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Calibration of the oxygen and clumped isotope thermometers for dolomite based on synthetic and natural carbonates.

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Abstract

Dolomite is a very common carbonate mineral in ancient sediments, but is rarely found in modern environments. Because of the difficulties in precipitating dolomite in the laboratory at low temperatures, the controls on its formation are still debated after more than two centuries of research. Two important parameters to constrain the environment of dolomitization are the temperature of formation and the oxygen isotope composition of the fluid from which it precipitated. Carbonate clumped isotopes (expressed with the parameter Δ_{47}) are increasingly becoming the method of choice to obtain this information. However, whereas many clumped isotope studies treated dolomites the same way as calcite, some recent studies observed a different phosphoric acid fractionation for Δ_{47} during acid digestion of dolomite compared to calcite. This causes additional uncertainties in the Δ_{47} temperature estimates for dolomites analyzed in different laboratories using different acid digestion temperatures.

To solve this problem we present here a dolomite-specific Δ_{47}-temperature calibration from 25 to 1100 °C with acid reaction temperature of 70 °C and anchored to widely available carbonate standards. For the temperature range 25 to 220 °C we obtain a linear Δ_{47}-T relationship:

$$\Delta_{47\ CDES\ 70^\circ C} = 0.0426 \pm 0.0022 \times \left(\frac{10^6}{T^2}\right) + 0.1492 \pm 0.0169$$ (T = temperature in Kelvin)

Including two isotopically scrambled dolomites formed at 1100 °C the best fit is obtained with a third order polynomial temperature relationship of

$$\Delta_{47\ CDES\ 70^\circ C}(‰) = -0.0002 \times \left(\frac{10^6}{T^2}\right)^3 + 0.0042 \times \left(\frac{10^6}{T^2}\right)^2 + 0.0113 \times \left(\frac{10^6}{T^2}\right) + 0.2219.$$

Applying a calcite Δ_{47}-T relationship results in 10 to 16 °C colder formation temperatures for dolomites than using the dolomite specific calibration presented here.

For the synthetic samples formed between 70 and 220 °C we also determined the temperature dependence of the oxygen isotope fractionation relative to the water. Based on the similarity between our results and two other recent studies we propose that a combination of the three datasets represents the most robust calibration for dolomite formed in a wide temperature range from 25 to 350 °C.

$$10^3 \alpha_{Dolomite-Water} = 2.9923 \pm 0.0557 \times \left(\frac{10^6}{T^2}\right) - 2.3592 \pm 0.4116$$

Because of the uncertainties in the phosphoric acid oxygen and clumped isotope fractionation for dolomite, we introduce three samples that are available in large amounts as possible inter-laboratory calibration standard for oxygen and clumped isotope measurements. A sample of the middle Triassic

San Salvatore dolomite from southern Switzerland, the NIST SRM 88b dolomite standard and a lacustrine Pliocene dolomite from La Roda (Spain).

This study demonstrates the necessity to apply dolomite specific Δ_{47}-T relationships for accurate temperature estimates of dolomite formation, ideally done at identical acid digestion temperatures to avoid acid digestion temperature corrections. In addition, the simultaneous analyses of dolomite standards will enable a much better comparison of published dolomite clumped and oxygen isotope data amongst different laboratories.

1. INTRODUCTION

The formation of dolomite ($Ca,Mg(CO_3)_2$) in nature has been subject to extensive research for more than two centuries. In spite of all the efforts it remains unclear how this mineral forms at Earth surface conditions and why it is so abundant during certain time intervals in the geological past (Land, 1985; Given and Wilkinson, 1987; Spencer and Hardie, 1990; Chai et al., 1995; Hardie, 1996; Holland et al., 1996; Wright, 1997; Land, 1998; Burns et al., 2000; Warren, 2000). In modern environments only few places of active (proto-)dolomite formation at the surface are known and in most of these cases microorganisms have been shown to play an active or passive role (e.g. Vasconcelos and McKenzie, 1997; Wright, 1999; Bontognali et al., 2010; Brauchli et al., 2016). However, the amount and geographic extent of recent dolomite formation is only very small compared to the amounts that were formed during specific time intervals in the past, such as the Triassic (Berra et al., 2010) or the Cryogenian (Hood et al., 2011; Hood and Wallace, 2012). Such episodes of widespread dolomite formation were followed and preceded by time intervals where limestone ($CaCO_3$) was the dominant carbonate sediment. These transitions between dolomite and limestone-rich time intervals in the geological record are thought to be triggered by changes in global seawater chemistry or by changes in the depositional environment (e.g. Hardie, 1996; Holland et al., 1996). To improve our models of dolomitization it is crucial to better characterize the temperature of formation and the composition of the fluid responsible for dolomite formation.

Many examples exist where microstructures and fossils in ancient dolomites point to a very early diagenetic formation in shallow seawater or lacustrine environment (e.g. Frisia, 1994; García del Cura et al., 2001; Hood and Wallace, 2012; Huang et al., 2014). In contrast, the absence of such signatures with a rather homogenous micritic matrix can indicate a secondary dolomite formation during early or burial diagenesis following dissolution of a primary carbonate phase or its conversion into well-ordered dolomite at a later stage. Complementary to microscopic methods, geochemical tools such as stable isotopes of oxygen, carbon or strontium were used to gain further insights in the

environment or the "parental fluid" in which the mineral precipitated (e.g. Land, 1980; Wilson et al., 1990; Preto et al., 2015).

During the last decade carbonate clumped isotope thermometry evolved as a promising tool to determine formation temperatures of carbonates and the oxygen isotope composition of the fluid source (e.g. Ghosh et al., 2006; Eiler, 2007; Ferry et al., 2011; Dale et al., 2014; Millán et al., 2016; Winkelstern and Lohmann, 2016; Rodríguez-Sanz et al., 2017; Suarez et al., 2017; Smeraglia et al., 2018). Thus it is now possible to gain important insights on the environment of carbonate mineral formation. Clumped isotope thermometry is a measure of the abundance of the ^{13}C-^{18}O bond within the carbonate mineral relative to its stochastic isotope distributions, which is solely temperature dependent. Carbonate clumped isotopes are measured on the CO_2 gas evolved from the reaction of the carbonate mineral with phosphoric acid as the mass 47 ($^{13}C^{18}O^{16}O$). The clumped isotope composition of carbonates is thus reported in the Δ_{47} notation:

$$\Delta_{47} = ((R^{47}/R^{47*}-1)-(R^{46}/R^{46*}-1)-(R^{45}/R^{45*}-1))*1000\ (‰),$$

where the measured ratios between the *m/z* 45 to 47 over the most abundant CO_2 isotopologue *m/z* 44 (R^i) are reported against their stochastic isotope distribution (R^{i*}), which is calculated from the bulk isotope composition of the sample gas ($\delta^{13}C$ and $\delta^{18}O$). The phosphoric acid reaction of the carbonate to CO_2 produces a temperature-dependent isotopic fractionation whose temperature dependence is relatively well constraint for calcite (e.g. Defliese et al., 2015; Murray et al., 2016) but not for dolomite. The temperature dependence of this acid fractionation factor (AFF) is of high importance as it is common practice to project the Δ_{47} value to an acid digestion temperature of 25 °C, the digestion temperature reported in the first clumped isotope studies (Ghosh et al., 2006) and to enable a direct comparison between different laboratories that use different acid digestion temperatures.

For dolomite the temperature dependence of the AFF is still debated. While earlier studies processed their Δ_{47} measurements of different carbonate minerals with the same acid fractionation correction factors as calcite, two recent studies on the temperature dependence of the AFF for dolomite came to contrasting conclusions (Defliese et al., 2015; Murray et al., 2016). Whereas Defliese et al. (2015) observed similar temperature sensitivities for the AFF of dolomite and calcite, Murray et al. (2016) observed a much steeper temperature sensitivity for the AFF of dolomite relative to calcite. In a study on the absolute Δ_{47} AFF at 70 °C acid digestion Müller et al. (2017a), in addition, observed significantly smaller AFF for aragonite (0.172 ‰), compared to calcite (0.197 ‰) and dolomite (0.226 ‰). In this study, Müller et al. (2017a) also determined the absolute AFF for dolomite at 100 °C and observed that the dolomite acid fractionation at this temperature is smaller than the one of calcite supporting the findings of Murray et al. (2016). Interestingly, the results of Müller et al. (2017a)

indicate that the Δ_{47} acid fractionation of dolomite and calcite seems to be identical at about 90 °C acid digestion temperature, the reaction temperature currently used by most clumped isotope laboratories using common acid bath systems for large samples. These inconclusive findings on the Δ_{47} acid fractionation of dolomite at different reaction temperatures can cause large uncertainties on the interpretation of the Δ_{47} based formation temperature of dolomites, especially when comparing studies that use different acid digestion temperatures.

Recently two dolomite-specific Δ_{47}-T calibrations were published (Winkelstern et al., 2016; Bonifacie et al., 2017) with the aim of eliminating additional uncertainties in the interpretation of dolomite clumped isotope temperatures. The study of Winkelstern et al. (2016) for 75 °C dolomite acid digestion revealed a slightly shallower slope than more recent and statistically more robust calcite specific calibrations (the ones corrected for negative backgrounds, in the absolute reference frame, wider calibration sample temperature range with sufficient replicates, see Fernandez et al., 2017). On the other hand, Bonifacie et al. (2017) for 90 °C acid digestion revealed that the temperature relationship of dolomite is within error of the one of calcite based on a compilation of many different published laboratories carried out in the same study. This proposed universal calibration was also statistically indistinguishable from the one for calcite of Kele et al. (2015) which was produced in our laboratory. However, the composition of the samples in Bonifacie et al. (2017) was not calculated with the new IUPAC parameters for the correction of the ^{17}O abundance (Daëron et al. 2016), thus it is not clear how much the calibration would change if it were recalculated with the new parameters. A recalculation of the Kele et al. (2015) by Bernasconi et al. (2018) showed that while the slope remained constant, the intercept decreased by 0.038 ‰.

Due to the uncertainties in the dolomite-specific Δ_{47} acid fractionation and its temperature-dependence and because dolomite reacts much faster at higher temperatures Bonifacie et al. (2017) published their calibration for an acid digestion temperature of 90 °C. In the ETH laboratory, dolomites and calcites are digested at 70 °C and at this temperature, a different dolomite specific Δ_{47} AFF is observed (Müller et al., 2017a). Because in many new laboratories single bath preparation systems allowing the measurement of sub-milligram samples at 70 °C are becoming the method of choice (Müller et al. 2017b, Bernasconi et al., 2018), it is crucial to produce a dolomite-specific Δ_{47}-temperature calibration at 70 °C and to evaluate potential differences with respect to the evaluation schemes using the calcite specific parameters. In addition, in this study we firmly anchor the results to the absolute reference frame using a carbonate based correction scheme using the widely distributed ETH Standards, which allows other laboratories to better compare the data to ours (Bernasconi et al., 2018). We produced a dolomite specific Δ_{47} temperature calibration using natural and in laboratory formed (proto-)dolomite samples covering a temperature range from 25 to 1100

°C. We evaluated this new calibration and show results of potential dolomite standards and the advantages of their regular analysis for an improved inter-laboratory dolomite Δ_{47} data comparison.

2. MATERIALS AND METHODS

2.1. Samples

To cover a wide temperature range we synthetized dolomites in the laboratory under controlled temperature conditions at 70, 140 and 220 °C. For low temperature we used samples of natural dolomites formed at 25 °C from Lagoa Vermelha (Brasil) the same lagoon from which Bonifacie et al. (2017) obtained their samples. Finally, we use two dolomites that were heated in a piston cylinder to 1100 °C to obtain a stochastic isotope composition. In total we analyzed 21 different samples between 6 and 87 times.

Dolomites synthesized in the laboratory at 70, 140 and 220 °C:

Laboratory (proto-) dolomites were synthesized following the recipe described in Rodriguez-Blanco et al. (2015). Equimolar aqueous solutions of Na_2CO_3, $CaCl_2$ and $MgCl_2$ were mixed at room temperature, which led to an instantaneous precipitation of a white, gel-like solid confirmed by X-ray diffraction to be amorphous. This gel was heated at 70, 140 and 220 ˚C for between 1 day and 12 weeks. At selected time points, experimental runs were quenched to room temperature, the solids separated from the supernatants via vacuum-filtration (0.2 µm polycarbonate Cyclopore filters) and dried with isopropanol. The end products were determined to be (proto-)dolomite by X-ray diffraction. Ordered crystalline dolomite forms from an initial amorphous calcium-magnesium carbonate phase that first crystallizes to a non-stoichiometric proto-dolomite, and that then transforms over hours to weeks, depending on the temperature, to fully ordered stoichiometric dolomite (Rodriguez-Blanco et al., 2015). For our calibration we analyzed multiple samples at each of the three temperatures (8 at 70 °C, 4 at 140 °C and 5 at 220 °C, respectively; see Table 1).

Microbial dolomite concretions from the Brazilian lagoon “Lagoa Vermelha”:

For the low temperature range we included two dolomite concretions from a sediment core of Lagoa Vermelha (LV 15cm, LV 71cm). The lagoon is located about 100 km East of Rio de Janeiro, Brazil (Van Lith et al., 2002) and is a very shallow isolated lagoon influenced by recharge from the sea and mixing with meteoric water and evaporation which seasonally exceeds precipitation. This causes an annual wet-dry seasonal cycle with hypersaline conditions during the summer months. The dolomite concretions form during intense evaporative conditions, where the precipitation process is mediated by the increase of microbial activity and the presence of extracellular polymeric substances (EPS;

Nascimento, 2018). The annual mean water temperature of Lagoa Vermelha is approximately 25 °C, and the recorded temperature in 20 cm sediment depth was 25.5±5.7 °C from November 2011 till May 2015 (Nascimento, 2018) using an identical water temperature logger setup as Bahniuk et al. (2015) applied for the nearby lagoon Brejo do Espinho. These microbial dolomite samples were cleaned as in previous studies with hydrogen peroxide (10 %) and rinsed several times with deionized water to remove organic matter. This to treat them identical to a recent calibration study of (Bonifacie et al., 2017), which also included samples from Lagoa Vermelha.

Dolomites heated to 1100 °C in a piston cylinder:

Fine powder of two natural dolomites (from Monte San Salvatore, Switzerland and La Roda, Spain) were heated during 4 hours at 1100 °C in a piston cylinder apparatus. More detail on these dolomite samples with stochastic isotope distribution are in (Müller et al., 2017a) where these samples, labelled as Sansa (H) and Rodolo (H), were used to determine the absolute Δ_{47} AFF. In this study these are the hottest calibration samples. These samples are important for a more accurate interpretation of natural dolomites that retained extremely hot temperature signals near magmatic intrusions (e.g. Lloyd et al., 2017; Ryb et al., 2017; Lloyd et al., 2018).

2.2. Natural dolomites from Monte San Salvatore, Switzerland, La Roda, Spain and the international standard NIST SRM 88b

The dolomite from Monte San Salvatore, Southern Switzerland, is a replacement dolomite that formed during the middle Triassic (Lehner 1952; Zorn, 1971) and was collected along the road leading southwards from Lugano at the locality Forca di San Martino. We named the sample “Sansa” to avoid confusion with the dolomites from San Salvador Island discussed by Murray and Swart (2017).

The other natural sample comes from La Roda, Spain and is a lacustrine dolomite that formed during the Pliocene probably induced by microbial activity (García del Cura et al., 2001). Additionally we analyzed the NIST (National Institute of Standards and Technology, Gaithesburg, MD, USA) dolomite standard SRM 88b, which is a natural dolomite from the Silurian Racine formation, northeastern Illinois. This widely available dolomite standard was already measured in other clumped isotope studies and enables a direct comparison between different laboratories.

2.3. X-ray diffraction and stable isotope analyses

All samples were drilled from the hand specimens with a hand-held dental drill taking care of not overheating the drill bit to avoid potential isotopic reordering. The mineralogy and degree of ordering was determined with a Powder X-ray Diffractometer Bruker AXS D8 Advance equipped with a Lynxeye detector. Oxygen, carbon and clumped isotope compositions were determined with a Kiel IV carbonate device coupled to a MAT 253 isotope ratio mass spectrometer (Thermo Fisher Scientific) as thoroughly described in earlier studies (Schmid and Bernasconi, 2010; Meckler et al., 2014; Müller et al., 2017b). Briefly, 130 to 160 µg of calcite standards (ETH-1 to -4) and samples are weighed in glass vials and placed in the Kiel IV carbonate device (46 samples per measurement sequence). The samples are reacted at 70 °C with three drops of 104 % phosphoric acid and during the reaction with the acid (300 seconds for calcite and 1200 seconds for dolomite) the released CO_2 gas is constantly frozen in the liquid nitrogen (LN_2) trap 1 of the Kiel device. After the reaction is completed trap 1 is heated to -100 °C and the gas is transferred through a tubing filled with 10 mm Porapak Type Q (50-80 mesh) embedded in silver wool into a second LN_2 trap. The Porapak trap was kept between -20 and -14 °C to remove potential contaminants such as halo-/hydrocarbons or reduced sulfur compounds. The samples were measured in the LIDI mode that measures the sample gas at once for 600 seconds and subsequently the working gas during 600 seconds. Usually the measurements start at 20 to 25 V on mass 44 and decrease by approx. 10 V during the 600 seconds (Hu et al., 2014; Müller et al., 2017b). Before starting a measurement sequence peak shape scans in the range of 30 to 10 V on *m/z* 44 are carried out at different gas pressures to determine the pressure dependence of the negative backgrounds to do a so-called pressure-sensitive baseline correction (PBL correction) according to (Bernasconi et al., 2013; Meckler et al., 2014; Müller et al., 2017a). The raw data are processed with the free Easotope software (John and Bowen, 2016), by first doing the PBL correction, then it calculates the carbon and oxygen isotope composition of the carbonates in the delta notation relative to the international Vienna PeeDee Belemnite standard, VPDB ($\delta^{13}C_{VPDB}$, $\delta^{18}O_{VPDB}$ in ‰) using the parameters recommended by Daëron et al., 2016). The calculated PBL-corrected clumped isotope composition (Δ_{47raw}) against our working gas ($\delta^{13}C_{VPDB}$ = -7.25 ‰, $\delta^{18}O_{VPDB}$ = +1.65 ‰) for each replicate was converted to $\Delta_{47\ CDES\ 70\ °C}$ (‰) using 32 standards before and after. The results a presented as the averages of replicates measured over a long period of time, from 2015 to 2017, where the conditions of the analytical instruments changed several times. Our measurement strategy involves the measurement of only few replicates of the same sample in the same measurement sequence of 46 samples. The distribution of replicates over multiple runs during different correction intervals often comes with the cost of a worse precision compared to measuring many replicates of the same sample in one analytical sequence or a short time interval, but we expect that this leads to more accurate Δ_{47} estimates as it removes possibly day to day biases. For the conversion into the absolute reference frame Easotope uses the accepted Δ_{47} values of the

calcite standards ETH-1 to -4 as reported in Bernasconi et al. (2018). Here we report the results for a reaction temperature of 70 °C ($\Delta_{47\ CDES\ 70\ °C}$) and refrain to project them to an acid digestion temperature of 25 °C due to the large uncertainties in the AFF of dolomite (see different observations in Defliese et al., 2015; Murray et al., 2016; Müller et al., 2017a). For $\delta^{18}O$ we used a AFF of 1.009926 for dolomite (Rosenbaum and Sheppard, 1986). Conversion from VPDB to the VSMOW scale was done using $\delta^{18}O_{SMOW}$ = 1.03091 * $\delta^{18}O_{PDB}$ + 30.91 (Coplen et al., 1983). The Δ_{47} temperatures of calcite samples are calculated with the fully recalculated calcite Δ_{47}-T calibration of Kele et al. (2015) using the isotopic parameters recommended in Daëron et al. (2016) including the fully recalculated accepted ETH standard values (Bernasconi et al., 2018; with ETH-1: Δ_{47} = 0.258 ‰, ETH-2: Δ_{47} = 0.256 ‰, ETH-3: Δ_{47} = 0.691 ‰ and ETH-4: Δ_{47} = 0.507 ‰ projected to a 25 °C acid digestion using a correction factor of 0.062 ‰).

Oxygen isotopes in waters from the experiments were measured with the CO_2 equilibration method. 200 µl of water are pipetted in 12 ml septum-capped vials which are subsequently filled with a mixture of 0.3 % CO_2 and He. After equilibration at 25 °C for at least 18 h the CO_2/He mixture is measured using a Thermo Scientific Gas Bench II connected to a Thermo Scientific Delta V plus isotope ratio mass spectrometer. The system is calibrated with the international standards SMOW, SLAP and GISP. The results are reported in the conventional delta notation with respect to VSMOW (Coplen, 1996). Reproducibility of the measurements based on repeated measurements of an internal standard was better than 0.06 ‰.

3. RESULTS

3.1. Dolomite mineralogy

The natural dolomites from Lagoa Vermelha, Brazil all show the main dolomite reflections 104, 110 and 113 at the corresponding 2θ space and the dolomite ordering reflections 015 and 021 (Bradley et al., 1953; Goldsmith and Graf, 1958; Gregg et al., 2015). Whereas the ordering reflection 001 is lacking in the XRD pattern of LV 15 cm. In LV 71 cm there could be a small reflection but it is masked by a large reflection from an unidentified phase (Fig. 1). In both samples the ordering reflection 015 is clearly smaller than the 110 reflection. In sample LV 71 cm the presence of halite (NaCl) is visible indicated by the green reflections at 32 and around 45 °, whereas for sample LV 15 cm it is not as clear as the reflection around 45 ° is not visible. With almost all dolomite ordering reflections expressed, the carbonate phase of LV 15 cm and LV 71 cm can be described as poorly ordered dolomite.

The XRD patterns of the 'dolomite samples' synthesized in the laboratory (Table 1 and Fig. 2) at 70 °C did not show the 'ordered' 001, 015 and 021 dolomite reflections, pointing to a crystal structure typical for proto-dolomite which is called by some authors very high Mg-calcite (VHMC). This observation was independent of the length of equilibration at the experiment temperature of 70 °C (1 to 12 weeks). Samples crystallized at 140 °C exhibited in their XRD pattern the 'ordered' dolomite reflections 015 and 021, but still lacked the 001 reflection pointing to a not fully ordered dolomite. Finally, the XRD patterns of the samples synthesized at 220 °C contained all three 'ordered' dolomite reflections, however, the intensity of the 015 peak was relatively smaller than the 110 peak, typical for a moderately well-ordered dolomite (see lower XRD pattern in Fig. 2).

The dolomites NIST SRM 88b, Sansa and Rodolo are well-ordered and stoichiometric. All ordered dolomite reflections are visible and the 015 reflections are almost as intense as the 110 (Fig. 3) similar to the "near perfect ordering" example Bonneterre dolomite described in Gregg et al. (2015). The Rodolo dolomite is a direct precipitate from solution in a lacustrine environment (García del Cura et al., 2001), in contrast to the other diagenetic dolomites that are a replacement of calcite or aragonite.

3.2. Dolomite-water oxygen isotope fractionation

The averages of the measurements of all samples used for the dolomite Δ_{47}-T calibration are displayed in Table 1 and 2 and the results of individual measurements are reported in Table S1. For the natural samples the fractionation ranges tightly between 32.01 to 32.19 ‰. The oxygen isotope composition of the water of Lagoa Vermelha is not exactly known and the value taken from van Lith et al. (2002) of 1.8 ‰ has an assigned larger uncertainty because of the annual variations in hydrology of the lagoon.

For the synthetic dolomites that were equilibrated with the solutions for variable times ranging from 1 to 12 weeks, we obtained a larger spread in the results (70 °C samples: 21.86 - 23.23 ‰; 140 °C samples: 14.94 – 16.49 ‰; 220 °C samples: 9.66 – 13.05 ‰), thereby the water value of sample 82 seems to be biased by evaporation during water sample transport prior to isotope analysis and the short 220 °C experiment Leeds 34 probably did not reach equilibrium. The uncertainty of the oxygen isotope composition of the (proto-)dolomite samples varies between ±0.03 – 0.44 ‰ at the 95% CI, which takes into account the number of replicates per sample (indicated in last column of Table 2).

Table 2 shows the average $\delta^{13}C_{VPDB}$ and $\delta^{18}O_{VPDB}$, the bulk isotope composition relative to our reference gas (δ^{47}) and the clumped isotope composition for an acid digestion temperature of 70 °C ($\Delta_{47\ CDES\ 70\ °C}$) of all samples. All uncertainties are reported at the 95% CI and range between 0.02 –

0.14 ‰ for $\delta^{13}C_{VPDB}$, 0.04 – 0.54 ‰ for $\delta^{18}O_{VPDB}$, 0.05 – 0.77 ‰ for δ^{47} and 0.010 – 0.054 ‰ for $\Delta_{47\ CDES\ 70\ °C}$.

The average $\Delta_{47\ CDES\ 70\ °C}$ values of the two "cold" natural dolomite calibration samples are 0.637 ‰ for LV 15 cm and 0.619 ‰ for LV 71 cm, both samples have similar oxygen isotope composition, but their carbon isotope compositions are more distinct with -8.32 ‰ for the more shallow sample and -10.21 ‰ for the deeper one. The $\delta^{13}C_{VPDB}$ and $\delta^{18}O_{VPDB}$ of the synthetic samples are quite similar to each other and the $\Delta_{47\ CDES\ 70\ °C}$ values range between 0.497 to 0.515 ‰ for samples synthesized at 70 °C, between 0.398 to 0.426 ‰ for samples synthesized at 140 °C and between 0.311 to 0.348 ‰ for the 220 °C samples. The two natural dolomites that where heated to 1100 °C to produce a stochastic isotope distribution were replicated much more and show almost identical $\Delta_{47\ CDES\ 70\ °C}$ values with 0.230±0.010 ‰ for Rodolo (H) and 0.228±0.011 ‰ for Sansa (H).

Using only the (proto-)dolomites synthesized under controlled laboratory conditions without the two heated dolomites and the two natural dolomites from the Brazilian lagoon, we obtain a temperature dependence with $R^2 = 0.9862$ for the oxygen isotope fractionation relative to water of

$$10^3\alpha_{Dolomite-Water} = 2.7757 \pm 0.2062 \times \left(\frac{10^6}{T^2}\right) - 0.6314 \pm 1.3916$$

For this temperature dependence we did not use sample Leeds 82 and sample Leeds 34 due to the aforementioned points. The natural samples of Lagoa Vermelha were not included due to the higher uncertainty in the $\delta^{18}O$ of the fluid source.

3.3 Clumped isotope fractionation

The clumped isotope composition of individual replicates and averages of samples formed between 25 to 220 °C is plotted in Fig. 4 against their reciprocal formation temperatures ($10^6/T^2$). From all analyzed individual replicates we obtained a linear regression for the $\Delta_{47\ CDES\ 70\ °C}$ – T relationship with $R^2 = 0.8513$ of

$$\Delta_{47\ CDES\ 70°C} = 0.0426 \pm 0.0022 \times \left(\frac{10^6}{T^2}\right) + 0.1492 \pm 0.0169$$

that is valid for acid digestion of dolomites at 70 °C and the temperature in Kelvin. The linear regression is based on 270 individual measurements of 19 different samples formed at 4 different

temperatures. Including the two measurements of the two dolomites that were heated and equilibrated during 4 hours at 1100 °C (Müller et al., 2017a) the best fit is obtained when using a polynomial function of third order with $R^2 = 0.9164$

$$\Delta_{47\ CDES\ 70\ °C}(‰) = -0.0002 \times \left(\frac{10^6}{T^2}\right)^3 + 0.0042 \times \left(\frac{10^6}{T^2}\right)^2 + 0.0113 \times \left(\frac{10^6}{T^2}\right) + 0.2219$$

based on a total of 416 individual measurements (Fig. 5).

3.4. Stable isotope data of proposed dolomite standards

The isotopic compositions of the three ordered dolomites are summarized in Table 3 and with the individual replicates in the supplementary Table S2. The lacustrine Rodolo dolomite has a $\delta^{13}C_{VPDB}$ of -3.71 ‰ and a relatively high $\delta^{18}O_{VPDB}$ of 2.77 ‰. Because of the large number of replicates (151) the Δ_{47} of 0.632 ‰ is well constrained with an uncertainty of only ±0.006 ‰ at the 95% CI giving a temperature of 25±2 °C and a fluid source with $\delta^{18}O$ of +1.7±0.04 ‰. The other two diagenetic dolomites have almost identical Δ_{47} with 0.526±0.014 ‰ for Sansa and 0.522±0.022 ‰ for NIST SRM 88b. Whereas their $\delta^{13}C$ are similar, their oxygen isotope composition is different with -3.56 ‰ for Sansa and -7.09 ‰ for NIST SRM 88b.

4. DISCUSSION

4.1. Dolomite specific Δ_{47}-temperature calibration

4.1.1. Clumped isotope temperature relationship for 70 °C acid digestion

The clumped isotope analysis of 19 (proto-)dolomite samples formed at temperatures between 25 and 220 °C with phosphoric acid digestion at 70 °C resulted in a linear regression of:

$$\Delta_{47\ CDES\ 70°C} = 0.0426 \pm 0.0022 \times \left(\frac{10^6}{T^2}\right) + 0.1492 \pm 0.0169$$

We start by comparing this calibration with the calcite calibration produced at ETH with the same instrumentation and normalized to the CDES using the same carbonate standards, because we can exclude artefacts due to methodological and data processing differences. Comparison with the calcite calibration of Kele et al. (2015) as recalculated in Bernasconi et al. (2018), shows a slightly shallower slope within the uncertainties of each other (0.0426±0.0022 vs. 0.0449±0.001), but the intercept of the calcite calibration is significantly lower so that the two calibrations do not overlap at their 95% CI's (see Fig. 6). Using this calcite calibration for dolomites (between 0 and 100 °C) leads to

calculated temperatures lower by 10 to 16 °C compared to the dolomite-specific calibration. Thus we conclude that calcite and dolomite have to be treated separately when measured for clumped isotopes, and published estimates of temperatures may have to be revised. This revision would however also take into consideration that the original data in many publications before 2017 were not processed using the parameters suggested by Daëron et al. (2016), thus the effect on the temperatures is difficult to predict. In the following we compare our new dolomite calibration with Bonifacie et al. 2017.

In the past clumped isotope analyses on natural dolomite samples were processed in the same way as calcite samples due to the facts that no dolomite specific Δ_{47} temperature calibrations and no dolomite specific AFF were available. This was based on the assumption that the clumped isotope fractionation during acid digestion is identical for the two minerals (e.g. Millán et al., 2016; Winkelstern and Lohmann, 2016). Ferry et al. (2011) on the other hand, added a correction factor of 0.02 ‰ and applied the theoretical calibration of Guo et al. (2009) to calculate formation temperatures. In recent years, two dolomite specific Δ_{47}-T calibrations were published, one of them reacting dolomite at 75 °C (Winkelstern et al., 2016) and the other at 90 °C (Bonifacie et al., 2017).

The comparison of calibrations established in different laboratories remains challenging, because of many factors: the lack of carbonate standards to compare across laboratories, the fact that clumped isotope data pre-2016 are not calculated using the "Brand parameters", and the uncertainties in phosphoric acid fractionation (Bernasconi et al., 2018). The absolute Δ_{47} AFF of various carbonate minerals was determined by Müller et al. (2017a) using carbonates with a stochastic isotope distribution. This study showed a that the AFF of dolomite is 29 ppm larger than the one of calcite and that due to the steeper temperature relationship for dolomite this difference would become increasingly larger at acid reaction temperatures below 90 °C. Defliese et al. (2015), on the other hand, determined that temperature dependence of the AFF of dolomite between 25 and 90 °C is identical to the one of calcite whereas Murray et al. (2016) observed a temperature dependence significantly steeper for dolomite.

Our new calibration allows now to address these uncertainties on potential differences of the Δ_{47} acid fractionation between dolomite. Because of the uncertainties in comparing data across labs discussed above we refrain to compare it with the Winkelstern et al. (2016) calibration, as we cannot directly compare any carbonate that was measured in their laboratory and we cannot recalculate it with the updated parameters. On the other hand we can compare our results with Bonifacie et al., 2017), even if that calibration is not recalculated with the new parameters because in both calibrations we use two samples from Lagoa Vermelha as a low temperature point, and thus we can directly compare the results of the two laboratories.

The calcite specific Δ_{47}-T calibration produced at the ETH clearly lies below our new dolomite calibration (around 30 ppm), but their slopes are similar. The difference between the intercepts of the dolomite and calcite calibrations produced at the ETH laboratory can be explained by the observed differences in the absolute Δ_{47} AFF between calcite and dolomite (Müller et al., 2017a). However, when reevaluating the data from Müller et al. (2017a) with the new accepted ETH standard values for consistency the offset increases to 0.04 ‰ (see Table 4, Table S3). The almost identical slopes supports the finding that the temperature dependence of clumped isotopes is the same for all minerals (Bonifacie et al., 2017). However, the offset of about 30 ppm shows the necessity to treat dolomites digested at 70 °C differently than calcites. In other words dolomite formed at 25 °C would be "made" 6 °C colder if calculated as a calcite and a dolomite formed at 80 °C would give 12 °C colder temperatures, with also a corresponding impact on the calculated $\delta^{18}O$ of the fluid source. A similar offset between the Δ_{47}-T relationship of dolomite and calcite was also predicted by theoretical calculations of Guo et al. (2009), however, the offset was of opposite sign.

The dolomite specific Δ_{47}-temperature calibration of Bonifacie et al. (2017) is based on 12 different samples formed at temperatures between 25 and 350 °C with a total of 67 individual measurements and contains one sample from Lagoa Vermelha and another one of a neighbouring lagoon (Brejo do Espinho) that formed under similar conditions as the ones we used in this study. In their study Bonifacie et al. (2017) reacted 5 mg samples with 104 % phosphoric acid in a common acid bath at 90 °C and obtained a linear regression of $\Delta_{47\ CDES\ 90\ °C} = (0.0428\pm0.0033)*10^6/T^2 + (0.1174\pm0.0248)$. This slope is almost identical to the slope of 0.0426 in this study and thus allows to directly evaluate the clumped isotope acid fractionation correction required to compare Δ_{47} measurements of the different laboratories to each other. For a direct comparison between the two studies we can compare the natural samples of Lagoa Vermelha where we obtained a $\Delta_{47\ CDES\ 70\ °C}$ of 0.637±0.022 ‰ for the upper one (LV 15cm, 16 replicates) and Bonifacie et al. (2017) obtained a $\Delta_{47\ CDES\ 90\ °C}$ of 0.591±0.022 ‰ (4 replicates) for their surface sample, an offset equal to 0.046 ‰. The average offset between our two sediment samples from Lagoa Vermelha and their two Brazilian lagoonal samples (CVLV and CVBE of their Table 2) would be approximately 0.029 ‰. In Fig. 7 we plotted the temperature calibration of Bonifacie et al. (2017) with the $\Delta_{47\ CDES\ 90\ °C}$ against the inverse temperature and applied the two differing published dolomite specific acid fractionations (Defliese et al., 2015; Murray et al., 2016) to project our dolomite data to 90 °C acid digestion temperature.

Applying an acid fractionation correction (AC) of 0.0204 ‰ derived from Defliese et al. (2015), which observed no significant differences between dolomite and calcite, our dolomite calibration lies parallel with an offset of about 10 ppm above the one of Bonifacie et al. (2017; see Fig. 7). Whereas with the AC of 0.0380 ‰ from Murray et al. (2016), which observed a much steeper temperature

relationship for dolomite compared to calcite, our calibration shifts down to about 8 ppm below the one of Bonifacie et al. (2017). The AC effectively needed to put the calibrations on the same level is an AC of approximately 0.030 ‰, which is located somewhere in between the two temperature sensitivity studies for dolomite and is equal to the observed average offset between our lagoonal proto-dolomite concretions and the ones of Bonifacie et al. (2017). An additional uncertainty in this comparison is the fact that the Bonifacie et al. (2017) was not corrected for the new "Brand " parameters, thus the exact difference remains unclear.

This example shows that applying an acid fractionation correction for Δ_{47} analyses on dolomite can result in large uncertainties and produce erroneous temperature estimates. Ideally laboratories apply temperature calibrations based on dolomite samples that were acid digested at the same temperature as already recommended by Bonifacie et al. (2017). Applying an AFF to Δ_{47} analysis on dolomite samples digested at 25 °C is expected to result in even larger uncertainties. The only way to remove these uncertainties for dolomite measurements is the use of dolomite standards in addition to calcite standards that are used to transfer the data to the CDES. The regular analysis of dolomite standards would drastically reduce the uncertainties arising from mineral specific acid fractionation correction and uncertainties arising from small differences in sample purification procedures and data processing (see also Bernasconi et al., 2018). This would be valuable not only for clumped isotopes but also for oxygen isotopes as well, as there are also uncertainties in oxygen isotope fractionation with different preparation systems. The international NIST SRM 88b is such an example of a dolomite that is often analyzed and two potential dolomite standards are presented below.

Our dolomite specific Δ_{47}-T calibration shows an almost identical slope than the calibration of Bonifacie et al. (2017), which also used a mixture of high temperature stoichiometric well-ordered dolomites and at lower temperature formed proto-dolomites. Their high temperature samples were synthesized by placing calcite or aragonite together with Ca-Ma-(Na)-Cl solutions in stainless steel reactor vessels that were heated for several days at the corresponding experiment temperature of 100 to 350 °C (see Horita, 2014 and Bonifacie et al., 2017). Thereby the starting carbonate phase converts first into high-Mg calcite, then into disordered dolomite to well-ordered near stoichiometric dolomite, which is similar to dolomite formation in this study, except that we did not use a solid carbonate starting phase. For their low temperature calibration samples Bonifacie et al. (2017) used similar samples than we from Brazilian hypersaline lagoons described in Vasconcelos and McKenzie, (1997) as well as bacterially-mediated precipitated proto-dolomites that were originally used to calibrate the oxygen isotope fractionation between the dolomite phase and the water (see Vasconcelos et al., 2005). At intermediate temperature of 80 °C Bonifacie and colleagues precipitated proto-dolomite from mixing solutions of $MgSO_4$, $Ca(NO_3)_2*4H_2O$ and Na_2CO_3 and keeping this mixture

for more than 41 days in a temperature controlled water bath. Despite the different ways forming (proto-)dolomite calibration samples the study of Bonifacie et al. and this study obtains a linear regression for the Δ_{47}-temperature relationship that is indistinguishable. Therefore our study supports their finding that there is no difference in the Δ_{47} between well-ordered stoichiometric dolomites and so-called proto-dolomite, or such differences if they exist, are well below the current analytical uncertainty. The minor differences to reported slopes of recent calcite specific calibrations (e.g. Bernasconi et al., 2018; Bonifacie et al., 2017; Breitenbach et al., 2018; Kelson et al., 2018; Peral et al., 2018) give further strong evidence that the slope of the clumped isotope temperature relationship is identical for different carbonates. However, for a "universal" clumped isotope calibration differences in the Δ_{47} acid fractionation of the various carbonate mineralogies need to be taken into account, notably at lower acid digestion temperatures where these effects seem to have a bigger impact (Murray et al., 2016; Müller et al., 2017a).

In Fig. 8 we additionally added the two dolomite samples heated to 1100 °C to expand the dolomite Δ_{47}-T relationship at elevated temperatures that can prevail in lower crustal environment or where magmatic intrusions penetrate sedimentary rocks (e.g. Lloyd et al., 2017; Ryb et al., 2017). The resulting Δ_{47}-T relationship is a third order polynomial fit that is largely identical to the theoretical dolomite calibration of Guo et al. (2009) displayed as grey dashed line in Fig. 8. Although the theoretical dolomite calibration of Guo et al. (2009) was calculated for 25 °C acid digestion temperature it fits well to our calibration without any correction and the small differences below 70 °C and above 500 °C might be due to the fact that we do not have enough different high temperature samples between the 220 °C and the 1100 °C samples as well as at low temperatures for a better higher order polynomial fitting. The linear regression for the dolomite specific Δ_{47}-T calibration for 70 °C acid digestion fits the theoretical dolomite calibration better in the low temperature range. The striking resemblance between our polynomial fit and the theoretical calculations show the necessity of applying one or the other for dolomites exposed to temperatures above ~400 °C in natural environments. Once more the regular analysis of dolomite standards would help to correct for offsets between laboratories digesting the carbonates at different reaction temperatures allowing laboratories without own temperature calibration the application of dolomite specific Δ_{47}-T calibrations with more confidence.

4.1.2. Oxygen isotope fractionation between (proto-)dolomites and water

Dolomite is known to have a different oxygen isotope fractionation to water compared to other carbonate minerals and its temperature dependency was thoroughly studied since many decades

(e.g. Northrop and Clayton, 1966; Fritz and Smith, 1970; Matthews and Katz, 1977; Zheng et al., 1999; Vasconcelos et al., 2005; Horita, 2014). Unfortunately all of these studies faced the challenge that in laboratory at temperatures below 100 °C it becomes difficult to synthesize dolomite, although naturally occurring dolomite samples in most cases formed at lower temperatures (e.g. via mixing of fluids, as diagenetic replacement phase or biologically mediated primary precipitate, see Warren at al., 2000 for a review). Some earlier studies produced dolomite at high temperatures >100 °C and extrapolated their results to lower temperatures (Northrop and Clayton, 1966; Matthews and Katz, 1977). Other studies precipitated with or without the help of microorganisms a carbonate phase that is not perfect stoichiometric dolomite (Gregg et al., 2015), but this proto-dolomite phase was formed at near surface temperatures (e.g. Fritz and Smith, 1970; Vasconcelos et al., 2005).

While these proto-dolomites are not well ordered, they show properties that distinguish them from calcite. The cultures of Vasconcelos et al. (2005) produced a mixture of calcite and proto-dolomite and before measurement they dissolved the calcite with EDTA, thus the Mg rich phase that has the main 104 XRD peak in the position of a dolomite, was more resistant to dissolution than all lower Mg calcite phases. We consider this a good indication that these phases, although not well ordered, are not very high magnesium calcites (Kaczmarek and Thornton, 2017), but poorly ordered dolomites.

Another approach to overcome the difficulty of precipitating low temperature dolomites was the theoretical modelling of the dolomite water oxygen isotope fractionation of Zheng (1999). Other studies, including ours, merged results from stoichiometric dolomites formed at temperatures above 140 °C with results from proto-dolomites formed at temperatures down to 70 °C (experiments down to 80 °C in Horita, 2014). A recent study of Murray and Swart (2017) discussed and evaluated the existing oxygen isotope calibrations for dolomite on Bahamian dolomites, on which they applied clumped isotope thermometry. In their figure 1 they show that for dolomite of a formation temperature of 25 °C depending on which calibration is used the $\delta^{18}O$ of the fluid source can vary by up to 3.6 ‰. Murray and Swart evaluated the various calibrations, by calculating the $\delta^{18}O_{fluid}$ from the Δ_{47} temperature estimates and the corresponding expected $10^3 \ln\alpha_{Dolomite\text{-}Water}$ to further test if the results are consistent with existing dolomitization models for the Bahamian dolomites. As outcome of their study they favor the use of the temperature relationship of Matthews and Katz (1977) for their Bahamian dolomites that presumably formed at temperatures between 15 to 35 °C. They ignore the low temperature dolomite calibrations covering this temperature range arguing that they were based on proto-dolomites or very-high Mg-calcite samples (Fritz and Smith, 1970; Vasconcelos et al., 2005).

The direct comparison of these studies on the temperature dependency of the oxygen isotope fractionation between dolomite and water is however difficult because they applied different acid

fractionation factors. In our study, we applied the acid fractionation factor correction for dolomite of Rosenbaum and Sheppard (1986), same as the two most recent studies of Vasconcelos et al. (2005) and Horita (2014). In contrast to that Northrop and Clayton (1966) use for 25 °C acid digestion a correction factor of 1.01090 and Fritz and Smith (1970) use at identical reaction temperature for their proto-dolomites the calcite acid fractionation factor of 1.01008 (both derived from Sharma and Clayton, 1965) and Matthews and Katz (1977) us for 25 °C acid digestion a factor of 1.01110 (from Friedman and O'Neil, 1977). Further uncertainties might originate from the oxygen isotope analyses of the water when comparing studies published during almost half a century. In Fig. 9 we compiled the oxygen isotope fractionation between (proto-)dolomites and water of this study with the two most recently published temperature relationships that applied the same acid fractionation correction (Vasconcelos et al., 2005; Horita, 2014) together with the temperature relationship of Matthews and Katz (1977) recommended in the study of Murray and Swart (2017). For this calibration we applied a correction factor of -0.68 ‰ to the intercept of their temperature relationship to correct for the different acid fractionations. The factor of -0.68 ‰ is the difference between the acid fractionation factor used by Matthews and Katz (1977) and the one for 25 °C acid digestion of Rosenbaum and Sheppard (1986). From this figure it appears that our new experimental data overlap well with those of Vasconcelos et al. (2005) and Horita (2014), whereas the Matthews and Katz (1977) calibration is slightly below the data compilation over the entire temperature range. Because of the uncertainties in the $\delta^{18}O_{H2O}$ of water from Lagoa Vermelha we do not include the oxygen isotope fractionations of these two natural samples in the temperature calibration in Fig. 9.

The study of Horita (2014) contains samples that cover a temperature range from 80 to 350 °C, whereas the study of Vasconcelos et al. (2005) covers a temperature range of 25 to 45 °C with a slightly more shallow temperature relationship. If the results of the proto-dolomites precipitated between 25 to 79 °C of Fritz and Smith (1970) are corrected for the difference of their applied acid fractionation at 25 °C, their calibration line is parallel to but slightly below the one of Vasconcelos et al. (2005).

Due to the before mentioned points and the similarity of our dataset with the two most recent studies (Vasconcelos et al., 2005 and Horita, 2014) we propose to combine the results of these three studies to derive a more accurate temperature dependence of the water-dolomite oxygen isotope fractionation because it is based on more data points and covers a wide temperature range of 25 to 350 °C (see Fig. 9). Based on observations from the statistical evaluation of Fernandez et al. (2017) of existing Δ_{47}-T calibrations that more samples covering a wider temperature range lead to more robust calibrations we therefore recommend to use this combined $10^3 \ln\alpha_{Dolomite\text{-}Water}$-T relationship

$$10^3 \ln\alpha_{Dolomite\text{-}Water} = 2.9923 \pm 0.0557 \times (10^6/T^2) - 2.3592 \pm 0.4116$$

to calculate the $\delta^{18}O$ of the fluid source of unknown samples. This makes extrapolations from calibrations based on high temperature dolomite samples to lower temperatures unnecessary.

4.3. New dolomite standards for improved inter-laboratory comparison

The comparison of the new dolomite specific Δ_{47}-T calibration of this study for 70 °C acid digestion with the calibration of Bonifacie et al. (2017) where they digested their dolomite samples at 90 °C shows that the discrepancy is due to poorly constrained understanding of the temperature dependence of the AFF for dolomite and possibly the use of the new Brand parameters, but the slope of the calibration is statistically indistinguishable. We observed a larger difference to the calibration of Winkelstern et al. (2016) (difference in slope and intercept) although it was realized with acid digestion temperature of 75 °C, closer to ours. This points to other unknown factors in the sample preparation or data processing as cause for the discrepancy, which may be overcome with carbonate standards (Bernasconi et al., 2018). These observed differences together with the inconclusive comparisons to other dolomite Δ_{47}-fluid inclusion studies that used calcite specific Δ_{47}-T calibrations (Came et al., 2017; Honlet et al., 2017) underline the urgent need of dolomite standards to reduce the uncertainties between laboratories. Simultaneous measurements of multiple dolomite standards with different bulk isotope composition and different Δ_{47} allows to detect differences due to stretching or background correction or calculations to transfer the isotope results to the CDES (see Bernasconi et al., 2018 for a detailed discussion of the advantages of carbonate standards). In addition, these dolomite standards, will help solving uncertainties in oxygen isotope fractionation. We propose three possible standards that have a range of compositions for this. Besides the already available NIST SRM 88b dolomite standard ($\Delta_{47\ CDES\ 70\ °C}$ of 0.522±0.022 ‰) that is distributed by the National Institute of Standards and Technology (Gaithesburg, MD, USA), we propose two potentially new dolomite standards, the lacustrine low temperature Rodolo dolomite ($\Delta_{47\ CDES\ 70\ °C}$ of 0.632±0.006 ‰) and the warmer Sansa dolomite ($\Delta_{47\ CDES\ 70\ °C}$ of 0.526±0.014 ‰), which is the product of diagenetic alteration of a primary marine carbonate (Table 3). All of these three dolomites show the XRD patterns of well-ordered stoichiometric dolomite (Fig. 3). The Rodolo and Sansa can be obtained directly from Stefano Bernasconi (stefano.bernasconi@erdw.ethz.ch). Rodolo and Sansa were also analyzed for their Δ_{47} in the laboratory of the MIT with a Nu Perspective mass spectrometer coupled to a Nu Carb device by Kristin D. Bergmann and reproduced well the results of the ETH laboratory (see Bernasconi et al., 2018).

5. CONCLUSIONS

Our dolomite specific Δ_{47}-T calibration for 70 °C acid digestion temperature covers a wide temperature range from 25 to 1100 °C and is based on 21 different (proto-)dolomite samples that formed at known temperatures and consists of a total of 416 individual measurements. This new dolomite calibration has identical slope but an offset of about 30 ppm to the one of Bonifacie et al. (2017) for 90 °C digestion. This offset corresponds to the dolomite isotope fractionation correction for acid digestions at 70 °C and 90 °C and lies in between the ones reported by Defliese et al. (2015) with a calcite similar behavior and by Murray et al. (2016) with a dolomite reaction temperature sensitivity much steeper than for calcite. However, the obtained offset of 30 ppm might change if the dataset of Bonifacie et al. (2017) will be recalculated with the newly recommended isotopic parameters ("Brand" parameters).

Comparing the novel dolomite specific Δ_{47}-T calibration to the calcite specific calibration of the same laboratory (Bernasconi et al., 2018) back-projected to 70 °C acid digestion, we observe a clear offset of about 30 ppm in average in the temperature range of 5 to 95 °C, whereas the slopes of both calibrations are within their uncertainties (0.0426±0.0022 for dolomite vs. 0.0449±0.001 for calcite). The offset between the two calibration sets corresponds to the different absolute Δ_{47} acid fractionations of dolomite and calcite already observed in Müller et al. (2017a).

We also propose a new dolomite-water oxygen fractionation equation based on samples from this study and from Vasconcelos et al. (2005) and Horita (2014) valid for temperatures between 25 and 350 °C.

The observed differences between the two carbonate mineralogies and the uncertainties in correcting Δ_{47} and $\delta^{18}O$ analyses of dolomites for different acid digestion temperatures underline the necessity of using dolomite specific Δ_{47}-T calibrations ideally constructed at identical sample reaction temperatures. The regular analysis of dolomite standards would also enable the use of dolomite specific Δ_{47}-T calibrations done in other laboratories and in general would allow a much better data comparison between different laboratories.

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REFERENCES

Assonov S. and Brenninkmeijer C. (2003) A redetermination of absolute values for $^{17}R_{VPDB\text{-}CO2}$ and $^{17}R_{VSMOW}$. *Rapid Communication to Mass Spectrometry* **17**, 1017-1029.

Baertschi P. (1976) Absolute ^{18}O content of standard mean ocean water. *Earth and Planetary Science Letters* **31**, 341-344.

Bahniuk A., McKenzie J.A., Perri E., Bontognali T.R.R., Vögeli N., Rezende C.E., Rangel T.P. and Vasconcelos C. (2015) Characterization of environmental conditions during microbial Mg-carbonate precipitation and early diagenetic dolomite crust formation: Brejo do Espinho, Rio de Janeiro, Brazil. From Bosence D.W.J., Gibbons K.A., LeHeron D.P., Morgan W.A., Pritchard T. and Vining B.A. (eds). *Microbial Carbonates in Space and Time: Implications for Global Exploration and Production*. Geological Society, London, Special Publications, **418**, 243-259.

Barkan E. and Luz B. (2005) High-precision measurements of $^{17}O/^{16}O$ ratios in H_2O. *Rapid Communications to Mass Spectrometry* **26**, 2733-2738.

Bernasconi S.M. (1991) Geochemical and microbial controls on dolomite formation and organic matter production/preservation in anoxic environments: a case study from the Middle Triassic Grenzbitumenzone, Southern Alps (Ticino, Switzerland). Dissertation ETH No. 9432.

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

Bernasconi S.M., Müller I.A., Bergmann K.D., Breitenbach S.F.M., Fernandez A., Hodell D.A., Jaggi M., Meckler A.N., Millan I. and Ziegler M. (2018) Reducing uncertainties in carbonate clumped isotope analysis through consistent carbonate-based standardization. *Geochemistry, Geophysics, Geosystems* **19**, 2895-2914.

Berra F., Jadoul F. and Anelli A. (2010) Environmental control on the end of the Dolomia Principale/Hauptdolomit depositional system in the central Alps: Coupling sea-level and climate changes. *Paleogeography, Palaeoclimatology, Palaeoecology* **290**, 138-150.

Bonifacie M., Calmels D., Eiler J. M., Horita J., Chaduteau C., Vasconcelos C., Agrinier P., Katz A., Passey B. H., Ferry J. M. and Bourrand J.-J. (2017) Calibration of the dolomite clumped isotope thermometer from 25 to 350 °C, and implications for a universal calibration for all (Ca, Mg, Fe)CO_3 carbonates. *Geochimica et Cosmochimica Acta* **200**, 255-279.

Bontognali T.R.R., Vasconcelos C., Warthmann R.J., Bernasconi S.M., Dupraz C., Strohmenger C.J. and McKenzie J.A. (2010) Dolomite formation within microbial mats in the coastal sabkha of Abu Dhabi (United Arab Emirates). *Sedimentology* **57**, 824-844.

Brauchli M., McKenzie J.A., Strohmenger C.J., Sadooni F., Vasconcelos C., Bontognali T.R.R. (2016) The importance of microbial mats for dolomite formation in the Dohat Faishakh sabkha, Qatar. *Carbonates and Evaporites* **31** (3), 339-345.

Bradley W.F., Burst J.F. and Graf D.L. (1953) Crystal chemistry and differential thermal effects of dolomite. *American Mineralogist* **38**, 207-217.

Breitenbach S.F.M., Mleneck-Vautravers M.J., Grauel A.-L., Lo L., Bernasconi S.M., Müller I.A., Rolfe J., Gázquez F., Greaves M. and Hodell D.A. (2018) Coupled Mg/Ca and clumped isotope analyses of foraminifera provide consistent water temperatures. *Geochimica et Cosmochimica Acta* **236**, 283-296.

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

Burns S.J., McKenzie J.A. and Vasconcelos C. (2000) Dolomite formation and biogeochemical cycles in the Phanerozoic. *Sedimentology* **47**, 49-61.

Came R.E., Azmy K., Tripati A. and Olanipekun B.-J. (2017) Comparison of clumped isotope signatures of dolomite cements to fluid inclusion thermometry in the temperature range of 73-176 °C. *Geochimica et Cosmochimica Acta* **199**, 31-47.

Chai L., Navrotsky A. and Reeder R.J. (1995) Energetics of calcium-rich dolomite. *Geochimica et Cosmochimica Acta* **59**, 939-944.

Chang T. and Li W. (1990) A calibrated measurement of the atomic weight of carbon. *Chinese Science Bulletin* **35**, 290-296.

Cocker J.D., Griffin B.J. and Muehlenbachs K. (1982) Oxygen and carbon isotope evidence for seawater-hydrothermal alteration of the Macquarie Island ophiolite. *Earth and Planetary Science Letters* **61**, 112-122.

Coplen T.B., Kendall C. and Hopple J. (1983) Comparison of stable isotope reference samples. *Nature* **302**, 236-238.

Coplen T.B. (1996) Atomic weights of the elements 1995 (Technical report). *Pure and Applied Chemistry* **68**, 2339-2359.

Daëron M., Blamart D., Peral M. and Affek H.P. (2016) Absolute isotopic abundance ratios and the accuracy of Δ_{47} measurements. *Chemical Geology* **442**, 83-96.

Dale A., John C.M., Mozley P.S., Smalley P.C. and Muggeridge A.H. (2014) Time-capsule concretions: Unlocking burial diagenetic processes in the Mancos Shale using carbonate clumped isotopes. *Earth and Planetary Science Letters* **394**, 30-37.

Defliese W. F., Hren M. T. and Lohmann K. C. (2015) Compositional and temperature effects of phosphoric acid fractionation on Δ_{47} analysis and implications for discrepant calibrations. *Chemical Geology* **396**, 51-60.

Del Cura M. A. G., Calvo J. P., Ordóñez S., Jones B. F. and Cañaveras J. C. (2001) Petrographic and geochemical evidence for the formation of primary, bacterially induced lacustrine dolomite: La Roda 'white earth' (Pliocene, central Spain). *Sedimentology* **48**, 897-915.

Dennis K. J., Affek H. P., Passey B. H., Schrag D. P. and Eiler J. M. (2011) Defining an absolute reference frame for "clumped" isotope studies of CO_2. *Geochimica et Cosmochimica Acta* **75**, 7117–7131.

Do Nascimento G.S. (2018) Influence of climatic and oceanographic conditions on bio-mineralization processes in hypersaline coastal lagoons (Rio de Janeiro – Brazil), Dissertation ETH.

Eiler J.M. (2007) "Clumped-isotope" geochemistry-The study of naturally-occurring, multiply-substituted isotopologues. *Earth and Planetary Science Letters* **262**, 309-327.

Epstein S. and Mayeda T. (1953) Variations of the O^{18}/O^{16} ratio in natural waters. *Geochimica et Cosmochimica Acta* **4**, 213-224.

Fernandez A., Müller I.A., Rodríguez-Sanz L., van Dijk J., Looser N. and Bernasconi S.M. (2017) A reassessment of the precision of carbonate clumped isotope measurements: implications for calibrations and paleoclimate reconstructions. *Geochemistry, Geophysics, Geosystems* **18**, 4375-4386.

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

Friedman I. and O'Neil J.R. (1977) Compilation of stable isotope fractionation factors of geochemical interest. Eds. Fleischer M., In Data of Geochemistry. Sixth Edition. *Geological Survey Professional Paper* **440**, KK1-KK9.

Frisia S. (1994) Mechanisms of complete dolomitization in a carbonate shelf: comparison between the Norian Dolomia Principale (Italy) and the Holocene of Abu Dhabi Sabkha. *Special Publication International Association of Sedimentologists* **21**, 55-74.

Fritz P. and Smith D.G.W. (1970) The isotopic composition of secondary dolomites. *Geochimica et Cosmochimica Acta* **34**, 1161-1173.

García del Cura A.M., Calvo J.P., Ordóñez S., Jones B.F. and Cañaveras J.C. (2001) Petrographic and geochemical evidence for the formation of primary, bacterially induced lacustrine dolomite: La Roda 'white earth' (Pliocene, central Spain). *Sedimentology* **48**, 897-915.

Ghosh P., Adkins J., Affek H., Balta B., Guo W., Schauble E.A., Schrag D. and Eiler J.M. (2006) ^{13}C-^{18}O bonds in carbonate minerals: A new kind of paleothermometer. *Geochimica et Cosmochimica Acta* **70**, 1439-1456.

Goldsmith J.R. and Graf D.L. (1958) Structural and compositional variations in some natural dolomites. *The Journal of Geology* **66**, 678-693.

Given R.K. and Wilkinson B.H. (1987) Dolomite abundance and stratigraphic age, constraints on rates and mechanisms of dolostone formation. *Journal of Sedimentary Petrology* **57**, 1068-1078.Gregg J. M., Bish D. L., Kaczmarek S. E. and Machel H. G. (2015) Mineralogy, nucleation and growth of dolomite in the laboratory and sedimentary environment: A review. *Sedimentology* **62**, 1749-1769.

Guo W., Mosenfelder J.L., Goddard III W.A. and Eiler J.M. (2009) Isotopic fractionations associated with phosphoric acid digestion of carbonate minerals: Insights from first-principles theoretical modeling and clumped isotope measurements. *Geochimica et Cosmochimica Acta* **73**, 7203-7225.

Hardie L.A. (1996) Secular variation in seawater chemistry: an explanation for the coupled secular variation in the mineralogies of marine limestones and potash evaporates over the past 600 m.y. *Geology* **24**, 279-283.

Hood A.vS., Wallace M.W. and Drysdale R.N. (2011) Neoproterozoic aragonite-dolomite seas? Widespread marine dolomite precipitation in Cryogenian reef complexes. *Geology* **39**, 871-874.

Hood A.vS. and Wallace M.W. (2012) Synsedimentary diagenesis in a Cryogenian reef complex: Ubiquitous marine dolomite precipitation. *Sedimentary Geology* **255-256**, 56-71.

Holland H.D., Horita J. and Seyfried W. (1996) On the secular variations in the composition of Phanerozoic marine potash evaporates. *Geology* **24**, 993-996.

Honlet R., Gasparrini M., Muchez P., Swennen R. and John C.M. (2017) A new approach to geobarometry by combining fluid inclusion and clumped isotope thermometry in hydrothermal carbonates. *Terra Nova* **30**, 199-206.

Horita J. (2014) Oxygen and carbon isotope fractionation in the system dolomite-water-CO_2 to elevated temperatures. *Geochimica et Cosmochimica Acta* **129**, 111-124.

Huang S., Huang K., Lü J. and Lan Y. (2014) The relationship between dolomite textures and their formation temperature: a case study from the Permian-Triassic of the Sichuan Basin and the Lower Paleozoic of the Tarim Basin. *Petroleum Science* **11**, 39-51.

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

John C. M. and Bowen D. (2016) Community software for challenging isotope analysis: First applications of "Easotope" to clumped isotopes. *Rapid Communications to Mass Spectrometry* **30**, 2285–2300.

Kaczmarek E.S. and Thornton B.P. (2017) The effect of temperature, cation ordering, and reaction rate in high-temperature dolomitization experiments. *Chemical Geology* **468**, 32-41.

Katz A., Bonifacie M., Hermoso M., Cartigny P. and Calmels D. (2017) Laboratory-grown coccoliths exhibit no vital effect in clumped isotope (Δ47) composition on a range of geologically relevant temperatures. *Geochimica et Cosmochimica Acta* **208**, 335–353.

Kele S., Breitenbach S. F. M., Capezzuoli E., Meckler A. N., Ziegler M., Millan I. M., Kluge T., Deák J., Hanselmann K., John C. M., Yan H., Liu Z. and Bernasconi S. M. (2015) Temperature dependence of oxygen- and clumped isotope fractionation in carbonates: A study of travertines and tufas in the 6-95 °C temperature range. *Geochimica et Cosmochimica Acta* **168**, 172-192.

Kelson J.R., Huntington K.W., Schauer A.J., Saenger C. and Lechler A.R. (2017) Toward a universal carbonate clumped isotope calibration: Diverse synthesis and preparatory methods suggest a single temperature relationship. *Geochimica et Cosmochimica Acta* **197**, 104-131.

Kim S.-T. and O'Neil J.R. (1997) Equilibrium and nonequilibrium oxygen isotope effects in synthetic carbonates. *Geochimica et Cosmochimica Acta* **61**, 3461-3475.

Kluge T., John C.M., Jourdan A.-L., Davis S. and Crawshaw J. (2015) Laboratory calibration of the calcium carbonate clumped isotope thermometer in the 25-250 °C temperature range. *Geochimica et Cosmochimica Acta* **157**, 213-227.

Land L.S. (1980) The isotopic and trace element geochemistry of dolomite: the state of the art. In: Zenger D.H., Dunham J.B. and Ethington R.L. (Eds.), Concepts and Models of Dolomitization. Spec. Publ. –*SEPM* **28**, 87-110.

Land L.S. (1985) The origin of massive dolomite. *Journal of Geological Education* **33**, 112-125.

Land L.S. (1998) Failure to precipitate dolomite at 25 degrees C from dilute solution despite 1000-fold oversaturation after 32 years. *Aquatic Geochemistry* **4**, 361-368.

Lehner P. (1952) Zur Geologie des Gebietes der Denti della Vecchia, des M. Boglia, des M. Brè, und des Monte Salvatore bei Lugano. *Eclogae geol. Helv.* **45**, 86–159.

Lloyd M.K., Eiler J.M. and Nabelek P.I. (2017) Clumped isotope thermometry of calcite and dolomite in a contact metamorphic environment. *Geochimica et Cosmochimica Acta* **197**, 323-344.

Lloyd M.K., Ryb U. and Eiler J.M. (2018) Experimental calibration of clumped isotope reordering in dolomite. *Geochimica et Cosmochimica Acta* **242**, 1-20.

Matthews A. and Katz A. (1977) Oxygen isotope fractionation during the dolomitization of calcium carbonate. *Geochimica et Cosmochimica Acta* **41**, 1431-1438.

Meckler A. N., Ziegler M., Millán M. I., Breitenbach S. F. M. and Bernasconi S. M. (2014) Long-term performance of the Kiel carbonate device with a new correction scheme for clumped isotope measurements. *Rapid Commun. Mass Spectrom.* **28**, 1705–1715.

Millán I.M., Machel H.G. and Bernasconi S.M. (2016) Constraining temperatures of formation and composition of dolomitizing fluids in the Upper Devonian Nisku Formation (Alberta, Canada) with clumped isotopes. *Journal of Sedimentary Research* **86**, 107-112.

Muehlenbachs K. and Clayton R.N. (1976) Oxygen isotope composition of the oceanic crust and its bearing on seawater. *Journal of Geophysical Research* **81**, 4365-4369.

Müller I. A., Violay M. E. S., Storck J. C., Fernandez A., van Dijk J., Madonna C. and Bernasconi S. M. (2017a) Clumped isotope fractionation during phosphoric acid digestion of carbonates at 70 °C. *Chem. Geol.* **449**, 1–14.

Müller I. A., Fernández A., Radke J., van Dijk J., Bowen D., Schwieters J. and Bernasconi S. (2017b) Carbonate clumped isotope analyses with the Long-integration dual-inlet (LIDI) workflow: Scratching at the lower sample weight boundaries. *Rapid Communcations to Mass Spectrometry* **31**, 1057-1066.

Murray S. T., Arienzo M. M. and Swart P. K. (2016) Determining the Δ_{47} acid fractionation in dolomites. *Geochimica et Cosmochimica Acta* **174**, 42-53.

Murray S.T. and Swart P.K. (2017) Evaluating formation fluid models and calibrations using clumped isotope paleothermometry on Bahamian dolomites. *Geochimica et Cosmochimica Acta* **206**, 73-93.

Northrop D.A. and Clayton R.N. (1966) Oxygen-isotope fractionations in systems containing dolomite. *The Journal of Geology* **74**, 174-196.

Peral M., Daëron M., Blamart D., Bassinot F., Dewilde F., Smialkowski N., Isguder G., Bonnin J., Jorissen F., Kissel C., Michel E., Vázquez Riveiros N. and Waelbroeck C. (2018) Updated calibration of the clumped isotope thermometer in planktonic and benthic foraminifera. *Geochimica et Cosmochimica Acta* **239**, 1-16.

Preto N., Breda A., dal Corso J., Spötl C., Zorzi F. and Frisia S. (2015) Primary dolomite in the Late Triassic Travenanzes Formation, Dolomites, Northern Italy: Facies control and possible bacterial influence. *Sedimentology* **62**, 697-716.

Rodriguez-Blanco J. D., Shaw S. and Benning L. G. (2015) A route for the direct crystallization of dolomite. *American Mineralogist* **100**, 1172-1181.

Rodríguez-Sanz L., Bernasconi S.M., Marino G., Heslop D., Müller I.A., Fernandez A., Grant K.M. and Rohling E.J. (2017) Penultimate deglacial warming across the Mediterranean Sea revealed by clumped isotopes in foraminifera. Scientific Reports 7: 16572, 1-11.

Rosenbaum J. and Sheppard S. M. (1986) An isotopic study of siderites, dolomites and ankerites at high temperatures. *Geochimica et Cosmochimica Acta* **50**, 1147-1150.

Ryb U., Lloyd M.K., Stolper D.A. and Eiler J.M. (2017) The clumped-isotope geochemistry of exhumed marbles from Naxos, Greece. *Earth and Planetary Science Letters* **470**, 1-12.

Sharma T. and Clayton R.N. (1965) Measurement of O^{18}/O^{16} ratios of total oxygen of carbonates. *Geochimica et Cosmochimica Acta* **29**, 1347-1353.

Schmid T. W. and Bernasconi S. M. (2010) An automated method for 'clumped-isotope` measurements on small carbonate samples. *Rapid Communications to Mass Spectrom*etry **24**, 1955-1963.

Smeraglia L., Bernasconi S.M., Berra F., Billi A., Boschi C., Caracausi A., Carminati E., Castorina F., Doglioni C., Italiano F., Rizzo A.L., Uysal I.T., Zhao J.-X. (2018) Crustal-scale fluid circulation and co-seismic shallow comb-veining along the longest normal fault of the central Apennines, Italy. *Earth and Planetary Science Letters* **498**, 152-168.

Spencer R.J. and Hardie L.A. (1990) Control of seawater composition by mixing of river waters and mid-ocean ridge hydrothermal brines. In: Spencer R.J., Chou I.M. (Eds.), Fluid Mineral Interactions: A tribute to H.P. Eugster. *Geochemical Society Special Publication* **2**, 409-419.

Stevenson E. I., Rickaby R. E. M., Tyler J. J., Minoletti F., Parkinson I. J., Mokadem F. and Burton K. W. (2014) Controls on stable strontium isotope fractionation in coccolithophores with implications for the marine Sr cycle. *Geochimica et Cosmochimica Acta* **128**, 225–235.

Suarez M.B., Ludvigson G.A., González L.A. and You H.-L. (2017) Continental paleotemperatures from an Early Cretaceous dolomitic Lake, Gansu Province, China. *Journal of Sedimentary Research* **87**, 486-499.

Van Lith Y., Vasconcelos C., Warthmann R., Martins J. C. F. and McKenzie J. A. (2002) Bacterial sulfate reduction and salinity: Two controls on dolomite precipitation in Lagoa Vermelha and Brejo do Espinho (Brazil). *Hydrobiologia* **485**, 35-49.

Vasconcelos C. and McKenzie J.A. (1997) Microbial mediation of modern dolomite precipitation and diagenesis under anoxic conditions (Lagoa Vermelha, Rio de Janeiro, Brazil). *Journal of Sedimentary Research*, Section A **67**, 378-390.

Vasconcelos C., McKenzie J. A., Warthmann R. and Bernasconi S. M. (2005) Calibration of the $\delta^{18}O$ paleothermometer for dolomite precipitated in microbial cultures and natural environments. *Geology* **33**, 317-320.

Warren J. (2000) Dolomite: occurrence, evolution and economically important associations. *Earth-Science Reviews* **52**, 1-81.

Wilson E.N. Hardie L.A. and Phillips O.M. (1990) Dolomitization front geometry, fluid flow patterns, and the origin of massive dolomite: the Triassic Latemar buildup, Northern Italy. *American Journal of Science* **290**, 741-796.

Winkelstern I. Z. and Lohmann K. C. (2016) Shallow burial alteration of dolomite and limestone clumped isotope geochemistry. *Geology* **44**, 463-466.

Winkelstern I. Z., Kaczmarek S. E., Lohmann K. C. and Humphrey J. D. (2016) Calibration of dolomite clumped isotope thermometry. *Chemical Geology* **443**, 32-38.

Wright D.T. (1997) An organogenic origin for widespread dolomite in the Cambrian Eilean Dubh Formation, northwestern Scotland. *Journal of Sedimentary Research* **67**, 54-64.

Wright D.T. (1999) The role of sulphate-reducing bacteria and cyanobacteria in dolomite formation in distal ephemeral lakes of the Coorong region, South Australia. *Sedimentary Geology* **126**, 147-157.

Zheng Y.-F. (1999) Oxygen isotope fractionation in carbonate and sulfate minerals. *Geochemical Journal* **33**, 109-126.

Zorn H. (1971) Paläontologische, stratigraphische und sedimentologische Untersuchungen des Salvatoredolomits (Mitteltrias) der Tessiner Kalkalpen. In: E. Kuhn-Schnyder und B. Peyer, Die Triasfauna der Tessiner Kalkalpen. XXI. *Schweizerische Paläontologische Abhandlungen* **91**, 1-90.

Figure Captions:

Fig. 1. X-ray diffraction pattern of the two natural calibration samples retrieved from the sediments of the Brazilian Lagoa Vermelha. The upper XRD pattern corresponds to sample LV 15 cm and the lower to sample LV 71 cm.

Fig. 2. XRD patterns of 'dolomite' samples synthesized under controlled laboratory conditions (Table 1); upper pattern 70 °C, 12 weeks; middle pattern 140 °C, 5.6 weeks; and lower pattern 220 °C, 12 weeks.

Fig. 3. XRD pattern of the ordered stoichiometric dolomites Rodolo (upper green XRD pattern) Sansa (middle XRD pattern) and the international dolomite standard NIST SRM 88b (lower XRD pattern).

Fig. 4. The clumped isotope composition of the synthetic and natural dolomite calibration samples digested at 70 °C is plotted against the reciprocal formation temperature. The linear relationship displayed in the top left is derived from the 270 individual replicates of the samples formed at temperatures between 25 and 220 °C. Averages of the 19 different samples are displayed as diamonds with their uncertainty at the 95% CI.

Fig. 5. Including the two dolomite samples that were heated to 1100 °C we obtain a third order polynomial Δ_{47}-T relationship based on 416 individual measurements covering the full range of potential temperature of dolomite rocks.

Fig. 6. The dolomite specific Δ_{47}-T calibration of this study is displayed as black line and lies above the calcite specific Δ_{47}-T calibration of the ETH (Kele et al., 2015 re-evaluated in Bernasconi et al., 2018) as grey line for 70 °C acid digestion. Both temperature relationships are embedded in 95% CI as dashed lines in the corresponding color.

Fig. 7. The new dolomite specific Δ_{47}-T calibration was projected to 90 °C acid digestion temperature using the AC of 0.0204 ‰ (Defliese et al., 2015, dashed black line), the AC of 0.0380 ‰ (Murray et al., 2016, black line with dashes and dots) to compare it directly to the dolomite calibration Bonifacie

et al., 2017 (grey line in the middle). The top left box shows a blow-up to better visualize the offsets at the temperature range between 70 to 92 °C.

Fig. 8. The black line corresponds to the third order polynomial fit (equation in figure) through all of our dolomite calibration samples between 25 and 1100 °C and the dashed black line corresponds to the theoretical dolomite Δ_{47}-T relationship from Guo et al. (2009).

Fig. 9. The oxygen isotope fractionation between (proto-)dolomites and precipitation solutions of the individual synthesized samples of this study (70, 140 and 220 °C, black hollow diamonds), samples of Horita, 2014 (black squares) and of Vasconcelos et al., 2005 (black triangles) are plotted against the inverse temperature. Combination of these three datasets resulted in the black dashed line giving the depicted linear relationship and covers a temperature range from 25 to 350 °C. As dashed grey line we also plotted the one of Matthew and Katz (1977; corrected for the acid digestion factor of Rosenbaum and Sheppard (1986) for consistent data treatment) lying slightly below the combined one.

Figure 1

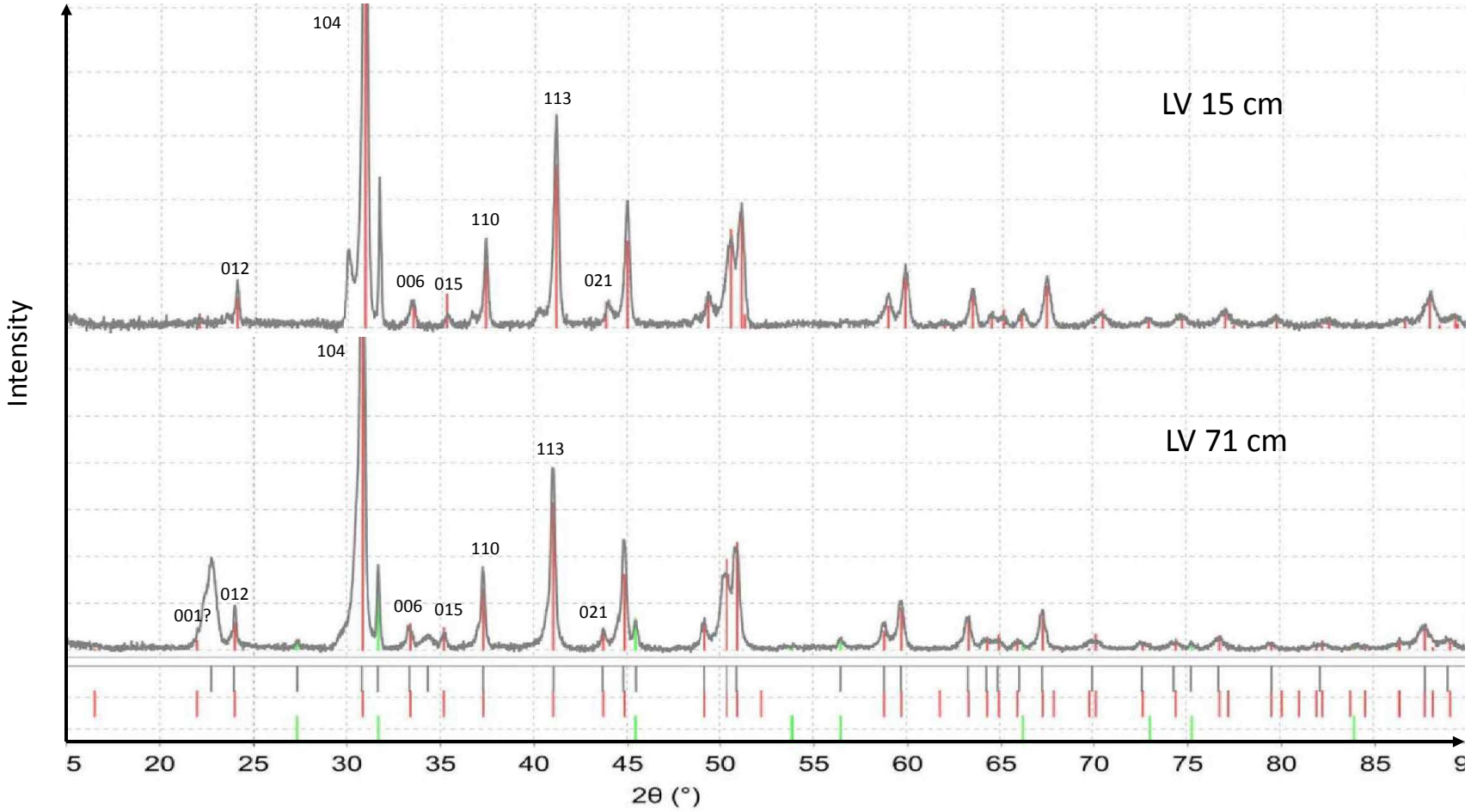
LV 15 cm
LV 71 cm
Intensity
2θ (°)
104
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Figure 2

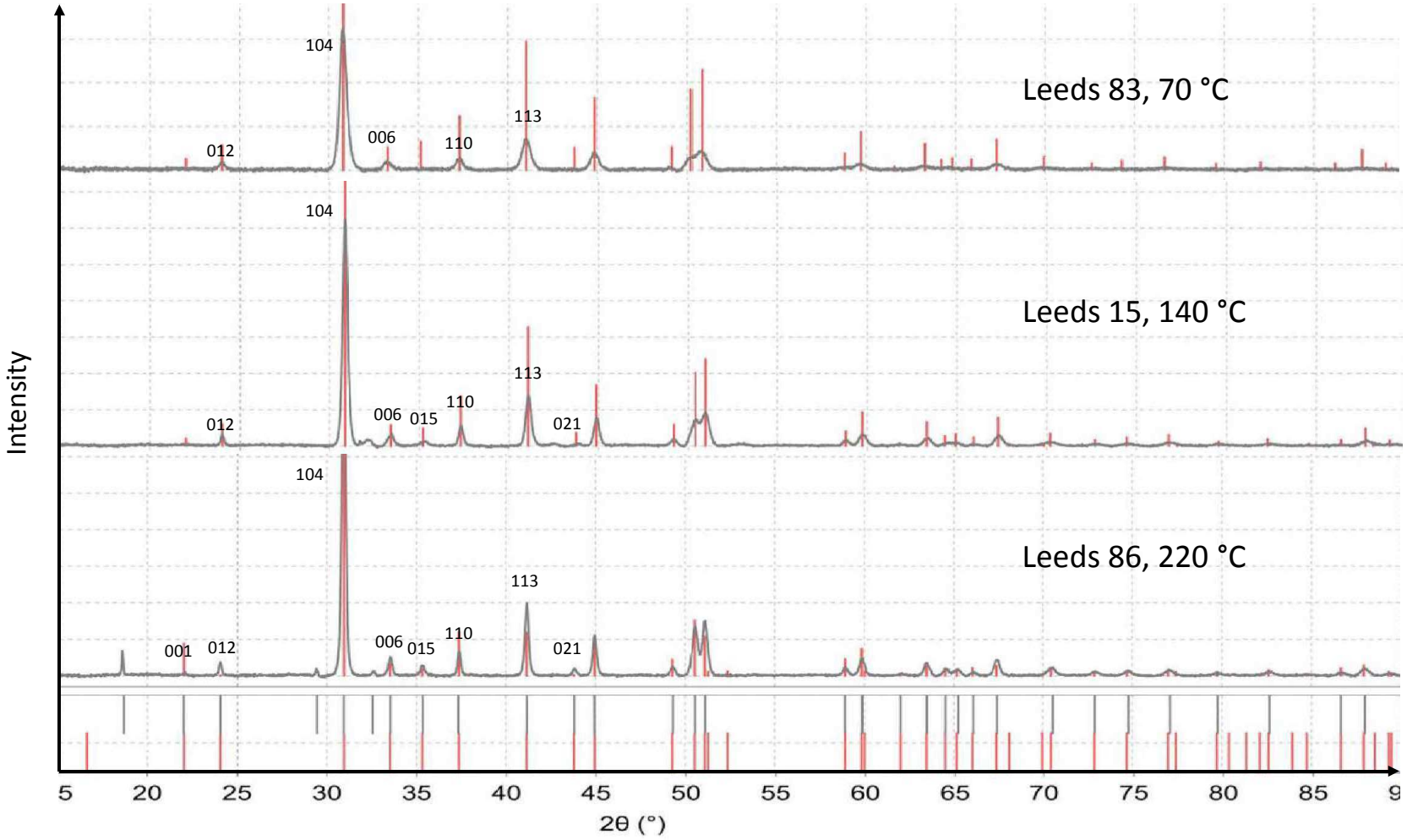
Leeds 83, 70 °C
Leeds 15, 140 °C
Leeds 86, 220 °C
Intensity
2θ (°)
104
012
006
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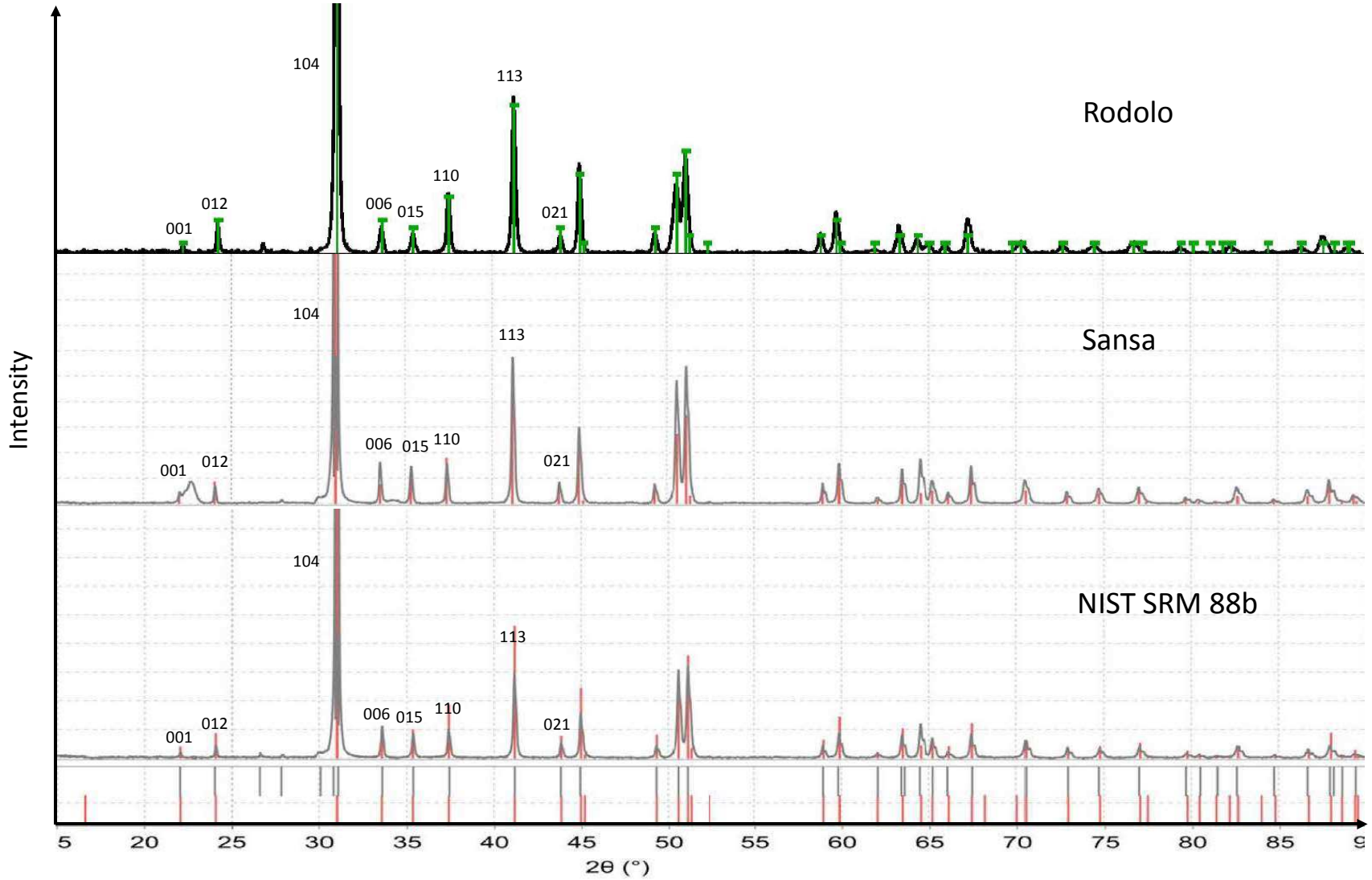
Figure 3


Rodolo
Sansa
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Intensity
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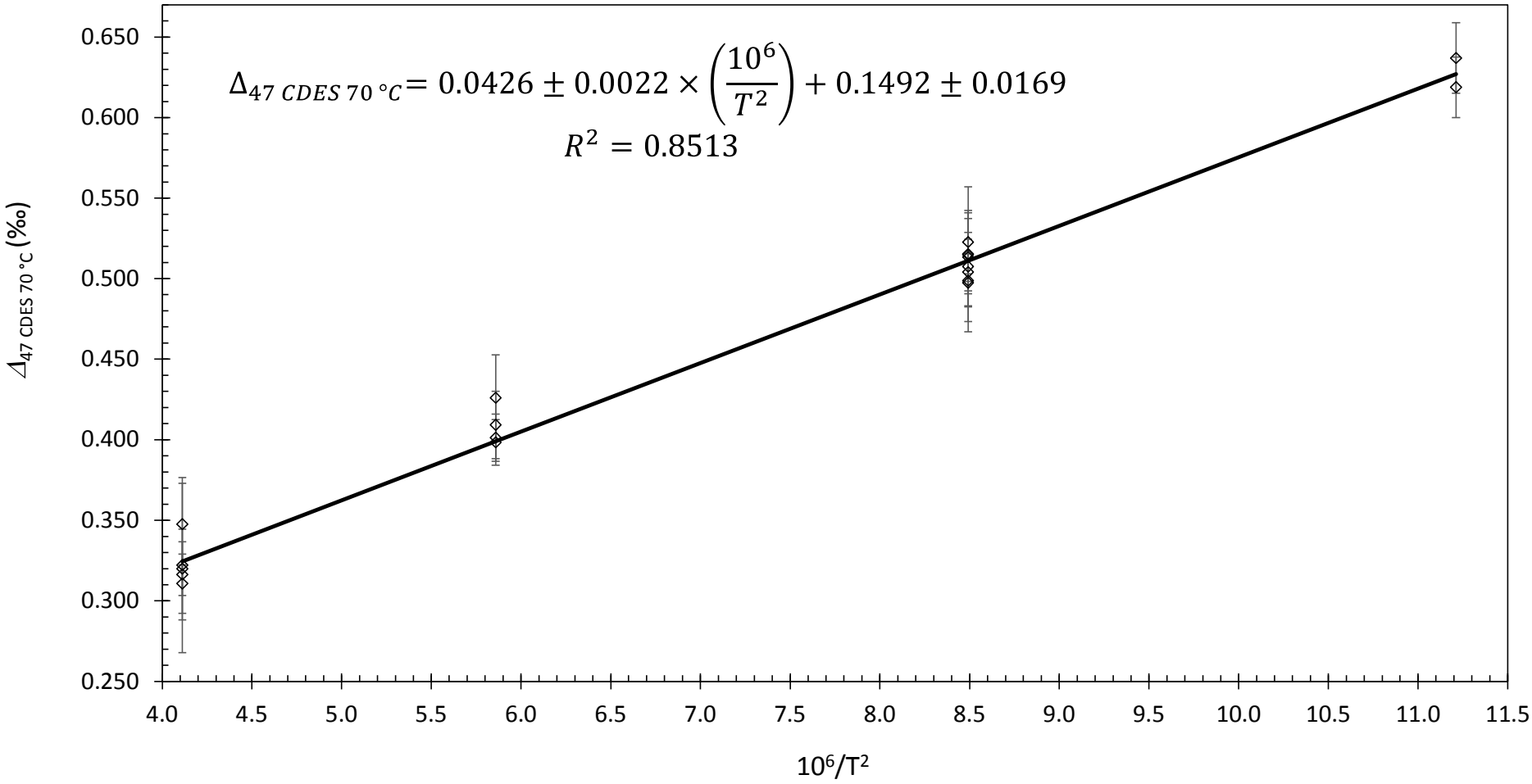
Figure 4


$\Delta_{47\ CDES\ 70\ °C} = 0.0426 \pm 0.0022 \times \left(\frac{10^6}{T^2}\right) + 0.1492 \pm 0.0169$
$R^2 = 0.8513$
$\Delta_{47\ CDES\ 70\ °C}$ (‰)
0.650
0.600
0.550
0.500
0.450
0.400
0.350
0.300
0.250
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
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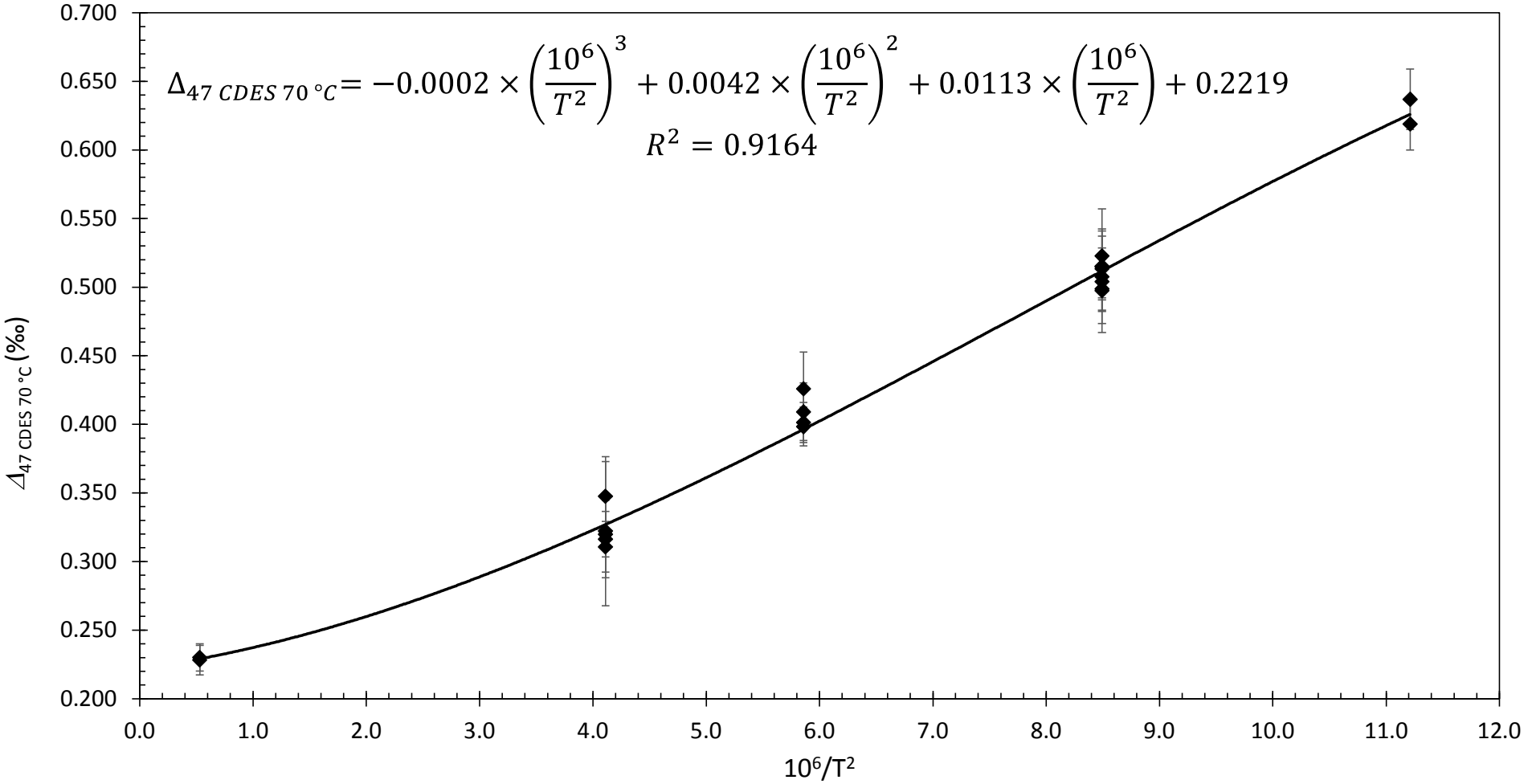
10.5
11.0
11.5
$10^6/T^2$

Figure 5


$\Delta_{47\ CDES\ 70\ °C} = -0.0002 \times \left(\frac{10^6}{T^2}\right)^3 + 0.0042 \times \left(\frac{10^6}{T^2}\right)^2 + 0.0113 \times \left(\frac{10^6}{T^2}\right) + 0.2219$
$R^2 = 0.9164$
$\Delta_{47\ CDES\ 70\ °C}$ (‰)
0.700
0.650
0.600
0.550
0.500
0.450
0.400
0.350
0.300
0.250
0.200
0.0
1.0
2.0
3.0
4.0
5.0
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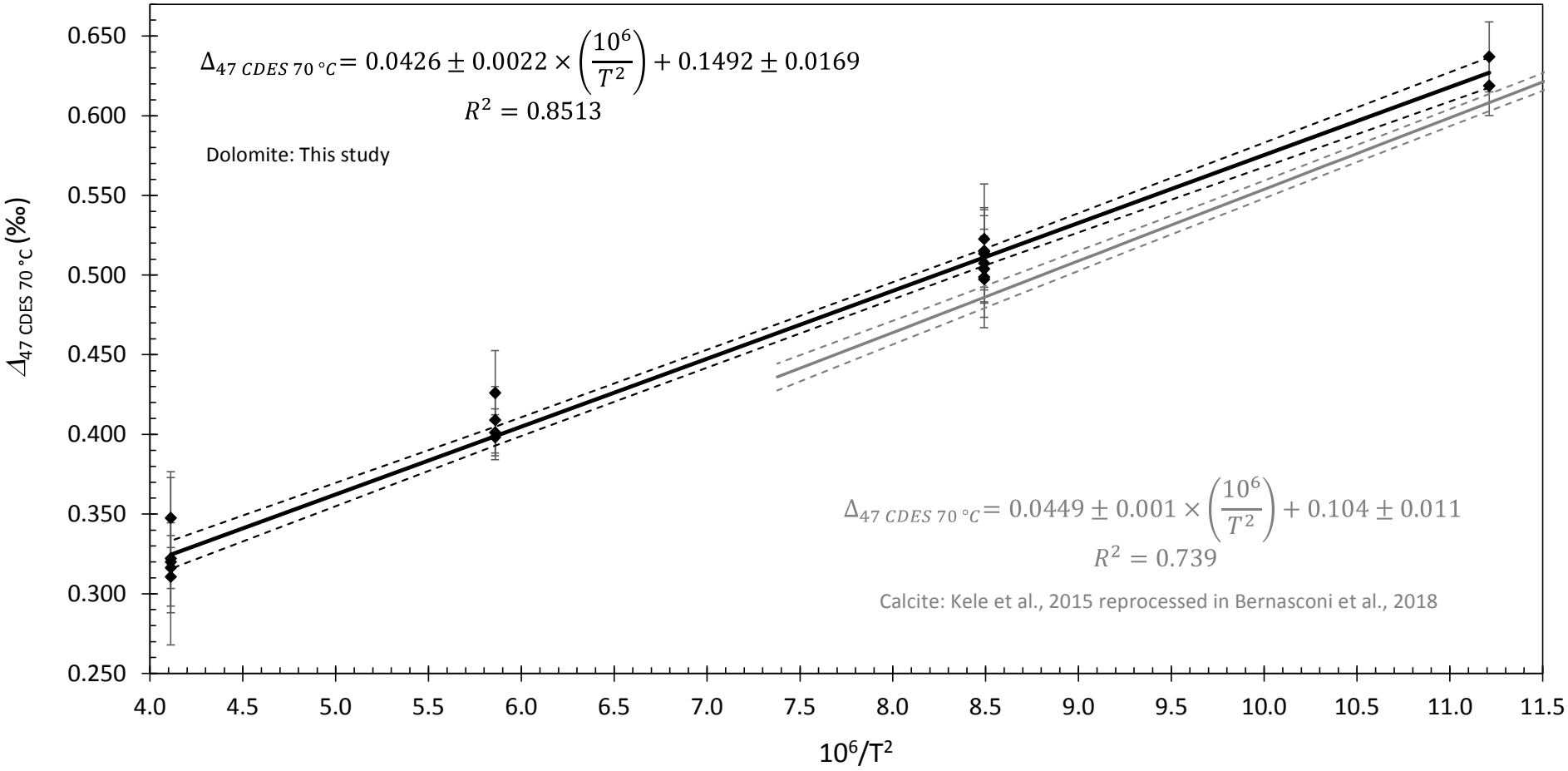
7.0
8.0
9.0
10.0
11.0
12.0
$10^6/T^2$

Figure 6


$\Delta_{47\ CDES\ 70\ °C} = 0.0426 \pm 0.0022 \times \left(\frac{10^6}{T^2}\right) + 0.1492 \pm 0.0169$
$R^2 = 0.8513$
Dolomite: This study
$\Delta_{47\ CDES\ 70\ °C} = 0.0449 \pm 0.001 \times \left(\frac{10^6}{T^2}\right) + 0.104 \pm 0.011$
$R^2 = 0.739$
Calcite: Kele et al., 2015 reprocessed in Bernasconi et al., 2018
$\Delta_{47\ CDES\ 70\ °C}$ (‰)
$10^6/T^2$
0.650
0.600
0.550
0.500
0.450
0.400
0.350
0.300
0.250
4.0
4.5
5.0
5.5
6.0
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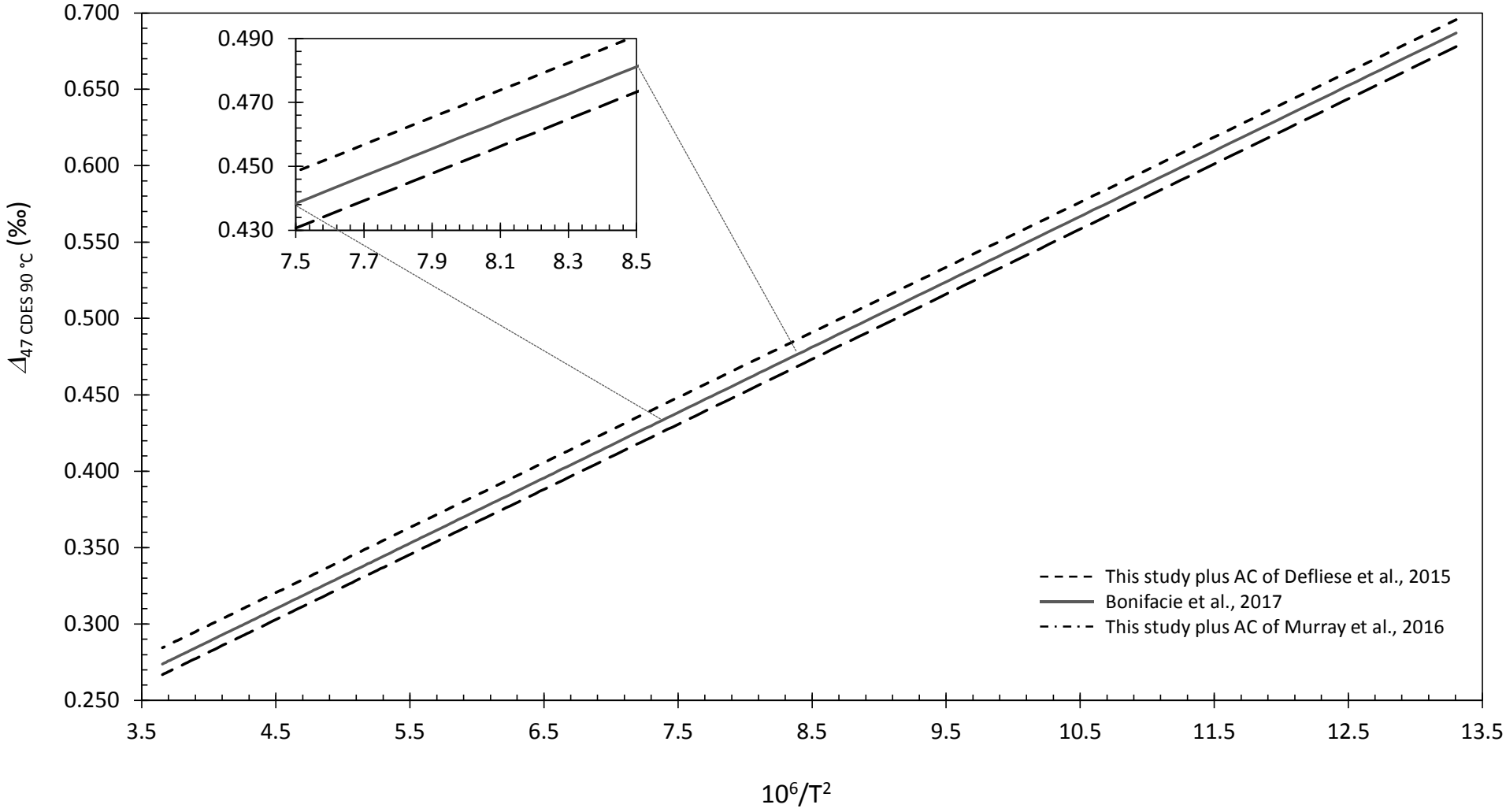
9.5
10.0
10.5
11.0
11.5

Figure 7


0.700
0.650
0.600
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0.450
0.400
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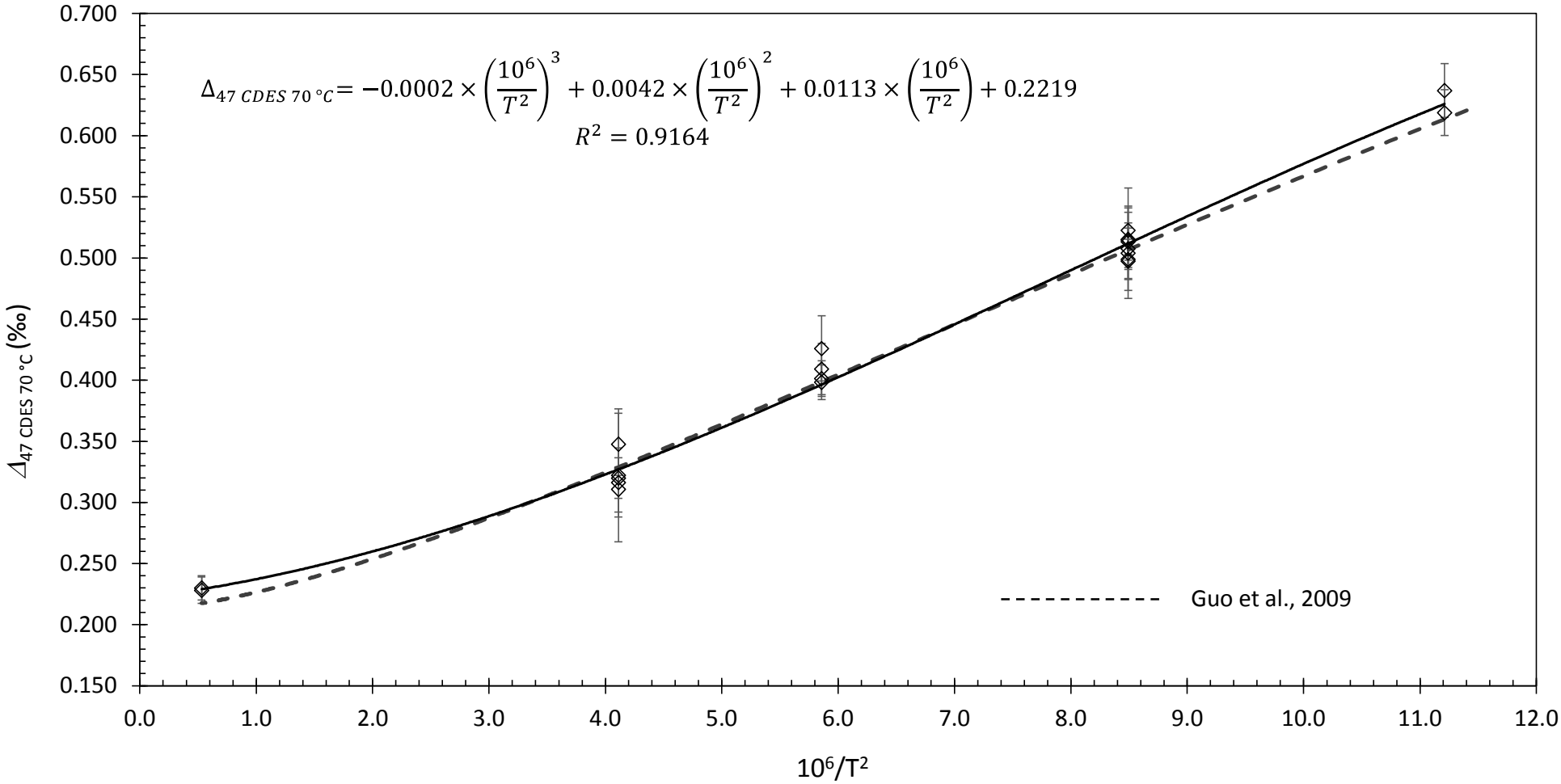
0.300
0.250
3.5
4.5
5.5
6.5
7.5
8.5
9.5
10.5
11.5
12.5
13.5
Δ47 CDES 90 °C (‰)
10^6/T^2
0.490
0.470
0.450
0.430
7.5
7.7
7.9
8.1
8.3
8.5
This study plus AC of Defliese et al., 2015
Bonifacie et al., 2017
This study plus AC of Murray et al., 2016

Figure 8


$\Delta_{47\ CDES\ 70\ °C} = -0.0002 \times \left(\frac{10^6}{T^2}\right)^3 + 0.0042 \times \left(\frac{10^6}{T^2}\right)^2 + 0.0113 \times \left(\frac{10^6}{T^2}\right) + 0.2219$
$R^2 = 0.9164$
Guo et al., 2009
$\Delta_{47\ CDES\ 70\ °C}$ (‰)
$10^6/T^2$
0.700
0.650
0.600
0.550
0.500
0.450
0.400
0.350
0.300
0.250
0.200
0.150
0.0
1.0
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12.0

Figure 9

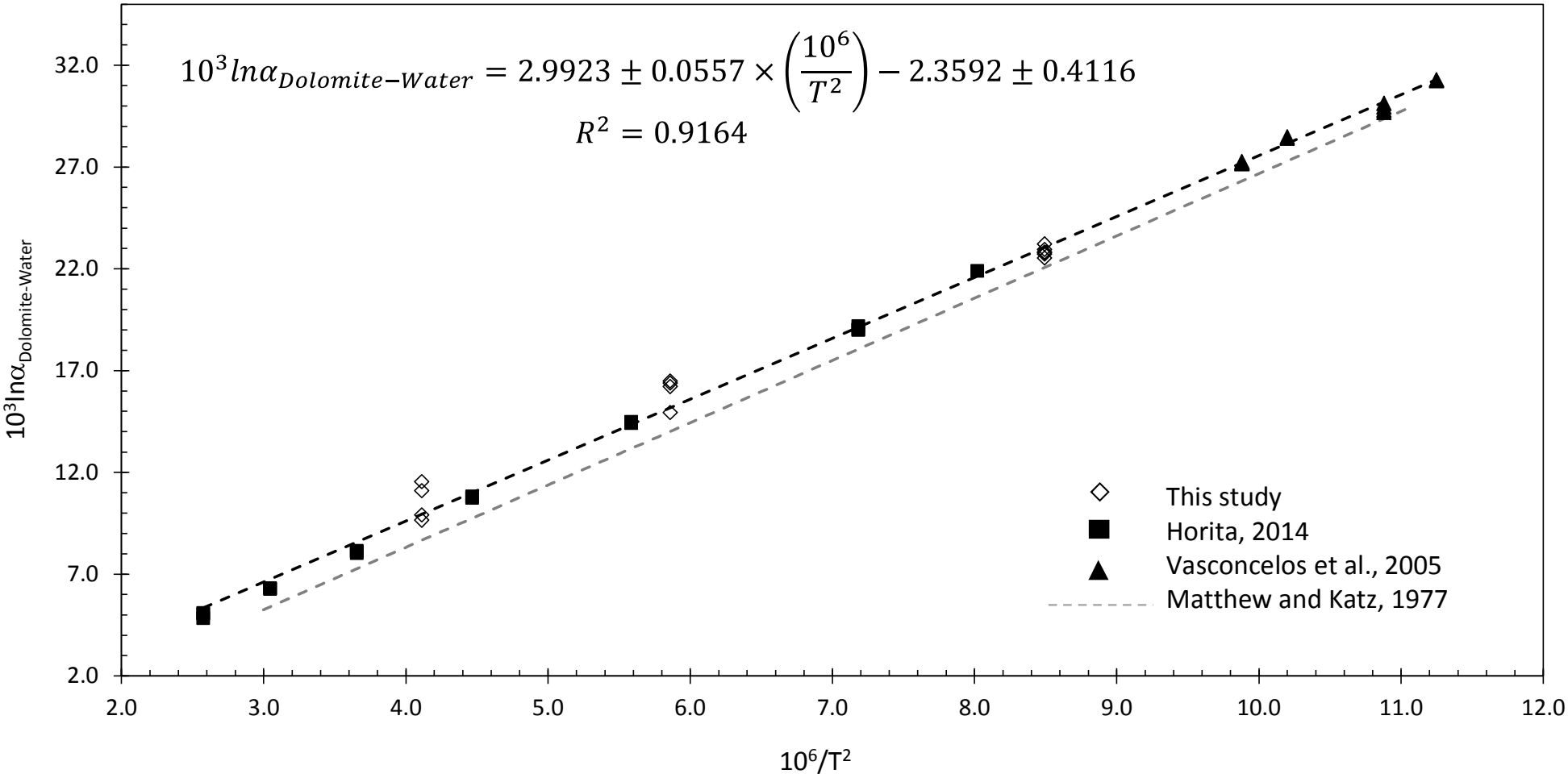
$10^3 ln\alpha_{Dolomite-Water} = 2.9923 \pm 0.0557 \times \left(\frac{10^6}{T^2}\right) - 2.3592 \pm 0.4116$
$R^2 = 0.9164$
$10^3 ln\alpha_{Dolomite-Water}$
$10^6/T^2$
This study
Horita, 2014
Vasconcelos et al., 2005
Matthew and Katz, 1977
32.0
27.0
22.0
17.0
12.0
7.0
2.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
12.0

Table 1

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Table 1. Oxygen isotope fractionation between Dolomite and Fluid source

Identifier	T (°C)	Time (weeks)	$\delta^{18}O_{VSMOW}$ (‰)	$\delta^{18}O_{H2O,VSMOW}$ (‰)	$10^3 \ln \alpha_{Dolomite\text{-}Water}$
LV 15 cm	25.5		34.58±0.05	1.8±1.0	32.19
LV 71 cm	25.5		34.39±0.04	1.8±1.0	32.01
Leeds 23	70	1.0	15.73±0.05	-7.31±0.1	22.95
Leeds 1	70	1.1	15.97±0.11	-7.35±0.1	23.23
Leeds 6	70	1.1	15.53±0.06	-7.36±0.1	22.79
Leeds 12	70	2.4	15.53±0.21	-7.28±0.1	22.72
Leeds 20	70	4.0	15.59±0.05	-7.33±0.1	22.82
Leeds 82	70	12.0	15.98±0.03	-5.99±0.1	21.86
Leeds 83	70	12.0	15.50±0.10	-7.12±0.1	22.53
Leeds 21	140	1.0	7.85±0.20	-7.31±0.1	14.94
Leeds 14	140	2.4	9.38±0.09	-7.13±0.1	16.49
Leeds 22	140	4.0	9.30±0.20	-7.10±0.1	16.39
Leeds 15	140	5.6	9.19±0.07	-7.05±0.1	16.22
Leeds 34	220	2.1	6.14±0.54	-6.91±0.1	13.05
Leeds 41	220	4.0	4.82±0.44	-6.71±0.1	11.54
Leeds 84	220	12.0	4.92±0.23	-4.74±0.1	9.66
Leeds 85	220	12.0	5.19±0.21	-4.72±0.1	9.91
Leeds 86	220	12.0	5.74±0.15	-5.37±0.1	11.10

All uncertainties are displayed at the 95% CL; oxygen isotope composition of the fluid source of samples LV 15 cm and 71 cm are derived from van Lith et al., 2002

Table 2

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Table 2. Averages of dolomite Δ_{47}-T calibration samples

Identifier	T (°C)	$\delta^{13}C_{VPDB}$ (‰)	$\delta^{18}O_{VPDB}$ (‰)	δ^{47} (‰)	$\Delta_{47\ CDES\ 70\ °C}$ (‰)	#
LV 15 cm	25.5	-8.32±0.02	3.56±0.05	10.87±0.08	0.637±0.022	16
LV 71 cm	25.5	-10.21±0.02	3.38±0.04	8.83±0.07	0.619±0.019	16
Leeds 23	70	-7.07±0.03	-14.72±0.05	-6.81±0.12	0.508±0.017	16
Leeds 1	70	-7.10±0.04	-14.51±0.11	-6.70±0.11	0.497±0.014	12
Leeds 6	70	-7.17±0.03	-14.90±0.06	-7.07±0.06	0.523±0.020	11
Leeds 12	70	-7.12±0.09	-14.92±0.21	-7.10±0.26	0.504±0.037	8
Leeds 20	70	-7.22±0.02	-14.86±0.05	-7.13±0.08	0.515±0.042	9
Leeds 81	70	-7.24±0.04	-14.89±0.10	-7.09±0.10	0.515±0.022	18
Leeds 82	70	-7.12±0.02	-14.48±0.03	-6.67±0.07	0.499±0.016	21
Leeds 83	70	-7.25±0.04	-14.94±0.10	-7.15±0.11	0.513±0.015	41
Leeds 21	140	-7.38±0.02	-22.37±0.20	-15.09±0.19	0.426±0.027	6
Leeds 14	140	-7.30±0.03	-20.88±0.09	-13.61±0.18	0.398±0.014	15
Leeds 22	140	-7.35±0.06	-20.96±0.20	-13.74±0.30	0.401±0.015	9
Leeds 15	140	-7.32±0.04	-21.07±0.07	-13.75±0.15	0.409±0.021	21
Leeds 34	220	-7.45±0.14	-24.03±0.54	-16.95±0.70	0.322±0.054	6
Leeds 41	220	-7.45±0.07	-25.31±0.44	-18.43±0.77	0.348±0.025	6
Leeds 84	220	-7.42±0.02	-25.21±0.23	-18.25±0.37	0.311±0.018	12
Leeds 85	220	-7.42±0.02	-24.95±0.21	-17.91±0.30	0.316±0.028	16
Leeds 86	220	-7.31±0.02	-24.42±0.15	-17.31±0.24	0.320±0.017	11
Rodolo (H)	1100	-3.89±0.02	1.78±0.04	13.16±0.05	0.230±0.010	87
Sansa (H)	1100	1.29±0.02	-3.68±0.04	12.54±0.06	0.228±0.011	59

All uncertainties are displayed at the 95% CL

Table 3

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Table 3. Dolomite Standards

Identifier	$\delta^{13}C_{VPDB}$ (‰)	$\delta^{18}O_{VPDB}$ (‰)	$\Delta_{47\ CDES,\ 70\ °C}$ (‰)	T (°C)	$\delta^{18}O_{fluid}$ (‰)	#
Rodolo	-3.71±0.01	2.77±0.02	0.632±0.006	25±2	1.7±0.4	151
Sansa	1.45±0.04	-3.56±0.09	0.526±0.014	64±6	2.8±1.0	19
NIST SRM 88b	2.12±0.06	-7.09±0.08	0.522±0.022	66±10	-0.5±1.5	14

All uncertainties are displayed at the 95% CI, $\delta^{18}O_{fluid}$ calculated by using combined T relationship of this study

Table 4
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Table 4. Heated Carbonates (Δ_{47} acid fractionations)

Identifier	$\delta^{13}C_{VPDB}$ (‰)	$\delta^{18}O_{VPDB}$ (‰)	$\Delta_{47\ CDES\ 70\ °C}$ (‰)	#
Aragonites				
Billin 1 (H)	3.10±0.01	-8.36±0.01	0.165±0.009	64
Billin 2 (H)	-10.99±0.06	-5.59±0.05	0.176±0.013	38
Average			0.169±0.007	102
Calcites				
MS 2 (H)	2.06±0.01	-1.91±0.02	0.183±0.008	88
ETH-4 (H)	-10.20±0.01	-18.72±0.02	0.187±0.008	107
Merck (H)	-41.91±0.02	-15.62±0.01	0.192±0.009	66
Average			0.187±0.005	258
Dolomites				
Rodolo (H)	-3.89±0.02	1.78±0.04	0.229±0.009	91
Sansa (H)	1.29±0.02	-3.68±0.04	0.226±0.010	57
Average			0.227±0.007	148

All uncertainties are displayed at the 95% CL