



Calibration of dolomite clumped isotope thermometry

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ARTICLE INFO

Article history:

Received 29 June 2016

Received in revised form 15 August 2016

Accepted 15 September 2016

Available online 16 September 2016

Keywords:

Dolomite

Clumped isotopes

Carbonate geochemistry

ABSTRACT

Use of the clumped isotope thermometer to decipher environments of dolomite formation has been inhibited by a lack of empirical data from dolomites formed at known temperatures. Calibrations for aragonite, calcite, siderite, and apatite indicate that a universal Δ_{47} – temperature relationship may exist across all carbonate-bearing mineral phases. However, theoretical modeling and proposed acid fractionation differences have suggested that dolomites may have different Δ_{47} values relative to calcites precipitated at the same temperature. To resolve this question, we analyzed five synthetic and four natural dolomites formed at known temperatures. These included synthetic dolomites grown in Mg–Ca–Cl solutions at temperatures of 200–250 °C, and natural samples constrained by fluid inclusion analyses (~70 °C), climate (~28 and ~27 °C), and deep ocean borehole temperature (~21 °C). When using calcite Δ_{47} acid fractionation values, these data result in a calibration line that is statistically indistinguishable from other clumped isotope calibrations. At least with current precision, we find no evidence for a consistent dolomite Δ_{47} offset. These results further support a universal calibration for carbonate clumped isotope thermometry and enable new investigations into conditions of dolomite formation.

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1. Introduction

Dolomite is common throughout the geologic record, but the usefulness of dolomite as a paleoenvironmental and diagenetic proxy has been inhibited by a general lack of understanding about the precise geochemical settings of its formation (Machel, 2004). As clumped isotope measurements provide temperature data that are independent of water isotopic composition (Ghosh et al., 2006), application to dolomite can help resolve longstanding questions about how the mineral forms. Understanding mineral-specific differences in dolomite clumped isotope thermometry, if any, will enable further studies on the temperature conditions of dolomite formation, help constrain the isotopic composition of formation waters, and in turn constrain the environments of precipitation.

Recent work has demonstrated the usefulness of the clumped isotope paleothermometer for calculating formation temperatures of other carbonates, as well as in carbonate ions within biogenic apatites (Eagle et al., 2010; Fernandez et al., 2014; Stolper and Eiler, 2015). The clumped isotope thermometer is based on the principle that, at cooler temperatures, the heavier oxygen (^{18}O) and carbon (^{13}C) isotopes are preferentially bonded to each other within a carbonate mineral lattice (Ghosh et al., 2006). The abundance of ^{13}C – ^{18}O bonds in CO_2 resulting from phosphoric acid digestion of a carbonate mineral, relative to their expected abundance from a stochastic isotope distribution, is expressed

as a Δ_{47} value (Eiler and Schauble, 2004). Using a set of calcites and aragonites formed at known temperatures and reacted with phosphoric acid at 25 °C, Ghosh et al. (2006) experimentally demonstrated that Δ_{47} is reflective of carbonate formation temperature.

Many temperature – Δ_{47} calibrations have been published since that of Ghosh et al. (2006). In general, though not exclusively, these roughly follow either the lower slope of the Dennis and Schrag (2010) calibration, or the original Ghosh et al. (2006) calibration (Fernandez et al., 2014; Defliese et al., 2015; Kele et al., 2015). These differences may be due to instrument-specific corrections or the way data is transferred into the Dennis et al. (2011) absolute reference frame (Spencer and Kim, 2015). The effects of acid digestion may also play a role (Fernandez et al., 2014). Though corrections are applied for the acid digestion fractionation at temperatures above the 25 °C of Ghosh et al. (2006) (e.g., Passey et al., 2010), these calibration differences may be attributable to unaccounted-for effects of phosphoric acid digestion methodology. This is because compiled data produced via acid digestion at 75 °C or higher gives a calibration line with a shallower slope that is statistically distinct from the calibration produced from compiled data produced with 25 °C acid (Defliese et al., 2015).

Within this framework, several studies have sought to understand mineralogical effects on clumped isotope acid fractionation and temperature calibration. The temperature sensitivity of acid fractionation of Δ_{47} values has been shown to be mineral-independent by Defliese et al. (2015), who observed statistically identical responses to acid temperature change for dolomite, calcite, and aragonite over an acid temperature range of 25 to 90 °C. However, theoretical models of kinetic

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isotope effects suggest that small acid fractionation factor differences for different mineralogies should exist (Guo et al., 2009). In theory, dolomite Δ_{47} is expected to be $\sim 0.02\%$ less than calcite Δ_{47} when reacted in 25 °C acid, and this difference has been applied to empirical work (Guo et al., 2009; Ferry et al., 2011). Murray et al. (2016) also reported a significantly different acid fractionation factor for dolomites compared to calcite and aragonite, indicating ongoing uncertainty regarding mineral-specific effects on the phosphoric acid fractionation.

No differences in the mineral-specific temperature – Δ_{47} relationships between calcite, aragonite, siderite, or biogenic apatite have been found empirically (Ghosh et al., 2007; Eagle et al., 2010; Fernandez et al., 2014; Kele et al., 2015; Kluge and John, 2015). No study has yet empirically tested this model for dolomite, perhaps largely because dolomite is very difficult essentially impossible to produce in a laboratory at sub-150 °C temperatures (e.g., Usdowski, 1994; Land, 1998; Gregg et al., 2015). Despite the lack of empirical data, several studies have applied clumped isotope thermometry to natural dolomite samples (e.g., Ferry et al., 2011; Loyd et al., 2012; Lechler et al., 2013; Van De Velde et al., 2013; Dale et al., 2014; Sena et al., 2014; MacDonald et al., 2015; Murray et al., 2016; Winkelstern and Lohmann, 2016; Millan et al., 2016). The Δ_{47} temperatures reported by these studies (albeit in some cases with various dolomite-specific correction schemes) have been generally reasonable, and dolomite and calcite formed under similar temperature conditions have similar Δ_{47} values (Winkelstern and Lohmann, 2016). This suggests that calcite and dolomite calibrations may not greatly differ. In fact, the similarity between other mineral-specific clumped isotope calibrations further suggests that a single temperature – Δ_{47} relationship may exist. The lack of empirical calibration data for dolomite, however, means that all dolomite clumped isotope interpretations assume this to be the case.

We used five synthetic dolomites formed at known temperatures between 200 and 250 °C and four natural dolomites formed under constrained, lower-temperature conditions to develop the first calibration for dolomite clumped isotope thermometry. By direct comparison with calcites and aragonites reacted at the same acid temperature in the same laboratory, we are able to explicitly test for mineral-specific differences in the temperature – Δ_{47} relationship. These data are a first step toward more precise use of dolomite clumped isotope thermometry for diagenetic and paleoenvironmental questions, as well as for insight into the formation of dolomite itself.

2. Methods

2.1. Synthetic dolomites

Synthetic dolomites were prepared as in Kaczmarek and Sibley (2007, 2014), with the exception that natural aragonite ooids harvested from the Ambergris Shoal (Caicos platform, British West Indies) were used as the starting material rather than crushed calcite. In summary, 100 mg whole ooids sieved to obtain the 300–354 μm size fraction and 15 ml 0.875 M Mg–Ca–Cl solution with a Mg/Ca ratio of 1.0 were loaded into Teflon-lined stainless steel acid-digestion Parr bombs. Sealed bombs were placed in a laboratory oven heated to temperatures ranging from 180 to 250 °C (see Table 1). Pressure was not controlled independently, and was equal to the saturation vapor pressure. Upon completion of the experiment, bombs were removed from the oven, and allowed to air-cool to room temperature, which took ~ 1 to ~ 1.5 h depending on temperature. Fluids were decanted and solid products were rinsed with DI water, filtered and dried. All solid products were analyzed by powder X-ray diffraction (XRD) analysis.

Three parameters were quantified for each sample via XRD (Table 1): (i) percent dolomite relative to the starting aragonite ooids, (ii) mol% MgCO_3 of the dolomite products (i.e. dolomite stoichiometry) as determined by position of the 104 reflection, and (iii) the degree of Mg–Ca cation ordering as determined by the relative heights of the 015 and 110 reflections. These parameters were determined following

Table 1

Composition of synthetic dolomite samples. 'Dolomite' is in quotes because some samples lack cation order; * indicates sample is VHMC as indicated by lack of cation order; see Gregg et al. (2015) for details. Uncertainties for all measurements are better than 1.0, and for cation order standard errors are <0.01 ($n = 3$).

| Sample ID | Formation temperature (°C) | % 'dolomite' | Mole % MgCO_3 | Cation order |
|-----------|----------------------------|--------------|------------------------|--------------|
| 250-I-7 | 250 | 93 | 47.8 | 0.12 |
| 235-O-12 | 235 | 94 | 46.5 | 0.08 |
| O-H-2 | 218 | 95 | 45.8 | 0.08 |
| O-T-5 | 218 | 99 | 50.5 | 0.25 |
| 200-P-30 | 200 | 91 | 40.8 | 0.00* |

the approach described by Kaczmarek and Sibley (2007, 2011, 2014), and are also described by Gregg et al. (2015). In general, high-temperature dolomitization reactions proceed via replacement of aragonite by very-high magnesium calcite (VHMC), which is then wholly replaced by poorly-ordered dolomite, and finally well-ordered dolomite.

2.2. Natural samples

2.2.1. Bonnetterre formation, viburnum trend, Missouri

We analyzed dolomite spar collected from the Ozark Lead Mine in southeastern Missouri. This cement formed within the upper Bonnetterre Formation, part of the Viburnum Trend Mississippi Valley Type lead/zinc deposit (Braunsdorf and Lohmann, 1983; Frank and Lohmann, 1986). These are petrographically identified as 100% gangue spar dolomites and are indicated by XRD to have near-perfect ordering (Gregg and Shelton, 1990). We base our temperature "error" estimates for this sample of 70 ± 10 °C on homogenization temperature-ice-melting relationships of Shelton et al. (1992) that indicate this dolomite likely precipitated from ~ 60 to ~ 80 °C saline waters. These measurements were conducted on dolomite from the same locality from which our sample is taken.

2.2.2. Barbados

We analyzed sample 1.10A of Humphrey (1988, 2000) from the late Pleistocene of Barbados. This is 100% calcium-rich dolomite with ~ 43 mol% MgCO_3 . An attenuated (015) ordering reflection indicates some degree of dolomite ordering, with an ordering ratio of 0.11. This dolomite has been interpreted by Humphrey (1988, 2000) to have precipitated from a mixture of fresh and saline waters. It must have formed during a late Pleistocene sea-level high stand near the Earth's surface, and thus formed under tropical conditions similar to today. We thus assign a formation temperature of 28 °C to this sample, based on local modern sea surface temperature (SST) (Locarnini et al., 2010) with an "error" of ± 5 °C, which likely exceeds realistic tropical climate change during the Cenozoic (Pearson et al., 2001). The calibration effects of such a shift in temperature are discussed below.

2.2.3. Andros Island

We also used core sample AC30 from 122 m below Andros Island, Bahamas. This sample is Plio-Pleistocene in age and was collected as part of the diagenetic study of Winkelstern and Lohmann (2016). It is $>95\%$ dolomite, and has an ordering ratio of 0.28. By similar logic to that applied to the Barbados dolomite, we assigned a 27 ± 5 °C formation temperature to the Andros dolomite based on local SST (Locarnini et al., 2010). Because it too formed during a high stand just north of the tropics, it is unlikely that Plio-Pleistocene local temperatures differed dramatically from modern mean annual temperatures.

2.2.4. Deep ocean

Sample DSDP is from a Deep Sea Drilling Project drillcore in the southern Gulf of California (Leg 64, core 29, hole 479; water depth 440 m). Dolomitization of this material is described by Kelts and McKenzie (1984) as the result of active methanogenesis. Via XRD, the

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