



## Invited Review

## Carbonate clumped isotope thermometry in continental tectonics

Katharine W. Huntington<sup>a,\*</sup>, Alex R. Lechler<sup>a,b</sup><sup>a</sup> Department of Earth and Space Sciences, University of Washington, Johnson Hall Rm-070, Box 351310, 4000 15th Avenue NE, Seattle, WA 98195-1310, United States<sup>b</sup> Department of Geosciences, Pacific Lutheran University, Rieke Rm-158, Tacoma, WA 98447-0003, United States

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## ABSTRACT

Reconstructing the thermal history of minerals and fluids in continental environments is a cornerstone of tectonics research. Paleotemperature constraints from carbonate clumped isotope thermometry have provided important tests of geodynamic, structural, topographic and basin evolution models. The thermometer is based on the  $^{13}\text{C}$ – $^{18}\text{O}$  bond ordering in carbonates (mass-47 anomaly,  $\Delta_{47}$ ) and provides estimates of the carbonate formation temperature independent of the  $\delta^{18}\text{O}$  value of the water from which the carbonate grew;  $\Delta_{47}$  is measured simultaneously with conventional measurements of carbonate  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values, which together constrain the isotopic composition of the parent water. Depending on the geologic setting of carbonate growth, this information can help constrain paleoenvironmental conditions or basin temperatures and fluid sources. This review examines how clumped isotope thermometry can shed new light on problems in continental tectonics, focusing on paleoaltimetry, basin evolution and structural diagenesis applications. Paleoaltimetry is inherently difficult, and the precision in carbonate growth temperature estimates is at the limit of what is useful for quantitative paleoelevation reconstruction. Nevertheless, clumped isotope analyses have enabled workers to address previously intractable problems and in many settings offer the best chance of understanding topographic change from the geologic record. The portion of the shallow crust residing at temperatures up to ca. 200 °C is important as host to economic resources and records of tectonics and climate, and clumped isotope thermometry is one of the few proxies that can access this critical range with sensitivity to temperature alone. Only a handful of studies to date have used clumped isotopes to investigate diagenesis and other sub-surface processes using carbonate crystallization temperatures or the sensitivity of  $\Delta_{47}$  values to a sample's thermal history. However, the thermometer is sufficiently precise to answer many important questions in this area, making the investigation of sub-surface processes an excellent target for future investigations.

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\* Corresponding author. Tel.: +1 206 543 1750.

E-mail address: [kate1@uw.edu](mailto:kate1@uw.edu) (K.W. Huntington).

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## 1. Introduction

The thermal history of minerals and fluids in both surface and subsurface environments on continents is a fundamental prediction of geodynamic, structural, topographic, and basin evolution models. Recently, the toolkit of thermochronometers and temperature proxies used to test such models has grown to include carbonate clumped isotope paleothermometry, a technique based on the thermodynamic tendency of the heavy isotopes of carbon and oxygen to bond, or “clump” together in carbonate minerals (Ghosh et al., 2006a; Schauble et al., 2006). Unlike conventional carbonate thermometers (Epstein and Mayeda, 1953; McCrea, 1950; Urey, 1947), clumped isotope thermometry does not require assumptions about the composition of the water from which the mineral grew. This feature makes the clumped isotope thermometer especially well suited for reconstructions of both surface and subsurface continental environments where such paleowaters typically are not preserved and their compositions are difficult to estimate (e.g., Eiler, 2007, 2011).

Although the methods are technically challenging (e.g., Bernasconi et al., 2013; Dennis et al., 2011; He et al., 2012; Hu et al., 2014; Huntington et al., 2009; Petrizzo and Young, 2014; Rosenheim et al., 2013; Yoshida et al., 2013), carbonate clumped isotope analysis offers a wealth of information that is not possible from conventional measurements of the carbon and oxygen isotopic compositions (i.e.,  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values)<sup>1</sup> of the carbonate alone. Combined with carbonate  $\delta^{18}\text{O}$  values and thermometry equations (e.g., Kim and O'Neil, 1997; Kim et al., 2007), carbonate growth temperatures determined from clumped isotope analysis can be used to calculate the  $\delta^{18}\text{O}$  value of the water from which the carbonate grew. Depending on the environment of carbonate growth, such information can give quantitative estimates of paleoenvironmental conditions (e.g., lake or soil temperatures, precipitation sources, aridity) or basin temperatures and fluid sources. As a result, clumped isotope thermometry has been applied to a broad array of problems relevant to continental tectonics, including terrestrial paleoclimate (Affek et al., 2008; Brand et al., 2014; Csank et al., 2011; Eagle et al., 2013; Frantz et al., 2014; Passey et al., 2010; Snell et al., 2013; Suarez et al., 2011; Tobin et al., 2014; VanDeVelde et al., 2013; Wang et al., 2013); paleoaltimetry (Carrapa et al., 2014; Fan et al., 2014; Garzione et al., 2014; Ghosh et al., 2006b; Huntington et al., 2010, 2014; Lechler et al., 2013; Leier et al., 2013; Quade et al., 2007, 2011, 2013; Snell et al., 2014); structural geology, diagenesis, fluid flow and water-rock interactions (Bergman et al., 2013; Bristow et al., 2011; Budd et al., 2013; Dale et al., 2014; Huntington et al., 2011, 2014; Loyd et al., 2012, 2014; Sena et al., 2014; Streit et al., 2012; Swanson et al., 2012); and metamorphism, cooling rates and basin thermal histories (Dennis and Schrag, 2010; Ferry et al., 2011; Henkes et al., 2014; Passey and Henkes, 2012; Shenton et al., 2015).

This review examines the application of carbonate clumped isotope thermometry to problems in continental tectonics, focusing on paleoaltimetry, basin evolution, diagenesis and structural geology studies. A growing number of studies explore other applications of clumped isotope thermometry to topics including marine organisms and paleoclimate (e.g., Brand et al., 2012; Came et al., 2007; Cummins et al., 2014; Dennis et al., 2013; Douglas et al., 2014; Finnegan et al.,

2011; Ghosh et al., 2007; Grauel et al., 2013; Keating-Bitonti et al., 2011; Price and Passey, 2013; Saenger et al., 2012; Thiagarajan et al., 2011, 2014; Tripathi et al., 2010), speleothems (Affek et al., 2008, 2013, 2014; Daëron et al., 2011; Kluge and Affek, 2012; Kluge et al., 2014; Wainer et al., 2011), meteorites (Guo and Eiler, 2007; Halevy et al., 2011), and extinct vertebrates (Eagle et al., 2010, 2011). Many of these studies are summarized in earlier comprehensive reviews (Eiler, 2007, 2013; Eiler et al., 2014) or reviews focused on paleoclimate applications (Affek, 2012; Eiler, 2011; Passey, 2012) and are not discussed here. Instead, the goal of this review is to equip researchers with the background and perspective needed to design future studies and critically evaluate the use of clumped isotopes to address problems in continental tectonics.

## 2. Clumped isotope geochemistry and the carbonate clumped isotope thermometer

Clumped isotope geochemistry investigates multiply-substituted isotopologues,<sup>2</sup> which are molecules or moieties that contain more than one heavy isotope (Eiler, 2007). Over the last decade, the theoretical framework (Affek, 2013; Cao and Liu, 2012; Eiler, 2013; Eiler et al., 2014; Guo et al., 2009; Hill et al., 2014; Ma et al., 2008; Schauble et al., 2006; Tang et al., 2014; Wang et al., 2004) and analytical methods (Bernasconi et al., 2013; Cao and Liu, 2012; Cui and Wang, 2014; Dennis et al., 2011; Eiler and Schauble, 2004; Eiler et al., 2013, 2014; Ghosh et al., 2006a; He et al., 2012; Hu et al., 2014; Huntington et al., 2009; Passey et al., 2010; Petrizzo and Young, 2014; Rosenheim et al., 2013; Schmid and Bernasconi, 2010; Tsuji et al., 2012; Yeung et al., 2012; Yoshida et al., 2013) in the field of clumped isotope geochemistry have co-evolved rapidly. Recent analytical developments have enabled clumped and site-specific isotopic measurements in a diverse array of molecules (Eiler, 2013; Eiler et al., 2013, 2014; Ono et al., 2014; Stolper et al., 2014a,b; Tsuji et al., 2012; Yeung et al., 2012), but by far the most developed application of clumped isotope geochemistry is in the area of carbonate thermometry. In carbonate minerals, clumping of the heavy isotopes of carbon and oxygen is temperature dependent, forming the basis of the carbonate clumped isotope thermometer (Ghosh et al., 2006a). Eiler (2007) presents an overview of the history and theoretical underpinnings of clumped isotope geochemistry, and the reader is referred to Affek (2012) for a complementary primer on carbonate clumped isotope thermometry.

Carbonate clumped isotope thermometry examines the proportion of heavy-heavy isotope bonds in a sample relative to the number of heavy-heavy bonds that would be predicted by probability (random chance) (Ghosh et al., 2006a; Schauble et al., 2006). An analogy with dice is useful to illustrate the concept (Passey, 2012). The probability of rolling two dice and getting “snake eyes,” or two ones, is dictated by the proportion of faces on each die showing the number one (i.e.,  $1/6 * 1/6 = 1/36$ , or 0.0278). Similarly, if bonding of heavy carbon and oxygen isotopes into

<sup>1</sup> Isotopic compositions are defined by ratios of heavy to light stable isotopes in a sample, reported using delta notation relative to the isotopic ratio of a standard. The ratios are small, and thus by convention they are multiplied by 1000 and reported in per mil (‰). For example,  $\delta^{18}\text{O} = [^{18}\text{O}/^{16}\text{O}_{\text{sample}} \div ^{18}\text{O}/^{16}\text{O}_{\text{standard}} - 1] \times 1000\text{‰}$ .

<sup>2</sup> Isotopologues are molecules of the same compound that are identical in chemical formula but differ in isotopic composition. For example,  $^{12}\text{C}^{16}\text{O}_2$ ,  $^{13}\text{C}^{16}\text{O}_2$ , and  $^{12}\text{C}^{17}\text{O}^{18}\text{O}$  are isotopologues of carbon dioxide;  $^{12}\text{C}^{16}\text{O}_2$  is the isotopically light and most abundant isotopologue, and  $^{12}\text{C}^{18}\text{O}^{16}\text{O}$  is an example of a singly substituted isotopologue having one heavy isotope ( $^{18}\text{O}$ ) substituted for a light isotope ( $^{16}\text{O}$ ). Multiply substituted (clumped) isotopologues have two or more heavy isotopes substituted for light isotopes, e.g.,  $^{12}\text{C}^{17}\text{O}^{18}\text{O}$ ,  $^{13}\text{C}^{18}\text{O}^{16}\text{O}$ , and  $^{13}\text{C}^{17}\text{O}_2$ . Clumped or multiply substituted isotopologues, molecules, or moieties (i.e., a part or functional group of a molecule) containing multiple heavy isotopes have lower vibrational energies, which makes them more thermodynamically stable (see Eiler, 2007).

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