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Invited Review

Carbonate clumped isotope thermometry in continental tectonics

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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 $^{13}C–^{18}O$ bond ordering in carbonates (mass-47 anomaly, Δ_{47}) and provides estimates of the carbonate formation temperature independent of the $\delta^{18}O$ value of the water from which the carbonate grew; Δ_{47} is measured simultaneously with conventional measurements of carbonate $\delta^{13}C$ and $\delta^{18}O$ 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 Δ_{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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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., δ^{13}C and δ^{18}O values)[1] of the carbonate alone. Combined with carbonate δ^{18}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 δ^{18}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; Tripati 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,[2] 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

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[1] 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, $\delta^{18}O = [^{18}O / ^{16}O_{sample} \div ^{18}O / ^{16}O_{standard} - 1] \times 1000‰$.

[2] Isotopologues are molecules of the same compound that are identical in chemical formula but differ in isotopic composition. For example, $^{12}C^{16}O_2$, $^{13}C^{16}O_2$, and $^{12}C^{17}O^{18}O$ are isotopologues of carbon dioxide; $^{12}C^{16}O_2$ is the isotopically light and most abundant isotopologue, and $^{12}C^{18}O^{16}O$ is an example of a singly substituted isotopologue having one heavy isotope (^{18}O) substituted for a light isotope (^{16}O). Multiply substituted (clumped) isotopologues have two or more heavy isotopes substituted for light isotopes, e.g., $^{12}C^{17}O^{18}O$, $^{13}C^{18}O^{16}O$, and $^{13}C^{17}O_2$. 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).

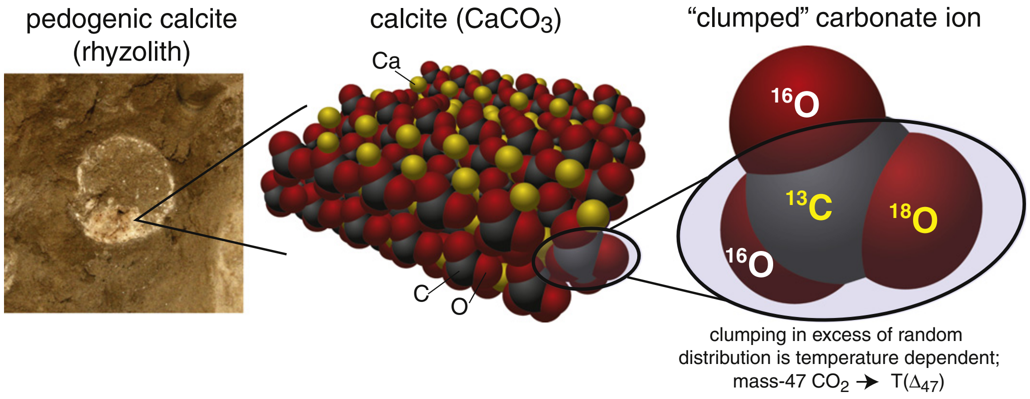

Fig. 1. Schematic of carbonate clumped isotope thermometry. The crystal lattices of carbonate minerals (e.g., pedogenic calcite, $CaCO_3$) contain carbonate ions (CO_3^{2-}) made up of carbon and oxygen atoms. Isotopically normal, or most abundant, is $^{12}C^{16}O^{16}O^{16}O$. 'Clumping' refers to the thermodynamic tendency for heavy isotopes of C and O to bond together with a greater proportion of ^{13}C–^{18}O clumping at colder temperatures. Δ_{47} refers to the measured abundance of ^{13}C–^{18}O bonds in CO_2 gas derived from acid digestion of carbonate in excess of a random (probability), or stochastic, distribution of ^{13}C–^{18}O bonds. The Δ_{47} value derived from mass-47 CO_2 is used to calculate carbonate formation temperature (T(Δ_{47})).

the same molecule were simply a function of random chance, the number of heavy–heavy ^{13}C–^{18}O bonds in a carbonate mineral sample would be dictated by the proportion of heavy carbon and oxygen isotopes in the sample (i.e., the sample's bulk isotopic composition, described by its $\delta^{13}C$ and $\delta^{18}O$ values). As summarized by Eiler (2007), this would be the case according to the "rule of the mean" (Bigeleisen, 1955). Bonds that contain one or more heavy isotopes have lower vibrational energies than bonds containing only light isotopes, and the "rule of the mean" assumes that the decrease in bond energy (increase in thermodynamic stability) for a double heavy isotope substitution is exactly twice that associated with a substitution of only one heavy isotope. That is, the total vibrational energy would be the same for a system containing a heavy–heavy isotopologue and a light–light isotopologue (e.g., $^{18}O^{18}O + {}^{16}O^{16}O$) as a system containing two heavy-light isotopologues ($^{18}O^{16}O + {}^{18}O^{16}O$). If this were strictly true, there would be no energetic advantage for heavy isotopes to clump into bonds with each other instead of being distributed into bonds with light isotopes. However, in reality bonds containing two heavy isotopes are slightly more than twice as thermodynamically stable as bonds containing only one heavy isotope. As a consequence, the actual number of heavy–heavy ^{13}C–^{18}O bonds in a sample is slightly greater at isotopic equilibrium than the number predicted by probability. In other words, the isotopic dice are "weighted," so that heavy–heavy bonds (rolling snake eyes) are favored. Due to enthalpy the "weighting of the dice" decreases with increasing temperature, resulting in fewer clumped isotopologues (relative to the number predicted by probability) for carbonates formed at high temperature. Thus the excess of clumped isotopologues in a carbonate mineral provides a direct, thermodynamically based estimate of the temperature of mineral growth.

Measuring clumped isotopes in carbonate minerals (e.g., calcium carbonate, $CaCO_3$) (Fig. 1) involves a modified version of the approach used to measure conventional or bulk carbon and oxygen isotope ratios ($\delta^{18}O$ and $\delta^{13}C$ values). Measurements are made not on the carbonate directly, but on CO_2 produced by reaction of the mineral with anhydrous phosphoric acid (H_3PO_4). Because only two out of the three oxygen atoms in carbonate are released as CO_2 in this reaction, kinetic oxygen isotope fractionation[3] accompanies the process; this causes the degree of ^{13}C–^{18}O "clumping" (and the $\delta^{18}O$ value) to differ between the reactant carbonate and product CO_2 by an amount that varies with acid digestion temperature (Defliese et al., 2015; Guo et al., 2009; Passey et al., 2010; Wacker et al., 2013). The CO_2 is analyzed with a mass spectrometer, which measures the ratios of CO_2^+ ions of different masses. For conventional analyses, $\delta^{13}C$ and $\delta^{18}O$ values of CO_2 are calculated from the ratios of the mass-45 and mass-46 CO_2 signals to the mass-44 CO_2 ($^{12}C^{16}O^{16}O$) signal, respectively, as per Santrock et al. (1985) and assuming specific mass-dependent fractionation between ^{17}O and ^{18}O. For clumped isotope analyses, the mass spectrometer is modified to also measure mass-47 CO_2 (mostly $^{13}C^{18}O^{16}O$), as well as mass 48 and sometimes 49 to screen for contaminants. The measured 47/44 ratio is compared to the calculated ratio predicted by probability to define the mass-47 anomaly (Δ_{47}; see Affek (2012) for a review of notation and details of Δ_{47} calculation). The Δ_{47} value describes a sample's heavy–heavy isotope bond enrichment, which depends only on the temperature of carbonate formation. Temperature (T(Δ_{47})) is then calculated from the Δ_{47} value of CO_2 released from phosphoric acid digestion of carbonate using an empirical calibration (e.g., Dennis and Schrag, 2010; Ghosh et al., 2006a; Passey and Henkes, 2012; Wacker et al., 2014; Zaarur et al., 2013).

General agreement between theoretical and empirical Δ_{47}-temperature calibrations suggests that most natural (biogenic and abiogenic) and synthetic calcites conform to conditions of mineral precipitation at isotopic equilibrium (Eiler, 2011). Speleothems are a notable exception (Affek et al., 2008; Daëron et al., 2011; Eiler, 2011; Kluge and Affek, 2012; Kluge et al., 2014; Meckler et al., 2009), with disequilibrium attributed to kinetic isotope effects associated with CO_2 degassing-driven calcite formation and/or high precipitation rates (e.g., Affek and Zaarur, 2014). Kinetic isotope effects during carbonate precipitation are also recognized in some corals (e.g., Ghosh et al., 2006a; Saenger et al., 2012), and may be important for some carbonate materials used to study continental interiors (e.g., caliche and other carbonate crusts). Detailed discussion of kinetic effects on clumped isotope compositions is beyond the scope of this paper. But as with any geothermometer based on equilibrium exchange reactions, including conventional carbonate-water $\delta^{18}O$ thermometry, potential departures from equilibrium mineral growth must be considered for clumped isotope study.

Usefully precise measurements of carbonate Δ_{47} values are considerably more challenging than conventional $\delta^{18}O$ and $\delta^{13}C$ analyses, with practical implications for applied clumped isotope thermometry studies. Challenges arise because the dice are only slightly weighted to favor heavy–heavy bonds, and the weighting of the dice changes only subtly with temperature. For natural carbonates, this results in very small Δ_{47} values—typically less than 1/1000, or 1‰—that vary only ~0.005‰ per degree. Measuring such small Δ_{47} values precisely enough to estimate carbonate formation temperature ± 1–2 °C requires large samples (3–8 mg of calcite per analysis; but c.f., Hu et al., 2014;

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[3] Isotopic fractionation refers to the enrichment of one isotope relative to another in a chemical or physical process. The extent of fractionation can be expressed by a fractionation factor (α), defined as the factor by which the abundance ratio of two isotopes will change during a chemical reaction or a physical process.

Schmid and Bernasconi, 2010), stringent purification procedures, hours of measurement time, replication of analyses on multiple aliquots of sample, and analysis of a large number of reference CO_2 gases and carbonate standards (e.g., Dennis et al., 2011; Huntington et al., 2009).

Although limits of sample size and throughput and precision and accuracy of temperature estimates impact experimental design and data interpretation (see Section 5, User's Guide), clumped isotopes can provide important, often unique constraints that make these challenges worth the effort. The following sections review recent applications to paleoelevation, diagenesis, basin evolution and structural geology, highlighting effective ways to exploit the advantages of clumped isotope thermometry to address problems in continental tectonics.

3. Clumped isotope thermometry in paleoelevation reconstructions

> Carbonate formation temperature and paleo-water $\delta^{18}O$ values obtainable through Δ_{47} analysis can be used to infer paleoelevation by exploiting the systematic decrease of surface temperature and the $\delta^{18}O$ value of meteoric water with elevation, provided samples record original depositional conditions and appropriate context exists for interpreting $T(\Delta_{47})$ and $\delta^{18}O$ values. Clumped isotope thermometry provides a measure of temperature and the paleowater $\delta^{18}O$ value at the time and place of carbonate formation (e.g., in lakes or soils), which may or may not represent average meteoric water $\delta^{18}O$ values or convenient climate variables such as mean annual surface temperature. Because of the complexity of relating isotopic values to earth-surface conditions and the influence of climate and other factors on temperature- and $\delta^{18}O$-elevation gradients through time, expanding information from carbonates to orogen-scale paleoelevation estimates is non-trivial. The accuracy of $T(\Delta_{47})$-derived paleoelevation estimates benefits from calibrations of $T(\Delta_{47})$-environment relationships in comparable modern carbonate systems and consideration of $T(\Delta_{47})$ and $\delta^{18}O$ records in the context of global and regional climate change and variability.

3.1. Previous methods and challenges of reconstructing paleoelevation

Topographic change impacts regional and global climate and is one of the best available measures of continental dynamics and deformation, yet reconstructing paleoelevation remains extremely difficult due to a lack of direct elevation proxies in the geologic record. Methods for reconstructing paleoelevation are diverse, relying on records of deposition, erosion or environmental variables that reflect the magnitude and timing of land surface elevation change. Where present and datable, depositional markers of elevation change including uplifted marine and terrestrial reference surfaces (e.g., Abbott et al., 1997; Bookhagen et al., 2006; Cosentino et al., 2009; Merritts and Bull, 1989; Perg et al., 2001; Schildgen et al., 2012) can provide precise constraints on surface uplift. Paleosurfaces dissected by river incision also can record the timing and magnitude of surface uplift (e.g., Clark et al., 2005; Gubbels et al., 1993; Schildgen et al., 2007), provided incision can be dated and the influence of other factors such as climate on river erosion is taken into account (e.g., Lease and Ehlers, 2013).

To investigate paleoelevation in cases where diagnostic reference paleosurfaces are not present, a range of methodologies have been proposed and used (see Kohn, 2007 for a complete review). Two of the few climate-independent measures of past elevation that have been proposed rely on estimates of paleo-atmospheric pressure at the site and time of basalt flow emplacement as recorded by basalt vesicularity (e.g., Sahagian et al., 2002; Xia et al., 2012; see also review by Sahagian and Proussevitch, 2007) or “fossil” cosmogenic nuclide production rates (Blard et al., 2005; Riihimaki and Libarkin, 2007). Basalt flows are straightforward to date radiometrically. However, the requirement of well-preserved basalt flows with simple emplacement histories precludes wide application of vesicularity methods, and paleoelevation interpretations derived from them remain controversial (e.g., Bondre, 2003; Libarkin and Chase, 2003; Sahagian et al., 2003a,b). Due to large uncertainties associated with the quantification of fossil cosmogenic nuclide production rates, cosmogenic paleoaltimetry techniques have been similarly limited in terms of application. The most commonly applied methods to infer paleoelevation exploit the systematic decrease of surface temperature and the oxygen and hydrogen isotopic compositions of meteoric water with elevation (Fig. 2), but they too suffer from important limitations (see reviews by Blisniuk and Stern, 2005; Meyer, 2007; Quade et al., 2007; Rowley, 2007; Rowley and Garzione, 2007).

Temperature-based methods for reconstructing paleoelevation are attractive for their apparent simplicity. The general approach is to combine estimates of surface paleotemperature with estimated temperature-elevation gradients (“lapse rates”). In the simplest case, the paleoelevation (in km) of a presently high-elevation surface can be estimated by dividing the difference in paleotemperature between that surface and an isochronous surface near sea level (°C) by the temperature lapse rate (°C/km) (see review by Meyer, 2007). Since the steepest climate gradients on earth are not latitudinal but vertical, with land surface temperatures decreasing 5.5 °C/km on average globally (Fig. 2b; e.g., Meyer, 1992, 2007), this approach can in theory yield usefully precise paleoelevation constraints if paleotemperature can be estimated with precisions of ~1–2 °C. But other uncertainties in the method are difficult to quantify; paleoelevation estimates depend critically on the choice of temperature lapse rate, which can vary from 4 to 8 °C/km regionally (e.g., Meyer, 2007), and on the often untestable assumption that all temperature change reflects elevation change. Moreover, obtaining precise and accurate paleotemperature estimates represents a significant hurdle in itself. Paleobotany-based temperature estimates have the longest history of application to paleoelevation reconstruction (e.g., Axelrod, 1997; Gregory and Chase, 1992; Gregory-Wodzicki, 2000; MacGinitie, 1953; Meyer, 1992; Spicer et al., 2003; Wolfe et al., 1997, 1998) but are limited by the requirement of pristine, dense fossil leaf assemblages and by debate over how to accurately quantify uncertainties in reconstructed temperature (e.g., Peppe et al., 2010; but c.f. Spicer and Yang, 2010).

A wide variety of geological materials archive isotopic information, making stable isotope paleoaltimetry by far the most extensively applied paleoelevation method. Conventional approaches reconstruct paleoelevation by taking advantage of the decrease in the heavy stable oxygen ($\delta^{18}O_{mw}$) and hydrogen ($\delta^{2}H_{mw}$ or δD_{mw}) isotopic compositions of meteoric water (i.e., precipitation and precipitation-derived surface and shallow groundwaters) with increasing elevation (e.g., Blisniuk and Stern, 2005; Craig and Gordon, 1965; Dansgaard, 1964; Poage and Chamberlain, 2001; Rowley and Garzione, 2007). Paleolevation estimates are then derived from inferred $\delta^{18}O_{mw}$ and/or δD_{mw} values interpreted using either a conventional ‘lapse rate’ approach based on empirical $\delta^{18}O_{mw}$ (or δD_{mw})-elevation gradients (global averages are ~−2.8‰/km for $\delta^{18}O_{mw}$ and ~−15 to −20‰/km for δD_{mw}; Fig. 2b; Poage and Chamberlain, 2001; Rowley, 2007) or Rayleigh distillation models, which describe the effects of evaporation–condensation on the oxygen and hydrogen isotopic compositions of cloud vapor and condensate as air masses cool and rise over high topography (e.g., Rowley and Garzione, 2007; Rowley et al., 2001). The ubiquity of paleo-meteoric water proxies in orogenic sedimentary basins makes this an attractive method, and stable isotopic evidence has played an important role in the development of paleotopographic records for the world's high-elevation landscapes (e.g., Cassel et al., 2009, 2014; Chamberlain et al., 1999; Dettman and Lohmann, 2000; Garzione et al., 2008; Lawrence and Rashkes Meaux, 1993; Leier et al., 2013; Mix et al., 2011; Mulch

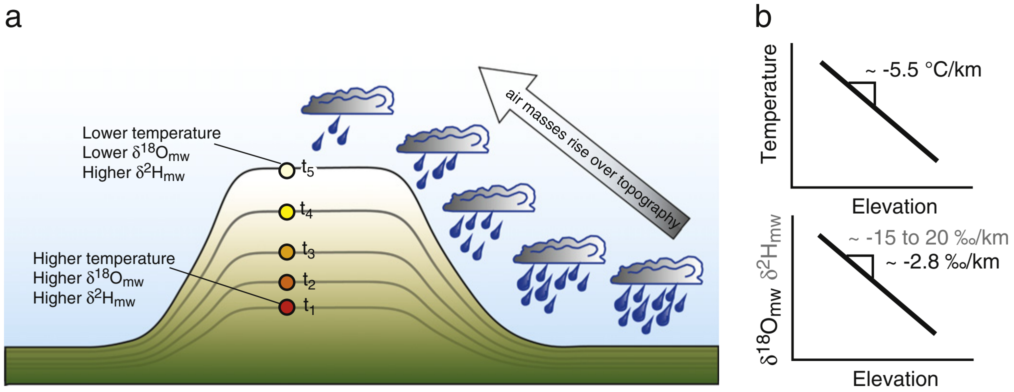

Fig. 2. Elevation dependence of Earth surface temperature and the oxygen ($\delta^{18}O_{mw}$) and hydrogen (δD_{mw}) isotopic compositions of meteoric water. (a) Topography forces air masses to rise and lose moisture, leading to a decrease in temperature and in $\delta^{18}O_{mw}$ and δD_{mw} values with increasing elevation. Samples (circles) deposited on top of an uplifting surface through time (t_1 to t_5) should record progressively cooler temperatures and lower $\delta^{18}O_{mw}$ and δD_{mw} values, all else being equal (schematic modified after Poage and Chamberlain, 2006). (b) Surface temperatures decrease with elevation by 5 to 6 °C/km on average, but local temperature 'lapse rates' can vary considerably (e.g., Meyer, 2007, and references therein). Globally, $\delta^{18}O_{mw}$ values decrease with elevation on average by 2.8‰/km (Poage and Chamberlain, 2001), with significant scatter around this average (Blisniuk and Stern, 2005).

et al., 2008; Polissar et al., 2009; Rowley and Currie, 2006; Rowley et al., 2001; Saylor et al., 2009).

However, several challenges can prevent the simple translation of isotopic records into quantitative paleoelevation estimates. Isotopic fractionation between minerals and the waters from which they form is temperature dependent (e.g., Kim and O'Neil, 1997; Kim et al., 2007); thus for carbonate records, which to date have been the most common type of records used for isotopic paleoaltimetry studies, temperatures of carbonate formation must be assumed in order to reconstruct $\delta^{18}O_{mw}$. Carbonate formation temperature uncertainties of 5–10 °C (a conservative range for many settings in which carbonates form) equate to $\delta^{18}O_{mw}$ uncertainties of ~1–2‰, or up to ± 1 km for calculated paleoelevations using average $\delta^{18}O_{mw}$-elevation gradients of ~ −1.5 to −3‰/km (Lechler and Niemi, 2011; Poage and Chamberlain, 2001). Furthermore, the reconstructed $\delta^{18}O_{mw}$ values may be higher than the actual values of precipitation because the oxygen isotopic values of surface waters are sensitive to modification (i.e., ^{18}O enrichment) by evaporation. Evaporation is especially important for shallow water bodies and/or in arid regions and can lead to significant (≥2 km) over- or under-estimates of paleoelevation (e.g., Quade et al., 2007).

Even when $\delta^{18}O_{mw}$ can be reliably reconstructed, extracting paleoelevation information from isotopic records is not straightforward. Values of $\delta^{18}O_{mw}$ (as well as $\delta^{2}H_{mw}$, or δD_{mw}) are sensitive to climate state (e.g., pCO_2 and associated feedbacks; Jeffery et al., 2012) and depend not only on elevation but also on moisture source, air mass temperature and trajectory, convection and seasonality of precipitation (e.g., Dansgaard, 1964; Galewsky, 2009; Garzione et al., 2000; Lechler and Galewsky, 2013; Rohrmann et al., 2014; Rowley and Garzione, 2007)—each of which can vary through time as a function of climatic and topographic change (Ehlers and Poulsen, 2009; Insel et al., 2012; Poulsen et al., 2010). As a result, it is inherently difficult to infer paleoelevation from the $\delta^{18}O$ values of carbonate samples deposited atop surfaces subject to climatic and elevation change, during which surface temperatures, $\delta^{18}O_{mw}$-elevation relationships, and evaporative influence may change simultaneously (e.g., Blisniuk and Stern, 2005; Ehlers and Poulsen, 2009; Poage and Chamberlain, 2001). These effects make it particularly challenging to isolate the influence of elevation on proxy $\delta^{18}O$ values in orogenic plateau and continental interior settings (e.g., Tibet, Basin and Range, Colorado Plateau, Altiplano), which are common targets for paleoaltimetry investigation. Consequently, the paleoelevation histories of many of the world's prominent high elevation regions remain equivocal (e.g., Lechler and Niemi, 2011; Quade et al., 2011), leaving the questions of how such high topography is built and sustained relatively open-ended.

3.2. Paleoelevation reconstruction using carbonate clumped isotope thermometry

3.2.1. Overview

Carbonate clumped isotope thermometry benefits investigations of continental paleoelevation by providing direct measures of surface temperature at the time and site of carbonate mineral precipitation, which, in turn, can help tease apart the contributions of elevation, climate and seasonality to continental $\delta^{18}O_{mw}$ and $T(\Delta_{47})$ records (e.g., Quade et al., 2007). The first improvement is that independent $T(\Delta_{47})$ measures eliminate the need to assume the temperature of carbonate growth, making possible the direct calculation of $\delta^{18}O_{mw}$ from carbonate $\delta^{18}O$ values. A second important advantage of clumped isotope thermometry is that it also provides paleoelevation estimates that are independent of $\delta^{18}O_{mw}$, based on the comparison of carbonate growth temperatures with inferred altitudinal gradients in surface temperature.

Previous workers have used a range of approaches to put these deceptively simple sounding concepts into practice, including:

- ☐ Applying conventional stable isotope paleoelevation approaches using paleo-$\delta^{18}O_{mw}$ values calculated directly from carbonate $T(\Delta_{47})$ and $\delta^{18}O$ values and appropriate carbonate-water fractionation equations (e.g., Carrapa et al., 2014; Ghosh et al., 2006b; Huntington et al., 2014; Leier et al., 2013; Quade et al., 2007, 2011).
- ☐ Integrating $T(\Delta_{47})$ data from analogous modern and ancient environments/carbonate systems to isolate respective influences of topographic and climatic change to $T(\Delta_{47})$ records (e.g., Huntington et al., 2010, 2014).
- ☐ Comparing carbonate $T(\Delta_{47})$ values at a known low paleoelevation, or near-sea-level, location with $T(\Delta_{47})$ values at a contemporaneous site of unknown paleoelevation, and calculating paleoelevation using an assumed adiabatic lapse rate or surface elevation-temperature gradient (e.g., Carrapa et al., 2014; Fan et al., 2014; Garzione et al., 2014; Huntington et al., 2010; Lechler et al., 2013; Snell et al., 2014).
- ☐ Estimating mean annual air temperature (MAAT) from proxy $T(\Delta_{47})$ using published transfer functions (e.g., Hren and Sheldon, 2012; Quade et al., 2013) and comparing $T(\Delta_{47})$-derived MAAT estimates with climate station data and GCM output (e.g., Garzione et al., 2014) and/or contemporaneous proxy MAAT estimates derived from independent (e.g., paleobotanical, MBT/CBT branched tetraether) methods (e.g., Lechler et al., 2013).
- ☐ Interpreting measured $T(\Delta_{47})$ and calculated $\delta^{18}O_{mw}$ values in the context of regional or global atmospheric models that simulate paleoclimate-topography scenarios (e.g., Leier et al., 2013).

In the following subsections we highlight examples from the Andes, western North America, and Tibet that showcase a range of sampling strategies and approaches for reconstructing paleoelevation using T(Δ_{47}) data. The examples illustrate the importance of evaluating (1) the influence of both topography and climate on surface temperatures and $\delta^{18}O_{mw}$ values, (2) the fidelity of the proxy based on analyses of modern carbonates, and (3) the method of translating carbonate temperature estimates into paleoelevation estimates, and provide insight into the mechanisms responsible for the rise of high topography.

3.2.2. Strategies for reconstructing paleoelevation: proof-of concept studies

The first clumped isotope paleoelevation investigations in the Andes and Colorado Plateau mapped out the basic "solution space" of sampling strategies for subsequent applications. Adapting the strategies of previous paleobotanical and stable isotopic paleoelevation studies, they quantified paleoelevation differences or changes through time, using either changes in T(Δ_{47}) and $\delta^{18}O_{mw}$ documented at a single site through time (Ghosh et al., 2006b) or comparison of T(Δ_{47}) at contemporaneous sites of known near-sea-level and unknown paleoelevation (Huntington et al., 2010).

Ghosh et al. (2006b) recognized that in some areas the effects of elevation and climate change can be discriminated based on the correlation between T(Δ_{47}) and $\delta^{18}O_{mw}$ values in a suite of related samples. They collected a chronosequence of Miocene pedogenic (i.e., formed in the soil) calcite from the Altiplano of the Bolivian Andes (Fig. 3a) and found that the pattern of T(Δ_{47}) and $\delta^{18}O_{mw}$ values inferred from clumped isotope analysis of the Miocene samples parallels the temperature versus $\delta^{18}O_{mw}$ trend observed along a modern elevation transect (Fig. 3b). Changes in variables other than elevation would result in an oblique T(Δ_{47}) versus $\delta^{18}O_{mw}$ trend (Fig. 3c), supporting the authors' interpretation that the observed decrease in both T(Δ_{47}) and $\delta^{18}O_{mw}$ values with time primarily reflects surface uplift over the sampled interval. The creative approach used by Ghosh et al. (2006b) and refined by Quade et al. (2007) illustrates the power of combining carbonate $\delta^{18}O$ and T(Δ_{47}) data to constrain paleoelevation—provided both surface temperature and $\delta^{18}O$ values of meteoric waters in the region of interest are sensitive to elevation.

However, $\delta^{18}O$ values are not good proxies for elevation in some regions of interest, a limitation Huntington et al. (2010) circumvented by distinguishing changes in climate and elevation using Δ_{47} temperature records alone. In the arid southwestern USA, evaporative ^{18}O enrichment prevented $\delta^{18}O$-based paleoelevation reconstructions of the Colorado Plateau. Instead, Huntington et al. (2010) based their estimates on measured T(Δ_{47}) values of Miocene–Pliocene lacustrine carbonates from the ~2 km-elevation plateau surface and adjacent near-sea-level lowlands, as well as modern lacustrine carbonates from a range of elevations in the region (Fig. 3d). The T(Δ_{47}) values for middle Miocene samples from the plateau surface record significantly warmer T(Δ_{47}) values than modern carbonates from similar elevations. If the warmer plateau paleotemperatures reflected deposition at low elevation prior to plateau uplift, paleotemperatures of contemporaneous plateau and lowland samples should be similar (Fig. 3e). Instead, the T(Δ_{47}) values for ancient lowland samples are warmer than the ancient plateau samples, and warmer than modern carbonates collected at low elevation today (Fig. 3f). Huntington et al. (2010) observed indistinguishable Miocene–Pliocene and modern carbonate temperature-elevation gradients, which they interpreted to indicate that topographic gradients changed little over this interval, suggesting Late Cenozoic cooling rather than plateau uplift was responsible for the warm middle Miocene T(Δ_{47}) values.

As well as providing a framework for more recent T(Δ_{47}) studies of paleoelevation, these initial studies hinted at the complexities of clumped isotope proxy interpretation and paleoelevation reconstruction. Both Ghosh et al. (2006b) and Huntington et al. (2010) examined the potential for diagenetic alteration of depositional isotopic values in their samples—an important issue that led to follow-up work on related sample suites (Eiler, 2007; Huntington et al., 2011) and that we discuss at length in Section 4. Ghosh et al. (2006b) acknowledged the potential for systematic errors due to bias toward an extreme of the seasonal variability in temperature, and the pairing of ancient and modern

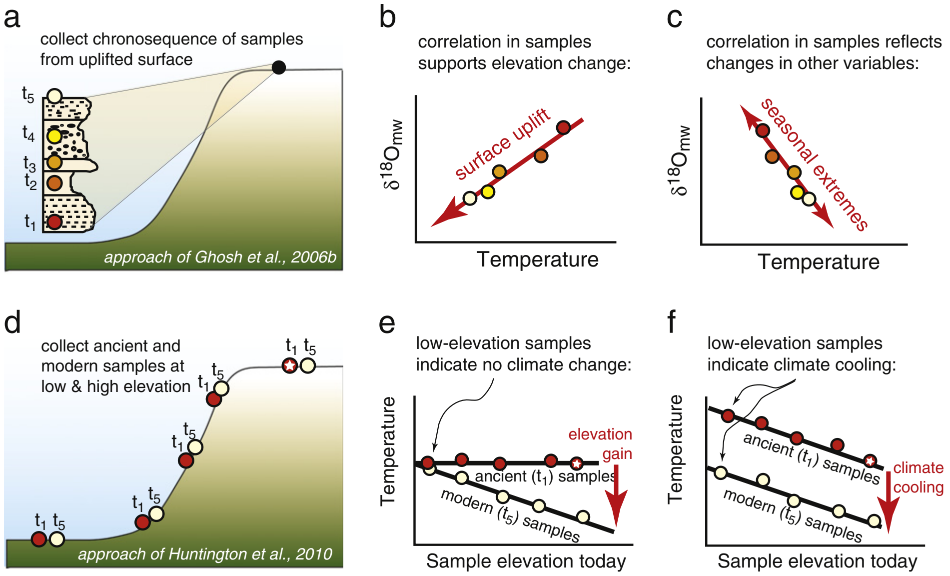

Fig. 3. Sampling strategies for reconstructing paleoelevation from clumped isotope thermometry data. (a) Ghosh et al. (2006b) collected a chronosequence of Miocene pedogenic carbonate samples from the Andean Altiplano in Bolivia. The authors compared paleosol temperatures and $\delta^{18}O$ values of soil waters inferred from clumped isotope analysis of the samples with modern altitudinal gradients in surface temperature and $\delta^{18}O_{mw}$ to distinguish the potential effects of elevation change versus other variables (i.e., changes in global climate or in the seasonality or amount of precipitation) on the isotopic record. (b) Both T(Δ_{47}) and $\delta^{18}O_{mw}$ values inferred from their samples decrease with time, paralleling the temperature versus $\delta^{18}O_{mw}$ trend observed along a modern elevation transect. (c) Changes in variables other than elevation would result in an orthogonal T(Δ_{47}) versus $\delta^{18}O_{mw}$ trend. (d) Huntington et al. (2010) investigated the uplift history of the Colorado Plateau by collecting Miocene–Pliocene lacustrine carbonates from the plateau surface and adjacent lowlands, as well as modern lacustrine carbonates from a range of elevations in the region. The authors found T(Δ_{47}) values for Late-Miocene samples from the plateau surface (~2 km a.s.l.) were significantly warmer than T(Δ_{47}) values for modern carbonates collected at similar elevations. (e) If the warmer paleotemperatures reflected deposition at low elevation prior to plateau uplift, similar paleotemperatures would be observed for the ancient lowland samples. (f) However, T(Δ_{47}) values for ancient lowland samples are also warmer than modern carbonates collected at similar elevations, suggesting Late Cenozoic cooling, not uplift is responsible for the temperature-elevation patterns.

lacustrine carbonate T(Δ_{47}) analyses in the study of Huntington et al. (2010) demonstrated a seasonal bias in lake carbonate formation and the need to understand modern systems in order to reliably interpret ancient T(Δ_{47}) records. The possibility that soil and lacustrine carbonate does not grow evenly throughout the year has important implications for paleoelevation (and terrestrial paleoclimate) studies.

3.2.3. Relating carbonate formation temperature to earth surface temperature

For any T(Δ_{47})-based paleoelevation (or paleoclimate) study, one must consider what it takes for carbonate to form in the relevant terrestrial environment (e.g., lake or soil) and how the processes of carbonate formation impact the relationship between proxy T(Δ47) and environment variables (such as MAAT, lake or soil temperatures) in these settings. Studies of modern carbonates and the environments in which they form elucidate such relationships and highlight the tendency for carbonate formation to be seasonally dependent (e.g., Hough et al., 2014; Huntington et al., 2010; Peters et al., 2013; Quade et al., 2013). As shown by the general reaction describing carbonate (calcite) precipitation (to the right) and weathering (to the left):

$$Ca^{+2}(aq) + 2HCO^{-}{}_{3}(aq) = CaCO_3(s) + CO_2(g) + H_2O \qquad (1)$$

carbonate formation is driven by evaporation and CO_2 degassing, both of which vary seasonally in lakes and soils. Since CO_2 solubility decreases at higher temperatures, carbonate formation also is favored by seasonal increases in soil and lake water temperature. In addition, the pH of the lake water or soil solution is a factor, and in general increasing pH (basic) promotes carbonate precipitation. In many earth surface environments, carbonate formation is likely concentrated when conditions are warm, evaporation is high, and CO_2 concentrations are reduced due to changes in photosynthetic activity.

In lakes, carbonate saturation conditions are most commonly met in the epilimnion (near surface water) photic zone during the warm half of the year. During the spring to fall, evaporative water loss and near-surface water temperatures are high, and algal blooms reduce pCO_2, increase pH and provide nucleation sites for growth of abiotic microcrystalline carbonate (micrite) (Dean and Megard, 1993; Duston et al., 1986; Effler and Johnson, 1987). The few clumped isotope data of Huntington et al. (2010), who analyzed modern carbonate from five lakes in the southwestern USA, give empirical evidence that bias toward warm season carbonate precipitation is in fact common for abiotic lake calcite. For different reasons, lacustrine aquatic snails from Tibet also appear to be biased toward warm-season shell aragonite growth (Huntington et al., 2014). This preliminary evidence of a warm season bias for both biogenic and abiogenic lake carbonate precipitation helps guide interpretations of lacustrine T(Δ_{47}) records. However, biogenic and abiogenic stromatolite microfabrics may grow under disparate lake conditions (Frantz et al., 2014). Additional systematic study is needed to confirm these trends and to assess how lake carbonate seasonality varies for different proxy materials in different physiographic and climatic settings (e.g., Mitsunaga et al., 2014).

More extensive calibration work has been performed in soils, showing warm season bias in most settings. By comparing the stable isotopic compositions of soil CO_2, soil water and modern pedogenic carbonate in New Mexico, Breecker et al. (2009) showed that carbonate formation conditions occur when soils are warm and dry. Initial clumped isotope thermometry observations of Passey et al. (2010) suggested a similar warm season bias in most settings. Later studies presented empirical evidence that pedogenic carbonates can be up to 10–15 °C warmer than mean annual air temperatures as a result of radiative solar heating effects and seasonality of carbonate growth, which commonly occurs during the warmest summer months (e.g., Burgener et al., 2013; Hough et al., 2014; Quade et al., 2013). Argentinian soils that receive extended warm-season precipitation are the exception, showing that pedogenic carbonate growth can occur at other times of the year (i.e., late fall) depending on when soil drying occurs (Peters et al., 2013).

Workers have used this basic understanding of carbonate proxy seasonality to reduce uncertainties in paleoelevation reconstructions by accounting for systematic offsets between T(Δ_{47}) and mean annual air temperature. In the case of lacustrine carbonates, Hren and Sheldon (2012) provided context for this exercise by documenting the relationship between seasonal air and lake water temperatures. Using a compilation of modern monitoring data from around the world, they produced transfer functions for calculating MAAT from mean annual or seasonal average lake surface water temperatures (Hren and Sheldon, 2012). Lechler et al. (2013) used these functions to estimate MAAT for Paleocene–Eocene lacustrine basins in the proto-Basin and Range for which T(Δ_{47}) values were measured, assuming different seasonal periods of lacustrine carbonate growth. Converting lacustrine carbonate T(Δ_{47}) to MAAT allows for direct comparison with published MAAT estimates obtained from other proxy records (Lechler et al., 2013). Garzione et al. (2014) used a similar T(Δ_{47})-to-MAAT conversion for paleosol carbonates (equation of Quade et al., 2013) to add new constraints on the Miocene surface uplift history of the Central Andes Altiplano of South America. Huntington et al. (2014) integrated this MAAT-transfer function approach with modern calibrations of gastropod-lake water temperature relationships to estimate Late Miocene–Pliocene elevation change on the southwestern Tibetan Plateau.

3.2.4. Converting surface temperature estimates to paleoelevation estimates

Proxy Δ_{47} values provide a direct measure not of paleoelevation, but of carbonate formation temperature—it is from temperature *differences* that (paleo)elevation difference or change through time can be quantified, assuming the appropriate surface temperature-elevation gradient can be estimated. For such T(Δ_{47}) differences to be interpreted in terms of (paleo)elevation, proxy T(Δ_{47}) should be compared to equivalent measures of surface temperatures (i.e., an 'apples-to-apples' comparison). The most simple apples-to-apples approach is to compare T(Δ_{47}) records from similar materials (e.g., pedogenic carbonate nodules). But the ability to translate T(Δ_{47}) from carbonate proxies into convenient climate variables like MAAT affords the opportunity to compare clumped isotope records with MAAT records derived from paleobotanical, MBT/CBT branched tetraether, and other methods.

While estimating temperature differences is simple in theory, in practice it is easier said than done, and recent studies illustrate how reasonable choices of reference temperature can lead to vastly different paleoelevation estimates interpreted from equivalent T(Δ_{47}) data. For example, Lechler et al. (2013) and Snell et al. (2014) obtained equivalent T(Δ_{47}) values for lacustrine carbonates of the Late Cretaceous–Eocene Sheep Pass Basin of east-central Nevada, an encouraging result suggesting a high degree of interlaboratory consistency. However, Lechler et al. (2013) compared T(Δ_{47})-derived Sheep Pass Basin MAAT with published MAAT estimates for the near-sea-level Eocene northern Sierra Nevada region derived from other proxy records (Fricke and Wing, 2004; Hren et al., 2010; Yapp, 2008), whereas Snell et al. (2014) used significantly warmer low-elevation paleosol T(Δ_{47}) values from central Utah for comparison. This difference in choice of low-elevation reference temperature resulted in calculated Sheep Pass Basin paleoelevations that differ by as much as 2 km between the two studies. In southwestern Tibet, Wang et al. (2013) and Huntington et al. (2014) obtained similar T(Δ_{47}) for aragonitic gastropod shells from the Zhada Basin. Wang et al. (2013) compared mid-Pliocene carbonate T(Δ_{47}) directly to modern MAAT, whereas Huntington et al. (2014) used measurements of modern gastropod shell T(Δ_{47}) and modern lake water temperatures to inform paleoelevation interpretations of Late Miocene–Pliocene lacustrine gastropod T(Δ_{47}). The difference in approach resulted in paleoelevation calculations that vary by up to 2 km despite equivalent ancient T(Δ_{47}) values.

In some instances, reference paleotemperatures from these and other proxy records are difficult to interpret or do not exist. A potential workaround is to interpret T(Δ_{47}) data in the context of paleoclimate-topography models that predict MAAT, precipitation seasonality (which may be an indicator of potential carbonate growth seasonality), and precipitation δ^{18}O values during the paleoclimate interval of interest. Leier et al. (2013) integrated climate model output (Insel et al., 2012; Poulsen and Jeffery, 2011) with $\delta^{18}O_{mw}$ estimates derived from clumped isotope analysis to infer multiple pulses of rapid surface uplift of the Central Bolivian Andes during the Neogene, and the success of this approach presents a viable method that should be considered for future paleoelevation studies.

3.2.5. Implications for continental dynamics

Advances in paleoelevation research have been made possible by incorporating carbonate clumped isotope thermometry into the research toolkit, improving understanding of continental dynamics in the western US Cordillera, Andes and Tibet.

Several studies have shed light on the mechanisms responsible for the rise and support of high topography in the western US Cordillera. The Colorado Plateau is an icon of the North American Southwest that has motivated over a century of debate regarding the geomorphic, tectonic and geodynamic processes that shape landscapes, but until recently constraints on its elevation history remained sparse and controversial (e.g., Pederson et al., 2002; Poulson and John, 2003). The clumped isotope data of Huntington et al. (2010) appear to rule out significant elevation gain or loss of the southwestern plateau since ~16 Ma. The inferred early (pre-middle Miocene) plateau uplift is consistent with paleorelief constraints for the southwestern plateau (e.g., Flowers and Farley, 2012; Flowers et al., 2008; Young, 1999) and favors explanations for topographic development including crustal thickening by lateral flow of deep crust (McQuarrie and Chase, 2000), hydration of the mantle lithosphere accompanying Laramide flat slab subduction (Humphreys et al., 2003), and/or dynamic topography associated with slab removal (Liu and Gurnis, 2010). Some of these mechanisms, specifically dynamic effects of Farallon slab removal, may also explain recent clumped isotope-derived interpretations of high mean topography in the Central Rockies during Eocene time (Fan et al., 2014). Even coarse constraints on the timing and magnitude of elevation change in the Basin and Range province provide important information about the region's geodynamic evolution. The T(Δ_{47})-derived interpretations from Lechler et al. (2013) indicate low-moderate paleoelevations, comparable to modern, in the pre-extensional Death Valley-domain of the central Basin and Range. These observations require that mass was not conserved in the extending lithospheric column during Middle Miocene-to-present extension of the region and imply that a compensation mechanism of synextensional magmatic addition likely played a major role in the geodynamic evolution of the region. Although interpretations of the pre-Miocene paleoelevation history for the adjacent northern Basin and Range remain equivocal at present (Lechler et al., 2013; Snell et al., 2014), T(Δ_{47}) paleoelevation methods are among the most promising ways to investigate the existence of a proto-Basin and Range orogenic plateau in the early Paleogene western US Cordilleran interior.

Extensive data in South America point to spatial variability in the timing of Andes-Altiplano surface uplift and provide new constraints on the protracted history of crust-upper mantle interactions in the Nazca subduction zone. Initial estimates of rapid late Miocene surface uplift of the north-central Altiplano in Bolivia provided by Ghosh et al. (2006b) and refined by Quade et al. (2007) could be explained by gravitational loss of dense lower crust and/or lithosphere (Eiler, 2007; Garzione et al., 2008; Ghosh et al., 2006b), consistent with the patterns of crustal thickening in the region (Elger et al., 2005; McQuarrie, 2002). The study of Leier et al. (2013) in the Eastern Cordillera to the northeast suggests multiple pulses of rapid surface uplift that do not correlate with the timing of upper crustal deformation. Far to the south in NW Argentina, Carrapa et al. (2014) suggest that the Puna Plateau likely attained its present height earlier than the Altiplano, and that the history of surface uplift in the Eastern Cordillera correlates with active shortening. Taken together with the extensive middle to late Miocene record of Garzione et al. (2014) for the southern Altiplano/Eastern Cordillera, clumped isotope studies in the region suggest that rapid surface uplift progressed from south to north, potentially caused by piecemeal lithospheric delamination or lower crustal flow (Garzione et al., 2014).

In contrast, T(Δ_{47}) paleoelevation study in the Himalayan–Tibetan Plateau system has been relatively limited. Quade et al. (2011) used insight from modern lacustrine and pedogenic carbonate clumped isotope temperatures in Tibet to recalculate $\delta^{18}O_{mw}$ values and $\delta^{18}O_{mw}$-based paleoelevation estimates, and suggest that much of Tibet attained its modern elevation by the mid-Eocene. The data are sparse, but may be consistent with high elevation inherited from orogeny prior to Indo-Asian collision (e.g., Kapp et al., 2007; Murphy et al., 1997; Volkmer et al., 2007). In the Zhada basin in southwestern Tibet, Huntington et al. (2014) added to the gastropod shell δ^{18}O dataset of Saylor et al. (2009) and T(Δ_{47}) dataset of Wang et al. (2013) to derive independent estimates of paleoelevation based on the temperature difference between modern and Miocene–Pliocene shells and on revised paleo-$\delta^{18}O_{mw}$ values. Both estimates call for a higher-than-modern southwestern Tibetan Plateau during the Late Miocene consistent with the $\delta^{18}O_{mw}$-based estimate of Saylor et al. (2009), and the authors suggest subsequent elevation loss probably related to local expression of east–west extension across much of the southern Tibetan Plateau at this time (Huntington et al., 2014). As discussed in Section 4, attempts at T(Δ_{47}) paleoaltimetry in the Nima basin in central Tibet failed due to diagenetic alteration (Huntington et al., 2014). Nevertheless, the presence of terrestrial carbonate proxies of desirable age and setting in this region make this a viable prospect for future T(Δ_{47}) studies.

4. Clumped isotope thermometry of carbonates altered or formed in the sub-surface

Post-depositional modification of clumping can confound efforts to reconstruct paleoelevation using paleotemperature and paleowater δ^{18}O values, but clumped isotope thermometry of samples altered or formed in the sub-surface can also provide new insights into diagenetic processes and fluid–rock interactions. Primary clumped isotope values can be altered either by solid-state C–O bond reordering or by dissolution and re-precipitation of the carbonate. Alteration may not modify the bulk isotopic composition of the sample or cause changes in sample mineralogy and texture, making it difficult to identify altered samples. Nevertheless, in some cases T(Δ_{47}) and δ^{18}O data for altered samples can be interpreted in the context of models that predict bond reordering as a function of a sample's thermal history or describe the isotopic evolution of water–rock systems under different diagenetic conditions. In other cases, T(Δ_{47}) and δ^{18}O values record conditions of carbonate formation in the sub-surface—accessing a critical temperature range for studying the influence of tectonics and structures on fluid flow and the thermal evolution of the shallow crust.

4.1. Previous constraints on the thermal and diagenetic histories of carbonates in the shallow crust

Although the shallow crust makes up a volumetrically tiny portion of our planet, it is disproportionately important as host to economic resources and records of climate and tectonic processes. Both the preservation of these records and the evolution of hydrocarbons, mineral deposits, aquifers and geothermal reservoirs depend on the thermal and diagenetic histories of rocks and fluids in this realm. Diagenesis refers to the chemical, biological or physical (e.g., mineralogical and textural) alteration of sediments, not only during lithification but also during deeper burial at temperatures up to ~300 °C and pressures less than those required for metamorphism (e.g., Milliken, 2003). Post-depositional alteration of authigenic carbonate can modify a sample's bulk stable and/or clumped isotopic composition, potentially erasing any useful information about the original depositional environment or paleoelevation—a long-standing problem in paleoenvironmental reconstruction from isotopic proxies (e.g., Brand and Veizer, 1980; Marshall, 1992). Diagenesis also plays an important role in the thermal and chemical evolution of basins (e.g., Morad et al., 2000) and fault systems (e.g., Laubach et al., 2010) and merits study in its own right—both for tectonics research (e.g., Eichhubl et al., 2004) and for a wide range of applications including subsurface carbon sequestration (e.g., Dockrill and Shipton, 2010), hydraulic fracturing (e.g., Cosgrove, 2001; Lee and Yasuhara, 2013) and hydrocarbon exploration (e.g., Olson et al., 2009).

Of particular concern to paleoaltimetry (and paleoclimate) studies is the diagenetic alteration of depositional carbonate stable isotopic compositions. Diagenetic alteration of carbonate $\delta^{18}O$ and $\delta^{13}C$ values can occur by mineral dissolution–reprecipitation or diffusional mass exchange with pore water or other phases (Brand and Veizer, 1980; Land, 1967; Schroeder, 1969). Recrystallization and cementation occur at or near earth-surface conditions during compaction and lithification of sediments (Bathurst, 1975), for example during the transformation of lime mud into limestone, and can continue after lithification during deeper burial. Open-system mineral recrystallization involves exchange of carbon and oxygen among the mineral, water and dissolved inorganic carbon species, which can cause changes in bulk isotopic composition and may be accompanied by changes in mineralogy, fabric, structure or the chemical distribution of minor and trace elements. This exchange also results in reordering of the carbonate clumped isotopic composition to reflect ambient conditions at the time and place of recrystallization (e.g., Huntington et al., 2011; Suarez and Passey, 2014). In the absence of recrystallization or diffusional mass exchange with co-existing phases, carbonate $\delta^{18}O$ and $\delta^{13}C$ values are not altered, but C–O bond reordering can still occur; at elevated temperatures (> ~100 °C), bond ordering is susceptible to modification by diffusion of carbon and oxygen through the solid mineral lattice (e.g., Bergmann, 2013; Dennis and Schrag, 2010; Ghosh et al., 2006a; Passey and Henkes, 2012).

Many approaches have been developed to identify diagenetic alteration of authigenic carbonate. For example, thin section inspection using petrographic and cathodoluminescence microscopy is commonly used to distinguish obvious secondary phases of carbonate from dense micrite, which is typically interpreted to be primary (e.g., Budd et al., 2002; Driese and Mora, 1993; Snell et al., 2013, 2014; Wieder and Yaalon, 1982). Such textural changes as well as mineralogical and chemical changes that accompany dissolution and re-precipitation of an original carbonate assemblage can be identified by petrographic or scanning electron microscopy (SEM); X-ray diffraction (XRD) and other methods sensitive to mineralogical changes (e.g., from aragonite to calcite, or from high-Mg calcite to low-Mg calcite); and measurements of minor and trace element variations (e.g., Brand and Veizer, 1980; Machel and Burton, 1991; Solomon and Walkden, 1985). Patterns of carbonate $\delta^{18}O$ and $\delta^{13}C$ values have also been used to screen for alteration, based on the idea that homogenization of isotopes in initially heterogeneous phases or structures would be expected if the carbon and oxygen bulk isotopic compositions of samples had been diagenetically altered since original deposition. This logic has been used to argue for excellent isotopic preservation of shell growth layers that exhibit inter-annual and seasonal variations in δ values (Ivany and Runnegar, 2010) and samples that pass an 'isotopic conglomerate test' of initially heterogeneous pedogenic carbonate and recycled marine limestone clasts (Leier et al., 2009). However, such approaches are imperfect indicators of sample recrystallization (e.g., Cummins et al., 2014; Cusack et al., 2008; Huntington et al., 2014; Pérez-Huerta et al., 2014) and remain insensitive to solid-state reordering.

These methods to assess sample preservation as well as a variety of temperature proxies also give insight into diagenetic processes, fluid flow and the origin of carbonates formed in sub-surface environments. Temperature constraints in basin evolution and diagenesis studies can be given by low-temperature thermochronometry (e.g., Farley, 2002; Gleadow et al., 1986; Green et al., 2004; Wolf et al., 1996), fluid-inclusion microthermometry (Goldstein, 2001), oxygen isotope thermometry of co-precipitating phases (Richards et al., 2005; Sharp and Kirschner, 1994), vitrinite reflectance (Barker and Pawlewicz, 1986) or other organic maturation indices (Tissot et al., 1987). However, few of these proxies provide information on shallow crustal conditions with sensitivity to temperature alone, and others are not applicable (e.g., thermochronology) or complicated to apply (fluid inclusion microthermometry) in carbonates. As a consequence, the difficulty of obtaining thermodynamically based mineral crystallization temperatures and thermal history constraints from carbonates presents a challenge to many basin evolution, diagenesis and structural geology investigations that are relevant to continental tectonics research.

4.2. Shallow crustal investigations using carbonate clumped isotope thermometry

4.2.1. Overview

Recent studies show that the ability to constrain both temperature and fluid $\delta^{18}O$ values using Δ_{47} data can shed light on processes of sample alteration relevant to paleoenvironmental reconstruction, and provide new constraints on basin thermal and diagenetic histories relevant to questions in continental tectonics. Nearly all clumped isotope studies of paleoelevation and paleoclimate address the possibility of diagenetic alteration to some degree, but published studies that seek to screen for or explain alteration of depositional T(Δ_{47}) values in detail or study sub-surface processes using clumped isotope thermometry are relatively limited. Published clumped isotopes research in these areas has focused on:

☐ Detailed screening for or study of the alteration of authigenic carbonate (e.g., Came et al., 2007; Douglas et al., 2014; Eiler et al., 2006; Huntington et al., 2011; Snell et al., 2013, 2014; VanDeVelde et al., 2013) and bioapatite (Eagle et al., 2010, 2011; Suarez and Passey, 2014) using a variety of approaches including Δ_{47} data.

☐ Experiments to recrystallize or reorder calcite at high temperature (Ghosh et al., 2006a; Henkes et al., 2014; Passey and Henkes, 2012; Stolper and Eiler, in revision).

☐ Analyses of high-temperature natural carbonates including regionally metamorphosed calcite and dolomite marbles (e.g., Eiler, 2007; Ferry et al., 2011; Ghosh et al., 2006a), carbonitites (Dennis and Schrag, 2010; Stolper and Eiler, in revision) and hydrothermal vein calcite (Bristow et al., 2011), with Δ_{47} values that may reflect "blocking" temperatures or metamorphic events.

☐ Experiments to quantify the Arrhenius behavior of C–O bond reordering in carbonate minerals (Henkes et al., 2014; Passey and Henkes, 2012; Stolper and Eiler, in revision).

☐ Interactions of geologic structures, fluid flow and cementation (Bergman et al., 2013; Budd et al., 2013; Swanson et al., 2012) and the evolution of basin fluid and temperature conditions recorded by concretion formation (Dale et al., 2014; Loyd et al., 2012, 2014).

☐ Δ_{47} constraints on subsurface water–rock reaction processes (Ferry et al., 2011; Huntington et al., 2011, 2014), low-temperature serpentinization and carbonation (Streit et al., 2012) or dolomitization (Sena et al., 2014).

☐ Modeling Δ_{47} values as a function of thermal history (Henkes et al., 2014; Huntington et al., 2014; Passey and Henkes, 2012; Shenton et al., 2015; Stolper and Eiler, in revision).

Previous reviews by Eiler (2007, 2011) give perspectives on behaviors of the carbonate clumped isotope thermometer and on the value

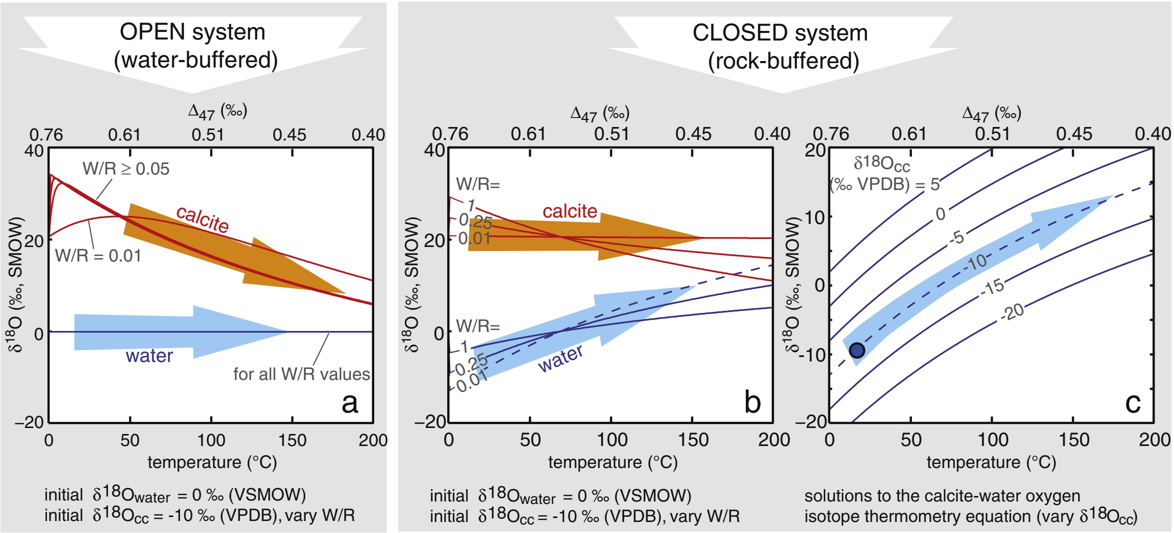

Fig. 4. Predictions of the isotopic evolution of water-calcite systems during open and closed system diagenesis at temperatures of 0–200 °C. Oxygen isotopic values for calcite and water are calculated using the methods of Banner and Hanson (1990) for open (water-buffered) and closed (rock-buffered) diagenetic scenarios in panels (a) and (b), respectively. The models assume a constant initial water $\delta^{18}O$ value of 0‰ (VSMOW) and an initial calcite $\delta^{18}O$ value of −10‰ (VPDB), and contours show solutions for different values of the water-to-rock ratio (W/R). Note that for the scenario shown in panel (a), because the water is replaced at each step of the reaction in the model, the effective water-to-rock ratio is much higher than indicated by W/R. Blue and orange arrows show how the modeled relationship between temperature and the $\delta^{18}O$ values of pore water and diagenetic calcite, respectively, vary between a water-buffered and rock-buffered system. The dashed blue line in (b) corresponds to the dashed blue line in (c). (c) Solutions to the calcite-water thermometry equation of Kim and O'Neil (1997) are shown for calcite (cc) $\delta^{18}O$ values of −20 to 5‰ (VPDB). In a dominantly rock-buffered diagenetic system, the depositional $\delta^{18}O_{cc}$ value (blue circle) remains unchanged while pore water $\delta^{18}O$ values and temperature increase (blue arrow).

of Δ_{47} constraints on the temperature and oxygen-isotopic composition of calcite and water during burial diagenesis and early metamorphism (e.g., Figs. 3 and 5 in Eiler, 2011). We build on these perspectives to discuss calcite-water stable isotope systematics and solid-state C–O bond reordering during burial diagenesis, and highlight recent applications of clumped isotope data to quantify the conditions and duration of fluid flow, diagenetic reactions and thermal histories in the shallow crust.

4.2.2. Changes in T(Δ_{47}) and $\delta^{18}O$ during diagenesis and subsurface water–rock interaction

Clumped isotope-based temperature estimates can provide straightforward constraints on conditions of diagenesis that are not possible using conventional oxygen isotope values alone. Whereas the $\delta^{18}O$ value of a carbonate mineral can be consistent with a wide range of physical environments and water sources (e.g., Eiler, 2011), due to the limited temperature range (~0–40 °C) in which carbonates precipitate at earth's surface, higher T(Δ_{47}) values provide a simple and direct indicator that authigenic carbonate has been subject to post-depositional alteration. Many applied studies have used clumped isotope temperatures or relationships between T(Δ_{47}) and burial depth or sample texture to evaluate the likelihood of alteration (e.g., Came et al., 2007; Carrapa et al., 2014; Eiler et al., 2006; Huntington et al., 2010, 2014; Lechler et al., 2013; Quade et al., 2015). For instance, T(Δ_{47}) values well in excess of plausible earth-surface temperatures have confounded paleoelevation reconstruction in studies of the Westwater Formation of the Colorado Plateau (Huntington et al., 2010), Goler Formation of the Basin and Range (Lechler et al., 2013), Nima basin of central Tibet (Huntington et al., 2014), and Angastaco Basin (Carrapa et al., 2014) and Yacoraite Formation (Quade et al., 2015) of Argentina. In other cases, high T(Δ_{47}) values enable new interpretations. For example, Bristow et al. (2011) observed extremely high T(Δ_{47}) values for Marinoan ‘snowball Earth’ cap carbonates of south China that point to a post-depositional hydrothermal origin for ^{13}C-depleted calcites, ruling out previously proposed calcite deposition in equilibrium with sea water linked to methane oxidation (e.g., Kennedy et al., 2001), and instead supporting reduced anaerobic oxidation of methane in Precambrian oceans. When interpreted together, the combination of T(Δ_{47}) and $\delta^{18}O$ data can provide even better leverage for describing the isotopic evolution and diagenetic conditions of subsurface water–rock systems.

The extent to which bulk stable isotope values are altered during dissolution/recrystallization depends on the conditions of water–rock reaction in the diagenetic environment. Fig. 4 illustrates how changes in the $\delta^{18}O$ value of the water and calcite that accompany changes in temperature can be modeled using the method of Banner and Hanson (1990). In an open system, continuous addition of water buffers the oxygen isotope budget of the rock and co-existing pore water (Fig. 4a). Therefore during burial or hydrothermal heating, the isotopic composition of the pore water reflects the source of the fluid circulating through the rock (a constant source $\delta^{18}O$ composition is shown in the example in Fig. 4a). In a rock subject to open-system diagenesis, the $\delta^{18}O$ values of precipitating calcite evolve as the calcite temperature increases and Δ_{47} value decreases (e.g., Fig. 4a), such that carbonate $\delta^{18}O$ values taken alone or interpreted together with T(Δ_{47}) values can indicate alteration. In the other end-member scenario of a closed, rock-buffered system with low water-to-rock ratio, the $\delta^{18}O$ value of the water increases with increasing temperature while the $\delta^{18}O$ value of the carbonate remains constant (Fig. 4b,c). This lack of variation in carbonate $\delta^{18}O$ values can make recrystallization difficult to detect on the basis of carbonate oxygen isotopic compositions alone in rocks that undergo rock-buffered diagenesis (e.g., Cummins et al., 2014).

In contrast, clumped isotope constraints on changes in the $\delta^{18}O$ values of calcite and co-existing water that accompany changes in temperature can indicate the conditions of alteration for both closed and open-system diagenesis. The evolution of calcite and pore-water $\delta^{18}O$ values with temperature is sensitive to the relative water-to-rock ratio (e.g., Fig. 4b) and the bulk isotopic compositional difference between the calcite and the water. Huntington et al. (2011) exploited this sensitivity by combining T(Δ_{47}) and $\delta^{18}O$ data and modeling with petrographic observations of early Eocene limestones from the Colorado plateau to explain the history of calcite precipitation and replacement via early lithification and later alteration associated with emplacement of a nearby lava flow in the late Miocene. But for many applications, end-member diagenetic behavior can be evaluated simply by plotting clumped isotope temperatures versus calculated $\delta^{18}O$ values of water for a suite of related samples on a contour plot showing solutions to the calcite-water oxygen isotope thermometry equations for constant carbonate $\delta^{18}O$ values; if closed-system reordering is responsible for the elevated clumped isotope temperatures, $T(\Delta_{47})$ is expected to increase along contours of constant $\delta^{18}O$ of carbonate (Fig. 4c).

Workers have used the combination of carbonate temperature and fluid $\delta^{18}O$ constraints in a wide range of applied studies. Ferry et al. (2011) used this approach to suggest that calcite associated with the Latemar carbonate buildup in the Dolomites of Italy formed from seawater and experienced later closed-system alteration during dolomitization. Plots of $T(\Delta_{47})$ vs. $\delta^{18}O$ were combined with petrographic screening of dolomitic paleosols from the Paleocene–Eocene boundary in Utah by VanDeVelde et al. (2013) to identify primary nodules that record warm soil paleotemperatures and heightened aridity. In other studies, $T(\Delta_{47})$ vs. $\delta^{18}O$ water data support interpretations of closed-system alteration in continental settings (e.g., Henkes et al., 2014; Huntington et al., 2014). In Oman, the combination of paleo-water temperature and $\delta^{18}O$ constraints shed light on low-temperature dolomitization and weathering. Sena et al. (2014) studied Lower Cretaceous shallow-water limestones from Oman, using $T(\Delta_{47})$ and $\delta^{18}O$ water values and other evidence to suggest early formation of dolomite affected by evaporated seawater and subsequent re-equilibration with fluids in a shallow burial setting. Alteration of the Samail Ophiolite, Oman, was shown to have occurred in a near-surface weathering environment by Streit et al. (2012) on the basis of carbonate vein $T(\Delta_{47})$ and $\delta^{18}O$ values consistent with precipitation from groundwater. These examples illustrate the potential for clumped isotope thermometry to impact tectonics research by providing insight into the alteration of carbonates deposited at earth's surface and the burial histories of basins.

4.2.3. Impact of thermal history on solid-state reordering of ^{13}C–^{18}O bonds

Carbonate Δ_{47} values are more susceptible to alteration than bulk carbon and oxygen isotopic compositions, both during recrystallization and in the absence of recrystallization due to thermally activated diffusive C–O bond reordering. However, it is difficult to predict the behavior of C–O bond ordering under geologically relevant diagenetic conditions using extrapolations of high temperature experiment-derived C and O diffusion coefficients (Anderson, 1969, 1972; Farver, 1994; Kronenberg et al., 1984; Labotka et al., 2004). Clumped isotope analysis of natural carbonates gets around this difficulty and provides first-order constraints on the temperature dependence of carbon and oxygen diffusion rates in carbonates. Measurements of marbles metamorphosed at ~500 °C and carbonatites cooled from temperatures of ~650 °C yield clumped isotope temperatures of ca. 100–300 °C, with the higher $T(\Delta_{47})$ values corresponding to the more rapidly cooled samples (Dennis and Schrag, 2010; Ghosh et al., 2006a). These observations show that diffusion of C and O atoms within the carbonate lattice can be sufficiently rapid over million-year timescales at elevated temperatures (typically >100 °C) to modify Δ_{47} values, and that the longer a sample resides at high temperature the more rearranging of ^{13}C–^{18}O bonds can occur.

Passey and Henkes (2012) and Henkes et al. (2014) made the first attempts to quantify this temperature sensitivity of clumped isotope reordering rates experimentally. They heated calcites with relatively high original Δ_{47} values to study order–disorder kinetics and observed a rapid initial change in Δ_{47} values followed by a slower change with progressive heating. Proposing a defect-annealing model to explain the initial rapid change in Δ_{47} values, they used the experimental results to constrain Arrhenius parameters describing the relationship between temperature and reaction progress over geologically relevant

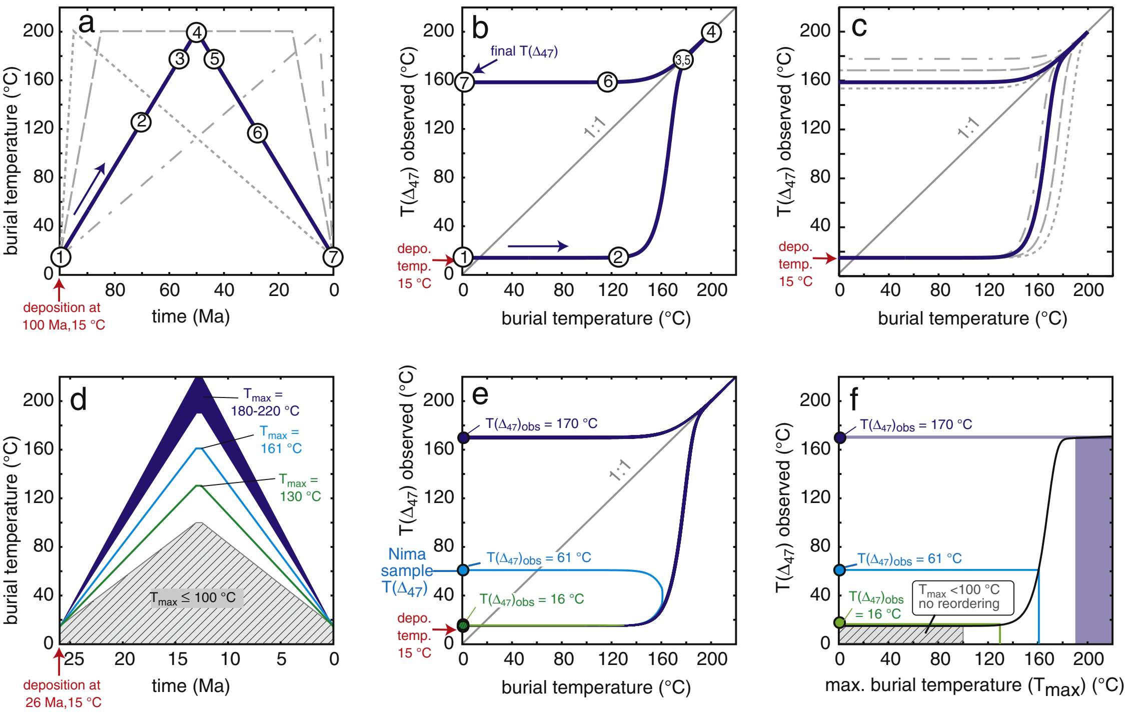

Fig. 5. Impact of thermal history on diffusive C–O bond reordering and $T(\Delta_{47})$ values in calcite. Panels (b, c, e, f) show solutions to the first-order reordering model of Henkes et al. (2014) for the thermal histories shown in (a) and (d). The purple curves in panels (a) and (b) are modified after the schematic in Fig. 5 of Henkes et al. (2014). After an initial period of heating during which the depositional $T(\Delta_{47})$ value remains unchanged (points 1 to 2), reordering commences and the sample $T(\Delta_{47})$ value begins to approach the ambient temperature of the burial environment (points 2 to 3). Once $T(\Delta_{47})$ reaches equilibrium with ambient temperature it continues to match ambient temperature above this threshold (points 3 to 4) and during retrograde cooling (points 4 to 5) following the 1:1 line. As the sample cools further the rate of reordering slows (points 5 to 6) and then effectively ceases (points 6 to 7), at which point the mineral "locks in" a final apparent $T(\Delta_{47})$ value. Gray dashed lines in (a) show variations on the purple temperature-time path, with the corresponding impact on the $T(\Delta_{47})$-burial temperature trajectory (c). Panels (d–f) show a subset of the scenarios modeled by Huntington et al. (2014) for the Nima basin, Tibet, constrained by the depositional age (26 Ma) of the carbonate and an assumed depositional temperature of 15 °C. See text for explanation. All solutions were calculated using the Arrhenius parameters for WACB13 (Henkes et al., 2014).

timescales. Using an elegant analogy to conventional solid-state diffusion studies in the field of thermochronology, Passey and Henkes (2012) developed an analytical solution for apparent equilibrium temperature analogous to Dodson's (1973) closure temperature equation. Unlike closure during cooling of a thermochronometer system that was previously open to the diffusive loss of radiogenic isotope decay products (i.e., daughter isotopes) via volume diffusion (e.g., Hodges, 2003), systems relevant to the reordering reaction:

$$Ca^{13}C^{16}O_3 + Ca^{12}C^{18}O^{16}O_2 \rightleftharpoons Ca^{13}C^{18}O^{16}O_2 + Ca^{13}C^{16}O_3 \qquad (2)$$

remain closed throughout the cooling process; nevertheless, both processes can be reasonably described by a first-order rate law given by a linear Arrhenius relationship between temperature and the log of diffusivity or reaction rate (Henkes et al., 2014; Passey and Henkes, 2012; but c.f. paired “reaction–diffusion” model of Stolper and Eiler, in revision). Arrhenius parameters determined for different calcites combined with a numerical model to predict Δ_{47} values as a function of sample thermal history show that calcite will undergo diffusional C–O bond reordering and associated Δ_{47} change when subjected to temperatures in excess of ~100–120 °C over million-year timescales (Henkes et al., 2014; Passey and Henkes, 2012). The uncertainties are large, but observed Δ_{47} values for marble, hydrothermal calcite and brachiopod calcite from sedimentary basins with independently constrained temperature histories generally agree with modeled Δ_{47} values, suggesting the experimental results are relevant to geologic time and temperature scales (Henkes et al., 2014; Passey and Henkes, 2012). Ongoing experimental work and natural case studies (e.g., Piasecki and Eiler, 2014; Lloyd et al., 2014; Clog et al., 2015; Stolper and Eiler, in revision) aim to better quantify reordering kinetics for calcite and other carbonate minerals.

These studies provide a useful framework for understanding sample alteration and constraining basin thermal histories by modeling Δ_{47} values of carbonates that have undergone solid-state reordering during burial heating and exhumation. Following Henkes et al. (2014), the top panels in Fig. 5 show the model predicted behavior of the Δ_{47} value of a calcite sample that is entirely reset by burial heating. After an initial period of heating during which the depositional $T(\Delta_{47})$ value remains unchanged, reordering commences and the sample $T(\Delta_{47})$ value begins to approach the ambient temperature of the burial environment. Once $T(\Delta_{47})$ reaches equilibrium with ambient temperature it continues to match ambient temperature at all temperatures above this threshold. As the sample cools below this threshold the rate of reordering slows and then effectively ceases, at which point the mineral “locks in” a final apparent $T(\Delta_{47})$ value. As shown in Fig. 5, the rates and threshold temperatures at which reordering commences and ceases depend on the particular sample thermal history. As a consequence, this type of model can be used with Δ_{47} data for samples that did not undergo recrystallization to place new constraints on cooling rates (Passey and Henkes, 2012) and the burial histories of sedimentary basins (Henkes et al., 2014; Shenton et al., 2015).

Model predictions are useful for assessing potential diffusive resetting of $T(\Delta_{47})$ values in paleoelevation and paleoclimate studies. For the model of Henkes et al. (2014), calcite ^{13}C–^{18}O bond reordering and Δ_{47} change is negligible during burial scenarios for which maximum burial temperature is ≤100 °C on the timescale of 10^6–10^8 years. Modeling the effect of likely burial heating scenarios on the Δ_{47} values of samples that may have experienced temperatures above ~100 °C in advance can help avoid wasted clumped isotope analyses. Alternatively, interpreting above-earth-surface temperature clumped isotope data in the context of models can help determine the cause of alteration after the fact. In an attempt to investigate the Neogene paleoelevation history of the Nima Basin in Tibet, Huntington et al. (2014) measured $T(\Delta_{47})$ values of up to 61 °C that are clearly indicative of post-depositional alteration. Constrained by the 26 Ma depositional age of the samples, they used the model of Passey and Henkes (2012) and Henkes et al. (2014) to explore possible temperature-time paths that could have produced the observed final apparent $T(\Delta_{47})$ value (e.g., Fig. 5d–f). Depending on the shape of the temperature-time path (i.e., short or long residence time at the maximum burial temperature, T_{max}), T_{max} of 145 to ~160 °C would be required to reproduce the observations (Fig. 5e, f). Actual maximum burial temperatures in the basin were likely no greater than 75–90 °C, ruling out solid-state reordering and pointing to recrystallization as the cause of the high $T(\Delta_{47})$ values.

This example is useful to illustrate the general behavior of Δ_{47} values for samples heated to a lesser or greater degree. Fig. 5f shows the relative insensitivity of Δ_{47} values to maximum burial temperatures above ~180 °C (for the short residence time burial scenarios in Fig. 5d), as well as the potential for depositional $T(\Delta_{47})$ values to be subtly modified by solid-state reordering at much lower temperatures. In this example, heating to $T_{max} = 130$ °C would cause observed and depositional carbonate temperatures to differ by 1 °C. Hotter temperatures or longer residence times at depth would increase the discrepancy. Clumped isotope temperatures consistent with earth-surface conditions that exhibit no systematic relationship between burial depth and temperature could indicate preservation of original depositional temperatures (e.g., Eiler et al., 2006). However, one takeaway from this exercise is that assessing sample preservation on the basis of $T(\Delta_{47})$ values may not be that straightforward; for a sample with this type of thermal history, a clumped isotope temperature of 30 °C—well within the range of plausible earth-surface temperatures—could reflect diffusive bond reordering in or partial recrystallization of a sample originally deposited at 15 °C. A similar difficulty would be expected if Δ_{47} values change in two distinct steps with heating as predicted by the paired reaction–diffusion model of Stolper and Eiler (in revision); for this model, burial heating to moderate temperatures of ~80–100 °C can cause observed $T(\Delta_{47})$ to increase by a small amount (0–25 °C) and then stabilize for long periods of time. Whether a linear Arrhenius model (Henkes et al., 2014; Passey and Henkes, 2012) or paired reaction–diffusion model (Stolper and Eiler, in revision) applies, a second takeaway is that the sensitivity of Δ_{47} values to temperature and time can be exploited to constrain plausible burial scenarios (e.g., Henkes et al., 2014), making pairing of carbonate $T(\Delta_{47})$ study with conventional thermochronometric approaches (e.g., apatite and zircon (U–Th)/He or fission track dating) an intriguing potential avenue for future research focused on the thermal evolution of basin systems.

4.2.4. Constraints on the conditions of carbonate formation in the sub-surface

Carbonates formed in the sub-surface record a snapshot of the temperature and isotopic composition of the fluids from which they precipitated. Distinct Δ_{47} crystallization temperatures can be preserved for multiple phases of carbonate within the same sample, providing the opportunity to develop detailed histories of temperature and fluid composition (Huntington et al., 2011). Workers have used this feature to assess the preservation of depositional temperatures and isotopic values in specific phases (e.g., Bristow et al., 2011; Csank et al., 2011; Douglas et al., 2014; Huntington et al., 2011; Snell et al., 2013, 2014; VanDeVelde et al., 2013), for example shell material and co-occurring void-filling or vein cement. But the potential is great for such information to provide new insight into the interactions of faults, fractures and fluid flow in basins (e.g., Bergman et al., 2013; Huntington et al., 2011). Compared to reconstructions of earth-surface paleotemperature (Affek, 2012; Eiler, 2011), applications of clumped isotope thermometry to subsurface problems are few to date. Nevertheless, initial attempts to apply clumped isotope thermometry to investigate fault systems and “structural diagenesis” (i.e., the relationship between deformation or deformation structures and chemical alteration of sediments; Laubach et al., 2010) show that the thermometer is sufficiently precise to answer many questions in this area—particularly when it is possible to target well-studied, geologically significant systems for which previous stable isotopic and other work guide sampling and provide hypotheses to be tested using clumped isotope data.

Clumped isotope analyses of fracture- and pore-filling cements and concretions have been used to constrain fault temperatures as well as paleo-fluid sources and pathways. In their study of carbonates in the Mormon Peak detachment fault in southern Nevada, Swanson et al. (2012) attempted to address two long-standing problems in structural geology: the origin of low-angle normal faults (e.g., Axen, 2007) and frictional heating of brittle faults during slip (e.g., Fulton et al., 2010; Scholz, 2002). Clumped isotope data revealed the presence of high-temperature (up to 139 °C) vein-filling carbonates in equilibrium with very low $\delta^{18}O$ value waters; although these results do not provide direct evidence of flash heating, they suggest the veins record deep (3–4 km) circulation of meteoric fluids, ruling out surficial landsliding as the origin of the structure (Swanson et al., 2012). The clumped isotope study of Bergman et al. (2013) targeted the Moab fault in Utah to study the relationship between deformation structures and paleofluid sources and pathways in what is arguably the best-studied brittle fault system in clastic rocks (e.g., Eichhubl et al., 2009; Johansen et al., 2005). Bergman et al. (2013) found cements derived from hot/deeply circulating fluids throughout the entire deformed zone, while cements from cold, meteoric fluids were restricted to highly fractured fault intersections, showing the extraordinary ability of these fault zones to rapidly conduct surface waters to 2 km depth.

Two recent studies have applied clumped isotope thermometry to study cementation in the classic Permian carbonate platform locality of the Guadalupe Mountains of New Mexico and Texas. Budd et al. (2013) combined detailed stratigraphic mapping, cement petrography, fluid inclusion analysis, stable isotopic data and clumped isotope temperatures of 16 to 96 °C to show that syndepositional fracture networks were repeatedly reactivated in younger diagenetic and fluid-flow events involving meteoric water and oil-filled brine. Based on geomechanical modeling of the cement-bearing fracture orientations, Budd et al. (2013) hypothesized that reactivation most likely occurred during Permo-Triassic burial and Miocene Basin and Range extension. Lloyd et al. (2014) analyzed additional calcite spars from the same locality and from a less fractured part of the platform, finding fluid penetration through the less fractured facies and a positive correlation between 30 and 75 °C temperatures and fluid $\delta^{18}O$ values indicating rock-buffered behavior. They interpret low fluid $\delta^{18}O$ values to be meteoric, and proposed that such waters would have infiltrated the basin during Tertiary uplift rather than during burial. Other recent work has shown the potential of concretion $T(\Delta_{47})$ values to understand pore water evolution and alteration of original pore water $\delta^{18}O$ values (Loyd et al., 2012, 2014) and the role of lithologic barriers to fluid flow (Dale et al., 2014).

These early studies show the potential of clumped isotope constraints on diagenesis and paleofluid compositions and temperatures to shed light on the geologic history of rocks and fluid flow in basins related to tectonic, topographic and/or structural events and processes. Considerable effort has gone into understanding the thermal and permeability properties of faults and sedimentary basins, particularly with application to hydrocarbon exploration. Future applications to characterizing oil and natural gas genesis, fossil geothermal reservoirs, mineral resources and crustal deformation could all benefit from quantifying temperatures of carbonate formation in the sub-surface. We expect our discussion of clumped isotope constraints in this area will soon be out-of-date as an abundance of “low-hanging fruit” makes this an excellent target for future study.

5. User's guide to applying carbonate clumped isotope thermometry to problems in continental tectonics

Recent studies have demonstrated the utility of clumped isotope thermometry for constraining the temperature and composition of paleo-fluids in both earth surface and subsurface environments for application to tectonic problems as well as the challenges inherent to the measurement and interpretation of $T(\Delta_{47})$ data. In this section we offer some perspective on the state of the art in carbonate clumped isotope thermometry and recommendations for how to approach applying the method to future investigations in continental tectonics. To design a successful clumped isotope study one must:

☐ select problems for which the precision and accuracy of the method are sufficient to address the research aim
☐ account for analytical limitations to sample size and number of analyses in the experimental design
☐ provide appropriate context for interpreting isotopic data (e.g., to assess sample preservation and homogeneity, evaluate the likelihood of solid-state reordering, understand proxy behavior, etc.)
☐ select the appropriate temperature-Δ_{47} calibration, and account for the impact of calibration uncertainties and other uncertainties on the results and conclusions.

Barring a radical change in analytical methods, $T(\Delta_{47})$ studies will continue to be limited by analytical precision on the order of 0.01‰ (1 s.e.) for a single Δ_{47} sample analysis, which when subjected to n replicate analyses results in a reported 1 s.e. Δ_{47} uncertainty equal to $0.01/\text{sqrt}(n)$‰. In cases where $n \geq 3$, such Δ_{47} uncertainties typically equate to *minimum* 95% temperature uncertainties of ~±2–3 °C. For questions requiring high-precision temperature estimates and/or involving impure carbonate or inhomogeneous materials (e.g., pedogenic carbonate), at least three replicates per sample, and ideally five or more is recommended. Two or three replicates may be sufficient for studies involving pure, homogeneous carbonate (e.g., vein calcite) that require lower precision (i.e., ±10 °C) temperature estimates. In other cases, heroic efforts (i.e., 10–12 replicates per sample) may enable small differences in temperature between closely related materials to be resolved (Thiagarajan et al., 2014).

Analytical time and sample size constraints also impact sampling strategy and project goals. Average mass spectrometer analysis time of ~2.5–3 h per sample limits the number of samples that can be run in a single day to ~10; this number of analyses is routinely achievable for laboratories with automated sample preparation and mass spectrometer inlet systems, but manually operated laboratories are typically limited to half the sample throughput or less. Of these analyses, 10–20% must be carbonate standards and reference CO_2 gases. Sample size requirements (~8 mg carbonate equivalent for most mass spectrometer setups; ≤4 mg for specialized configurations, e.g., Schmid and Bernasconi, 2010; Zaarur et al., 2011) also impact experimental goals and design. For example, high temporal resolution studies common for conventional carbonate stable isotope analysis using micromilling techniques (e.g., Dettman and Lohmann, 1995) may be limited by these sample size requirements.

Taken together, these requirements limit the number of unique samples that can be reasonably analyzed for a given $T(\Delta_{47})$ study. For example, the number of samples in a clumped isotope study is more along the lines of a bedrock thermochronology study (tens of samples) than a detrital zircon U–Pb sampling strategy (hundreds to thousands of grains). Moreover, compared to conventional carbonate stable isotope analysis, for which sample throughput can be an order of magnitude higher, researchers must be far more discriminating when selecting and prioritizing clumped isotope samples. In most applications, this requires preliminary isotopic analysis and screening (e.g., for diagenetic influence and sample context) for the complete sample set prior to selection of sample subsets for Δ_{47} analysis.

Finally, the accuracy of temperature estimates depends on the choice of empirical calibration based on analyses of synthetic or natural carbonates used to convert Δ_{47} values to carbonate growth temperature. Synthetic calibrations vary by method of mineral precipitation and analysis (Fig. 6), and recent workers have suggested that lab-specific carbonate acid digestion methods are responsible for the

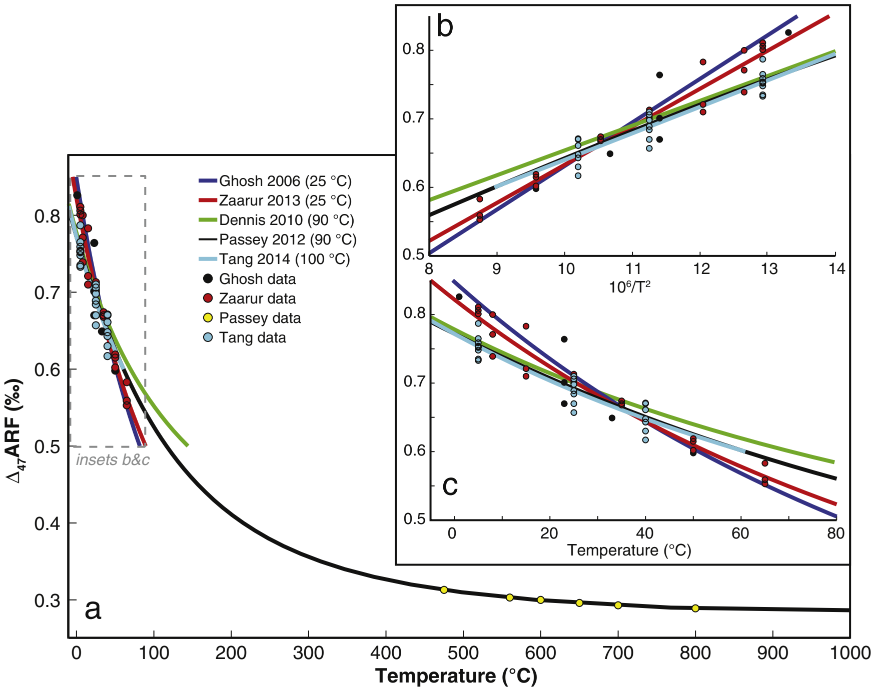

Fig. 6. Compilation of published Δ_{47}-temperature calibrations. (a, b) Calibrations derived from experimental methods using manual, ~8–12 h, 25 °C carbonate-acid digestion (Ghosh et al., 2006a; Zaarur et al., 2013) are characterized by steeper Δ_{47}-T slopes than calibrations derived from automated, ~10 min, 90–100 °C digestions (Dennis et al., 2011; Passey and Henkes, 2012; Tang et al., 2014). The thick solid black line represents the theoretical prediction of temperature-dependent clumping in CO_3 (Δ_{63}; Schauble et al., 2006), adjusted by a constant offset to fit the Δ_{47} measurements made by Passey and Henkes (2012) of CO_2 derived from acid digestion of high-temperature equilibrium reordered calcites; see Passey and Henkes (2012) for details and equation. The black line is in better agreement with calibrations derived from 90 to 100 °C acid digestions than from 25 °C acid digestions. (b) Inset plots show the divergence of low-temperature (<100 °C) calibrations for temperatures outside the 20–30 °C T(Δ_{47}) range ($\Delta_{47} = 0.68$–0.71). All Δ_{47} data and Δ_{47}-T regressions are presented in the absolute reference frame (ARF) of Dennis et al. (2011). See original sources for calibration equations. See text for discussion and Tang et al. (2014) and Came et al. (2014) for similar compilations.

discrepancy (e.g., Came et al., 2014; Tang et al., 2014; Wacker et al., 2014). Manual sample preparation involves acid digestion at 25 °C in reaction vessels where the product CO_2 remains in contact with the acid for ~8–12 h; automated devices perform ~10 minute reactions at 90 °C, with product CO_2 immediately isolated using a cold trap. Acid digestion at different temperatures produces an offset in Δ_{47} values (e.g., Guo et al., 2009) that is accounted for using a constant correction factor (e.g., Defliese et al., 2015; Henkes et al., 2014; Passey et al., 2010; Wacker et al., 2013). However, a discrepancy between the 25 °C and 90 °C reaction calibrations remains (Fig. 6), with 90 °C-reaction calibrations in better general agreement with theoretical calculations (Guo et al., 2009; Schauble et al., 2006). The possibility that different synthetic calcite precipitation methods used in these studies may contribute to calibration differences has not been ruled out (Fernandez et al., 2014; Kelson et al., 2014). In addition, small sample size (4 mg, compared to the more typical ~8 mg) may lead to systematically higher Δ_{47} values for 25 °C reaction methods (Wacker et al., 2013; but c.f. Zaarur et al., 2011). Calibrations for different natural and biogenic carbonates are in general agreement with synthetic calibrations developed using similar analytical methods (e.g., Eiler, 2011), but as discrepancies due to analytical procedures are resolved, subtle differences in calibrations for different materials may prove to be robust.

For now the recommended best practice is to apply the Δ_{47}-T calibration that most closely matches the materials and analytical methods used for a particular study, and to explore how application of different calibrations affects results in order to ensure the most robust interpretation is presented. Published calibrations based on data for synthetic calcites grown at temperatures <100 °C agree in the ~20–30 °C range, which encompasses many surface environments in both the present and past. However, divergence of calibrations below and above this 20–30 °C range (Fig. 6) significantly increases uncertainty for T(Δ_{47}) investigations in cold (e.g., icehouse, high latitude, high elevation) climates and high-temperature subsurface (i.e., diagenetic) environments. Published calibration data for >100 °C calcites are relatively few, but appear consistent with one another. These data include calcites recrystallized or re-equilibrated (i.e., driven to clumped isotope equilibrium) at temperatures of 450–1165 °C (Ghosh et al., 2006a; Guo et al., 2009; Passey and Henkes, 2012; Stolper and Eiler, in revision). A calibration for synthetic dolomite precipitated at temperatures of 25–350 °C has been presented only in abstract form (Bonifacie et al., 2011) but appears consistent with the calcite data (Bristow et al., 2011; Ferry et al., 2011). With multiple independent labs moving toward a common absolute reference frame (Dennis et al., 2011) and working in parallel to investigate calibration gaps and discrepancies, we expect rapid progress in this area.

Since the first Δ_{47}-temperature calibration data were published in 2006, the field has grown to more than a dozen labs worldwide capable of making the extraordinarily high precision measurements required for useful Δ_{47} analysis (Eiler, 2011). Yet carbonate clumped isotope analysis is still not for the casual user—both because of stringent analytical requirements and because of rapid developments in methods of analysis and calibration associated with the novelty of the technique. The development of methods that do not require a specialized mass spectrometer (e.g., 'peak-hopping'; Petrizzo and Young, 2014) and the potential for clumped isotopologue measurements of CO_2 to be made by laser-spectroscopic methods (e.g., Karlovets et al., 2014) may improve access in the future. Until the field matures, clumped isotope studies can be performed in collaboration with an expert and associated lab. The following paragraphs outline strategies for approaching such investigations.

Paleoaltimetry is inherently difficult, and the precision in carbonate growth temperature estimates is at the limit of what is useful for quantitative paleoelevation reconstruction. Thus it is essential to first identify a tractable and important question for which the obtainable temperature resolution is sufficient. Resolvable Δ_{47} temperatures with uncertainties of 2–3 °C are currently the best-case scenario. Accordingly, even in cases for which surface lapse rates, carbonate seasonality, and other factors impacting paleoelevation calculations (Section 3) are known or can be controlled for, many sample replicates are needed. With surface temperature lapse rates of 4–8 °C/km (e.g., Hren and Sheldon, 2012; Meyer, 2007), uncertainties of ±2–3 °C result in minimum paleoelevation uncertainties on the order of ±0.25 to 0.5 km, and more conservatively on the order of ±1 km given inherent uncertainties and variability in carbonate seasonality and setting.

Given the inherent uncertainties, careful experimental design and sample screening can improve the odds of success. It is advisable to: (1) obtain coeval samples (see Snell et al., 2014, for a viable method to correct for cases for which coeval samples are not obtainable), (2) evaluate potential diffusive resetting by modeling C–O bond reordering for different thermal histories and burial scenarios (e.g., Henkes et al., 2014; Huntington et al., 2014), and (3) screen for diagenetic alteration. Even basic screening for diagenesis (i.e., petrographic and CL microscopy of thin sections, mineralogy, and isotopic analysis of apparently primary and secondary phases) can decrease the number of suspect Δ_{47} analyses and increase confidence (but not prove) that samples preserve earth-surface temperatures. It is also important to complement ancient carbonate Δ_{47} study with modern carbonate analysis and monitoring data for analogous modern environments, as well as to integrate independent geologic and environmental information, and climate model output where appropriate. Extracting robust paleoelevation information from Δ_{47} data is non-trivial, but the potential for understanding fundamental tectonic and geodynamic processes makes the task worth the effort.

For many high temperature (>50 °C) applications (e.g., structural diagenesis or basin evolution), lower precision temperature estimates may be sufficient. For example, determining whether vein filling calcite cement precipitated from shallow groundwater at 20 °C or at elevated temperatures of >50 °C may rule out a suite of hypotheses; in such cases precisions of 2–3 °C may be overkill, and since samples consisting of a single generation of vein filling calcite tend to be homogeneous, budgeting for 2–3 replicates per sample would be sufficient for this type of investigation. This replicate advantage counterbalances the current limitations resulting from uncertainty of Δ_{47}-temperature calibrations at high temperatures (Fig. 6). Observed Δ_{47} values for calcites that were reordered at high temperature combined with theoretical predictions provide an initial calibration for high temperature studies (Eq. (5); Passey and Henkes, 2012). We are aware of unpublished data from two laboratories that support use of this or a similar calibration for both calcite and dolomite, but accuracy of high temperature $T(\Delta_{47})$ estimates will remain uncertain until consensus is reached among published calibrations. For studies of metamorphism and basin thermal history, Δ_{47} data do not provide the most sensitive cooling rate constraints (Passey and Henkes, 2012). Nevertheless, clumped isotope data can help refine maximum burial temperature estimates and provide important burial history constraints where other proxy data are lacking (Henkes et al., 2014). For such applications workers should select the Arrhenius parameters for the materials (e.g., optical calcite, Passey and Henkes, 2012; brachiopod calcite, Henkes et al., 2014) that most closely match the studied samples, and explore the sensitivity of Δ_{47} predictions to the choice of parameters and reordering model.

For subsurface investigations, sample context is the key to prioritizing analyses. The likelihood of success is enhanced by sampling strategies that test a specific hypothesis generated from detailed geologic and structural mapping, stable isotopic records, textural, CL, and/or trace element analysis. It is also best to identify representative samples to analyze for clumped isotope compositions based on structural position, texture, and isotopic composition—realizing that Δ_{47} is an independent dimension and may be a more sensitive recorder of environmental change than other analysis types. While still in its early stages, diagenesis and basin history research using Δ_{47} methods is ripe for expansion and will likely prove to be a fruitful endeavor given the importance of accurate diagenetic and burial thermal histories for our understanding of continental basin evolution.

6. Summary and opportunities for continental tectonics research

The field of clumped isotope geochemistry is rapidly evolving and presents a wealth of research opportunities not only for carbonates but for methane (Stolper et al., 2014a,b) and beyond. To date, applications of carbonate clumped isotope thermometry to studies under the umbrella of continental tectonics research have mostly focused on paleoaltimetry, but a handful of recent studies demonstrate the great potential for applications to the shallow crust. These include both better assessment of paleoenvironmental records relevant to paleoelevation and paleoclimate reconstruction, and also understanding of diagenetic processes, subsurface water-rock reactions, basin thermal histories and the influence of deformation structures on fluid pathways.

Challenges associated with relating carbonate $T(\Delta_{47})$ to convenient climate variables like mean annual air temperature and fundamental uncertainties and variability for seasonality of carbonate formation and terrestrial lapse rates limit the accuracy of paleoelevations derived from carbonate $T(\Delta_{47})$ study. As a result, carbonate clumped isotope paleoelevation studies should be complemented by independent paleotemperature and paleoenvironmental datasets as well as relevant climate models whenever possible. In addition, success of clumped isotope paleoelevation studies requires careful evaluation of whether carbonate proxies retain primary (i.e., depositional) stable and clumped isotope signatures or if $T(\Delta_{47})$, $\delta^{13}C$ and/or $\delta^{18}O$ values have been diagenetically altered. Carbonate clumped isotope temperature estimates are currently at the analytical precision limit necessary for quantitative paleoelevation study, but, nevertheless, incorporation of the method into the paleoaltimetry toolkit has enabled workers to address previously intractable problems and in many settings offers the most viable approach to reconstructing paleoelevations from the geologic record.

Future applications of carbonate clumped isotope thermometry for paleoelevation study should target several lines of research, including but not limited to (1) developing robust methods to assess the degree and type of diagenetic influence to carbonate proxies and (2) adding to existing modern field calibrations and datasets in order to improve understanding of how carbonate depositional environment impacts $T(\Delta_{47})$-environment relationships. The latter is complicated but vital for translation of proxy $T(\Delta_{47})$ into paleoelevation estimates. For $T(\Delta_{47})$ paleoaltimetry, the carbonate environments of interest are most commonly soils and lakes. Modern lake systems are an especially good target for future work because of the paucity of existing $T(\Delta_{47})$ data from these settings, in addition to the fact that lake carbonate $\delta^{18}O$ values are commonly evaporatively enriched which makes temperature-based methods more viable than conventional isotopic approaches for reconstructing paleoelevation.

In comparison to relatively well established paleoelevation applications, the field for $T(\Delta_{47})$ subsurface studies is in its early stages. In particular, new understanding of solid-state diffusive C–O bond reordering in calcite in combination with the capability of carbonate ^{13}C–^{18}O clumping to record sub-surface crystallization temperatures opens up new opportunities to examine thermal histories of basins and fluid flow in the shallow crust. Recent work has used carbonate clumped isotope thermometry to explore the thermal histories of faults and basins and the interactions of deformation structures, diagenesis and fluid flow—the sorts of constraints needed to develop predictive models of subsurface carbon sequestration studies and the role of fault sealing processes in maintaining injection reservoir stability. To maximize the potential of these and related subsurface $T(\Delta_{47})$ studies, it is critical to develop (1) a robust high temperature (>100 °C) T-Δ_{47} calibration; (2) a better understanding of C–O bond reordering; and (3) a framework for interpreting $T(\Delta_{47})$ data together with other temperature proxy data commonly incorporated into basin evolution and diagenesis studies (e.g., low-T thermochronometry, fluid-inclusion microthermometry, organic maturation indices and other proxies).

This is an exciting time in carbonate clumped isotope thermometry research. More labs are coming online and contributing new expertise each year. Opportunities for researchers with backgrounds in sedimentology, metamorphic petrology, structural geology, thermochronology and other "staples" of continental tectonics research abound and it will be from integration of these varied backgrounds that new research avenues will emerge and the field will continue to grow and develop. We hope the perspectives presented here serve as a point of departure for tectonicists to embrace new research opportunities applying carbonate clumped isotope thermometry to new and outstanding problems in continental tectonics.

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References

Abbott, L.D., Silver, E.A., Anderson, R.S., Smith, R., Ingle, J.C., Kling, S.A., Haig, D., Small, E., Galewsky, J., Sliter, W.S., 1997. Measurement of tectonic surface uplift rate in a young collisional mountain belt. Nature 385, 501–507.

Affek, H.P., 2012. Clumped isotope paleothermometry: principles, applications, and challenges. In: Ivany, L.C., Huber, B. (Eds.), Reconstructing Earth's Deep-Time Climate — The State of the Art in 2012. Paleontological Society Papers, pp. 101–114.

Affek, H.P., 2013. Clumped isotopic equilibrium and the rate of isotope exchange between CO_2 and water. Am. J. Sci. 313, 309–325.

Affek, H.P., Zaarur, S., 2014. Kinetic isotope effect in CO_2 degassing: Insight from clumped and oxygen isotopes in laboratory precipitation experiments. Geochim. Cosmochim. Acta 143, 319–330.

Affek, H.P., Bar-Matthews, M., Ayalon, A., Matthews, A., Eiler, J.M., 2008. Glacial/interglacial temperature variations in Soreq cave speleothems as recorded by "clumped isotope" thermometry. Geochim. Cosmochim. Acta 72, 5351–5360.

Affek, H.P., Matthews, A., Ayalon, A., Bar-Matthews, M., Burstyn, Y., Zaarur, S., Zilberman, T., 2014. Accounting for kinetic isotope effects in Soreq Cave (Israel) speleothems. Geochim. Cosmochim. Acta 143, 303–318.

Anderson, T.F., 1969. Self-diffusion of carbon and oxygen in calcite by isotope exchange with carbon dioxide. J. Geophys. Res. 74, 3918–3932.

Anderson, T.F., 1972. Self-diffusion of carbon and oxygen in dolomite. J. Geophys. Res. 77, 857–861.

Axelrod, D.I., 1997. Paleoelevation estimated from Tertiary floras. Int. Geol. Rev. 39, 1124–1133.

Axen, G.J., 2007. Research Focus: significance of large-displacement, low-angle normal faults. Geology 35, 287–288. http://dx.doi.org/10.1130/0091-7613(2007)35[287:RFSOLL]2.0.CO;2.

Banner, J.L., Hanson, G.N., 1990. Calculation of simultaneous isotopic and trace element variations during water-rock interaction with applications to carbonate diagenesis. Geochim. Cosmochim. Acta 54, 3123–3137.

Barker, C.E., Pawlewicz, M.J., 1986. The correlation of vitrinite reflectance with maximum temperature in humic organic matter. Paleogeothermics. Springer, pp. 79–93.

Bathurst, R.G., 1975. Carbonate sediments and their diagenesis. 2nd ed. Elsevier, Amsterdam, the Netherlands (657 pp.).

Bergman, S.C., Huntington, K.W., Crider, J.G., 2013. Tracing paleofluid sources using clumped isotope thermometry of diagenetic cements along the Moab Fault Utah. Am. J. Sci. 313, 490–515. http://dx.doi.org/10.2475/05.2013.03.

Bergmann, K.D., 2013. Constraints on the carbon cycle and climate during the early evolution of animals. (Dissertation (Ph.D.)). California Institute of Technology.

Bernasconi, S.M., Hu, B., Wacker, U., Fiebig, J., Breitenbach, S.F., Rutz, T., 2013. Background effects on Faraday collectors in gas-source mass spectrometry and implications for clumped isotope measurements. Rapid Commun. Mass Spectrom. 27, 603–612.

Bigeleisen, J., 1955. Statistical mechanics of isotopic systems with small quantum corrections. 1. General considerations and the rule of the geometric mean. J. Chem. Phys. 23, 2264–2267.

Blard, P.-H., Lavé, J., Pik, R., Quidelleur, X., Bourlès, D., Kieffer, G., 2005. Fossil cosmogenic ^{3}He record from K–Ar dated basaltic flows of Mount Etna volcano (Sicily, 38° N): Evaluation of a new paleoaltimeter. Earth Planet. Sci. Lett. 236, 613–631.

Blisniuk, P.M., Stern, L.A., 2005. Stable isotope paleoaltimetry: a critical review. Am. J. Sci. 305, 1033–1074.

Bondre, N.R., 2003. Analysis of vesicular basalts and lava emplacement processes for application as a paleobarometer/paleoaltimeter: a discussion. J. Geol. 111, 499–502.

Bonifacie, M., Ferry, J., Horita, J., Vasconcelos, C., Passey, B., Eiler, J., 2011. Calibration and applications of the dolomite clumped isotope thermometer to high temperatures. Mineralogical Magazine 75 (3), 551.

Bookhagen, B., Echtler, H.P., Melnick, D., Strecker, M.R., Spencer, J.Q.G., 2006. Using uplifted Holocene beach berms for paleoseismic analysis on the Santa María Island, south-central Chile. Geophys. Res. Lett. 33.

Brand, U., Veizer, J., 1980. Chemical diagenesis of a multicomponent carbonate system-1: trace elements. J. Sediment. Res. 50.

Brand, U., Posenato, R., Came, R., Affek, H., Angiolini, L., Azmy, K., Farabegoli, E., 2012. The end-Permian mass extinction: a rapid volcanic CO_2 and CH_4-climatic catastrophe. Chem. Geol. 322, 121–144.

Brand, U., Came, R.E., Affek, H., Azmy, K., Mooi, R., Layton, K., 2014. Climate-forced change in Hudson Bay seawater composition and temperature, Arctic Canada. Chem. Geol. 388, 78–86.

Breecker, D.O., Sharp, Z.D., McFadden, L.D., 2009. Seasonal bias in the formation and stable isotopic composition of pedogenic carbonate in modern soils from central New Mexico USA. Geol. Soc. Am. Bull. 121, 630–640.

Bristow, T.F., Bonifacie, M., Derkowski, A., Eiler, J.M., Grotzinger, J.P., 2011. A hydrothermal origin for isotopically anomalous cap dolostone cements from south China. Nature 474, 68–71.

Budd, D.A., Pack, S.M., Fogel, M.L., 2002. The destruction of paleoclimatic isotopic signals in Pleistocene carbonate soil nodules of Western Australia. Palaeogeogr. Palaeoclimatol. Palaeoecol. 188, 249–273.

Budd, D.A., Frost, E.L., Huntington, K.W., Allwardt, P.F., 2013. Syndepositional deformation features in high-relief carbonate platforms: long-lived conduits for diagenetic fluids. J. Sediment. Res. 83, 12–36. http://dx.doi.org/10.2110/jsr.2013.3.

Burgener, L.K., Huntington, K.W., Hoke, G.D., Schauer, A.J., Samek, K., 2013. Applications of clumped-isotope thermometry: precipitation season as a control on the timing of pedogenic carbonate growth in the central Andes. AGU Fall Meeting Abstracts.

Came, R.E., Eiler, J.M., Veizer, J., Azmy, K., Brand, U., Weidman, C.R., 2007. Coupling of surface temperatures and atmospheric CO_2 concentrations during the Palaeozoic era. Nature 449, 198–201.

Came, R.E., Brand, U., Affek, H.P., 2014. Clumped isotope signatures in modern brachiopod carbonate. Chem. Geol. 377, 20–30.

Cao, X., Liu, Y., 2012. Theoretical estimation of the equilibrium distribution of clumped isotopes in nature. Geochim. Cosmochim. Acta 77, 292–303.

Carrapa, B., Huntington, K.W., Clementz, M., Quade, J., Schoenbohm, S.B.-R., Lindsay, M., Canavan, R.R., 2014. Uplift of the Central Andes of NW Argentina associated with upper crustal shortening, revealed by multi-proxy isotopic analyses. Tectonics 33. http://dx.doi.org/10.1002/2013TC003461.

Cassel, E.J., Graham, S.A., Chamberlain, C.P., 2009. Cenozoic tectonic and topographic evolution of the northern Sierra Nevada, California, through stable isotope paleoaltimetry in volcanic glass. Geology 37, 547–550.

Cassel, E.J., Breecker, D.O., Henry, C.D., Larson, T.E., Stockli, D.F., 2014. Profile of a paleo-orogen: high topography across the present-day Basin and Range from 40 to 23 Ma. Geology http://dx.doi.org/10.1130/G35924.1.

Chamberlain, C.P., Poage, M.A., Craw, D., Reynolds, R.C., 1999. Topographic development of the Southern Alps recorded by the isotopic composition of authigenic clay minerals, South Island, New Zealand. Chem. Geol. 155, 279–294.

Clark, M.K., House, M.A., Royden, L.H., Whipple, K.X., Burchfiel, B.C., Zhang, X., Tang, W., 2005. Late Cenozoic uplift of southeastern Tibet. Geology 33, 525–528.

Clog, M., Stolper, D., Eiler, J.M., 2015. Kinetics of $CO_{2(g)}$–$H_2O_{(l)}$ isotopic exchange, including mass 47 isotopologues. Chem. Geol. 395, 1–10.

Cosentino, D., Cipollari, P., Di Bella, L., Esposito, A., Faranda, C., Giordano, G., Gliozzi, E., Mattei, M., Mazzini, I., Porreca, M., Funiciello, R., 2009. Tectonics, sea-level changes and palaeoenvironments in the early Pleistocene of Rome (Italy). Quat. Res. 72, 143–155.

Cosgrove, J.W., 2001. Hydraulic fracturing during the formation and deformation of a basin: a factor in the dewatering of low-permeability sediments. AAPG Bull. 85, 737–748.

Craig, H., Gordon, L.I., 1965. Deuterium and oxygen 18 variations in the ocean and the marine atmosphere.

Csank, A.Z., Tripati, A.K., Patterson, W.P., Eagle, R.A., Rybczynski, N., Ballantyne, A.P., Eiler, J.M., 2011. Estimates of Arctic land surface temperatures during the early Pliocene from two novel proxies. Earth Planet. Sci. Lett. 304, 291–299.

Cui, L., Wang, X., 2014. Determination of clumped isotopes in carbonate using isotope ratio mass spectrometer: effects of extraction potential and long-term stability. Int. J. Mass Spectrom. 372, 46–50.

Cummins, R.C., Finnegan, S., Fike, D.A., Eiler, J.M., Fischer, W.W., 2014. Carbonate clumped isotope constraints on Silurian ocean temperature and seawater $\delta^{18}O$. Geochim. Cosmochim. Acta 140, 241–258.

Cusack, M., Pérez-Huerta, A., Janousch, M., Finch, A.A., 2008. Magnesium in the lattice of calcite-shelled brachiopods. Chem. Geol. 257, 59–64.

Daëron, M., Guo, W., Eiler, J., Genty, D., Blamart, D., Boch, R., Drysdale, R., Maire, R., Wainer, K., Zanchetta, G., 2011. ^{13}C ^{18}O clumping in speleothems: observations from natural caves and precipitation experiments. Geochim. Cosmochim. Acta 75, 3303–3317.

Dale, A., John, C.M., Mozley, P.S., Smalley, P.C., Muggeridge, A.H., 2014. Time-capsule concretions: unlocking burial diagenetic processes in the Mancos Shale using carbonate clumped isotopes. Earth Planet. Sci. Lett. 394, 30–37.

Dansgaard, W., 1964. Stable isotopes in precipitation. Tellus 16, 436–468.

Dean, W.E., Megard, R.O., 1993. Environment of deposition of $CaCO_3$ in Elk Lake Minnesota. Geol. Soc. Am. Spec. Pap. 276, 97–114.

Defliese, W.F., Hren, M.T., Lohmann, K.C., 2015. Compositional and temperature effects of phosphoric acid fractionation on D_{47} analysis and implications for discrepant calibrations. Chem. Geol. http://dx.doi.org/10.1016/j.chemgeo.2014.12.018.

Dennis, K.J., Schrag, D.P., 2010. Clumped isotope thermometry of carbonatites as an indicator of diagenetic alteration. Geochim. Cosmochim. Acta 74, 4110–4122.

Dennis, K.J., Affek, H.P., Passey, B.H., Schrag, D.P., Eiler, J.M., 2011. Defining an absolute reference frame for "clumped" isotope studies of CO_2. Geochim. Cosmochim. Acta 75, 7117–7131.

Dennis, K.J., Cochran, J.K., Landman, N.H., Schrag, D.P., 2013. The climate of the Late Cretaceous: new insights from the application of the carbonate clumped isotope thermometer to Western Interior Seaway macrofossil. Earth Planet. Sci. Lett. 362, 51–65.

Dettman, D.L., Lohmann, K.C., 1995. Microsampling carbonates for stable isotope and minor element analysis: physical separation of samples on a 20 micrometer scale. J. Sediment. Res. 65.

Dettman, D.L., Lohmann, K.C., 2000. Oxygen isotope evidence for high-altitude snow in the Laramide Rocky Mountains of North America during the Late Cretaceous and Paleogene. Geology 28, 243–246.

Dockrill, B., Shipton, Z.K., 2010. Structural controls on leakage from a natural CO_2 geologic storage site: Central Utah USA. J. Struct. Geol. 32, 1768–1782.

Dodson, M.H., 1973. Closure temperature in cooling geochronological and petrological systems. Contrib. Mineral. Petrol. 40, 259–274.

Douglas, P.M., Affek, H.P., Ivany, L.C., Houben, A.J., Sijp, W.P., Sluijs, A., Schouten, S., Pagani, M., 2014. Pronounced zonal heterogeneity in Eocene southern high-latitude sea surface temperatures. Proc. Natl. Acad. Sci. 111, 6582–6587.

Driese, S.G., Mora, C.I., 1993. Physico-chemical environment of pedogenic carbonate formation in Devonian vertic palaeosols, central Appalachians, USA. Sedimentology 40, 199–216.

Duston, N.M., Owen, R.M., Wilkinson, B.H., 1986. Water chemistry and sedimentological observations in Littlefield Lake Michigan implications for lacustrine marl deposition. Environ. Geol. Water Sci. 8, 229–236.

Eagle, R.A., Schauble, E.A., Tripati, A.K., Tütken, T., Hulbert, R.C., Eiler, J.M., 2010. Body temperatures of modern and extinct vertebrates from $^{13}C–^{18}O$ bond abundances in bioapatite. Proc. Natl. Acad. Sci. 107, 10377–10382.

Eagle, R.A., Tütken, T., Martin, T.S., Tripati, A.K., Fricke, H.C., Connely, M., Cifelli, R.L., Eiler, J.M., 2011. Dinosaur body temperatures determined from isotopic ($^{13}C–^{18}O$) ordering in fossil biominerals. Science 333, 443–445.

Eagle, R.A., Risi, C., Mitchell, J.L., Eiler, J.M., Seibt, U., Neelin, J.D., Li, G., Tripati, A.K., 2013. High regional climate sensitivity over continental China constrained by glacial-recent changes in temperature and the hydrological cycle. Proc. Natl. Acad. Sci. 110, 8813–8818.

Effler, S.W., Johnson, D.L., 1987. Calcium carbonate precipitation and turbidity in Otisco Lake. Wiley Online Library, New York.

Ehlers, T.A., Poulsen, C.J., 2009. Influence of Andean uplift on climate and paleoaltimetry estimates. Earth Planet. Sci. Lett. 281, 238–248.

Eichhubl, P., Taylor, W.L., Pollard, D.D., Aydin, A., 2004. Paleo-fluid flow and deformation in the Aztec Sandstone at the Valley of Fire, Nevada—evidence for the coupling of hydrogeologic, diagenetic, and tectonic processes. Geol. Soc. Am. Bull. 116, 1120–1136.

Eichhubl, P., Davatz, N.C., Becker, S.P., 2009. Structural and diagenetic control of fluid migration and cementation along the Moab fault, Utah. AAPG Bull. 93 (5), 653–681. http://dx.doi.org/10.1306/02180908080.

Eiler, J.M., 2007. "Clumped-isotope" geochemistry—the study of naturally-occurring, multiply-substituted isotopologues. Earth Planet. Sci. Lett. 262, 309–327.

Eiler, J.M., 2011. Paleoclimate reconstruction using carbonate clumped isotope thermometry. Quat. Sci. Rev. 30, 3575–3588.

Eiler, J.M., 2013. The isotopic anatomies of molecules and minerals. Annu. Rev. Earth Planet. Sci. 41, 411–441.

Eiler, J.M., Schauble, E., 2004. ^{18}O ^{13}C ^{16}O in Earth's atmosphere. Geochim. Cosmochim. Acta 68, 4767–4777.

Eiler, J., Garzione, C., Ghosh, P., 2006. Response to comment on "Rapid Uplift of the Altiplano Revealed Through $^{13}C–^{18}O$ Bonds in Paleosol Carbonates". Science 314, 760c.

Eiler, J.M., Clog, M., Magyar, P., Piasecki, A., Sessions, A., Stolper, D., Deerberg, M., Schlueter, H.-J., Schwieters, J., 2013. A high-resolution gas-source isotope ratio mass spectrometer. Int. J. Mass Spectrom. 335, 45–56.

Eiler, J.M., Bergquist, B., Bourg, I., Cartigny, P., Farquhar, J., Gagnon, A., Guo, W., Halevy, I., Hofmann, A., Larson, T.E., Levin, N., Schauble, E.A., Stolper, D., 2014. Frontiers of stable isotope geoscience. Chem. Geol. 372, 119–143.

Elger, K., Oncken, O., Glodny, J., 2005. Plateau-style accumulation of deformation: southern Altiplano. Tectonics 24.

Epstein, S., Mayeda, T., 1953. Variation of ^{18}O content of waters from natural sources. Geochim. Cosmochim. Acta 4, 213–224.

Fan, M., Hough, B.G., Passey, B.H., 2014. Middle to late Cenozoic cooling and high topography in the central Rocky Mountains: constraints from clumped isotope geochemistry. Earth Planet. Sci. Lett. 408, 35–47.

Farley, K.A., 2002. (U–Th)/He dating: techniques, calibrations, and applications. Rev. Mineral. Geochem. 47, 819–844.

Farver, J.R., 1994. Oxygen self-diffusion in calcite: dependence on temperature and water fugacity. Earth Planet. Sci. Lett. 121, 575–587.

Fernandez, A., Tang, J., Rosenheim, B.E., 2014. Siderite 'clumped' isotope thermometry: A new paleoclimate proxy for humid continental environments. Geochim. Cosmochim. Acta 126, 411–421. http://dx.doi.org/10.1016/j.gca.2013.11.006.

Ferry, J.M., Passey, B.H., Vasconcelos, C., Eiler, J.M., 2011. Formation of dolomite at 40–80 °C in the Latemar carbonate buildup, Dolomites, Italy, from clumped isotope thermometry. Geology 39, 571–574.

Finnegan, S., Bergmann, K., Eiler, J.M., Jones, D.S., Fike, D.A., Eisenman, I., Hughes, N.C., Tripati, A.K., Fischer, W.W., 2011. The magnitude and duration of Late Ordovician–Early Silurian glaciation. Science 331, 903–906.

Flowers, R.M., Farley, K.A., 2012. Apatite $^{4}He/^{3}He$ and (U–Th)/He evidence for an ancient Grand Canyon. Science 338, 1616–1619.

Flowers, R.M., Wernicke, B.P., Farley, K.A., 2008. Unroofing, incision, and uplift history of the southwestern Colorado Plateau from apatite (U–Th)/He thermochronometry. Geol. Soc. Am. Bull. 120, 571–587.

Frantz, C.M., Petryshyn, V.A., Marenco, P.J., Tripati, A., Berelson, W.M., Corsetti, F.A., 2014. Dramatic local environmental change during the Early Eocene Climatic Optimum detected using high resolution chemical analyses of Green River Formation stromatolites. Palaeogeogr. Palaeoclimatol. Palaeoecol. 405, 1–15.

Fricke, H.C., Wing, S.L., 2004. Oxygen isotope and paleobotanical estimates of temperature and $\delta^{18}O$–latitude gradients over North America during the early Eocene. Am. J. Sci. 304, 612–635.

Fulton, P.M., Harris, R.N., Saffer, D.M., Brodsky, E.E., 2010. Does hydrologic circulation mask frictional heat on faults after large earthquakes? J. Geophys. Res. 115, B09402. http://dx.doi.org/10.1029/2009JB007103.

Galewsky, J., 2009. Orographic precipitation isotopic ratios in stratified atmospheric flows: Implications for paleoelevation studies. Geology 37, 791–794.

Garzione, C.N., Dettman, D.L., Quade, J., DeCelles, P.G., Butler, R.F., 2000. High times on the Tibetan Plateau: paleoelevation of the Thakkhola graben, Nepal. Geology 28, 339–342.

Garzione, C.N., Hoke, G.D., Libarkin, J.C., Withers, S., MacFadden, B., Eiler, J., Ghosh, P., Mulch, A., 2008. Rise of the Andes. Science 320, 1304–1307.

Garzione, C.N., Auerbach, D.J., Jin-Sook Smith, J., Rosario, J.J., Passey, B.H., Jordan, T.E., Eiler, J.M., 2014. Clumped isotope evidence for diachronous surface cooling of the Altiplano and pulsed surface uplift of the Central Andes. Earth Planet. Sci. Lett. 393, 173–181.

Ghosh, P., Adkins, J., Affek, H., Balta, B., Guo, W., Schauble, E.A., Schrag, D., Eiler, J.M., 2006a. $^{13}C–^{18}O$ bonds in carbonate minerals: a new kind of paleothermometer. Geochim. Cosmochim. Acta 70, 1439–1456.

Ghosh, P., Garzione, C.N., Eiler, J.M., 2006b. Rapid uplift of the Altiplano revealed through $^{13}C–^{18}O$ bonds in paleosol carbonates. Science 311, 511–515.

Ghosh, P., Eiler, J., Campana, S.E., Feeney, R.F., 2007. Calibration of the carbonate "clumped isotope" paleothermometer for otoliths. Geochim. Cosmochim. Acta 71, 2736–2744.

Gleadow, A.J.W., Duddy, I.R., Green, P.F., Lovering, J.F., 1986. Confined fission track lengths in apatite: a diagnostic tool for thermal history analysis. Contrib. Mineral. Petrol. 94, 405–415.

Goldstein, R.H., 2001. Fluid inclusions in sedimentary and diagenetic systems. Lithos 55, 159–193.

Grauel, A.-L., Schmid, T.W., Hu, B., Bergami, C., Capotondi, L., Zhou, L., Bernasconi, S.M., 2013. Calibration and application of the "clumped isotope" thermometer to foraminifera for high-resolution climate reconstructions. Geochim. Cosmochim. Acta 108, 125–140.

Green, P.F., Crowhurst, P.V., Duddy, I.R., 2004. Integration of AFTA and (U–Th)/He thermochronology to enhance the resolution and precision of thermal history reconstruction in the Anglesea-1 well, Otway Basin, SE Australia. Eastern Australian Basins Symposium II. Petroleum Exploration Society of Australia, Special Publication. Petroleum Exploration Society of Australia, West Perth, pp. 117–131.

Gregory, K.M., Chase, C.G., 1992. Tectonic significance of paleobotanically estimated climate and altitude of the late Eocene erosion surface, Colorado. Geology 20, 581–585.

Gregory-Wodzicki, K.M., 2000. Uplift history of the Central and Northern Andes: a review. Geol. Soc. Am. Bull. 112, 1091–1105.

Gubbels, T.L., Isacks, B.L., Farrar, E., 1993. High-level surfaces, plateau uplift, and foreland development, Bolivian central Andes. Geology 21, 695–698.

Guo, W., Eiler, J.M., 2007. Temperatures of aqueous alteration and evidence for methane generation on the parent bodies of the CM chondrites. Geochim. Cosmochim. Acta 71, 5565–5575.

Guo, W., Mosenfelder, J.L., Goddard III, W.A., Eiler, J.M., 2009. Isotopic fractionations associated with phosphoric acid digestion of carbonate minerals: insights from first-principles theoretical modeling and clumped isotope measurements. Geochim. Cosmochim. Acta 73, 7203–7225.

Halevy, I., Fischer, W.W., Eiler, J.M., 2011. Carbonates in the Martian meteorite Allan Hills 84001 formed at 18 ± 4 ° C in a near-surface aqueous environment. Proc. Natl. Acad. Sci. 108, 16895–16899.

He, B., Olack, G.A., Colman, A.S., 2012. Pressure baseline correction and high-precision CO_2 clumped-isotope (Δ_{47}) measurements in bellows and micro-volume modes. Rapid Commun. Mass Spectrom. 26, 2837–2853.

Henkes, G.A., Passey, B.H., Grossman, E.L., Shenton, B.J., Pérez-Huerta, A., Yancey, T.E., 2014. Temperature limits for preservation of primary calcite clumped isotope paleotemperatures. Geochim. Cosmochim. Acta 139, 362–382.

Hill, P.S., Tripati, A.K., Schauble, E.A., 2014. Theoretical constraints on the effects of pH, salinity, and temperature on clumped isotope signatures of dissolved inorganic carbon species and precipitating carbonate minerals. Geochim. Cosmochim. Acta 125, 610–652.

Hodges, K.V., 2003. Geochronology and thermochronology in orogenic systems. In: Rudnick, R.L. (Ed.), The Crust. Elsevier, New York, pp. 263–292.

Hough, B.G., Fan, M., Passey, B.H., 2014. Calibration of the clumped isotope geothermometer in soil carbonate in Wyoming and Nebraska USA: implications for paleoelevation and paleoclimate reconstruction. Earth Planet. Sci. Lett. 391, 110–120.

Hren, M.T., Sheldon, N.D., 2012. Temporal variations in lake water temperature: paleoenvironmental implications of lake carbonate $\delta^{18}O$ and temperature records. Earth Planet. Sci. Lett. 337, 77–84.

Hren, M.T., Pagani, M., Erwin, D.M., Brandon, M., 2010. Biomarker reconstruction of the early Eocene paleotopography and paleoclimate of the northern Sierra Nevada. Geology 38, 7–10.

Hu, B., Radke, J., Schlüter, H.J., Heine, F.T., Zhou, L., Bernasconi, S.M., 2014. A modified procedure for gas-source isotope ratio mass spectrometry: the long-integration dual-inlet (LIDI) methodology and implications for clumped isotope measurements. Rapid Commun. Mass Spectrom. 28 (13), 1413–1425.

Humphreys, E., Hessler, E., Dueker, K., Farmer, G.L., Erslev, E., Atwater, T., 2003. How Laramide-age hydration of North American lithosphere by the Farallon slab controlled subsequent activity in the western United States. Int. Geol. Rev. 45, 575–595.

Huntington, K.W., Eiler, J.M., Affek, H.P., Guo, W., Bonifacie, M., Yeung, L.Y., Thiagarajan, N., Passey, B., Tripati, A., Daëron, M., et al., 2009. Methods and limitations of “clumped”CO_2 isotope (Δ_{47}) analysis by gas-source isotope ratio mass spectrometry. J. Mass Spectrom. 44, 1318–1329. http://dx.doi.org/10.1002/jms.1614.

Huntington, K.W., Wernicke, B.P., Eiler, J.M., 2010. Influence of climate change and uplift on Colorado Plateau paleotemperatures from carbonate clumped isotope thermometry. Tectonics 29, TC3005. http://dx.doi.org/10.1029/2009TC002449.

Huntington, K.W., Budd, D.A., Wernicke, B.P., Eiler, J.M., 2011. Use of clumped-isotope thermometry to constrain the crystallization temperature of diagenetic calcite. J. Sediment. Res. 81, 656–669.

Huntington, K.W., Saylor, J., Quade, J., Hudson, A.M., 2014. High Late Miocene–Pliocene elevation of the Zhada basin, SW Tibetan plateau, from clumped isotope thermometry. Geol. Soc. Am. Bull. B31000–1. http://dx.doi.org/10.1130/B31000.1.

Insel, N., Poulsen, C.J., Ehlers, T.A., Sturm, C., 2012. Response of meteoric δ^{18}O to surface uplift—implications for Cenozoic Andean Plateau growth. Earth Planet. Sci. Lett. 317, 262–272.

Ivany, L.C., Runnegar, B., 2010. Early Permian seasonality from bivalve δ^{18}O and implications for the oxygen isotopic composition of seawater. Geology 38, 1027–1030.

Jeffery, M.L., Poulsen, C.J., Ehlers, T.A., 2012. Impacts of Cenozoic global cooling, surface uplift, and an inland seaway on South American paleoclimate and precipitation δ^{18}O. Geol. Soc. Am. Bull. 124, 335–351.

Johansen, T.E.S., Fossen, H., Kluge, R., 2005. The impact of syn-faulting porosity reduction on damage zone architecture in porous sandstone; an outcrop example from the Moab Fault, Utah. J. Struct. Geol. 27 (8), 1469–1485. http://dx.doi.org/10.1016/j.jsg.2005.01.014.

Kapp, P., DeCelles, P.G., Gehrels, G.E., Heizler, M., Ding, L., 2007. Geological records of the Lhasa-Qiangtang and Indo-Asian collisions in the Nima area of central Tibet. Geol. Soc. Am. Bull. 119, 917–933.

Karlovets, E.V., Campargue, A., Mondelain, D., Kassi, S., Tashkun, S.A., Perevalov, V.I., 2014. High sensitivity Cavity Ring Down spectroscopy of ^{18}O enriched carbon dioxide between 5850 and 7000 cm^{-1}: part II—analysis and theoretical modeling of the $^{12}C^{18}O_2$, $^{13}C^{18}O_2$ and $^{16}O^{13}C^{18}O$ spectra. J. Quant. Spectrosc. Radiat. Transf. 136, 71–88.

Keating-Bitonti, C.R., Ivany, L.C., Affek, H.P., Douglas, P., Samson, S.D., 2011. Warm, not super-hot, temperatures in the early Eocene subtropics. Geology 39, 771–774.

Kelson, J., Lechler, A.R., Huntington, K., Schauer, A.J., Smith, R., 2014. Influence of dissolved inorganic carbon species equilibrium on clumped isotope values of synthetic calcite. 4th International Workshop on Clumped Isotopes, Zurich Switzerland, p. 4.

Kennedy, M.J., Christie-Blick, N., Sohl, L.E., 2001. Are Proterozoic cap carbonates and isotopic excursions a record of gas hydrate destabilization following Earth's coldest intervals? Geology 29, 443–446.

Kim, S.-T., O'Neil, J.R., 1997. Equilibrium and nonequilibrium oxygen isotope effects in synthetic carbonates. Geochim. Cosmochim. Acta 61, 3461–3475.

Kim, S.-T., O'Neil, J.R., Hillaire-Marcel, C., Mucci, A., 2007. Oxygen isotope fractionation between synthetic aragonite and water: influence of temperature and Mg^{2+} concentration. Geochim. Cosmochim. Acta 71, 4704–4715.

Kluge, T., Affek, H.P., 2012. Quantifying kinetic fractionation in Bunker Cave speleothems using Δ_{47}. Quat. Sci. Rev. 49, 82–94.

Kluge, T., Affek, H.P., Zhang, Y.G., Dublyansky, Y., Spötl, C., Immenhauser, A., Richter, D.K., 2014. Clumped isotope thermometry of cryogenic cave carbonates. Geochim. Cosmochim. Acta 126, 541–554.

Kohn, M.J., 2007. Paleoaltimetry: geochemical and thermodynamic approaches. Mineralogical Society of Amer.

Kronenberg, A.K., Yund, R.A., Giletti, B.J., 1984. Carbon and oxygen diffusion in calcite: effects of Mn content and P H_2O. Phys. Chem. Miner. 11, 101–112.

Labotka, T.C., Cole, D.R., Riciputi, L.R., Fayek, M., 2004. Diffusion of C and O in calcite from 0.1 to 200 MPa. Am. Mineral. 89, 799–806.

Land, L.S., 1967. Diagenesis of skeletal carbonates. J. Sediment. Res. 37.

Laubach, S.E., Eichhubl, P., Hilgers, C., Lander, R.H., 2010. Structural diagenesis. J. Struct. Geol. 32, 1866–1872.

Lawrence, J.R., Rashkes Meaux, J., 1993. The stable isotopic composition of ancient kaolinites of North America. Clim. Chang. Cont. Isot. Rec. 249–261.

Lease, R.O., Ehlers, T.A., 2013. Incision into the Eastern Andean plateau during Pliocene cooling. Science 341, 774–776.

Lechler, A.R., Galewsky, J., 2013. Refining paleoaltimetry reconstructions of the Sierra Nevada, California, using air parcel trajectories. Geology 41, 259–262.

Lechler, A.R., Niemi, N.A., 2011. Controls on the spatial variability of modern meteoric δ^{18}O: empirical constraints from the western US and East Asia and implications for stable isotope studies. Am. J. Sci. 311, 664–700.

Lechler, A.R., Niemi, N.A., Hren, M.T., Lohmann, K.C., 2013. Paleoelevation estimates for the northern and central proto–Basin and Range from carbonate clumped isotope thermometry. Tectonics 32, 295–316.

Lee, D.S., Yasuhara, H., 2013. An evaluation of the effects of fracture diagenesis on hydraulic fracturing treatment. Geosyst. Eng. 16, 113–118.

Leier, A., Quade, J., DeCelles, P., Kapp, P., 2009. Stable isotopic results from paleosol carbonate in South Asia: paleoenvironmental reconstructions and selective alteration. Earth Planet. Sci. Lett. 279, 242–254.

Leier, A., McQuarrie, N., Garzione, C., Eiler, J., 2013. Stable isotope evidence for multiple pulses of rapid surface uplift in the Central Andes Bolivia. Earth Planet. Sci. Lett. 371, 49–58.

Libarkin, J.C., Chase, C.G., 2003. Timing of Colorado Plateau uplift: initial constraints from vesicular basalt-derived paleoelevations: Comment and Reply COMMENT. Geology 31, 191.

Liu, L., Gurnis, M., 2010. Dynamic subsidence and uplift of the Colorado Plateau. Geology 38, 663–666.

Lloyd, M., Eiler, J., Nabelek, P., 2014. Carbonate clumped isotope thermometry of the Notch Peak Contact Metamorphic Aureole. Goldschmidt Abstracts 2014 p. 1502.

Loyd, S.J., Corsetti, F.A., Eiler, J.M., Tripati, A.K., 2012. Determining the diagenetic conditions of concretion formation: assessing temperatures and pore waters using clumped isotopes. J. Sediment. Res. 82, 1006–1016.

Loyd, S.L., Dickson, J.A.D., Boles, J.R., Tripati, A.K., 2014. Clumped-isotope constraints on cement paragenesis in septarian concretions. J. Sediment. Res. 84, 1170–1184. http://dx.doi.org/10.2110/jsr.2014.91.

Ma, Q., Wu, S., Tang, Y., 2008. Formation and abundance of doubly-substituted methane isotopologues ($^{13}CH_3D$) in natural gas systems. Geochim. Cosmochim. Acta 72, 5446–5456. http://dx.doi.org/10.1016/j.gca.2008.08.014.

MacGinitie, H.D., 1953. Fossil plants of the Florissant beds. Carnegie Institution of Washington, Colorado.

Machel, H.G., Burton, E.A., 1991. Causes and spatial distribution of anomalous magnetization in hydrocarbon seepage environments (1). AAPG Bull. 75, 1864–1876.

Marshall, J.D., 1992. Climatic and oceanographic isotopic signals from the carbonate rock record and their preservation. Geol. Mag. 129, 143–160.

McCrea, J.M., 1950. On the isotopic chemistry of carbonates and a paleotemperature scale. J. Chem. Phys. 18, 849–857.

McQuarrie, N., 2002. The kinematic history of the central Andean forld-thrust belt, Bolivia: implications for building a high plateau. Geol. Soc. Am. Bull. 114, 950. http://dx.doi.org/10.1130/0016-7606(2002)1140950:TKHOTC2.0.CP;2.

McQuarrie, N., Chase, C.G., 2000. Raising the Colorado plateau. Geology 28, 91–94.

Meckler, A.N., Adkins, J.F., Eiler, J.M., Cobb, K.M., 2009. Constraints from clumped isotope analyses of a stalagmite on maximum tropical temperature change through the late Pleistocene. Geochim. Cosmochim. Acta 73, A863.

Merritts, D., Bull, W.B., 1989. Interpreting Quaternary uplift rates at the Mendocino triple junction, northern California, from uplifted marine terraces. Geology 17, 1020–1024.

Meyer, H.W., 1992. Lapse rates and other variables applied to estimating paleoaltitudes from fossil floras. Palaeogeogr. Palaeoclimatol. Palaeoecol. 99, 71–99.

Meyer, H.W., 2007. A review of paleotemperature–lapse rate methods for estimating paleoelevation from fossil floras. Rev. Mineral. Geochem. 66, 155–171.

Milliken, K.L., 2003. Late diagenesis and mass transfer in sandstone shale sequences. Treatise Geochem. 7, 159–190.

Mitsunaga, B.A., Mering, J., Petryshyn, V.A., Robert, D., Cohen, A., Liu, X., Kaufman, D.S., Eagle, R., Tripati, A., 2014. A clumped isotope calibration for lacustrine carbonates. Geol. Soc. of Amer. Abstract 209–8.

Mix, H.T., Mulch, A., Kent-Corson, M.L., Chamberlain, C.P., 2011. Cenozoic migration of topography in the North American Cordillera. Geology 39, 87–90.

Morad, S., Ketzer, J.R.M., De Ros, L.F., 2000. Spatial and temporal distribution of diagenetic alterations in siliciclastic rocks: implications for mass transfer in sedimentary basins. Sedimentology 47, 95–120.

Mulch, A., Sarna-Wojcicki, A.M., Perkins, M.E., Chamberlain, C.P., 2008. A Miocene to Pleistocene climate and elevation record of the Sierra Nevada (California). Proc. Natl. Acad. Sci. 105, 6819–6824.

Murphy, M.A., Yin, A., Harrison, T.M., Dürr, S.B., Chen, Z., Ryerson, F.J., Kidd, W.S.F., Wang, X., Zhou, X., 1997. Did the Indo-Asian collision alone create the Tibetan plateau? Geology 25, 719–722.

Olson, J.E., Laubach, S.E., Lander, R.H., 2009. Natural fracture characterization in tight gas sandstones: integrating mechanics and diagenesis. AAPG Bull. 93, 1535–1549.

Ono, S., Wang, D.T., Gruen, D.S., Sherwood Lollar, B., Zahniser, M., McManus, B.J., Nelson, D.D., 2014. Measurement of a doubly-substituted methane isotopologue, $^{13}CH_3D$, by tunable infrared laser direct absorption spectroscopy. Analytical Chemistry 86, 6487–6494. http://dx.doi.org/10.1021/ac5010579.

Passey, B.H., 2012. Reconstructing terrestrial environments using stable isotopes in fossil teeth and paleosol carbonates. In: Ivany, L.C., Huber, B. (Eds.), Reconstructing Earth's Deep-Time Climate — The State of the Art in 2012. Paleontological Society Papers 18, pp. 167–193.

Passey, B.H., Henkes, G.A., 2012. Carbonate clumped isotope bond reordering and geospeedometry. Earth Planet. Sci. Lett. 351, 223–236.

Passey, B.H., Levin, N.E., Cerling, T.E., Brown, F.H., Eiler, J.M., 2010. High-temperature environments of human evolution in East Africa based on bond ordering in paleosol carbonates. Proc. Natl. Acad. Sci. 107, 11245–11249.

Pederson, J.L., Mackley, R.D., Eddleman, J.L., 2002. Colorado Plateau uplift and erosion evaluated using GIS. GSA Today 12, 4–10.

Peppe, D.J., Royer, D.L., Wilf, P., Kowalski, E.A., 2010. Quantification of large uncertainties in fossil leaf paleoaltimetry. Tectonics 29.

Pérez-Huerta, A., Aldridge, A.E., Endo, K., Jeffries, T.E., 2014. Brachiopod shell spiral deviations (SSD): implications for trace element proxies. Chem. Geol. 374, 13–24.

Perg, L.A., Anderson, R.S., Finkel, R.C., 2001. Use of a new ^{10}Be and ^{26}Al inventory method to date marine terraces, Santa Cruz, California, USA. Geology 29, 879–882.

Peters, N.A., Huntington, K.W., Hoke, G.D., 2013. Hot or not? Impact of seasonally variable soil carbonate formation on paleotemperature and O-isotope records from clumped isotope thermometry. Earth Planet. Sci. Lett. 361, 208–218. http://dx.doi.org/10.1016/j.epsl.2012.10.024.

Petrizzo, D.A., Young, E.D., 2014. High-precision determination of ^{13}C–^{18}O bonds in CO_2 using multicollector peak hopping. Rapid Commun. Mass Spectrom. 28, 1185–1193.

Piasecki, A., Eiler, J., 2014. The blocking temperature for ‘clumped’ isotope thermometry in aragonite. Goldschmidt Abstractsp. 1959.

Poage, M.A., Chamberlain, C.P., 2001. Empirical relationships between elevation and the stable isotope composition of precipitation and surface waters: considerations for studies of paleoelevation change. Am. J. Sci. 301, 1–15.

Poage, M.A., Chamberlain, C.P., 2006. Rising mountain ranges. Science 311, 478–479.

Polissar, P.J., Freeman, K.H., Rowley, D.B., McInerney, F.A., Currie, B.S., 2009. Paleoaltimetry of the Tibetan Plateau from D/H ratios of lipid biomarkers. Earth Planet. Sci. Lett. 287, 64–76.

Poulsen, C.J., Jeffery, M.L., 2011. Climate change imprinting on stable isotopic compositions of high-elevation meteoric water cloaks past surface elevations of major orogens. Geology 39, 595–598.

Poulsen, C.J., Ehlers, T.A., Insel, N., 2010. Onset of convective rainfall during gradual late Miocene rise of the central Andes. Science 328, 490–493.

Poulson, S.R., John, B.E., 2003. Stable isotope and trace element geochemistry of the basal Bouse Formation carbonate, southwestern United States: implications for the Pliocene uplift history of the Colorado Plateau. Geol. Soc. Am. Bull. 115, 434–444.

Price, G.D., Passey, B.H., 2013. Dynamic polar climates in a greenhouse world: evidence from clumped isotope thermometry of Early Cretaceous belemnites. Geology 41, 923–926.

Quade, J., Garzione, C., Eiler, J., 2007. Paleoelevation reconstruction using pedogenic carbonates. Rev. Mineral. Geochem. 66, 53–87.

Quade, J., Breecker, D.O., Daëron, M., Eiler, J., 2011. The paleoaltimetry of Tibet: an isotopic perspective. Am. J. Sci. 311, 77–115.

Quade, J., Eiler, J., Daeron, M., Achyuthan, H., 2013. The clumped isotope geothermometer in soil and paleosol carbonate. Geochim. Cosmochim. Acta 105, 92–107.

Quade, J., Dettinger, M., DeCelles, P., Carrapa, B., Huntington, K., Murray, K., 2015. The growth of the Central Andes 22–26°S. In: DeCelles, P.G., Ducea, M., Kapp, P., Carrapa, B. (Eds.), The Geodynamics of a Cordilleran Orogenic System: The Central Andes of Argentina and northern Chile. Geol. Soc. Am. Memoir 212. http://dx.doi.org/10.1130/2015.1212(15) XXX-XXX (in press).

Richards, I.J., Connelly, J.B., Gregory, R.T., Gray, D.R., 2005. The importance of diffusion, advection, and host-rock lithology on vein formation: a stable isotope study from the Paleozoic Ouachita orogenic belt Arkansas and Oklahoma. Geol. Soc. Am. Bull. 114 (11), 1343–1355.

Riihimaki, C.A., Libarkin, J.C., 2007. Terrestrial cosmogenic nuclides as paleoaltimetric proxies. Rev. Mineral. Geochem. 66, 269–278.

Rohrmann, A., Strecker, M.R., Bookhagen, B., Mulch, A., Sachse, D., Pingel, H., Alonso, R.N., Schildgen, T.F., Montero, C., 2014. Can stable isotopes ride out the storms? The role of convection for water isotopes in models, records, and paleoaltimetry studies of the central Andes. Earth Planet. Sci. 407, 187–195. http://dx.doi.org/10.1016/j.epsl.2014.09.021.

Rosenheim, B.E., Tang, J., Fernandez, A., 2013. Measurement of multiply substituted isotopologues ('clumped isotopes') of CO_2 using a 5 kV compact isotope ratio mass spectrometer: performance, reference frame, and carbonate paleothermometry. Rapid Commun. Mass Spectrom. 27, 1847–1857.

Rowley, D.B., 2007. Stable isotope-based paleoaltimetry: theory and validation. Rev. Mineral. Geochem. 66, 23–52.

Rowley, D.B., Currie, B.S., 2006. Palaeo-altimetry of the late Eocene to Miocene Lunpola basin, central Tibet. Nature 439, 677–681.

Rowley, D.B., Garzione, C.N., 2007. Stable isotope-based paleoaltimetry. Annu. Rev. Earth Planet. Sci. 35, 463–508.

Rowley, D.B., Pierrehumbert, R.T., Currie, B.S., 2001. A new approach to stable isotope-based paleoaltimetry: implications for paleoaltimetry and paleohypsometry of the High Himalaya since the Late Miocene. Earth Planet. Sci. Lett. 188, 253–268.

Saenger, C., Affek, H.P., Felis, T., Thiagarajan, N., Lough, J.M., Holcomb, M., 2012. Carbonate clumped isotope variability in shallow water corals: temperature dependence and growth-related vital effects. Geochim. Cosmochim. Acta 99, 224–242.

Sahagian, D., Proussevitch, A., 2007. Paleoelevation measurement on the basis of vesicular basalts. Rev. Mineral. Geochem. 66, 195–213.

Sahagian, D., Proussevitch, A., Carlson, W., 2002. Timing of Colorado Plateau uplift: initial constraints from vesicular basalt-derived paleoelevations. Geology 30, 807–810.

Sahagian, D., Proussevitch, A., Carlson, W., 2003a. Analysis of vesicular basalts and lava emplacement processes for application as a paleobarometer/paleoaltimeter: a reply. J. Geol. 111, 502–504.

Sahagian, D., Proussevitch, A., Carlson, W., 2003b. Reply. Geology 31, 192.

Santrock, J., Studley, S.A., Hayes, J.M., 1985. Isotopic analyses based on the mass spectra of carbon dioxide. Anal. Chem. 57, 1444–1448.

Saylor, J.E., Quade, J., Dettman, D.L., DeCelles, P.G., Kapp, P.A., Ding, L., 2009. The late Miocene through present paleoelevation history of southwestern Tibet. Am. J. Sci. 309, 1–42.

Schauble, E.A., Ghosh, P., Eiler, J.M., 2006. Preferential formation of ^{13}C–^{18}O bonds in carbonate minerals, estimated using first-principles lattice dynamics. Geochim. Cosmochim. Acta 70, 2510–2529.

Schildgen, T.F., Hodges, K.V., Whipple, K.X., Reiners, P.W., Pringle, M.S., 2007. Uplift of the western margin of the Andean plateau revealed from canyon incision history, southern Peru. Geology 35, 523–526.

Schildgen, T.F., Cosentino, D., Bookhagen, B., Niedermann, S., Yıldırım, C., Echtler, H., Wittmann, H., Strecker, M.R., 2012. Multi-phased uplift of the southern margin of the Central Anatolian plateau Turkey: a record of tectonic and upper mantle processes. Earth Planet. Sci. Lett. 317, 85–95.

Schmid, T.W., Bernasconi, S.M., 2010. An automated method for "clumped-isotope" measurements on small carbonate samples. Rapid Commun. Mass Spectrom. 24, 1955–1963.

Scholz, C.H., 2002. The mechanics of earthquakes and faulting. 2nd ed. Cambridge Univ. Press, Cambridge, U.K. (471 pp.).

Schroeder, J.H., 1969. Experimental dissolution of calcium, magnesium, and strontium from recent biogenic carbonates: a model of diagenesis. J. Sediment. Res. 39.

Sena, C.N.H., John, C.M., Jourdan, A.L., Vandeginste, V., Manning, C., 2014. Dolomitization of Lower Cretaceous peritidal carbonates by modified seawater: constraints from clumped isotope paleothermometry, elemental chemistry and strontium isotopes. J. Sed. Res. 84, 552–566. http://dx.doi.org/10.2110/jsr.2014.45.

Sharp, Z.D., Kirschner, D.L., 1994. Quartz-calcite oxygen isotope thermometry: a calibration based on natural isotopic variations. Geochim. Cosmochim. Acta 58, 4491–4501.

Shenton, B.J., Grossman, E.L., Passey, B.H., Henkes, G.A., Becker, T.P., Laya, J.C., Perez-Huerta, A., Becker, S.P., Lawson, M., 2015. Clumped isotope thermometry in deeply buried sedimentary carbonates: The effects of bond reordering and recrystallization. Geol. Soc. Amer. Bull. http://dx.doi.org/10.1130/B31169.1.

Snell, K.E., Thrasher, B.L., Eiler, J.M., Koch, P.L., Sloan, L.C., Tabor, N.J., 2013. Hot summers in the Bighorn Basin during the early Paleogene. Geology 41, 55–58.

Snell, K.E., Koch, P.L., Druschke, P., Foreman, B.Z., Eiler, J.M., 2014. High elevation of the "Nevadaplano" during the Late Cretaceous. Earth Planet. Sci. Lett. 386, 52–63.

Solomon, S.T., Walkden, G.M., 1985. The application of cathodoluminescence to interpreting the diagenesis of an ancient calcrete profile. Sedimentology 32, 877–896.

Spicer, R.A., Yang, J., 2010. Quantification of uncertainties in fossil leaf paleoaltimetry: does leaf size matter? Tectonics 29, 1–13.

Spicer, R.A., Harris, N.B., Widdowson, M., Herman, A.B., Guo, S., Valdes, P.J., Wolfe, J.A., Kelley, S.P., 2003. Constant elevation of southern Tibet over the past 15 million years. Nature 421, 622–624.

Stolper, D.A., Eiler, J.M., 2015. The kinetics of solid-state isotope-exchange reactions for clumped isotopes in carbonates: a study of inorganic calcites and apatites from natural and experimental samples. American Journal of Science (in revision).

Stolper, D.A., Lawson, M., Davis, C.L., Ferreira, A.A., Santos Neto, E.V., Ellis, G.S., Lewan, M.D., Martini, A.M., Tang, Y., Schoell, M., Sessions, A.L., Eiler, J.M., 2014a. Formation temperatures of thermogenic and biogenic methane. Science 344, 1500–1503.

Stolper, D.A., Sessions, A.L., Ferreira, A.A., Santos Neto, E.V., Schimmelmann, A., Shusta, S.S., Valentine, D.L., Eiler, J.M., 2014b. Combined ^{13}C–D and D–D clumping in methane: methods and preliminary results. Geochim. Cosmochim. Acta 126, 169–191.

Streit, E., Kelemen, P., Eiler, J., 2012. Coexisting serpentine and quartz from carbonate-bearing serpentinized peridotite in the Samail Ophiolite Oman. Contrib. Mineral. Petrol. 164, 821–837.

Suarez, M.B., Passey, B.H., 2014. Assessment of the clumped isotope composition of fossil bone carbonate as a recorder of subsurface temperatures. Geochim. Cosmochim. Acta. 140, 142–159.

Suarez, M.B., Passey, B.H., Kaakinen, A., 2011. Paleosol carbonate multiple isotopologue signature of active East Asian summer monsoons during the late Miocene and Pliocene. Geology 39, 1151–1154.

Swanson, E.M., Wernicke, B.P., Eiler, J.M., Losh, S., 2012. Temperatures and fluids on faults based on carbonate clumped–isotope thermometry. Am. J. Sci. 312, 1–21.

Tang, J., Dietzel, M., Fernandez, A., Tripati, A.K., Rosenheim, B.E., 2014. Evaluation of kinetic effects on clumped isotope fractionation (Δ_{47}) during inorganic calcite precipitation. Geochim. Cosmochim. Acta 134, 120–136.

Thiagarajan, N., Adkins, J., Eiler, J., 2011. Carbonate clumped isotope thermometry of deep-sea corals and implications for vital effects. Geochim. Cosmochim. Acta 75, 4416–4425.

Thiagarajan, N., Subhas, A.V., Southon, J.R., Eiler, J.M., Adkins, J.F., 2014. Abrupt pre-Bolling-Allerod warming and circulation changes in the deep ocean. Nature 511, 75–78.

Tissot, B.P., Pelet, R., Ungerer, P.H., 1987. Thermal history of sedimentary basins, maturation indices, and kinetics of oil and gas generation. AAPG Bull. 71, 1445–1466.

Tobin, T.S., Wilson, G.P., Eiler, J.M., Hartman, J.H., 2014. Environmental change across a terrestrial Cretaceous–Paleogene boundary section in eastern Montana, USA, constrained by carbonate clumped isotope paleothermometry. Geology 42, 351–354.

Tripati, A.K., Eagle, R.A., Thiagarajan, N., Gagnon, A.C., Bauch, H., Halloran, P.R., Eiler, J.M., 2010. ^{13}C–^{18}O isotope signatures and "clumped isotope" thermometry in foraminifera and coccoliths. Geochim. Cosmochim. Acta 74, 5697–5717.

Tsuji, K., Teshima, H., Sasada, H., Yoshida, N., 2012. Spectroscopic isotope ratio measurement of doubly-substituted methane. Spectrochim. Acta A Mol. Biomol. Spectrosc. 98, 43–46.

Urey, H.C., 1947. The thermodynamic properties of isotopic substances. J. Chem. Soc. 562–581.

VanDeVelde, J.H., Bowen, G.J., Passey, B.H., Bowen, B.B., 2013. Climatic and diagenetic signals in the stable isotope geochemistry of dolomitic paleosols spanning the Paleocene–Eocene boundary. Geochim. Cosmochim. Acta 109, 254–267.

Volkmer, J.E., Kapp, P., Guynn, J.H., Lai, Q., 2007. Cretaceous–Tertiary structural evolution of the north central Lhasa terrane, Tibet. Tectonics 26.

Wacker, U., Fiebig, J., Schoene, B.R., 2013. Clumped isotope analysis of carbonates: comparison of two different acid digestion techniques. Rapid Commun. Mass Spectrom. 27, 1631–1642.

Wacker, U., Fiebig, J., Tödter, J., Schöne, B.R., Bahr, A., Friedrich, O., Tütken, T., Gischler, E., Joachimski, M.M., 2014. Empirical calibration of the clumped isotope paleothermometer using calcites of various origins. Geochim. Cosmochim. Acta 141, 127–144.

Wainer, K., Genty, D., Blamart, D., Daëron, M., Bar-Matthews, M., Vonhof, H., Dublyansky, Y., Pons-Branchu, E., Thomas, L., van Calsteren, P., et al., 2011. Speleothem record of the last 180 ka in Villars cave (SW France): Investigation of a large $\delta^{18}O$ shift between MIS6 and MIS5. Quat. Sci. Rev. 30, 130–146.

Wang, Z., Schauble, E.A., Eiler, J.M., 2004. Equilibrium thermodynamics of multiply substituted isotopologues of molecular gases. Geochim. Cosmochim. Acta 68, 4779–4797.

Wang, Y., Xu, Y., Khawaja, S., Passey, B.H., Zhang, C., Wang, X., Li, Q., Tseng, Z.J., Takeuchi, G.T., Deng, T., et al., 2013. Diet and environment of a mid-Pliocene fauna from southwestern Himalaya: Paleo-elevation implications. Earth Planet. Sci. Lett. 376, 43–53.

Wieder, M., Yaalon, D.H., 1982. Micromorphological fabrics and developmental stages of carbonate nobular forms related to soil characteristics. Geoderma 28, 203–220.

Wolf, G., Lerchner, J., Schmidt, H., Gamsjäger, H., Königsberger, E., Schmidt, P., 1996. Thermodynamics of $CaCO_3$ phase transitions. J. Therm. Anal. 46, 353–359.

Wolfe, J.A., Schorn, H.E., Forest, C.E., Molnar, P., 1997. Paleobotanical evidence for high altitudes in Nevada during the Miocene. Science 276, 1672–1675.

Wolfe, J.A., Forest, C.E., Molnar, P., 1998. Paleobotanical evidence of Eocene and Oligocene paleoaltitudes in midlatitude western North America. Geol. Soc. Am. Bull. 110, 664–678.

Xia, G., Yi, H., Zhao, X., Gong, D., Ji, C., 2012. A late Mesozoic high plateau in eastern China: evidence from basalt vesicular paleoaltimetry. Chin. Sci. Bull. 57, 2767–2777.

Yapp, C.J., 2008. $^{18}O/^{16}O$ and D/H in goethite from a North American Oxisol of the early Eocene climatic optimum. Geochim. Cosmochim. Acta 72, 5838–5851.

Yeung, L.Y., Young, E.D., Schauble, E.A., 2012. Measurements of $^{18}O^{18}O$ and $^{17}O^{18}O$ in the atmosphere and the role of isotope-exchange reactions. J. Geophys. Res. Atmos. 1984–2012 117.

Yoshida, N., Vasilev, M., Ghosh, P., Abe, O., Yamada, K., Morimoto, M., 2013. Precision and long-term stability of clumped-isotope analysis of CO_2 using a small-sector isotope ratio mass spectrometer. Rapid Commun. Mass Spectrom. 27, 207–215.

Young, R.A., 1999. Nomenclature and ages of late Cretaceous (?)-Tertiary strata in the Hualapai Plateau region, northwest Arizona. US Government Printing Office.

Zaarur, S., Olack, G., Affek, H.P., 2011. Paleo-environmental implication of clumped isotopes in land snail shells. Geochim. Cosmochim. Acta 75, 6859–6869.

Zaarur, S., Affek, H.P., Brandon, M.T., 2013. A revised calibration of the clumped isotope thermometer. Earth Planet. Sci. Lett. 382, 47–57.