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Geochimica et Cosmochimica Acta 126 (2014) 411–421

Geochimica et Cosmochimica Acta

www.elsevier.com/locate/gca

Siderite ‘clumped’ isotope thermometry: A new paleoclimate proxy for humid continental environments

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Received 19 July 2013; accepted in revised form 6 November 2013; available online 21 November 2013

Abstract

Clumped isotope measurements can be used to exploit the paleoclimatic potential of pedogenic siderite ($FeCO_3$); however, the applicability of this method is held back by the lack of clumped isotope calibrations of mineralogies other than calcite and aragonite. Here we present an inorganic calibration of siderites grown in the laboratory between 21 and 51 °C. Linear regression of Δ_{47} values and temperature ($10^6/T^2$, K) yields the following relationship ($r^2 = 0.997$):

$$\Delta_{47\text{-RF}} = \frac{(0.0356 \pm 0.0018) \times 10^6}{T^2} + (0.172 \pm 0.019)$$

We demonstrate that this calibration is indistinguishable from calcite at current levels of analytical precision. Our observations suggest that there is likely no large systematic bias in the clumped isotope acid fractionation factors between the two different carbonate minerals. We also present clumped isotope measurements of a natural siderite collected from Holocene sediments of the Mississippi River Delta. We find that siderites record warm season marsh water temperatures instead of mean annual temperatures as it has long been presumed. This finding has important implications for the accuracy of siderite stable isotope and clumped isotope based climate reconstructions.

1. INTRODUCTION

Siderite ($FeCO_3$) has the potential to become an important archive of paleoclimate in humid continental environments because it forms in poorly drained/anoxic wetland soils where pedogenic calcite is not typically found (Ludvigson et al., 1998, 2013; Sheldon and Tabor, 2009). The oxygen isotope composition of siderite can be used to solve the carbonate-water isotope exchange paleothermometer equation for temperatures of mineral precipitation or for the $\delta^{18}O$ values of soil waters during mineral formation (White et al., 2001; Ufnar et al., 2004; Suarez et al., 2011). The paleothermometer equation, however, is a function of two independent variables (temperature and the $\delta^{18}O$ of the fluids from which the mineral forms) and one of them must be known independently to determine the other.

Like other carbonate minerals, $\delta^{18}O$ values of siderites can only be used when there are independent constraints on either the formation temperature or the $\delta^{18}O$ value of coexisting fluids. White et al. (2001) used the oxygen isotope composition of middle Cretaceous pedogenic siderites along with paleotemperature estimates from a general circulation model (GMC) to estimate meteoric water $\delta^{18}O$ values and, ultimately, arrive at an estimate for precipitation rate. While this approach is useful when direct observations are lacking, it uses model data in place of recorded observations. For instance, Suarez et al. (2011) used the pedogenic siderite data of Ufnar et al. (2002) along with new proxy data in a mass balance model to quantify the mid-Cretaceous hydrologic cycle. They found that the estimated rainfall rates depend strongly on the chosen Cretaceous

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http://dx.doi.org/10.1016/j.gca.2013.11.006

temperature reconstruction. Even if accurate, GCM temperature estimates may not be adequately precise, both temporally and spatially, to reflect local conditions during the time of mineral precipitation. For instance, solar heating can result in soil temperatures hotter than local air temperature (Passey et al., 2010; Quade et al., 2013); and, more importantly, it is not clear whether siderites record mean annual air temperatures (MAAT) or seasonally biased soil temperatures like pedogenic calcites (Breecker et al., 2009; Passey et al., 2010; Peters et al., 2013; Quade et al., 2013). This must be known before we can confidently interpret paleotemperature estimates from this archive.

Recent work has demonstrated that the carbonate clumped isotope paleothermometer is useful for solving both temperature and $\delta^{18}O_w$ problems simultaneously because it provides temperature estimates that are independent of fluid isotopic compositions (e.g., Ghosh et al., 2006; Schauble et al., 2006; Eiler, 2011). This effectively reduces the paleothermometer equation to one variable that can be reliably measured in the laboratory. The clumped isotope proxy exploits the observation that in the carbonate lattice the rare, heavier carbon and oxygen isotopes preferentially bond to each other with decreasing temperature. Isotopic ‘clumping’ is determined by measuring the $^{13}C^{18}O^{16}O$, $^{12}C^{18}O^{17}O$, and $^{13}C^{17}O^{17}O$ isotopologues of CO_2 (collectively comprising the mass 47 ion beam, with the vast majority of species at that mass being $^{13}C^{18}O^{16}O$) extracted from a carbonate mineral via reaction with concentrated phosphoric acid. It is reported as a Δ_{47} value, which is the enrichment of the mass 47 isotopologue in a sample relative to a stochastic distribution of isotopes (Eiler and Schauble, 2004; Wang et al., 2004).

Most of the published measurements of clumped isotopes have been obtained from calcite- or aragonite-bearing materials, and there is no consensus yet on whether the existing calcite calibrations are appropriate for other minerals. Guo et al. (2009) used the theoretical predictions of Schauble et al. (2006) and a model of kinetic effects during phosphoric acid digestion of carbonates to calculate the temperature vs. Δ_{47} relationship for several carbonate minerals. They predict that several types of carbonates are offset from the calcite calibration to lower or higher Δ_{47} values. Their work does not include a prediction for siderite because Schauble et al. (2006) did not consider this mineral in their calculations; however, they do provide an estimate for the Δ_{47} value expected in CO_2 extracted at 25 °C from siderites with a stochastic distribution of ^{13}C–^{18}O bonds. Their estimate shows that the siderite calibration should be offset to lower Δ_{47} values by approximately 0.03‰ relative to calcite (outside the accepted external reproducibility of clumped isotope measurements of 0.02‰). This prediction, however, has not been validated by empirical studies of siderites grown in the laboratory at known temperatures.

Additionally, there are no empirical studies that show what effect the temperature of phosphoric acid digestion has on Δ_{47} values for minerals other than calcite. Siderites are commonly reacted at elevated temperatures because acid digestion of siderite can be extremely slow at 25 °C (on the order of days or weeks, e.g., Rosenbaum and Sheppard, 1986). The most widely used calibration (Ghosh et al., 2006) was generated from calcite samples reacted at 25 °C, and siderite data generated at elevated acid digestion temperatures (>25 °C) must first be normalized to that reaction temperature in order to use any of the existing (both empirical and theoretical) carbonate calibrations.

Here we present an inorganic calibration for the siderite clumped isotope paleothermometer using minerals precipitated in the laboratory under controlled temperature conditions. We demonstrate that this calibration is indistinguishable from calcite at current levels of analytical precision. We also present clumped isotope measurements of a natural siderite sample collected from Holocene sediments of the Mississippi River Delta that suggest that siderites record warm season marsh water temperatures instead of MAATs as has long been presumed.

2. METHODS

2.1. Synthetic siderite

Siderite was precipitated under controlled temperature conditions (4, 9, 21, 39, 51 ± 1 °C) following the procedures of Wiesli et al. (2004) who used a method similar to that described by Kim and O’Neil (1997) for Ca, Cd, and Ba carbonates, along with several precautions intended to prevent oxidation of dissolved Fe(II). The reactor temperature was controlled with the aid of a temperature controlled water bath (Fisher Scientific®, Isotemp 110), which has an observed precision of ±1 °C. Experimental solutions of $FeCl_2$ and $NaHCO_3$ were prepared in two Erlenmeyer flasks using 18 MΩ water that had been made anoxic by continuous flushing with N_2 for ~2 h (Fig. 1). The N_2 was first bubbled through water to saturate the gas and minimize evaporation in the experimental solutions. One flask contained 100 ml of a 0.05 mM solution of $FeCl_2$ and the other 300 ml of a 0.05 mM solution of $NaHCO_3$. Both flasks were acidified until the $NaHCO_3$ solution reached a pH ~ 6.7 by

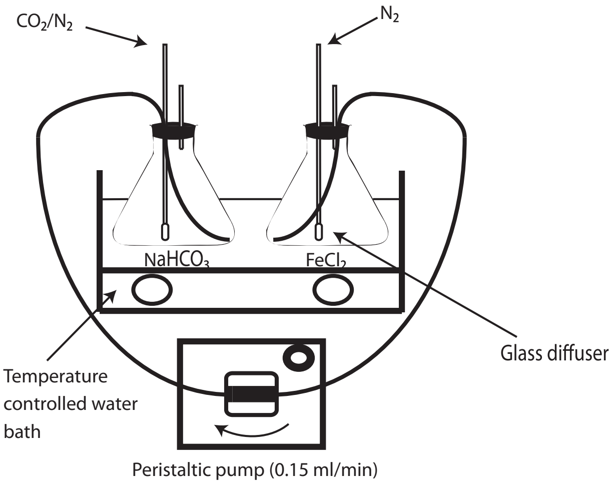

Fig. 1. Schematic of the experimental apparatus used for siderite synthesis experiments. An $FeCl_2$ solution was slowly titrated into a flask containing a $NaHCO_3$ solution. Precipitation was achieved by degassing of CO_2. See text for details.