Geochemistry of the Earth's Surface meeting, GES-10

Modeling coupled chemical and isotopic equilibration rates

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Abstract

We present a model for coupled chemical and isotopic equilibration rates based on Transition State Theory (TST) type rate laws and apply it to Ca isotope kinetic fractionation in natural systems. The model, in contrast to the steady state model proposed by DePaolo (2011), explicitly considers isotopic equilibration in the absence of bulk chemical disequilibrium by making use of a solid-solution model for the precipitating (and potentially) dissolving mineral phase. The model is applied to the subsequent isotopic equilibration of the isotopically light bulk or surface layer on calcite formed as a result of kinetic Ca fractionation associated with precipitation. The model is then applied to Ca isotopic re-equilibration at marine Site 984 in the mid-Atlantic using the Ca isotope data of Turchyn and DePaolo (2011) based on a modification of the reactive transport model presented in Maher et al. (2006). The simulations with the new model CrunchTope demonstrate that it is impossible to match the observed Ca isotope profiles at Site 984 using the same rate constants as were used to describe calcite precipitation. To match the isotopic data requires re-equilibration rate constants that are about 4 orders of magnitude smaller than those for bulk precipitation using a linear TST rate law.

1. Introduction

Calcium carbonate in sedimentary marine settings constitutes the principal source of paleoceanographic information in the geological record. The isotopic record provides an important tool in the reconstruction of ocean chemistry and paleoclimate, with the isotopes of calcium being considered in a number of more recent analyses (De la Rocha and DePaolo, 2000; Fantle and DePaolo, 2005; Farkas et al., 2007; Fantle and DePaolo, 2007; Fantle et al., 2010; Turchyn and DePaolo, 2011). In deep marine sedimentary sequences below the zone of aerobic respiration, a series of microbially mediated reactions oxidizing buried organic carbon take place, with sulfate reduction and methanogenesis the most important pathways. These reactions result in the production of CO_2, which typically

drives secondary carbonate mineral (especially calcite) precipitation. The calcium required for calcite precipitation is present in the buried seawater, as well as derived from dissolution of primary phases like feldspar and clays (Maher et al., 2006). The precipitation of calcite is associated with the kinetic fractionation of Ca isotopes, reported as the ratio of ^{44}Ca/^{40}Ca in standard delta notation (δ^{44}Ca) using a bulk Earth calcium isotope standard (Simon and DePaolo, 2010), with enrichment of the precipitate in the lighter isotopologue, and enrichment of the residual fluid in the heavier (^{44}Ca) isotopologue (DePaolo, 2011; Druhan et al., 2013). Subsequent re-equilibration of the calcite drives the calcium isotopic composition of the fluid and solid surface back towards equivalent values, reversing the kinetic enrichment observed over shorter time scales (Fantle and DePaolo, 2007; Jacobsen and Holmden, 2008; Fantle et al., 2010; Turchyn and DePaolo, 2011; Druhan et al., 2013). As suggested by Fantle and DePaolo (2007), the equilibrium fractionation factor, $\alpha_{s-f} = 0.9987\pm0.0002$, that has been reported based on shorter duration laboratory experiments, may be an artifact of the slow isotopic re-equilibration rate of carbonate, and that the true equilibrium fraction is closer to 1.0000.

In this paper, we explore this topic further with the use of a newly developed multicomponent model that formally couples chemical and isotopic equilibration rates (Druhan et al., 2013). The kinetic model is most closely related to that presented recently by DePaolo (2011), but with the important additional capability that it considers transient isotopic equilibration as opposed to a strictly steady-state surface layer isotopic composition during mineral precipitation. In other words, a dynamic isotopic composition for the solid phase is considered in the new model. This is in addition to the ability to simulate kinetic fractionation during mineral precipitation. The model is based on a Transition State Theory (TST) formulation for reversible mineral dissolution and precipitation (Aagaard and Helgeson, 1982; Lasaga, 1984; DePaolo, 2011). The model describes the incorporation of the isotopologues in the mineral structure in terms of an ideal solid-solution model, with the rate of isotopic equilibration driven by the departure from equilibrium (Druhan et al., 2013). The initial premise is that the isotopologues present in the mineral structure function like other chemical components, affecting the departure from equilibrium (the thermodynamics) in a similar fashion. However, we evaluate the strict applicability of this assumption by comparing model results to observations from Site 984 in the Mid-Atlantic Ocean.

2. Reversible TST rate law for coupled chemical and isotopic equilibration

The rate law presented here is based on a Transition State Theory (TST) formulation that assumes microscopic reversibility of the dissolution and precipitation rates (Aagaard and Helgeson, 1982; Lasaga, 1984; DePaolo, 2011). The mathematical formulation for the rate law, which couples the isotopologue mineral end-members, presented below, followed by a brief description of the numerical implementation in the code CrunchTope.

2.1. Mathematical formulation

Following the presentation of DePaolo (2011) and Druhan et al. (2013), the net rate of reaction, R_{net}, is given by the difference between the dissolution and precipitation fluxes:

$$R_{net} = R_f - R_b \qquad (1)$$

where R_f is the forward rate (precipitation) and R_b is the backward rate (dissolution). At equilibrium $R_{net} = 0$, which requires that $R_f = R_b$. Based on the formulation of the backward and forward rates shown in Fig. 1, this implies that:

$$k_f a_{Ca^{2+}} a_{CO_3^{2-}} = k_b a_{CaCO_3(s)} \qquad (2)$$

or at equilibrium:

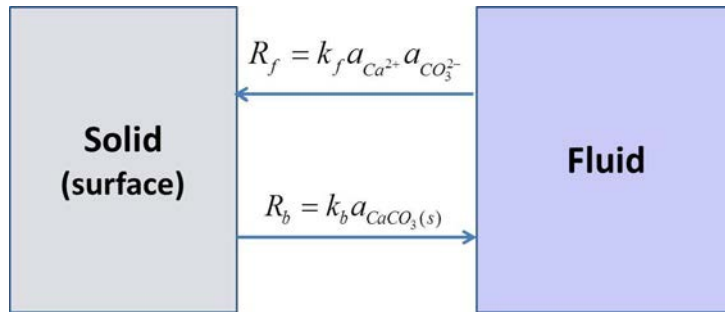$$\frac{k_b}{k_f} = \frac{a_{Ca^{2+}} a_{CO_3^{2-}}}{a_{CaCO_3(s)}} = K_{eq} \tag{3}$$

Fig. 1. Schematic representation of the reversible dissolution and precipitation fluxes for calcite (modified after DePaolo, 2011).

Eqn. 1 can be rewritten so as to eliminate the backward (dissolution) rate constant by making use of Eqn. 3:

$$R_{net} = a_{CaCO_3(s)} k_f K_{eq} \left[\frac{a_{Ca^{2+}} a_{CO_3^{2-}}}{a_{CaCO_3(s)}} \frac{1}{K_{eq}} - 1 \right] \tag{4}$$

Where the mineral is pure (only Ca), the activity of the solid phase equals unity, and may be neglected. However, in the case of a solid solution, particularly where the mineral composition is dynamic (either due to incorporation of isotopes or trace elements), the activity of the solid phase should be retained (in contrast to the treatment by DePaolo, 2011). The rates of the individual isotopologue end-members, $^{40}CaCO_3(s)$ and $^{44}CaCO_3(s)$, then should be written as:

$$^{40}R_{net} = a_{^{40}CaCO_3(s)} \, ^{40}k_f \, ^{40}K_{eq} \left[\frac{a_{^{40}Ca^{2+}} a_{CO_3^{2-}}}{a_{^{40}CaCO_3(s)}} \frac{1}{^{40}K_{eq}} - 1 \right]$$

$$^{44}R_{net} = a_{^{44}CaCO_3(s)} \, ^{44}k_f \, ^{44}K_{eq} \left[\frac{a_{^{44}Ca^{2+}} a_{CO_3^{2-}}}{a_{^{44}CaCO_3(s)}} \frac{1}{^{44}K_{eq}} - 1 \right] \tag{5}$$

Note that as discussed by Druhan et al (2013), who presented Eqn. 1-5, the formulation implies that the isotopic composition of the solid phase (which may change with time) can affect the thermodynamic driving force (the "affinity term") for the solid solution. In the case of an ideal solid solution, the activity of the solid phase is typically written as the mole fraction (e.g., for ^{44}Ca: $X_{44CaCO3}$)

$$a_{^{44}CaCO3} = X_{^{44}CaCO3} = \frac{n_{^{44}CaCO3}}{n_{^{40}CaCO3} + n_{^{44}CaCO3}} \tag{6}$$

where $n_{^{44}CaCO3}$ and $n_{^{40}CaCO3}$ are the moles of ^{44}Ca and ^{40}Ca in the calcite, respectively.

This derivation was utilized by Druhan et al. (2013) to simulate the isotopic partitioning of calcium isotopes during carbonate mineral precipitation driven by biogenic oxidation of acetate. The model accurately reproduced measured fluid δ^{44}Ca values that could not be reproduced by simple Rayleigh distillation. However, the dataset was insufficient to consider the full extend of the model capability to simulate isotopic re-equilibration. This capability is noted by first writing the net reaction for the heavy (^{44}Ca) mineral component using the terminology of DePaolo

(2011), in terms of the activities of the common isotopologue, ^{40}Ca, as:

$$^{44}R_{net} = \frac{^{44}N_s}{^{40}N_s} a_{^{40}CaCO_3(s)} \Gamma^f_{44/40} \, ^{40}k_f \alpha_{eq} \, ^{40}K_{eq} \left[\frac{^{40}N_s}{^{44}N_s} \frac{^{44}N_f}{^{40}N_f} \frac{a_{^{40}Ca^{2+}} a_{CO_3^{2-}}}{a_{^{40}CaCO_3(s)}} \frac{1}{\alpha_{eq} \, ^{40}K_{eq}} - 1 \right]$$

$$^{40}R_{net} = a_{^{40}CaCO_3(s)} \, ^{40}k_f \, ^{40}K_{eq} \left[\frac{a_{^{40}Ca^{2+}} a_{CO_3^{2-}}}{a_{^{40}CaCO_3(s)}} \frac{1}{^{40}K_{eq}} - 1 \right]$$

(7)

where $\alpha_{eq} = {^{44}K_{eq}} / {^{40}K_{eq}}$ is the equilibrium fractionation factor, $\Gamma^f_{44/40} = {^{44}k_f} / {^{40}k_f}$ is the kinetic fractionation factor, and N_f and N_s refer to the moles of the isotopologue in the fluid and solid phase, respectively. Note that the ion activity product inside the square brackets is here written in terms of the common isotopologue, ^{40}Ca, and this value is nearly (but not precisely) identical to the bulk calcite ion activity product, Q_{cc}, normally computed.

Several limiting cases can be derived from Eqn. 7. For far from equilibrium dissolution, the rate of dissolution of the rare isotopologue, ^{44}Ca, is given by:

$$^{44}R_{diss} \approx \Gamma^f_{44/40} \, ^{40}k_f \alpha_{eq} \, ^{40}K_{eq} \left[-\frac{^{44}N_s}{^{40}N_s} \right].$$

(8)

For highly supersaturated precipitation of calcite, the rate is given by:

$$^{44}R_{ppt} \approx \Gamma^f_{44/40} \, ^{40}k_f \alpha_{eq} \, ^{40}K_{eq} \left[\frac{^{44}N_f}{^{40}N_f} \frac{Q_{cc}}{\alpha_{eq} \, ^{40}K_{eq}} \right]$$

(9)

If kinetic fractionation results in a change in the ratios in the fluid and solid phases, even in the absence of equilibrium fractionation, then the saturation states of the two isotopologues will not remain the same over time in the surface layer of the precipitate. This is the principal distinction from the DePaolo (2011) model as implemented, since the isotopic composition of the solid phase is not retained in that steady-state treatment. To the extent that this isotopic disequilibrium can drive recrystallization and thus isotopic re-equilibration, there should be a natural tendency to return to equilibrium if recrystallization rates are sufficiently high (i.e., the kinetic fractionation associated with bulk precipitation will be reversed). In this model, for isotopic re-equilibration **not** to occur, the saturation states of the two isotopologue end-members should be the same:

$$\frac{a_{^{44}Ca^{2+}} a_{CO_3^{2-}}}{a_{^{44}CaCO_3(s)}} = \frac{a_{^{40}Ca^{2+}} a_{CO_3^{2-}}}{a_{^{40}CaCO_3(s)}}$$

(10)

This is again for the case even where there is no equilibrium fractionation—in the case where there is an equilibrium fractionation factor, the expression in Eqn. 10 is corrected according to the ratio of the equilibrium constants for the two end-members ($^{40}Keq/^{44}Keq$). Eqn. 7 states therefore that where the ratio of the isotopologues is not the same in the fluid and solid phase, isotopic equilibration should occur.

To represent the case where no back-reaction occurs (in which case the composition of the mineral in bulk or at its surface has no impact on the rate), one can write the rate in terms of the aqueous mole fractions and the bulk saturation state using Eqn. 5:

$$^{44}R_{net} = \frac{^{44}N_f}{^{40}N_f} \Gamma^f_{44/40} \, ^{40}k_f \alpha_{eq} \, ^{40}K_{eq} \left[\left(\frac{Q_{cc}}{\alpha_{eq} \, ^{40}K_{eq}} \right) - 1 \right].$$

(11)

This formulation (which is used in the analysis of the Site 984 Ca isotope profiles below) provides similar results to what is obtained with the DePaolo (2011) model utilizing the assumption of a steady state mineral surface isotopic composition (compare to Eqn. 7 above).

2.2. Numerical implementation

The solid solution model for isotopic exchange and kinetic fractionation is implemented in the general purpose reactive transport simulator CrunchTope, a modification of the code CrunchFlow (Steefel et al., 2014). The solid phase isotopic end members (for example, $^{40}CaCO_3$ and $^{44}CaCO_3$) are treated in the code as separate minerals, except insofar as they are coupled through the mineral activity (mole fraction) term (Eqn. 6). At runtime, the user of the code may choose either a mole fraction based on the bulk or surface mineral composition using Eqn. 5. Alternatively, back-reaction may be suppressed altogether by using the aqueous rather than mineral volume fractions (Eqn. 11). The contrasting behavior of these two formulations is shown in the first examples involving calcite precipitation in a batch system below. Or the options can be combined as essentially parallel rate laws, one with no back-reaction, a second for re-equilibration with either the bulk or surface mineral composition. This approach makes it possible to consider different reaction rates for bulk precipitation (and associated kinetic fractionation, as in DePaolo, 2011) and isotopic re-equilibration, as we do in simulating the ODP Site 984 data of Turchyn and DePaolo (2011). To handle the problem using Newton's method, as is conventionally done in modern reactive transport simulators (Steefel et al., 2014), additional entries are included that couple the isotopologues in the Jacobian matrix.

3. Isotopic re-equilibration in a batch system

As an illustration of the effects discussed above, we use the CrunchTope model to simulate a simple batch system (no transport) which begins supersaturated with respect to calcite (log Q/Keq = 1.9 initially). With the rate constants chosen (Table 1), the system approaches equilibrium within about 4 days. Using the "no back reaction" option in CrunchTope in which the aqueous mole fraction is used (so there is no isotopic equilibration with the mineral phase), we see from Fig. 2 that isotopic fractionation only extends in time as long as the system remains out of chemical equilibrium. There is no return to the isotopic equilibrium value, so the fractionation only reflects the kinetic enrichment associated with mineral precipitation. In contrast, with the formulation presented in Eqn. 7 (with isotopic equilibration), the batch system takes as much as 30 days to return to the isotopic equilibrium value, reversing the enrichment in the light isotopologue associated with kinetic fractionation during the precipitation stage. In this case, the same rate constants are used for the re-equilibration stage as were used for the kinetic fractionation during precipitation. The actual time scale depends on the mass of calcite initially present as well as the number of moles of calcite precipitated during the chemical equilibration stage.

Table 1. Initial compositions and parameters relevant to batch simulation of calcite precipitation. Equilibrium fractionation factor is 1.0.

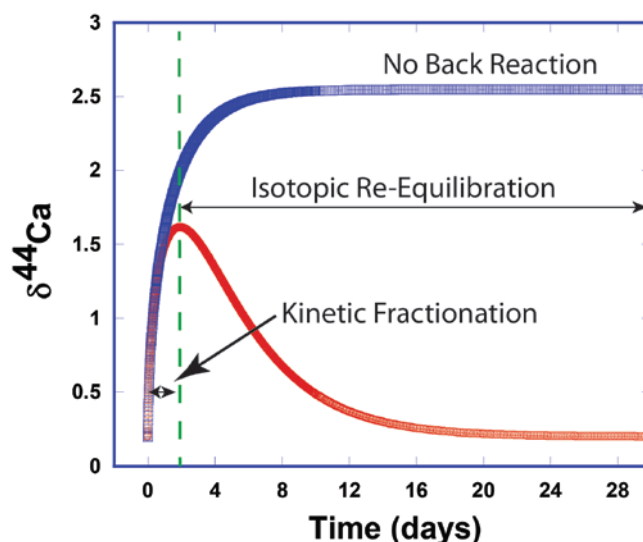| Parameter	Value	Unit
Ca^{2+}	5.4	mM
$\delta^{44}Ca$ of fluid and solids	0.2	‰
pH	8.1	
HCO_3^-	20	mM
Calcite precipitation rate constant	-4.1	log(mol m^{-2} s^{-1})
Calcite kinetic fractionation $\Gamma^f_{44/40}$	0.998	

Fig. 2. Comparison of the isotopic fractionation of the fluid phase associated with calcite precipitation in a batch system. In the case of no back-reaction (Eqn. 11), fractionation only occurs during bulk chemical equilibration and there is no reversal due to isotopic re-equilibration. In the case of the full chemical-isotopic rate law given in Eqn. 5 or 7, an initial stage of fractionation associated with the bulk mineral precipitation is followed by a longer stage of isotopic re-equilibration. In this case, re-equilibration is with the bulk mineral rather than the mineral surface, although the surface case produces a similar shape but with lower amplitude and a shorter re-equilibration time.

4. Isotopic fractionation and re-equilibration in a marine sedimentary sequence

The example of isotopic re-equilibration presented in Fig. 2 is an artificial one that honors the models as presented in Eqn. 5-7 and Eqn. 11, but does it have any basis in reality? Can the same set of rate constants be used to describe bulk calcite precipitation and dissolution and isotopic equilibration? To begin to answer this question, we need observations from an experimental or natural system where isotopic equilibration rates can be determined. Fortunately, chemical and isotopic profiles extending over geological periods of time have been collected from the marine sedimentary record in a few cases (Fantle and DePaolo, 2005; Turchyn and DePaolo, 2011). The preferred marine sedimentary record will be one in which both chemical and isotopic data are available so that the question of how isotopic equilibration rates relate to chemical equilibration rates can be addressed.

The model for isotopic re-equilibration (Eq. 5 and 7) is well suited to describe isotopic ratios associated with recrystallization in marine carbonates. To demonstrate this capability, we extend the CrunchFlow simulation of the Ocean Drilling Program (ODP) site 984 presented by Maher et al. (2006) to the δ^{44}Ca profile reported by Turchyn and DePaolo (2011). The site has the advantage that it has been intensively analyzed with a comprehensive reactive transport model that captures the important components of the biogeochemical reaction network, as well as the porosity distribution and burial rate for the site. Model parameters are described in Maher et al. (2006), and are briefly reported here with emphasis on values necessary to explicitly incorporate the stable isotopes of calcium (Table 2). Both porosity and burial rates as a function of depth were extended using the Maher et al (2006) fits to consider the values of calcium concentration and δ^{44}Ca reported by Turchyn and DePaolo (2011) down to 270 meters below the sea floor.

A full analysis of the isotopic equilibration rates at ODP Site 984 is beyond the scope of this contribution, but we present here two simulations of the Ca isotope profile using rate laws presented above (a combination of Eqn. 7 and 11) and the geochemical reactive transport model previously developed for the site (Maher et al., 2006). In the first case, Eqn. 5 (or 7) is applied without modification, with the same set of rate constants used for both the bulk chemical equilibration and isotopic equilibration rate. Calcium concentrations in the simulations as a function of depth accurately reproduce the values reported in Turchyn and DePaolo (2011), well below the depth of the previous Maher et al., (2006) simulation (Fig. 3A). But Fig. 3b indicates that the simulations predict an effectively

instantaneous isotopic equilibration, or at least sufficiently rapid that it cannot be observed in the profile (isotopic equilibrium is achieved in the first grid cell within the domain).

Table 2. Initial compositions and parameters relevant to incorporation of calcium isotopes in the Maher et al., (2006) model of ODP 984. All fluid and Ca-bearing minerals are initially set to a δ^{44}Ca of 0‰. Marine calcite precipitation is the only fractionating reaction considered in the model. Equilibrium fractionation factor is 1.0. $^{40}k_{bulk}$ and $^{40}k_{reCr}$ are the rate constants for bulk precipitation and isotopic equilibration, respectively.

| Parameter	Case 1	Case 2	Units
Ca^{2+}	10.02	10.02	mM
δ^{44}Ca of fluid and solids	0	0	‰
Calcite bulk precipitation rate constant ($^{40}k_{bulk}$)	-6.19	-6.19	log(mol m^{-2} s^{-1})
Calcite recrystallization rate constant ($^{40}k_{reCr}$)	-6.19	-10.05	log(mol m^{-2} s^{-1})
Calcite kinetic fractionation $\Gamma^f_{44/40}$	0.996	0.996	
Illite	-19	-19	log(mol m^{-2} s^{-1})
Plagioclase	-17.59	-17.59	log(mol m^{-2} s^{-1})
Smectite	-18.5	-18.5	log(mol m^{-2} s^{-1})
Hydroxylapatite	-10.0	-10.0	log(mol m^{-2} s^{-1})
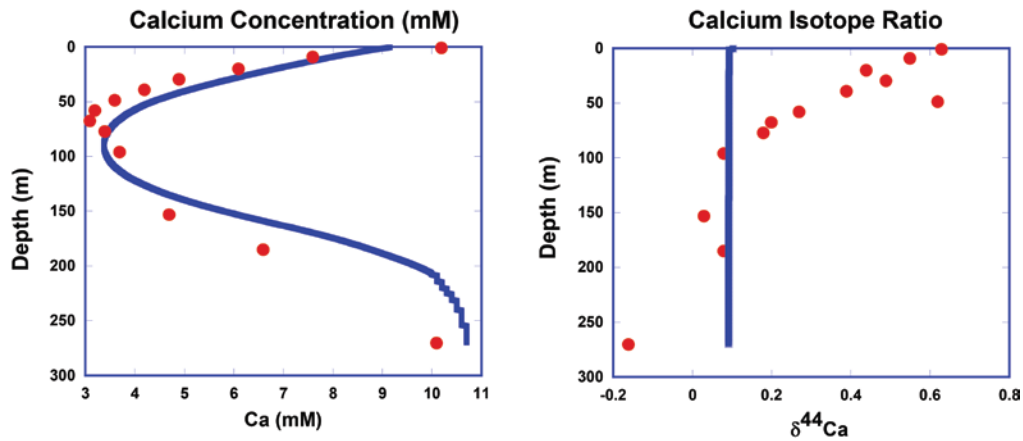
Fig. 3. Case 1 in Table 2. A. Calcium concentration profile in the pore fluid (symbols: data, solid lines: model results) for ODP Site 984 in the Mid-Atlantic Ocean. The bulk Ca profile is modeled reasonably well with the rate constants used. B. Calcium isotopic ratio simulated using the same rate constants for bulk chemical reaction and isotopic re-equilibration (Table 2). Note that the slow isotopic re-equilibration suggested by the data cannot be matched with the high rate constants. Data from Turchyn and DePaolo (2011).

In agreement with Turchyn and DePaolo (2011), the simulations carried out here indicate that the same set of rate constants cannot be used for both bulk chemical kinetics and isotopic re-equilibration, at least in the case of calcite in such a deep marine sedimentary sequence. This is despite the fact that the bulk Ca profile is matched fairly well.

Fig. 3 (Case 1 in Table 2) presents the results of a simulation in which Eqn. 7 (with back-reaction) is solved using the same rate constants for bulk calcite precipitation and for isotopic re-equilibration. To evaluate what combination of rate constants and reaction pathways might describe the isotopic data better, we use in Case 2 (see Table 2) different rate constants for bulk calcite precipitation and for isotopic re-equilibration. This is implemented by using

two separate but parallel rate laws, one for calcite bulk precipitation with no isotopic back-reaction (Eqn. 11), a second with full isotopic re-equilibration (Eqn. 7).

$$^{44}R_{bulk} = \frac{^{44}N_f}{^{40}N_f} \Gamma_{44/40}^f \, ^{40}k_{bulk} \alpha_{eq} \, ^{40}K_{eq} \left[\left(\frac{Q_{cc}}{\alpha_{eq} \, ^{40}K_{eq}} \right) - 1 \right]; \text{. Bulk precipitation}$$

$$^{44}R_{reCr} = \frac{^{44}N_s}{^{40}N_s} a_{^{40}CaCO_3(s)} \Gamma_{44/40}^f \, ^{40}k_{reCr} \alpha_{eq} \, ^{40}K_{eq} \left[\frac{^{40}N_s}{^{44}N_s} \frac{^{44}N_f}{^{40}N_f} \frac{a_{^{40}Ca^{2+}} a_{CO_3^{2-}}}{a_{^{40}CaCO_3(s)}} \frac{1}{\alpha_{eq} \, ^{40}K_{eq}} - 1 \right]; \text{. Isotopic equilibration}$$

(11)

where $^{40}k_{bulk}$ and $^{40}k_{reCr}$ are the rate constants for bulk precipitation and isotopic equilibration, respectively. Note that in this Case 2, as summarized in Table 2, the rate constants for bulk precipitation and isotopic re-equilibration are different by nearly 4 orders of magnitude. The simulation results are summarized in Fig. 4. Except for these changes, the simulation presented in Fig. 4 is the same as that used for Fig. 3.

The match with the pore fluid Ca values is again good, as one expects from the fact that the same rate constant is used for bulk calcite precipitation as in Case 1. Enrichment of fluid δ^{44}Ca is accomplished by allowing a kinetic fractionation of 0.996 during the formation of marine calcite coupled to a parallel, non-fractionating recrystallization rate. All other mineral precipitation (illite) and dissolution (plagioclase, smectite and hydroxyapatite) processes involving calcium are non-fractionating and do not consider isotopic re-equilibration (eq. 11). This approach produces an accurate depth profile of fluid phase δ^{44}Ca in comparison to the Turchyn and DePaolo (2011) dataset, with the rate of isotopic re-equilibration controlled by the smaller rate constant used in Case 2.
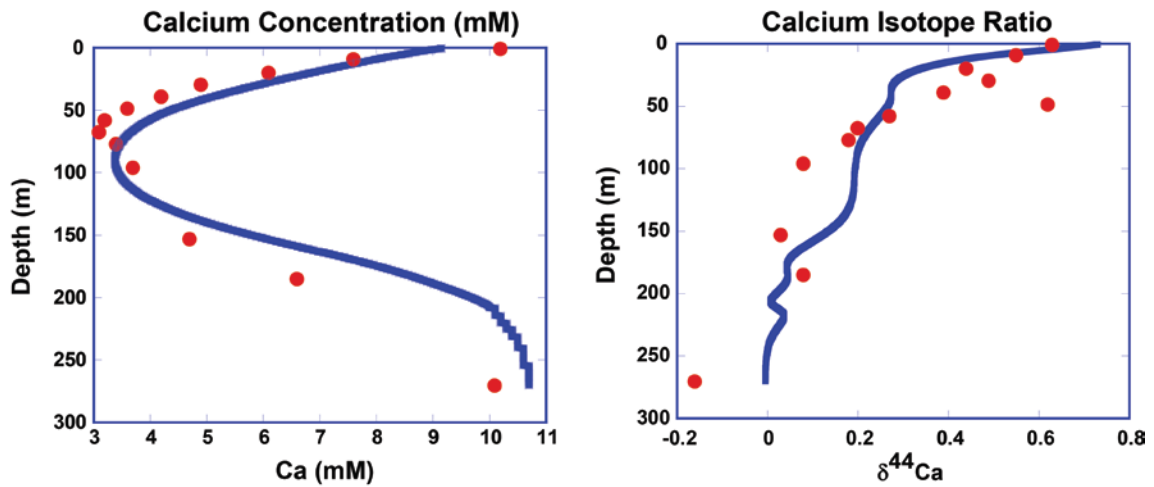

Fig. 4. Case 2 in Table 2. A. Calcium concentration profile (data in symbols, model results solid lines) for ODP Site 984. B. Calcium isotopic ratio simulated using rate constants for isotopic re-equilibration about 4 orders of magnitude smaller than for bulk mineral precipitation (Table 2). Data from Turchyn and DePaolo (2011).

In the ODP Site 984 simulations presented above, it should be noted that we have assumed a linear TST formulation for calcite precipitation and recrystallization, which may not be appropriate. A more highly nonlinear rate law, with much slower rates close to equilibrium, might provide an improved fit to the Ca isotope data using a single rate constant. This possibility has not yet been quantitatively evaluated, but it should be noted that the rate law would have to be highly nonlinear in order to capture the approximately 4 orders of magnitude change in the rate between very close to and further from equilibrium conditions. A second possibility is that the TST rate laws, driven as they are by the departure from equilibrium, may not be strictly applicable. Criticisms of the thermodynamically driven TST rate laws have become more widespread in recent years (e.g., Teng and Dove, 2000; Nielsen et al., 2012; Wolthers et al., 2012; Bracco et al., 2013), so it is conceivable that a more realistic ion by ion

model based on the evolving calcite crystal surface would yield more realistically slow rates, especially close to equilibrium.

5. Conclusions

We have presented a dynamic model that couples chemical and isotopic equilibration rates within the framework of a multicomponent reactive transport simulator. The model, which allows for the transient evolution of the isotopic composition of a bulk mineral phase or its surface layer, is based on Transition State Theory (TST) type rate laws in which thermodynamics drives both chemical and isotopic equilibration. The model, therefore, differs from the steady state model presented previously by DePaolo (2011). Applied to a case in which calcite precipitates in a batch chemical system, the model is able to capture both the initial kinetic fractionation associated with bulk mineral precipitation and the subsequent re-equilibration of the surface or bulk phase after chemical equilibrium has been achieved. When applied to a dataset from ODP Site 984, however, the model over-predicts the rate of isotopic equilibration when the same set of rate constants are used for both bulk mineral precipitation/dissolution and isotopic equilibration. In order to match the Ca isotopic data of Turchyn and DePaolo (2011) for the site, it is necessary to use a rate constant for isotopic equilibration that is nearly 4 orders of magnitude smaller than the rate constant for bulk mineral precipitation/dissolution.

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