Clumped isotope thermometry of calcite and dolomite in a contact metamorphic environment

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Abstract

Clumped isotope compositions of slowly-cooled calcite and dolomite marbles record apparent equilibrium temperatures of roughly 150–200 °C and 300–350 °C, respectively. Because clumped isotope compositions are sensitive to the details of T–t path within these intervals, measurements of the Δ_{47} values of coexisting calcite and dolomite can place new constraints on thermal history of low-grade metamorphic rocks over a large portion of the upper crust (from ∼5 to ∼15 km depth). We studied the clumped isotope geochemistry of coexisting calcite and dolomite in marbles from the Notch Peak contact metamorphic aureole, Utah. Here, flat-lying limestones were intruded by a pluton, producing a regular, zoned metamorphic aureole. Calcite Δ_{47} temperatures are uniform, 156 ± 12 °C (2σ s.e.), across rocks varying from high-grade marbles that exceeded 500 °C to nominally unmetamorphosed limestones >5 km from the intrusion. This result appears to require that the temperature far from the pluton was close to this value; an ambient temperature just 20 °C lower would not have permitted substantial re-equilibration, and should have preserved depositional or early diagenetic Δ_{47} values several km from the pluton. Combining this result with depth constraints from overlying strata suggests the country rock here had an average regional geotherm of 22.3–27.4 °C/km from the late Jurassic Period until at least the middle Paleogene Period. Dolomite Δ_{47} in all samples above the talc + tremolite-in isograd record apparent equilibrium temperatures of 328^{+13}_{-12} °C (1σ s.e.), consistent with the apparent equilibrium blocking temperature we expect for cooling from peak metamorphic conditions. At greater distances, dolomite Δ_{47} records temperatures of peak (anchi)metamorphism or pre-metamorphic diagenetic conditions. The interface between these domains is the location of the 330 °C isotherm associated with intrusion. Multiple-phase clumped isotope measurements are complemented by bulk $\delta^{13}C$ and $\delta^{18}O$ dolomite–calcite thermometry. These isotopic exchange thermometers are largely consistent with peak temperatures in all samples within 4 km of the contact, indicating that metamorphic recrystallization can occur even in samples too low-grade to produce growth of conventional metamorphic index minerals (i.e., talc and tremolite). Altogether, this work demonstrates the potential of these methods to quantify the conditions of metamorphism at sub-greenschist facies.
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1. INTRODUCTION

There are relatively few quantitative geothermometers that can be used to investigate the thermal histories and temperatures of chemical processes occurring in the upper ∼15 km of the crust. Below ∼300 °C, most heterogeneous equilibria, including the cation and stable isotope exchange reactions upon which most geothermometers are based, proceed too slowly to reach thermodynamic equilibrium. Some established thermometers, such as oxygen isotope fractionation in quartz–calcite veins (Kirschner et al.,

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1995) or fluid inclusion phase equilibria and microthermometry (Mullis et al., 1994), are applicable in this range of relatively low temperatures, but only to narrow types of samples. Other methods are more widely applicable, but yield only semi-quantitative constraints, such as a relative ranking of thermal maturity (e.g., illite crystallinity; conodont color alteration; vitrinite reflectance; Frey, 1987). One method of thermometry that might seem to offer a useful approach to shallow crustal settings — the carbonate–water oxygen isotope thermometer (which rapidly equilibrates at most diagenetic and low-grade metamorphic conditions; Epstein et al., 1953) is rarely useful because one generally lacks precise constraints on the $\delta^{18}O$ of crustal waters (Sheppard, 1986).

Carbonate clumped isotope thermometry offers a relatively new approach to determine the thermal histories of surface and shallow crustal processes (see review by Eiler, 2011). Because it is based on a homogeneous equilibrium recorded by the carbonate mineral lattice, and carbonates appear to often grow at or near isotopic equilibrium, it is potentially useful (as good as est. $\pm 10\,°C$) as a recorder of crustal processes up to $\sim 300\,°C$. While most uses of this technique have focused on paleoclimate problems using biogenic and soil carbonates, proof-of-concept studies have already demonstrated its usefulness for the study of early diagenesis (Huntington et al., 2011), dolomitization (Ferry et al., 2011), cementation (Dale et al., 2014), and hydrothermal alteration at temperatures relevant to the shallow crust (Bristow et al., 2011).

Carbonate clumped isotope thermometry in sub-surface environments is complicated because apparent temperatures may be modified by solid state diffusion, which re-orders bonds between rare isotopes on geologic timescales (Dennis and Schrag, 2010). Studies of C–O bond reordering kinetics in calcite predict that measurable resetting should occur at temperatures as low as $\sim 115\,°C$ on timescales of hundreds of millions of years (Passey and Henkes, 2012; Henkes et al., 2014; Stolper and Eiler, 2015). Moreover, the exact clumped isotope composition preserved in a crystal, and the degree to which it is reset from an initial value, can depend on the specific T–t path through the window where C–O reordering can occur. This phenomenon presents a problem for the interpretation of paleoclimate records in deeply buried samples, but also presents an opportunity for a new tool to study the thermal histories of rocks — a 'clumped isotope geospeedometry' — i.e., the constraint of cooling rate (or other features of a cooling history) based on the preservation of apparent temperatures. This concept has been successfully employed in some initial studies to predict the cooling rate of a metamorphic core complex (Passey and Henkes, 2012), the maximum burial depths of carbonate fossils in depositional basins (Henkes et al., 2014; Shenton et al., 2015), and the geotherm traversed by buried and exhumed soils (Stolper and Eiler, 2015).

Here we examine the clumped isotope systematics of calcite and dolomite in a contact metamorphic environment, compare these results with the heterogeneous C and O isotope exchange equilibria between these two minerals, and interpret these findings with respect to experimental determinations of the kinetics of clumped isotope re-ordering

and intermineral exchange of stable isotopes. To the best of our knowledge, this is the first study to integrate constraints from multiple simultaneous clumped isotope equilibria with each other and with more conventional stable isotope geothermometers. Our purpose is both to illuminate the thermal history surrounding a shallow crustal intrusion, including locations and times that are poorly constrained by other techniques, and to illustrate a general methodology that may be helpful in studying thermal histories of other metamorphic settings.

2. BACKGROUND

The formation of bonds between the rare, heavy isotopes of C and O in carbonates (i.e., ^{13}C–^{18}O bearing carbonate ion groups) is governed by the thermodynamic balance between minimization of vibrational energy (lowest when heavy isotopes are bonded to each other), and maximization of configurational entropy (highest when all carbon and oxygen isotopes are randomly distributed among all isotopologues of CO_3^{-2} — a state referred to as the stochastic distribution). This balance can be expressed by the isotope exchange reaction (for calcite):

$$Ca^{13}C^{16}O_3 + Ca^{12}C^{18}O^{16}O_2 = Ca^{12}C^{16}O_3 + Ca^{13}C^{18}O^{16}O_2.$$
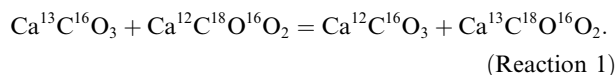
(Reaction 1)

The equilibrium constant for this reaction, K_{eq1}, is measured by digestion of a carbonate phase in phosphoric acid and analysis of the isotopic composition of the evolved CO_2 by sector mass spectrometry (or potentially other methods, such as absorption spectroscopy); the essential point here is that the proportion of ^{13}C–^{18}O bonds in the evolved CO_2 is fractionated by acid digestion but (apparently) not re-equilibrated by exchange. Thus, just as for an acid-digestion measurement of the $\delta^{18}O$ of carbonates, one can indirectly observe the state of isotopic ordering in reactant $(CO_3)_2$ groups by observing that in the product CO_2 molecules. The degree to which multiple isotopic substitution — or isotopic "clumping" — is present in a sample of CO_2 is expressed as:

$$\Delta_{47} = \left[\left(\frac{R^{47}}{R^{47*}} - 1 \right) - \left(\frac{R^{46}}{R^{46*}} - 1 \right) - \left(\frac{R^{45}}{R^{45*}} - 1 \right) \right] \times 1000,$$

where R^{47}, R^{46}, and R^{45} are the measured intensity ratios of masses 47, 46, and 45 over mass 44, respectively, of the evolved CO_2, and * denotes the expected value for a ratio given a stochastic distribution of isotopes among all isotopologues (Eiler and Schauble, 2004; Wang et al., 2004; Ghosh et al., 2006). Because K_{eq1} in carbonate is temperature-dependent, the measured Δ_{47} value of CO_2 evolved from that carbonate depends on the growth temperature (assuming the carbonate grew at or near equilibrium with respect to Reaction 1).

2.1. The kinetics of clumped isotope reordering in carbonate

If a crystal is not in clumped isotopic equilibrium with its ambient temperature, the clumped isotope composition can evolve toward equilibrium by C–O bond reordering,