A modified surface kinetic model for calcium and strontium isotope fractionation during calcite precipitation

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Abstract

The Ca and Sr isotope fractionation factors (\(\Delta^{44/40}\text{Ca}\) and \(\Delta^{88/86}\text{Sr}\)), as well as the bulk Sr partition coefficient (\(K\)), depend on calcite precipitation rates in both experimental and natural settings. These processes are expected to be controlled by surface kinetics. Ten years ago, Depaolo (2011) proposed a surface reaction model that successfully explained the kinetic effects on \(\Delta^{44/40}\text{Ca}\) and \(K\). With new observations of \(\Delta^{88/86}\text{Sr}\), the limitation of this model emerges. Here, we develop a modified surface reaction model with separate contributions from two underlying precipitation mechanisms, namely spiral growth and surface nucleation. We derive the most representative model by synthesizing general forms with simple but justifiable assumptions of surface reaction kinetics. Our modified model successfully explains observations of the precipitation rate dependence of \(\Delta^{44/40}\text{Ca}\), \(\Delta^{88/86}\text{Sr}\), and \(K\), as well as their correlations. Our findings suggest that surface reactions during calcite precipitation solely regulate these parameters, regardless of diffusion. The revised model can be readily integrated with existing stoichiometric models and offers important implications for interpreting carbonate stable Ca and Sr isotope compositions, as well as the partitioning and isotope fractionation of other trace elements during carbonate precipitation.

Keywords: kinetics, calcium isotopes, strontium isotopes, Sr partitioning, isotope fractionation

1. Introduction

The elemental and isotope compositions of carbonate minerals have been widely used as tracers and proxies in geochemical, geobiological, and environmental sciences. Crystal growth
kinetics and trace element partitioning during calcium carbonate precipitation have been studied observationally and theoretically for decades (e.g., Lorens, 1981; Burton et al., 1951; Carpenter and Lohmann, 1992; Nancollas and Reddy, 1971; Meyer, 1984; Dove and Hochella, 1993; Zuddas and Mucci, 1994; Paquette and Reeder, 1995; Teng et al., 1998, 2000; Morse and Arvidson, 2002; Nehrke et al., 2007; Nielsen et al., 2012; Sand et al., 2016). More recently, studies focused on the fractionation of Ba, Ca, Li, Mg, Sr and other elements have provided additional constraints (e.g., Dietzel et al., 2009; Gabitov et al., 2012; Tang et al., 2008a,b; Böhm et al., 2012; Mavromatis et al., 2013, 2020; Zhang and DePaolo, 2020; Füger et al., 2022). The main block-building element, calcium, and its most common substitution, strontium, have received considerable attention. While pioneering investigations initially pointed to equilibrium isotope fractionation (e.g., Nägler et al., 2000; Lemarchand et al., 2004; Gussone et al., 2005), more recent observations of Ca and Sr isotope fractionation in experimental and natural systems point more toward kinetic control (e.g., Skulan and DePaolo, 1999; Fietzke and Eisenhauer, 2006; Fantle and DePaolo, 2007; Jacobson and Holmden, 2008; Tang et al., 2008a,b; Böhm et al., 2012; AlKhatib and Eisenhauer, 2017; Shao et al., 2021; Wang et al., 2021). Specifically, Ca isotope fractionation ($\Delta^{44/40}\text{Ca}$), Sr isotope fractionation ($\Delta^{88/86}\text{Sr}$), and bulk Sr partition coefficient ($K$) all depend on calcite precipitation rate, and linearly correlate with each other (Tang et al., 2008a,b; Böhm et al., 2012; AlKhatib and Eisenhauer, 2017).

To explain kinetic effects, Watson (2004) invoked the “growth entrapment” model developed by Watson and Liang (1995) and suggested that diffusion through a boundary layer surrounding the near-surface region of growing crystals controls the incorporation of elements and isotopes. This model assumes that the surface of the growing crystal remains in equilibrium with the aqueous solution (Watson, 2004). However, in order to achieve equilibrium, the crystal surface must undergo sufficient mass exchange with the aqueous solution before isolation by newly-precipitated crystal, which requires the net rate of crystal growth to be much smaller than the rate of ion detachment from crystal surfaces (e.g., DePaolo, 2011). For most growth experiments (e.g., Tang et al., 2008a,b; AlKhatib and Eisenhauer,
2017), net calcite precipitation rates are comparable to or greater than the detachment rates estimated by Chou et al. (1989). This implies that the crystal surface and aqueous solution are rarely equilibrated, such that the kinetics of surface mass exchange plays an important role. DePaolo (2011) proposed a surface reaction model and suggested that the rate of mass exchange between crystal surfaces and the aqueous solution underlies the precipitation rate dependency of $\Delta^{44/40}\text{Ca}$ and $K$ for synthetic calcite. The model provides a straightforward framework to explain observations using a minimal number of adjustable parameters. Nonetheless, despite the model’s success, it cannot explain the rate control of $\Delta^{88/86}\text{Sr}$ nor the relationship between $\Delta^{44/40}\text{Ca}$ and $\Delta^{88/86}\text{Sr}$ provided by new experimental observations (Bohm et al., 2012; AlKhatib and Eisenhauer, 2017, see discussion in Sec. 3).

In this contribution, we develop a modified surface reaction model, employing general descriptions of surface reaction kinetics and microscopic calcite growth observations. The model provides a coherent and internally consistent framework for predicting observed relations among $\Delta^{44/40}\text{Ca}$, $\Delta^{88/86}\text{Sr}$, and $K$. In Sec. 2, we start with the most general forms of reaction kinetics to establish a fundamental surface reaction model. In Sec. 3, we recover the model of DePaolo (2011) and supplement it with the expression for $\Delta^{88/86}\text{Sr}$ using the general framework provided in Sec. 2; we also discuss how the observed relationships among $\Delta^{44/40}\text{Ca}$, $\Delta^{88/86}\text{Sr}$, and $K$ exert challenges for the model of DePaolo (2011). In Sec. 4, we reconcile this discrepancy by modifying the model to two common precipitation mechanisms (i.e., spiral growth and surface nucleation), which have been identified by in situ microscopic observations (e.g., Dove and Hochella, 1993; Teng et al., 1998, 2000). Our model strengthens and expands the current understanding of kinetics effects on isotope and trace element fractionation during calcite precipitation and further has important implications for interpreting the chemical and isotope compositions of natural carbonates.

2. The general formulation for surface reaction models

2.1. Calcium isotope fractionation

Like crystal growth reactions, ion attachment (precipitation) and detachment (dissolution) are treated here as two independent processes (Fig. 1a). Net crystal growth occurs
when the rate of ion attachment exceeds the rate of ion detachment. When considering individual isotopes of calcium ($^{40}$Ca and $^{44}$Ca), the rates of their change in calcite are

$$\frac{dN(^{40}Ca)}{dt} = r_a(^{40}Ca) - r_d(^{40}Ca),$$

(1)

$$\frac{dN(^{44}Ca)}{dt} = r_a(^{44}Ca) - r_d(^{44}Ca),$$

(2)

where $t$ is time, $N(^{40}Ca)$ and $N(^{44}Ca)$ are the total amounts of $^{40}$Ca and $^{44}$Ca in the calcite crystal, $r_a$ and $r_d$ are the ion attachment (precipitation) and ion detachment (dissolution) rates. Taking the ratio of Eq. 2 and Eq. 1 leads to

$$\frac{dN(^{44}Ca)}{dN(^{40}Ca)} = \frac{r_a(^{44}Ca) - r_d(^{44}Ca)}{r_a(^{40}Ca) - r_d(^{40}Ca)}. \quad (3)$$

To facilitate the analysis, we normalize the $^{40}$Ca attachment rate, $r_a(^{40}Ca)$, against the $^{40}$Ca detachment rate, $r_d(^{40}Ca)$, and define a normalized $^{40}$Ca attachment rate

$$s = \frac{r_a(^{40}Ca)}{r_d(^{40}Ca)}. \quad (4)$$

As $^{40}$Ca is the dominant isotope of calcium, we can use the attachment and detachment rates of this isotope to represent the precipitation and dissolution reaction rates of calcite. Therefore, $s$ is also used to represent the ratio of precipitation and dissolution rates of calcite. Substituting Eq. 4 into Eq. 3 and after some algebra, we obtain

$$\frac{dN(^{44}Ca)}{dN(^{40}Ca)} = \frac{s[r_a(^{44}Ca)/r_a(^{40}Ca)] - [r_d(^{44}Ca)/r_d(^{40}Ca)]]}{s - 1}. \quad (5)$$

The attachment rates of calcium isotopes are controlled by their concentrations in the aqueous solution. Here, we assume that the ratio of the attachment rates of the two isotopes, $r_a(^{44}Ca)/r_a(^{40}Ca)$, is proportional to the ratio of the two isotopes in the aqueous solution, $(^{44}Ca/^{40}Ca)_{aq}$, i.e.,

$$r_a(^{44}Ca)/r_a(^{40}Ca) = k_{44}(^{44}Ca/^{40}Ca)_{aq}, \quad (6)$$

where $k_{44}$ describes the preference of $^{44}$Ca over $^{40}$Ca being attached onto calcite crystal from the aqueous solution. A similar relation was also provided by DePaolo (2011), but under
the assumptions of \( r_a(^{40}\text{Ca}) = k_{40}^*[^{40}\text{Ca}^{2+}]_{\text{aq}}[^{40}\text{Ca}^2]_{\text{aq}} \) and \( r_a(^{44}\text{Ca}) = k_{44}^*[^{44}\text{Ca}^{2+}]_{\text{aq}}[^{44}\text{Ca}^2]_{\text{aq}} \), which lead to \( r_a(^{44}\text{Ca})/r_a(^{40}\text{Ca}) = (k_{44}^*/k_{40}^*)(^{44}\text{Ca}[^{44}\text{Ca}^2]_{\text{aq}}/^{40}\text{Ca}[^{40}\text{Ca}^2]_{\text{aq}}) \), where \( k_{40}^* \) and \( k_{44}^* \) are reaction coefficients. In this paper, we do not introduce these assumptions because they are not supported by calcite growth experiments (e.g., Mucci and Morse, 1983; Mucci, 1986; Zuddas and Mucci, 1994; Lopez et al., 2009); we suggest that Eq. 6 stays valid regardless of the specific formulas of the attachment rates, without violating experimental observations. Similarly, we assume that the ratio of the two detachment rates, \( r_d(^{44}\text{Ca})/r_d(^{40}\text{Ca}) \), is proportional to the ratio of the two isotopes in the crystal (on the crystal surface), \( (^{44}\text{Ca}/^{40}\text{Ca})_{\text{cal}} \), and write

\[ r_d(^{44}\text{Ca})/r_d(^{40}\text{Ca}) = k_{44}'(^{44}\text{Ca}/^{40}\text{Ca})_{\text{cal}}, \tag{7} \]

where \( k_{44}' \) describes the preference of \( ^{44}\text{Ca} \) over \( ^{40}\text{Ca} \) being detached from the calcite crystal surface. Substituting Eqs. 6-7 into Eq. 5, we write

\[ dN(^{44}\text{Ca})/dN(^{40}\text{Ca}) = s k_{44}(^{44}\text{Ca}/^{40}\text{Ca})_{\text{aq}} - k_{44}'(^{44}\text{Ca}/^{40}\text{Ca})_{\text{cal}}, \tag{8} \]

Hereafter, we focus on steady state precipitation (i.e., aqueous conditions do not change with time such that the growth rate and chemical and isotope compositions of the crystal stay constant). In this case, the net precipitation of \( ^{44}\text{Ca} \) and \( ^{40}\text{Ca} \) in an infinitesimal time interval would follow the \( ^{44}\text{Ca}/^{40}\text{Ca} \) ratio in the existing crystal, i.e., \( dN(^{44}\text{Ca})/dN(^{40}\text{Ca}) = (^{44}\text{Ca}/^{40}\text{Ca})_{\text{cal}} \). Substituting this into Eq. 8 and after some algebra, we get

\[ \alpha_{\text{cal-aq}}^{44/40} = \frac{(^{44}\text{Ca}/^{40}\text{Ca})_{\text{cal}}}{(^{44}\text{Ca}/^{40}\text{Ca})_{\text{aq}}} = \frac{s k_{44}}{s + (k_{44}' - 1)}. \tag{9} \]

where \( \alpha_{\text{cal-aq}}^{44/40} = (^{44}\text{Ca}/^{40}\text{Ca})_{\text{cal}}/(^{44}\text{Ca}/^{40}\text{Ca})_{\text{aq}} \) is the Ca isotope fractionation factor. Introducing \( \delta \)-notation, \( \delta^{44/40}\text{Ca} = 1000\%_{\text{e}} \times \left[ (^{44}\text{Ca}/^{40}\text{Ca})/(^{44}\text{Ca}/^{40}\text{Ca})_{\text{std}} - 1 \right] \), we rewrite the definition of the fractionation factor as \( \alpha_{\text{cal-aq}}^{44/40} = (1000\%_{\text{e}} + \delta^{44/40}\text{Ca}_{\text{cal}})/(1000\%_{\text{e}} + \delta^{44/40}\text{Ca}_{\text{aq}}) \). The calcium isotope fractionation can be expressed using \( \Delta \)-notation, \( \Delta^{44/40}\text{Ca} = \delta^{44/40}\text{Ca}_{\text{cal}} - \delta^{44/40}\text{Ca}_{\text{aq}} \). The two parameters are related as \( \Delta^{44/40}\text{Ca} = (1000\%_{\text{e}} + \delta^{44/40}\text{Ca}_{\text{aq}}) \times \left( \alpha_{\text{cal-aq}}^{44/40} - 1 \right) \). Typically, the magnitude of \( \delta^{44/40}\text{Ca}_{\text{aq}} \) is much smaller than \( 1000\%_{\text{e}} \), so we write approximately \( \Delta^{44/40}\text{Ca} = 1000\%_{\text{e}} \times \left( \alpha_{\text{cal-aq}}^{44/40} - 1 \right) \). Substituting Eq. 9 into this equation, we write
expression the calcium isotope fractionation as
\[
\Delta ^{44/40}\text{Ca} = 1000\% \times \frac{s(k_{44} - 1) - (k'_{44} - 1)}{s + (k'_{44} - 1)},
\] (10)

which can be rewritten, after some algebra, as
\[
\Delta ^{44/40}\text{Ca} = 1000\% \times (k_{44} - 1) - 1000\% \times \frac{k_{44}(k'_{44} - 1)}{s + (k'_{44} - 1)}.\] (11)

2.2. Strontium partitioning and isotope fractionation

Strontium commonly substitutes for calcium in calcite because Ca\(^{2+}\) and Sr\(^{2+}\) have similar ionic radii. The derivation of Eq. 9 can be directly applied to \(^{86}\)Sr and \(^{88}\)Sr provided that the concentration of aqueous Sr is sufficiently low such that (1) Sr reaction rates are proportional to Sr concentrations in the calcite and the aqueous solution and (2) SrCO\(_3\) inclusions do not affect the precipitation or dissolution of calcite. In this case, the attachment and detachment of \(^{86}\)Sr and \(^{88}\)Sr can be expressed using equations similar to those of \(^{44}\)Ca (Eqs. 2-8), and the incorporation of the Sr isotopes is expressed as

\[
K_{\text{cal-aq}}^{^{86/40}\text{Sr}} = \frac{(^{86}\text{Sr} / ^{40}\text{Ca})_{\text{cal}}}{(^{86}\text{Sr} / ^{40}\text{Ca})_{\text{aq}}} = \frac{sk_{86}}{s + (k'_{86} - 1)},
\] (12)

\[
K_{\text{cal-aq}}^{^{88/40}\text{Sr}} = \frac{(^{88}\text{Sr} / ^{40}\text{Ca})_{\text{cal}}}{(^{88}\text{Sr} / ^{40}\text{Ca})_{\text{aq}}} = \frac{sk_{88}}{s + (k'_{88} - 1)},\] (13)

where \(k_{86}\) and \(k_{88}\) are coefficients describing the preference of \(^{86}\)Sr and \(^{88}\)Sr over \(^{40}\)Ca being precipitated from aqueous solution to calcite, and \(k'_{86}\) and \(k'_{88}\) are coefficients describing the preference of \(^{86}\)Sr and \(^{88}\)Sr over \(^{40}\)Ca being dissolved from the calcite crystal. These coefficients are defined explicitly as

\[
k_{86} = \frac{r_{a}(^{86}\text{Sr})}{(^{86}\text{Sr} / ^{40}\text{Ca})_{\text{aq}}} / \frac{r_{a}(^{40}\text{Ca})}{(^{40}\text{Sr} / ^{40}\text{Ca})_{\text{aq}}}, \quad k_{88} = \frac{r_{a}(^{88}\text{Sr})}{(^{88}\text{Sr} / ^{40}\text{Ca})_{\text{aq}}} / \frac{r_{a}(^{40}\text{Ca})}{(^{40}\text{Sr} / ^{40}\text{Ca})_{\text{aq}}},
\] (14)

\[
k'_{86} = \frac{r_{d}(^{86}\text{Sr})}{(^{86}\text{Sr} / ^{40}\text{Ca})_{\text{cal}}} / \frac{r_{d}(^{40}\text{Ca})}{(^{40}\text{Sr} / ^{40}\text{Ca})_{\text{cal}}}, \quad k'_{88} = \frac{r_{d}(^{88}\text{Sr})}{(^{88}\text{Sr} / ^{40}\text{Ca})_{\text{cal}}} / \frac{r_{d}(^{40}\text{Ca})}{(^{40}\text{Sr} / ^{40}\text{Ca})_{\text{cal}}},
\] (15)

where \(r_{a}(^{86}\text{Sr})\) and \(r_{a}(^{88}\text{Sr})\) are the attachment rates of \(^{86}\)Sr and \(^{88}\)Sr, and \(r_{d}(^{86}\text{Sr})\) and \(r_{d}(^{88}\text{Sr})\) are the detachment rates of \(^{86}\)Sr and \(^{88}\)Sr, respectively. These coefficients are often
considered as constants (as in the simple model that will be discussed in Sec. 3). However, it should be noted that the formulations derived in this section would remain valid even if these coefficients vary with precipitation rate (as presented in the modified model in Sec. 4).

Taking the ratio of Eq. 13 and Eq. 12, we write

$$\alpha_{\text{cal-aq}}^{88/86} = \frac{(88\text{Sr}/86\text{Sr})_{\text{cal}}}{(88\text{Sr}/86\text{Sr})_{\text{aq}}} = \frac{(k_{88}/k_{86}) s + (k'_{86} - 1)}{s + (k'_{88} - 1)}.$$  

(16)

where $\alpha_{\text{cal-aq}}^{88/86} = (88\text{Sr}/86\text{Sr})_{\text{cal}}/(88\text{Sr}/86\text{Sr})_{\text{aq}}$ is the Sr isotope fractionation factor. Introducing $\delta$-notation for Sr isotope composition, $\delta^{88/86}\text{Sr} = 1000/\text{permil} \times \left[(88\text{Sr}/86\text{Sr})_{\text{cal}}/(88\text{Sr}/86\text{Sr})_{\text{std}} - 1\right]$ and the $\Delta$-notation for the Sr isotope fractionation factor, $\Delta^{88/86}\text{Sr} = \delta^{88/86}\text{Sr}_{\text{cal}} - \delta^{88/86}\text{Sr}_{\text{aq}}$, and applying the approximate relation $\Delta^{88/86}\text{Sr} = 1000/\text{permil} \times (\alpha_{\text{cal-aq}}^{88/86} - 1)$, we express the strontium isotope fractionation as

$$\Delta^{88/86}\text{Sr} = 1000/\text{permil} \times (k_{88}/k_{86} - 1)(s - 1) + (k_{88}/k_{86})k'_{86} - k'_{88}s,$$

(17)

which can be shown (after some algebra) to be equivalent to

$$\Delta^{88/86}\text{Sr} = 1000/\text{permil} \times (k_{88}/k_{86} - 1) - 1000/\text{permil} \times \frac{(k_{88}/k_{86})(1 - k'_{86}/k'_{88})k_{88}s}{s + (k'_{88} - 1)}.$$

(18)

The elemental abundance of Sr in calcite is also an important proxy. The incorporation of Sr into calcite is often described by the partition coefficient, $K$, which is defined as

$$K = \frac{(\text{Sr}/\text{Ca})_{\text{cal}}}{(\text{Sr}/\text{Ca})_{\text{aq}}},$$

(19)

where $(\text{Sr}/\text{Ca})_{\text{cal}}$ and $(\text{Sr}/\text{Ca})_{\text{aq}}$ are the Sr/Ca elemental ratios in calcite and the aqueous solution. Typically, the fractionation of Sr isotopes and Ca isotopes during precipitation are both very small, and $K^{86/40}_{\text{cal-aq}}$ and $K^{88/40}_{\text{cal-aq}}$ (defined in Eqs. 12 and 13) are both very close to the value of $K$. Because $^{88}\text{Sr}$ is the most abundant Sr isotope, we use the partitioning of $^{88}\text{Sr}$ (which is determined by $K^{88/40}_{\text{cal-aq}}$ in Eq. 13) to approximate that of the element,

$$K = \frac{sk_{88}}{s + (k'_{88} - 1)} = k_{88} - \frac{k_{88}(k'_{88} - 1)}{s + (k'_{88} - 1)}.$$

(20)

Thus far, we have used the normalized $^{40}\text{Ca}$ attachment rate, $s = r_{a}(^{40}\text{Ca})/r_{d}(^{40}\text{Ca})$, to formulate the Ca isotope fractionation factor ($\Delta^{44/40}\text{Ca}$), the Sr isotope fractionation factor
(Δ^{88/86}Sr), and the Sr partition coefficient (K). These expressions can be easily expanded to other trace elements in calcite and potentially other mineral systems following surface-controlled kinetics, although we note that the behaviors of carbon and oxygen isotopes in calcite are often complicated by the hydration and exchange processes among different species in dissolved carbon species (e.g., Zeebe and Wolf-Gladrow, 2001; Zeebe, 2009). Nevertheless, the resulting framework is quite simple, which reflects that the calcium and strontium isotope fractionation, as well as strontium partitioning, are fundamentally controlled by calcite precipitation and dissolution rates. In the following sections, we discuss the choices and formulations of the coefficients k and k’ for the involved nuclides (^{40}Ca, ^{86}Sr, and ^{88}Sr) and compare the model predictions with experimental results.

3. The model of DePaolo (2011) and the challenge from new observations

For the formulas derived above (Eqs. 11, 18, and 20), the simplest assumption is to treat all k and k’ coefficients as constant (DePaolo, 2011). In this case, all the coefficients can be determined by extrapolating experimental observations to extreme conditions (i.e., the limit of equilibrium on one end and rapid precipitation rates on the other). At s = 1 (no net growth, which implies the crystal and the aqueous solution are in equilibrium; recall that s is the ^{40}Ca attachment rate normalized by the ^{40}Ca detachment rate), Δ^{44/40}Ca, Δ^{88/86}Sr, and K take the values of equilibrium. In this case, Eqs. 11, 18, and 20 reduce to

\[ \Delta^{44/40}\text{Ca}_{\text{eq}} = 1000 \times \left( k_{44} / k'_{44} - 1 \right), \]  

(21)

\[ \Delta^{88/86}\text{Sr}_{\text{eq}} = 1000 \times \left[ (k_{88} / k_{86}) / (k'_{88} / k'_{86}) - 1 \right], \]  

(22)

\[ K_{\text{eq}} = k_{88} / k'_{88}, \]  

(23)

where Δ^{44/40}Ca_{eq}, Δ^{88/86}Sr_{eq}, and K_{eq} are values of Δ^{44/40}Ca (Ca isotope fractionation), Δ^{88/86}Sr (Sr isotope fractionation), and K (Sr partition coefficient) at equilibrium. When s \rightarrow \infty (precipitation is fast enough such that the fractionation no longer changes with
precipitation rate), $\Delta^{44/40}\text{Ca}$, $\Delta^{88/86}\text{Sr}$, and $K$ take the values of the large precipitation rate limit. In this case, Eq. [11], [18] and 20 reduce to

$$\Delta^{44/40}\text{Ca}_{\text{inf}} = 1000\%_0 \times (k_{44} - 1),$$  \hspace{1cm} (24)$$

$$\Delta^{88/86}\text{Sr}_{\text{inf}} = 1000\%_0 \times (k_{88}/k_{86} - 1),$$ \hspace{1cm} (25)$$

$$K_{\text{inf}} = k_{88},$$ \hspace{1cm} (26)$$

where $\Delta^{44/40}\text{Ca}_{\text{inf}}$, $\Delta^{88/86}\text{Ca}_{\text{inf}}$, and $K_{\text{inf}}$ are the values of $\Delta^{44/40}\text{Ca}$, $\Delta^{88/86}\text{Sr}$, and $K$ in the large precipitation rate limit (the kinetic limit). Solving the $k$ and $k'$ coefficients from Eqs. [21],[26] we obtain

$$k_{44} = 1 + \frac{\Delta^{44/40}\text{Ca}_{\text{inf}}}{1000\%_0}, \quad k'_{44} = \frac{1000\%_0 + \Delta^{44/40}\text{Ca}_{\text{inf}}}{1000\%_0 + \Delta^{44/40}\text{Ca}_{\text{eq}}},$$ \hspace{1cm} (27)$$

$$k_{88}/k_{86} = 1 + \frac{\Delta^{88/86}\text{Sr}_{\text{inf}}}{1000\%_0}, \quad k'_{88}/k'_{86} = \frac{1000\%_0 + \Delta^{88/86}\text{Sr}_{\text{inf}}}{1000\%_0 + \Delta^{88/86}\text{Sr}_{\text{eq}}},$$ \hspace{1cm} (28)$$

$$k_{88} = K_{\text{inf}}, \quad k'_{88} = K_{\text{inf}}/K_{\text{eq}}.$$ \hspace{1cm} (29)$$

Substituting Eq. [27] into Eq. [11] we express the Ca isotope fractionation factor as

$$\Delta^{44/40}\text{Ca} = \Delta^{44/40}\text{Ca}_{\text{inf}} - \frac{(1000\%_0 + \Delta^{44/40}\text{Ca}_{\text{inf}})(\Delta^{44/40}\text{Ca}_{\text{inf}} - \Delta^{44/40}\text{Ca}_{\text{eq}})}{s(1000\%_0 + \Delta^{44/40}\text{Ca}_{\text{eq}}) + (\Delta^{44/40}\text{Ca}_{\text{inf}} - \Delta^{44/40}\text{Ca}_{\text{eq}})}.$$ \hspace{1cm} (30)$$

Typically, the magnitudes of $\Delta^{44/40}\text{Ca}_{\text{eq}}$ and $\Delta^{44/40}\text{Ca}_{\text{inf}}$ are both much smaller than 1000\% (see the next paragraph for details). In this paper, we focus on growing (not dissolving) calcite crystals, which implies that the normalized $40\text{Ca}$ attachment rate $s$ is always greater than one. In this case, the following approximations apply

$$1000\%_0 + \Delta^{44/40}\text{Ca}_{\text{inf}} \approx 1000\%_0,$$ \hspace{1cm} (31)$$

$$s(1000\%_0 + \Delta^{44/40}\text{Ca}_{\text{eq}}) + (\Delta^{44/40}\text{Ca}_{\text{inf}} - \Delta^{44/40}\text{Ca}_{\text{eq}}) \approx s \times 1000\%_0.$$ \hspace{1cm} (32)$$
Implementing these approximations in Eq. 30, the Ca isotope fractionation factor simplifies to

$$\Delta^{44/40}\text{Ca} = \Delta^{44/40}\text{Ca}_{\text{inf}} - (\Delta^{44/40}\text{Ca}_{\text{inf}} - \Delta^{44/40}\text{Ca}_{\text{eq}})/s. \quad (33)$$

Clearly, this relation satisfies the constraints from both the equilibrium and kinetic limits (i.e., $\Delta^{44/40}\text{Ca} = \Delta^{44/40}\text{Ca}_{\text{eq}}$ at $s = 1$ and $\Delta^{44/40}\text{Ca} = \Delta^{44/40}\text{Ca}_{\text{inf}}$ at $s \to \infty$). Substituting Eqs. 28-29 into Eqs. 18 and 20, we similarly express the Sr isotope fractionation factor and element partition coefficient as

$$\Delta^{88/86}\text{Sr} = \Delta^{88/86}\text{Sr}_{\text{inf}} - (\Delta^{88/86}\text{Sr}_{\text{inf}} - \Delta^{88/86}\text{Sr}_{\text{eq}}) \frac{K_{\text{inf}}/K_{\text{eq}}}{s + (K_{\text{inf}}/K_{\text{eq}} - 1)}, \quad (34)$$

$$K = K_{\text{inf}} - (K_{\text{inf}} - K_{\text{eq}}) \frac{K_{\text{inf}}/K_{\text{eq}}}{s + (K_{\text{inf}}/K_{\text{eq}} - 1)}. \quad (35)$$

The $K_{\text{inf}}/K_{\text{eq}}$ ratio is around $\sim 10$ (see next paragraph for details), and the magnitude of $(K_{\text{inf}}/K_{\text{eq}} - 1)$ is greater than or at least comparable to the magnitude of $s$, unless the precipitation rate is very rapid. For this reason, the approximation that we invoke to simplify Eq. 30 to Eq. 33 cannot be applied to Eqs. 34-35. We note that the above results are consistent with the formulas for Ca isotope fractionation and Sr partitioning given by DePaolo (2011), despite Sr isotope fractionation was not considered therein.

With the formulations provided above (Eqs. 33-35), $\Delta^{44/40}\text{Ca}$, $\Delta^{88/86}\text{Sr}$, and $K$ are expressed as functions of the normalized $^{40}\text{Ca}$ attachment rate, $s$, if their values in the equilibrium limit ($\Delta^{44/40}\text{Ca}_{\text{eq}}$, $\Delta^{88/86}\text{Ca}_{\text{eq}}$, and $K_{\text{eq}}$) and the kinetic limit ($\Delta^{44/40}\text{Ca}_{\text{inf}}$, $\Delta^{88/86}\text{Ca}_{\text{inf}}$, and $K_{\text{inf}}$) are given. The Ca isotope fractionation factor between carbonate and precipitating solution ranges from $-0.1\%_\circ$ to $-1.6\%_\circ$ under different laboratory conditions (e.g., Lemarchand et al., 2004; Tang et al., 2008a) with an average of approximately $-1.4\%_\circ$ in natural settings (e.g., De La Rocha and DePaolo, 2000; DePaolo, 2004; Fantle and DePaolo, 2005; Gussone et al., 2005, 2009; Kısıkirek et al., 2011; Gussone and Dietzel, 2016) and approaches zero at equilibrium (e.g., Fantle and DePaolo, 2007; Jacobson and Holmden, 2008). Here, we chose $\Delta^{44/40}\text{Ca}_{\text{inf}} = -2\%_\circ$, a value that is slightly larger than the largest fractionation has ever been observed ($-1.8\%_\circ$ in ikaite) in ikaite, Gussone et al. (2011), for fractionation at
infinite precipitation rate and $\Delta^{44/40}\text{Ca}_{\text{eq}} = 0\%$ for equilibrium Ca isotope fractionation. With respect to Sr, controlled laboratory studies have long investigated kinetic control of Sr partitioning in calcite (e.g., Lorens, 1981; Tesoriero and Pankow, 1996; Gabitov and Watson, 2006; Tang et al., 2008b) and the results consistently suggest that partitioning at the kinetic limit ($K_{\text{inf}}$) equals $\sim 0.24$ while the equilibrium partitioning ($K_{\text{eq}}$) is one order of magnitude smaller. A recent study of deep-sea sediments and associated pore fluids also derives the equilibrium Sr partition coefficient to be $K_{\text{eq}} = 0.025\pm 0.05$ at 25°C (Zhang and DePaolo, 2020). Therefore, $K_{\text{inf}} = 0.24$ (DePaolo, 2011) and $K_{\text{eq}} = 0.025$ are chosen here to represent Sr partitioning at the kinetic and equilibrium limits. For Sr isotope fractionation, Böhm et al. (2012) and AlKhatib and Eisenhauer (2017) found that $\Delta^{88/86}\text{Sr}$ spans between $-0.35\%$ and $-0.07\%$ under different precipitation rates in synthetic experiments, similar to the range observed in natural settings (e.g., Fietzke and Eisenhauer, 2006; Krabbenhöft et al., 2010; Stevenson et al., 2014; Voigt et al., 2015). Limited fractionation observed in slowly-precipitated oceanic crust calcite suggests that $\Delta^{88/86}\text{Sr}_{\text{eq}}$ is close to zero (Böhm et al., 2012). Thus, we assume $\Delta^{88/86}\text{Sr}_{\text{eq}} = 0\%$. Molecular dynamics simulations suggest that the maximum fractionation (associated with the kinetic limit) of an isotope system is ultimately determined by the mass and that the maximum fractionation between $^{88}\text{Sr}$ and $^{86}\text{Sr}$ is $\sim 20\%$ the maximum fractionation between $^{44}\text{Ca}$ and $^{40}\text{Ca}$ (Hofmann et al., 2012). Thus, we assume $\Delta^{88/86}\text{Sr}_{\text{inf}} = -0.4\%$.

To compare the model predictions with experimental observations, we also need to calculate the absolute net growth rate of calcite crystal. For simplicity, we use the net precipitation of the dominant calcium isotope, $^{40}\text{Ca}$, to represent the net growth of calcite. The net growth rate, $r_g(^{40}\text{Ca})$, is given by the difference between attachment and the detachment rates of $^{40}\text{Ca}$, i.e.,

$$r_g(^{40}\text{Ca}) = r_a(^{40}\text{Ca}) - r_d(^{40}\text{Ca}) = (s - 1)r_d(^{40}\text{Ca}).$$  \(36\)

We first assume that the detachment rate is constant, $r_d(^{40}\text{Ca}) = 6 \times 10^{-7} \text{ mol}/(m^2 \cdot s)$ (Chou et al., 1989), as in Model 1 of DePaolo (2011) (Fig. 2 solid curves). To better fit data of Ca isotope fractionation, DePaolo (2011) described Model 2, where the detachment rate is
reduced at near equilibrium or low precipitation rate conditions (Fig. 2, dashed curves). With the preferred values of parameters described above (and summarized in Tab. I), the simple model explains the dependence of $\Delta^{44/40}$Ca on precipitation rate (Fig. 2h) and the linear relation between $\Delta^{88/86}$Sr and $K$ (Fig. 2f). However, it does not provide good fits to the dependence of $K$ and $\Delta^{88/86}$Sr on precipitation rate (Fig. 2b-c). DePaolo (2011) obtained good fits of $K$ by assuming an elevated equilibrium Sr partition coefficient, $K_{eq} = 0.07$ (Fig. 2 gray curves). However, even with this assumption, the model output does not fit observed $\Delta^{88/86}$Sr well (Fig. 2). More importantly, it predicts a non-linear relation between $\Delta^{44/40}$Ca and $\Delta^{88/86}$Sr (Fig. 2f) and a non-linear relation between $\Delta^{44/40}$Ca and $K$ (Fig. 2h), which are inconsistent with experimental observations (Bohm et al., 2012; AlKhatib and Eisenhauer, 2017). Moreover, such a large equilibrium Sr partition coefficient ($K_{eq} = 0.07$) is inconsistent with the natural observation of Zhang and DePaolo (2020). To reconcile the experimental Sr partitioning data of Tang et al. (2008b) and observations of natural equilibrium Sr partitioning, Zhang and DePaolo (2020) suggested a stronger detachment rate reduction than that assumed in Model 2 of DePaolo (2011). Here, implementing the reduced detachment rates suggested by Zhang and DePaolo (2020), the model better fits $K$ (Fig. 2f, dotted curve) and $\Delta^{88/86}$Sr (Fig. 2c; dotted curve), but simultaneously yields poor fits for $\Delta^{44/40}$Ca (Fig. 2a, dotted curve). In addition, this scenario does not resolve the challenge of simulating the linear $\Delta^{44/40}$Ca-$\Delta^{88/86}$Sr correlation (Fig. 2f). Assuming a constant $^{40}$Ca detachment rate (DePaolo, 2011, Model 1) or variable/reduced $^{40}$Ca detachment rates (DePaolo, 2011, Model 2; Zhang and DePaolo, 2020) affects how the normalized net growth rate converts to the absolute net growth rate (and thus produces the results in Fig. 2b-c), but it does not influence correlations between $\Delta^{44/40}$Ca, $\Delta^{88/86}$Sr, and $K$ (i.e., in Fig. 2d-f, the solid, dashed, and dotted curves coincide with each other). Therefore, the linear correlation between $\Delta^{44/40}$Ca and $\Delta^{88/86}$Sr challenges for the simple surface reaction model, although we note that $\Delta^{88/86}$Sr data reported in Bohm et al. (2012) and AlKhatib and Eisenhauer (2017) were not available when this model was first developed by DePaolo (2011).
4. A new model incorporating different precipitation mechanisms

In situ microscopic observations have demonstrated that the precipitation of calcite involves two different but likely concurrent mechanisms, spiral growth and surface nucleation (e.g., Dove and Hochella, 1993; Teng et al., 1998, 2000). At low saturation states, the attachment force is lower than the critical value for surface nucleation; dislocations in crystal lattices dominate the new crystal growth, and screw dislocations by lattice fault stacking yields spiral growth. With increasing saturation state, the nucleation rate increases and leads to a rough surface where ion attachment occurs non-selectively on crystal surfaces (e.g., De Yoreo and Vekilov, 2003). Therefore, we suggest that the precipitation (ion attachment) step should be separated into two contributions, spiral growth and surface nucleation (Fig. 1b).

To explicitly express the contributions of the two precipitation mechanisms, we write

\[ r_a(\text{40Ca}) = r_s(\text{40Ca}) + r_n(\text{40Ca}), \]  

(37)

where \( r_a(\text{40Ca}) \) is the overall rate of \( ^{40}\text{Ca} \) attachment (see Eq. 1), \( r_s(\text{40Ca}) \) is the rate of \( ^{40}\text{Ca} \) attachment due to spiral growth, and \( r_n(\text{40Ca}) \) is the rate of \( ^{40}\text{Ca} \) attachment due to surface nucleation. Most of our analysis presented above reflects the normalized \( ^{40}\text{Ca} \) attachment rate, \( s = r_a(\text{40Ca})/r_d(\text{40Ca}) \). Here, to maintain consistency, we also normalize the \( ^{40}\text{Ca} \) attachment rate due to spiral growth, \( r_s(\text{40Ca}) \), and that due to surface nucleation, \( r_n(\text{40Ca}) \), against the \( ^{40}\text{Ca} \) detachment rate, \( r_d(\text{40Ca}) \), and define

\[ s_s = r_s(\text{40Ca})/r_d(\text{40Ca}), \quad s_n = r_n(\text{40Ca})/r_d(\text{40Ca}). \]  

(38)

Given that the \( ^{40}\text{Ca} \) attachment rates due to spiral growth and surface nucleation add up to the total \( ^{40}\text{Ca} \) attachment rate (Eq. 37), their normalized values (\( s_s \) and \( s_n \), as defined in Eq. 38) add up the normalized rate of total \( ^{40}\text{Ca} \) attachment (\( s \)), i.e.,

\[ s_s + s_n = s. \]  

(39)

The two precipitation mechanisms likely trap impurity cations (e.g., \( \text{Sr}^{2+} \)) differently (e.g., De Yoreo and Vekilov, 2003; De Yoreo et al., 2009). Therefore, we assign two distinct
coefficients for $^{88}\text{Sr}$ attachment,

$$k_{88(s)} = \frac{r_s(^{88}\text{Sr})}{(^{88}\text{Sr}/^{40}\text{Ca})_{aq}}$$

$$k_{88(n)} = \frac{r_n(^{88}\text{Sr})}{(^{88}\text{Sr}/^{40}\text{Ca})_{aq}},$$

where $r_s(^{88}\text{Sr})$ is the attachment rate of $^{88}\text{Sr}$ associated with spiral growth, and $r_n(^{88}\text{Sr})$ is the attachment rate of $^{88}\text{Sr}$ associated with surface nucleation. The coefficient $k_{88(s)}$ describes the relative preference of $^{88}\text{Sr}$ over $^{40}\text{Ca}$ being attached during spiral growth, while the coefficient $k_{88(n)}$ describes the relative preference of $^{88}\text{Sr}$ over $^{40}\text{Ca}$ being attached during surface nucleation, with both considered constant. The total $^{88}\text{Sr}$ attachment rate is then the sum of the contributions of the two mechanisms, $r_a(^{88}\text{Sr}) = r_s(^{88}\text{Sr}) + r_n(^{88}\text{Sr})$. Applying this relation and the two coefficients defined in Eq. (40), we express the total $^{88}\text{Sr}$ attachment rate as

$$r_a(^{88}\text{Sr})/r_a(^{40}\text{Ca}) = [k_{88(s)}(s_s/s) + k_{88(n)}(s_n/s)] (^{88}\text{Sr}/^{40}\text{Ca})_{aq},$$

where $s_s/s = r_s(^{40}\text{Ca})/r_a(^{40}\text{Ca})$ is the fractional contribution from spiral growth and $s_n/s = r_n(^{40}\text{Ca})/r_a(^{40}\text{Ca})$ is fractional contribution from surface nucleation relative to the total $^{40}\text{Ca}$ attachment (recall that $s_s$ and $s_n$ are normalized spiral growth and surface nucleation rates of $^{40}\text{Ca}$ attachment, as defined in Eq. (38) and $s = r_a(^{40}\text{Ca})/r_a(^{40}\text{Ca})$ is the normalized rate of total $^{40}\text{Ca}$ attachment). Similarly, the total $^{86}\text{Sr}$ attachment rate can be expressed as

$$r_a(^{86}\text{Sr})/r_a(^{40}\text{Ca}) = [k_{86(s)}(s_s/s) + k_{86(n)}(s_n/s)] (^{86}\text{Sr}/^{40}\text{Ca})_{aq},$$

where $k_{86(s)}$ describes the relative preference of $^{86}\text{Sr}$ over $^{40}\text{Ca}$ being attached during spiral growth, $k_{86(n)}$ describes the relative preference of $^{86}\text{Sr}$ over $^{40}\text{Ca}$ being attached during surface nucleation, with both considered constant. When we derived the general formulation of the surface reaction model in Sec. 2, we defined the following coefficients in Eq. (14), $k_{88} = (r_a(^{88}\text{Sr})/r_a(^{40}\text{Ca}))/(^{88}\text{Sr}/^{40}\text{Ca})_{aq}$ and $k_{86} = (r_a(^{86}\text{Sr})/r_a(^{40}\text{Ca}))/(^{86}\text{Sr}/^{40}\text{Ca})_{aq}$, to describe the preference of $^{88}\text{Sr}$ and $^{86}\text{Sr}$ over $^{40}\text{Ca}$ attaching onto crystal surfaces from aqueous solution during calcite precipitation, and we suggested that the derived formulations remain valid even if such coefficients are not constant but depend on precipitation rate. Comparing the definition of coefficients $k_{88}$ and $k_{86}$ (Eq. (14)) with Eqs. (41) and (42) we suggest that the
modified model developed in this section is an example of the general formulation derived in Sec. 2 (for $\Delta^{88/86}\text{Sr}$ and $K$, Eqs. 18 and 20), with coefficients $k_{88}$ and $k_{86}$ varying as

$$k_{88} = k_{88(s)}(s_s/s) + k_{88(n)}(s_n/s),$$

$$k_{86} = k_{86(s)}(s_s/s) + k_{86(n)}(s_n/s).$$

(43)

Similarly, the general formulation of Ca isotope fractionation (Eq. 11) could also be written, with the coefficient $k_{44}$ varying with precipitation as

$$k_{44} = k_{44(s)}(s_s/s) + k_{44(n)}(s_n/s),$$

(44)

where $k_{44(s)}$ describes the relative preference of $^{44}\text{Ca}$ over $^{40}\text{Ca}$ being attached during spiral growth, the coefficient $k_{44(n)}$ describes the relative preference of $^{44}\text{Ca}$ over $^{40}\text{Ca}$ being attached during surface nucleation, with both considered constant.

Now that we have increased the number of unknowns by three (i.e., the three coefficients, $k_{88}$, $k_{86}$, and $k_{44}$ are expressed using six new coefficients, $k_{88(s)}$, $k_{88(n)}$, $k_{86(s)}$, $k_{86(n)}$, $k_{44(s)}$, and $k_{44(n)}$, in Eqs. 43-45), we need to also introduce three new constraints to the system. We attempt to maintain the number of input parameters of the theoretical framework at the minimum level (with prescribed values for $K$, $\Delta^{88/86}\text{Ca}$, and $\Delta^{44/40}\text{Ca}$ at the equilibrium and kinetic limits only). Therefore, we seek the new constraints through theoretical considerations rather than introducing new observations. Given that the preferential uptake of isotopes in chemical reactions is fundamentally determined by their relative atomic masses (e.g., Criss, 1999), DePaolo (2011) suggested that the attachment and detachment processes have the same relative preference for $^{44}\text{Ca}$ over $^{40}\text{Ca}$, which explains the absence of Ca isotope fractionation at equilibrium. Analogously, we assume that spiral growth and surface nucleation have the same relative preferences for $^{44}\text{Ca}$ over $^{40}\text{Ca}$, i.e.,

$$k_{44(s)} = k_{44(n)} = k_{44}.$$  

(46)

With the same argument, we also assume that spiral growth and surface nucleation have the same relative preferences for $^{88}\text{Sr}$ over $^{86}\text{Sr}$, i.e.,

$$k_{88(s)}/k_{86(s)} = k_{88(n)}/k_{86(n)} = k_{88}/k_{86}.$$  

(47)
These assumptions provide two additional constraints (Eqs. 46, 47). The third new constraint is introduced in the following text through another assumption. To separately discuss the effects of different assumptions and approximations, we first provide the model formulations incorporating the assumptions that are so far introduced. As a reminder, the general formulation of the surface reaction model is given by Eqs. 11, 18, and 20. The analysis proceeds by considering the values of Ca isotope fractionation, Sr isotope fractionation, and Sr partition coefficient between the limits of equilibrium ($s = 1$) and infinitely rapid precipitation ($s \to \infty$). The basic logic of the following analysis is somewhat similar to that in Sec. 3 and some (although not all) equations in Sec. 3 still apply.

With the assumption that spiral growth and surface nucleation have the same relative preferences for $^{44}\text{Ca}$ over $^{40}\text{Ca}$ (i.e., Eq. 46), the analysis on Ca isotope fractionation in Sec. 3 still applies, and Eq. 33 still provides the expression for $\Delta^{44/40}\text{Ca}$. With the assumption that spiral growth and surface nucleation have the same relative preferences for $^{88}\text{Sr}$ over $^{86}\text{Sr}$ (i.e., Eq. 47), Eq. 22 and Eq. 25 still describe Sr isotope fractionation at equilibrium ($s = 1$) and infinitely rapid precipitation rate ($s \to \infty$). Consequently, Eq. 28 remains valid (although Eq. 29 does not, see discussion below). Substituting Eq. 28 (but not Eq. 29) into Eq. 18 we rewrite the Sr isotope fractionation ($\Delta^{88/86}\text{Sr}$) as

$$\Delta^{88/86}\text{Sr} = \Delta^{88/86}\text{Sr}_{\text{inf}} - (\Delta^{88/86}\text{Sr}_{\text{inf}} - \Delta^{88/86}\text{Sr}_{\text{eq}}) \frac{k'_{88}}{s + (k'_{88} - 1)}.$$  (48)

Substituting Eq. 43 into the general formulation for Sr partitioning (Eq. 20), we write

$$K = \frac{s}{s + (k'_{88} - 1)} \left[ k_{88(s)}(s/s) + k_{88(n)}(s_n/s) \right].$$  (49)

In the limit of equilibrium ($s = 1$), surface nucleation is sufficiently suppressed and all ion attachment occurs through spiral growth (e.g., Dove and Hochella, 1993; Teng et al., 1998, 2000), i.e., $s_s/s = 1$ and $s_n/s = 0$. Therefore, we write the equilibrium Sr partitioning (by substituting $s_s/s = 1$, $s_n/s = 0$, and $s = 1$ into Eq. 49) as

$$K_{\text{eq}} = k_{88(s)}/k'_{88}.$$  (50)

When the solution is infinitely oversaturated, the precipitation rate is infinitely large ($s \to \infty$) and is dominated by the contribution of surface nucleation (i.e., $s_s/s \to 0$ and $s_n/s \to 1$;
Thus, we express the Sr partition coefficient at the kinetic limit by substituting $s_s/s \to 0$, $s_n/s \to 1$, and $s \to \infty$ into Eq. 49 to obtain

$$K_{\text{inf}} = k_{88(n)}.$$  

(51)

Substituting Eqs. 50 and 51 into Eq. 49, we express the Sr partition coefficient as

$$K = \frac{s}{s + (k'_{88} - 1)[k'_{88} K_{\text{eq}}(s_s/s) + K_{\text{inf}}(s_n/s)]}.$$  

(52)

To make specific predictions that can be compared with observations, we also need to formulate the relative contributions of the two precipitation mechanisms (i.e., the $s_s/s$ and $s_n/s$ terms). The net rate of calcite precipitation is commonly described with $(\Omega - 1)^n$, where $\Omega = [\text{Ca}^{2+}]_{\text{aq}}[\text{CO}_3^{2-}]_{\text{aq}}/C_{\text{sp}}$ is the saturation state (in which $[\text{Ca}^{2+}]_{\text{aq}}$ and $[\text{CO}_3^{2-}]_{\text{aq}}$ are concentrations of Ca$^{2+}$ and CO$_3^{2-}$ in the aqueous solution, and $C_{\text{sp}}$ is the solubility product) and $n$ is an exponent (e.g., Nancollas and Reddy, 1971; Reddy and Nancollas, 1973; Reddy, 1977; Mucci and Morse, 1983; Mucci, 1986; Zuddas and Mucci, 1994; Lopez et al., 2009). For simplicity, we use the attachment and detachment rates of the dominant calcium isotope, $^{40}\text{Ca}$, to represent the precipitation and dissolution reaction rates of calcite and write

$$r_{\text{g}}(^{40}\text{Ca}) = r_{\text{a}}(^{40}\text{Ca}) - r_{\text{d}}(^{40}\text{Ca}) = c(\Omega - 1)^n,$$  

(53)

where $c$ is a coefficient with units of mol/(m$^2$·s). The exponent has been suggested to be either $n \approx 2$ (Reddy and Nancollas, 1973; Reddy, 1977) or $n \approx 3$ (Mucci and Morse, 1983; Mucci, 1986). Teng et al. (2000) further suggested that different precipitation mechanisms are associated with different exponents (for spiral growth, $n \approx 2$; for surface nucleation, $n \approx 3$ or greater). Assuming the two mechanisms operate concurrently, we write

$$[r_s(^{40}\text{Ca}) + r_n(^{40}\text{Ca})] - r_d(^{40}\text{Ca}) = c_s(\Omega - 1)^2 + c_n(\Omega - 1)^3,$$  

(54)

where $c_s$ and $c_n$ are coefficients associated with spiral growth and surface nucleation, respectively. When $(\Omega - 1)$ is small, the parabolic term dominates, and Eq. 54 reduces to Eq. 53 with $n = 2$; when $(\Omega - 1)$ is large, the cubic term dominates, and Eq. 54 reduces to Eq. 53 with $n = 3$. This is consistent with experimental observations of calcite growth.
at different saturation states (e.g., Dove and Hochella, 1993; Teng et al., 2000). The coefficients \( c_s \) and \( c_n \) depend on temperature and chemical conditions (e.g., pH and \( \text{Ca}^{2+} : \text{CO}_3^{2-} \)) of the aqueous solution and thus cannot be uniquely constrained (Nielsen et al., 2012, 2013; Sand et al., 2016; Mills et al., 2021). For illustrative purposes, we provide a specific example of this parametrization \( (c_s = 2.4 \times 10^{-8} \text{ mol/(m}^2 \cdot \text{s}) \) and \( c_n = 1.2 \times 10^{-8} \text{ mol/(m}^2 \cdot \text{s}) \)).

The comparison with net growth rates observed in synthetic experiments (e.g., Tang et al., 2008a,b; AlKhatib and Eisenhauer, 2017) suggests that this parametrization is reasonable (Fig. 3a). Although countless synthetic calcite precipitation experiments exist other than those cited in Fig. 3a, we focus on Tang et al. (2008a,b) and AlKhatib and Eisenhauer (2017) because these experiments are the sources of the data on \( \Delta^{44/40}\text{Ca}, \Delta^{88/86}\text{Sr} \), and \( K \), which are of primary interest for the present contribution. At near equilibrium conditions (with \( \Omega \) close to one), surface nucleation is absent, and precipitation occurs through spiral growth only (e.g., Dove and Hochella, 1993; Teng et al., 1998, 2000). To satisfy this constraint (i.e., \( r_n(40\text{Ca}) = 0 \) and \( r_s(40\text{Ca}) = r_a(40\text{Ca}) = r_d(40\text{Ca}) \) at \( \Omega = 1 \)), we express the contributions of the spiral growth and surface nucleation on \( 40\text{Ca} \) attachment as

\[
\begin{align*}
  r_n(40\text{Ca}) &= r_d(40\text{Ca}) + c_s(\Omega - 1)^2, \\
  r_n(40\text{Ca}) &= c_n(\Omega - 1)^3. 
\end{align*}
\]

At temperature of 25 °C and pH ≈ 8 (i.e., conditions of the aforementioned experiments), we assume a constant detachment rate \( r_d(40\text{Ca}) = 6 \times 10^{-7} \text{ mol/(m}^2 \cdot \text{s}) \) (Chou et al., 1989; DePaolo, 2011). We note that the detachment rate is potentially smaller than this value at near equilibrium conditions (e.g., DePaolo, 2011, Model 2), but the effects of this complexity on the conclusions offered here are minor (see below for details). In the example with \( c_s = 2.4 \times 10^{-8} \text{ mol/(m}^2 \cdot \text{s}) \) and \( c_n = 1.2 \times 10^{-8} \text{ mol/(m}^2 \cdot \text{s}) \), the variation in spiral growth rate is much smaller than the variation in surface nucleation rate (Fig. 3b). In evaluating the relative contribution of the two precipitation mechanisms, the spiral growth rate can be treated approximately as a constant, i.e., \( r_s(40\text{Ca}) \approx r_d(40\text{Ca}) \) or by the definition of \( s_s \) in Eq. 38 \( s_s \approx 1 \) (Fig. 3c, dashed curves). In this case, the relative contributions of spiral growth and surface nucleation are approximated as

\[
\begin{align*}
  s_s/s &= 1/s, \\
  s_n/s &= 1 - 1/s, 
\end{align*}
\]
in which the relation \( s_s + s_n = 1 \) (Eq. 39) has also been substituted. Now, we evaluate the effect of the potential reduction in detachment rate at near equilibrium conditions (DePaolo, 2011, Model 2). At large saturation states, the detachment rate is not reduced, and the above discussion is not at all influenced. At near equilibrium conditions (with saturation states close to one), the detachment rate is potentially reduced, but meanwhile, surface nucleation is also strongly suppressed; precipitation predominantly proceeds through spiral growth (Dove and Hochella, 1993; Teng et al., 1998, 2000), and \( s_s \approx s \approx 1 \) still applies (\( s_s \approx s \) because spiral growth dominates, and \( s \approx 1 \) because the system is near equilibrium). Therefore, considering the potential reduction of detachment rate at near equilibrium conditions (DePaolo, 2011, Model 2) would not influence our conclusion here. With the approximation of Eq. 56, the coefficients \( c_s \) and \( c_n \) are eliminated from the formulation, and the Sr partition coefficient (Eq. 52) is re-expressed as

\[
K = \frac{s}{s + (k'_{88} - 1)} \left[ k'_{88} K_{eq}(1/s) + K_{inf}(1 - 1/s) \right].
\] (57)

Next, we introduce the third assumption regarding the coefficients. Thus far, only one coefficient, \( k'_{88} \), remains unconstrained. This coefficient describes the preference of Sr over Ca being detached from the calcite crystal (see Eq. 15 for the formal definition). Here, we assume that Sr\(^{2+}\) cation and Ca\(^{2+}\) cation have similar probabilities of being detached from the crystal surface within a given time interval (i.e., \( k'_{88} \approx 1 \)). In this case, we can approximately write \( k'_{88} \approx 1 \) and \( s + (k'_{88} - 1) \approx s \) (we only consider growing calcite crystals, and \( s \) is always greater than one). With these approximations, Eq. 57 and Eq. 48 become

\[
K = K_{inf} - (K_{inf} - K_{eq})/s.
\] (58)

\[
\Delta^{88/86}\text{Sr} = \Delta^{88/86}\text{Sr}_{inf} - (\Delta^{88/86}\text{Sr}_{inf} - \Delta^{88/86}\text{Sr}_{eq})/s,
\] (59)

As discussed earlier in this section, introducing two different precipitation mechanisms does not affect the expression for the Ca isotope fractionation factor; i.e., Eq. 33 still applies. To facilitate the discussion, we repeat this expression (Eq. 33) here,

\[
\Delta^{44/40}\text{Ca} = \Delta^{44/40}\text{Ca}_{inf} - (\Delta^{44/40}\text{Ca}_{inf} - \Delta^{44/40}\text{Ca}_{eq})/s.
\] (60)
With these assumptions, we obtain expressions for all variables of interest, including $\Delta^{44/40} \text{Ca}$, $\Delta^{88/86} \text{Sr}$, and $K$. These expressions successfully predict the observed precipitation rate dependence of $\Delta^{44/40} \text{Ca}$, $\Delta^{88/86} \text{Sr}$, and $K$ (Fig. 4a-c). In the simplified expressions, $\Delta^{44/40} \text{Ca}$, $K$, and $\Delta^{88/86} \text{Sr}$ are all linear to $1/s$ thus linearly correlated to each other, which closely matches the experimentally observed linear correlation among these variables (Fig. 4d-f; Tang et al. 2008a,b; Böhm et al. 2012; AlKhatib and Eisenhauer 2017).

Two assumptions/approximations are involved in the expressions of Sr partitioning and Sr isotope fractionation shown in Eq. 59 and 58: (1) The variation in spiral growth rate with oversaturation is much smaller than that in surface nucleation rate so that we can approximately take $s_s/s = 1/s$; and (2) Sr$^{2+}$ and Ca$^{2+}$ have similar probabilities of being detached from the crystal surface within a given time interval so that we can approximately take $k'_{88} = 1$. To analyze how these approximations affect the model predictions, we performed sensitivity analysis (1) with the parametrization of spiral growth and surface nucleation rates given by Eq. 55 while maintaining the $k'_{88} = 1$ approximation (Fig. 4 dashed curves), and (2) with $k'_{88} = 0.7$ or $k'_{88} = 1.5$ while maintaining the $s_s/s = 1/s$ approximation (Fig. 4 red and blue dotted curves). The predicted $\Delta^{44/40} \text{Ca}-\Delta^{88/86} \text{Sr}$ relation becomes less linear as the magnitude of $k'_{88}$ deviates from one. If $k'_{88}$ falls out of the range of our sensitivity analysis (from 0.7 to 1.5), then the deviation from experimental observations could be significant. From this point of view, that Sr$^{2+}$ and Ca$^{2+}$ have similar probabilities of being detached from the crystal surface within a given time interval, or more quantitatively, $k'_{88} = r_{a(88 \text{Sr})}/r_{a(40 \text{Ca})}/(88 \text{Sr}/40 \text{Ca})_{aq} \in (0.7, 1.5)$, is also a prediction of our model that can be tested by additional investigations. Within the range of parameters covered in the present sensitivity analysis, the results are close to our simplified model, Eqs. 58, 60. The benefit of this simplified model is that it requires a minimal number of free parameters making our model readily applicable to aqueous solutions with different temperature and pH conditions.
5. Discussion

5.1. The origin of kinetic effects during calcite precipitation

The trace element partitioning and isotope fractionation during calcite precipitation are experimentally observed depend on precipitation rate (e.g., Lorens, 1981; Gabitov and Watson, 2006; Tang et al., 2008a,b; Böhm et al., 2012; AlKhatib and Eisenhauer, 2017), but the origin of such kinetic effects remains debated. Two types of models have been proposed: (1) the growth entrapment model (Watson, 2004), which assumes that the crystal surface is in equilibrium with the aqueous solution and fractionation is controlled by diffusion in near-surface regions of the calcite crystal, and (2) the surface reaction model (DePaolo, 2011; Nielsen et al., 2012, 2013), which assumes that diffusive transport inside the calcite crystal is negligible and fractionation is controlled by mass exchange at the solid-liquid interface. To distinguish between the two models, one may examine their basic assumptions. The efficiency of diffusion in growing calcite remains controversial. To explain observed kinetic fractionation with the growth entrapment model, it is necessary to invoke a diffusion coefficient that is around sixteen orders of magnitude higher than that in the regular calcite lattice (e.g., Tang et al., 2008a,b). Atomic diffusion in the near-surface region has been suggested to occur much faster than that in the regular lattice (Watson, 2004), but whether such rapid diffusion occurs needs to be tested. The plausibility of surface equilibrium depends on the relative rate of ion attachment and detachment (DePaolo, 2011). If the net growth rate is much smaller than the detachment rate, then the crystal surface can be exposed for long enough time to undergo sufficient mass exchange with the aqueous solution before it is isolated by newly precipitated solid. In this case, the crystal surface is likely to be in equilibrium with the aqueous solution. If the net growth rate is comparable to or greater than the detachment rate, the crystal surface only undergoes restricted mass exchange with the aqueous solution before it is isolated by further precipitation. As a result, surface equilibrium is unlikely to be reached. In most calcite growth experiments (e.g., Tang et al., 2008a,b; AlKhatib and Eisenhauer, 2017), the net precipitation rates are greater than the ion detachment rate estimated by the dissolution experiments of Chou et al. (1989). When
the net growth rate exceeds the detachment rate, the crystal surface is unlikely to be in equilibrium with the aqueous solution, and surface reaction kinetics likely play a significant role (DePaolo, 2011). The model of DePaolo (2011) provides a straightforward framework to explain kinetic effects by considering only the surface reaction processes. However, it does not explain the linear $\Delta^{44/40}\text{Ca}-\Delta^{88/86}\text{Sr}$ relation observed in the precipitation experiments (Sec. 3; Fig. 2).

Here, we suggest that this problem can be readily resolved by introducing spiral growth and surface nucleation (Sec. 4; Fig. 4), without invoking diffusion or additional free parameters. This implies that surface reaction processes exclusively control kinetic effects during calcite precipitation from aqueous solutions (DePaolo, 2011; Nielsen et al., 2012, 2013). More fundamentally, the kinetics of surface reaction (i.e., the rate of ion attachment/detachment) is probably controlled by the rate of ion dehydration/rehydration (e.g., DeBoer, 1977; Mucci and Morse, 1983). The breaking of hydration spheres of light isotopes is slightly favored than that of heavy isotopes (e.g., Hofmann et al., 2012). Consequently, the dehydration (attachment) of $^{44}\text{Ca}$ is less favored than $^{40}\text{Ca}$ (i.e., $k_{44} = 1 + \Delta^{44/40}\text{Ca}_{\text{inf}}/1000\permil < 1$), and the dehydration (attachment) of $^{88}\text{Sr}$ is less favored than $^{86}\text{Sr}$ (i.e., $k_{88}/k_{86} = 1 + \Delta^{88/86}\text{Sr}_{\text{inf}}/1000\permil < 1$). The suggestion that the dehydration rates control isotope fractionation during the ion attachment step also supports our assumption that spiral growth and surface nucleation have same relative preferences of different isotopes of the same element (i.e., $k_{44(s)} = k_{44(n)}$ and $k_{88(s)}/k_{86(s)} = k_{88(n)}/k_{86(n)}$). The release of ions from crystal surfaces would also favor light isotopes. Thus, the detachment of $^{44}\text{Ca}$ is less frequent than $^{40}\text{Ca}$ (i.e., $k'_{44} = (1000\permil + \Delta^{44/40}\text{Ca}_{\text{inf}})/(1000\permil + \Delta^{44/40}\text{Ca}_{\text{eq}}) < 1$) and the detachment of $^{88}\text{Sr}$ is less frequent than that of $^{86}\text{Sr}$ (i.e., $k'_{88}/k'_{86} = (1000\permil + \Delta^{88/86}\text{Sr}_{\text{inf}})/(1000\permil + \Delta^{88/86}\text{Sr}_{\text{eq}}) < 1$). As to the incorporation of trace elements (e.g., Sr), our model suggests that the difference between equilibrium and kinetic partitioning is originated from the different probabilities of impurity cations (e.g., $\text{Sr}^{2+}$) to be trapped during spiral growth and surface nucleation.

Our model also provides a comprehensive framework for the kinetic controls of other
impurity elements, such as Cd, Mn, Ba, Co, and perhaps Mg, if treated as a trace element. The formulas for element partitioning and isotope fractionation in our model can easily be generalized to other systems, provided the behaviors of the considered elements at extreme conditions (i.e., chemical equilibrium and oversaturation) are well-understood. If the assumptions in Sec. 4 apply, then the partition coefficient or isotope fractionation of such an element would also be expected to linearly correlate with $\Delta^{44/40}\text{Ca}$. This prediction points to a potential means to test our model with new observations of synthetic and natural calcite.

5.2. Implications of the kinetic $\delta^{44/40}\text{Ca}-\delta^{88/86}\text{Sr}$ relationship

During most physical and chemical processes, isotope variations arise from differences in mass. For two or more elements that occur as different isotopes, similar mass-dependent variations may be observed. The hydrogen and oxygen isotope composition of meteoric water provides a canonical example, where $\delta D = 8 \times \delta^{18}O + 10^\circ$ (Global Meteoric Water Line or GMWL; Craig 1961). This relationship has been widely used to investigate the hydrological cycle at local and global scales.

Analogously, the kinetic relationship between $\Delta^{44/40}\text{Ca}$ and $\Delta^{88/86}\text{Sr}$ can be applied to trace variable rates of carbonate precipitation. For calcite crystals precipitated from an aqueous solution comprising Ca and Sr with isotope compositions of $\Delta^{44/40}\text{Ca}_{\text{aq}}$ and $\Delta^{88/86}\text{Sr}_{\text{aq}}$, corresponding compositions of calcite ($\delta^{44/40}\text{Ca}_{\text{cal}}$ and $\delta^{88/86}\text{Sr}_{\text{cal}}$) are given by

$$\delta^{44/40}\text{Ca}_{\text{cal}} = \delta^{44/40}\text{Ca}_{\text{aq}} + \Delta^{44/40}\text{Ca},$$  

$$\delta^{88/86}\text{Sr}_{\text{cal}} = \delta^{88/86}\text{Sr}_{\text{aq}} + \Delta^{88/86}\text{Sr},$$

where $\Delta^{44/40}\text{Ca}$ and $\Delta^{88/86}\text{Sr}$ represent the Ca and Sr isotope fractionation factors during the precipitation of the calcite crystals. If the isotope compositions of the aqueous solution are fixed, then the variations in $\delta^{44/40}\text{Ca}_{\text{cal}}$ and $\delta^{88/86}\text{Sr}_{\text{cal}}$ would be controlled by the effects of kinetics on fractionation. In this case, the slope of the $\delta^{44/40}\text{Ca}_{\text{cal}}-\delta^{88/86}\text{Sr}_{\text{cal}}$ relation, $\beta$, can be expressed as

$$\beta = \frac{d(\delta^{88/86}\text{Sr}_{\text{cal}})}{d(\delta^{44/40}\text{Sr}_{\text{cal}})} = \frac{d(\Delta^{88/86}\text{Sr})}{d(\Delta^{44/40}\text{Ca})}.$$
Through a modified surface reaction model for kinetic isotope fractionation, we suggest that $\Delta^{44/40}\text{Ca}$ and $\Delta^{88/86}\text{Sr}$ exhibit a linear relation (see Eqs. 59-60). In other words, the slope $\beta$ is constant,

$$
\beta = \frac{d(\Delta^{88/86}\text{Sr})}{d(\Delta^{44/40}\text{Ca})} = \frac{\Delta^{88/86}\text{Sr}_{\text{inf}} - \Delta^{88/86}\text{Sr}_{\text{eq}}}{\Delta^{44/40}\text{Ca}_{\text{inf}} - \Delta^{44/40}\text{Ca}_{\text{eq}}}.
$$

(64)

Therefore, the $\delta^{44/40}\text{Ca}$ and $\delta^{88/86}\text{Sr}$ data should fall along the same line with the “kinetic” slope. If the observed carbonate $\delta^{44/40}\text{Ca}$ and $\delta^{88/86}\text{Sr}$ correlate linearly with a slope identical to the model predicted “kinetic” slope, it reflects that the variations of $\delta^{44/40}\text{Ca}$ and $\delta^{88/86}\text{Sr}$ values are induced by precipitation rate and the Ca and Sr isotope compositions of precipitating fluid are likely constant (i.e., the aqueous reservoir is large enough such that its isotope composition is not affected by calcite precipitation). In contrast, if the carbonate $\delta^{44/40}\text{Ca}$ and $\delta^{88/86}\text{Sr}$ fractionate from fluid with changing isotope compositions, they should not produce the same “kinetic” slope, despite that they may still exhibit a linear relationship. The equilibrium fractionation of calcium and strontium isotopes may be affected by the coordination number (CN) of cation in the crystal. Nelson et al. (2021) found that the equilibrium fractionation of Ca isotopes in zeolite (lowest CN = 7) is different from that in calcite (CN = 6). Therefore, our model predicts that the slope may be different from different minerals. Specifically, for calcite, with values of isotope fractionation in the equilibrium and kinetic limits discussed in Sec. 3 (and listed in Tab. 1), we suggest a slope around $\beta = 0.2$, which is consistent with the experimental observations of Böhm et al. (2012).

Given that both mass flux imbalance and changes in carbonate kinetics may cause variations in $\delta^{44/40}\text{Ca}$ and $\delta^{88/86}\text{Sr}$, this information is particularly useful for biogeochemical studies in paleoceanographic settings. Since carbonate precipitation is mainly controlled by seawater carbonate chemistry, being able to distinguish kinetically-driven signals paves a way for independently tracing paleo-oceanic carbonate saturation states and solving for other parameters in composing seawater carbonate buffering system. For instance, Wang et al. (2021) detected a kinetic fractionation line of slope 0.19, which is consistent with the experimental observation of Böhm et al. (2012) and theoretical prediction of the present contribution, in Early Cretaceous biogenic carbonate spinning Oceanic Anoxia Event 1a (OAE1a) and argued
for precipitation rate reduction induced by ocean acidification during this interval. An important complementary benefit is that recovery of the $\delta^{44/40} \text{Ca-} \delta^{88/86} \text{Sr}$ kinetic relationship readily excludes any potential origins from diagenetic alteration. The signal from diagenetic overprinting essentially originates from mixing between primary and recrystallized carbonate minerals. The chemical and isotope compositions of lowly-precipitated diagenetic calcite can be described by $(\text{Sr}/\text{Ca})_{\text{dgt}} = (\text{Sr}/\text{Ca})_{\text{aq}} K_{eq}$, $\delta^{44/40} \text{Ca}_{\text{dgt}} = \delta^{44/40} \text{Ca}_{\text{aq}} + \Delta^{44/40} \text{Ca}_{eq}$, and $\delta^{88/86} \text{Sr}_{\text{dgt}} = \delta^{88/86} \text{Sr}_{\text{aq}} + \Delta^{88/86} \text{Sr}_{eq}$. If a fraction $x$ of this slowly-precipitated carbonate is mixed with the original primary carbonate having chemical and isotope compositions described by $(\text{Sr}/\text{Ca})_{\text{cal}} = (\text{Sr}/\text{Ca})_{\text{aq}} K$ and Eqs. (61)-(62), then the Ca and Sr isotope compositions of the resulting mixed carbonate, $\delta^{44/40} \text{Ca}_{\text{mix}}$ and $\delta^{88/86} \text{Sr}_{\text{mix}}$, can be calculated from mass balance as

$$\delta^{44/40} \text{Ca}_{\text{mix}} = \delta^{44/40} \text{Ca}_{\text{aq}} + x \Delta^{44/40} \text{Ca}_{eq} + (1 - x) x \Delta^{44/40} \text{Ca}, \quad (65)$$

$$\delta^{88/86} \text{Sr}_{\text{mix}} = \delta^{88/86} \text{Sr}_{\text{aq}} + \frac{x K_{eq}}{x K_{eq} + (1 - x) K} \Delta^{88/86} \text{Sr}_{eq} + \frac{(1 - x) K}{x K_{eq} + (1 - x) K} \Delta^{88/86} \text{Sr}. \quad (66)$$

The $\Delta^{44/40} \text{Ca}$, $\Delta^{88/86} \text{K}$, and $K$ values can be correlated through Eqs. (58)-(60). As illustrated by the dashed curves in Fig. 5, this mixing leads to non-linear relations between $\delta^{44/40} \text{Ca}$ and $\delta^{88/86} \text{Sr}$ of the carbonates. Therefore, if the $\delta^{44/40} \text{Ca}$ and $\delta^{88/86} \text{Sr}$ values of natural carbonate samples follow a linear relation of the “kinetic” slope, then signals are most reasonably interpreted as primary [Wang et al., 2021]. Moreover, if syn-precipitated minerals other than carbonate (e.g., apatite or barite in oceanic settings) produced mass-dependent fractionation lines with different “kinetic” slopes, then Ca and Sr isotope compositions of original precipitating fluid could be uniquely determined by the intercept of two fractionation lines.

6. Conclusions

The mass exchange between the crystal surface and the aqueous solution controls the kinetics of crystal growth and likely plays a crucial role in the kinetic processes of trace element partitioning and isotope fractionation. The surface reaction model of DePaolo [2011] provides the first simple framework to explain these kinetic effects with a minimum number
of free parameters. Nevertheless, despite the model’s success in explaining the precipitation rate dependence of calcium fractionation ($\Delta^{44/40}\text{Ca}$) and Sr partition coefficient ($K$), it cannot explain rate control of strontium isotope fractionation ($\Delta^{88/86}\text{Sr}$) nor observed linear relation between $\Delta^{41/40}\text{Ca}$ and $\Delta^{88/86}\text{Sr}$. Here, we developed a new surface reaction model by considering two parallel precipitation mechanisms, spiral growth and surface nucleation, which have been identified directly through in situ microscopic observations (e.g., Dove and Hochella, 1993; Teng et al., 1998, 2000). With this modification, the new surface reaction model successfully explain the rate dependence of $\Delta^{44/40}\text{Ca}$, $\Delta^{88/86}\text{Sr}$, and $K$, as well as their observed linear correlations (Tang et al., 2008a,b; Böhm et al., 2012; AlKhatib and Eisenhauer, 2017). Although it is impractical to exclude other processes (e.g., Watson, 2004), our model suggests that the kinetics of calcite precipitation could largely be controlled by the surface reaction processes, especially in low temperature systems (e.g., DePaolo, 2011; Nielsen et al., 2012, 2013). This model also has important implications for interpreting $\delta^{44/40}\text{Ca}$ and $\delta^{88/86}\text{Sr}$ values of natural carbonate. When precipitating from a fluid with constant isotope compositions (i.e., the aqueous reservoir is large enough such that its isotope composition is not affected by calcite precipitation), kinetics isotope effects should control variations of carbonate $\delta^{44/40}\text{Ca}$ and $\delta^{88/86}\text{Sr}$ values, and the values should fall along a kinetic fractionation line with a characteristic slope, as observed in laboratory experiments. In other words, if the observed carbonate $\delta^{44/40}\text{Ca}$ and $\delta^{88/86}\text{Sr}$ correlate linearly with a slope identical to the model predicted “kinetic” slope, it reflects that the variations of $\delta^{44/40}\text{Ca}$ and $\delta^{88/86}\text{Sr}$ are induced by variable precipitation rates, and the Ca and Sr isotope compositions of precipitating fluid are likely constant (Wang et al., 2021). In contrast, if the seawater varies during carbonate precipitation or diagenetic process alters the primary carbonate, $\delta^{44/40}\text{Ca}$ and $\delta^{88/86}\text{Sr}$ do not correlate. This implication points towards a new way to distinguish primary versus secondary $\delta^{44/40}\text{Ca}$ signals and quantify seawater carbonate chemistry.
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A nuclide of element X with mass number M

Detachment rate of $^M X$ from calcite surface to aqueous solution

Attachment rate of $^M X$ from aqueous solution onto calcite surface

Attachment rate of $^M X$ onto calcite surface due to spiral growth

Attachment rate of $^M X$ onto calcite surface due to surface nucleation

Normalized $^{40}\text{Ca}$ attachment rate, $s = r_{a(40\text{Ca})}/r_{d(40\text{Ca})}$

Normalized spiral growth rate of $^{40}\text{Ca}$ attachment, $s_s = r_{a(40\text{Ca})}/r_{d(40\text{Ca})}$

Normalized surface nucleation rate of $^{40}\text{Ca}$ attachment, $s_n = r_{n(40\text{Ca})}/r_{d(40\text{Ca})}$

Concentration ratio of $^{M_1}X_1$ and $^{M_2}X_2$ in aqueous solution

Concentration ratio of $^{M_1}X_1$ and $^{M_2}X_2$ in calcite crystal (on its surface)

The relative preference of $^M X$ over $^{40}\text{Ca}$ being attached from aqueous solution onto calcite surface, $k_M = (r_{a(40\text{Ca})}/r_{a(40\text{Ca})})(^{M X}/^{40\text{Ca}})_{\text{aq}}$

The relative preference of $^M X$ over $^{40}\text{Ca}$ being attached during spiral growth, $k_{M(s)} = (r_{a(40\text{Ca})}/r_{a(40\text{Ca})})(^{M X}/^{40\text{Ca}})_{\text{aq}}$

The relative preference of $^M X$ over $^{40}\text{Ca}$ being attached during surface nucleation, $k_{M(n)} = (r_{n(40\text{Ca})}/r_{d(40\text{Ca})})(^{M X}/^{40\text{Ca}})_{\text{aq}}$

The relative preference of $^M X$ over $^{40}\text{Ca}$ being detached from calcite surface to aqueous solution, $k'_M = (r_{d(40\text{Ca})}/r_{d(40\text{Ca})})(^{M X}/^{40\text{Ca}})_{\text{cal}}$

Sr partition coefficient, $K = (\text{Sr}/\text{Ca})_{\text{cal}}/(\text{Sr}/\text{Ca})_{\text{aq}}$

Ca isotope fractionation factor, $\Delta^{44/40\text{Ca}} = 1000^\% \times (\delta^{44/40\text{Ca}}_{\text{cal}} - \delta^{44/40\text{Ca}}_{\text{aq}})$

Sr isotope fractionation factor, $\Delta^{88/86\text{Sr}} = 1000^\% \times (\delta^{88/86\text{Sr}}_{\text{cal}} - \delta^{88/86\text{Sr}}_{\text{aq}})$

Sr partition coefficient at equilibrium, assumed to be $K_{eq} = 0.025$

Sr partition coefficient at equilibrium, assumed to be $\Delta^{44/40\text{Ca}}_{eq} = 0^\%$

Sr partition coefficient at equilibrium, assumed to be $\Delta^{88/86\text{Sr}}_{eq} = 0^\%$

Sr partition coefficient at the kinetic limit, assumed to be $K_{inf} = 0.24$
\[ \Delta^{44/40}\text{Ca}_{\text{inf}} \]

Ca isotope fractionation factor at the kinetic limit, assumed to be \( \Delta^{44/40}\text{Ca}_{\text{inf}} = -2\% \)

\[ \Delta^{88/86}\text{Sr}_{\text{inf}} \]

Sr isotope fractionation factor at the kinetic limit, assumed to be \( \Delta^{88/86}\text{Sr}_{\text{inf}} = -0.4\% \)

| Variable          | Definition                                                                 |
|-------------------|---------------------------------------------------------------------------|
| \( \Delta^{44/40}\text{Ca}_{\text{inf}} \) | Ca isotope fractionation factor at the kinetic limit, assumed to be \( \Delta^{44/40}\text{Ca}_{\text{inf}} = -2\% \) |
| \( \Delta^{88/86}\text{Sr}_{\text{inf}} \) | Sr isotope fractionation factor at the kinetic limit, assumed to be \( \Delta^{88/86}\text{Sr}_{\text{inf}} = -0.4\% \) |

Table 1: Variables used in this study
Figure 1: Schematic of the surface reaction models for calcite precipitation from aqueous solutions. (a) The general reaction rate dependent model (see Sec. 2 for details). Ions are attached onto the crystal surfaces from the aqueous solute ion and detached from the crystal surfaces into the solution. The attachment and detachment fluxes determine the chemical compositions of the crystal. In the simplest model (Sec. 3 also in DePaolo 2011), the composition of the aqueous solution solely determines the composition of the attachment flux. (b) A modified surface reaction model (see Sec. 4 for details). Ion attachments occur through two parallel mechanisms, spiral growth and surface nucleation. The composition of the total attachment flux varies with the relative contributions of the two attachment mechanisms.
Figure 2: The predictions from the simplest surface reaction model described in Sec. 2 (Eqs. 33-35). (a) Ca isotope fractionation ($\Delta^{44/40}$Ca) versus net growth rate; (b) Sr partition coefficient ($K$) versus net growth rate; (c) Sr isotope fractionation ($\Delta^{88/86}$Sr) versus net growth rate; (d) Ca isotope fractionation ($\Delta^{44/40}$Ca) versus Sr partition coefficient ($K$); (e) Sr isotope fractionation ($\Delta^{88/86}$Sr) versus Sr partition coefficient ($K$); (f) Sr isotope fractionation ($\Delta^{88/86}$Sr) versus Ca isotope fractionation ($\Delta^{44/40}$Ca). The black curves display results with the preferred values of the parameters according to observational constraints; the gray curves show results with $K_{eq} = 0.07$, which was assumed by DePaolo (2011). The solid curves are predictions assuming a constant detachment rate (DePaolo, 2011, Model 1); the dashed curves are predictions assuming variable detachment rates (DePaolo, 2011, Model 2); the dotted curves are predictions assuming the detachment rates adopted by Zhang and DePaolo (2020) to fit the experimentally reported Sr partitioning data with the naturally observed value for equilibrium Sr partitioning. In (d)-(f), the dashed and dotted curves are not visible because they completely coincide with the solid curves. The black, blue, and gray circles are data from experiments at temperature of 25 °C and pH ≈ 8 reported by Böhm et al. (2012), Tang et al. (2008a,b), and AlKhatib and Eisenhauer (2017), respectively. The red squares are observations of oceanic crust calcite (Böhm et al., 2012). The red bar in (c) gives the range of $K$ at very low net precipitation rates reported by Zhang and DePaolo (2020).
Figure 3: An example of the parametrization of spiral growth and surface nucleation rates as a function of calcite saturation state. (a) Net calcite growth rates change with oversaturation ($\Omega - 1$). The red curve indicates the contribution of spiral growth (the parabolic term in Eq. 54), the blue curve represents the contribution of surface nucleation (the cubic term in Eq. 54), and the black curve denotes the overall normalized net growth. The crosses and circles indicate observations of net growth rate reported by Tang et al. (2008a,b) and AlKhatib and Eisenhauer (2017), respectively, at 25 °C and pH $\approx$ 8. (b) The variation of attachment rate with oversaturation ($\Omega - 1$). The red curve represents the contribution of spiral growth, the blue curve represents the contribution of surface nucleation, and the black curve is the overall attachment rate. The dotted curves are approximations under the assumption of constant spiral growth rate. (c) The variation of relative contribution of spiral growth ($s_s/s$) and surface nucleation ($s_n/s$) with overall attachment rate. The dashed curve gives the approximation of constant spiral growth rate ($s_s/s = 1/s$ and $s_n/s = 1-1/s$). In all panels, the solid curves indicate results of the example with $c_s = 2.4 \times 10^{-8}$ mol/(m$^2$ · s) and $c_n = 1.2 \times 10^{-8}$ mol/(m$^2$ · s).
Figure 4: The predictions with the new surface reaction model. The solid black curves are the results with the simplest approximations (i.e., $s/s = 1/s$ and $k_{88}' = 1$, which lead to Eqs. [58-60]). Sensitivity tests on these approximations are illustrated by dashed and dotted curves. The dashed curves indicate results with $k_{88}' = 1$ but $s/s$ and $s$ parametrized following Eq. [51]. The dotted curves indicate results with $s/s = 1/s$ but $k_{88}' = 1.5$ (blue dotted curves) or $k_{88}' = 0.7$ (red dotted curves). The black, blue, and gray circles are observations from experiments at 25 °C and pH ≈ 8 by Böhm et al. (2012), Tang et al. (2008a,b), and AlKhatib and Eisenhauer (2017), respectively. The red squares are observations of oceanic crust calcite (Böhm et al., 2012). The red bar in (c) gives the range of $K$ at very low net precipitation rates (Zhang and DePaolo, 2020). In (a)-(c), the absolute net growth rates were converted to normalized net growth rates with a constant detachment rate $6 \times 10^{-7}$ mol·m$^{-2}$·s$^{-1}$ (Chou et al., 1989; DePaolo, 2011, Model 1).
Figure 5: Behaviors of carbonate Ca and Sr isotope compositions according to different processes. (1) Kinetic process: If the isotope compositions of seawater remained constant, then all precipitating carbonates should fall along the kinetic isotope fractionation line and their $\delta^{44/40}$Ca and $\delta^{88/86}$Sr should linearly correlate. This process is best represented by the Cretaceous OAE 1a samples shown as red circles \(\text{(Wang et al., 2021)}\). (2) Seawater mixing process: If the isotope compositions of seawater varied through time, although individual carbonate still precipitates diagonally along the kinetic fractionation line, their $\delta^{44/40}$Ca and $\delta^{88/86}$Sr values will not correlate. This process is suggested to occur during the end-Permian mass extinction, as shown by grey triangles \(\text{(Wang et al., 2019)}\). (3) Diagenetic alteration: If diagenetic alteration overprints the original $\delta^{44/40}$Ca and $\delta^{88/86}$Sr values (i.e., the primary carbonate is mixed with secondary carbonate), then the $\delta^{44/40}$Ca and $\delta^{88/86}$Sr of the bulk altered carbonate will not linearly correlate and will instead fall along curved mixing arrays (given by Eqs. \(65\) and \(66\)). An example of this process could be recrystallization during early diagenesis, as suggested by \(\text{Higgins et al., 2018)}\).
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