



Evaluating formation fluid models and calibrations using clumped isotope paleothermometry on Bahamian dolomites

Sean T. Murray*, Peter K. Swart

Department of Marine Geosciences, Rosenstiel School of Marine and Atmospheric Science, University of Miami, Miami, FL 33149, USA

Received 11 July 2016; accepted in revised form 18 February 2017; Available online 27 February 2017

Abstract

The use of stable oxygen isotopes to understand the mechanisms of dolomite formation has been hampered by the inability to precipitate well-ordered dolomite under normal Earth surface conditions. Several studies have attempted to address this problem, either by precipitating high-temperature ordered dolomites and extrapolating the data to low temperatures or by using more disordered very-high Mg-calcites as a proxy for low temperature dolomites. The result is eight equations that disagree significantly from each other (by as much as $\sim 3.6\text{‰}$ in the $\delta^{18}\text{O}$ value of the precipitating fluid at 25 °C), and produce differences which can greatly affect the interpretation of the formation mechanisms for low temperature dolomites. However, by combining the recently developed clumped-isotope paleothermometer, an independent isotopic measurement (Δ_{47}) that directly relates to the temperature of formation, to Late Miocene to Pleistocene aged dolomites from the Bahamas with a well-constrained thermal and fluid history, we have attempted to narrow down the viable equations used to interpret the $\delta^{18}\text{O}$ values of dolomites.

The clumped-isotope temperatures measured on the Bahamian dolomites (16–37 °C) agrees with the range of temperatures expected in the Bahamas. Pairing these temperatures with geological and mineralogical arguments, we favor the equation suggested by Matthews and Katz (1977), as it is the only one that produces realistic $\delta^{18}\text{O}$ fluid values across the range of clumped-isotope temperatures. Both the clumped-isotope temperatures and $\delta^{18}\text{O}$ values of the precipitating fluid show a strong positive covariance that we have interpreted as reflecting the mixing of surface brines that have undergone varying amounts of evaporation and normal seawater. The different mechanisms driving these fluids included formation by normal marine seawater driven by the compensatory flow of the mixing zone, bank wide Kohout convection, and evaporative brine reflux.

© 2017 Elsevier Ltd. All rights reserved.

Keywords: Clumped isotope; Dolomite; Bahamas; Fluid composition

1. INTRODUCTION

It is well known that massive dolomites commonly replace shallow-water carbonate sediments formed at Earth surface temperatures (Land, 1980, 1998), yet the failure of laboratory studies to reproduce ordered stoichiometric dolomite under similar conditions has limited our ability to understand their formation. Modern seawater for exam-

ple is significantly over saturated with respect to dolomite (Arvidson and Mackenzie, 1999), yet the mineral does not readily precipitate from marine waters and most attempts to precipitate dolomite in the laboratory at reasonable sedimentary temperatures have met with failure; the exception being studies in which very high Mg-calcites, sometimes referred to as protodolomites, which lack evidence of cation ordering (Gregg et al., 2015), were formed at temperatures between 25 and 100 °C (Fritz and Smith, 1970; Vasconcelos and McKenzie, 1997).

* Corresponding author.

E-mail address: smurray@rsmas.miami.edu (S.T. Murray).

Although the $\delta^{18}\text{O}$ value of dolomite ($\delta^{18}\text{O}_{\text{dolomite}}$) has been frequently employed to understand dolomite formation, the estimates of equilibrium $\delta^{18}\text{O}$ values for dolomites have varied widely (Land, 1980). Several approaches have been employed to establish the fractionation factor (α) between the $\delta^{18}\text{O}_{\text{dolomite}}$ and the $\delta^{18}\text{O}$ of the precipitating fluid ($\delta^{18}\text{O}_{\text{fluid}}$) (Eq. (1)). The fractionation factor varies as a function of temperature and usually has the form as defined in Eq. (2). In Eq. (2), variables A and B vary according to the mineral under consideration and T is temperature in degrees Kelvin (K).

$$\alpha_{\text{Dolomite-Fluid}} = \frac{\delta^{18}\text{O}_{\text{Dolomite}} + 1000}{\delta^{18}\text{O}_{\text{Fluid}} + 1000} \quad (1)$$

$$1000 \ln \alpha_{\text{Dolomite-Fluid}} = A(10^6 T^{-2}) + B \quad (2)$$

New equations defining α are still being proposed with little agreement as to which relationship is correct (Land, 1980, 1983; Horita, 2014). Some of the earliest attempts to determine the α value for dolomites involved examining co-occurring calcites and dolomites (Friedman and Hall, 1963; Degens and Epstein, 1964; Sheppard and Schwarz, 1970) and were based on the premise that the dolomite and calcite formed at the same time and from the same fluid in isotopic equilibrium. Working under the assumption that the equilibrium relationship between calcite and its parent fluid has been fairly well constrained (Friedman and O'Neil, 1977; Kim and O'Neil, 1997), any oxygen isotopic difference between co-evolved calcite and the dolomite could then be attributed to the equilibrium fractionation value of the dolomite and the parent fluid (Land, 1980, 1983; Budd, 1997). While many studies did show a consistent enrichment of the ^{18}O of dolomites compared to calcite by 3–6‰, this method was hindered by the difficulty in establishing that the calcites and dolomites being studied were cogenetic.

Later studies approached the problem by examining the equilibrium isotopic fractionation of well-ordered dolomites precipitated at elevated temperatures (Northrop and Clayton, 1966; O'Neil and Epstein, 1966; Matthews and Katz, 1977; Horita, 2014) and extrapolating these results to lower temperatures. This method proved to be unsatisfactory as the extrapolation to sedimentary temperatures resulted in significant error. Other studies precipitated very-high Mg-calcites or protodolomites at lower temperatures (Fritz and Smith, 1970; Vasconcelos et al., 2005). However, as it is known that $\delta^{18}\text{O}_{\text{dolomite}}$ values are sensitive to both ordering and stoichiometry (Vahrenkamp and Swart, 1994), there is some doubt whether these equations are applicable to well-ordered, more stoichiometric forms of the mineral (Gregg et al., 2015). A final method used a theoretical approach (Zheng, 1999) based on a modified increment method, but it is uncertain if this equation is applicable to naturally occurring dolomite as well (Horita and Clayton, 2007). If all of these various calibrations are considered together, the result is a range in the $\delta^{18}\text{O}_{\text{dolomite}} - \delta^{18}\text{O}_{\text{fluid}}$ fractionation (α) of ~ 1.0315 – 1.0351 for a dolomite precipitated at 25 °C. Assuming the temperature of formation is known, this range is large enough (~ 3.6 ‰ at 25 °C) to render the $\delta^{18}\text{O}_{\text{fluid}}$ value of little use in distin-

guishing between the different types of fluids that are reasonable for dolomite formation (Fig. 1).

1.1. Clumped Isotopes

The clumped isotope paleothermometer (Ghosh et al., 2006; Huntington et al., 2009) is dependent upon the systematic change in the abundance of carbonate molecules that have multiple substitutions of rare, heavy isotopes in their structure (e.g. $^{13}\text{C}^{18}\text{O}^{16}\text{O}_2$). A number of studies (Ghosh et al., 2006, 2007; Dennis and Schrag, 2010; Eagle et al., 2010; Tripathi et al., 2010; Daëron et al., 2011; Thiagarajan et al., 2011; Passey and Henkes, 2012; Saenger et al., 2012; Eagle et al., 2013; Grauel et al., 2013; Henkes et al., 2013; Zaarur et al., 2013; Came et al., 2014; Fernandez et al., 2014; Tang et al., 2014; Wacker et al., 2014; Defliese et al., 2015; Kele et al., 2015; Kluge et al., 2015; Tripathi et al., 2015; Bonifacie et al., 2016; Kelson et al., 2016; Winkelstern et al., 2016) have shown a measurable difference in the abundance of these multiply substituted “clumped” isotopologues with changes in temperature within a variety of organic and inorganic carbonates that have formed at known temperatures. This technique has enabled a new approach to the problems of studying dolomites as the change in abundance of clumped isotopes is strictly controlled by the temperature of the system and is therefore completely independent of the composition of the parent fluid.

The measurement of clumped isotopes is based on the mass 47 of CO_2 , primarily focused on the most abundant multiply substituted species $^{13}\text{C}^{18}\text{O}^{16}\text{O}$, derived from the acid digestion of carbonates. The variable Δ_{47} (Wang et al., 2004) is used to describe the deviation of mass 47 CO_2 isotopologues in carbonate samples (R_{47}) relative to the same bulk isotopic composition except that it has been stochastically redistributed (R_{47}^*).

$$\Delta_{47} = \left(\frac{R_{47}}{R_{47}^*} - 1 \right) \times 1000 \quad (3)$$

Changes in the Δ_{47} value are then directly related to temperature through calibrations, with decreasing Δ_{47} values associated with increasing formation temperatures.

The work described in this paper applies clumped-isotope paleothermometry to dolomites that have formed on secluded Cenozoic aged islands in the Bahamas. While dolomite is commonplace in the ancient, the context of its formation is often difficult to establish as increasing age often positively correlates with increased burial depth, diagenesis, metamorphism, and exposure to variable environmental settings that all could overprint the original dolomite composition. By examining dolomites that have formed in the more recent past, the variables which have contributed to a dolomites formation can be better constrained.

1.2. Interpreting $\delta^{18}\text{O}_{\text{fluid}}$ values

In this study, the calculated clumped-isotope temperatures have been utilized to better constrain how each of the different $\delta^{18}\text{O}_{\text{dolomite}} - \delta^{18}\text{O}_{\text{fluid}}$ –temperature calibra-

Download English Version:

<https://daneshyari.com/en/article/5783413>

Download Persian Version:

<https://daneshyari.com/article/5783413>

[Daneshyari.com](https://daneshyari.com)