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Surface kinetic model for isotopic and trace element fractionation during precipitation of calcite from aqueous solutions

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A surface reaction kinetic model is developed for predicting Ca isotope fractionation and metal/Ca ratios of calcite as a function of rate of precipitation from aqueous solution. The model is based on the requirements for dynamic equilibrium; i.e. proximity to equilibrium conditions is determined by the ratio of the net precipitation rate ($R_p$) to the gross forward precipitation rate ($R_f$), for conditions where ionic transport to the growing crystal surface is not rate-limiting. The value of $R_p$ has been experimentally measured under varying conditions, but the magnitude of $R_f$ is not generally known, and may depend on several factors. It is posited that, for systems with no trace constituents that alter the surface chemistry, $R_f$ can be estimated from the bulk far-from-equilibrium dissolution rate of calcite ($R_b$ or $k_b$), since at equilibrium $R_f = R_b$, and $R_p = 0$. Hence it can be inferred that $R_f \approx R_p + R_b$. The dissolution rate of pure calcite is measurable and is known to be a function of temperature and pH. At given temperature and pH, equilibrium precipitation is approached when $R_p (= R_f - R_b) << R_b$. For precipitation rates high enough that $R_p >> R_b$, both isotopic and trace element partitioning are controlled by the kinetics of ion attachment to the mineral surface, which tend to favor more rapid incorporation of the light isotopes of Ca and discriminate weakly between trace metals and Ca. With varying precipitation rate, a transition region between equilibrium and kinetic control occurs near $R_p \approx R_b$ for Ca isotopic fractionation. According to this model, Ca isotopic data can be used to estimate $R_f$ for calcite precipitation. Mechanistic models for calcite precipitation indicate that the molecular exchange rate is not constant at constant T and pH, but rather is dependent also on solution saturation state and hence $R_p$. Allowing $R_b$ to vary as $R_p^{1/2}$, consistent with available precipitation rate studies, produces a better fit to some trace element and isotopic data than a model where $R_b$ is constant. This model can account for most of the experimental data in the literature on the dependence of $^{44}$Ca/$^{40}$Ca and metal/Ca fractionation in calcite as a function of precipitation rate and temperature, and also accounts for $^{18}$O/$^{16}$O variations with some assumptions. The apparent temperature dependence of Ca isotope fractionation in calcite may stem from the dependence of $R_b$ on temperature; there should be analogous pH dependence at pH < 6. The proposed model may be valuable for predicting the behavior of isotopic and trace element fractionation for
a range of elements of interest in low-temperature aqueous geochemistry. The theory presented is based on measurable thermo-kinetic parameters in contrast to models that require hyper-fast diffusivity in near-surface layers of the solid.

1. INTRODUCTION

Recent work on mid-mass stable isotope systems like Ca, Mg, Fe, Cr, and Mo suggests that minerals that form by precipitation from aqueous solution do not do so at isotopic equilibrium, especially when the precipitation is done at rates fast enough to be readily observed in laboratory experiments (Johnson et al., 2004). Furthermore, it has also been shown that in most instances the solid phase is enriched in the light isotope species relative to the solution phase. While some studies have suggested that these fractionations associated with precipitation from solution may represent isotopic equilibrium (e.g. Lemarchand et al., 2004), and the reports of temperature dependence of fractionations can be viewed as broadly consistent with this interpretation (e.g. Gussone et al., 2005), the precipitation rate dependence (Tang et al., 2008) and preference for the light isotopes in the solid phase (Skulan et al., 1997; Skulan and DePaolo, 1999) suggest that the fractionations are mostly kinetic in origin. The recent observations on mid-mass stable isotope systems have potentially important implications for all stable isotope and trace element studies. Deviations from equilibrium fractionation behavior are common, and a more complete understanding of their origins is critical to fully capitalizing on the potential of isotopic and trace element measurements to provide information on geochemical processes and paleoenvironment (e.g. Smith et al., 1979; Beck et al., 1992; Zachos et al., 2002; Marshall and McCulloch, 2002; Fantle and DePaolo, 2005; Eisenhauer et al., 2010; Coggon et al., 2010).

It is the purpose of this contribution to propose a framework to help understand the many, and partly contradictory observations on calcium isotopic fractionation that have been made thus far, and to help define the additional data needed to more fully understand isotopic fractionation during mineral precipitation. The proposed model also accounts for the essential features of the incorporation of Sr and Mn into calcite, although trace element
partitioning, as opposed to isotopic fractionation, is likely to require additional parameters to achieve a full description. The approach taken is one using a macroscopic treatment of chemical kinetics, and can be viewed as an extension of one component of the box model of Fantle and DePaolo (2007). It is expected that this macroscopic treatment can be extended to include a molecular scale description of the processes involved in mineral growth (e.g. Teng et al., 2000; DeYoreo et al., 2009; Morse et al., 2007), and how they relate to isotopic fractionation.

1.1. Surface reaction effects, transport-control, and isotopic equilibrium

The conditions necessary for isotopic equilibrium are analogous to those for chemical equilibrium. Chemical reactions are conceptualized as the net result of a forward and backward reaction. At equilibrium, the rate of the forward reaction ($R_f$) is balanced exactly by the rate of the backward reaction ($R_b$). Equilibrium can be maintained only through the rapid and continual exchange of material between reactant and product phases. In order for a reaction to proceed (such that the amounts of the product phases increase at the expense of the reactants) at equilibrium requires that the net reaction rate ($R_p = R_f - R_b$) be much smaller than either the gross forward or gross backward reaction rates. This requirement can be stated simply in the form $R_p << R_b$. This same requirement applies to isotopic equilibrium. It is also to be expected, because the zero-point vibrational energy and the mean molecular velocity of light isotopes are higher than those for heavy isotopes, that the rate constants for both the forward and backward reactions are greater for light isotopic species than for heavier isotopic species (e.g. O’Neil, 1986; Criss, 1999; Zeebe and Wolf-Gladrow, 2001).

The requirement that the net precipitation rate is small relative to the gross exchange fluxes is necessary but not sufficient to ensure equilibrium. It is also necessary that the net rate of reaction is small in comparison to the transport of reactants to the sites of reaction. Hence, the precipitation of minerals from solution can occur in at least four different regimes (Figure 1).
In regime 1, the net precipitation rate is much slower than the gross exchange rates \((R_f - R_b) << R_b\), and slow enough that there are no transport limitations of ions to the surface of growing crystals. In this regime, which is restrictive, it can be expected that equilibrium will describe the isotopic and elemental fractionation between the aqueous species and solid phase.

In regime 2, the net precipitation rate is much slower than the gross exchange rate, but fast enough that there are transport limitations in the fluid phase. In this case, it is a good approximation that the fluid phase in contact with the crystal surface is at or very near equilibrium with the crystal surface, but the solid is not growing in equilibrium with the bulk aqueous reservoir due to fractionation during transport (e.g. diffusion) of the aqueous species to the mineral surface. It is shown below that this condition is unlikely to be applicable to precipitation of calcite from aqueous solution.

In regime 3, the net precipitation rate is larger than the gross exchange rate \((R_f - R_b) \geq R_b\) but slow enough that there are no transport limitations in the fluid phase. In this case, the composition of the solid phase is determined mainly by the attachment-detachment kinetics of the species at the interface (i.e. surface reaction control), which means that the solid phase will tend to be enriched in the light isotopic species, in excess of whatever the equilibrium fractionation should be.

In regime 4, the net precipitation rate is larger than the gross exchange rate and fast enough that there are also transport limitations in the fluid phase. This case is similar to regime 3, but the composition of the solid is affected by both attachment/detachment kinetics and mass transport in the fluid. Because light isotopic species will be transported faster, the solid phase will tend to be enriched in the light isotopic species, in excess of the equilibrium fractionation.

This qualitative summary of the relationships between fluid - mineral surface reaction kinetics provides a framework that is adequate to begin discussion of isotopic fractionation effects. It can be quantified further as discussed below, but may also need further modification to account for variations in reaction mechanism. This summary does not account for solid phase transport effects, which may affect the relationship between solid
and fluid phase isotopic composition under near-equilibrium (near-zero net crystal growth) conditions.

1.2. Examples of Regime 1 and Regime 2 condensation

Examples of precipitation (*sensu lato*) in regimes 1 and 2 with important isotopic fractionation consequences are provided by the condensation of water and ice from saturated and supersaturated air. An example of equilibrium, or near-equilibrium precipitation (Regime 1), is afforded by the condensation of water droplets from vapor-saturated air. Condensation occurs at very slight water vapor oversaturation values (< 1%), and the exchange fluxes at the liquid surface are >1000 times the net condensation flux. Regime 2 is illustrated by the condensation of ice crystals from vapor-oversaturated air in mixed (ice plus water droplets) clouds (Jouzel and Merlivat, 1984). Due to the co-existence of water vapor droplets and ice crystals, air in clouds can be oversaturated with respect to ice by 30% or more (Pruppacher and Klett, 1997; Libbrecht, 2005). At this level of oversaturation, the growth of ice crystals is limited by vapor phase transport of water molecules to the ice surface, the difference in vapor phase diffusivity between water isotope species has a large effect, and the ice crystals that form are enriched in light isotopes *relative to equilibrium values*. In this example, it is also the case that exchange at the ice surface between the solid and vapor is fast relative to the net condensation rate.

In the above mentioned examples of condensation of water from a gas phase, the exchange rate at the vapor-condensate interface can be estimated using the collision rate of water vapor molecules with the condensate surface (Knudsen, 1950; Hirschfelder et al., 1965; Richter, 2004), multiplied by a sticking coefficient (or accommodation coefficient, $\gamma$), as discussed in Pruppacher and Klett (1997) and Seinfeld and Pandis (1998). Although there is uncertainty in the accommodation coefficient, for water recent estimates place the value between 0.1 and 1 (Davidovits et al., 2004). Using a conservative value of 0.1, the implied exchange rate of molecules between saturated vapor and a liquid water surface is about $R_b = 20$ mol/m$^2$/sec at 25°C. A typical condensation rate ($R_f - R_b$) is about 0.003 mol/m$^2$/sec (for a 100 µm–radius droplet in 1% oversaturated air), about four orders of magnitude
smaller. The condensation flux varies as the inverse of the radius of the droplet, so indeed condensation of water droplets larger than 10 µm is expected to be a near-equilibrium process.

For ice at -15°C, the accommodation coefficient is estimated to be close to 1 (Libbrecht, 2005), and the implied exchange rate of molecules between the vapor and the ice surface is therefore 20 mol/m²/sec (the higher value of γ is offset by lower temperature and lower saturation water vapor pressure). Ice condensation rates can be up to about 0.005 mol/m²/sec (for a 100 µm–radius ice grain in 30% oversaturated air). The ice condensation rates are slow in comparison to the (theoretical) surface exchange rates, i.e. \((R_f - R_b) \ll R_b\) but they are fast enough, and occur at substantial vapor phase oversaturation and at low water vapor concentration, so that the growth is limited by diffusive transport of H₂O in the vapor phase. Hence ice condensation (or vapor deposition) occurs under conditions described by Regime 2. The kinetic isotopic effects associated with ice crystal growth in air can be simply described with a radial diffusion model because it can be assumed that the water vapor concentration in air at the ice surface is the equilibrium value (Jouzel and Merlivat, 1984; Seinfeld and Pandis, 1998). The kinetic effects cause large deviations from equilibrium (Figure 2) because the equilibrium fractionation favors the heavy isotopologue (e.g. H²¹⁸O) in the solid phase (\(\alpha_{eq} = 1.018\) at -15°C) whereas the diffusivity of the light isotopologue (H₂¹⁶O) is larger in air so that the diffusive kinetic fractionation factor (\(D_{18}/D_{16} = 0.972\)) is less than 1.

1.3. Equations for surface reaction control of CaCO₃ precipitation

The precipitation of minerals from aqueous solution is likely to occur in Regimes 3 and 4. However, as with the vapor phase condensation examples, the critical parameter is the exchange rate between fluid and mineral surface. For a vapor phase, the collision frequency can be calculated from kinetic theory. If the accommodation coefficient cannot be estimated, the exchange rate can be determined experimentally by evaporation into infinitely undersaturated vapor (or into vacuum) under conditions where there are no transport limitations (e.g. Richter, 2004). It is argued here, and this should be regarded as
a postulate that needs further proof, that the exchange rate for the mineral – aqueous fluid system can be measured experimentally as well, and is given by the mineral dissolution rate into a highly undersaturated solution under surface reaction controlled conditions (i.e. no transport limitations). This assumption is the initial thesis that is evaluated below. However, studies of calcite growth from aqueous solution strongly suggest that the surface exchange rate is a function of saturation state of the solution, which correlates with growth mechanism (e.g. Teng et al., 2000; DeYoreo et al., 2009). A second version of the model is also discussed where the surface exchange rate is allowed to be a function of oversaturation, with the functional form approximated based on experimental data on the relationship between calcite precipitation rates and solution oversaturation.

In the following section, equations describing Ca isotopic fractionation during calcite precipitation from aqueous solution are developed and then compared to recent experimental measurements. The available data fit the model well. This success has implications for the application of isotope ratio measurements to the understanding of mineral precipitation, and for understanding fluid-rock systems in nature. A key result is that experimentally measured dissolution rates can be used to infer whether mineral precipitation is likely to be occurring under near-equilibrium or kinetically controlled conditions.

The precipitation rate ($R_f$; the forward rate) and dissolution rate ($R_b$; backward rate) for calcite in a solution where pH ≥ 7.5 can be written in simplified form as (Lopez et al., 2009):

$$ R_f = k_f \gamma_{Ca} \gamma_{CO_3}{Ca^{2+}}_{fs}[CO_3^{2-}]_{fs} = k_f [Ca^{2+}]_{fs}[CO_3^{2-}]_{fs} \quad (1a) $$

$$ R_b = k_b [CaCO_3] \quad (1b) $$

where “$fs$” denotes the fluid at the mineral surface, $k_f$ is the (forward) rate constant for precipitation and $k_b$ is the (backward) rate constant for dissolution. The units of $k_f$ and $k_b$ depend on the units used for concentration. If the concentrations are expressed in
dimensionless units relative to a standard state (hypothetical 1 molal solution for aqueous species; pure CaCO₃ for the solid), then the units of \( k_f \) and \( k_b \) will be fluxes, such as mol/m²/sec. At equilibrium the forward and backward rates are equal, and hence the equilibrium constant for the dissolution reaction is \( K_{eq} = k_b / k'_f \) (cf. Lasaga, 1998).

It follows from equations 1a and 1b and the expression for \( K_{eq} \) that the net precipitation rate \( (R_p) \) can be written in the form:

\[
R_p = R_f - R_b = k_f' \left( [Ca^{2+}]_f [CO_3^{2-}]_f - [Ca^{2+}]_{eq} [CO_3^{2-}]_{eq} \right)
\] (2a)

For the conditions prevalent in marine waters, namely \([Ca^{2+}] >> [CO_3^{2-}]\), this equation can be simplified to:

\[
R_p = k_f' [Ca^{2+}]_{sol} \left( [CO_3^{2-}]_f - [CO_3^{2-}]_{eq} \right)
\] (2b)

where \([Ca^{2+}]_{sol}\) is the Ca ion concentration in the bulk solution, and it can be assumed that \([Ca^{2+}]_{sol} = [Ca^{2+}]_{fs} \approx [Ca^{2+}]_{eq}\) to a sufficiently good approximation. The concentration of dissolved Ca\(^{2+}\) (= 10.4 mmol/L) in the oceans varies little. In general it is not possible to measure \([CO_3^{2-}]_{fs}\), which could potentially be somewhat smaller than \([CO_3^{2-}]_{sol}\), but when calcite growth is occurring under conditions where diffusive transport of \([CO_3^{2-}]\) to the mineral surface is not limiting the growth rate, it is possible to substitute \([CO_3^{2-}]_{sol}\) for \([CO_3^{2-}]_{fs}\) with little loss of accuracy. The equation can then be cast in the following form:

\[
R_p = k_f' K_{sp} (\Omega_c - 1) = k_f^* \left( \Omega_c - 1 \right)
\] (3a)

where \(\Omega_c\) is the saturation state of the solution with respect to calcite and \(K_{sp} = [Ca^{2+}]_{eq} [CO_3^{2-}]_{eq}\) and \(k_f^*\) is defined as equal to \(k_f K_{sp}\). It has been found experimentally that precipitation rates are not proportional to \((\Omega_c - 1)\), but rather vary as this quantity to a power of up to or even greater then 3 (e.g. Zuddas and Mucci, 1994, 1998; Lopez et al., 2009). It is likely that this higher order dependence stems from changes in the reaction...
mechanism with saturation state (e.g. Teng et al., 2000; DeYoreo et al., 2009) and hence equation 3a might better be written:

\[ R_p = k_f K_{sp} (\Omega_c - 1) = k_f^* (\Omega_c) (\Omega_c - 1) \]  

(3b)

where the notation is meant to show \( k_f^* \) as a function of \( \Omega_c \). Since \( k_f^* \) constitutes an estimate for the gross exchange flux at the mineral surface, this point is important in evaluating the isotope fractionation model and its application to trace element partitioning described below. It is also noteworthy that recent studies have shown that \( k_f^* \) is dependent on the \( \text{Ca}^{2+}/\text{CO}_3^{2-} \) ratio of the solution (Nehrke et al., 2007; Larsen et al., 2010), which is important for evaluating how the exchange flux \( R_b \) relates to \( k_f^* \).

2. MODEL FOR ISOTOPIC FRACTIONATION WITH SURFACE REACTION CONTROL

It is expected that isotopic species such \( ^{44}\text{Ca}^{2+} \) and \( ^{40}\text{Ca}^{2+} \), as well as \( ^{13}\text{CO}_3^{2-} \) and \( ^{12}\text{CO}_3^{2-} \) will have slightly different \( k_f \) and \( k_b \) values and hence different rates of reaction. The behavior of the C and O isotopes in the carbonate anions is complicated by exchange among dissolved species (e.g. Zeebe and Wolf-Gladrow, 2001), so the analysis here will be restricted to the simpler case of the isotopes of \( \text{Ca}^{2+} \). The simplified equations for the rate of attachment (precipitation) of the two Ca isotopic species as mineral crystal growth proceeds can be written:

\[ ^{40}R_f = ^{40}k_f [^{40}\text{Ca}^{2+}]_f [^{CO}_3^{2-}]_f \]  

(4a)

\[ ^{44}R_f = ^{44}k_f [^{44}\text{Ca}^{2+}]_f [^{CO}_3^{2-}]_f \]  

(4b)

The dissolution rates are:

\[ ^{40}R_b = ^{40}k_b [^{40}\text{CaCO}_3] \]  

(5a)
Implicit in these expressions are the two kinetic isotopic fractionation factors associated with precipitation and dissolution:

$$\alpha_f = \frac{^{44}k_f}{^{40}k_f}$$  \hspace{1cm} (6a)$$

$$\alpha_b = \frac{^{44}k_b}{^{40}k_b}$$  \hspace{1cm} (6b)$$

The equilibrium isotopic fractionation factor is:

$$\alpha_{eq} = \frac{\alpha_f}{\alpha_b} = \frac{^{44}K_{eq}}{^{40}K_{eq}} = \left(\frac{r_{solid}}{r_{fs_{eq}}}\right)$$  \hspace{1cm} (7)$$

where \( r \) is shorthand for the isotopic ratio \(^{44}\text{Ca}/^{40}\text{Ca}\). If the above expressions are substituted into the previous equations, two equations can be derived that relate the isotope-specific forward and backward rates (Figure 3):

$$^{44}R_f = \alpha_f^{40}k_f^{40}r_{fs_{eq}}^{40}[^{40}\text{Ca}^{2+}]_{fs}[^{40}\text{CO}_3^{2-}]_{fs} = \alpha_f^{40}R_f$$  \hspace{1cm} (8)$$

and

$$^{44}R_b = \alpha_b^{40}k_b^{40}r_{solid}^{40}[^{40}\text{CaCO}_3] = \alpha_b^{40}R_b = \frac{\alpha_f}{\alpha_{eq}}r_{solid}^{40}R_b$$  \hspace{1cm} (9)$$

These equations can be used to derive a general equation for the fractionation attending mineral precipitation under steady state, surface reaction controlled conditions. It should be noted that if the precipitation and dissolution fluxes are equal, the equilibrium condition is recovered. Also, the isotopic effects are not dependent on the exact form of the kinetic rate expression (e.g. equations 2); they are only dependent on the rates themselves.

The effective isotopic fractionation factor for steady state precipitation can be derived starting first with the rate of change of the isotopic ratio of the solid surface layer:

$$^{44}R_b =^{44}k_b[^{44}\text{CaCO}_3]$$  \hspace{1cm} (5b)$$
where \( N \) designates number of atoms (or moles of atoms), and at steady state:

\[
\frac{dr_{\text{solid}}}{dt} = 0 = \frac{1}{N_{40\text{Ca}}} \left( \frac{dN_{44\text{Ca}}}{dt} - r_{\text{solid}} \frac{dN_{40\text{Ca}}}{dt} \right) = \frac{1}{N_{40\text{Ca}}} \left( \frac{44R_p - r_{\text{solid}} 40R_p}{1} \right)
\]

Steady state in this case means that the isotopic composition of the surficial layer of the solid is not changing with time as the crystal grows. After substitution of equation 8 and 9 into 10 and some algebraic manipulation, the following expression is obtained for the steady condition \((r_{\text{solid}} = \text{constant})\):

\[
\alpha_p = \frac{r_{\text{solid}}}{r_{\text{fluid}}} = \frac{\alpha_f}{1 + \frac{R_b}{R_f} (\frac{\alpha_f}{\alpha_{eq}} - 1)} = \frac{\alpha_f}{1 + \frac{R_b}{R_p + R_b} (\frac{\alpha_f}{\alpha_{eq}} - 1)}
\]

This function is plotted in Figure 4 for arbitrary values of \(\alpha_{eq}\) and \(\alpha_f\). The equation describes the instantaneous isotopic fractionation of the material being added to a growing solid phase under conditions where there is no transport limitation. The crossover from equilibrium \((\alpha_p = \alpha_{eq})\) to kinetically controlled \((\alpha_p = \alpha_f)\) precipitation occurs at \(R_p \approx R_b\). The equation does not take account of any transport in the solid phase that might affect the isotopic composition of the solid surface layer (e.g. Watson, 2004), which at low temperature (ca. 25°C) should be far too slow to affect the process. Transport effects are considered in a later section of the paper.

According to equation 11 and as shown in Figure 4, a critical parameter in assessing isotopic fractionation is the backward (dissolution) rate, \(R_b\), or equivalently the difference between the gross forward precipitation rate \(R_f\) and the net forward precipitation rate \(R_p\). For conditions under which \(R_p \gg R_b\) (or \(R_f \approx R_p\)) the effective fractionation is dominated by the kinetic fractionation factor associated with precipitation \((\alpha_f)\). In this limit, as shown in Figure 4, the fractionation factor \(\alpha_p\) is not sensitive to precipitation rate unless the rate becomes high enough that fluid phase transport limitations start to have an effect. In the other extreme, \(R_p \ll R_b\) (or \(R_f\)
The effective fractionation factor ($\alpha_p$) is sensitive to precipitation rate mainly in the range where $R_p \approx R_b \approx 2R_f$. The behavior illustrated in Figure 4 and described in equation 11 is what should be expected in the absence of transport effects in the fluid or the solid, and assuming that $R_b$ is not a function of $R_p$. Comparing with Figure 1, this behavior corresponds to that expected for the conditions represented by the uppermost part of the diagram. It should be noted that $R_b$, and the values of the kinetic and equilibrium fractionation factors, can be functions of temperature, solution composition, and other variables, but it is inescapable that the approach to equilibrium must depend on the ratio $R_p/R_b$ (or alternatively $R_p/R_f$).
3. WHAT IS THE VALUE OF $R_b$?

To apply equation 11 to Ca isotopes in calcite requires values for three parameters – $R_b$ (or $R_f$), $\alpha_f$, and $\alpha_{eq}$. Several studies have reported dissolution rates (i.e. $R_b$) for calcite. A relatively complete study covering a range of pH values at 25°C was presented by Chou et al. (1989); their data are reproduced in Figure 5. Chou et al. (1989) determined that there is in general more than one dissolution mechanism operating, and the dominant mechanism changes with pH (cf. Alkatten et al., 2009). The available experimental data on Ca isotopic fractionation were obtained using solutions with a relatively narrow pH range of 7.5 to 9 (LeMarchand et al., 2004; Tang et al., 2008), and in this range the value for $R_b$ is invariant with pH and equal to $6 \times 10^{-7}$ mol/m$^2$/sec at 25°C. For the value of $\alpha_{eq}$, Fantle and DePaolo (2007) have suggested the value $\alpha_{eq} = 1.0000$. For $\alpha_f$ it could be argued based on available data that the value is approximately $0.9985\pm 3$, which is the largest fractionation so far observed. However, it is possible that both $\alpha_{eq}$ and $\alpha_f$ vary with temperature, and possibly also with solution composition. The experimental data can also be used to deduce values for $\alpha_{eq}$ and $\alpha_f$ using the proposed model.

The dissolution rate studies in the literature are virtually all done under conditions far from equilibrium; i.e. $\Omega_c << 1$. In this case, by reference to equation 3b, the value of $R_b$ should be equivalent to the precipitation rate constant:

$$R_b = k_f K_{sp} (\Omega_c - 1) = -k_f K_{sp} = -k_f^*$$

(12a)

As noted above, however the value of $k_f^*$ is generally found to be a function of $\Omega_c$, which means that the exchange rate between the mineral surface and the solution is not a constant, but instead tends to vary systematically with oversaturation, especially as $(\Omega_c - 1)$ approaches zero. It is even more problematical that $k_f^*$ is a function of $\text{Ca}^{2+}/\text{CO}_3^{2-}$ in the solution (Nehrke et al., 2007; Larsen et al., 2010) because, whereas calcite can precipitate from solutions of arbitrary $\text{Ca}^{2+}/\text{CO}_3^{2-}$, it can dissolve only stoichiometrically. Hence the dissolution rate constant $k_b$ (or $R_b$) is not likely to be equivalent to the precipitation rate.
constant $k_f^*$ except when $\text{Ca}^{2+}/\text{CO}_3^{2-} = 1$. Nehrke et al (2007) show that $k_f^*$ is roughly 10 times smaller for a seawater-like $\text{Ca}^{2+}/\text{CO}_3^{2-}$ ($\approx 200$) than for $\text{Ca}^{2+}/\text{CO}_3^{2-} = 1$.

As shown by Teng et al. (2000), the mechanism of calcite mineral growth varies as a function of saturation index, and hence as a function of growth rate. The velocity and spacing of steps, and the density of kinks on the crystal surface determine the growth rate. As oversaturation increases, the spacing of the steps decreases and the step velocities increase, resulting in faster growth rates. Since most of the attachment of ions from solution happens at steps and kinks, the rate of exchange between the mineral surface and the solution is presumably a function of the concentration of steps and kinks, which is also a function of growth rate. The observed growth rate effectively varies as $(\Omega-1)^n$, where $n > 1$. A similar conclusion has been reached in other studies although without the benefit of a mechanistic model (e.g. Zuddas and Mucci, 1994; Lopez et al., 2009).

No researcher has proposed a formula relating $k_f^*$ to $\Omega$ based on the detailed topography and structural evolution of calcite surfaces (cf. DeYoreo et al., 2009). However, a first-order estimate for the variation of the exchange flux with oversaturation can be inferred from available experimental data on calcite growth rates. If it is assumed that the precipitation rate can be expressed by the following equation:

$$R_p = k_f^*(\Omega)(\Omega_c - 1)$$

the exchange flux might vary much like the rate constant $k_f^*(\Omega_c)$, corrected for the solution $\text{Ca}^{2+}/\text{CO}_3^{2-}$. Apparent values of $k_f^*$ are derivable from the values of $R_p$ and $\Omega_c$ measured in the experiments: $k_f^*(\Omega) = R_p/(\Omega-1)$. A plot of this apparent exchange rate versus $R_p$ is shown as Figure 6, using data from Tang et al. (2008) and Lopez et al. (2009) acquired at three different temperatures. The data suggest that the apparent rate constant varies roughly as $R_p^{0.5\pm0.2}$ at constant temperature (Figure 6) and for values of $R_p$ between $10^{-9}$ and $5 \times 10^{-6} \text{ mol/m}^2/\text{sec}$. It may be noteworthy that in the experiments summarized in Figure 6, in no case is the 25°C value of $k_f^*$ greater than the value of $k_b$ determined by Chou et al.
In all cases, the deduced value of $k_f^*$ is substantially smaller than $k_b$. In the discussion below, two versions of the model are used; one with $R_b = \text{constant}$ (Model 1), and one in which $R_b$ is allowed to vary with $R_p$ (Model 2) as shown in Figure 6.

3. APPLICATION TO CALCITE PRECIPITATION

3.1 Ca isotopic fractionation in precipitated inorganic calcite

The constant-$R_b$ version of the model applied to Ca isotope fractionation in calcite is shown as Figure 7a. For this calculation, a constant value of $R_b = 6 \times 10^{-7} \text{ mol/m}^2/\text{sec}$ at 25°C is assumed, and the resulting model curve is juxtaposed with 25°C data of Tang et al (2008). The dark dashed line in the figure corresponds to limiting fractionation factors of $\alpha_{eq} = 0.9995$ and $\alpha_f = 0.9984$. The data fit the model well, which is noteworthy because the inflection point for the curve is set by the value of $R_b$ from Chou et al. (1989) and is not an adjustable parameter. The value of $\alpha_f$ of 0.9984 that fits the data best is consistent with available experimental data. However, the value of $\alpha_{eq}$ that must be used to get a good fit to the data is not that suggested by Fantle and DePaolo (2007), but rather a lower value. The data do not appear to allow for a value of $\alpha_{eq} = 1.0000$ for the constant-$R_b$ model, as shown by the significantly poorer fit obtained when the model curve is forced to this value. The good fit of the Tang et al (2008) data suggests that the value of $R_b$ derived from the dissolution rate data of Chou et al. (1989) is in fact close to the actual gross molecular exchange flux for Ca between the growing calcite and solution at 25°C, at least in the range of $R_p$ where it is close to the calcite dissolution rate measured by Chou et al. (1989).

A second version of the model is plotted in Figure 7b, where in this case $R_b$ is allowed to vary with $R_p$. The exact form of the variation of $R_b$ with $R_p$ (or with $\Omega_c$) is not known, although the isotopic data could provide constraints. To evaluate the effect of allowing $R_b$ to vary along the lines of the observations in Figure 6, Model 2 uses an $R_b$ equal to the Chou value at $R_p \geq R_b$, and lets $R_b$ vary as $R_p^{1/2}$ at $R_p$ values lower than the Chou et al. value. The use of values of $R_b$ that are greater than the deduced $k_f^*$ values is consistent with the
observations of Nehrke et al. (2007) and Larsen et al. (2010) as noted above, and is required by the fit of the data shown in Figure 7a. The use of a variable $R_b$ value at low precipitation rates provides a fit to the Ca isotopic data that is similar in quality to that obtained with the constant – $R_b$ model, but it allows the value of $\alpha_{eq}$ to be closer to 1.00; in this case a good fit is obtained with $\alpha_{eq} = 0.9998$. The other endmember value, is slightly different as well ($\alpha_f = 0.9983$), but not significantly different from that deduced for the constant-$R_b$ model.

3.2. Effect of temperature on Ca isotopic fractionation

At higher and lower temperature, the value of $R_b$ changes relative to that at 25°C, which shifts the model curve shown in Figure 7 (i.e. $\alpha_f$ versus $R_p$) toward lower $R_p$ values at lower temperature and higher $R_p$ values at higher temperature. Tang et al. (2008) report data for Ca isotope fractionation at 5°C and 40°C, so the model can be tested against these data. The temperature dependence of the dissolution rate has been determined recently by Gledhill and Morse (2006), albeit in salt-rich brines, and by Pokrovsky et al. (2009). Both studies were done in solutions with lower pH. Here the T-dependence proposed by Pokrovsky et al. (2009) is used; which implies that $R_b$ is $1.55 \times 10^{-6}$ mol/m²/sec at 40°C and $1.5 \times 10^{-7}$ mol/m²/sec at 5°C, when applied to the 25°C data of Chou et al. (1989) for solutions with pH in range 7.5 to 9. Figures 8a and 8b show the constant-$R_b$ model fits to the Tang et al. (2008) data for 5°C and 40°C. It is evident that the shift in the $R_b$ values due to temperature does well in accounting for most of the data. The model curves were calculated for the same values of $\alpha_f$ and $\alpha_{eq}$ as used for the 25°C model curve.

The curves from Figures 7 and 8 can be used to make inferences about the temperature dependence of the Ca isotope fractionation factor in nature (Figure 9). For example, if $R_p$ is constant and close to the value of $6 \times 10^{-7}$ mol/m²/sec, there will be a T-dependence to the fractionation factor, with $\alpha_p$ tending toward unity as T increases. This feature is similar to the expectation for equilibrium fractionation, and hence could be confused with the temperature dependence of an equilibrium fractionation factor (e.g. Gussone et al., 2003).
However, the kinetically controlled T-dependence will depend in turn on the precipitation rate. Figure 8 shows the expected T-dependence of $\alpha_p$ for five different values of $R_p$. At $R_p = 6 \times 10^{-7}$ mol/m$^2$/sec, there is the maximum T-dependence, and over the range of temperature appropriate to the oceans (0 to 40°C), the value of $1000\ln \alpha_p$ shifts by about 0.6‰. However, at higher and lower values of $R_p$, there is less T-dependence.

For biogenic calcite formation, organisms may produce calcite from solutions that are oversaturated by a factor of 5 to 10 (slightly in excess of that of surface seawater; e.g. Bentov and Erez, 2005), hence the attendant $R_p$ values may be close to $10^{-6}$ mol/m$^2$/sec or somewhat lower due to the inhibiting effect of Mg ions. At this rate one would expect approximately the observed variation of about 0.5‰ as shown on Figure 9. Since aragonite dissolves at about the same rate as calcite (i.e. $R_b$ for aragonite is the same as that for calcite; Chou et al., 1989), the temperature variability for aragonite is likely to be similar to that for calcite at the same precipitation rate, as is indicated by the data of Gussone et al (2003), although the fractionation factor is somewhat larger. The data and model curves shown in Figure 9 suggest that the temperature dependence of $R_b$ could play a significant role in determining isotopic fractionation in biogenic as well as abiogenic calcite. However, it is well known that many organisms produce microenvironments from which calcite is precipitated, and therefore other effects could also contribute to the observed fractionations (e.g. Bentov and Erez, 2005; Sime et al, 2005; Carre et al., 2006).

### 3.3. Trace element incorporation into calcite

The incorporation of trace metal cations (e.g. Sr, Ba, Mn, Cd, U) into calcite is analogous in many ways to isotopic fractionation and hence may also be treatable with an appropriate modification of equation 11. One difference between trace element-to-Ca ratios and Ca isotope ratios, is that the former vary over a factor of 10 or more with varying precipitation rate rather than over just a few tenths of a percent. As shown here, this difference may be important for constraining the precipitation rate-dependence of the molecular exchange rates at the mineral surface.
For illustration, the Sr/Ca ratio of calcite is used, where there are data from several sources relating Sr/Ca to precipitation rate (Tang et al., 2008; Tesoriero and Pankow, 1996; Lorens, 1981; Gabitov and Watson, 2006). The model can be applied to the Sr/Ca elemental ratio in a straightforward manner if it is assumed that the range of Sr concentrations is well within the Henry’s law regime for the solid; i.e. that the activity coefficient for Sr in calcite is a constant. Making this assumption, the above equations for isotopes need only be modified by substituting Sr for $^{44}$Ca, and Ca for $^{40}$Ca, and $\alpha$ is replaced with “$K$” as defined below.

$$K_{p, Sr} \left( \frac{(Sr/Ca)_{solid}}{(Sr/Ca)_{fluid}} \right) = \frac{K_f}{1 + \frac{R_b}{R_p + R_b} \left( \frac{K_f}{K_{eq}} - 1 \right)}$$

(13)

where $K_f = k_{f, Sr} / k_{f, Ca}$ is the forward kinetic fractionation factor for Sr/Ca in the precipitation reaction, and $K_{eq}$ is the equilibrium Sr/Ca partition coefficient applicable to extremely slow precipitation and determined by the activity coefficient of SrCO$_3$ dissolved in calcite. As with Ca isotope fractionation, $K_{p, Sr}$ has been determined experimentally to be dependent on precipitation rate. At low precipitation rates ($\leq 10^{-8}$ mol/m$^2$/sec) the value is ostensibly between about 0.02 and 0.07, and at high precipitation rates it is in the range 0.24 to 0.4 (Gabitov and Watson, 2006).

Figure 10 shows plots of equation 13, with constant $R_b$, juxtaposed against 25°C experimental data from Tang et al. (2008), Tesoriero and Pankow (1996), and Lorens (1981). In each case, the input parameters are the calcite dissolution rate from Chou et al. (1989) (adjusted for temperature and at the appropriate pH), $K_{eq}$ and $K_f$. In all cases, a value of $K_f = 0.24$ is used. For the Tang et al. (2007) data, $K_{eq}$ is set equal to 0.07, whereas for the Tesoriero and Pankow (1996) data $K_{eq}$ is set equal to 0.03, and for Lorens (1981) $K_{eq}$ is set equal to 0.035. The data for the Tesoriero and Pankow (1996) study were obtained at pH $\approx 6.2$, substantially lower than the pH $\approx 8$ used in the Tang et al. (2008) study and the pH $\approx 7.4$ used by Lorens (1981). Tang et al. (2008) give reasons why $K_{eq}$ could be pH-dependent, but in any case, to fit the data the only parameter that needs to be
adjusted between the three studies is $K_{eq}$, and this adjustment is unavoidable because the three studies obtained different values of $K_{p,Sr}$ at similar $R_p$ values of about $10^{-7}$ mol/m²/sec. The lower pH of the Tesoriero and Pankow (1996) study also necessitates the use of a slightly higher value of $R_b$ at 25°C of $1 \times 10^{-6}$ mol/m²/sec (see Figure 5). All of the Sr/Ca partitioning data are well described by the constant-$R_b$ model, given the adjustment of $K_{eq}$ with pH. The Lorens (1981) data could be fit better if a lower value of $K_f$ were used, but there is also some uncertainty about their precipitation rates, since they did not carefully control the reacting surface area. The model fits the data of Gabitov and Watson (2006) also; they found a relatively large range of $K_p$ values at very high precipitation rates, but the value of $K_f = 0.24$ fits with the lower range of their values. The one worrisome aspect of the data shown in Figure 10 is the difference between the Tang et al. (2008) results and those of Lorens (1981) and Tesoriero and Pankow (1996). The results from the latter two studies are similar, especially if corrected for pH. The Tang et al (2008) Sr/Ca data appear to be shifted to lower $R_p$ values, which could mean that they have slightly underestimated the precipitation rates for their experiments. If they have, it would require some revision to the interpretations of the Ca isotope data given above.

Given the good fit of the Sr/Ca data it follows that the model could also be applicable to U, Cd, Ba, Mn, and other trace elements in calcite. The data for Mn/Ca partitioning from Lorens (1981) are among the best available for testing the model and are interesting because the apparent equilibrium Mn/Ca ratio (i.e. the value at low $R_p$ values) is much larger than the kinetically-controlled Mn/Ca, and both values are far from unity. Figure 11 shows the Lorens (1981) Sr/Ca data compared to a fit using the variable – $R_b$ model (Model 2), and also shows the Lorens (1981) Mn/Ca data with curves representing both the constant – $R_b$ (Model 1) and the variable-$R_b$ (Model 2) versions of the model. The Model 2 fit to the Lorens Sr/Ca data is marginally better than the Model 1 fit shown in Figure 10. For the Lorens Mn/Ca data, however, the two models differ substantially, and only Model 2 appears to fit the entire data set reasonably well. This result could be regarded as evidence that the molecular exchange rate does indeed vary substantially at low $\Omega_c$ and $R_p$ values.
3.4. Oxygen isotopes in precipitated calcite

Kinetic effects on oxygen isotope fractionation during calcite precipitation are of broad interest for paleo-environmental studies. Dietzel et al (2009) present data showing that the fractionation of $^{18}$O/$^{16}$O between calcite and solution grown in the laboratory at constant temperature and pH is dependent on precipitation rate. Analysis of this effect is more complicated than that for Ca isotopes. Traditionally, most workers have discussed O isotope fractionation in terms of the difference between calcite and water. This difference is large – close to $+30\%$ at $25^\circ$C. Zeebe (1999) and Zeebe and Gladrow (2001), on the other hand, propose that the important fractionation factors are between calcite and the dissolved carbonate species (mostly HCO$_3^-$ and CO$_3^{2-}$) in solution in the water. Zeebe (1999) has noted that the equilibrium fractionation between calcite and the average carbonate species in solution is close to zero (i.e. $\alpha_{eq} = 1.0000$ relative to bulk DIC) and that calcite tends to inherit the average isotopic composition of the dissolved inorganic carbon (DIC).

For our purposes, comparing the $\delta^{18}$O of calcite CO$_3$ to that of total DIC is analogous to comparing the $\delta^{44}$Ca of calcite with that of dissolved Ca$^{2+}$. Dietzel et al give the $\delta^{18}$O values of their precipitated calcite relative to $\delta^{18}$O of the water from which the calcite was precipitated. From the calcite - water fractionation values and inter-species fractionation factors given by Beck et al. (2005) it is possible to calculate the $\delta^{18}$O of the carbonate species in solution, and from those and the pH the $\delta^{18}$O of the bulk DIC. A plot of $\delta^{18}$O of precipitated calcite relative to bulk DIC (at $25^\circ$C; from Dietzel et al., 2009) versus precipitation rate is shown as Figure 12. The data follow the predicted trends reasonably well for either the constant-$R_b$ or variable-$R_b$ models. This result suggests that the fractionation of O isotopes may not be so different from that of Ca in that the equilibrium fractionation between the solid phase and dissolved species is small, and much of the observed variation may be due to kinetic effects during non-equilibrium precipitation of CaCO$_3$. This result does not mean that carbonate $\delta^{18}$O does not reflect temperature, just that the temperature effects are associated with isotopic exchange between the dissolved carbonate species and water.
4. DISCUSSION AND IMPLICATIONS

4.1 Isotopic effects due to transport limitations in the fluid phase

The agreement of the Tang et al. (2008) Ca isotope results and the model curves shown above would not be expected if the Tang et al. precipitations occurred under conditions where the delivery of Ca\(^{2+}\) ions to the mineral surfaces was transport-controlled. There are strong arguments why the Tang et al. experiments must have been in the surface reaction control regime. The experimental conditions were such that [Ca\(^{2+}\)] >> [CO\(_3^{2-}\)], so the surface reaction control limit to the precipitation rate is determined by the delivery of carbonate ions to the mineral surface, not the delivery of Ca ions. Also, the Tang et al. precipitation rates as a function of oversaturation are very close to those of Lopez et al. (2009), who employed a fluidized bed arrangement, which should guarantee surface reaction control at pH > 7. Hence it is highly likely that the Tang et al (2008) data represent a surface reaction-controlled condition for Ca isotope fractionation.

To evaluate other experiments, and the limits of the surface reaction model, it is useful to derive an approximate formulation for the effects of transport. If the advance of a growing calcite crystal face is limited by diffusion of CO\(_3^{2-}\) through a boundary layer of thickness \(h_{bl}\) (Figure 13), the following equation must be satisfied:

\[
D_{CO_3} \frac{\left[CO_3^{2-}\right]_{sl} - \left[CO_3^{2-}\right]_{fs}}{h_{bl}} = k_f \left[Ca^{2+}\right]_{sl} \left(\left[CO_3^{2-}\right]_{fs} - \left[CO_3^{2-}\right]_{eq}\right)
\]  

(13a)

This equation results from equating the rate of diffusion of CO\(_3^{2-}\) ions through the boundary layer (left side) to the deposition rate on the surface of the crystal (from equation 2b). This formulation is valid because the rate of crystal growth is small enough that the condition \(v h_{bl} / D_{CO_3} \ll 1\) is satisfied, where \(v\) is the growth velocity of the crystal. Rearranging equation 13a, we can write:
The conditions under which the right side of this equation is equal to unity can be defined as the point where diffusion and surface reaction are of equal importance. The critical boundary layer thickness at which this transition point occurs is:

\[
\frac{D_{CO_3}}{h_{k_f}[Ca^{2+}]_{sol}} = \frac{[CO_3^{2-}]_{fs} - [CO_3^{2-}]_{eq}}{[CO_3^{2-}]_{sol} - [CO_3^{2-}]_{fs}} \quad (13b)
\]

where the subscript \(CO_3\) is meant to imply the critical boundary layer thickness under the condition that \([Ca^{2+}] > [CO_3^{2-}]\).

Using the values \(D_{CO_3} = 8 \times 10^{-10}\) m²/sec, \(k_f^* = 6 \times 10^{-8}\) mol/m²/sec (a mid-range experimental value, from Figure 6), and \([CO_3^{2-}] = 0.043\) mol/m³ (corresponding to equilibrium with seawater; \(Ca^{2+} = 10\) mol/m³), results in \(h_{*CO_3} = 0.6\) mm. If stirring a beaker at 150 to 300 rpm produces diffusional boundary layers that are similar to those of a rotating disk at the same rates (e.g. Alkatten et al., 2007), then the diffusive boundary layer thicknesses would be in the range 15-25 µm, well below the critical boundary layer thickness. Consequently, stirred experiments at high pH should be in the surface reaction controlled regime. However, the rate of calcite precipitation in an unstirred precipitation experiment could be affected by transport because boundary layer thicknesses are likely to be much larger. However, for a solution where \([Ca^{2+}] >> [CO_3^{2-}]\) it is less likely for Ca supply to be transport controlled because, if the rate of delivery of \(Ca^{2+}\) by diffusion is to be equal to the rate of delivery of \(CO_3^{2-}\), the drawdown in \([Ca^{2+}]\) near the crystal surface cannot be greater than \([CO_3^{2-}]\), which is small relative to \([Ca^{2+}]\).

It should be noted that equation 14 indicates that the critical boundary layer thickness is dependent on \([Ca^{2+}]\). At lower \([Ca^{2+}]\), for example if it is equal to \([CO_3^{2-}]\) so that both are 0.66 mol/m³, the critical boundary layer thickness increases to \(h_{*CO_3} \approx 9\) mm. Hence it may be easier to achieve conditions of surface reaction controlled precipitation if the solution
has \([\text{Ca}^{2+}] = [\text{CO}_3^{2-}]\), although this effect could be offset by changes in \(k_f^*\) as a function of \(\text{Ca}^{2+}/\text{CO}_3^{2-}\). In the other extreme, for a solution with very high \([\text{Ca}^{2+}]\), for example, 150 mol/m³ (Lemarchand et al., 2004), the calculated critical boundary layer thickness decreases to 40 µm, which creates conditions where it may be more difficult to avoid transport limitations on the precipitation rate even in stirred solutions.

Experimental results of Richter et al. (2006) indicate that the ratio of the diffusivities of \(^{44}\text{Ca}^{2+}\) and \(^{40}\text{Ca}^{2+}\) in chloride solution is approximately 0.9945. Assuming that this value applies to the experimental solutions of Tang et al. (2008), if calcite growth were controlled by transport of \(\text{Ca}^{2+}\) ions to the crystal surface, we would expect a fractionation of \(\Delta^{44}\text{Ca} = -0.55\) permil \((\alpha_{\text{diff}} = 0.9945)\). The larger fractionations observed suggest that transport effects do not dominate the results.


Lemarchand et al (2004) report Ca isotope fractionation factors for calcite precipitated from \(\text{CaCl}_2 – \text{NH}_4\text{Cl}\) solutions. They also found a relationship between calcite precipitation rate and Ca isotope fractionation, although the relationship is opposite to that of the Tang et al (2008) results even though the estimated range of precipitation rates is similar. At high precipitation rates Lemarchand et al (2004) found small fractionations approaching \(\Delta^{44}\text{Ca} = 0\), and at slower precipitation rates they found larger fractionations approaching \(\Delta^{44}\text{Ca} = -1.3\). In most of their experiments, they diffused \(\text{CO}_2\) into the solutions from the top and did not stir the solutions. As they describe, their solutions were heterogeneous, with high \([\text{CO}_3^{2-}]\) at the liquid surface and strong diffusive gradients downward into the solution. With no stirring, the precipitation rates may have been transport – controlled. Lemarchand et al did not measure the precipitation rates, but rather calculated them from an equation given by Zuddas and Mucci (1994), which gives a relationship between precipitation rate and solution oversaturation. However, the equation given by the latter authors was determined for surface reaction-controlled conditions using a fluidized bed experimental arrangement. It is unclear whether the reported, calculated precipitation rates of Lemarchand et al are accurate. Also, because of the geometry of the experiments, it is likely
that the rates were variable, both in space and time. As crystallization occurred along the sides of the shallow (3 cm deep, 8 cm diameter) beaker, CO$_3^{2-}$ ions could have been delivered from the top surface while Ca$^{2+}$ ions need to diffuse laterally. In this geometry it is possible that Ca$^{2+}$ gradients could have been large enough to produce isotopic effects due to diffusive transport. However, because they observed fractionations that are smaller than -0.55 permil, the fractionation must not have been controlled by a steady state process such as that depicted in Figure 13, but either to depletion of aqueous Ca in a boundary layer near the growing calcite crystals or a different mechanism of precipitation that is accessed only at very high solution oversaturation.

To evaluate whether aqueous Ca depletion is likely in the Lemarchand et al. experiments, consider a hypothetical situation where the precipitation rate is controlled independent of solution chemistry. The thickness of a boundary layer where depletion of Ca by precipitation onto a growing crystal is balanced by diffusion into the layer is:

$$h_{Ca} = \frac{D_{Ca}[Ca^{2+}]}{R_p}$$

(15)

In the Lemarchand et al. un-stirred experiments with the highest precipitation rates (estimated at $10^{-5}$ mol/m$^2$/sec), and for $[Ca^{2+}]_{sol} = 15 - 150$ mol/m$^3$, the value of $h_{Ca}$ is about 1.2 mm to 12 mm. In un-stirred conditions, this could be in a regime where Ca transport is limiting since these estimated $h_{Ca}$ values are smaller than the 40 mm radius of the beaker. The actual precipitation rates could locally have been higher or lower than the authors’ estimates. In general, however, as the precipitation rate is lowered toward $10^{-7}$ mol/m$^2$/sec, transport should be less important and the surface reaction control limit should be approached, which could explain the relationship Lemarchand et al. observed between precipitation rate and Ca isotope fractionation. However, it is still not possible to reconcile the results of the two studies unless the precipitation rate estimates in one or both studies are in error by a large factor (cf. Tang et al., 2008). In addition, Gussone et al. (2005) found a relationship between Ca isotope fractionation and precipitation rate in aragonite that is similar to that determined by Lemarchand et al. for calcite.
4.4. Previously proposed growth entrapment models

An alternative model for the control on trace element incorporation into calcite has been advanced by Watson (2004), who describes a “growth entrapment model,” whereby the precipitation rate dependence of Sr/Ca (and other ratios involving trace constituents) in calcite arises from a competition between mineral growth rate, expressed in terms of a growth velocity ($v$) normal to the crystal surface, and the redistribution of the trace constituent back to the mineral surface by solid state diffusion. The growth velocity is proportional to the precipitation rate used here according to: 

$$v = \frac{R_p M_s}{\rho_s},$$

where $M_s$ is the molecular weight of the solid and $\rho_s$ the density. In the Watson (2004) model the competition is expressed as a Peclet number that compares the timescale to accumulate a thickness $L$ of new mineral material ($L/v$), with the timescale required for diffusion within this layer ($L^2/D$) to allow expulsion of excess Sr back to the surface. The value of $L$ needs to be in the range of a few molecular dimensions (or ca. $10^{-9}$ m) for the model to apply, because it is the thermodynamic properties of these near surface layers that drive the inferred diffusion, and Fenter et al (2004) for example, have shown that only the outermost one or two molecular layers of calcite are different from the bulk in terms of bond lengths and orientation.

For a typical growth rate of $10^{-6}$ mol/m²/sec, the growth velocity is $v = 3.7 \times 10^{-11}$ m/sec. In order for Sr diffusion in the solid to compete with growth, the diffusivity needs to be about $10^{-20}$ m²/sec. The expected value of the volume diffusivity of Sr in calcite at 25 °C (extrapolated from higher temperature data) is $1.5 \times 10^{-36}$ m²/sec (Cherniak, 1997), about $10^{16}$ times smaller. This result would seem to indicate that diffusion within the crystal is not significant, and the explanation for the growth rate dependence must lie elsewhere. Recognizing the disparity, Watson (2004) postulates that there is an effective diffusivity of just the right order of magnitude (ca. $10^{-15}$ to $10^{-20}$ m²/sec) that applies only over a distance of about one atomic layer at the crystal surface, and that the diffusivity decreases systematically over a distance of one or two molecular layers into the crystal. He suggests
that this is not really diffusion but ionic mobility or exchange between near-surface layers. Nevertheless, the process is formulated as diffusion in the model.

A key postulate of the Watson (2004) model, taken from the original model for sector zoning in igneous minerals (Watson and Liang, 1995; Watson, 1996), is that the surface layer of the calcite crystal is maintained in equilibrium with the solution during growth. The model posits that the surface layer, of one or two molecular dimensions thickness (ca. 0.5 nm), has a different crystal structure and hence different equilibrium concentration of trace elements and isotopes. It is the difference in the equilibrium chemical potential (or activity coefficient) between the crystal interior and the surface layer that drives diffusion and the approach to the new (crystal interior) equilibrium concentration as the crystal grows. As noted above, however, the surface layer is not likely to be in equilibrium with the solution except at very slow crystal growth rates. Most calcite grown in the laboratory (or biogenically) is precipitated under conditions of substantial oversaturation, and there is no reason to expect that equilibrium can be maintained. If the surface layer is not kept at equilibrium with the solution by infinitely fast exchange, then the surface boundary condition for the Watson (2004) model is not correct, and the driving force for uphill diffusion to the surface is undefined.

The Watson (2004) surface entrapment model (SEMO; see also Gaetani and Cohen, 2006; Tang et al., 2008) yields growth rate dependence that is similar to the model presented here, although not identical. The kinetic effects in both models are controlled by a dimensionless number, which relates the growth velocity ($v$ or $R_p M_s / \rho_s$) to a “relaxation velocity” ($D_s / L$ or $R_b M_s / \rho_s$). In applying the SEMO model to their Ca isotope data obtained at different temperatures, Tang et al (2008) show that it is necessary to systematically change the parameter $F_{44Ca}$, which is analogous to the parameter $\alpha$ in the model presented here. Hence the SEMO model requires that this parameter have substantial temperature dependence whereas in the model presented here, the Tang et al. (2008) data can be fit with no change in $\alpha$ between 5°C and 40°C. Hence the two models predict substantially different behavior in the high precipitation rate (high $R_p$) limit. Interestingly, Tang et al.
(2008) were able to fit their data with the SEMO model with a low temperature limit of $\alpha_{eq} = 1.000$. They also show that temperature dependence similar to that shown in Figure 9 for $\Delta^{44}$Ca can be obtained from the SEMO model with the appropriate choice of parameters.

The model presented here is also in effect a “growth entrapment model,” but the competition is between the growth rate and the rate of molecular exchange between the mineral surface and solution. In comparison to the Watson (2004) model, the model presented here is attractive in that the approximate value of $\nu$ (or $R_p$) at which there are strong effects on trace element and isotopic partitioning, is predictable from measureable rates of dissolution or from the experimentally determined kinetic rate constants for the precipitation reaction.

4.5. Ultra-slow reaction rates and surface exchange rates

As noted above, the apparent equilibrium Ca isotope fractionation factor at slow precipitation rates approaching $10^{-8}$ mol/m²/sec is 0.99955 (or 1000 ln $\alpha_{eq} = -0.5$) for the constant- $R_b$ version of the model (Model 1), and 0.9998 for the variable-$R_b$ version of the model (Model 2). Neither value is exactly the value 1.0000 inferred from deep-sea sediment pore fluids from ODP Site 807 by Fantle and DePaolo (2007). The differences are subtle, but probably significant. The discrepancy may relate to the extremely slow inferred rate of precipitation of calcite in the Site 807 pore fluids (see also Richter and Liang, 1993), which are far slower than in the experiments. To illustrate the difference between the pore fluids and the available laboratory experiments, if precipitation in the Site 807 sediments were distributed over the available surface area of the sediment, the rate would be $10^{-17}$ to $10^{-18}$ mol/m²/sec (Fantle and DePaolo, 2007), some 9 to 10 orders of magnitude slower than those accessed by laboratory experiments. If the active surface area of the Site 807 sediments is, for example, $10^4$ times smaller than the total surface area, the observed precipitation rate is still 4 to 5 orders of magnitude smaller than those of the laboratory experiments. In the formulations provided here of the Ca exchange rate at the mineral surface, it is shown that if the exchange rate decreases at low $\Omega_c$ (and $R_p$), it is possible to bring the laboratory results for Ca isotopic fractionation closer to agreement with the
results from deep sea pore fluids. The Mn/Ca data of Lorens (1981), and the many studies of calcite precipitation mechanisms, provide evidence that the exchange rate does decrease as equilibrium conditions are approached. Fantle and DePaolo (2007) argue that $\Omega_c$ must be indistinguishable from unity in Site 807 pore fluid, so the system is very close to equilibrium. For conditions that are incrementally displaced from equilibrium, and for systems that are allowed to mature for millions of years, we do not know what the surface exchange rates are; they could be even slower than would be inferred by extrapolation of the data in Figure 6. Ultimately, to fully reconcile the laboratory and pore fluid observations, a better measure of (or model for) the molecular exchange rates at the mineral surface is necessary. Additional complications can arise from the effects of the presence of trace constituents, including organic compounds, which may significantly change the rates of molecular exchange (e.g. Morse et al., 1997; Wasylkenki et al., 2005a, b; Stephenson et al, 2008). Also, at extremely slow growth rates it is possible that solid state diffusion could play a role, if for example the diffusivity is larger than would be indicated by extrapolation from higher temperature experimental data (e.g. Marshall et al., 1986), and if there is somewhat accelerated atomic exchange between near surface layers as hypothesized by Watson (2004).

4.7. Origins of kinetic fractionation during precipitation

Although there is as yet no definitive information on the origin of kinetic isotopic and trace element fractionations during precipitation, it may be a useful working hypothesis that the kinetic effects are associated with dehydration of dissolved ions during the precipitation step, and rehydration during the dissolution step. In any reaction where a chemical bond must be broken to release the reactant, it is expected that the rate of bond breaking, and hence the rate of reaction, will be higher for the light isotopic species (e.g. Criss, 1999; Zeebe, 2001). Bond breaking involving the light isotopic species is favored because it has a higher zero-point vibrational energy and hence has a slightly smaller potential energy barrier to overcome. The attachment of $\text{Ca}^{2+}$ ions to a calcite mineral surface may involve an initial step of formation of an outer sphere complex, in which the $\text{Ca}^{2+}$ is still surrounded by a shell of water molecules, followed by formation of an inner sphere complex that
requires dehydration (e.g. Morse et al., 2007). It is likely that the kinetics of dehydration favor the light isotope, and it is possible that this step is the one that results in the forward isotopic fractionation factor $\alpha_f$ having a value less than unity. For analogous reasons the release of Ca$^{2+}$ from the mineral surface back to solution is also likely to favor the light isotope so that $\alpha_b$ is less than unity. If these two fractionation factors are close in value, then the equilibrium fractionation factor should be close to unity.

If the dehydration/rehydration of Ca$^{2+}$ ions is the major factor controlling the kinetic fractionation factors, then any perturbation to the stability of the hydration shell, such as effects due to other constituents in solution, could alter the kinetic fractionation factors as well as the reaction rates. Relative rates of dehydration might also partly explain the forward kinetic fractionation factors for Sr/Ca partitioning. The relatively larger ionic radius of Sr$^{2+}$ relative to Ca$^{2+}$ presumably makes it easier to dehydrate, and this may be the reason that the forward precipitation reaction favors the incorporation of Sr in calcite in excess of the equilibrium value. As with isotopic partitioning, changes in the strength of ion hydration due to solution chemistry could affect the kinetic fractionation factor for Sr/Ca. However, it cannot be ignored that the presence of impurities like Sr and Mg on the calcite surface also affects the mineral growth rate and mechanism (Wasylenki et al., 2005a, b; Katz, 1973; Davis et al., 2000), and hence there may be complex feedbacks between growth rate, kinetic fractionation factors, and molecular exchange rates between mineral and solution.

5. CONCLUSIONS

The Ca and O isotopic fractionation during precipitation of calcite from aqueous solution provides critical information on the molecular exchange fluxes at the mineral-solution interface during mineral growth. These fluxes are not easily measureable by other methods, but are critical for understanding the dynamics of the interface and for understanding isotopic partitioning. A relatively simple model describing how isotopic fractionation during precipitation should depend on precipitation rate is presented. The key parameters in the model are the forward (precipitation reaction) fractionation factor,
\( \alpha_p \), the equilibrium fractionation factor, \( \alpha_{eq} \), and the bulk backward reaction rate \( R_b \). The latter is effectively the value of the gross exchange flux at the interface. The ratio of the net precipitation rate \( R_p \) to the exchange flux \( R_b \) determines whether the isotopic fractionation during precipitation is close to the equilibrium value \( (R_p/R_b << 1) \) or the forward kinetic fractionation factor \( (R_p/R_b \geq 1) \). A key question is how to estimate \( R_b \). It is posited here that \( R_b \) is equal to the dissolution rate of the mineral into a highly undersaturated solution, assuming that there are no transport limitations affecting the dissolution rate. This assumption leads to a first version of the model (Model 1) in which \( R_b \) is assumed to be constant, i.e. independent of solution saturation state and precipitation rate. Model 1 achieves excellent fits of available Ca and O isotope data (from Tang et al., 2008; and Dietzel et al., 2009), and for Sr/Ca partitioning for pH of 7 to 9 (from Tang et al., 2008; Tesoriero and Pankow, 1996; Lorens, 1981; and Gabitov and Watson, 2006), which suggests that it has merit.

The far-from-equilibrium dissolution rate may be only a starting point for understanding the dynamics of precipitation and their effects on isotopic and trace element partitioning. The primary success shown here is that the transition between near-equilibrium isotopic fractionation and fractionation controlled by the forward kinetic fractionation factor, occurs as predicted at a value of \( R_p \approx R_b \), where \( R_b \) is the value of the calcite dissolution rate determined by Chou et al (1989) at the appropriate pH and temperature. But, available data suggest that the value of \( R_b \) decreases at low solution oversaturation and low net precipitation rates (e.g. Teng et al., 2000; DeYoreo et al., 2009). To account for this effect, a second version of the model (Model 2) is presented where \( R_b \) is allowed to vary as \( R_p^{1/2} \) at low \( R_p \) values. This second version of the model fits the Ca and O isotopic data, and the Sr/Ca partitioning data, no better than the constant-\( R_b \) version of the model, but it fits the Mn/Ca data of Lorens (1981) much better. Model 1 does not allow for extrapolation of the laboratory Ca isotope fractionation data to an equilibrium fractionation factor of \( \alpha_{eq} = 1.0000 \), as suggested by Fantle and DePaolo (2007) from studies of deep sea pore fluids. Model 2 comes close to allowing the laboratory and pore fluid data to be reconciled. Both models suggest that the Ca isotope fractionation factor for the forward reaction is close to
\( \alpha = 0.9984 \). Any extension to the model may need to account for potential changes in \( R_b \) as a function of solution composition (e.g. presence of Mg, Sr, Na, K, and other anion components and organic solutes).

The model described here derives from standard macroscopic formulations of the kinetic controls on mineral precipitation, and the precipitation rate dependence arises from the inescapable consideration that the net precipitation rate can be either similar to or much smaller than the gross precipitation flux. The model is also anchored on a measurable parameter – the far-from-equilibrium dissolution rate of calcite. The implication of the agreement between model and data is that the major control on both Ca isotope composition and Sr/Ca in calcite is the competition between net and gross precipitation rates.

The model presented here explains the precipitation rate dependence of isotopic and trace element partitioning into calcite by means of a “growth entrapment model,” where there is an implicit competition between the mineral-solution exchange rate (represented by the far-from-equilibrium dissolution rate \( R_b \)), and the net precipitation rate \( (R_p) \). Watson (2004) presents an alternative growth entrapment model to explain the same precipitation rate dependence in terms of a competition between solid-state diffusion within the growing calcite crystal and the net precipitation rate. There is an unsatisfactory aspect of the Watson model in that the measured solid state diffusion rate is many orders of magnitude too small to be competitive with the precipitation rate, and hence it may be that the model presented here is a better description of the mineral surface processes controlling isotopic and trace element partitioning at low temperatures. However, solid-state transport may come into play at sufficiently slow mineral growth rates and at higher temperatures (e.g. Watson and Liang, 1995; Watson, 1996), especially if low-temperature diffusivities are anomalously high and if atomic exchange among a few near-surface molecular layers is significantly faster than bulk diffusion.

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7. REFERENCES


Figure captions

Figure 1: Precipitation regimes for mineral precipitation under surface reaction limited and transport (diffusion) limited conditions. Horizontal axis is the ratio of the net mineral precipitation rate ($R_p$) to the gross backward (dissolution) rate during precipitation ($R_b$). The $y$ axis is the ratio of the critical diffusive boundary layer thickness in the aqueous solution above the growing mineral surface ($D_{Caq}/R_p$) to the actual diffusive boundary thickness ($h_{bl}$).

Figure 2: Calculated fractionation factor associated with condensation of liquid water droplets from air at 25°C and ice crystals from air at -15°C. In both cases the fractionation factor ($\alpha_p$) is shown as a function of vapor oversaturation ($S - 1$), where $S$ is the ratio of water vapor concentration in air to the equilibrium water vapor concentration. The calculation is done assuming that the growth of the condensed phase is limited by radial diffusion of water vapor through air to the surface of a growing droplet or ice crystal with no ventilation (i.e. the condensed phase is not falling through the air; c.f. Jouzel and Merlivat, 1984). As oversaturation goes to zero, the water and ice form at equilibrium ($\alpha_p = \alpha_{eq}$). At extremely high water vapor oversaturations (not generally realized in nature) the fractionation factor approaches the ratio of the diffusivities in air of the two isotopologues of water. Water droplets generally form at near-zero values of $S-1$ and hence form near isotopic equilibrium. Ice crystals typically form under oversaturated conditions where $S-1$ is up to 0.5, hence do not form at isotopic equilibrium. For this calculation it is assumed that the molecular exchange flux at the condensed phase surface is much larger than the net condensation rate, which should be true as discussed in the text, but is not the case for calcite precipitation from aqueous solutions. Equilibrium isotope fractionation values are from Horita and Wesolowski (1994). Molecular diffusivities are from Merlivat (1978).

Figure 3: Schematic of the Ca isotope fractionation model for the case of surface reaction rate controlled precipitation. The parameters $r_{fluid}$ and $r_{solid}$ are the Ca isotopic ratios
(\(^{44}\text{Ca}/^{40}\text{Ca}\)), in the fluid and solid respectively. Upper case \(R\) represents a flux (e.g. \(\text{mol/m}^2/\text{sec}\)). The parameters \(\alpha_f\) and \(\alpha_{eq}\) are the kinetic and equilibrium isotopic fractionation factors associated with precipitation.

Figure 4: Calculated model curve for the effective isotopic fractionation factor for precipitation \((\alpha_p)\), for arbitrary values of the equilibrium \((\alpha_{eq} = 1.009)\) and forward \((\alpha_f = 0.9985)\) isotopic fractionation factors. \(R_p\) is the net precipitation rate and \(R_b\) is the backward (dissolution) rate during precipitation. When the fractionation factors are close to unity, the inflection point lies at approximately \(R_p = R_b\) (equation 11). This model carries the assumption that \(R_b\) is independent of \(R_p\) (meaning it is also independent of \(\Omega_c\)).

Figure 5: Calcite dissolution rate into pure water with regulated pCO\(_2\) at 25°C from Chou et al. (1989). The dashed line corresponds to \(R_b = k_b = 6 \times 10^{-7}\) \(\text{mol/m}^2/\text{sec}\).

Figure 6: Compilation of apparent first order rate constant versus precipitation rate. Data are from calcite precipitation experiments of Tang et al. (2007) and Lopez et al. (2009). The dashed line illustrates \(R_p^{1/2}\) dependence fit roughly through the 25°C data. The black solid line represents the Model 1 version of \(R_b\) versus \(R_p\) at 25°C, used to calculate the curves in Figures 7a and 8. The red line represents the Model 2 version of \(R_b\) versus \(R_p\).

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Figure 7b: Illustration of the alternative formulation of the model in which the dissolution rate “constant” is not constant but a function of fluid saturation state and thus also a function of precipitation rate. For this calculation it is assumed that $R_b$ is described by the solid red line in Figure 6. The values used for the fractionation factors are $\alpha_f = 0.9983$ and $\alpha_{eq} = 0.9998$. This model is closer to being consistent with a value of 1.000 for $\alpha_{eq}$, but also suggests a slightly lower value of $\alpha_f$. This version of the model is based on the expectation that the surface exchange flux between mineral and aqueous solution is markedly reduced as equilibrium conditions are approached, as suggested by the studies of Teng et al. (2000) and DeYoreo et al. (2009).

Figure 8: Model fits to Tang et al (2008) data for 5°C and 40°C show that the data can be explained by the temperature dependence of $R_b$. Because the dissolution rate of calcite varies with temperature, the value of $R_b$ is lower for 5°C (estimated to be $1.5 \times 10^{-7}$ mol/m²/sec) and higher for 40°C ($1.55 \times 10^{-6}$ mol/m²/sec). The model curves for $R_b$ shown in Figure 6b are therefore shifted accordingly. All but two of the data fit the model curves reasonably well.

Figure 9: Representative foraminifer and coccolith data showing the $^{44}$Ca/$^{40}$Ca fractionation factor and comparison with predicted kinetic fractionations as a function of temperature for different calcite growth rates using the model presented in the text. The $\Delta^{44}$Ca exhibit a temperature dependence (cf. Gussone et al., 2000; Schauble, 2009) of about 0.02 per °C. This diagram shows that this effect could arise from the dependence of $R_b$ on temperature if the natural biogenic precipitation rates are in a limited range between about $3 \times 10^{-7}$ and $3 \times 10^{-6}$ mol/m²/sec. For this calculation Model 1 was used, and it is also assumed that $\alpha_{eq}$ and $\alpha_f$ are independent of temperature. There could in addition be some dependence of either or both of the fractionation factors on temperature, and biological effects could also be important. Circles represent the foraminifer $G. \ ornatissima$, diamonds the coccolith $E. \ huxleyi$, both from De La Rocha and DePaolo (2000). Squares are data for $O. \ universa$ from Gussone et al. (2003).
Figure 10: The experimental values of $K_{Sr} = (Sr/C_{a_{solid}})/(Sr/C_{a_{fluid}})$ plotted versus precipitation rate and compared to Model 1 predictions using equation 16 in the text. For all three calculations it is assumed that $K_f = 0.24$.

Figure 11: (a) Lorens (1981) data fit using Model 2. With Model 2 the inferred value of $K_{eq}$ is slightly smaller than for Model 1, but the data are fit well with either model. (b) Lorens (1981) Mn/Ca data shown with fits using both Model 1 and Model 2. Model 1 does not fit the data well at $R_p$ values smaller than $10^{-7}$ mol/m$^2$/sec. Model 2 fits the data well. The Mn data are different from the other data available to test the models in that they clearly discriminate between the two models and indicate that only Model 2 can match the data. The Mn/Ca data strongly suggest that mineral-fluid exchange rates decrease at low precipitation rates (i.e. as $\Omega_c \rightarrow 1$); the other available experimental isotopic and trace element data do not strongly constrain the exchange rates at low $R_p$.

Figure 12. Plot of experimental measurements of $\delta^{18}O$ of calcite versus precipitation rate (Dietzel et al., 2009). The left hand scale gives the fractionation factor relative to bulk DIC; the right hand side gives the fractionation factor relative to H$_2$O. Solid line assumes $R_b = constant = 6 \times 10^{-7}$ mol/m$^2$/sec. Dashed line is for Model 2 (see Figure 6). The assumed values for $\alpha_f$ and $\alpha_{eq}$ can be read from the diagram for Model 1; for Model 2 the values are $\alpha_f = 0.9945$ and $\alpha_{eq} = 1.0000$ relative to DIC.

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