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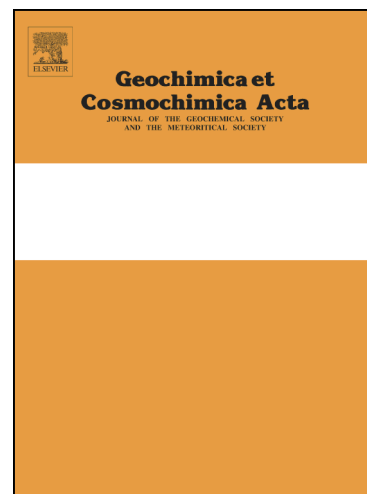
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Calibration of the dolomite clumped isotope thermometer from 25 to 350°C, and implications for a universal calibration for all (Ca, Mg, Fe)CO₃ carbonates

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Abstract

Carbonate clumped isotope thermometry is based on the temperature-dependent formation of $^{13}C^{18}O^{16}O_2^{2-}$ ion groups within the lattice of solid carbonate minerals. At low temperatures the bonds between rare, heavy ^{13}C and ^{18}O isotopes are thermodynamically favored, and thus at equilibrium they are present in higher than random abundances. Here we calibrate the use of this temperature proxy in a previously uncalibrated carbonate phase — dolomite [$CaMg(CO_3)_2$] — over a temperature range that extends to conditions typical of shallow crustal environments, by determining the Δ_{47} values of CO_2 extracted from synthetic or natural (proto)dolomites grown at known temperatures from 25 to 350ºC and analyzed in two different laboratories using different procedures for sample analysis, purification and post-measurement data treatment. We found that the $\Delta_{47} - 1/T^2$ dependence for (proto)dolomite is linear between 25 and 350°C, independent of their Mg/Ca compositions or cation order (or the laboratory in which they were analyzed), and offset from, but parallel to, the theoretical predictions of the Δ_{63} dependence to temperature of the abundance of the $^{13}C^{18}O^{16}O_2$ isotopologue inside the dolomite and calcite mineral lattices as expected from ab-initio calculations (Schauble et al., 2006). This suggests that neither the equilibrium constant for ^{13}C–^{18}O clumping in (proto)dolomite lattice, nor the experimental fractionation associated with acid digestion to produce CO_2, depend on their formation mechanism, degree of cation order and/or stoichiometry (ie., Mg/Ca ratio) and/or $\delta^{18}O$ and $\delta^{13}C$ compositions (at least over the range we explored). Thus, we suggest the following single $\Delta_{47} - 1/T^2$ linear regression for describing all dolomite minerals:

$$\Delta_{47CDES90} = 0.0428 \, (\pm 0.0033) * 10^6/T^2 + 0.1174 \, (\pm 0.0248) \quad (r^2 = 0.997),$$

with T in kelvin and Δ_{47} in the Carbon Dioxide Equilibrium Scale (CDES) of Dennis et al. (2011) and referring to CO_2 extracted by phosphoric acid digestion at 90°C. The listed uncertainties on slope and intercept are 95% confidence intervals. The temperature sensitivity (slope) of this relation is lower than those based on low temperature acid digestion of carbonates, but comparable to most of those based on high temperature acid digestion (with however significantly better constraints on the slope and intercept values, notably due to the large range in temperature investigated and the large number of Δ_{47} measurements performed here, n = 67). We also use this dataset to empirically determine that the acid fractionation factor associated with phosphoric acid digestion of dolomite at 90°C ($\Delta^*_{dolomite90}$) is about + 0.176‰. This is comparable

to the $\Delta^*_{calcite90}$ experimentally obtained for calcite (Guo et al., 2009), suggesting that the acid fractionation Δ^* for acid digestion of dolomite and calcite are the same within error of measurement, with apparently no influence of the cation identity. This hypothesis is also supported by the fact that our dolomite calibration data are indistinguishable from published calibration data for calcite, aragonite and siderite generated in similar analytical conditions (ie., carbonate digested at T $\geq$ 70°C and directly referenced into CDES), demonstrating excellent consistency among the four $(Ca,Mg,Fe)CO_3$ mineral phases analyzed in seven different laboratories (this represents a total of 103 mean Δ_{47} values resulting from more than 331 Δ_{47} measurements). These data are used to calculate a composite Δ_{47}–T universal relation for those carbonate minerals of geological interest, for temperatures between -1 and 300°C, that is found to be statistically indistinguishable from the one described by dolomite only:

$$\Delta_{47CDES90} = 0.0422 \,(\pm\, 0.0019) * 10^6/T^2 + 0.1262 \,(\pm\, 0.0207) \qquad (r^2 = 0.985)$$

Thus, in order to standardize the temperature estimates out of different laboratories running high temperature digestion of $(Ca,Mg,Fe)CO_3$ carbonate minerals, we recommend the use of this single Δ_{47}-T calibration to convert Δ_{47CDES} data into accurate and precise temperature estimates. More widely, this study extends the use of the Δ_{47} thermometry to studies of diagenesis and low-grade metamorphism of carbonates with unprecedented precision on temperature estimates based on Δ_{47} measurements — environments where many other thermometers are generally empirical or semi-quantitative.

1- INTRODUCTION

Temperature is a significant parameter for many processes operating in various Earth systems and reservoirs (e.g., atmosphere, oceans, crusts, deep Earth). Geoscientists attempt to reconstruct past temperature variations in Earth's surface, the shallow-crust, magmatic and metamorphic systems. One of the most widely used quantitative thermometric methods is based on the thermodynamically-based exchange of oxygen isotopes between two phases (fluid or solid), the so-called $\delta^{18}O$ thermometry (Urey, 1947, Epstein et al., 1953). However, such thermometers generally constrain temperature only when two or more cogenetic phases mutually equilibrated and each can be measured or estimated for

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$\delta^{18}O$, reducing its usefulness where thermodynamic equilibrium cannot be proven or when one or more of the phases of interest are not preserved. Many alternative paleothermometers have been used or combined to circumvent some of the problems inherent to oxygen isotope thermometry, particularly as applied to surface and shallow crustal environments, including: the molecular structure of organic biomarkers (Muller et al., 1996), the partitioning of elements between seawater and biogenic carbonates (e.g., Delaney et al. 1995), indices of structural and chemical maturation of organic matter (e.g., Lafargue et al., 1998), vitrinite reflectance or apatite fission track thermochronology (e.g., Arne and Zentilli 1994), the T-max parameter from kerogen pyrolysis (Espitalié et al., 1985), fluid inclusion microthermometry (e.g., Barker and Goldstein 1990), the illite crystallinity index (e.g., Kübler and Jaboyoff 2000). However most of these temperature proxies are often restricted to a small range of materials and conditions, and/or rely on empirical calibrations that are unsuitable for extrapolation to conditions beyond their calibrations, and/or represent an integration of temperature-time histories and therefore require independent estimation of duration of heating.

Carbonate clumped isotope thermometry (or 'Δ_{47} thermometry') (Ghosh et al., 2006; Schauble et al., 2006, Eiler et al., 2007, 2011) contributes new constraints to such problems because it is based on the temperature dependent formation of $^{13}C^{18}O^{16}O_2^{2-}$ ion groups within solid carbonate minerals: at lower temperatures $^{13}C-^{18}O$ bonds are thermodynamically favored and thus enriched relative to a random distribution, whereas at higher temperatures (T > 1000°C) the abundance of $^{13}C-^{18}O$ bonds more nearly approaches the random, or stochastic abundance of $^{13}C-^{18}O$ bonds in the crystal lattice. Interest in this method partly results from the fact that it is based on an intramineralic equilibrium ($X^{12}C^{18}O^{16}O_2 + X^{13}C^{16}O_3 \Leftrightarrow X^{13}C^{18}O^{16}O_2 + X^{12}C^{16}O_3$; where X is a metal ion), and thus can rigorously constrain temperature using measured isotopic species of a single phase (the carbonate) – avoiding the need to assume an isotopic composition of water (as one often must do when applying conventional oxygen isotope paleothermometers). Carbonate clumped isotope thermometry has thus been particularly useful for reconstructing temperatures in times and locations where the isotopic composition of water is unknown, as for reconstructing paleoenvironmental or diagenetical histories (Came et al., 2007, Bristow et al., 2011, Ferry et al., 2011, Finnegan et al., 2011, Dale et al., 2014, Loyd et al., 2015). Moreover Δ_{47} measurements are always accompanied by simultaneous $\delta^{18}O$ measurements of the analyzed carbonate, allowing the $\delta^{18}O$ of the water from which carbonate grew to be calculated – in some applications, a more important parameter than the carbonate growth temperature (e.g., paleoaltimetry, Ghosh et al., 2006).

Existing methods for precise carbonate clumped isotope analysis require CO_2 as an analyte; results are typically reported as values of Δ_{47} in ‰ variations reflecting the overabundance of $^{13}C^{18}O^{16}O$ relative to the stochastic distribution (Eiler 2007). Until now, the carbonate clumped isotope thermometer has

been experimentally calibrated for synthetic inorganic calcite (Ghosh et al., 2006; Dennis and Schrag, 2010; Zaarur et al., 2013; Tang et al., 2014; Defliese et al., 2015; Kluge et al., 2015), siderite (Fernandez et al., 2014) and a variety of biogenic carbonates: aragonitic otholith (Ghosh et al., 2007), foraminifera (Tripati et al., 2010; Grauel et al., 2013), deep-sea corals (Thiagarajan et al., 2011), calcitic and aragonitic mollusks and brachiopods (Eagle et al., 2013; Henkes et al., 2013, Came et al., 2014), bio-apatite (Eagle et al., 2010) or empirically on a variety of biogenic calcites (Wacker et al., 2014) (Figure 1). All materials used in these studies had growth temperatures below 70°C, except for the recent studies of Kele et al., (2015) and Kluge et al., (2015), which include samples having growth temperatures up to 95 and 250°C, repectively. Prior to 2013, most (though not all) calibration studies report correlations of Δ_{47} *vs.* T that are relatively uniform and similar to the initial study of Ghosh et al. (2006), despite examining a wide range of biogenic and abiogenic minerals. [A noteable exception are carbonates formed by rapid CO_2 degassing, including most natural speleothems; Affek et al., 2008, Daëron et al. 2011].

However, since 2013, the emergence of additional calibration studies on various materials resulted in increasing differences among published Δ_{47}-T calibration lines, illustrated by the large dispersion of published Δ_{47} calibration data in Figure 1 (see also examples of compilations of the published slopes and intercepts on calculated Δ_{47}-T linear regressions in Wacker et al., 2014 or Defliese et al., 2015), that appear to reduce both the precision and accuracy of the temperature estimates made on the basis of Δ_{47} data (even if only similar digestion temperatures are considered). [Indeed, Figure 1 shows a typical 50 ppm dispersion of Δ_{47} data for a given temperature, that can result, for instance, in uncertainties of about ± 8°C for growth temperatures close to 25°C, and higher uncertainties for higher temperatures].

Possible factors that could partly explain the dispersion of data in Fig. 1 are differences in: (1) methodological/analytical procedures for data acquisition, (2) post-measurement data processing, or (3) intrinsic properties of the analyzed carbonates.

(1) Strikingly, when considering published calibration datasets, most of "steep-slope" Δ_{47}-T calibration lines found (Ghosh et al., 2006, Tripati et al., 2011, Thiagarajan et al., 2011, Zaaruur et al., 2013, Came et al., 2014) were obtained with analytical protocols involving CO_2 extraction via 25°C acid digestion in sealed vessels followed by CO_2 purification via gas chromatography using capillary columns used for the early Δ_{47} measurements at Caltech (and still in use at Yale University). In contrast, most of "shallow-slope" Δ_{47}-T calibration lines (Dennis and Schrag 2010, Henkes et al., 2013, Wacker et al., 2013, Eagle et al., 2013, Fernandez et al., 2014, Tang et al., 2015, Defliese et al. 2015, Kluge et al., 2015, Kele et al., 2015, Winkelstern et al., 2016) were obtained with analytical protocols involving CO_2 extraction via T ≥ 70°C acid digestion (now in use in most laboratories generating Δ_{47} data), continuous trapping of CO_2 over its generation followed by CO_2 purification by gas chromatography

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using either filled columns flushed by an He flow or one tube filled with porapak where CO_2 is cryogenically transferred through it. However, despite substantial effort by the carbonate clumped isotope community to understand such differences (notably through regular workshops), no consensus explanation has been found.

(2) Dennis et al. (2011) presented an inter-laboratory "absolute" standardization scheme (or CDES for Carbon Dioxide Equilibrated Scale) that can correct all Δ_{47} values to a proposed absolute reference frame, free of fragmentation/recombination and non-linearity effects in the source of the mass spectrometer, but requiring concurrent analyses of samples and standards of CO_2 gas equilibrated at known temperatures. However, it is likely that retrospectively projecting published data into this absolute reference frame using global "tertiary transfer functions" (TTF) could lead to artifacts in the data, particularly when there is insufficient information about standards that were co-analyzed with the calibration samples.

In parallel, various values for the difference between acid fractionation factors at 25°C and X°C (Δ^*_{25-X}) have been previously used to convert Δ_{47} data from high temperature digestion reactions into the 25°C acid digestion reference frame (e.g., Δ^*_{25-90} varying between 0.069 and 0.092‰ for digestions at 90°C) and could also partly contribute to the dispersion of data along the *y-axis* of Figure 1. Also, the variety of Δ_{47}–$(1/T^2)$ slopes and intercepts found might also partly result from different statistical treatments of data that were not uniform in previous studies: with for instance some data points in Figure 1 representing averages out of 2 to 27 replicate Δ_{47} measurements. However, even when homogenizing data treatment (weighted by both the number of replicate and the uncertainties on growth temperatures) and/or replacing acid fractionation to a single common value, the discrepancy between Δ_{47}–$(1/T^2)$ trends with digestion at 25°C versus higher temperatures remains (Defliese et al., 2015), as does the dispersion of data in Figure 1.

(3) Given the diversity of carbonate minerals used for generating previous Δ_{47}-T calibrations it is still unclear whether or not (some of) the dispersion observed in calibration data (Figure 1) might also partly result from variations in ^{13}C–^{18}O clumping associated with the intrinsic characteristics of the calibration samples themselves. In other words, the dispersion observed in Figure 1 might also partly reflect some true (i.e., not due to measurement and/or data treatment bias) characteristics of the carbonate clumped isotope systematics as for example: i/ isotopic disequilibrium of ^{13}C–^{18}O clumping (as observed by Affek et al., 2008; Daëron et al., 2011; Saenger et al., 2012); ii/ Δ_{47} vital effects for some biogenic minerals; iii/ variations in ^{13}C–^{18}O clumping distribution with the structure or chemical compositions of the carbonate either inside the mineral lattice (as suggested by Schauble et al., 2006, Hill et al., 2014) or into CO_2 generated by H_3PO_4 acid digestion (as suggested by Guo et al., 2009)]. Such "material-specific explanations" for the dispersion of Δ_{47} data in Figure 1 find support from analogy with the conventional

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oxygen isotope systematics. Indeed, oxygen isotope fractionations between both carbonate-water and carbonate-extracted CO_2 vary with: i/ mineralogy of the carbonate (i.e., inorganic calcite, aragonite, dolomite and other types of carbonates all show their own oxygen isotope fractionation factors; e.g., Kim and O'Neil, 1997 for calcite, Kim et al., 2007 for aragonite and Rosenbaum and Sheppard 1986 and Horita, 2014 for dolomite); ii/ variations of structure or chemical composition inside of a single type of carbonate (e.g., for dolomite: Hardie et al., 1997; Schmidt et al., 2005 also suggesting a dependence to the degree of cation ordering and/or stoichiometry – ie., Mg/Ca composition); or iii/ mechanisms of biomineralization for biogenic carbonates – for example deep-sea corals or coccolliths (Adkins et al., 2003; Hermoso et al., 2013). Thus, the complexity of the oxygen isotope systematics in carbonates raises the possibility that ^{13}C–^{18}O 'clumping' could also depend on mineralogy, degree of cation order and chemical compositions. So far only a small proportion of the carbonate group variety has been experimentally or empirically calibrated (mainly calcium carbonate, but see recent calibration for siderite in Fernandez et al., (2014) or carbonate groups in phosphate ; e.g., Eagle et al., 2010). This underlines questions related to other minerals, structures, and chemical compositions including the applicability of the Δ_{47} thermometry for studying material presenting a mixed mineralogy.

Thus, although Δ_{47} thermometry can theoretically provide temperature estimates with uncertainties of ± 1-2°C at T < 50°C (when the most precise Δ_{47} data achievable with currently used analytical methods for Δ_{47} measurements are considered), in practice, such precision has not yet been definitively attained. This stems from the large dispersion of the previously published Δ_{47} calibration datasets that may lead to temperature estimates varying by several 10's of degrees, particularly at the extremes of the calibration temperature range (see Zaarur et al., 2013 for an example of error that arises when data fall out of the calibration range); with even more uncertainty when converting Δ_{47} data into temperatures using a calibration generated in another laboratory.

Here we report a Δ_{47} calibration for dolomite samples that were precipitated at known temperatures from 25 to 350°C – that is across almost the entire range of ambient temperatures in which dolomite and other carbonate minerals can be found – and that differ from one another in " intrinsic characteristics" such as formation mechanisms, bulk stable isotopic ($\delta^{13}C$ and $\delta^{18}O$) or Mg/Ca compositions, and cation ordering. For the first time the same suite of samples with highly varying Δ_{47} and bulk isotopic compositions (namely $\delta^{13}C$ and $\delta^{18}O$) were analyzed in two different laboratories using different techniques for CO_2 extraction, purification and post-measurement data processing [i.e., reported *directly* and *indirectly* into the absolute reference frame at Institut de Physique du Globe de Paris and California Institute of Technology, respectively]. In parallel, those data are used to discuss

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some of the key issues related to the use of carbonate-clumped isotope thermometry discussed above, including inter-comparison of laboratories using different procedures for sample analyses, purification and data treatment, Δ_{47} dependence on mineral structure or chemical composition, fractionation factor for phosphoric acid digestion of carbonate minerals (Δ^*), *real* uncertainties on temperature estimates based on replicate measurements of Δ_{47} of unknown samples, and differences with previously published Δ_{47}-T dependence. This study ultimately aims to provide more accurate, precise and standardized (when different laboratories running high temperature acid digestion are compared) temperature estimates than currently possible based on Δ_{47} measurements, particularly for temperatures above 50°C. More broadly, this study aims to strengthen and expand the use of Δ_{47} thermometry for high temperature applications in which this tool has been only sparsely applied likely due to a lack of precision on temperature estimates relying only on theoretical predictions (since previous calibration studies have focused on a relatively narrow range of low-temperatures). This objective has importance in several fields of research because, when applied to materials subjected to burial and anchimetamorphic environments (generally < 250°C) only a few geothermometers can actually provide accurate temperatures for carbonate minerals.

2- SAMPLES

Table 1 reports four parameters characterizing the samples investigated in this study: (i) the duration of the experiment; (ii) the position of the 104 reflection; (iii) the relative content of Mg cations (dolomite stoichiometry) as determined by position of the 104 reflection (following Lumdsen and Chimahusky, 1980); and (iv) the degree of Mg-Ca cation ordering as determined by the relative heights of the 015 and 006 reflections (Redfern et al. 1989; Dove and Powell 1989; Hammouda et al. 2011, Zucchini et al., 2012). Cation ordering reflects the degree of alternating layers of Mg^{2+} and Ca^{2+} interspersed with CO_3^{2-} groups in the lattice structure. Dolomites with varying degrees of cation ordering thus have varying crystal structures. Samples investigated here are showing a large range of degree of cation ordering and stoichiometry. Some of the experimental low-temperature samples are poorly ordered (that is cation-ordering reflections are attenuated because cations occupy increasingly random positions within lattice) and/or not stoichiometric and are referred as protodolomite. Historically, Graf and Golsdsmith (1956) first used the term protodolomite to describe the poorly ordered transitional stage through which dolomites went during hydrothermal synthesis in the laboratory. Since then, protodolomite is usually defined as rhombohedral carbonate with slight Ca-excess and dolomite basal reflections, but lacking major superstructure-reflections of cation-ordering,

which progressively increase as cations order within the mineral lattice with time.

2.1. Laboratory products

2.1.1. Laboratory high temperature dolomites

These laboratory syntheses of (proto)dolomites were originally conducted for studying the oxygen isotope fractionation between dolomite and water at high temperature (Horita, 2014). The protocols used to generate these samples [e.g., duration, heating and cooling procedures as well as initial $CaCO_3$ materials (with different structures, chemical and bulk isotopic compositions; Table S1) and solutions (with various ionic strengths and Mg/Ca ratios; Table S1)] as well as some characteristics of the produced samples (e.g., stoichiometry, degree of cation ordering) are detailed in Horita (2014) and briefly described below and in Table 1.

Protodolomite precipitation at 80°C: Ca-Mg carbonate was synthesized by preparing separate solutions of $MgSO_4$, $Ca(NO_3)_2.4H_2O$, and Na_2CO_3 to reach an initial compositions of 0.256, 0.238, and 0.483 molal, respectively. Milky solids precipitated immediately upon mixing and the mixed solution was placed in a sealed (air tight) glass bottle, which was then placed within a water bath controlled at 80.2 ± 1°C and remained immersed at this temperature over 41 days. Atomic absorption and XRD analysis shows that the Ca-Mg carbonate precipitated has the chemical composition of almost perfectly stoichiometic dolomite ($Ca_{0.51}Mg_{0.49}CO_3$), but lacks a (015) super-lattice peak indicating Mg-Ca ordering (Table 1, Figure S1 and Horita 2014); thus, this material has the properties of so-called protodolomite.

Dolomitization of calcite or aragonite (100-350°C): Dolomite synthesized at temperatures from 100 to 350°C was grown by reacting powdered $CaCO_3$ (either reagent calcite or natural aragonite; Table 1 and S1) with Ca-Mg-(Na)-Cl solutions following: $2CaCO_3 + Mg^{2+} \Leftrightarrow CaMg(CO_3)_2 + Ca^{2+}$. The reaction proceeds from the starting $CaCO_3$ to very high-Mg (35-40 mol % $MgCO_3$) calcite to Ca-rich disordered dolomite to well-ordered near-stoichiometric dolomite. About 100-150 mg of ground natural aragonite (Minglanilla, Spain) or reagent calcite were transferred to a Teflon cup along with 80 – 120 g of a Ca-Mg-(Na)-Cl solution. The Teflon cup was then placed and sealed inside a 300 mL bolted-closure 316 stainless steel reactor vessel, which was in turn placed inside a furnace in the vertical position at the target temperature. The temperature of the reactor vessel, which reached the target temperature within 1-2 hours, was controlled within ± 2 °C for durations of 6 to 85 days (Table 1). At the end of the experiments, the reactor was pulled out of the furnace, and cooled quickly by blowing with compressed air (the reactor typically reached less than 50°C in less than 30 minutes). The recovered powder

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samples were washed several times with distilled water. Their mineralogy and Ca/Mg ratios were determined with XRD and atomic absorption spectroscopy (Table 1 and Horita, 2014). The Ca-Mg carbonate samples synthesized at 102°C have a slight excess of Ca relative to stoichiometric dolomite (56-58 mol % $CaCO_3$) and an attenuated (015) ordering reflection indicates some degree of dolomite ordering (Figure S1). Interestingly the sample 100-A3 (synthesized over 85 days) shows a higher degree of cation ordering than the sample 100-A2 (synthesized over 36 days), suggesting that time allows progressive ordering of cations. Other samples synthesized at higher temperatures are stoichiometric, or nearly so, and exhibit a (015) ordering peak as strong as that seen in ordered hydrothermal dolomite (Figure S1 and Horita, 2014).

Some of these laboratory syntheses were conduced to test possible experimental artifacts such as: (i) isotopic inheritance, (ii) pre-mature reaction, and (iii) kinetic isotope effects (Horita, 2014). (i) To test a possible isotopic inheritance effect during dolomitization, two different starting $CaCO_3$ polymorphs were used at 100°C (aragonite and calcite with very different $\delta^{18}O$ and $\delta^{13}C$ isotopic compositions of $\delta^{18}O_{SMOW} = 24‰$ and $\delta^{13}C_{PDB} = -2.41‰$ or $\delta^{18}O_{SMOW} = 7.87‰$ and $\delta^{13}C_{PDB} = -36.4‰$, for samples 100-A2 and 100-A3, respectively; Table S1). (ii) In parallel, dolomitization might have started before reaching the target temperatures. This effect of pre-mature reaction was examined at the highest experimental temperature (350°C), with an experiment where the vessel was heated up from room temperature (sample 350-A7). (iii) Finally, in the conversion of calcium carbonate to dolomite, kinetic (rather that equilibrium) isotope effects could have controlled the reaction. This hypothesis was tested by conducting experiments using solutions with different Mg/Ca ratios and ionic strengths at 150°C, 250°C, 300°C and 350°C (since dolomitization is considered to proceed faster in solutions with high ionic strengths and higher Mg/Ca ratios; e.g., Kaczmarek and Sibley, 2011) as well as conducting the dolomitization reactions with two different $CaCO_3$ polymorphs at 100°C (since aragonite is more promptly dolomitized than calcite).

2.1.2. Bacterially-mediated precipitated samples

Some of the bacterially-mediated protodolomites analyzed here were originally synthesized in order to determine the oxygen isotope fractionation between dolomite and water at low temperature (Vasconcelos et al., 2005). The protocol used and sample characteristics are described in detail in (Vasconcelos et al., 2005), and only briefly summarized here and in Table 1. The precipitation experiments were performed under anaerobic conditions with a pure microbial strain isolated from Lagoa Vermelha, Rio de Janeiro, Brazil (Warthmann et al., 2000; Vasconcelos and McKenzie, 1997). These sulfate-reducing bacteria (*Desulfovibrio* strain LV form1) were grown in bottles in an anoxic liquid medium at three different temperatures (30, 40 and 45°C) maintained in thermostat-controlled

incubators. The synthetic growth medium was a solution with an ion concentration similar to that of the natural Lagoa Vermelha water. Sterile control samples were prepared and maintained under the same conditions but showed no evidence of carbonate precipitation. As the lower temperatures are below the growth optimum for the bacteria (~37-38ºC), experiments were run for 4–6 months to obtain sufficient mineral precipitate. The Ca-Mg carbonates precipitated have Mg contents between 41 and 53% and dolomite *d*-spacing, but lacks the (015) super-lattice peak (Figure S2, Table 1 and Vasconcelos et al., 2016). At 30 and 40ºC, calcite and high-Mg calcite co-precipitate with protodolomite. These mixed carbonate samples were treated with a 0.1*M* EDTA solution for ~15 min to dissolve the calcite and high Mg calcite, leaving a pure protodolomite residue to be analyzed for its isotopic composition. The purity of the samples after pre-treatment was confirmed by XRD. The samples were treated with sodium hypochlorite or H_2O_2 to eliminate organic contaminants.

2.2. Natural low temperature dolomites

We analyzed two samples from hypersaline lagoons: CVLV and CVBE. Sample CVLV is a natural dolomite from Lagoa Vermelha (Vasconcelos and McKenzie, 1997). The youngest sediments in Lagoa Vermelha are a mixture of calcite, high-Mg calcite, and Ca-rich dolomite. During the annual change from wet to dry seasons, the salinity of the lagoon water undergoes large variations from brackish to seawater values, reaching hypersaline values at the height of the evaporative conditions. The temperature of the lagoon water averages 25°C annually and varies little over the year (± 4˚C). XRD analysis shows that dolomite from Lagoa Vermelha is ordered and nearly stoichiometric (Table 1, Figure S1).

Sample CVBE is a natural dolomite from Brejo do Espinho lagoon that is a very shallow (< 0.5 m) hypersaline coastal lagoon located east of Lagoa Vermelha about 100 km east of Rio de Janeiro (Brazil). The lagoon water has a typical seawater Mg/Ca molar ratio of ~ 5, indicating a seawater origin modified by evaporation and dilution processes (Van Lith et al., 2002). The temperature of the lagoon water averages 25°C annually and varies little over the year (maximum ± 4˚C, Bahniuk et al., 2015). Brejo do Espinho sediments contain pure dolomite as well as high-Mg calcite and Ca-dolomite (45 to 47% Mg) on the top sediment (Van Lith et al., 2002). Those mixed carbonate samples were treated with a 0.1*M* EDTA solution for ~15 min to dissolve the calcite and high-Mg calcite, leaving a pure dolomite (ordered and stoichiometric) residue to be analyzed for its stable isotope composition (Table 1, Figure S1).

For both samples, organic contaminants were removed prior to analysis by oxidation with H_2O_2.

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3. METHODS

Here we describe the methods used over the course of this study at both Institut de Physique du Globe de Paris (France) and California Institute of Technology (USA) for Δ_{47} measurements and post-measurements data treatment on similar samples. The procedures used at IPGP and Caltech differ from each other on several points, the most critical ones being the procedures for CO_2 extraction and purification (e.g., digestion time, sample grain size, purification steps, quantification of extracted CO_2) as well as the data reduction procedures used to transfer raw Δ_{47} into the absolute reference frame (i.e., mostly direct versus indirect data transfer into the absolute reference frame, with also "shallow and stable" versus "steep and fast moving" slopes for heated gases, respectively used at IPGP and Caltech).

3.1. Carbonate digestion, CO_2 purification and stable isotopes measurements

3.1.1. Analytical procedure at IPGP

Measurements performed at Institut de Physique du Globe de Paris were made from 2013 to 2015 with a manual acid digestion and gas purification system and then introduced into a dual-inlet Thermo Scientific™ MAT 253™ gas source isotope ratio mass spectrometer (in the Laboratoire de Géochimie des Isotopes Stables at IPGP), configured to simultaneously measure masses 44-49. Since this is the first time that the IPGP setup is described, we here detail the procedure. Carbonate samples are reacted for 20 min for calcite and 2h for (proto)dolomite in a common acid bath (CAB) held at 90°C. Classically, circa. 5 mg of carbonates (8 mg on the first measurements of this study) are loaded in silver capsules and left under high-vacuum for at least 3 hours before being dropped in the acid bath. Up to 16 samples are successively reacted in the same batch of phosphoric acid (~ 104%; ρ=1.914). The gas produced by acid digestion of carbonate is directly collected in a liquid nitrogen (LN$_2$) trap.

After complete digestion, non-condensable gases are pumped away to less than 10^{-5}-10^{-4} mbar and the CO_2 (plus the trapped H_2O + acid vapor produced during the digestion step) is then slowly unfrozen (3-4 min) to be eventually collected in a second LN$_2$ trap after passing through a LN$_2$-ethanol trap (-117 ± 6°C) to remove water and acid vapor. Purified CO_2 was quantified and CO_2 extraction/purification yields checked (i.e., recovered CO_2 divided by expected CO_2 for a given reacted carbonate sample) for all the samples and standards with a calibrated capacitive gauge. Over the course of this study extraction/purification yields were 100.2 ± 2.5% for calcite standards and 100.4 ± 4.6% for dolomite samples, except sample 350-A9 that shows a reproducible yield of ~ 75% due to the occurrence of magnetite. Purified CO_2 is then allowed to pass (by differential pressure) through a 10 cm long U-trap

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(6mm, ID) packed with silver wool to remove sulfur compounds and 7-8cm of Porapak-Q, 50-80 mesh to remove remaining traces of water or volatile organic compounds. This latter trap is enclosed in an aluminum block held at -28°C using two Peltier cells. The Porapak-Q trap is cleaned every night or after any samples showing traces of contamination by heating at 150°C. The purified CO_2 is then collected into a sample tube and introduced into the MAT 253 within 10 min after purification. CO_2 samples are analyzed versus a reference CO_2 working gas tank provided by Oztech Trading Corporation and with bulk isotopic compositions normalized with international reference material NBS19 (and daily with our carbonate standards – mainly Carrara IPGP and 102-GC-AZ01b – normalized to NBS19). The Oztech CO_2 working gas tank used over the course of this study has carbon and oxygen isotopic compositions of $\delta^{13}C$ = - 3.63‰ PDB and $\delta^{18}O$ = -15.79‰ PDB. Each sample, standard, or reference gas is analyzed at 12V signal on the Faraday cup measuring mass 44 (16V for the few carbonates for which 8 mg of powder were reacted). Each measurement consisted of 7 acquisitions of 10 cycles of comparison between the CO_2 extracted from sample versus Oztech working gas, with a signal integration time of 26 s (total integration time of 1820s).

Accuracy on Δ_{47} data was reached by correcting data to CO_2 gases driven to isotopologue equilibrium at 1000 and 25°C and checked with carbonate reference materials that were also analyzed in the inter-lab comparison study of Dennis et al. (2011): Cararra marble and 102-GCAZ-01. To construct the Carbon Dioxide Equilibrated Scale (CDES) we regularly analyze CO_2 Heated Gases (HG, held at 1000°C for 3h) and Equilibrated Gases (EG at 25°C) which were alternatively analyzed every 3-4 analyses of carbonate samples. The bulk isotopic composition of HG and EG spans a range of δ^{47} values from -52 to +30‰, which almost entirely covers the variation range of unknown dolomitic samples (from -68 to +12‰) and calcite standards (from +3 to +18‰) analyzed in this study.

3.1.2. Analytical procedure at Caltech

Measurements performed at California Institute of Technology (USA) were made in 2008-2009 with an automated acid digestion and gas purification device coupled to a dual inlet Thermo MAT253 as described in (Passey et al., 2010). Briefly, samples weighed into silver capsules (~ 8 mg) were reacted in a common phosphoric acid bath (~ 103%; 1.90 < ρ < 1.92) for 20 minutes at 90°C under static vacuum (evacuated to < 0.5 Torr at the beginning of the reaction). Up to 15 samples are successively reacted in the same batch of phosphoric acid. The evolved CO_2 was passed through an ethanol/dry ice U-trap (~ - 80 °C) before being collected on a liquid nitrogen temperature (-196 °C) U-trap. Following the 20 minute reaction period, the CO_2 was carried through a Porapak Q 120/80 mesh gas chromatography column held at -20° C using He as the carrier gas. Unlike the setup at IPGP, yields of gaseous CO_2 were not precisely quantified, but were qualitatively monitored relative to yields observed

for pure calcite samples using the pressure gauge in the bellows volume of the dual-inlet system. The purified CO_2 was analyzed using a Thermo Scientific™ MAT 253™ Mass Spectrometer configured to collect masses 44–49. Each measurement consisted of eight acquisitions (16V on m/z = 44) of 7 cycles of unknown sample CO_2 versus Oztech working CO_2 gases (with $\delta^{18}O$ = 24.97‰ VSMOW and $\delta^{13}C$ = -3.60‰ PDB and verified through measurements of the NBS-19 standard, analyzed using the same methods used for samples analyses). Signal integration time is 26 s, resulting in total integration time of 1456s each for the sample and the working CO_2 gas. Because at the time the measurements were made at Caltech the complexity and potential evolution through time of the dissociation-recombination reactions of CO_2 in the ion source were not fully recognized, only HG standards (δ^{47} values from ~ -40 to +10‰) were run concurrently to unknown samples to correct from mass spectrometer effects such as non-linearity and scale compression. Note however that accuracy of such corrections was checked with carbonate standards that were concurrently run to samples (notably Cararra marble and in-house standards, for which accepted values in the CDES are now available).

3.2. Post-measurement data processing

In both laboratories, traditional $\delta^{18}O$ and $\delta^{13}C$ data were acquired as part of each Δ_{47} analysis and ^{17}O correction were made following Santrock et al. (1985). In order to account for the temperature dependent oxygen isotope fractionation between CO_2 gas and dolomites resulting from the reaction with phosphoric acid at 90ºC, a fractionation factor of 1.0093 was used, following Rosenbaum and Sheppard (1986). Both the $\delta^{18}O$ and $\delta^{13}C$ of the carbonate samples are referenced to the V-PDB scale as determined using the pre-calibrated Oztech CO_2 tank as the reference working gas.

Post-analysis Δ_{47} data reduction was done according to two reference frames previously outlined: the "stochastic distribution reference frame" (also called "heated gas line – HGL" reference frame or "intra-laboratory reference frame" or "Ghosh scale"; defined in detail in Huntington et al., 2009) and the "absolute reference frame" or "inter-laboratory reference frame" defined by Dennis et al., (2011) and also called "CDES" for Carbon Dioxide Equilibrated Scale. In the former case, as recommended by Huntington et al. (2009), our raw Δ_{47} data were corrected for non-linearity effects based on results for CO_2 gases heated at 1000°C only, and for scale compression effects based on the nominal value of -0.8453‰ (i.e., the intercept of the heated gas line at the time the data from Ghosh et al., (2006) were acquired). [Note however that this procedure relies on the implicit assumption that different batches of Oztech working gas have identical Δ_{47} compositions that do not vary with time]. Alternatively, for transferring our raw Δ_{47} data into the absolute reference frame, non-linearity effects were corrected

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using CO_2 gases driven to isotopologue equilibrium at both 1000 and 25°C at IPGP (and only 1000°C at Caltech). Scale compression effects were corrected either: (1) with empirical transfer functions (ETF) based on theoretical predictions of the abundances of multiply-substituted isotopologues in gaseous CO_2 at thermodynamic equilibrium at IPGP (as recommended when analyses of gas equilibrated at various temperatures were performed concurrently to unknown samples), or (2) with and a tertiary transfer function (TTF) at Caltech (as recommended when only heated gases and carbonate standards that have now accepted values in CDES were analyzed concurrently with unknown samples).

Finally, Δ_{47} data are then corrected for acid reaction temperature in order to normalize values to acid digestion performed at 25°C using Δ^*_{25-90} (the difference between raw Δ_{47} obtained at 25 and 90°C acid digestion reactions) = 0.081‰ using the 'Ghosh scale' (experimentally determined by Passey et al., 2010) and = 0.092‰ using the CDES (experimentally determined by Henkes et al., 2013 for calcitic minerals and confirmed at IPGP, Calmels et al., 2014). For each laboratory dataset, we report three different values of Δ_{47} depending on the scheme of data reduction used (Table S2 and S3): $\Delta_{47Ghosh}$ values are reported in the 25°C acid digestion stochastic reference frame; $\Delta_{47CDES25}$ and $\Delta_{47CDES90}$ are both reported into the CDES absolute reference frame, for acid digestion temperatures of 25°C and 90°C, respectively (i.e., the $\Delta_{47CDES90}$ value was not corrected for acid reaction temperature). However, for dolomite samples, we only provide $\Delta_{47CDES90}$ values because the fractionation factor between 25 and 90°C acid digestion reactions (Δ^*_{90-25}) is still debated, with Δ^*_{90-25} values varying from 0.082 to 0.153‰ as determined on the same reference dolomite NIST 88b (Defliese et al., 2015 and Murray et al., 2016, respectively). Interestingly, it is notable that for NIST 88b the Δ_{47} values obtained in both studies are similar when acid digestion was made at 90°C but differ by 0.07‰ (that is beyond the analytical uncertainty) when acid digestion was made at 25°C. [This feature might stem from the fact that H_3PO_4 digestion of most dolomite samples at 25°C are hard to perform and take several days]. We thus think that reporting our dolomite data into the 25°C reference frame is still uncertain, particularly until this discrepancy will be solved.

3.2.1   *Reduction of raw Δ_{47} data acquired at IPGP*

All samples were measured over the course of seven sessions of analyses distributed over a two-year period. Table S2 compiles all isotopic data for samples, carbonate reference materials and equilibrated gases as well as information on the slopes and intercepts of equilibrated gas lines, and empirical transfer functions (ETF).

Importantly, in contrast with the conditions for Δ_{47} measurements made at Caltech, HGL and EG slopes are very shallow (i.e., only small linearity corrections are applied to the raw Δ_{47} data) and both

slopes and intercepts only slightly vary (e.g. from 0.0019 to 0.0042 and -0.8123 to -0.7886 over time, respectively for heated gases) over the course of the 2 years of analyses at IPGP (i.e., limiting uncertainties associated with a fast moving HGL when not enough or inappropriate standard material were run concurrently with the samples). The Δ_{47} values were corrected for linearity using a fixed slope fitted to both the heated and equilibrated gases. The Δ_{47} values were thereafter transferred into the CDES reference frame ($\Delta_{47CDES25}$ and $\Delta_{47CDES90}$) using Empirical Transfer Functions (ETF) that were determined for a block of typically 30 raw analyses, with ETF slopes and intercepts only slightly varying from 1.1093 to 1.1379 and from 0.9160 to 0.9331‰ respectively over the two year period.

The accuracy in Δ_{47} values with the IPGP analytical setup has been tested on carbonate standards previously shared by four laboratories producing clumped isotope data (Caltech, Johns Hopkins, Yale and Harvard, see Dennis et al. 2011): Carrara marble and 102-GC-AZ01b. One of these two carbonate reference materials was analyzed every 5 analyses to check for analytical stability, reproducibility and accuracy of Δ_{47} measurements at IPGP. Over the course of this study, the average Δ_{47} data obtained for those carbonate standards are $\Delta_{47CDES25}$ = + 0.403 ± 0.014‰ (1S.D., n=24; corresponding to $\Delta_{47CDES90}$ = + 0.311‰) for IPGP-Carrara and $\Delta_{47CDES25}$ = + 0.717 ± 0.013‰ (1S.D., n=20; corresponding to $\Delta_{47CDES90}$ = + 0.625‰) for 102-GC-AZ01b. Note that the $\Delta_{47CDES25}$ values are indistinguishable from those obtained in previous studies (e.g., Dennis et al., 2011, Henkes et al., 2013) and that the standard deviations on the twenty-ish replicate Δ_{47} measurements made over the course of this study are consistent with those obtained at IPGP for these two carbonate reference materials over three years (typically of ± 14 ppm, 1 S.D., n > 300). Over the course of this study, the average Δ_{47} data obtained for ETH1 standard (Carrara Marble heated at 600°C, 155 MPa, 10h and distributed by S. Bernasconi, ETH Zurich) are $\Delta_{47CDES25}$ = + 0.289 ± 0.07‰ (1S.D., n=4; corresponding to $\Delta_{47CDES90}$ = + 0.197‰) and indistinguishable, when respective uncertainties are considered, from the "accepted value" reported in Meckler et al., (2014) [$\Delta_{47CDES25}$ = + 0.267 and $\Delta_{47CDES90}$ = + 0.183‰].

3.2.2. *Reduction of raw Δ_{47} data acquired at Caltech*

Measurements performed at California Institute of Technology were made over the course of five different analytical sessions distributed over approximately 9 months (details of analyses are given in Table S3). We first transferred Δ_{47} data into the stochastic and 25°C acid digestion reference frames ($\Delta_{47Ghosh}$). Briefly, raw Δ_{47} data were corrected for instrumental nonlinearity, scale compression, acid reaction temperature (by adding the Δ^*_{25-90} = + 0.081‰). For three out of five sessions and the raw Δ_{47}

values of heated CO_2 gases drifted over time due to changes in the physical state of the mass spectrometer, a phenomenon previously observed by other authors (Huntington et al., 2009; Passey et al., 2010). In order to correct for this drift we used a MATLAB script that models changes in the slope and intercept of the heated gas line as low-order polynomial functions of time using a least squares approximation (Passey et al., 2010). A fixed (time invariant) heated gas line was used for the two remaining sessions of data acquisition at Caltech. It is noteworthy that over the whole period of this study HGL slopes and intercepts varied considerably (from -0.0135 to 0.0201 and from -0.8453 to -0.7618‰ respectively, with most of the variation observed during a two month period), reflecting fast changes in the mass spectrometric source conditions. In order to evaluate the potential effect of such rapid changes on the accuracy and reproducibility of the post-measurements reduction of the Δ_{47} values of the carbonate samples ran in various sessions of analyses, we tested several types of corrections (including moving or fixed heated gas lines and/or including heated gases with depleted δ^{47} values or not). Distinct extractions of Carrara marble standard analyzed together with unknown samples over the course of these four sessions of analyses yielded a mean $\Delta_{47Ghosh} = 0.358 \pm 0.008$‰ (1SD, n=12), and NBS19 yielded a mean $\Delta_{47Ghosh} = 0.350 \pm 0.013$‰ (1SD, n=11); that are both indistinguishable from the previously published values for those reference material (e.g., Dennis et al., 2011).

The Δ_{47} data were also translated into the inter-laboratory absolute reference frame using the global tertiary transfer function (GTTF) given in Table 4 of Dennis et al. (2011) for reporting data obtained at Caltech before 2011 into the absolute reference frame. Using this transfer function, distinct extractions of Carrara marble yielded a mean $\Delta_{47CDES25} = 0.402 \pm 0.018$‰ (1SD, n=12 and corresponding to $\Delta_{47CDES90} = 0.310$‰) and NBS19 show a mean $\Delta_{47CDES25} = 0.402 \pm 0.018$‰ (1SD, n=11). We also estimated, for each session of analysis, a laboratory tertiary transfer function (LTTF) based on measured Δ_{47} values of gases heated at 1000°C and in-house carbonate standards that have now accepted 'absolute' Δ_{47} values (before acid correction) determined on multiple analyses made later on – that is when it was then possible to directly project their nominal Δ_{47} values into the absolute reference frame. With the LTTF, distinct measurements of Carrara marble yielded a mean $\Delta_{47CDES25}$ of 0.408 ± 0.020‰ (1SD, n=12), and NBS-19 yielded a mean $\Delta_{47CDES25}$ of 0.406 ± 0.020‰ (1SD, n=11). Importantly, when comparing Δ_{47} data calculated with these two methods to *indirectly* transfer Δ_{47} data into the absolute reference frame, we observe no difference in the calculated Δ_{47CDES} data (at least at the analytically resolvable level), with the exception of one session for which insufficient numbers of standards were co-analyzed with unknown

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samples to permit construction of a reliable LTTF. This hypothesis finds support in the fact that the standard deviation of replicate Δ_{47} measurements obtained on the carbonate standards for the different analytical sessions at Caltech seemed to be slightly better when the GTTF was used. We therefore report, in Table 2, data based on this correction scheme. [Note here that such observations are inherent to our own dataset and scheme of correction and do not apply to every dataset acquired at Caltech or another laboratory before 2011].

Finally, the potentially larger uncertainties in Δ_{47CDES} values obtained for dolomite samples ran at Caltech before 2011 (resulting from: (i) indirectly reporting Δ_{47} data obtained at Caltech into the absolute reference frame; (ii) correcting raw Δ_{47} data from linearity and stretching conditions with steep and fast-moving heated gas lines; and (iii) the fact that we remarked that after 20 minutes at 90°C some other dolomite samples were not totally digested) motivated the additional analytical work at IPGP (described above) where linearity, scale-compression and extraction yields were more routinely and accurately monitored.

4. RESULTS

Table 2 summarizes stable isotopic data for carbon (δ^{13}C), oxygen (δ^{18}O) and carbonate clumped isotopes (Δ_{47}) values for individual extractions of CO_2 from powdered (proto)dolomite samples together with their known growth temperatures. Table 2 shows Δ_{47} values reported into the absolute CDES reference frame for acid digestion temperatures of 90°C (ie. the $\Delta_{47CDES90}$ value was not corrected for acid reaction temperature). The total range in $\Delta_{47CDES90}$ values among all the investigated samples varies from 0.604‰ to 0.215‰ (n = 67 measurements in total) for growth temperatures from 25 to 351°C, respectively. The sub-set of bacterially-mediated protodolomite grown in the laboratory from 30 to 45°C shows $\Delta_{47CDES90}$ varying from 0.574‰ to 0.541‰. The sub-set of natural dolomites CVLV and CVBE grown at 25°C has $\Delta_{47CDES90}$ of 0.591 and 0.604‰. The sub-set of hydrothermal (proto)dolomites grown in the laboratory from 100 to 350°C has $\Delta_{47CDES90}$ varying from 0.430 to 0.215‰. Notably, this study shows that $\Delta_{47CDES90}$ data on (proto)dolomite samples with formation temperatures ranging from 25 to 350°C and acquired in two different laboratories using different procedures for data acquisition and processing are indistinguishable, at the analytically resolvable level, from each other (Figure 2a). Most importantly, despite the relatively large diversity of analyzed (proto)dolomites in their "intrinsic characteristics" (i.e., different conditions of precipitation – notably natural/laboratory or inorganically/bacterially-mediated precipitations – and other characteristics such as their Mg/Ca ratios

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or degree of cation ordering, or their highly variable bulk isotopic compositions) they all define a single trend in $\Delta_{47} - (1/T^2)$ space (with a correlation coefficient $R^2 = 0.99$ if all data are input to a single least squares linear regression).

5. DISCUSSION

5.1. Data Treatment

Here we discuss our dataset in terms of accuracy (i.e., consistency between the two laboratories using different procedures for data acquisition and processing), sample homogeneity, isotopic equilibrium, and degree of ordering or stoichiometry; we conclude that, for a given growth temperature, we can average data independently of their way of formation and/or the laboratory in which they have been analyzed. Most importantly, we conclude that none of the "intrinsic characteristics" of the (proto)dolomite samples seems to influence $^{13}C-^{18}O$ clumping either in the mineral lattice or during CO_2 generation through H_3PO_4 reaction of acid digestion (at least at the 1 SD analytically resolvable level) and then that a single $\Delta_{47} - (1/T^2)$ relationship can fit through all analyzed (proto)dolomites.

5.1.1. Comparison of data between IPGP and Caltech

Our dataset allows comparison of various steps of the procedures used for data acquisition and processing in two different laboratories on a single suite of samples. While only one or two reference materials (often Carrara marble) are generally common to Δ_{47} measurements made in various laboratories, the comparison of data on our suite of samples covering almost the full ranges of Δ_{47} and $\delta^{13}C$ and $\delta^{18}O$ found for natural carbonate samples provides a unique opportunity to identify whether potential analytical artifacts related to these procedures might explain some inconsistencies observed when comparing data from different laboratories [and, in turn, the diversity in published calibrations (Fig. 1)]. There are four main differences between the procedures used at IPGP and Caltech: (1) the length of the reaction between H_3PO_4 and the reacted carbonate powder (2 hours at IPGP on dolomite samples versus 20 minutes at Caltech with quantitative extraction only checked at IPGP), or the sample size reacted (from 5 to 8mg), or the acid concentration (~104% and ~103% at IPGP and Caltech, respectively) [both were made in common acid bath with approximately 10 mL of acid and a maximum of 16 samples dissolved in the same acid. The acid concentration after a series of digestion was not measured, but it is likely that it increased with increasing number of digestions (as qualitatively

monitored by the progressive decrease of the residual pressure above the acid bath)]; (2) the purification procedures for CO_2 generated from acid digestion of the reactant carbonate (cryogenically transferred through a trap filled with Porapak at IPGP versus transferred with He flow through gas chromatographic (GC) columns filled with the same polymer at Caltech); (3) the linearity corrections made using slopes of both heated gas lines (HGL) and, at IPGP, equilibrated gas lines (EGL), which are shallow and vary little with time at IPGP versus steeper and fast-moving at Caltech; (4) the stretching corrections made by direct transfer of Δ_{47} data into CDES at IPGP (with empirical transfer functions based on equilibrated CO_2 gases at both 1000 and 25°C run concurrently to unknown samples) versus indirect transfer at Caltech (with the tertiary transfer function given in Table 4 of Dennis et al., 2011).

When comparing data acquired in the two laboratories, several features are observed. First, the mean Δ_{47} values obtained for Carrara marble analyzed in both laboratories are indistinguishable from each other ($\Delta_{47CDES25}$ = 0.402‰ at IPGP and Caltech) and from the previously published recommended values (e.g., Dennis et al., 2011, Henkes et al., 2013). Second, internal precision for raw Δ_{47} values ran at IPGP and Caltech are comparable (typical SE of 9 ppm and 11 ppm, respectively; Tables S2 and S3) and consistent with the shot noise limit of Δ_{47} measurements (for detailed explanations see Huntington et al., 2009; Zaarur et al., 2013). Third, external reproducibility (SD) on several replicate Δ_{47} measurements of the same dolomite sample inside of the same laboratory tends to be substantially poorer at Caltech, compared to IPGP on comparable samples with similar number of replicates ran (with SD ranging from 4 to 22 ppm at Caltech compared to 0 to 11 ppm at IPGP). In parallel, the good consistency observed between the Δ_{47CDES} data out of the two laboratories suggests that transferring dolomite $\Delta_{47Ghosh}$ data acquired at Caltech in the "old" reference frame into the CDES using GTTF defined in Table 4 of Dennis et al. (2011) did not generate significant (i.e., analytically resolvable) additional uncertainties in Δ_{47CDES} values. [This means that the composition of the CO_2 tank used as a working gas at Caltech at the time dolomite data were acquired was similar to those used both at the time of Ghosh et al., 2006 and Dennis et al. 2011 data were obtained – note however that it might not be the case for all datasets acquired at Caltech over all times (i.e., with various aliquots of Oztech CO_2 tanks)].

We thus conclude that we can here average Δ_{47} values obtained for various replicate measurements independent of the laboratory in which they were measured, and that none of the differences in the analytical or post-measurements data processing procedures used at IPGP or Caltech can explain the scatter in calibration data shown in Figure 1.

5.1.2. *Isotopic equilibrium reached for $^{13}C–^{18}O$ bond distribution and $^{18}O/^{16}O$ ratios into the mineral lattice*

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The Δ_{47} values obtained for (proto)dolomite samples investigated decrease with increasing growth temperature, reflecting thermodynamically-controlled $^{13}C-^{18}O$ clumping during carbonate precipitation. However, it has been previously suggested that rapid laboratory mineral precipitation may sometimes lead to kinetic fractionation of isotopes preventing isotopic equilibrium to be reached while relations between $\delta^{18}O$ and growth temperatures may still exist (as discussed for oxygen isotopes in Kim and O'Neil, 1997). Another potential difficulty specific to $^{13}C-^{18}O$ clumping may arise from solid-state diffusion that can drive partial $^{13}C-^{18}O$ bond reordering to a "more clumped" state (i.e., leading to artificially higher Δ_{47} values than those expected at a given growth temperature) when high temperature carbonate samples were cooled down to room temperature. Indeed, solid-state diffusion has been suggested to drive isotopic exchange and $^{13}C-^{18}O$ bonds reordering upon cooling of high temperature carbonates as suggested for natural marbles or carbonatites (e.g., Dennis and Schrag 2010, Bonifacie et al., 2013, Stolper and Eiler, 2015), or experimentally heated carbonates (Passey and Henkes, 2012, Stolper and Eiler 2015). Based on three main arguments, we suggest that conditions prevailing during the crystallization of (proto)dolomites investigated here allowed reaching and retaining equilibrium for both $^{18}O/^{16}O$ isotope ratios and $^{13}C-^{18}O$ bonds abundance.

First, there are remarkable consistencies between $\delta^{18}O$ or Δ_{47} values for dolomites that grew from different batches of synthesis at a given growth temperature, with different conditions of durations (Table 1), differences in starting seed materials (e.g., sample 100A-2 and 100A-3 respectively crystallized after 36 and 85 days from aragonite and calcite seeds with very different bulk isotopic compositions; Table S1) or starting solutions (with different Mg/Ca ratios and ionic strengths) used for syntheses at 150°C, 250°C, 300°C and 350°C (Table S1). Indeed, despite those different experimental conditions at each investigated temperatures from 100 to 350°C, duplicate experiments all show very reproducible Δ_{47} results with standard deviation in the range of ± 0.015‰ to ± 0.022‰ (2σ) and standard error between ± 0.005‰ and ± 0.009‰ (Table 2) – a feature also observed on $\delta^{18}O$ analyses (Horita, 2014). This suggests sample homogeneity regarding their $\delta^{18}O$ and Δ_{47} compositions, as also suggested by the good external reproducibilities for their $\delta^{13}C$ and $\delta^{18}O$ values determined on various sizes of samples (i.e., 1 mg of carbonate reported in Vasconcelos et al., 2005 and Horita, 2014 compared to 5-8 mg used for simultaneous determination of Δ_{47}, $\delta^{13}C$ and $\delta^{18}O$ at IPGP and Caltech) – but also that equilibrium conditions were reached for both oxygen isotopes and $^{13}C-^{18}O$ bonding over the various batches of syntheses (see also discussion in Horita, 2014 for $\delta^{18}O$ values only).

Second, there is no simple way to prove that the equilibrium $^{13}C-^{18}O$ bond distribution in carbonate is preserved during rapid quenching from a high temperature carbonate (particularly from those above, or close to, the closure temperature of carbonate minerals with respect to solid-state reordering of C–O bonds; that is about 200-300°C, Bonifacie et al., 2013). However this seems to be a reasonable

hypothesis given that the dolomites close to this blocking temperature (samples 200-A1, 250-A1 and A5, 300-A2 and A5, and 350-A7 and A9) show Δ_{47} values aligning well with the lower temperature samples (Fig. 2), which were held at temperatures too low to be affected by solid state $^{13}C–^{18}O$ reordering over short timescales (minutes to hours), according to kinetic results from previous studies (Bristow et al., 2011; Passey and Henkes, 2012; Bonifacie et al., 2013; Henkes et al., 2014, Stolper and Eiler, 2015). Alternatively, the possibility that dolomitization reactions might have proceed prior to reaching the experimental temperatures has been tested with the 350-A7 experiment, which started from room temperature. However, the Δ_{47} (and $\delta^{18}O$) results suggest that such premature reactions are very likely negligible since sample 350-A7 shows an average Δ_{47} value of 0.203‰ (n= 3 replicate measurements) that is, in fact, slightly lower than the average Δ_{47} of 0.233‰ obtained for the sample 350-A9 (n= 2) synthesized in "normal experimental conditions" (which is opposite in direction to the expected effect of inheritance of material grown at lower temperature), but indistinguishable from each other when our 1 SD external reproducibility on carbonate standards is considered.

Third, perhaps most importantly, while samples studied here were generated from various types of dolomite-forming processes (microbially-mediated precipitation *versus* hydrothermal dolomite formed by replacement of pre-existing calcite *versus* precipitation from a mixture of solutions) they all follow a single trend in the measured Δ_{47} of CO_2 versus $1/T^2$ space that is parallel to the theoretical prediction for Δ_{63} dependence to temperature of the abundance of the $^{13}C^{18}O^{16}O_2$ in the dolomite mineral lattice as expected from ab-initio calculations (Schauble et al., 2006) (Figure 2). It is unlikely that these features would be (fortuitously) observed if equilibrium in distribution of $^{13}C–^{18}O$ bonds were not reached during laboratory and natural crystallizations of the (proto)dolomite samples studied here.

5.1.3. No measurable effect of cation ordering or Mg/Ca ratio on $^{13}C–^{18}O$ clumping in the mineral lattice or its extracted CO_2

Samples investigated here show a range of characteristics found in naturally occurring (proto)dolomites with various degrees of cation ordering and stoichiometry (Table 1). Because the oxygen isotope fractionation factor for phosphoric acid digestion of carbonates can vary with its crystal structure (Hardie, 1987; Schmidt et al., 2005), we paid particular attention to determine if various Mg/Ca composition or degree of cation ordering would significantly affect $^{13}C–^{18}O$ clumping. However, the conformance of all data to a single linear trend with a correlation coefficient $r^2 > 0.99$ argues against significant clumped isotope effects related to cation ordering and stoichiometry (Fig. 2). In particular, high temperature samples (highly ordered and stoichiometric dolomite, that are samples synthesized at $T \geq 150°C$, would not align with lower temperature samples (and particularly protodolomite which are

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poorly ordered and non-stoichiometric). Importantly, when only high temperature samples (i.e., fully ordered and stoichiometrical dolomites strictly) are considered in the regression calculation, the resulting regression line is indistinguishable from the one fitting through all samples. As importantly, while (proto)dolomite samples studied here show various degrees of cation ordering and stoichiometry, they all fit through one single Δ_{47}–$(1/T^2)$ regression line ($r^2 > 0.99$) that is parallel to the theoretical prediction of the Δ_{63} dependence to temperature of the abundance of the $^{13}C^{18}O^{16}O_2$ isotopologue in the dolomite mineral lattice (Schauble et al., 2006) in the 25 – 350°C range of temperature investigated (Fig. 2b).

We thus conclude that the degree of ^{13}C–^{18}O clumping both in the carbonate lattice and in the CO_2 extracted by acid digestion of the reactant carbonate does not depend, at least at the analytically resolvable level, on the degrees of ordering and/or stoichiometry of the analyzed dolomite samples. Therefore, we conclude that a single Δ_{47}–$(1/T^2)$ calibration trend can be used to convert $\Delta_{47CDES90}$ data into temperature estimates of unknown (proto)dolomite samples across a range of "intrinsic characteristics" and ambient temperatures common in shallow crustal and surficial environments.

5.2. Δ_{47} dependence with growth temperatures for dolomite

5.2.1. Linear Δ_{47}-$1/T^2$ dependence for 25-350°C temperatures

Here we calculate least square regression analysis fitting through the (proto)dolomite data according to Minster et al. (1979) modified from York (1969), which takes into account the independent and weighted errors on the growth temperature and the Δ_{47} data. The following dependence is found:

$$\Delta_{47CDES90} = 0.0428 \, (\pm 0.0033) * 10^6/T^2 + 0.1174 \, (\pm 0.0248) \qquad (r^2 = 0.998) \qquad [Eq. 1]$$

with temperature (T) reported in Kelvin, $\Delta_{47CDES90}$ reported in per mil and into the 90°C acid digestion and CDES reference frames. We emphasize that Equation [1] was calculated for Δ_{47} data averaged by growth temperatures and weighed from the well-known (ie., determined with large number of replicate Δ_{47} measurements n) standard deviation on carbonate reference materials corrected with the t-distribution factor for the 95% confidence interval (Figure 3). This approach takes into account a "small" number of analyses n of unknown samples. The uncertainties on the slope and intercept are given for the 95% confidence interval. Note that if average Δ_{47} dolomite data are weighted with their respective standard error of the mean (1 SE) (like for most of previously published Δ_{47}-$(1/T^2)$

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calibration equations), the calculated slope and intercept are comparable to those from Equation [1] (0.0428 and 0.1173, respectively), but reported errors are about five times less than those we report in Equation [1] (with errors as 1 SD being ± 0.0007 and ± 0.0050 on the slope and intercept, respectively). These low uncertainties are amongst (if not) the best reported so far for a Δ_{47}-T calibration of the clumped isotope thermometer. This likely reflects both the small dispersion of the large number of replicate Δ_{47} measurements ran on (proto)dolomites crystallized at a given temperature, as well as the very large range of formation temperatures investigated (the largest range to date).

Finally, it is noteworthy that we chose here to use linear fitting of the data in the investigated 25-350°C temperature range (rather than polynomial sometimes used for describing large ranges of temperatures) because equations of linear regressions are easier to manipulate and because our statistical test of the use of a squared term to fit our dolomite data was found to be negligible (i.e., a Student t-test lead to rejection of the hypothesis that the Δ_{47} dependency to T^{-4}, with a confidence degree much larger than 95%). Note however that our (proto)dolomite data are thereafter used together with previously published experimental data on calcites of higher temperature to provide a Δ_{47}-T polynomial fit for growth temperature up to ~1600°C; section 4.3.

5.2.2. Uncertainties on temperature estimates for unknown dolomite samples

Figure 3b illustrates the 95% confidence interval of temperature estimates based on Δ_{47} data of unknown samples using dolomite calibration from Eq. [1]. The 95% confidence interval uncertainties on temperature estimates resulting from Equation [1] are less than ± 3°C below 50°C, ± 5°C at 100°C, ± 7°C at 150°C and ± 10°C at 200°C. Importantly, those uncertainties: (1) would be about two times smaller if only the 66% confidence interval level is chosen instead (which is the case in most geological studies), (2) apply only to data obtained using 90°C acid digestion reaction and/or for conditions of analyses for which Δ^*_{x-90} is precisely known, and (3) are larger when uncertainties on Δ_{47} data are considered. As importantly, those uncertainties on determining growth temperatures based on Δ_{47} measurements are only relevant for temperatures below the blocking temperature of the considered carbonate mineral (that are 200 and 300°C for calcite and dolomite respectively; Bonifacie et al., 2013) since, at higher temperatures, solid-state diffusion can change the $^{13}C-^{18}O$ bond distribution originally recorded in the mineral lattice during its crystallization.

5.3. Kinetic fractionation of Δ^* during acid digestion

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5.3.1. Empirical determination of $\Delta^*_{dolomite90}$ and comparison to $\Delta^*_{calcite90}$

The kinetic fractionation factor during acid digestion of dolomite at 90°C ($\Delta^*_{dolomite90}$) is here estimated by calculating the difference between our Δ_{47} measurements of CO_2 extracted from dolomite grown at known temperature and the Δ_{63} abundance of $^{13}C^{18}O^{16}O_2$ isotopologues in the dolomite lattice theoretically expected at a given temperature from ab-initio calculations (Schauble et al., 2006) (see Figure 4 for a graphical representation of those calculations). For doing so, we implicitly make the assumption that the Δ_{47}-$(1/T^2)$ relationship empirically obtained on dolomites only reflects a combination of both the initial ^{13}C–^{18}O clumping state in the mineral lattice and of the kinetic fractionation factor $\Delta^*_{dolomite}$ associated to CO_2 generation at a given temperature for acid digestion (a reasonable hypothesis as discussed in part 5.1). For a given growth temperature, the calculated difference empirically obtained in between Δ_{63} from ab-initio calculations and Δ_{47} values on our investigated dolomites, averages to 0.176‰ with only a small uncertainty (i.e., 1SD of $\pm$ 0.006‰ and a total variation range of +0.166‰ to 0.189‰). Such small range in this calculated difference suggests that $\Delta^*_{dolomite90}$ varies little (i.e., less than the analytically resolvable level of $\pm$ 0.014‰, that is the 1 SD long-term external reproducibility reached at IPGP on carbonate reference materials) with either: i/ the cation ordering and Mg/Ca ratios of the analyzed carbonates (as discussed in 5.1.3.); and ii/ the intrinsic Δ_{47} and δ^{47} values of the considered carbonate (at least for the ranges investigated here: $\Delta_{47CDES90}$ values from 0.215 to 0.604‰ and δ^{47} values from -68 to +12‰). [These latter two features are *qualitatively* consistent with the theoretical model of Guo et al. (2009) that predicted only slight Δ_{47} changes of 0.035‰ in reacted carbonates associated with a 1‰ increase in Δ_{63} and Δ_{47} changes of 0.002‰ per 50‰ increase in $\delta^{13}C$ of the reacted carbonate]. It is noteworthy that while our approach to determine $\Delta^*_{dolomite90}$ conceptually applies only to the 25-350°C temperature range we examined, the $\Delta^*_{dolomite90}$ estimated here is indistinguishable from the Δ^* estimated using the same approach for calcite digested at 90°C (hereafter $\Delta^*_{calcite90}$) of Passey and Henkes (2012) (Figure 4). Indeed, the six calcite samples with ^{13}C–^{18}O bonds re-equilibrated at temperatures between 475°C and 800°C show an average difference of $\Delta^*_{calcite90}$ = + 0.198‰ (with 1ΣD of $\pm$ 0.009‰) between their $\Delta_{47CDES90}$ values (that are Δ_{47} values from Table 1 in Passey and Henkes 2012 from which we subtracted the + 0.081‰ value to "uncorrect" for the acid fractionation factor they added to account for a 25°C digestion reference frame) and the theoretical Δ_{63} abundance of $^{13}C^{18}O^{16}O_2$ isotopologues into calcite lattice out of ab-initio calculations (Schauble et al., 2006). Here, we chose to compare our calculated Δ^* for dolomite ($\Delta^*_{dolomite90}$) to that for calcite ($\Delta^*_{calcite90}$) calculated out of Passey and Henkes (2012) rather than to other studies reporting low-

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temperature synthesis of carbonates, because (similarly to in our study): acid digestion was made at 90°C, Δ_{47} data were directly reported into the CDES, and perhaps most importantly, isotopic equilibrium was more likely to have been reached in their calcite samples heated at high temperatures. Such similarity in empirically calculated $\Delta^*_{dolomite90}$ and $\Delta^*_{calcite90}$ suggests that: (1) using the same $\Delta^*_{dolomite90}$ for dolomite for the whole range of growth temperature (not just the 25-350°C range investigated here) is likely a reasonable hypothesis; and (2) more broadly, Δ^*_{90} for dolomite and calcite digested at 90°C are indistinguishable and thus that, as discussed in part 5.1.3, the kinetic isotope fractionation over acid digestion Δ^* seems to be independent of the structure or Mg/Ca ratio of the analyzed carbonate (at least at the level of current analytical capacities in laboratories making Δ_{47} measurements) and close to the + 0.176‰ value determined here.

5.3.2. Comparison to the experimentally determined $\Delta^*_{calcite25}$

Guo and co-workers (2009) have experimentally determined the kinetic fractionation factor associated to the 25°C acid digestion of calcite minerals ($\Delta^*_{calcite25}$) by measuring the Δ_{47} value of calcites that were formerly melted and recrystallized during quenching from high temperature (T > 1550°C) [with the assumption that the Δ_{47} value of the CO_2 extracted from those disordered calcite minerals should then equal 0‰ (i.e., the Δ_{63} value for a carbonate showing a stochastic bond distribution) plus $\Delta^*_{calcite25}$]. They measured $\Delta_{47Ghosh25}$ values averaging + 0.232‰ (reported in the "stochastic" reference frame) with a variation of ± 0.015‰ (1ΣD) on their three disordered calcites. In order to compare their average $\Delta^*_{calcite25}$ value to our estimate of the $\Delta^*_{dolomite90}$, we transferred their $\Delta_{47Ghosh25}$ average into both CDES and 90° acid digestion reference frames by: (1) using the relationship $\Delta_{47CDES} = 1.0381 * \Delta_{47Ghosh} + 0.0266$ (that is the tertiary transfer function given in Table 4 of Dennis et al. (2011) for reporting old Caltech data into the absolute reference frame), giving a $\Delta_{47CDES25} = + 0.267‰$ and (2) then subtracting the 0.092‰ (i.e., the difference between 25°C and 90°C acid digestion measured for calcite in CDES; Henkes et al., 2013) to obtain a $\Delta_{47CDES90} = + 0.175‰$. Despite the fact that both of these values likely have significant uncertainties that are difficult to evaluate (although independent), the Δ^*_{90} values recalculated here for both calcite and dolomite are remarkably similar to each other (as well as to the value calculated from Passey and Henkes (2012)). This suggests that calcite and dolomite have the same absolute kinetic fractionation Δ^* over acid digestion at both 25 and 90°C. This hypothesis also finds support in the fact that when we calculate a polynomial fit based on these three sets of experimental data on both calcite and dolomite in the 25-1600°C temperature range, the resulting relation [Equation 2] is remarkably consistent with the relation defined by adding the fractionation

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factor $\Delta^*_{90} = 0.176‰$ (estimated here for both dolomite and calcite) to the theoretical Δ_{63} dependence to temperature for dolomite and calcite predicted from ab-initio calculations (Schauble et al., 2006) (Figure 4b). Equation 2 is defined as :

$$\Delta_{47CDES90} = + 1.0771 * 10^{-3}(10^6/T^2)^2 + 2.5885 * 10^{-2}(10^6/T^2) + 0.1745 \qquad \text{[Eq. 2]}$$

with temperature (T) reported in Kelvin, $\Delta_{47CDES90}$ reported in per mil into both the 90°C acid digestion and CDES reference frames. Note that we recommend using [Eq. 2] only if very high temperatures (T > 300°C) are relevant (e.g., for experimentally driven high temperature equilibration of $^{13}C–^{18}O$ bonds), the Equations [1 and 3] being more appropriate for the low temperature ranges.

5.4 Comparison to previous calibrations

Our dolomite samples digested at 90°C describe a linear regression with a shallower slope than carbonates digested at 25°C, as already noticed in many previous comparisons of high (ie. T ≥ 70°C) versus low digestion temperatures for other carbonate minerals (calcite, aragonite, siderite) [see the latest compilation in Defliese et al., 2015]. With the aim to reduce uncertainties when comparing datasets based on low versus high temperature of acid digestion, and because, despite large efforts from the clumped isotope community, it is still difficult to understand such discrepancy, we here compare our dolomite data only to those acquired with high-temperature phosphoric acid digestion reactions (i.e., 70°C < digestion temperature < 100°C). In parallel, in order to minimize bias due to the data treatment used in different studies we also chose to *only* compare Δ_{47} data that were *directly* projected into the CDES and to report those data into the 90°C acid digestion reference frame instead of the 25°C reference frame used so far – that is samples digested at temperatures other than 90°C have been converted into the 90°C acid digestion reference frame subtracting or adding the fractionation Δ^*_{90-X} value recommended by Defliese et al., (2015). In addition to being more practical (since most of laboratories that are currently generating Δ_{47} data are running 90°C acid digestion reactions) this approach has the advantage of eliminating uncertainties from transferring Δ_{47} data into the 25°C acid digestion reference frame when variable Δ^*_{25-90} were previously used (e.g., from 0.069 to 0.092‰ for calcite).

5.4.1. *Consistency of most (Ca, Mg, Fe)CO₃ carbonates digested at high-temperatures*

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When only carbonates digested at high temperatures ($T \geq 70°C$) are considered, most of the suites of carbonate minerals of various origins (inorganic or biogenic calcites, aragonites, siderites from Henkes et al., 2013, Wacker et al., 2014, Fernandez et al., 2014, Tang et al., 2014, Defliese et al., 2015, Kele et al., 2015) are remarkably similar to our (proto)dolomite dataset – with the exception of the calcite data from Kluge et al., (2015) – and all fit inside the 95% confidence envelop defined by our dataset (Figure 5) although measurements were made in seven different laboratories (i.e., with different reaction times, nature of phosphoric acid used, number of replicate analyses made, long-term external reproducibilities on carbonate reference materials, etc.). [See also Figure S3 for another graphical representation of the Kluge et al.'s data offset relative to our data as well as other previously published data on high-temperature calcites and theoretical predictions]. In addition, all data are distributed around the polynomial trend calculated here for the 25-1600°C temperature range [Equation 2] and the one defined by adding the fractionation factor $\Delta^*_{90} = + 0.176‰$ (empirically determined here) to the theoretical predictions of the Δ_{63} dependence on temperature calculated by Schauble et al., (2006) (Figures 5 and S3). This observation about experimental data from seven laboratories supports the hypothesis made above that calcites and dolomites (and possibly aragonites and siderites) have similar kinetic fractionation Δ^* over acid digestion, at least for high digestion temperatures (with apparently no influence of the cation identity or mineral structure). This feature is however not consistent with the data reported by Kluge et al. (2015) that show significantly higher (i.e., circa $\geq + 50$ ppm) Δ_{47} values for a given growth temperature than other data reported in Figures 5 and S3. This offset could result from either intrinsic characteristics of the synthesized samples and/or different methods used for data acquisition or reduction. For instance the heated gas lines used to correct data in Kluge et al. (2015) were both moving fast and with a strong-slope. Such analytical conditions might in some cases lead to: (1) less accurate processing of raw Δ_{47} data (as shown by their 1SD long-term external reproducibility of ± 30 ppm obtained on carbonate reference materials, compared to the ± 14 ppm obtained at IPGP and Caltech) and (2) poorer knowledge on the slope and intercept reported for their Δ_{47}-T relation that are 2 to 3 times larger than in [Eq. 1] when calculated similarly (Figure S4). However, even though the total variation range in Δ_{47} values reported for Carrara reference material in Kluge et al. (2015) is two times larger than that obtained over the course of this study (Fig. S5), the fact that average $\Delta_{47CDES90}$ values found for Carrara marble in those two laboratories are indistinguishable when respective uncertainties are taken into account (i.e., $\Delta_{47CDES90} = 0.335 \pm 0.030‰$, 1SD, n=71; $0.310 \pm 0.014‰$, 1SD, n=24; $0.310 \pm 0.018‰$, 1SD, n=12; respectively found at Imperial College by Kluge et al., 2015 and at IPGP and Caltech in this study only – and confirmed by hundreds of measurements made since) does not argue in favor of a systematic analytical bias between those laboratories. On the other hand, it is notable that samples from Kluge et al. (2015) that show the largest offset from the other published data

are those synthesized using the "pressurized reaction vessel" method (Fig S3, and fitting systematically outside the 95% confidence envelops in Figure 5), which might reflect potential artifacts associated with the method of synthesis of these samples. Alternatively, the offset might also partly result from the choice of ^{17}O correction parameters that could influence both data accuracy (as recently suggested by Daëron et al., 2016) and agreement between calibration datasets out of different laboratories. Thought it is not simple to predict how re-processing published data with ^{17}O correction parameters different from those initially used for corrections in respective studies will influence the magnitude and direction of changes for Δ_{47} data, it is unclear why only the samples from Kluge et al. (2015) (or only those synthesized using the "pressurized reaction vessel") would be affected by such artifacts and not the other calibration samples/data considered here (out of five different studies/laboratories). Finally, because it is difficult to clearly identify the reasons of the observed ~ 50 ppm offset with all the comparable data (i.e., acquired via digestion at high temperatures ≥ 70°C and *direct* transfer into CDES) published to date, the data from Kluge et al., (2015) are treated separately in the following calculations of the composite Δ_{47}-T calibration.

5.4.2. Master calibration for all (Ca, Mg, Fe)CO₃ carbonates digested at high temperatures

Previous attempts were made to provide "universal" Δ_{47}-$(1/T^2)$ relationships from a variety of combinations of published calibration datasets (Zaarur et al., 2013, Wacker et al., 2014, Rosenheim et al., 2013, Klugge et al., 2015, Defliese et al., 2015, Stolper and Eiler, 2015) with the aim of either understanding the reasons of the divergences in Δ_{47}-T relations measured in different laboratories and/or increase the statistical number of data used for calculation of the Δ_{47}-$(1/T^2)$ relationship (to decrease the "artificial/biased" uncertainties on the slopes and intercepts of the calculated linear regression) and thus smooth out differences and standardize temperature estimates based on Δ_{47} data for the whole community. Examples of these attempts include gathering data with various methodological treatment and/or origins (i.e., intrinsic characteristics of analyzed carbonates) for which the consistency is contested and/or not proven yet, as for instance gathering data: (1) for different acid digestion temperatures (e.g., Kluge et al., 2015, Stolper and Eiler, 2015); (2) reported in various reference frames, with some transfer of old data made without knowing the long-term external reproducibility (or number) of equilibrated CO_2 gases or carbonate standards ran together with unknown samples (Zaarur et al., 2013, Defliese et al., 2015, Stolper and Eiler, 2015); (3) corrected for acid digestion fractionation with Δ^*_{25-90} varying from 0.069 to 0.100‰ (Wacker et al., 2014, Rosenheim et al., 2013, Kluge et al., 2015) (with acid corrections sometimes made before the transfer into the absolute reference frame); (4) on experimentally grown abiogenic carbonates with natural biogenic carbonates for which, besides the

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possible influence of minor vital effects or possible mixing of seasonal growth bands, the growth temperatures is often known with much less precision (Zaarur et al., 2013; Wacker et al., 2014; Defliese et al., 2015); and/or (5) on various mineral phases (Stolper and Eiler, 2015, Defliese et al., 2015). However, it is possible that gathering Δ_{47} data from so many origins and characteristics (ie., different procedures for data acquisition and post-measurement corrections, different intrinsic properties of the analyzed carbonates, or different statistical treatment of data – that is with some data points representing Δ_{47} averages out of 2 to 27 replicate measurements) might reduce the accuracy and precision of temperature estimates from Δ_{47} measurements.

Here, with the aim of both improving the accuracy and reconciling temperature estimates (and their associated uncertainties) of different laboratories digesting carbonate samples at temperatures T $\geq$ 70°C, we formulate a composite calibration for all (Ca, Mg, Fe)CO$_3$ carbonate minerals by compiling data (directly transferred to CDES only) on dolomite, calcite, aragonite and siderite out of seven different laboratories (IPGP, Caltech, ETH and Universities of Tulane, Michigan, Johns Hopkins and Frankfurt). In order to statistically treat all Δ_{47} data in the same way (and thus eliminates a degree of uncertainty when comparing different datasets), all Δ_{47} data were averaged by growth temperature and weighted from the well-known standard deviation on carbonate standards in respective studies corrected with the t-distribution factor for the 95% confidence interval and the considered number of replicate Δ_{47} measurements of unknown samples. [This approach takes into account the small number of replicate Δ_{47} measurements in respective studies – which is between 4 and 11 in our study, but is mostly around 3 in other calibration studies]. This represents a total number of 103 mean Δ_{47} values resulting from more than 331 Δ_{47} measurements. Figure 6 shows mean Δ_{47} data and the calculated equations of the least-square regression fitting through the data on inorganic carbonates only (Fig. 6a) or inorganic plus biogenic carbonates (Fig. 6b). Although considering the whole inorganic dataset for the calculation of the Δ_{47}-$(1/T^2)$ linear regression slightly changes the slope, intercept and the 2SD uncertainties (i.e., slope = 0.0438 ± 0.0024‰ and intercept = 0.1144 ± 0.0229‰; Fig. 6a) compared to those determined for dolomite only in [Eq. 1], neither the absolute values nor the uncertainties of the temperature estimated from Δ_{47} data are significantly changed. This feature likely results from the fact that dolomite Δ_{47} data have high statistical weight in the calculation of this regression line [i.e., statistical weight of ~ 42%, with only 12 mean Δ_{47} values out of 48 considered in total. This reflects the low 95% confidence interval uncertainties associated to our data compared to some other considered here]. In contrast, when considering the whole dataset including biogenic samples (Fig. 6b), the statistical weight of the dolomite data is lowered to less than 29% (with only 12 out of a total population of 103 mean Δ_{47} values considered here), and the calculated linear regression is:

$$\Delta_{47CDES90} = 0.0422\ (\pm\ 0.0019) * 10^{6}/T^{2} + 0.1262\ (\pm\ 0.0207) \qquad (r^2 = 0.985) \qquad [\text{Eq. 3}]$$

with temperature (T) reported in Kelvin, $\Delta_{47CDES90}$ in per mil with both 90°C acid digestion and CDES reference frames, and uncertainties on slope and intercept reported in 2SD. Finally, if average $\Delta_{47\ CDES90}$ data are weighted with their respective standard error of the mean (1SE) like for most of previously published Δ_{47}-T calibration equations, the calculated slope and intercept are comparable (0.0424 and 0.1257‰, respectively) to those from Equation [3] [however with uncertainties more than three times less (i.e., 1SD uncertainties of $\pm$ 0.0003 and $\pm$ 0.0035‰, respectively) and the statistical weight of the dolomite dataset lowered to less than 16%].

Most importantly, the absolute values of the slope and intercept of Equation [3] considering Δ_{47} data on inorganic and biogenic calcite, aragonite, dolomite and siderite from seven different laboratories are remarkably consistent with those defined based on the dataset acquired on dolomite only at IPGP and Caltech. In other words, for a given $\Delta_{47CDES90}$ value, temperature estimates resulting from Equations [3] and [1] only slightly differ from each other (i.e., a difference of less than 1°C for temperatures below 50°C and 2°C for temperatures up to 150-200°C). It is noteworthy that those differences are irrelevant when uncertainties on replicate Δ_{47} measurements are also considered (at least at the level of current analytical capabilities in laboratories making Δ_{47} measurements). Thus, we propose that this single composite Δ_{47}-$(1/T^2)$ calibration can be used to convert $\Delta_{47CDES90}$ data from different laboratories using comparable analytical conditions into accurate and standardized temperature estimates for all (Ca, Mg, Fe)CO$_3$ carbonates of geological interest (e.g., calcite, dolomite, aragonite, siderite, magnesite).

A discussion about possible Δ_{47} vital effects is beyond the scope of this study, but the fact that biogenic carbonates reported in Figure 6 are remarkably consistent with Δ_{47} data for inorganic carbonates acquired under comparable analytical conditions supports the lack of significant vital effects on Δ_{47} (at least at the analytically resolvable level) for some biogenic carbonates (e.g., Henkes et al., 2013; Zaarur et al., 2013, Wacker et al., 2013; Tripati et al., 2010; Thiagarajan et al., 2010). Thus, in order to standardize temperature estimates and associated uncertainties out of Δ_{47} data from different laboratories using high temperature acid digestion, we also recommend the use of [Eq. 3] for biogenic carbonates for which the absence of vital effects have been demonstrated.

6. SUMMARY AND BROADER IMPLICATIONS

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We present carbonate clumped isotope analyses of natural and synthetic (proto)dolomites grown at known temperatures from 25 to 350°C. This dataset allows formulation of a Δ_{47}-$(1/T^2)$ calibration that is linear in the 25-350°C temperature range, and allows determination of formation (or possibly reequilibration) temperatures of dolomites with the highest precision that is currently possible by multiple replicate Δ_{47} measurements of the same unknown carbonate sample. This represents the first experimental calibration dataset: (1) concurrently acquired in two different laboratories with different methods used for both data acquisition and post-measurement processing; (2) for dolomite minerals; and (3) for a wide range of temperature spanning more than 300°C (that is close to the total range of temperature observed in the Earth's surface and shallow crust). Our dolomite data are used to discuss some key issues related to the use of the carbonate-clumped isotope thermometry, including Δ_{47} dependence on mineral structure and elemental composition (notably Mg content), fractionation factor during phosphoric acid digestion of carbonate minerals (Δ^*), uncertainties in temperature estimates based on replicate Δ_{47} measurements of unknown samples, consistency of Δ_{47} data (and the resulting temperature estimates and uncertainties) acquired in different laboratories as well as the potential difference in Δ_{47}-$(1/T^2)$ calibrations for various types of carbonate with significant geological interest (e.g., calcite, aragonite, dolomite, siderite, magnesite). We conclude that:

(1) None of the intrinsic characteristics of the (proto)dolomite samples investigated here (i.e., formation mechanism, degree of cation ordering, Mg/Ca ratios and/or $\delta^{18}O$ and $\delta^{13}C$ compositions) seem to influence ^{13}C–^{18}O clumping either within the mineral lattice or in the CO_2 generated through H_3PO_4 acid digestion (at least at the analytically resolvable level) and then that a single Δ_{47}-$(1/T^2)$ relationship can adequately represent all analyzed dolomite samples. The 1SD uncertainties in temperature estimates resulting from the dolomite calibration [Equation 1] are less than ± 1.5°C below 50°C, ± 2°C at 100°C, ± 3.5°C at 150°C and ± 5°C at 200°C, and only apply to temperatures under the blocking temperature of dolomite (i.e., at higher temperatures, solid-state diffusion can change the ^{13}C–^{18}O bond distribution originally acquired by the mineral lattice during crystallization).

(2) Kinetic fractionation factor Δ^*_{90} over acid digestion for calcite and dolomite are identical (at least at the level of current analytical capabilities in laboratories making Δ_{47} measurements), close to the + 0.176‰ value determined here. This suggests that Δ^*_{90} over acid digestion does not depend on the nominal Δ_{63} value, the cation identity or the mineral structure of the analyzed carbonate (which is also supported by the good agreement between our dolomite dataset and the previously published calibration datasets on calcite, aragonite and siderite). More widely, this confirms the previous suggestion that the difference in Δ_{47} observed between natural calcite and dolomitic

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marbles (Bonifacie et al., 2013) actually reflects a real difference in their blocking temperatures (that are about 200 and 300°C, respectively).

(3) For a given growth temperature, (proto)dolomite Δ_{47} data acquired in this study at both IPGP and Caltech are indistinguishable from most previously published Δ_{47} data for inorganic and biogenic calcites, aragonites and siderites analyzed under comparable analytical conditions (i.e., digestion temperature above 70°C with Δ_{47} data directly transferred into CDES) in seven different laboratories – with however data from Kluge et al., (2015) being statistically resolved from this group. This suggests that the kinetic fractionation factor during acid digestion is similar for calcite and dolomite (as suggested above) but also likely for aragonite and siderite (at least for high temperature digestion of carbonates). This also suggests that a single composite Δ_{47}–$(1/T^2)$ calibration can be used to convert $\Delta_{47CDES90}$ data measured in different laboratories using comparable analytical conditions into accurate and standardized temperature estimates for these four $(Ca,Mg,Fe)CO_3$ minerals of geological interest. The 1SD uncertainties on temperature estimates resulting from the composite Δ_{47}–$(1/T^2)$ calibration are less than ± 0.7°C at 25°C, ± 1°C below 50°C, and comparable to those from Equation [1] for higher temperature.

(4) This study allows the use of Δ_{47} for accurate and precise determination of carbonate growth temperature (or reequilibration temperature) for almost the whole range of temperature over which carbonate minerals form, and particularly for T > 50°C (that were poorly constrained by previous Δ_{47} calibration studies). It thus provides better constraints on the carbonate formation temperature (and associated uncertainties) and, consequently, on the $\delta^{18}O$ of the water from which it grew (provided the sample did not experience solid-state diffusion).

   More widely, in addition to providing new insights to several specific challenges that are facing the clumped isotope community, this study strengthens and standardizes the use of Δ_{47} thermometry in high temperature problems for which only few geothermometers can provide accurate temperature estimates for material (and particularly carbonates) that have experienced temperatures lower than 200°C. Indeed, some of the most widely applied thermometric methods for such environments are actually measurements of integrated temperature–time history and therefore require independent estimation of duration of heating (or, more generally, a temperature time path) in order to provide a meaningful estimate of the maximum temperature attained by a rock. As importantly, Δ_{47} thermometry allows simultaneous determination of both the temperature and oxygen isotopic composition of the mineralizing fluid – a feature that helps to elucidate questions relative to the nature and origin of the mineralizing fluid, or the conditions of water-rock interactions – for temperatures up to 200°C for calcites and 300°C for dolomites (Bonifacie et al., 2013). Δ_{47} thermometry also holds promises in

contributing to some longstanding questions in Earth Science like for instance determining the debated origin of dolomite minerals in sedimentary successions (sometimes referred as the "dolomite problem"). Since this gap in our understanding of dolomite formation and diagenesis partly results from the difficulty in determining its formation temperature, we anticipate that these questions should benefit from our development of the dolomite clumped isotope thermometer.

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Table and Figure caption

Table 1: Summary of the characteristics of the (proto)dolomite samples investigated here.

Table 2: Summary table of isotopic data out of replicate analyses of the dolomite samples analyzed in this study both at IPGP and Caltech. Stable isotope compositions of carbon ($\delta^{13}C$) and oxygen ($\delta^{18}O$) are reported on the PDB scale. Δ_{47} data are reported relative to the absolute reference frame (Carbon Dioxide Reference Frame – CDES) defined in Dennis et al., (2011), for acid digestion temperatures of 90°C (ie. the $\Delta_{47CDES90}$ value was not corrected for acid reaction temperature). "Av. $\Delta_{47CDES90}$" are replicate $\Delta_{47CDES90}$ measurements averaged by growth temperature. "n" is the number of replicate Δ_{47} measurements of dolomite samples for a given growth temperature. Uncertainties on mean $\Delta_{47CDES90}$ values are given both as: "± 1 S.E." = one standard error of the mean (1SD/√n ; ie., uncertainties considered in previous Δ_{47} calibration studies) and "± 95% C.I.∀ = uncertainties at the 95% confidence interval (ie. long-term external reproducibility on carbonate standards corrected with the student's t-distribution factor at the 95% confidence level for each n considered – this approach takes into account the small sample size for unknown samples – ie., 4 < n < 11 here). More details on each single replicate Δ_{47} measurement are reported in Table S2 and S3.

Figure 1: Compilation of previously published calibration data on carbonate minerals into the absolute and 25°C acid digestion reference frames in the temperature range of 0-80°C. Each datapoint represents an average of several analyses of the same carbonate sample (from n = 2 to sometimes up to 27; e.g. Wacker et al., 2014), the only exception being the study of Zaarur et al. (2013) for which one data point represents one measurement of one synthesized sample. Data are reported as given in the publication or projected using tertiary transfer functions (TTF) given in Table 4 of Dennis et al. (2011). Only data that could be placed into the absolute reference frame were included. No uncertainties are reported for clarity of the figure. Note that similar (if not larger) dispersion of data can be observed if data are reported in the stochastic reference frame (not shown). Data are also grouped "by type" of acid digestion temperatures (i.e., T = 25°C versus T ≥ 70°C). Note that we here prefer to show actual data points instead of the published calculated regression lines (like plotted in some previous papers) because those Δ_{47}-T relations were calculated with various statistical treatments (e.g., Δ_{47} data averaged by sample or growth temperatures and/or weighted (or not) by the number of replicate measurements and/or by the uncertainty on growth temperatures) that bias rigorous comparison of those datasets. The dashed lines represent the Δ_{47} dependence with growth temperature for the CO_2 extracted from calcite,

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aragonite and dolomite minerals as theoretically calculated by Guo et al., (2009). Here, we stress that those calculations, in contrast to their use in some recent papers, are based on transition state theory that should not change whenever the absolute (CDES) or the stochastic reference frames are considered (since those reference frames are related to analytical bias on mass spectrometric measurements and should thus *only* affect Δ_{47} data, not theoretical calculations).

Figure 2: Δ_{47} values for dolomite samples investigated here plotted against their assigned formation temperature. All data are reported in the absolute [CDES] reference frame and refer to CO_2 extracted by phosphoric acid digestion at 90°C. **Panel a**: All single Δ_{47} value (n = 67) acquired both at IPGP and Caltech: open diamonds = dolomite data acquired at IPGP after 2012 and *directly* reported into the CDES; open circles = dolomite data acquired at Caltech before 2011 and *indirectly* transferred into the CDES. Uncertainties on each Δ_{47} measurement and temperature estimate are included in the symbol size. Note that the IPGP Δ_{47} data show less dispersion than the Caltech Δ_{47} data, probably due to more stable (and/or better monitored) conditions of analyses. Alternatively, some of the scatter in the Caltech data might also partly result from the fact that the reactant H_3PO_4 acid was more dilute than at IPGP [ie., due to either lower starting concentration and/or the fact that the analyzed samples were larger at Caltech (that implies more water produced over the reaction, and thus more dilution of the acid)]. **Panel b:** Δ_{47} data averaged by formation temperatures. Filled squares = synthetic dolomites; open triangles = natural samples. In both panels, the solid line represents the Δ_{63} dependence on temperature of the abundance of the $^{13}C^{18}O^{16}O_2$ isotopologue inside the dolomite mineral lattice as expected from ab-initio calculations (Schauble et al., 2006). Uncertainties on mean $\Delta_{47CDES90}$ values are reported for the 95% confidence interval.

Figure 3: Panel a - Dolomite Δ_{47} –T calibration reported relative to the CDES and referring to CO_2 extracted by phosphoric acid digestion at 90°C. Plotted uncertainties on mean $\Delta_{47CDES90}$ values are the same as in Fig. 2b. The plain thick black line represents the least square regression line calculated according to Minster et al. (1979) modified from York (1969) [Equation 1], with uncertainties on slopes and intercepts given in 2σ [note that if S.E. were considered instead, as in previous studies, the reported uncertainties on slopes and intercepts are significantly smaller – about five times less; see text]. The dashed grey curves show the 95% confidence envelops for the calculated least square calibration line. The plain grey curves show the 95% confidence envelop for a temperature prediction for a single Δ_{47} measurement. **Panel b -** Graphical summary of 95% confidence domain of uncertainty on temperature estimates based on Δ_{47} data of unknown

samples using Equation [1]. The uncertainty on temperature estimates is shown as a function of both the temperature (*y-axis*) and the uncertainty on Δ_{47} measurements (contours) for an unknown sample. The uncertainty for the calibration alone is given by the solid black contours. Note that the reported uncertainties apply only to data obtained after 90°C acid digestion reaction and/or for conditions of analyses for which $\Delta^*_{X-90°C}$ is precisely known.

Figure 4: **Panel a-** Graphic representation of the ($\Delta_{47CDES90}$ data used for the) calculations for estimating Δ^* over acid digestion for dolomite and calcite plotted in the Δ_{47} versus $10^6/T^2(K^{-2})$ space (see details in part 5.3) in the 0-1600°C temperature range. All Δ_{47} data are reported relative to the absolute CDES reference frame and refer to CO_2 extracted by phosphoric acid digestion at 90°C. Black circles are dolomite from this study and the plain thick line is the same as in Figure 3 (i.e., Equation [1]). Light grey diamonds are inorganic calcites equilibrated at high temperatures from Passey and Henkes (2013). Dark grey diamonds are inorganic calcites equilibrated at T $\geq$ 1550°C from Guo et al. (2009). Though it is difficult to rigorously estimate uncertainties on previously published data, they should be larger than those reported here for dolomites (since the former are averages of a maximum of three measurements versus a minimum of 4 measurements for the latter). The dashed curves represent the Δ_{63} dependence of $^{13}C–^{18}O$ bonds distribution with temperature inside the dolomite and calcite lattices (blue and grey respectively) as expected from ab-initio calculations (Schauble et al., 2006). The reported Δ^*_{90} values were either empirically (in italic font) or experimentally (underlined font) determined. **Panel b-** Same data plotted in the Δ_{47} versus temperature (in °C) space. The plain green curve shows the polynomial fit calculated based on the three sets of experimental data (Eq. [2]). The red trends represent the Δ_{47} dependence on temperature for the CO_2 extracted from both dolomite and calcite (that are superimposed in this space) predicted by adding the fractionation factor $\Delta^*_{90} = + 0.176‰$ (estimated here for both dolomite and calcite) to the Δ_{63} theoretical predictions from Schauble et al., (2006) for these two minerals.

Figure 5: Comparison of all Δ_{47} data directly reported relative to the CDES and digested at high temperatures (T $\geq$ 70°C) only (panel **a** = temperature range of 0-350°C; panel **b** = zoom in the 0-80°C range). Δ_{47} data are averaged by sample and errors are not reported for more clarity. The plain black line as well as the grey dashed and plain envelops are the same than plotted in Figure 3 (i.e., Equation [1]). Note that Kluge et al (2015) data are statistically offset from the group formed by the rest of the data (see Figure S3 and S4 for more details). In panel b only, the long-dashed curves show: the polynomial trend from Equation [2] for the 25-1600°C temperature

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range (green curve) and the theoretical Δ_{47} dependence with growth temperature for the CO_2 extracted from both dolomite and calcite (both superimposed - red curves) predicted by adding the fractionation factor Δ^*_{90} = + 0.176‰ to the Δ_{63} theoretical predictions from Schauble et al., (2006) for these two minerals.

Figure 6: Composite universal calibrations for all (Ca, Mg, Fe)CO_3 carbonate minerals digested at high temperatures (T $\geq$ 70°C) and directly reported into CDES. **Panel 6a** shows $\Delta_{47CDES90}$ data and equations for inorganic minerals only (calcite, dolomite, aragonite and siderite determined at IPGP, Caltech, ETH, Tulane, and Michigan Universities – this represents a total of 48 mean Δ_{47} values). **Panel 6b** shows the same data together with those from biogenic calcites and aragonites acquired at Johns Hopkins and Frankfurt universities (this represents a total of 103 mean Δ_{47} values resulting from more than 331 Δ_{47} measurements). All $\Delta_{47CDES90}$ data were averaged by growth temperature and weighted from the standard deviation on carbonate standards corrected with the t-distribution factor for the 95% confidence interval and the considered number of replicate Δ_{47} measurements in respective studies. [For clarity of the figure, the uncertainties on average Δ_{47} values are plotted here only for inorganic samples – see Fig. S6 for a full report of the 95% confidence interval uncertainties as considered in our calculations]. This method presents the advantage that all Δ_{47} data are statistically treated in the same way, which eliminates a degree of uncertainty when comparing different datasets. In both panels: plain thick line = least square regression line calculated according to Minster et al. (1979) modified from York (1969); the dashed black curves show the 95% confidence envelop for the calculated least square calibration lines; the plain grey curves show the 95% confidence envelop for a temperature prediction for a single Δ_{47} measurement. On both panels we report the equation of the least-square regression fitting the data with uncertainties on slopes and intercepts given in 2σ – note that if S.E. were considered instead, as in previous studies, the reported uncertainties on slopes and intercepts are significantly smaller (about three times less – see text for details). **Panel c :** Graphic summary of 95% confidence domain of uncertainty on temperature estimates out of Equation [3]. The uncertainty on temperature estimates is shown as a function of both the temperature (*y-axis*) and the uncertainty on Δ_{47} measurements (contours) for an unknown sample. The uncertainty for the calibration alone is given by the solid black contours and is lower than ± 0.7°C at 25°C, ± 1°C at 50°C (1σ) and comparable to those resulting from Equation [1] for higher temperatures. [Note that those uncertainties apply to data obtained for conditions of analyses for which $\Delta^*_{X-90°C}$ is precisely known and are larger when uncertainties on replicate Δ_{47} measurements are considered].

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Supplementary materials

Table S1: Isotopic and chemical compositions of the initial materials ($CaCO_3$, CO_2 and solutions) used for the dolomitization experiments.

Table S2: Full table of the data acquired at IPGP

Table S3: Full table of the data acquired at Caltech.

Figure S1: XRD spectra of the investigated samples. For the two samples generated at 100°C (100-A2 and 100-A3), the onsets figures show longer counting times with smaller steps in the area on interest.

Figure S2: High-resolution transmission electron microscopy image of the bacterially-mediated precipitated samples shows *d*-spaces of the crystal lattice of 2.89 Å, which corresponds to the mineral dolomite. See Vasconcelos et al., (2016) for more details.

Figure S3: Graphical representation of Kluge et al. (2015)'s data offset compared to theoretical and previously published data on high-temperature calcites. See Figure 4a caption for more details.

Figure S4: Correlation ellipses between the slopes and intercepts for the Δ_{47} - $10^6/T^2$ regression lines calculated for both this study and the data from Kluge et al. (2015). The big square and circle represent the calculated respective slopes and intercept, with their 2σ uncertainties, showing that the two calibrations are statistically different from each other. All $\Delta_{47CDES90}$ data were, in respective studies, averaged by growth temperatures and weighted from the long-term external reproducibility obtained on carbonate standards (that is well-known since determined with large number of replicate Δ_{47} measurements) corrected with the t-distribution factor for the 95% confidence interval and the considered number of replicate Δ_{47} measurements of unknown samples. [This approach takes into account the small number of analyses n of unknown samples.]

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Figure S5: Compilation of Δ_{47} values reported for Carrara reference material in Kluge et al., (2015) and this study only (hundreds of additional measurements were made since). Average $\Delta_{47CDES25}$ values found for Carrara marble in the considered laboratories (IPGP, Caltech and Imperial College) are indistinguishable when respective uncertainties are taken into account. In contrast, the total variation range in Δ_{47} values reported in Kluge et al., (2015) is two times larger than that obtained over the course of this study.

Figure S6: Same figure as Figure 6b with uncertainties on biogenic samples.

Figure 1 EPS

Figure 1

Figure 2 EPS

Figure 2

Figure 3s

Figure 5

Figure 5

Figure 6 EPS

Figure 6