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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.

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Keywords: Isotopic fractionation; reactive transport modeling; kinetic fractionation; calcium isotopes

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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

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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, $\alpha_{s\text{-}f} = 0.9987 \pm 0.0002$, 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:

$$R_{net} = R_f - R_b \tag{1}$$

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:

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

or at equilibrium: