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A process-based model for non-equilibrium clumped isotope effects in carbonates

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ABSTRACT

The equilibrium clumped isotope composition of carbonate minerals is independent of the composition of the aqueous solution. However, many carbonate minerals grow at rates that place them in a non-equilibrium regime with respect to carbon and oxygen isotopes with unknown consequences for clumped isotopes. We develop a process-based model that allows one to calculate the oxygen, carbon, and clumped isotope composition of calcite as a function of temperature, crystal growth rate, and solution pH. In the model, carbon and oxygen isotope fractionation occurs through the mass-dependent attachment/detachment kinetics of the isotopologues of HCO_3^- and CO_3^{2-} to and from the calcite surface, which in turn, influence the clumped isotope composition of calcite. At experimental and biogenic growth rates, the mineral is expected to inherit a clumped isotopic composition that is similar to that of the DIC pool, which helps to explain (1) why different organisms share the same clumped isotope versus temperature calibration curves, (2) why many inorganic calibration curves are slightly different from one another, and (3) why foraminifera, coccoliths, and deep sea corals can have near-equilibrium clumped isotope compositions but far-from-equilibrium carbon and oxygen isotope compositions. Some aspects of the model can be generalized to other mineral systems and should serve as a useful reference in future efforts to quantify kinetic clumped isotope effects.

1. Introduction

Clumped isotope geochemistry, or the study of bond ordering in molecules, is at the frontier of efforts to use temperature proxies for reconstructing ocean chemistry (Came et al., 2007), estimating the uplift rate of mountains (Ghosh et al., 2006b), studying diagenetic processes (Dennis and Schrag, 2010), sourcing methane (Stolper et al., 2014, 2015; Wang et al., 2015), identifying signatures of biology in the atmosphere (Yeung et al., 2015) and even investigating the thermal physiology of dinosaurs (Eagle et al., 2011). The most widely-used clumped isotope thermometer is based on the homogeneous reaction (Ghosh et al., 2006a):

$$\underbrace{{}^{13}C^{16}O_3^{2-}}_{\text{mass 61}} + \underbrace{{}^{12}C^{18}O^{16}O_2^{2-}}_{\text{mass 62}} \rightleftharpoons \underbrace{{}^{13}C^{18}O^{16}O_2^{2-}}_{\text{mass 63}} + \underbrace{{}^{12}C^{16}O_3^{2-}}_{\text{mass 60}}, \qquad (1)$$

which describes the extent to which the rare isotopes ^{13}C and ^{18}O are bound together as 'clumps' among the carbonate molecules. The equilibrium constant for this reaction, which can be applied to either dissolved carbonate molecules or carbonate molecules in minerals such as calcite, has a well-defined temperature-dependence based on equilibrium thermodynamics (Wang et al., 2004; Schauble et al., 2006) and is measured by expressing the proportion of mass 63 isotopologues relative to what one would expect for a stochastic distribution of isotopes among the carbonate isotopologues (Ghosh et al., 2006a).

Because the clumped isotope thermometer is based on equilibrium thermodynamics, it potentially suffers from the same issue as oxygen isotope thermometry: many carbonates that form in nature grow at rates that place them in a non-equilibrium regime (Dietzel et al., 2009). There are clear instances, for example in speleothems and surface corals, where clumped isotope compositions yield significant over- or under-estimates of temperature, representing clear departures from equilibrium (Affek et al., 2008; Daëron et al., 2011; Saenger et al., 2012; Affek, 2012; Eiler et al., 2014). There are other cases, namely in deep-sea corals, where clumped isotope compositions are apparently equilibrated even when there are significant departures from carbon and oxygen isotope equilibrium (Thiagarajan et al., 2011; Eiler et al., 2014). Several ideas have been put forth to explain these observations, but because of the complexity of clumped iso-

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tope systematics relative to oxygen or carbon isotope systematics, the models have remained largely conceptual (Tang et al., 2014; Tripati et al., 2015) or based on analogies to gas phase processes such as Knudsen diffusion and mixing of indestructible molecules (Thiagarajan et al., 2011; Henkes et al., 2013).

In this paper we employ a process-based crystal growth model to investigate the complex interplay between carbon, oxygen, and clumped isotope systematics during carbonate growth under non-equilibrium conditions. The non-equilibrium isotope effects attending carbonate precipitation are quantified by considering the mass-dependent transport of isotopologues of CO_3^{2-} and HCO_3^- to and from the mineral surface. In this framework, the carbon isotope composition is calculated from the ratio of $^{13}C^{16}O^{16}O^{16}O$ (mass 61) to $^{12}C^{16}O^{16}O^{16}O$ (mass 60) ions incorporated into the mineral, and the oxygen isotope composition is calculated from the ratio of $^{12}C^{18}O^{16}O^{16}O$ (mass 62) to $^{12}C^{16}O^{16}O^{16}O$ (mass 60) incorporated into the mineral. Since each dissolved inorganic carbon (DIC $= CO_2(aq) + HCO_3^- + CO_3^{2-}$) species has a different equilibrium carbon, oxygen, and clumped isotopic composition (Zeebe and Wolf-Gladrow, 2001; Beck et al., 2005; Hill et al., 2014), the net carbon and oxygen isotopic composition of calcite depends on the relative proportions of HCO_3^- and CO_3^{2-} participating in calcite growth, the isotopic compositions of dissolved HCO_3^- and CO_3^{2-}, and any isotopic fractionations (equilibrium or kinetic) between calcite and each species that arise during ion transport onto, or away from, the mineral surface. The processes could include aqueous diffusion, isotope exchange reactions in aqueous solution, desolvation, surface diffusion and isotope exchange reactions at or near the aqueous–mineral interface. For clumped isotopes, the $^{13}C^{18}O^{16}O^{16}O$ isotopologue (mass 63) is postulated to follow a mass fractionation law that is mathematically related to the behavior of the mass 62 and mass 61 isotopologues.

2. Notation

2.1. Notation for carbon and oxygen isotopes

The difference in isotope composition between any two chemical species or phases can be expressed in terms of an isotopic fractionation factor (α). The fractionation factors between calcite and DIC (for carbon isotopes) and calcite and water (for oxygen isotopes) are given by:

$$\alpha^{C}_{xtl-DIC} = \frac{\left(\frac{[^{13}C]}{[^{12}C]}\right)_{xtl}}{\left(\frac{[^{13}C]}{[^{12}C]}\right)_{DIC}}, \tag{2}$$

and

$$\alpha^{O}_{xtl-w} = \frac{\left(\frac{[^{18}O]}{[^{16}O]}\right)_{xtl}}{\left(\frac{[^{18}O]}{[^{16}O]}\right)_{w}}, \tag{3}$$

where the subscript 'xtl' refers to calcite and 'w' refers to water. The *equilibrium* isotope compositions for species dissolved in aqueous solution are plotted as curves in Fig. 1. The fractionation factors used to construct these curves are provided in Table 1 along with the appropriate references. Note that the oxygen isotope composition of DIC varies with pH because it represents a weighted average of the isotopic composition of individual species. The carbon isotope composition of DIC is also a weighted average of DIC, but is constant with pH because DIC is the only carbon in the system (there is no carbon in H_2O). Hence, the carbon isotope composition of each dissolved species must vary as a consequence of mass balance (cf. Zeebe and Wolf-Gladrow, 2001).

All model calculations in this paper will be done under the assumption that the system is water buffered such that the equilibrium $^{18}O/^{16}O$ values of the DIC species are controlled solely by temperature and the $^{18}O/^{16}O$ of the water. We also assume an infinite reservoir such that the DIC concentration and $^{13}C/^{12}C$ of DIC are constant in all calculations; i.e., there is no distillation of carbon isotopes or change in pH as the carbonate precipitates.

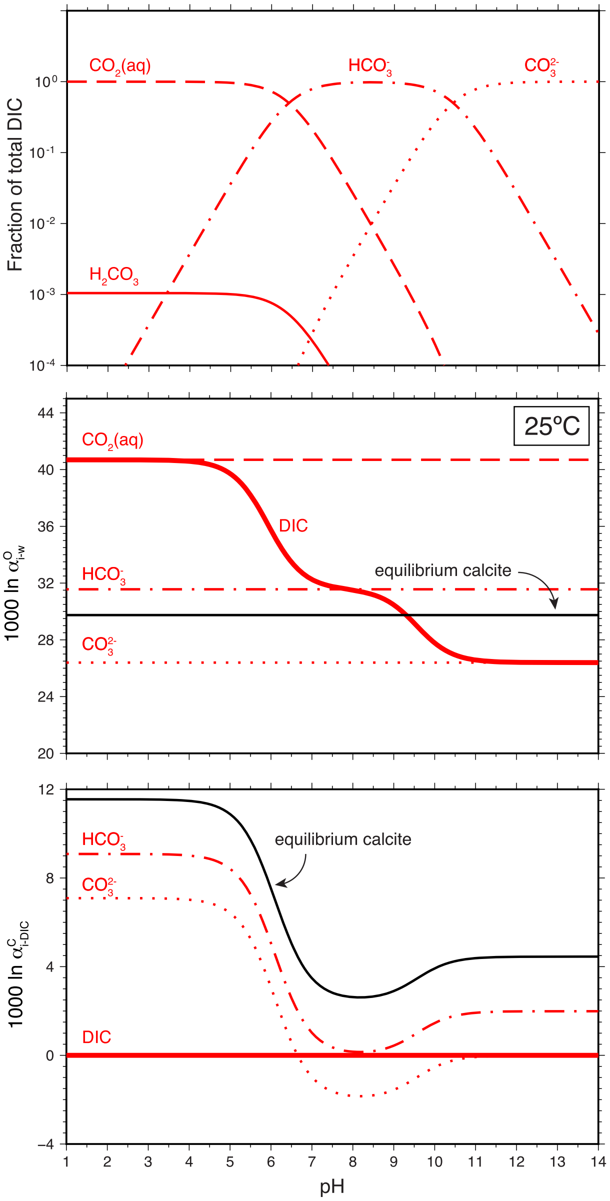

Fig. 1. Equilibrium stable isotope composition of calcite and dissolved inorganic carbon (DIC) species in aqueous solution. *Top*: Distribution of DIC species in aqueous solution as a function of pH. *Middle*: Oxygen isotope compositions expressed relative to water. Since water is by far the predominant oxygen-bearing species in aqueous solution, mass balance dictates that the oxygen isotope composition of DIC vary with pH. *Bottom*: Carbon isotope compositions expressed relative to DIC. Since all of the carbon in aqueous solution is stored in DIC, mass balance dictates that the carbon isotope composition of DIC be constant with pH. Also shown are proposed curves for the equilibrium stable isotope composition of calcite. See Table 2 for the equilibrium fractionation factors used to construct these curves.

2.2. Notation for clumped isotopes

The clumped isotope composition of calcite, denoted Δ^{63}_{xtl}, is given by

$$\Delta^{63}_{xtl} = 1000\left(\frac{r^{63}_{xtl}}{r^{63}_{xtl*}} - 1\right), \tag{4}$$