



Influence of water on clumped-isotope bond reordering kinetics in calcite

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Abstract

Oxygen self-diffusion in calcite and many other minerals is considerably faster under wet conditions relative to dry conditions. Here we investigate whether this “water effect” also holds true for solid-state isotope exchange reactions that alter the abundance of carbonate groups with multiple rare isotopes (‘clumped’ isotope groups) via the process of solid-state bond reordering. We present clumped-isotope reordering rates for optical calcite heated under wet, high-pressure (100 MPa) conditions. We observe only modest increases in reordering rates under such conditions compared with rates for the same material reacted in dry CO₂ under low-pressure conditions. Activation energies under wet, high-pressure conditions are indistinguishable from those for dry, low-pressure conditions, while rate constants are resolvably higher (up to ~3 times) for wet, high-pressure relative to dry, low-pressure conditions in most of our interpretations of experimental results. This contrasts with the water effect for oxygen self-diffusion in calcite, which is associated with lower activation energies, and diffusion coefficients that are $\geq 10^3$ times higher compared with dry (pure CO₂) conditions in the temperature range of this study (385–450 °C). The water effect for clumped-isotopes leads to calculated apparent equilibrium temperatures (“blocking temperatures”) for typical geological cooling rates that are only a few degrees higher than those for dry conditions, while O self-diffusion blocking temperatures in calcite grains are ~150–200 °C lower in wet conditions compared with dry conditions. Since clumped-isotope reordering is a distributed process that occurs throughout the mineral volume, our clumped-isotope results support the suggestion of Labotka et al. (2011) that the water effect in calcite does not involve major changes in bulk (volume) diffusivity, but rather is primarily a surface phenomenon that facilitates oxygen exchange between the calcite surface and external fluids. We explore the mechanism(s) by which clumped isotope reordering rates may be modestly increased under wet, high-pressure conditions, including changes in defect concentrations in the near surface environment due to reactions at the water–mineral interface, and lattice deformation resulting from pressurization of samples.

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1. INTRODUCTION

The presence of water can affect the chemical reactions and rates of those reactions that occur in a variety of geolog-

ical systems including in igneous, metamorphic, and sedimentary systems. Water appears to significantly change (by orders of magnitude) reaction rates and pathways during solid-state diffusion both between and within minerals (Kronenberg et al., 1984; Hochella and White, 1990a; Farver, 1994; Labotka et al., 2000; Behrens and Zhang, 2001; Wang et al., 2004; Hier-Majumder et al., 2005; Brown et al., 1999; Brown, 2001). For example, the presence of water enhances, by a factor of 10–50, Fe–Mg interdiffusion

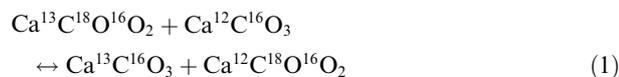
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in olivine (Wang et al., 2004; Hier-Majumder et al., 2005), Ar diffusion in rhyolitic and albitic melts (Behrens and Zhang, 2001), and the diffusivity of oxygen in carbonate minerals (Kronenberg et al., 1984; Farver, 1994; Labotka et al., 2000; Labotka et al., 2011). Here we focus on how water affects isotope-exchange rates between carbonate groups within calcite as studied in the laboratory using the distribution of multiply isotopically substituted carbonate molecules (commonly referred to as “clumped” isotopes).

Within the past decade, carbonate clumped-isotope thermometry has emerged as an important tool for answering for geologic questions ranging from the temperature evolution of Earth’s oceans over the Phanerozoic (e.g., Ghosh et al., 2006a; Came et al., 2007; Bernasconi et al., 2011; Eiler, 2011; Finnegan et al., 2011; Dennis et al., 2013; Grauel et al., 2013; Cummins et al., 2014; Drury and John, 2016), Cenozoic uplift history of Earth’s major mountain ranges (Ghosh et al., 2006b; Huntington et al., 2010, 2014; Quade et al., 2011; Leier et al., 2013; Huntington and Lechler, 2015; Kar et al., 2016), sedimentary basin burial histories pertinent to fossil fuel exploration (Dale et al., 2014; Henkes et al., 2014; Shenton et al., 2015), and low-temperature (<400 °C) metamorphism (Ferry et al., 2011; Lloyd et al., 2017). The carbonate clumped-isotope thermometer is based on the temperature-dependence of isotope-exchange reactions between carbonate groups with two or more rare, heavy isotopes (clumped isotopologues) in chemically equilibrated systems. In calcium carbonate minerals, the predominant clumped isotopologue exchange reaction is:



For an isotopically equilibrated system, the abundance of multiply substituted carbonate isotopologues relative to a random isotopic distribution is a monotonic function of temperature (Ghosh et al., 2006a; Schauble et al., 2006). At low temperature, clumped isotopologue abundances are more enriched relative to a random distribution for an isotopically equilibrated system than at high temperature (Ghosh et al., 2006a; Schauble et al., 2006). This temperature dependence provides the basis for carbonate clumped-isotope geothermometry (Ghosh et al., 2006a; Schauble et al., 2006).

Carbonates that precipitate in internal isotopic equilibrium will have a clumped-isotope signature that reflects the minerals’ formation temperatures. Non-equilibrium clumped-isotope distributions can also occur in nature. For example, growth of carbonate minerals at fast rates prevents CO_3^{2-} groups from maintaining isotopic equilibrium with water (and thus internal isotopic equilibrium between carbonate groups) and can result in non-equilibrium clumped isotope abundances (e.g., Affek et al., 2008; Daëron et al., 2011; Saenger et al., 2012; Kluge et al., 2014; Affek and Zaarur, 2014; Tripathi et al., 2015). These processes all involve isotope-exchange reactions between carbonate and water.

Isotope-exchange processes also occur in minerals such as when C–O bonds are broken and remade within the

mineral lattice, resulting in the exchange of oxygen atoms between differing carbonate ion groups (Ghosh et al., 2006a; Dennis and Schrag, 2010; Eiler, 2011; Passey and Henkes, 2012; Henkes et al., 2014; Stolper and Eiler, 2015). Such solid-state isotope-exchange processes can alter the clumped-isotope compositions of carbonate minerals in a variety of scenarios including burial (Henkes et al., 2014; Shenton et al., 2015), exhumation (Ghosh et al., 2006b; Huntington et al., 2010; Huntington and Lechler, 2015), and contact and regional metamorphism (Ferry et al., 2011; Lloyd et al., 2017). We use the term ‘reordering’ for these solid-state isotopic exchange reactions that occur within the calcite crystal lattice in response to a thermal perturbation. Reordering refers to the change in the degree of internal isotopic order for C–O bonding of the mineral when it is out of thermodynamic equilibrium. Order relates to the abundance of clumped isotopologue groups—calcite formed in isotopic equilibrium at a lower versus higher temperature has a higher concentration of clumped isotopologue groups relative to that expected for a random distribution of isotopes amongst all isotopologue groups and is thus more ordered than the calcite formed at higher temperature. Some potential factors that may influence the rates of these reordering reactions include the mineral type (Ferry et al., 2011; Lloyd et al., 2017; Ryb et al., 2017), minor element substitution in the mineral lattice (Kronenberg et al., 1984), water fugacity (Kronenberg et al., 1984; Farver, 1994; Labotka et al., 2011), pressure (Labotka et al., 2000, 2004), the pH and dissolved ion composition of fluid in contact with the mineral (Hill et al., 2014; Tripathi et al., 2015), and deformation (Siman-tov et al., 2016; Ryb et al., 2017). Understanding the importance of these various factors to reordering kinetics is necessary to evaluate and use carbonate clumped-isotope measurements in systems where reordering reactions have occurred.

The temperature dependence of clumped-isotope reordering kinetics in calcite has been studied in detail under dry (low $f_{\text{H}_2\text{O}}$) conditions (Passey and Henkes, 2012; Henkes et al., 2014; Stolper and Eiler, 2015). However, the other factors discussed above have not been thoroughly investigated, except for a study of the effect of mineralogy (clumped-isotope reordering in the carbonate component of apatite mineral; Stolper and Eiler, 2015) and limited experiments on the influence of water (Passey and Henkes, 2012). Most shallow crustal processes, including burial diagenesis and contact metamorphism, occur in the presence of water and under elevated pressures (Ferry and Dipple, 1991; Beckert et al., 2016). Therefore, it is important to understand how the presence of water influences the kinetics of clumped-isotope reordering.

It is well known, based on tracer diffusion studies, that solid-state oxygen diffusivities differ in wet versus dry conditions (Kronenberg et al., 1984; Farver, 1994; Labotka et al., 2011). These tracer diffusion studies evaluate diffusivities in the near-surface (outer few micrometers) of the sample as, on laboratory timescales, tracers only diffuse a relatively short distance into the sample (typically $\leq 2 \mu\text{m}$) (Kronenberg et al., 1984; Farver, 1994; Labotka et al., 2000, 2004, 2011). The diffusivities obtained in these studies

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