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The influence of kinetics on the oxygen isotope composition of calcium carbonate

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ABSTRACT

Paleotemperature reconstructions rely on knowledge of the equilibrium separation of oxygen isotopes between aqueous solution and calcium carbonate. Although oxygen isotope separation is expected on theoretical grounds, the temperature-dependence remains uncertain because other factors, such as slow exchange of isotopes between dissolved CO_2-species and water, can obscure the temperature signal. This is problematic for crystal growth experiments on laboratory timescales and for interpreting the oxygen isotope composition of crystals formed in natural settings. We present results from experiments in which inorganic calcite is precipitated in the presence of 0.25 μM dissolved bovine carbonic anhydrase (CA). The presence of dissolved CA accelerates oxygen isotope equilibration between the dissolved carbon species CO_2, H_2CO_3, HCO_3^-, CO_3^{2-} and water, thereby eliminating this source of isotopic disequilibrium during calcite growth. The experimental results allow us to isolate, for the first time, kinetic oxygen isotope effects occurring at the calcite–water interface. We present a framework of ion-by-ion growth of calcite that reconciles our new measurements with measurements of natural cave calcites that are the best candidate for having precipitated under near-equilibrium conditions. Our findings suggest that isotopic equilibrium between calcite and water is unlikely to have been established in laboratory experiments or in many natural settings. The use of CA in carbonate precipitation experiments offers new opportunities to refine oxygen isotope-based geothermometers and to interrogate environmental variables other than temperature that influence calcite growth rates.

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1. Introduction

Paleotemperature reconstructions using biogenic and other natural carbonate minerals are based on equilibrium fractionation of oxygen isotopes between calcium carbonate and water. Equilibrium oxygen isotope fractionation is determined by the thermodynamic properties of the exchanging phases, but natural mineral growth typically occurs under non-equilibrium conditions, as does precipitation of calcite in laboratory experiments (Dietzel et al., 2009; Gabitov et al., 2012). Non-equilibrium oxygen isotope effects occur in the transfer of anions from solution to the growing crystal surface, and in the exchange of isotopes between dissolved CO_2 species and water. These non-equilibrium, or kinetic, effects are likely ubiquitous and therefore problematic for the interpretation of oxygen isotope ratios, as well as "clumped" isotope ratios, as paleotemperature indicators (Ghosh et al., 2006; Dietzel et al., 2009; Dennis and Schrag, 2010; Lachniet, 2009; Tripati et al., 2010).

Kinetic isotope effects are relatively well understood for Ca isotopes in calcite because the treatment of Ca isotopes is relatively simple; there is only one dissolved Ca^{2+} species in solution (DePaolo, 2011; Nielsen et al., 2012). Oxygen isotopes, on the other hand, have the complication that there are multiple dissolved oxygen-bearing carbonate species in solution, and if those species are not isotopically equilibrated, there is no way that the precipitated calcite can be in equilibrium. In this study, we use the enzyme, carbonic anhydrase, to achieve rapid oxygen isotopic equilibration among dissolved inorganic carbon species in the solution from which we precipitate calcite. This effectively eliminates the equilibration of the dissolved carbonate species as an uncertainty in measuring O isotope fractionation factors by experiment, allowing us to isolate non-equilibrium isotope fractionations arising at the mineral–solution interface.

We adapt a model that represents the effects of ion-by-ion growth of calcite to show how experimental measurements (almost certainly controlled by kinetics) can be reconciled with measurements of natural calcites formed under near-equilibrium conditions.

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The model is based on the realistic assumption that ion attachment to, and detachment from, the calcite surface is mass dependent. The experimental results indicate that oxygen isotope-based paleothermometry works reasonably well because the kinetic fractionation factors, which describe oxygen isotope fractionation between calcite and dissolved carbon species, are relatively insensitive to temperature.

1.1. *Background on oxygen isotopes and dissolved carbon species*

The fractionation of oxygen isotopes between phases such as calcite and water is expressed in terms of a fractionation factor

$$\Delta^{18}O_{c-w} = 1000 \ln \alpha_{c-w}, \tag{1}$$

where

$$\alpha_{c-w} = \frac{[^{18}O/^{16}O]_{calcite}}{[^{18}O/^{16}O]_{water}}. \tag{2}$$

Values of $\Delta^{18}O_{c-w} > 0$ or $\alpha_{c-w} > 1$ indicate enrichment of the heavy isotope ^{18}O in calcite (c) relative to water (w). In carbonate crystal growth experiments, $\Delta^{18}O_{c-w}$ correlates with temperature, providing the basis for empirical calibrations of the oxygen isotope thermometer for inorganic and biogenic carbonates (Urey, 1947; McCrea, 1950; Epstein et al., 1953; O'Neil et al., 1969; Kim and O'Neil, 1997; Dietzel et al., 2009; Gabitov et al., 2012). Although carbonate isotope compositions are expressed relative to water, it has been suggested that the oxygen isotope fractionation between calcite and water is not controlled by calcite–water exchange, but by exchange between calcite and dissolved inorganic carbon ($DIC = [CO_2] + [H_2CO_3] + [HCO_3^-] + [CO_3^{2-}]$; brackets denote molar concentration) (Zeebe, 1999).

The relative abundance of DIC species depends primarily on *p*H, with a lesser dependence on temperature (Fig. 1a). At equilibrium, each DIC species exhibits its own temperature-dependent degree of ^{18}O enrichment relative to water (McCrea, 1950; Usdowski et al., 1991; Zeebe, 1999; Zeebe and Wolf-Gladrow, 2001; Beck et al., 2005). In fact, most of the temperature-dependence of ^{18}O in calcite, and its utility as a paleothermometer, can be attributed to the strong temperature-dependence of ^{18}O partitioning between DIC and water. An open question is whether the CO_3^{2-} groups incorporated into calcite are derived from the various dissolved species (Zeebe, 1999), whose proportions vary with temperature and *p*H, or strictly from the CO_3^{2-} ions, whose $^{18}O/^{16}O$ relative to H_2O is fixed for a given temperature regardless of *p*H (Watson, 2004; Dietzel et al., 2009). In either scenario, it is important to assess the kinetics of oxygen isotope exchange between DIC species and water during precipitation of calcite.

1.1.1. *Uncatalyzed kinetics of ^{18}O exchange between $CO_2(aq)$ and water*

Direct exchange of oxygen isotopes between DIC and water occurs through CO_2 hydration and CO_2 hydroxylation reaction mechanisms (Zeebe and Wolf-Gladrow, 2001):

$$CO_2 + H_2O \underset{k_{-2}}{\overset{k_{+2}}{\rightleftharpoons}} H_2CO_3 \rightleftharpoons HCO_3^- + H^+ \tag{3a}$$

$$CO_2 + OH^- \underset{k_{-4}}{\overset{k_{+4}}{\rightleftharpoons}} HCO_3^- \tag{3b}$$

where the *k*'s are forward and backward reaction rate coefficients (Zeebe and Wolf-Gladrow, 2001). The hydration of CO_2 is the predominant reaction mechanism at low-*p*H, whereas at high *p*H the greater abundance of OH^- ions favors the hydroxylation reaction.

The time required for 99% ^{18}O equilibration between DIC and water is given by (Usdowski et al., 1991; Zeebe and Wolf-Gladrow, 2001; Uchikawa and Zeebe, 2012)

$$t_{99\%} = -\ln(0.01)\tau, \tag{4}$$

where

$$\tau^{-1} = (0.5)\{k_{+2} + k_{+4}[OH^-]\} \times \left\{1 + \frac{[CO_2]}{S} - \left[1 + \frac{2}{3}\frac{[CO_2]}{S} + \left(\frac{[CO_2]}{S}\right)^2\right]^{0.5}\right\}. \tag{5}$$

Here, $S = [H_2CO_3] + [HCO_3^-] + [CO_3^{2-}]$. Eq. (5) states that the time required to achieve oxygen isotope equilibrium between DIC and water depends on the temperature-dependent forward reaction rate constants (k_{+2} and k_{+4}), and DIC speciation, which varies with temperature, salinity and *p*H. Fig. 1b shows $t_{99\%}$ versus *p*H using experimentally-determined k_{+2} and k_{+4} (Pinsent et al., 1956; Uchikawa and Zeebe, 2012). For HCO_3^- – dominated solutions, the timescales are hours to days, and for CO_3^{2-} – dominated solutions, the timescales are months to years. Although these timescales are short by geological standards, they are comparable to or greater than the duration of inorganic calcite growth experiments used to measure the equilibrium $\Delta^{18}O_{c-w}^{eq}$ (O'Neil et al., 1969; Kim and O'Neil, 1997; Dietzel et al., 2009; Gabitov et al., 2012). The kinetic parameters describing rates of ^{18}O exchange among dissolved species were not known until recently (Beck et al., 2005), but they suggest that previous calibrations of the ^{18}O calcite thermometer suffer from non-equilibrium effects due to incomplete exchange of ^{18}O between DIC and water, in addition to those due to crystal growth kinetics.

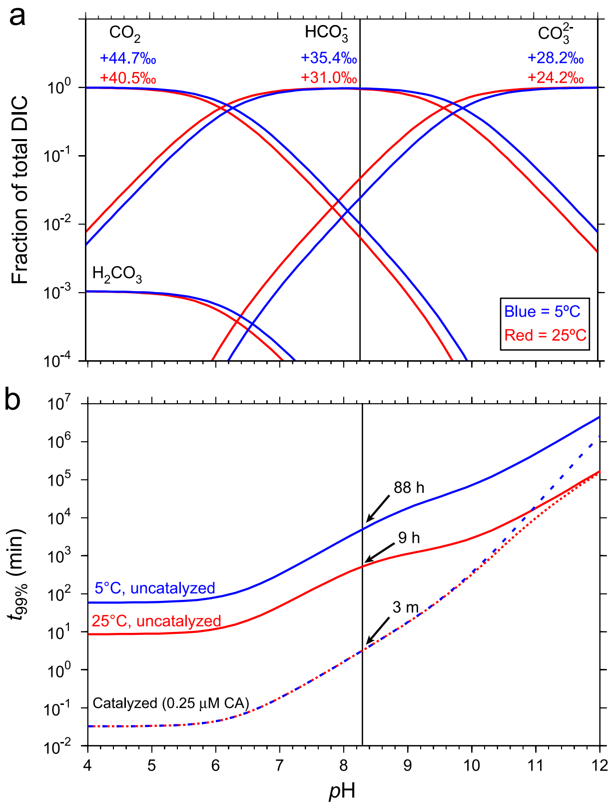

Fig. 1. (a) Speciation of dissolved inorganic carbon ($DIC = [CO_2] + [H_2CO_3] + [HCO_3^-] + [CO_3^{2-}]$) as a function of *p*H at 5 °C and 25 °C. Numbers under the species labels are permil enrichments in ^{18}O for each of the dissolved inorganic carbon species relative to water at 5 °C and 25 °C (Beck et al., 2005) and (b) solid lines show the time required to reach 99% equilibration ($\tau_{99\%}$) of oxygen isotopes among DIC species at 5 °C and 25 °C. Dashed lines show the calculated $t_{99\%}$ in the presence of 0.25 μM bovine carbonic anhydrase (CA), which is a catalyst for the hydration of dissolved CO_2.