kristallinen Substanzen, *Chem. Erde* **39**, 321–334.
- Sharp Z. D. and Kirschner D. L. (1994) Quartz–calcite oxygen isotope thermometry: A calibration based on natural isotopic variations *Geochim. Cosmochim. Acta* **58**, 4491–4501.
- Shiro Y. and Sakai H. (1972) Calculation of the reduced partition function ratios of α -, β -quartzes and calcite Bull, *Chem. Soc. Japan* **45**, 2355–2359.
- Shmulovich K. I., Landwehr D., Simon K. and Heinrich W. (1999) Stable isotope fractionation between liquid and vapor in water-salt systems up to 600 °C, *Chem. Geol.* **157**, 343–354.
- Sommer II M. A. and Rye D. M. (1978) Oxygen and carbon isotope internal thermometry using benthic calcite and aragonite foraminifera pairs. In: *Short papers of the Fourth International Conference on Geochronology, Cosmochronology and Isotope Geology* (ed. R.E. Zartman), pp. 78–701:408–410, USGS Open-File Report.
- Smyth J. R. (1989) Electrostatic characterization of oxygen sites in minerals, *Geochim. Cosmochim. Acta* **53**, 1101–1110.
- Tarutani T., Clayton R. N. and Mayeda T. K. (1969) The effect of polymorphism and magnesium substitution on oxygen isotope fractionation between calcium carbonate and water, *Geochim. Cosmochim. Acta* **33**, 987–996.
- Taube H. (1954) Use of oxygen isotope effects in the study of hydration of ions, *J. Phys. Chem.* **58**, 523–528.
- Thorrold S. R., Campana S. E., Jones C. M. and Swart P. K. (1997) Factors determining $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ fractionation in aragonitic otoliths of marine fish, *Geochim. Cosmochim. Acta* **61**, 2909–2919.

- Urey H.C. (1947) The thermodynamic properties of isotopic substances. *J. Chem. Soc. (London)* 562–581.
- Uzdowski E., Michaelis J., Boettcher M. E. and Hoefs J. (1991) Factors for the oxygen isotope equilibrium fractionation between aqueous and gaseous CO₂, carbonic acid, bicarbonate, carbonate, and water (19 °C), *Zeitschr. Phys. Chem.* **170**, 237–249.
- Uzdowski E. and Hoefs J. (1993) Oxygen isotope exchange between carbonic acid, bicarbonate, carbonate, and water: A re-examination of the data of McCrea (1950) and an expression for the overall partitioning of oxygen isotope between the carbonate species and water, *Geochim. Cosmochim. Acta* **57**, 3815–3818.
- Vasconcelos C., McKenzie J. A., Warthmann R. and Bernasconi S. M. (2005) Calibration of the $\delta^{18}\text{O}$ paleothermometer for dolomite precipitated in microbial cultures and nature environments, *Geology* **33**, 317–320.
- Wary J. L. and Daniels F. (1957) Precipitation of calcite and aragonite, *J. Am. Chem. Soc.* **79**, 2031–2034.
- Xia J., Ito E. and Engstrom D. R. (1997) Geochemistry of ostracode calcite: Part 1. An experimental determination of oxygen isotope fractionation, *Geochim. Cosmochim. Acta* **61**, 377–382.
- Zeebe R. E. (1999) An explanation of the effect of seawater carbonate concentration on foraminiferal oxygen isotope, *Geochim. Cosmochim. Acta* **63**, 2001–2007.
- Zheng Y.-F. (1991) Calculation of oxygen isotope fractionation in metal oxides, *Geochim. Cosmochim. Acta* **55**, 2299–2307.
- Zheng Y.-F. (1992) Oxygen isotope fractionation in wolframite, *Eur. J. Mineral.* **4**, 1331–1335.
- Zheng Y.-F. (1993a) Calculation of oxygen isotope fractionation in anhydrous silicate minerals, *Geochim. Cosmochim. Acta* **57**, 1079–1091.
- Zheng Y.-F. (1993b) Calculation of oxygen isotope fractionation in hydroxyl-bearing silicates, *Earth Planet. Sci. Lett.* **120**, 247–263.
- Zheng Y.-F. (1995) Oxygen isotope fractionation in magnetites: structural effect and oxygen inheritance, *Chem. Geol.* **121**, 309–316.
- Zheng Y.-F. (1996) Oxygen isotope fractionations involving apatites: Application to palaeo-temperature determination, *Chem. Geol.* **127**, 177–187.
- Zheng Y.-F. (1997) Prediction of high-temperature oxygen isotope fractionation factors between mantle minerals, *Phys. Chem. Mineral* **24**, 356–364.
- Zheng Y.-F. (1998) Oxygen isotope fractionation between hydroxide minerals and water, *Phys. Chem. Mineral* **25**, 213–221.
- Zheng Y.-F. (1999) Oxygen isotope fractionation in carbonate and sulfate minerals, *Geochem. J.* **33**, 109–126.
- Zheng Y.-F., Satir M., Metz P. and Sharp Z. D. (1999) Oxygen isotope exchange and disequilibrium between calcite and forsterite in an experimental C–O–H fluid, *Geochim. Cosmochim. Acta* **63**, 1781–1786.
- Zheng Y.-F., Satir M. and Metz P. (2004) Oxygen isotope exchange and disequilibrium between calcite and tremolite in the absence and presence of an experimental C–O–H fluid, *Contrib. Mineral. Petrol.* **146**, 683–695.
- Zhou G.-T. and Zheng Y.-F. (2001) Chemical synthesis of CaCO₃ minerals at low temperatures and implication for mechanism of polymorphic transition, *N. Jb. Miner. Abh.* **176**, 323–343.
- Zhou G.-T. and Zheng Y.-F. (2002) Kinetic mechanism of oxygen isotope disequilibrium in precipitated witherite and aragonite at low temperatures: An experimental study, *Geochim. Cosmochim. Acta* **66**, 63–71.

- Zhou G.-T. and Zheng Y.-F. (2003) An experimental study of oxygen isotope fractionation between inorganically precipitated aragonite and water at low temperatures, *Geochim. Cosmochim. Acta* **67**, 387–399.
- Zhou G.-T., Yu J. C., Wang X.-C. and Zhang L.-Z. (2004) Sonochemical synthesis of aragonite-type calcium carbonate with different morphologies, *New J. Chem.* **28**, 1027–1031.
- Zhou G.-T. and Zheng Y.-F. (2005) Effect of polymorphic transition on oxygen isotope fractionation between aragonite, calcite and water: A low-temperature experimental study, *Am. Mineral.* **90**, 1121–1130.