On the utility of quantitative modeling to the interpretation of Ca isotopes

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ABSTRACT

Though the utility of calcium isotopes is broad, examples of application are still relatively sparse. Some of this, as with many metal isotope systems, may derive from a perception that the analytical tool is difficult to access. Alternatively, potential users may be deterred by a sense that calcium isotopes are ambiguous, difficult to interpret, and/or complicated by too many interrelated processes. Here we provide an overview of the quantitative modeling approaches available to facilitate interpretation of the distribution and signatures of calcium isotopes in Earth systems, in particular their ability to push interpretations beyond the qualitative. While no method is perfect, the variety of approaches described here offer an accessible toolset that is incredibly valuable. We suggest that the calcium isotope community should be expanding the use of such techniques, noting their limitations and striving to improve upon current methods over time.

1. Introduction

Over the past twenty years, the use of calcium (Ca) isotopes has reached into almost every sub-discipline in the geosciences and is now gaining ground in archeological, medical, and forensic applications (Tacail et al., this volume). Ca is a major element in the important sedimentary carbonate archive, it is correspondingly difficult to alter diagenetically (Fantle & Tipper, 2014; Fantle, 2015), and its chemistry in surface environments is relatively simple (e.g., not impacted by overly complex speciation or redox processes). We now have a reasonably robust understanding of how Ca fractionates when calcite precipitates and we are becoming increasingly sophisticated in the interpretation of this signal. Calcium isotopes are thus emerging as a robust tool both for probing the past (Gussone et al., this volume) and understanding the present (Griffith et al., this issue).

Though the potential is evident, the application of Ca isotopes to a host of questions remains relatively sparse. This may stem, at least in part, from a perception of analytical difficulty, or perhaps as a result of perceived complexity or ambiguity in the interpretation of Ca isotopes in natural systems. For example, the Ca isotopic composition of marine carbonates have been interpreted to reflect secular seawater evolution, sea surface temperature, local mineralogical and fractionation factor variability, and diagenetic alteration (e.g., De La Rocha and DePaolo, 2000; Fantle and DePaolo, 2005; Sime et al., 2007; Farkas et al., 2007; Fantle, 2010; Fantle and Higgins, 2014; Du Vivier et al., 2015; Lau et al., 2017; Higgins et al., 2018). Other questions remain to be answered, such as why the world's largest rivers show a surprisingly narrow range of Ca isotope values at high flow rates despite the complexity of water-rock interaction and riverine drainage networks (Tipper et al. 2010). Here, we argue that observations such as these are not a reason to *avoid* Ca isotopes as an analytical tool but are instead the motivation for delving more deeply into them. Ultimately, these are the critical clues to the underlying function and balance of the Earth system that Ca (and other metal) isotopes uniquely report.

Our ability to leverage the information contained in such complex signals and thus advance application of Ca isotopes across the geoscience community depends on the development of quantitative models capable of deconvolving complex signals. For our present discussion a "model" is considered any quantitative framework designed to combine external sources and internal processes to reproduce or even predict a dataset (or, more usefully, datasets). The primary objective of such work is to identify and even quantify the dominant controls on a system of interest. This distinction is important, as it focuses the remainder of our present discussion on process-based frameworks, thus excluding regression, component analysis, and interpolation methods. Such a modeling approach may be a simple mixing analysis, a box model with one or more reservoirs, a single- or multi-component reactive transport model, or an *ab initio* molecular simulation (Figure 1). Models are a quantitative means of testing hypotheses across scales, thus serving a critically important service in deconvolving complex signals and developing confidence in proxies.

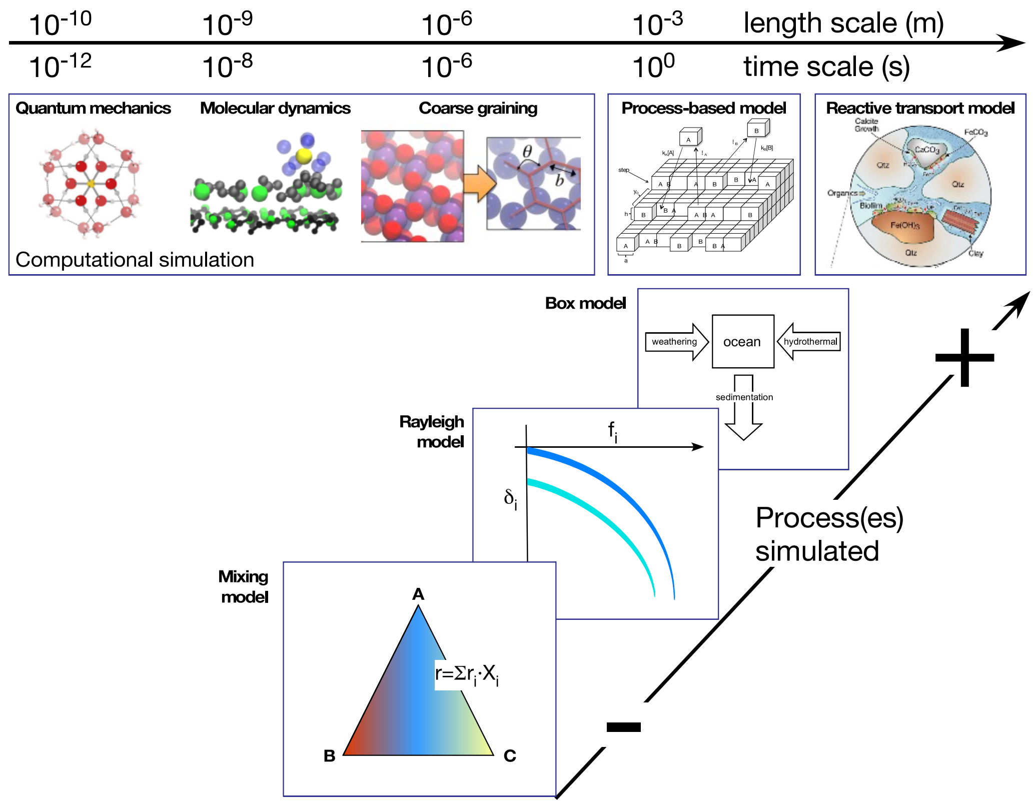

Figure 1: Hierarchy of multiscale modeling techniques indicating typical accessible length- and time-scales (horizontal axis). Hierarchy of processes assimilated into modeling techniques indicating typical progression of complexity and coupling (diagonal axis).

Combining models and stable isotopes, in addition to other geochemical parameters, removes degrees of freedom in poorly constrained problems. For example, the concentration of calcium in a given reservoir may appear to be stable through time, and thus we may suggest (multiple) simple steady state mixing model(s) of inputs and outputs that create this unique value. Yet variations in the δ^{44}Ca values, if measured, could indicate that changes are indeed occurring, and could be used to either rule out certain combinations of input and output fluxes or constrain endmember compositional shifts through time. Thus, isotopes add important constraints to the models that integrate information, simplifying complex systems and isolating key processes.

The only perfect example of a system is the system itself. Models are fundamentally imperfect in their representations of reality, seeking to achieve reasonable approximations while simplifying the myriad of processes and underlying mechanisms. Becoming an experienced modeler is then largely a process of learning how to define what is a reasonable approximation for the datasets available and the hypotheses one wishes to test. To those unfamiliar with a given modeling tool, the learning curve for such model development can be steep. Difficulty commonly arises when new users wish to test hypotheses or explore behavior that requires a more elaborate modeling framework than an individual on their own could reasonably construct. Just as a researcher new to Ca isotopes would not be expected to purchase and operate a multi-collector mass spectrometer in order to produce their first dataset, many model applications require software that is already built by others, such as common open source and commercially available reactive transport packages (e.g., Steefel et al. 2015). For the inexperienced user, entering values into an input file or graphical user interface and then launching the simulation creates a 'black box' situation in which it becomes difficult to establish a clear understanding of what the model results have achieved or why a particular set of input parameters fails to run. Another common issue arises from the preconceived expectation that a model should reproduce observations or else it has failed. The frustration that results in such a situation can often cause a user to abandon the particular quantitative approach, when in fact the inability of a well-constructed modeling framework to reproduce expectations can be a direct test of underlying hypotheses.

Overcoming such barriers is crucial to the development of the Ca isotope proxy, given the value that models offer. Increasing familiarity with models will foster the ability to communicate in more certain terms about the capabilities of any given proxy. We suggest that such a collective proficiency can be initiated via a basic understanding of modeling language and techniques, which does not require years of (re)training. Just as we depend on specialists in field work, mass spectrometry, and laboratory experiments, the calcium isotope community will have to include and collaborate with specialists in model development. This does not mean that a 'modeler' is required in order to apply such quantitative techniques. Simply that a basic, shared language and understanding are necessary in order for the broader community to better integrate quantitative models into interpretive frameworks. For example, all models require some information to be input in order to generate a solution, and this information should be appropriate to the system of interest. Endmembers must be established for a mixing model, and these values should reflect realistic Ca mass and isotope compositions. Rayleigh models require a fractionation factor that is appropriate to the pathway of interest, and a rationale that justifies applying a single fractionating pathway to a multi-process system. Numerical solutions for reactive transport equations require a starting point (initial conditions) and information regarding the mass and isotope ratio of reservoirs surrounding the domain (boundary conditions). Such values are the responsibility of the researchers to identify and constrain before a model can be applied.

To this end, and with our overall motivation to advance the development of the Ca isotope proxy, we present an overview of the general classes of models applicable to Ca isotope studies of the Earth system. To date, the majority of quantitative interpretations of Ca isotopic data have been accomplished using mixing, box model, and Rayleigh approaches, and we begin with these methods. Advancing from this more familiar foundation, we step through simple reactive transport frameworks to modern multi-component simulation approaches, finally turning to a new generation of highly-resolved mechanistic models that isolate the mass-dependent partitioning of calcium isotopes. In each section, we highlight areas in which these approaches have proven utility and success, as well as situations in which the relevant assumptions suggest that we require a more nuanced approach. An overall theme of the paper is that each modeling technique described offers the potential to impact interpretations and guide future research when they are appropriately developed, and the results carefully considered.

Before proceeding, we wish to clarify that this review focuses on Ca isotopes. However, in many instances, the descriptions and conclusions drawn are applicable to an array of stable isotope systems. Given the focus on Ca in this special issue, and for simplicity's sake, we will not discuss the diversity of metal isotopes. As a result, we may refer to the inapplicability of a given modeling technique, for example Rayleigh distillation describing precipitation of new mineral phases, that would be sound for a different isotope system. We ask the reader to keep this qualification in mind when utilizing the material herein.

2. Reservoir Models

This classification refers to models that are applied to describe mass and isotopic distributions of reservoirs, such as ocean and crust, porous media and groundwater, and vegetation and soil, without explicitly resolving length scales or interfaces among and between these reservoirs. Mass transfer is thus accomplished through a process that is not physically resolved, such as an instantaneous or sequential mixing between endmembers, a coefficient of input, removal or exchange between reservoirs, or a direct relationship between reaction progress and fractionation independent of travel path. Such approaches are broadly applicable and highly adaptive as they require only minimal representation or understanding of the physical systems to which they are applied. For example, a simple box model of riverine inputs to a lake or ocean averages over the broad range of drainage pathways, fluid residence times, seasonal variations, and lithologies, information that may be unavailable or poorly constrained.

2.1 Mixing analysis

Mixing analysis approaches are used over a range of length scales, and time is not explicitly considered. They offer a powerful means of interpreting large-scale phenomena, such as the effect of organic matter burial on the global carbon cycle (e.g., Schidlowski and Junge, 1981), and hold proven value in smaller-scale processes, such as the diagenetic alteration of carbonates (e.g., Banner and Hanson, 1990). In the world of Ca isotopes, mixing approaches are used regularly. For instance, Chanda et al. (2019) used a simple mixing analysis to explore the impact of surface reaction in nannofossil oozes on the interpretation of the equilibrium fractionation factor (Fantle and DePaolo, 2007). Jacobson et al. (2015) used mixing models to apportion riverine Ca fluxes between silicates and carbonates in Iceland. Holmden (2009), Fantle and Higgins (2014), and Lau et al. (2017) used mixing models to explore carbonate diagenesis and its impact on the global Ca cycle, while Gussone et al. (2009) used similar techniques to explore the Ca isotopic composition of foraminiferal carbonate.

There are many advantages to mixing analysis, chief among them is that it is a simple and flexible technique which is easily applied to both elemental and isotopic data. Mixing equations can be derived by the researcher in a straightforward manner and are readily reportable in the literature and thus reproducible for use by others in the scientific community. Here we briefly present a such a derivation for those wishing to gain proficiency with the approach. Additional resources include Albarede (1995) and Banner and Hanson (1990).

All mixing equations begin with a simple statement of mass conservation:

$$N_{mix}^{A} = \sum_{q=1}^{n} N_{q}^{A} \qquad [1]$$

where N is mass (in moles) of element A in either the mixture or the qth endmember. From there, mixing equations that deal with isotopic or elemental ratios are simply derived by factoring out the ratio of interest. For the example of an elemental ratio mixing expression:

$$N_{mix}^{B} \cdot \frac{N_{mix}^{A}}{N_{mix}^{B}} = \sum_{q=1}^{n} N_{q}^{B} \cdot \frac{N_{q}^{A}}{N_{q}^{B}} \quad [2]$$

where N_i^A/N_i^B is the molar ratio of element A to element B (e.g., Mg/Ca or Sr/Ca). This results in a familiar expression:

$$\frac{N_{mix}^{A}}{N_{mix}^{B}} = \sum_{q=1}^{n} X_{q}^{B} \cdot \frac{N_{q}^{A}}{N_{q}^{B}} \quad [3]$$

where X_q^B is the mole fraction of element B contributed to the mixture by the qth endmember. For the example of Mg/Ca, Eqn. 3 becomes:

$$\left(\frac{N^{Mg}}{N^{Ca}}\right)_{mix} = \sum_{q=1}^{n} X_{q}^{Ca} \cdot \left(\frac{N^{Mg}}{N^{Ca}}\right)_{q} \quad [4]$$

The mole fraction of Ca contributed by each endmember can be recast to something more useful, such as the mass fraction of mineral ($M_{minl,i}$ in this example) or fluid contributed to the mixture:

$$X_{q}^{Ca} = \frac{N_{q}^{Ca}}{N_{mix}^{Ca}} = \frac{m_{Ca,minl,q}[mol/g] \cdot mass_{minl,q}[g]}{m_{Ca,minl,mix}[mol/g] \cdot mass_{minl,mix}[g]} = \frac{m_{Ca,minl,q}[mol/g]}{m_{Ca,minl,mix}[mol/g]} M_{minl,q} \quad [5]$$

where $m_{A,phase,i}$ is the concentration of element A in a given phase (i.e., solid or fluid) in either the mixture or qth endmember.

An isotopic mixing expression is derived in exactly the same way for the nuclide-specific mole fraction term (${}^{j}X_{q}^{A}$):

$$\left(\frac{{}^{i}N^{A}}{{}^{j}N^{A}}\right)_{mix} = \sum_{q=1}^{n} {}^{j}X_{q}^{A} \cdot \left(\frac{{}^{i}N^{A}}{{}^{j}N^{A}}\right)_{q} \quad [6]$$

Typically for these isotopic expressions, an assumption is made regarding the abundance of the *jth* nuclide (^{40}Ca, for instance), which is usually similar across all endmembers and the mixture. This allows the expression to be recast in terms of the isotope ratio so that ${}^{i/j}r_{mix}^{A} = \sum_{q=1}^{n} {}^{j}X_{q}^{A} \cdot {}^{i/j}r_{q}^{A}$, which may be further cast in terms of delta notation: $\delta^{i/j}A_{mix} = \sum_{q=1}^{n} X_{q}^{A} \cdot \delta^{i/j}A_{q}$. This is reasonable in cases where the variability in isotopic composition is low (as for Ca isotope system). However, use of the ^{44}Ca/^{42}Ca ratio instead of the ^{44}Ca/^{40}Ca ratio requires a correction for the abundance of the *jth* nuclide.

The primary disadvantage of the mixing approach is that there is no explicit time component, no kinetics, and no chemistry included in the calculation. Thus, no process (e.g. transport, chemical reaction, or biological uptake) and/or temporal evolution along a pathway (e.g., a fluid flow pathway) are considered or accounted for. Instead, mixing analysis provides a time-integrated snapshot of a given system, which can be quite informative. In some cases, however, it may be advantageous to consider the impact of transport and extent of reaction on the interpretation of the data. This bring us then to consider other approaches that offer more flexibility.

2.2 Rayleigh models

Rayleigh models are often the next step for those that wish to think about the evolution of a given system as a function of reaction progress (Druhan & Winnick 2019). In the Ca isotope community, Rayleigh models have been used to explore and/or interpret experimental data, processes occurring in the soil environment, marine pore fluids, biomineral formation, plant uptake, and the deep Earth (e.g., Teichert et al., 2009; Schmitt et al., 2013; Harouaka et al., 2014; Inoue et al., 2015; Millière et al., 2019; Amsellem et al., 2019; Brazier et al., 2019). The primary advantage of using a Rayleigh model is that it is a simple means of considering the effects of a fractionating pathway on the system while requiring relatively few inputs (i.e., a fractionation factor and an initial isotopic composition). The expression that describes the evolution of a reservoir containing element A upon removal or consumption of A by some mechanism (e.g., mineral precipitation), and assuming a constant fractionation factor (α), is (Rayleigh, 1902):

$$\left(\frac{{}^{i/j}r^{A}}{{}^{i/j}r_0^{A}}\right) = f_A^{\alpha-1} \qquad [7]$$

where r is the isotope ratio of the reservoir at any point in the reaction, r_0 is the initial isotope ratio (i.e., before any reaction has occurred; f=1), and f_A is the fraction of element A remaining in that reservoir (relative to the initial mass). In cases where both isotopes are similar in abundance relative to one another (e.g. when considering the $^{44}Ca/^{42}Ca$ ratio instead of the $^{44}Ca/^{40}Ca$), the Rayleigh equation becomes (Criss, 1999):

$$\left(\frac{{}^{i/j}r^{A}}{{}^{i/j}r_0^{A}}\right) = \left(\frac{\left(1+{}^{i/j}r_0^{A}\right)\cdot f_A}{1+{}^{i/j}r^{A}}\right)^{\alpha-1} \qquad [8]$$

for a two-isotope system.

A primary disadvantage of a Rayleigh model is that it simulates a single process that must adhere to specific behavior. For systems in which there is more than one process playing a significant role in the transport or transformation of element A between phases, a Rayleigh model may not be acceptable. In addition, the simplest and most common versions of this model framework do not account for a variable fractionation factor. Thus, if more than one fractionating process influences a system, or if the relative influence of different processes (both fractionating and non-fractionating) shift through space and/or time, such models will be inaccurate. Take the example of a soil in which two fractionating processes, sorption and mineral precipitation, both affect the isotopic composition of a pore fluid. If we wish to interpret the data from such a system, and both processes operate on the same time scale, a Rayleigh model is not appropriate for simulating the pore fluid isotopic data.

Finally, a significant potential drawback of a Rayleigh model is that it does not account for any reversibility or return of mass removed back into the reservoir (i.e., a “back reaction” in the case of a solid precipitating from a fluid (e.g., Druhan et al., 2013; Harouaka et al., 2019; Fernandez et al., 2019). Instead, a Rayleigh model instantaneously and permanently segregates the material removed from the reservoir, which is why a basic form is commonly referred to as a "distillation" model. In the case of minerals, there is often back reaction (that is, the mass held in the solid and surrounding fluid phases can exchange); in such cases, the Rayleigh model is not appropriate. The same is true in cases where material is introduced into the reservoir (i.e. the system is open) and/or the system is close enough to equilibrium that it can fluctuate between precipitation and dissolution, sorption and desorption, etc.

Ultimately, a Rayleigh model is versatile and simple to apply. It allows one to test hypotheses in relatively complex systems and generate more concrete conclusions as a result. Although good agreement between such a model and a given dataset does not inherently provide mechanistic information, a well-designed study involving complementary modeling and experimental/analytical approaches can help one to identify possible mechanisms. Application of Rayleigh models, however, require clear justification, and an applicable constraint on the fractionation factor. Otherwise, an interpretation that depends on the output of the model may be based on flawed assumptions.

2.3 Box models

In the Ca isotope community, box models have been used extensively to examine the global Ca cycle (e.g., De La Rocha and DePaolo, 2000; DePaolo, 2004; Du Vivier et al., 2015; Fantle and DePaolo, 2005; Heuser et al., 2005; Sime et al., 2007; Fantle, 2010; Griffith et al., 2011; Vollstaedt et al., 2014; Jost et al., 2017) and the terrestrial Ca cycle (e.g., Fantle and Tipper, 2014), as well as the effects of diagenesis on carbonate isotopic composition (e.g., Fantle and Higgins, 2014). In a box model, the user simulates a single (or multiple) homogeneous reservoir(s) (i.e., box(es) that represent a system of interest, e.g., the ocean-atmosphere system) that evolve(s) over time as a consequence of inputs to and outputs from a given reservoir. While processes within a reservoir are not simulated in a spatially-resolved manner, a box model can consider processes within a reservoir that affect the output flux (e.g., mineral transformations, dissolution, complexation, sorption, etc). Box models are used at large spatial scales (e.g., the global Ca cycle), but can also be useful in quantifying smaller scale systems such as the mineral-fluid interface (Fantle and DePaolo, 2007), bench-scale experiments (Ryu et al., 2011) and basin-scale systems (Harouaka et al., 2014).

The general approach to using a box model for the simulation of isotopic composition begins by designing a model construct that appropriately describes the system of interest. This mainly involves deciding how many boxes are needed. For instance, in the global ocean, seawater might be modeled as one reservoir, the sedimentary column another, and the atmosphere in communication with the ocean a third. In theory, a box model can consist of as many reservoirs as the user requires, their evolutions coupled by the relevant fluxes which transfer mass between them. For example, mineral precipitation can affect the isotopic composition of the fluid, which then determines the isotopic composition of the solid removed from the system at any point in time.

After a model has been conceptualized, differential equations are written that describe the inputs to, and outputs from, each box in the model (note that "sources" and "sinks" are simply included as inputs and outputs, respectively). The most straightforward way to write such an equation is to recognize that the derivative of an isotope ratio (dr/dt) is, by the chain rule:

$$ {}^{j}N_l \frac{dr_l}{dt} = \frac{d\,{}^{i}N_l}{dt} - r_l \frac{d\,{}^{j}N_l}{dt} \qquad [9] $$

where ${}^{j}N_l$ is the mass (in moles) of nuclide j in reservoir l, r is the isotope ratio (i/j), and t is time. One can then write expressions for each of the nuclides in ratio i/j and combine them. The two nuclide-specific expressions are related to each other by isotope ratios and, where applicable, fractionation factors. A generic result of this procedure is:

$$ {}^{j}N_l \frac{dr_l}{dt} = \sum_m {}^{j}F_{m,input}\,(r_m - r_l) - r_l \sum_n {}^{j}F_{n,output}\,\left(\alpha_{n-l}^{i/j} - 1\right) \qquad [10] $$

where ${}^{j}F_m$ is the mth mass flux (in moles/time) of nuclide j (i.e., the denominator nuclide) into reservoir l and $\alpha_{n-l}^{i/j}$ is the isotopic fractionation factor between the nth output and the reservoir l. As with the mixing equations above, an abundance correction can be applied to convert the flux of nuclide j to the total elemental flux, where the error incurred when modeling isotopic ratios such as $^{40}Ca/^{44}Ca$ is negligible. This is the only assumption that is made in deriving the box model equations using this approach. In delta notation, Eqn. 10 becomes:

$$ N_l \frac{d\delta^{i/j}A_l}{dt} = \sum_m F_{m,input}\left(\delta^{i/j}A_m - \delta^{i/j}A_l\right) - \sum_n F_{n,output}\,\Delta^{i/j}A_{n-l} \qquad [11] $$

where $\delta^{i/j}A_l$ indicates the isotopic composition of element A (ratio i/j) in reservoir l, input m, or output n, and $\Delta^{i/j}A_{n-l}$ is the isotopic fractionation factor ($= \delta^{i/j}A_n - \delta^{i/j}A_l$). Note that dividing by N_l results in F/N terms on the righthand side of Eqns. 10 and 11. These terms have units of [1/time] and are the inverse of the response or "replacement" times for a given flux (τ_m or τ_n; e.g., Berner and Berner, 1996). These values reflect the time scale over which a given flux can influence the reservoir under consideration. At steady state ($dN/dt = d\delta/dt = 0$) and the input and output fluxes balance; the time scale associated with this condition is referred to as the **residence time** of the species (or isotope ratio) being modeled (e.g., $\delta^{44}Ca$).

Box models can be solved by assuming steady state or in a time-dependent manner. The former is common and aids development of an intuitive feel for the behavior of large or complex systems. Where simplifications such as steady state are prohibited, the differential equations are often solved numerically, as analytical solutions are rarely possible (examples of numerical approaches can be found in Richter and DePaolo, 1987; 1988; Boudreau, 1997; etc). The behavior of the mass fluxes is quite flexible: they can be set to constant values or they can vary, for example as functions of the reservoir mass or as a function of time. An example of the application of a box model approach to evaporite formation in a semi-open basin, in which the output flux of Ca in gypsum is a function of saturation state, is provided in Harouaka et al. (2014).

The primary advantage of box models is that they are extremely flexible; in theory, they can be applied to systems at any spatial scale. While there is no real restriction on the number of reservoirs, the more that are modeled, the greater the number of free parameters (and thus constraints) needed. Box models can incorporate any mass flux of interest, including rudimentary transport and reaction (e.g., Fantle and Higgins, 2014), and can be built to include chemistry, such as the use of simple saturation state expressions to parametrize mineral precipitation fluxes (e.g., Harouaka et al., 2014). Such utility can be used to identify the processes occurring in a system, given the proper data constraints. A recent example of this is given by Chanda et al. (2019), who explained the extent to, and manner in, which foraminiferal tests reacted under experimental conditions. The box model in this case was constrained by multiple datasets (^{45}Ca radiotracer, Mg, Sr, and Ca), as well as expectations for foraminiferal Mg/Ca as a function of temperature (e.g., Anand et al., 2003), which allowed the authors to deduce that dissolution of Mg-rich carbonate and recrystallization of low-Mg calcite occurred over the ~90 day experimental time scale. The multi-box model was also used to constrain rate, a calculation that can be considerably impacted by the choice of model (Gorski and Fantle, 2017; Harouaka et al., 2019).

A key disadvantage of box models is that as model complexity increases with the number of boxes and/or fluxes, the speed, ease of use and intuitive nature quickly degrade. For problems that must resolve (i) transport at finer spatial scales or (ii) processes that occur within a reservoir (e.g., solute diffusion, water mass mixing, remineralization of organic matter in deep waters), the user will move towards reactive transport or Earth System model (e.g., Ridgwell et al., 2007) frameworks. In box models, critical factors such as speciation, pH, diffusion, and mineral reaction are difficult to consider and are typically omitted, or overly simplified. There is, in situations where these factors exert a critical influence, a need for more process-based model frameworks.

3. Reactive Transport Models

This classification is distinguished from the prior examples in that the spatial domain over which mass transfer and transformation occurs is explicitly represented by partial differential equations that describe changes in mass or concentration through space and time:

$$\frac{\partial \phi C_i}{\partial t} = \nabla \cdot (\phi D \nabla C_i) - \nabla \cdot (\boldsymbol{q} C_i) - \sum_{r=1}^{N_r} \nu_{ir} R_r - \sum_{m=1}^{N_m} \nu_{im} R_m \qquad [12]$$

where the term on the left-hand side describes the change in concentration of a compound, element or isotope (C_i) multiplied by the porosity (ϕ). The terms on the right-hand side include transport due to dispersion and diffusion (D), transport due to advective flow ($\boldsymbol{q}$ tensor) and a set of mass source and sink terms that represent chemical reactions. These are divided into two classes, aqueous phase (r) and mineral reactions (m), which are the sum of the product of the stoichiometric coefficients for the species (i) and the associated reaction rate (R) (e.g. Steefel et al. 2015 and many others). Clearly there is a lot of information contained within this framework, yet the version provided above is already relatively simplified. For example, the inclusion of reactions involving gas phases is omitted, which also implies that the open pore space (ϕ) is fully fluid saturated. If not, a saturation term would appear alongside ϕ in the accumulation and dispersion terms. Furthermore, the function is essentially written for a fluid solute, yet a comparable form could be generated for the corresponding solid phases, where fluid flow rate might be replaced with an erosion or burial term and dispersion might be used to represent bioturbation or some other form of mechanical mixing. The feedback between these co-evolving phases is then tracked through changes in ϕ which occur as a result of R_m.

Though potentially more complex, the basic structure of this framework is not that different from the box models presented above. The key distinction is that spatial derivatives (∇) now appear, and the potential inclusion of a wide range of chemical transformations is more feasible. The partial differential equation(s) for each species of interest are solved for at any location in the model domain. Again, in some cases, the system of equations is simplified by the assumption of steady state, and the time derivative set to zero (e.g., Jacobson and Holmden, 2008). Where the steady state assumption is reasonable, only boundary conditions are necessary, for example the composition of seawater at the sediment-water interface. Where transient effects are unavoidable, the model must be run forward in time from some initial condition, for example the moment CO_2 is injected into a geologic reservoir. This process requires the choice of a 'timestep' over which the calculation of transport and reactivity will be made. Ideally this timestep would be large in order to allow the simulation to complete quickly, but not so big that instabilities or poor approximations to the real solution are incurred.

A key feature of the explicit spatial derivatives is that each location (or node) across the domain is then a representative elementary volume (REV) with associated parameters, and these REVs are connected to one another and summed up to represent either the entire volume of a reservoir or a profile across that reservoir. Typically, such profiles are constructed along a principle direction of transport (e.g., vertical distance from the sediment water interface). The model then simulates explicit mass transfer through space (and time), for example solute advection along a fluid flow path or diffusion along a concentration gradient. These transport processes are parameterized using measured values such as flow velocity and diffusion coefficients and are simulated along with chemical reaction(s).

A principle inference of this modeling framework is the balance between relative rates of mass transport and reaction(s), essentially building off of the characteristic timescales described by the box modeling structure above. These relative rates are often cast in terms of a dimensionless parameter referred to as the Damkhöler number (Da). High Da values describe systems in which the timescale of transport is much faster than the timescale of reactivity, such that the effects of chemical reaction are only discernable over long distances (likely influencing how a given system is sampled). In contrast, low Da values suggest chemical controls over small distances, and thus cases in which a reactive front may be missed over coarse observational length scales.

Thus, the ability to account for transport in a fundamental manner not only informs how we observe systems of interest, but also allows for constraints to be placed on the rates of chemical transformations that occur in such systems. Below, we address the use of reactive transport models in the field of Ca isotope geochemistry, distinguishing between single- and multi-component models that have been used in the past and developments that offer utility in the future.

3.1 Single-component models

Single-component reactive transport models are highly useful simplifications of Eqn. 12 that can be used to simulate transport (diffusion and/or advection), physical processes (e.g., burial and compaction), simple speciation, and chemical reaction. While they can simulate the evolution of more than one element and its isotopes (e.g., Fantle et al., 2010), their representation of reaction pathways and in particular the complete stoichiometry of all relevant species is simplified (or even omitted) in comparison to the multi-component models described next. In some cases, such simplifications are justified and sufficient to address the questions at hand. For example, Fantle and DePaolo (2007), Turchyn and DePaolo (2011), and Fantle (2015) simulated carbonate recrystallization and its impact on Ca, Mg, and Sr elemental and isotopic ratios without the need to include pH, associated shifts in dissolved organic carbon content or speciation, or contemporaneous chemical reactions involving Mg or Sr.

In this approach, the elemental and/or isotopic evolution of a given system, such as a marine sediment, is described by a differential equation of the form (see Fantle et al., 2010 for a more detailed summary)

$$\frac{\partial C_{i,f}}{\partial t} = D\frac{\partial^2 C_{i,f}}{\partial x^2} - v\frac{\partial C_{i,f}}{\partial x} + \frac{\rho_s(1-\phi)}{\rho_f \phi} \cdot R\left(C_{i,s} - K_i C_{i,f}\right) \qquad [13]$$

where C_i is the concentration of the element i in the fluid (f) or solid (s), D is the elemental diffusion coefficient (L^2/time), v is the advection velocity (L/time), ρ is the density of either the solid or fluid, ϕ is the porosity, R is the recrystallization rate in g/g/time, and K_i is the elemental partition coefficient ($=C_{i,s}/C_{i,f}$). This particular example would be appropriate to describe the evolution of the pore fluid for the case of a recrystallizing mono-mineralic solid.

In the Ca isotope community, for example, such single-component reactive transport models have been used to interpret the Ca isotopic compositions of pore fluids as reflective of carbonate recrystallization rates (Fantle and DePaolo, 2007; Fantle et al., 2010; Turchyn and DePaolo, 2011; Fantle, 2015), following the earlier work of Richter and DePaolo (1987;1988) and Richter and Liang (1993) on Sr concentrations and Sr isotopes ($^{87}Sr/^{86}Sr$) in their seminal studies of deep-sea marine carbonates. Key to the ability to constrain this rate of mineral alteration is a reasonable representation of transport, which is difficult to implement in box models. With transport constrained, and assuming that there is one dominant process that controls pore fluid Ca isotopic composition (i.e., carbonate recrystallization) and a geochemical gradient to interrogate, the rate of recrystallization can be quantified.

For example, the use of a single-component reactive transport model was integral to interpreting observations made by Fantle and DePaolo (2007) in their study of Ca isotopes in pore fluids and nannofossil ooze. The primary observation was that pore fluid $\delta^{44}Ca$ decreased sharply with depth from seawater-like values to carbonate-like values, whereas Ca concentrations were largely invariant. The use of a single-component reactive transport model was vital to showing that net dissolution, which was widely hypothesized at the time, could not explain the $\delta^{44}Ca$ distribution, as well as Sr elemental and isotopic data. Instead, recrystallization was required. The model was also crucial to discerning that the recrystallization rates constrained by Sr (Fantle and DePaolo, 2006) did not explain the shallowest δ^{44}Ca datum, leading to improved resolution of carbonate recrystallization rates in young carbonate sediments (to which Sr is less sensitive).

The observations made by Fantle and DePaolo (2007) hinged on the use of a reactive transport model framework to elucidate the utility of Ca isotopes, ultimately extending and cementing interpretations. At the time of the study, calcite precipitation experiments suggested that the calcium isotopic fractionation factor at equilibrium was as low as -1.5‰ (Lemarchand et al., 2004), a value similar to the global fractionation factor between biogenic carbonates and seawater (e.g., De La Rocha and DePaolo, 2000; DePaolo, 2004; Gussone et al., 2006; Gussone et al., 2007; Langer et al., 2007; see Fig. 7 of Fantle and Tipper, 2014 for summary). The similarity between the equilibrium and observed fractionation factor was significant, as it suggested at the time that Ca isotopes might not be a sensitive indicator of calcite recrystallization. However, the suggestion of an equilibrium fractionation factor much different than that associated with the formation of biogenic carbonates meant the existence of an isotopic gradient in marine pore fluids. This gradient suggested Ca isotopes as a tool for constraining carbonate recrystallization rates in relatively young sediments (Fantle and DePaolo, 2007; Fantle et al., 2010; Fantle, 2015). The hypothesis of a small fractionation factor close to chemical equilibrium was subsequently confirmed by the experimental work of Tang et al. (2008; 2012).

3.2 Multi-component models

Modern, widely-available reactive transport software packages, such as PHREEQC, CrunchFlow, TOUGHREACT, MIN3P, etc. are generally ‘multi-component’, meaning that they consider the transport and transformation of multiple chemically coupled elements or compounds within or between phases. Such models account for mass and charge balance across a user-defined chemical system, often considering a mixture of both kinetic and equilibrium reactions, such that all species involved in these transformations must be accounted for. For instance, the precipitation of a carbonate mineral from solution removes not only Ca^{2+} from the fluid, but also CO_3^{2-}, which results in an attendant shift in the distribution of aqueous carbonate species subject to their equilibrium relationships. This redistribution in turn alters the activity of protons (H^+), and thus the pH, in the system, which impacts the solubility of the carbonate mineral. Such feedbacks offer a powerful means of predicting controls on solubility and thus the locations in a spatial domain where a given mineral is stable or a given reaction may favorably proceed.

The adoption of a complete accounting of mass for all relevant elements and compounds of each phase participating in a given reactive transport system inherently creates a complex mathematical problem that requires numerical methods to solve. The basic formulation involves both the transport of mass and the transformation between compounds and phases in each timestep. This numerical calculation is accomplished either sequentially (e.g. operator splitting approaches) or collectively (e.g. global implicit approach) and there are benefits and drawbacks to each, which influence the stability and speed of the numerical scheme. The interdependence of these partial derivatives with respect to one another is one common source of convergence errors in solutions of these systems. For example, the rate of change of one variable may be orders of magnitude different than another and thus misinform the chosen timestep or spatial scale over which a solution is attempted. Though beyond the scope of the present paper, many resources exist which describe these numerical methods in the context of Earth Science applications (e.g. Steefel et al. 2015; Druhan and Tournassat, 2019).

A significant utility of such a multi-component framework is that it imposes rigorous stoichiometric constraints on the reactive transformations that are being simulated. Thus, one must impact both the calcium and inorganic carbon budgets in a model system when simulating carbonate mineral precipitation or dissolution. The formation of new carbonate mineral does not simply remove mass from solution, but adds mass to the solid, so that all phases are accounted for explicitly. Often simpler single-component frameworks will instead rely on assumptions such as a fixed mass and isotope ratio of the solid phase, so that this component of the system is no longer solved for or tracked directly. While this sort of simplification can be appropriate and greatly simplifies the modeling process, the complete mass balance approach offers a means of testing where such assumptions fail.

Continuing with the example of diagenetic alterations to marine sediments, it is often reasonable to assume that the extremely small mass of calcium in the pore fluid relative to the solid phase will impart negligible influence on the isotope ratio of the latter. Using a multi-component reactive transport simulation incorporating the isotopes of calcium, such a system is simulated using parameter values reported by Huber et al. (2017) (Fig. 2). Importantly, the simulation includes contemporaneous burial of both the solids and pore fluids at equivalent rates of 150 m/Ma. The overall saturation state of calcite remains close to equilibrium throughout the entire simulation, but the calcium isotope ratios of the pore fluid and solid phase are clearly distinct at the sediment-water interface. As the fluid and solid phase are slowly buried and thus move downward, the large difference in mass between the calcium in the pore fluid and the calcium in the carbonate causes the former to shift over to the solid phase value through recrystallization. At this burial rate, the system reaches a steady state, where the fluid isotope ratio reaches an equivalence to the solid phase by approximately 150 m below the sediment-water interface (i.e. roughly 1 Ma). Under such conditions, the solid phase isotope ratio is invariant, and a simpler model leveraging such assumptions would be valid (Huber et al., 2017). However, using the complete mass-balance accounting of the multi-component numerical model, we can explore the conditions under which this assumption would no longer be appropriate. For example, setting the burial rate to a negligibly low value and rerunning the simulation, we find that a steady state is no longer achievable. Under these conditions, the solid phase is not resupplied at the top of the domain, and thus there is no source of replenishment for the solid phase isotope ratio. In contrast, the fluid phase solutes are still in communication with the upper boundary condition seawater interface through diffusion. As a result, the fluid phase isotope ratio profile is sustained as a balance between diffusive solute flux and recrystallization with the solid phase, whereas the solid isotope ratio is slowly becoming replaced. After 20 Ma, we begin to see this replacement showing up in the solid phase isotope ratio, despite the significant difference in mass between the phases. Ultimately, were such a model run out to sufficient timescales, the solid isotope ratio would be completely replaced with the seawater $\delta^{44}Ca$ value.

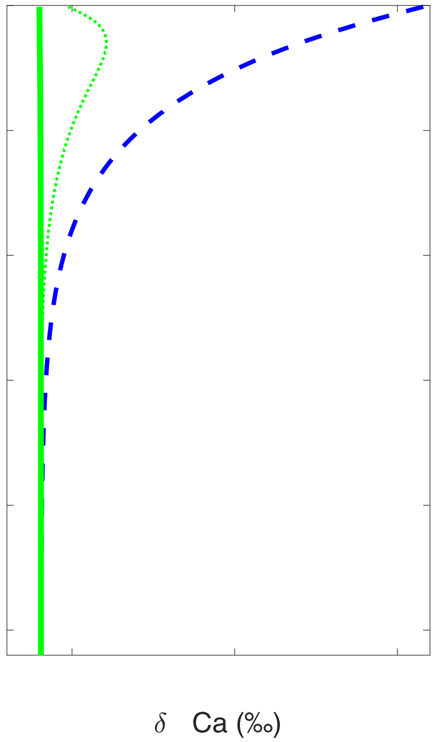

Figure 2: CrunchTope reactive transport simulation of contemporaneous pore fluid (dashed blue line) and carbonate (solid green line) δ^{44}Ca as a function of depth from the seawater – sediment interface run to steady state for a burial rate of 150 m/Ma. All relevant parameter values including reaction rate are reported in Huber et al. (2017). The same simulation is repeated without burial and run to a duration of 20 Ma, over which time the resulting carbonate isotope ratio begins to shift towards the fluid value (dashed green line). Implications for the conditions under which alteration of the solid is expected vs. not are discussed extensively in Huber et al. (2017).

The results of this exercise highlight the utility of a complete mass balance framework to test the sensitivity of simpler model predictions with respect to key assumptions. In the present example, the assumption of a solid phase whose isotopic composition is invariant with respect to depth or time is valid only under timescales and burial rates that are sufficient to avoid extensive replacement by the fluid (Huber et al. 2017). From another perspective, the ability to run a model forward in time in order to either achieve steady state or suggest that the system is not capable of such a balance affords a high degree of generalized utility. In terrestrial groundwater systems, for example, the formation and dissolution of carbonate minerals as a result of changes in solution chemistry are frequent and often hold environmental and engineering implications.

This leads to a second key advantage of a multi-component reactive transport framework, affording the capacity to combine multiple reactive pathways, including mixtures of equilibrium and kinetic effects, in transient or rapidly evolving systems. For example, the remediation of heavy metals and actinides from contaminated aquifers commonly leverages the capacity of microbial populations to catalyze redox transformations (e.g. Long et al. 2015). The process involves supplying excess labile organic carbon sources to these populations in order to enhance their activity, which inherently results in high rates of oxidation and thus increased alkalinity. This elevated carbonate concentration in turn frequently leads to the precipitation of carbonate minerals, which can adversely impact the conductivity of injection well screens and surrounding flow fields. Such scaling effects are broadly relevant both in contaminant remediation and enhanced oil recovery. The utility of calcium isotopes to constrain and quantify such mineral formation pathways has only recently begun to be explored but holds great potential (if they can be appropriately simulated) in such dynamic environments. The key challenge is to simulate the calcium isotope composition associated with rapid deposition and dissolution which inherently involves both the equilibrium partitioning between phases and the kinetic signatures of mineral growth and dissolution.

As a case study, we consider the calcium isotope composition of carbonates formed in a well bore during biostimulation of a uranium contaminated aquifer, which indicated a clear signature of fractionation in the fluid phase as the well became clogged by carbonate formation (Druhan et al., 2013; Fig. 3A). This example affords an opportunity to revisit the sequence of modeling options reviewed thus far in our discussion. How would we begin to quantify this dataset? Were the environmental conditions which lead to these data unknown, we might begin our analysis by considering whether the data could be explained by a sequential mixture of two end-members, one with high calcium and low $\delta^{44}Ca$, the other with low calcium and high $\delta^{44}Ca$. For the present measurements, using the first and last data points to represent our endmembers results in a mixture where the $\delta^{44}Ca$ is consistently too low for the corresponding change in calcium concentration to reproduce the observed trend. Furthermore, we know that the conditions of the system were such that the change in calcium concentration through time occurred due to mineral precipitation, rather than the introduction of some low concentration fluid. Turning to a Rayleigh model approach, the decrease in calcium concentration through time is easily recast as the fraction of reaction progress. Using several different fractionation factors, we see that the data are still not reproduced (Fig. 3B) and importantly the fractionation factor appears to decrease through time. This observation also limits application of box model approaches, as the partitioning of the isotopes between the fluid and solid phases appears to evolve through the course of the reaction in a way that is not immediately obvious.

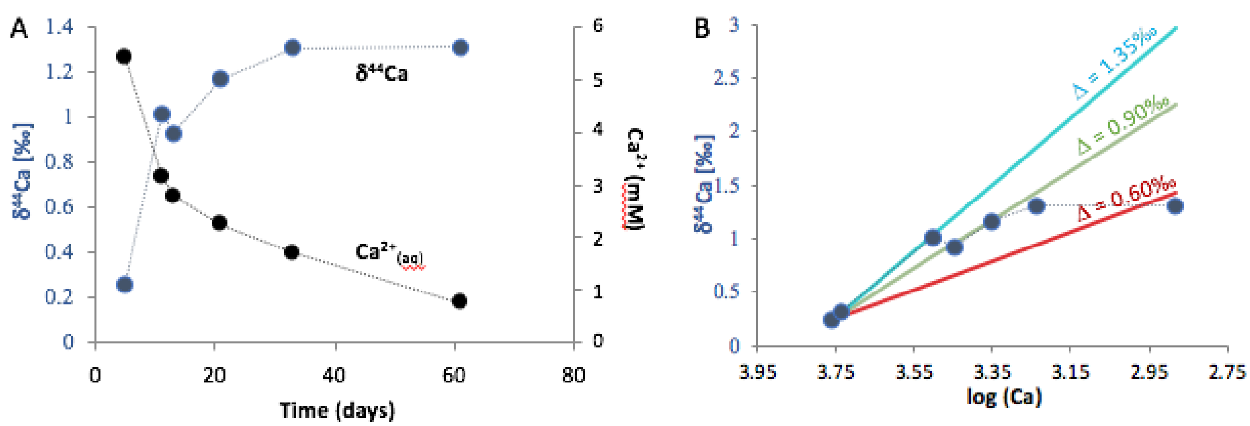

Figure 3: (A) Ca concentration and isotope ratio in the fluid phase of a clogged well bore through time during carbonate precipitation. (B) Associated Rayleigh models fail to reproduce the data. Adapted from Druhan et al. (2013).

This ultimately brings us a to a multi-component reactive transport framework, in which an initially high organic carbon content is oxidized to produce alkalinity through time, altering the saturation state of the system with respect to calcite, and driving the formation of new mineral. As the reaction proceeds, the decrease in calcium concentration allows the system to approach equilibrium, such that an initial period of kinetically dominated enrichment of the fluid $\delta^{44}Ca$ value associated with formation of the solid is followed by a subsequent decrease in the fractionation factor towards values closer to 1.0 (Druhan et al., 2013). This shift from large fractionation factors at high oversaturation, to smaller fractionation near equilibrium is consistent with much simpler systems designed to isolate isotopic partitioning under controlled saturation states (e.g. Tang et al. 2008) but the process is complicated by the 'free drift' conditions of the transient field-scale setting.

The two examples of marine diagenesis (Fig. 2) and well bore scaling (Fig. 3) shown above illustrate distinct aspects of the reactive transport approach. In the marine sediment model, the role of transport (e.g. burial) played a critical factor in the distribution of isotopes between phases. In the clogged well bore, the need for a transient multi-component reaction network was apparent in order to resolve the isotope ratios through time. Taken together, the capacity to handle such complex chemical reactivity in systems subject to a variety of transport pathways illustrates the malleable architecture and broad applicability of such reactive transport frameworks.

4. Molecular and Process-Based Models

As shown in the previous sections, the processes that dictate the Ca isotope composition of solids and fluids in natural systems are complex. Yet all of the macroscopic quantitative modeling approaches described above are founded on a common assumption that a subset of critical controlling processes (referred to as "first-order processes" here) can be isolated that play a disproportionate role in determining Ca isotope systematics. As isotope geochemists, a key challenge we face is to identify these first-order processes and then to develop quantitative expressions relating Ca isotope composition to the geochemical variables controlling them. Put another way, we aim to describe each process that leads to Ca isotope separation with a mathematical function or set of functions that takes geochemical variables (pH, temperature, pressure, and composition) as inputs. Despite the major emphasis on Big Data and machine learning approaches in the sciences today, our collective expertise is still required to complete the task of model development, because these artificial intelligence methods rely on humans to identify a dataset encompassing the key variables controlling the model outcome (i.e. "attributes").

In the following section, we discuss models that provide an increasingly explicit representation of the physiochemical mechanisms that lead to Ca isotopic fractionation in real systems, and address why they are needed to make quantitative predictions at larger scales. The critical trade-off that is made when developing highly mechanistic models is that the length- and/or time-scales explicitly represented by the models are decreased. Thus, we also provide several examples of how these process-based models can be "up-scaled" or integrated into larger length-scale and longer time-scale macroscopic models (Fig. 1). The need to develop predictive, mechanistic, up-scaled models for complex biogeochemical systems is perhaps one of the most difficult challenges we face as geochemists today.

The study of Ca isotopic fractionation during crystal growth has been a major emphasis of the Ca isotope community since the discovery that biomineralization leads to significant and measurable depletion of the light isotope in the solid phase compared to the calcifying fluid (cf. Skulan et al., 1997). The uptake of isotopically light Ca in the solid phase during carbonate mineral growth is thought to play a key role in regulating the Ca isotope composition of the ocean over geologic timescales (Skulan et al., 1997; Zhu & MacDougall, 1998). Subsequent kinetic studies of synthetic crystal growth in the laboratory revealed that Ca isotopic fractionation during crystal growth is kinetically controlled (Lemarchand et al., 2004; Tang et al. 2008, 2012). These laboratory studies were largely conducted in fluids undersaturated with respect to amorphous calcium carbonate, such that the process of crystal growth is likely classical, meaning growth is driven by the attachment of monomer ions to active growth sites on the crystal surface (cf. DeYoreo et al, 2015). Together, these studies motivated the development of process-based models (e.g. DePaolo, 2011) for kinetic Ca isotopic fractionation during classical crystal growth.

4.1 Crystal growth models

Process-based models for classical crystal growth were first developed in the mid-20th century with the seminal work of Burton, Cabrera and Frank (BCF; Burton et al., 1951). The predicted mineral surface structures and rate relationships were later confirmed with the advent of nanoscale imaging by Atomic Force Microscopy (AFM; De Yoreo et al., 1994; Onuma et al., 1995; Teng et al., 1998, 2000). Consistent with the predictions laid out in the seminal BCF paper, it has been observed that ionic mineral growth at low supersaturations occurs by a classical mechanism (Fig. 4), where ionic monomers attach to and detach from active growth sites (kink sites) on the mineral surface (cf. Zhang & Nancollas, 1990, 1998). At relatively low supersaturations, growth unit attachment and detachment occur primarily at kink sites along monomolecular steps on the surface. Under these conditions, surface normal growth occurs when steps propagate outward parallel to the surface, and new steps are generated either at spiral dislocations or by 2D nucleation.

Figure 4. Schematic of classical growth features typical of low supersaturations with respect to the growing crystal. Image is modified from Burton et al. (1951).

Calcite was the subject of some of the first studies linking nano-scale observations of surface structures to classical growth theories (Teng et al., 1998, 2000). Mechanistic "ion-by-ion" models for calcite growth have been developed that quantify the net (and gross) fluxes of ions to and from kink sites on the growing crystal surface (Wolthers et al., 2012a,b; Wolthers et al., 2013; Nielsen et al., 2012, 2013). Although relatively complicated in appearance, these models integrate two very simple descriptions for ion fluxes at kink sites: a first-order rate law for ion attachment and a zeroth order rate law for ion detachment. Because the overall growth rate depends on the surface area normalized density of kink sites, ion-by-ion models must quantify the surface step and kink site density as a function of solution composition, making them somewhat more complicated to implement than typical empirical rate laws.

The advantage of adopting a more complicated process-based modelling approach is that such models can be applicable to a wider range of solution conditions than simpler models based on similar principles. From the stable isotope geochemistry perspective, process-based models allow the development of separate rate expressions for each individual isotopologue. Moreover, because calcium ions can only attach to carbonate kink sites and vice versa, the influence of solution stoichiometry and surface speciation on both growth rate (Wolthers et al., 2012a, 2013) and stable isotopic fractionation can be studied (Nielsen et al., 2012). The ion-by-ion approach can thus be used to model kinetic stable isotopic fractionation both as a function of aqueous supersaturation and of solution stoichiometry or pH (Watkins et al., 2013).

Several key assumptions are made in the implementation of ion-by-ion growth models. First and foremost, the models assume that the calcite being studied has grown by a kink-limited classical growth process. Fortunately, this assumption can be validated in synthetic systems using AFM or other nanoscale imaging techniques. However, for biogenic material, calcification by non-classical mechanisms is commonplace (Politi et al., 2004; DeYoreo et al., 2015), and Ca isotopic fractionation factors associated with diverse biomineralization pathways are not well understood. Second, and less easily proven, these models assume that a first order rate law for ion attachment to a kink and zero order rate law for detachment from a kink give a valid and reasonable representation of kink dynamics. Currently no experimental techniques exist that can probe the dynamics of individual ion attachment reactions, so the tools of computational chemistry must be used for future validation of rate laws for ion attachment and detachment dynamics at mineral surfaces (cf. Stack, 2012). Finally, current versions of the ion-by-ion model assume that rate coefficients for ion attachment (and detachment) reactions at kink sites for each ion mass are invariant with surface and solution conditions. There is, however, evidence that these kinetic parameters are conditional and dependent on factors such as aqueous electrolyte concentration and composition (Tang et al., 2012; Nielsen et al., 2012; Lammers et al*., this volume*). These findings again motivate an investigation of shorter length- and time-scale processes to better predict large-scale Ca isotope systematics in complex geochemical systems.

4.2 Molecular modeling

As discussed in the previous sections, the development of general, predictive models for Ca isotope systematics in natural environments will require that the basic physiochemical mechanisms driving isotope separation are known. Computational chemistry techniques including *ab initio* quantum mechanical calculations, classical molecular mechanics simulations (e.g., molecular dynamics), and coarse-grained models are gaining traction as quantitative modeling tools that facilitate the exploration of process mechanisms. Simulations can provide numerous essential insights to isotope geochemists. First, molecular modeling of the vibrational frequencies of chemical species can be used to quantify equilibrium fractionation factors between chemical environments (for excellent reviews see Schauble et al., 2004 and Blanchard et al., 2017). Second, molecular dynamics simulations are fully deterministic, such that the time-dependent trajectory of each individual atom or isotopologue is known. This allows us to identify the molecular level details of reaction pathways involving calcium as well as the exact mechanisms responsible for the mass-dependence of studied processes. Finally, these techniques can be used to simulate both real and fictitious isotope masses, enabling the systematic study of mass-dependent reaction rates and free energies. These molecular modeling approaches provide a quantitative toolkit that can be used to probe the physiochemical processes driving Ca isotope separation.

A hierarchy of simulation techniques exists that can access different length- and time-scales (Fig. 1), and each technique is best suited to a distinct subset of applications (Frenkel & Smit, 2001). The lowest level (least abstract/most explicit) technique is based on quantum mechanical calculations that solve for the electronic structures of chemical species. These *ab initio* (e.g. from physical "first principles") simulations are the most chemically detailed, and thus the most computationally expensive. They are most appropriate to use when the chemical process being probed is controlled by bond formation and breaking involving a transfer of electrons or shared electron density. For calcium, which participates in bonds that are dominantly ionic in nature, molecular mechanics simulations are usually favored. This technique uses simplified force-field models that are usually derived from *ab initio* calculations to solve the Newton-Euler equations of motion for many body systems. These include molecular dynamics (MD) simulations that are extremely useful for investigating the structure and dynamics of chemical species both in bulk solution and at interfaces, as MD systems can include multiple phases such as bulk liquid water and a solid. Typically, they do not allow bond breaking and formation to occur, but hybrid *ab initio* molecular dynamics (AIMD) and reactive force-field techniques are also available. Coarse-grained (CG) models lump together multiple atoms into a single center of mass and can be used to simulate larger length-scales and longer time-scales. As with MD, CG models are typically parameterized based on the results of lower-level molecular mechanics calculations. Fractionation of Ca isotopes can be due to thermodynamic and/or kinetic factors, and these molecular modeling tools are increasingly being used to study the physical basis of Ca isotope separation.

4.3 Simulation studies of aqueous calcium

Dissolved Ca^{2+} is ubiquitous in nature, and quantitative modeling of Ca isotope separation requires a rigorous understanding of the (mass-dependent) properties of Ca dissolved in liquid water. The equilibrium and kinetic behavior of dissolved calcium influences its fate both in the environment and within living organisms (cf. Moynier & Fuji, 2017), through, for example differential transport or uptake of isotopically distinct aqueous species. Quantum mechanical calculations show that the Ca^{2+}(aq) ion forms a relatively stable aquo-complex, where the Ca ion is strongly coordinated by on average six coordination water molecules, but with weak discrimination among the 6-, 7- and 8- fold coordinated states (Megyes et al., 2004; Ikeda et al., 2007). Because the strength of the coordination complex influences the vibrational zero-point energy of the complex, equilibrium isotopic fractionation is expected between these coexisting coordination states. Rustad et al. (2010) and Colla et al. (2013) report a significant (2.6‰ and 5.5‰ respectively) enrichment of ^{44}Ca relative to ^{40}Ca in the six-fold coordination state compared to seven- and eight-fold coordinated Ca. A later study considering an extended coordination environment gives fractionation factors approximately half as large (Moynier & Fuji, 2017), highlighting the fact that simulation study results can only be considered quantitative insofar as the setup and parameterization (or choice of basis sets) is accurate.

In real solutions, calcium exists in the presence of ligands other than water that can also form stable complex species. Quantum mechanical calculations have been used to quantify mass discrimination among a wide variety of aqueous Ca complexes at isotopic equilibrium. The trend of heavy Ca enrichment in lower coordination number complexes appears to hold for ligands other than water, including phosphate, citrate and oxalate, where the sevenfold complexes are consistently lighter by 0.7-0.9‰ than the sixfold (Moynier & Fuji, 2017). In general, equilibrium Ca isotopic fractionation among dissolved aqueous complexes agrees with long-standing isotope theory, wherein the heavier isotope is concentrated in the species with the strongest bonding environment.

Molecular modeling has also been used to probe the stable isotope mass dependence of Ca dynamics in solution, including the diffusion coefficient and water exchange rate (Bourg et al., 2010; Hofmann et al., 2012). The latter factor is important in understanding kinetic stable isotopic fractionation during the growth of mineral phases by dissociative desolvation rate-limited mechanism (cf. Casey & Rustad, 2007; Lammers et al., this volume). Molecular dynamics simulations of Ca^{2+} in bulk liquid water are typically performed over a wide range of Ca isotope masses to quantify the mass-dependence of Ca ion solvation dynamics. These studies take advantage of the ability to simulate fictitious isotope masses to emphasize Ca isotope separation during transport. Both ion diffusion coefficients (Bourg et al., 2010) and the rates of water molecule exchange in the first solvation shell of calcium (Hofmann et al., 2012) follow an inverse power law mass dependence, causing faster diffusion of and water exchange around isotopically light Ca. However, the observed magnitude of the mass dependence of the diffusion coefficient is much smaller than predictions from kinetic theory. Based on a careful analysis of the physiochemical factors regulating isotope separation, Bourg et al. (2010) determined that the mass-dependent diffusivity of aqueous alkali and alkaline earth elements is attenuated by hydrodynamic friction, particularly for ions like Ca^{2+} that form a strong solvation complex.

4.4 Simulation studies of calcium isotope separation between solid and aqueous phases

One of the main processes regulating the fractionation of Ca isotopes, both in marine settings and within organisms, is mineral growth. Some of the first molecular simulations of Ca isotopic fractionation applied the principles developed in the seminal Biegeleisen & Mayer (1947) and Urey (1947) papers to determine equilibrium isotopic fractionation factors between coexisting aquo-complexes and crystalline carbonate solids (Zhang et al., 1988; Rustad et al., 2010; Colla et al., 2013). Results of these thermodynamic calculations show that solid phases should be enriched in isotopically heavy Ca compared to aqueous solution at equilibrium. Rustad et al. (2010) calculated a $\Delta^{44/40}Ca_{s\text{-}aq}$ for calcite of +1.5‰ for six-fold coordinated Ca^{2+} (aq) and of +4.1 for the sevenfold aqueous coordination state. Excepting the hydrated Ca minerals that appear to rapidly attain isotopic equilibrium with aqueous solution (Colla et al., 2013), this conclusion conflicts with abundant natural and laboratory data showing preferential enrichment of light Ca in crystalline solids (Nägler, 2000; Gussone et al., 2005; Tang et al., 2008; Hippler et al., 2009; Harouaka et al., 2017 among many others).

Molecular modeling results have been used to rationalize the presence of isotopically light Ca in crystalline solids in various ways, and it is likely that a mixture of equilibrium surface and aqueous speciation factors and surface kinetic effects contribute to the bulk measured fractionation factors between solid and aqueous calcite in real systems. Bone apatite, for example, is isotopically light compared with blood calcium, and Moynier & Fuji (2017) attribute this to the fact that osteoblasts may scavenge free blood Ca^{2+}(aq), which is isotopically light compared to Ca complexed by ligands including phosphate, citrate, and oxalate. In the case of carbonate minerals, equilibrium aqueous speciation may counteract to some extent a kinetic isotope effect. Simulations show that water exchange around isotopically light Ca^{2+}(aq) is more rapid than for heavy calcium both in bulk aqueous solution (Hofmann et al., 2013) and for Ca adsorbed to kink sites at the calcite surface (Lammers et al., this volume). Because Ca^{2+} uptake at calcite is rate-limited by desolvation, this effect translates to solids depleted in ^{44}Ca relative to ^{40}Ca with increasing growth rate. The magnitude of the kinetic isotope effect due to desolvation determined by molecular simulation is much larger than measured kinetic fractionation factors, which may either be due to inaccuracies in the simulation approach or due to aqueous or surface speciation effects that attenuate the kinetic isotope effect. For example, Colla et al. (2013) propose that isotopically heavy six-fold coordinated Ca may make a disproportionately large contribution to mineral growth. It is clear that the presence of isotopically distinct aqueous complexes will influence measured bulk fractionation factors (Watkins et al., 2013), so understanding the contribution of aqueous complexes during both classical and non-classical (e.g. crystallization by particle attachment, CPA; DeYoreo et al., 2015) growth is a ripe area for future research.

Equilibrium adsorption reactions or enrichment of ions at surfaces relative to bulk aqueous solution have also been suggested as potential drivers of Ca isotopic fractionation in natural settings. One early experimental paper reports more than -1‰ Ca isotope fraction during incomplete Ca elution from a column resin, with the solid depleted in heavy Ca relative to the eluent (Russell & Pamanastassiou, 1978). While the mechanism of fractionation was not clearly established, the authors suggest that surface complexed-Ca on the resin is isotopically light at equilibrium with aqueous Ca. Although numerous simulation studies have investigated the surface complexation behavior of Ca on various mineral surfaces including smectite clay (Bourg et al., 2011) and calcite (Kerisit & Parker, 2004; Duckworth et al., 2004), molecular simulation studies of equilibrium Ca isotopic fractionation during adsorption and diffusion through nanopores appear to present additional opportunities for future work.

4.5 Application of computational chemistry techniques to natural systems

The intrinsic shortcoming of these techniques when interpreting natural samples is the extremely small length- and time-scales that are currently accessible compared to macroscopic systems. A leading challenge of modern geochemistry is thus one of up-scaling: How molecular level information can best be used to accurately predict the fate of macroscopic systems remains an open question. Currently, the process of interpreting macroscopic experimental observables using molecular level simulation tools is an iterative one. Experimental data, including spectroscopic data bearing molecular level information, can often be interpreted in multiple different ways with often diverging hypotheses. Computational chemistry techniques can then be employed to test the leading hypotheses. Additional experiments, in turn, are used to refine the parameterization of force field models or other model inputs that control the outcomes of the simulations themselves. In an ideal scenario, such deliberate coupling of experiments and complementary simulations allows us to develop accurate mechanistic models of processes that exert first-order controls over the transport and reactivity of chemical species in complex natural systems. In isolation, neither technique is sufficient to establish causality.

5. Acknowledgements

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