Clumped isotope fractionation during phosphoric acid digestion of carbonates at 70 °C.

Inigo A. Müller^{a*}, Marie E.S. Violay^c, Julian-Christopher Storck^b, Alvaro Fernandez^a, Joep vanDijk^a,
Claudio Madonna^a, Stefano M. Bernasconi^a

^aGeological Institute, ETH Zurich, Sonneggstr. 5, 8092 Zurich, Switzerland

^bInstitute of Geochemistry and Petrology, ETH Zurich, Sonneggstr. 5, 8092 Zurich, Switzerland

^cLEMR, EPFL Lausanne, GC D1 401, 1015 Lausanne, Switzerland

Abstract

The application of clumped isotopes (Δ_{47}) in carbonate minerals as a sensitive temperature proxy in paleo-environments depends on a well-constrained clumped isotope fractionation for the necessary step of phosphoric acid digestion of the carbonate mineral to produce CO₂. Published estimates for clumped isotope fractionations vary, and the effect of different carbonate mineralogies is still under debate. Differences in the sample preparation design and sample digestion temperatures are potential sources for varying acid fractionations and could be a source for discrepant Δ_{47} -temperature calibrations observed in different laboratories. To evaluate the clumped isotope acid fractionation at 70 °C and simultaneously account for a potential cation effect we analyzed a set of eight carbonate minerals (calcite, aragonite, dolomite and magnesite) that were driven to a stochastic isotope distribution by heating them to temperatures of 1000 °C. Our study reveals significant cation- and mineral- specific differences for the Δ_{47} acid fractionation of carbonate minerals digested at 70 °C or 100 °C. The Δ_{47} acid fractionation at 70 °C for calcite is 0.197 ± 0.002 ‰, for aragonite 0.172 ± 0.003 ‰, whereas dolomite has a significantly larger acid fractionation of 0.226 ± 0.002 ‰. For magnesite digested at 100 °C we observed a Δ_{47} acid fractionation of 0.218 ± 0.020 ‰. Projected to an acid digestion at 25 °C, our acid fractionation for calcite of 0.260 ‰ is statistically indistinguishable from existing studies. We further show that the Δ_{47} of the calcite standards ETH-1 and ETH-2 of 0.265 ‰ and 0.267 ‰, respectively, are in the range of the determined acid fractionation projected to 25 °C suggesting that they have an identical and near stochastic isotope distribution. The observed differences in the Δ_{47} acid fractionation between calcite and aragonite ($\Delta\Delta_{47} = -0.025$ ‰) and between calcite and dolomite ($\Delta\Delta_{47} = -0.029$ ‰) does not correlate with the phosphoric acid fractionation of oxygen isotopes, but rather depends on the radius of the cation as well as on the mineral structure. Our results reveal that the acid fractionation of dolomite at 70 °C is significantly distinct from the one of calcite, but at 90 °C the two are within error

of each other due to the different acid fractionation temperature dependence of calcite and dolomite. Thus it is necessary to use a mineral-specific Δ_{47} acid fractionation factor for dolomite to avoid differences in the final Δ_{47} signal from dolomites digested at 90 °C and dolomites digested at lower temperatures. Similar effects may apply also to other carbonates such as magnesite and siderite. However, their mineral specific Δ_{47} acid fractionation at digestion temperatures around 90 °C might be also similar to the one of calcite so that potential differences could be within the range of the analytical error.

1. INTRODUCTION

The application of clumped isotopes in carbonate minerals has attracted increasing interest in the fields of paleo-climate research (e.g. Ghosh et al., 2006a; Passey et al., 2010; Grauel et al., 2013; Henkes et al., 2013; Grauel et al., 2016), paleoaltimetry (e.g. Ghosh et al., 2006b; Huntington and Lechler, 2015) and to unravel diagenetic processes that occur during burial or contact metamorphism (e.g. Huntington et al., 2011; Stolper and Eiler, 2015; Millan et al., 2016).

Schauble et al. (2006) showed that in carbonate minerals there is an excess abundance of the multiply substituted isotopologue $^{13}\text{C}^{18}\text{O}^{16}\text{O}_2^{2-}$ (m/z 63) compared to a stochastic distribution, which solely depends on the temperature during its formation. This excess is a consequence of the homogenous isotope exchange reaction between the relevant carbonate isotopologues:

with M being the metal cation of the corresponding carbonate mineral (e.g. calcite and aragonite (CaCO_3), dolomite ($\text{CaMg}(\text{CO}_3)_2$), magnesite (MgCO_3), siderite (FeCO_3), witherite (BaCO_3)). Having attained equilibrium this exchange reaction (Eq. 1) is thermodynamically controlled and produces an excess in the doubly substituted isotopologue relative to a stochastic isotope distribution (0.5 ‰ at 0 °C), which decreases with increasing temperature and approaches a stochastic isotope composition at 1000 °C (Schauble et al., 2006). Ghosh et al. (2006a) demonstrated the feasibility to analyze clumped isotopes in carbonates by phosphoric acid digestion to CO_2 gas and the measurement of the abundance of m/z 47. Mass 47 mainly consists of the $^{13}\text{C}^{18}\text{O}^{16}\text{O}$ isotopologue (96%) and the remainder is made up by the isotopologues $^{12}\text{C}^{18}\text{O}^{17}\text{O}$ and $^{13}\text{C}^{17}\text{O}^{17}\text{O}$ (Eiler and Schauble, 2004). The study by Ghosh et al. (2006a) showed that the temperature dependent abundance of the $^{13}\text{C}^{18}\text{O}$ bond in the carbonate molecule (m/z 63) is retained during acid digestion to CO_2 gas within the isotopologue of m/z 47 and thus can be used to determine the formation temperature of the carbonate mineral. The abundance of the multiply substituted isotopologue $^{13}\text{C}^{18}\text{O}^{16}\text{O}$ is expressed

with the parameter Δ_{47} , which represents the difference of the measured ratios versus theoretical ratios if the analyzed sample would have stochastic isotope distribution:

$$\Delta_{47} = \left[\left(\frac{R^{47}}{R^{47*}} - 1 \right) - \left(\frac{R^{46}}{R^{46*}} - 1 \right) - \left(\frac{R^{45}}{R^{45*}} - 1 \right) \right] \times 1000 \text{ ‰}, \quad \text{Eq. 2}$$

With R^{47} , R^{46} , R^{45} being the measured ratios $^{47}/_{44}$, $^{46}/_{44}$, $^{45}/_{44}$, respectively and with R^{47*} , R^{46*} , R^{45*} corresponding to the mass ratios for a stochastic isotope distribution derived from the traditional isotope composition of the sample gas ($\delta^{13}\text{C}_{\text{VPDB}}$, $\delta^{18}\text{O}_{\text{VSMOW}}$). The bulk isotope composition of the sample gas is expressed in the conventional delta notation against the working gas used in the mass spectrometer:

$$\delta_{(SG \text{ vs. } WG)}^{47} = \left(\frac{R_{SG}^{47}}{R_{WG}^{47}} \right) \times 1000 \text{ ‰}. \quad \text{Eq. 3}$$

In contrast to the carbonate $\delta^{18}\text{O}$ paleothermometer, which depends on the two unknowns, the oxygen isotope composition of the parent fluid and the temperature during carbonate formation (e.g. Epstein et al., 1953; Kim and O'Neil, 1997; Dietzel et al., 2009), the Δ_{47} paleothermometer depends solely on the ambient temperature and is independent of the oxygen isotope composition of the water. However, analytical challenges arise as the $^{13}\text{C}^{18}\text{O}^{16}\text{O}$ isotopologue is very rare, with an abundance of approximately 46 ppm, and the exposure of CO_2 to water vapor during sample preparation and measurement can lead to rapid re-equilibration of the clumped isotope signatures. In addition, organic impurities within the sample or contaminants within the sample preparation system such as halocarbons, hydrocarbons or reduced sulfur compounds can form isobaric interferences in the source of the mass spectrometer that affect mass 47 to 49 (Eiler and Schauble, 2004; Huntington et al., 2009). Thus special care has to be taken during sample preparation, phosphoric acid digestion and CO_2 purification before the gas can be analyzed with a gas source isotope ratio mass spectrometer (see Spencer and Kim, 2015 for a recent review).

The study of Ghosh et al. (2006) demonstrated that the abundance of the $^{13}\text{C}^{18}\text{O}$ bond in CO_2 evolved from phosphoric acid digestion of the carbonate mineral is proportional to the one in the carbonate mineral, but with an offset corresponding to the phosphoric acid fractionation factor Δ_{47}^* :

$$\Delta_{47}^* = \Delta_{47} - \Delta_{63}, \quad \text{Eq. 4}$$

This isotopic fractionation occurs because only 2/3 of the CO_3^{2-} oxygen atoms are transferred into the CO_2 phase whereas one oxygen atom forms water as illustrated in the following equations (Guo et al., 2009):

$$95 \quad \text{H}_2\text{CO}_3 \rightarrow \text{H}_2\text{O} + \text{CO}_2 \quad \text{Eq. 6}$$

96 Ghosh and colleagues observed that the clumped isotope acid fractionation is temperature
 97 dependent, analogously to the extensively studied acid fractionation for the oxygen isotope system
 98 (Sharma and Clayton, 1965; Rosenbaum and Sheppard, 1986; Swart et al., 1991; Kim and O'Neil,
 99 1997; Kim et al., 2007; Guo et al., 2009) and changes by approximately 0.0016 ‰ per °C. They also
 100 tried to determine an absolute value for the clumped isotope acid fractionation at 25 °C, however,
 101 their results were ambiguous, ranging between 0.14 ‰ - 0.28 ‰. A study by Guo et al. (2009)
 102 investigated the acid fractionation during phosphoric acid digestion of carbonates to CO₂ more
 103 thoroughly by applying a combined experimental and theoretical modeling approach. They
 104 calculated the absolute theoretical value for the clumped isotope phosphoric acid fractionation at 25
 105 °C to be 0.220 ‰ and found a similar temperature dependence to the one observed by Ghosh et al.
 106 (2006). The theoretical model of Guo et al. (2009) predicts that heating to about 1300 °C is necessary
 107 to reach a stochastic isotope distribution. For this reason they produced three calcites with stochastic
 108 isotope distribution by exposing them for several hours to temperatures about 1600 °C. They
 109 obtained an experimental value for the absolute clumped isotope acid fractionation of $\Delta_{47}^* =$
 110 0.232 ± 0.015 ‰. Once this value is transferred into the absolute reference frame, a standardization
 111 frame in use since 2011 to enable better inter-laboratory comparison, it becomes about 0.268 ± 0.015
 112 ‰ (determined with the transfer function of Table 4 in Dennis et al., 2011) and thus is 0.047 ‰
 113 larger than the theoretical fractionation. Guo and colleagues also attempted to evaluate the effect of
 114 different cations on the acid fractionation factor and their model could show that various cations
 115 might interact in a different way with the proposed intermediate H₂CO₃. They suggest that the cation
 116 radius plays the major role in affecting the clumped isotope fractionation.

117 While pioneering studies digested their carbonate minerals at 25 °C in a sealed McCrea-type reaction
 118 vessel over several days (e.g. Ghosh et al., 2006; Guo et al., 2009), new phosphoric acid digestion
 119 setups were introduced to decrease the reaction time and increase the sample throughput. To date,
 120 three main types carbonate digestion devices are used, the sealed vessel method at 25 °C, the
 121 common acid bath operated at temperatures between 75 and 100 °C (e.g. Wacker et al., 2013,
 122 Fernandez et al., 2014; Defliese et al., 2015) and the automated Kiel IV carbonate device operated at
 123 70 °C (Schmid and Bernasconi, 2010; Meckler et al., 2014). To enable a direct comparison of clumped
 124 isotope data it has become common to project the data to an acid digestion temperature of 25 °C,
 125 which requires a correction factor for laboratories that digest carbonates at higher temperatures.
 126 The temperature-dependence of the acid fractionation factor of calcite was determined in several
 127 studies by digesting the same samples at different temperatures in offline preparation systems and
 128 seem to match the theoretical estimates (Guo et al., 2009; Henkes et al., 2013; Wacker et al., 2013;

Defliese et al., 2015; Murray et al., 2016). However, a redetermination of the absolute acid fractionation has not been carried out since Guo et al. (2009).

The effect of different carbonate mineralogies on the phosphoric acid fractionation is not conclusive. Theoretical studies attempted to simulate the cation effect, but did not observe significant differences in the resulting clumped isotope composition of the evolved CO₂ gas (Schauble et al., 2006; Guo et al., 2009). Observations during experimental studies diverge from each other. Whereas the temperature dependence of the phosphoric acid fractionation between 25 °C and 90 °C was found to be identical for the two CaCO₃ polymorphs calcite and aragonite (Wacker et al., 2013; Defliese et al., 2015), the one for dolomite is still unclear. Defliese et al. (2015) determined a similar dependence as for calcite, whereas Murray et al. (2016) measured a much stronger temperature dependence (Murray et al., 2016). Further support of the influence of different cations on the clumped isotope acid fractionation of carbonates comes from Tripathi et al. (2015) who determined a 0.025 ‰ smaller isotope fractionation for witherite (BaCO₃) than for calcite at 25 °C. On the other side, a study on the Δ_{47} temperature sensitivity for siderites acid digested at 100 °C shows a similar temperature relationship than for calcite (Fernandez et al., 2014), although one would expect a large cation effect in the iron carbonate with its stronger electronegativity that would cause a distinct temperature relationship.

With this study we aimed at solving the discrepancies discussed above, by analyzing a set of carbonates of different mineralogy and bulk isotope composition driven to stochastic isotope composition. This allowed us to establish an absolute isotope fractionation factor at 70°C, rather than only determining differences between reaction temperatures. The choice of the reaction temperature and digestion method was guided by the demonstrated performance of the Kiel IV-MAT253 system to measure small samples (2-3 mg for 20 to 30 replicate aliquots of each sample) with very high reproducibility (1 SD 0.016 ‰; Meckler et al., 2014), which makes it the system of choice for the measurement of small samples. Additionally, we reacted two dolomite samples offline at 100 °C to verify the temperature dependence of dolomite and one magnesite sample was reacted at 100 °C as its reaction kinetics at 70 °C is too slow to be applicable.

A second aim was to compare the compositions determined for carbonates with stochastic isotope composition with the one of the calcite standards ETH-1 and ETH-2 (Meckler et al., 2014, Kele et al., 2015), which were distributed to a large number of laboratories for a laboratory inter-comparison exercise. The new data helps to put strong constraints on the composition of these samples, and thus on the correction scheme we proposed in Meckler et al. (2014).

2. METHODOLOGY

2.1. Heating of carbonate minerals

The clumped isotope composition of carbonate minerals is reported as the difference between the measured R^{47} and the stochastic R^{47*} of the CO_2 gas that evolved from the acid digestion of the carbonate mineral. To determine the isotopic fractionation during this acid digestion step we need to ensure that the isotopologues of the carbonate mineral are stochastically distributed. Our calcite standards ETH-1 and 2 were heated during 10 h to 600 °C with a hot isostatic press (Sinter-HIP-Kompaktanlage; ABRA Fluid AG, Switzerland) which cooled to room temperatures on time scales of hours, and still have a near stochastic Δ_{47} composition. From this observation we concluded that the more rapid cooling of the two high pressure devices used would most probably preserve the high temperature clumped isotope signature. The theoretical model of Guo et al. (2009) predicts that it would be necessary to heat the carbonate minerals to temperatures above 1300 °C to produce a stochastic isotopic composition. However, the Δ_{47} values of our heated calcite standards ETH-1 and 2 (see section 2.3) display almost identical values to the carbonates heated to about 1600 °C in Guo et al. (2009) if we project our results to 25 °C acid fractionation temperature. From this observation we conclude that heating carbonate minerals for several hours to approximately 1000 °C is sufficient to obtain stochastic isotope distribution. The 0.004 ‰ difference between 1000 °C and 1300 °C predicted by Guo et al. (2009) is not resolvable with the current Δ_{47} measurement precision. At elevated temperatures different carbonate minerals have specific p-T-stability fields, thus we heated our carbonate minerals in two different devices, in a “Paterson” apparatus (Paterson, 1990) or in a piston cylinder under higher confining pressure (see individual heating conditions on Table 1). The advantage of the Paterson apparatus is that it allows producing samples in 1-2 gram quantities compared to the Piston cylinder that only allows about hundred mg of sample to be heated.

For calcite, we heated a Carrara Marble (MS2) and a synthetic calcite (ETH-4 standard) to 1000 °C in a Paterson apparatus at the Rock Deformation Laboratory of the ETH Zürich. Several grams of powder were first cold pressed in a small capsule (diameter 15 mm, length 10 mm). The capsules were held between alumina and zirconia pistons in an iron jacket (Fig. 1a). These assemblies were then confined and heated individually during 4 hours to 1000 °C at a confining pressure of 0.15 GPa. The temperature was monitored during the course of the experiment by a type K thermocouple and the temperature gradient on the sample was less than 1 °C. After 4 hours exposure to these conditions the calcite specimens were cooled down to room temperature within 45 minutes.

For the dolomite heating experiments we used two natural dolomites, Rodolo a primary lacustrine dolomite that was deposited during the upper Pliocene in La Roda, Spain (Del Cura et al., 2001) and

San Salvatore dolomite (Sansa) deposited in the middle Triassic in shallow subtidal to intertidal environment in the southern Alps, Switzerland (Bernasconi, 1994). Dolomite requires much higher confining pressure than calcite at 1000 °C (Tao et al., 2014; Buob et al., 2006), thus the heating of dolomite was performed in a piston cylinder with a graphite furnace similar to the heating experiments of Guo et al. (2009) and Tripathi et al. (2015). Approximately 70 mg of dolomite powder was sealed in a small platinum capsule (diameter 2-3 mm, length 5-7 mm), placed in the piston cylinder (Fig. 1b) and exposed during 4 hours to 1100 °C under 2.5 GPa confining pressure.

A hydrothermal magnesite sample was heated with the Paterson apparatus during 4 hours at 655 °C to ensure that the experiments were carried out within the magnesite stability field. Approximately 2 g of the ground hydrothermal magnesite were cold pressed in a small capsule and treated similarly as the calcites, but as mentioned before at 655 °C and a pressure of 0.124 GPa. From the heating conditions of ETH-1 and 2 we would expect that the 655 °C enable a near-stochastic isotope distribution in magnesite. Considering the theoretical calculations of Guo et al. (2009) at 655 °C a carbonate would be expected to be approximately 0.017 ‰ higher than the stochastic value.

The powder of two aragonite crystals (Bilin 1 and Bilin 2) from Bohemia, Czech Republic (Mineral collection, Department Earth Science, ETH Zurich) were exposed 4 hours to 850 °C at 3.5 GPa using a piston cylinder to remain in the stability field of aragonite (Li et al., 2015). According to the theoretical model of Guo et al. (2009) the temperature of 850 °C would produce a Δ_{47} that is 0.007 ‰ higher than the stochastic isotope distribution. To examine the impact of different cooling rates of the two heating devices on potential re-equilibration of Δ_{47} we heated a third artificial calcite (Merck) with the piston cylinder during 4 hours at 1000 °C and 2.5 GPa. The heating experiments in the piston cylinder were quenched to room temperature in less than 30 sec by switching off the graphite furnace. Prior to isotopic analysis all heated carbonate minerals were finely ground with a pestle and mortar and their mineralogy verified by powder X-ray diffraction (XRD patterns in Appendix B).

2.2. Instrumental setup and Δ_{47} analysis

Stable isotope measurements were performed on a Kiel IV carbonate device connected to a MAT253 isotope ratio mass spectrometer (*Thermo Fisher Scientific*, Bremen, Germany) following the methodology of Schmid and Bernasconi (2010) with the improvements described in Meckler et al. (2014). Small aliquots (90 – 130 µg) of carbonates are loaded in a Kiel IV carbonate device, which is constantly kept at 70 °C. The carbonate sample is digested by three drops of 104 % phosphoric acid while the evolved CO₂ is continuously frozen in a first liquid nitrogen (LN₂) trap. After complete acid reaction, non-condensable gases are pumped away, then the CO₂ gas of the sample is heated to -100

°C and transferred through a Porapak Type Q 50-80 mesh trap, embedded with silver wool on both ends, to a second LN₂ trap. The Porapak trap is kept at approximately -15 °C by four Peltier cooling elements and the gas transfer through the trap takes 300 seconds. The design of our Peltier cooling system cannot reach the low temperatures possible in offline purification setups that use a mixture of cooling agents, but is adequate for the small and clean samples of this study. The sample gas is released at 30 °C from the second LN₂ trap to the MAT253 and the *m/z* 44, 45, 46, 47, 48, 49 of the gas is measured in micro volume mode during 8 cycles against our reference gas ($\delta^{13}\text{C}_{\text{VPDB}} = -7.25 \text{ ‰}$, $\delta^{18}\text{O}_{\text{VPDB}} = +1.65 \text{ ‰}$). Each of the 8 cycles is comprised of 26 sec integration of sample gas, 26 sec integration of reference gas with a 10 sec idle time after the changeover switches, taking about 35 min per aliquot. Every measurement run is loaded with 6 replicates of each ETH standard and the rest of the 46 turret positions are filled with sample aliquots (3 to 4 aliquots per sample). The accepted Δ_{47} values of the ETH standards that are used for normalization and data correction were determined in Meckler et al. (2014). Briefly, Meckler et al. (2014) measured the ETH standards during a 3 week period, they applied first a PBL correction, added an acid fractionation correction to project the values to 25 °C acid digestion temperature, then the data were converted into the absolute reference frame using an empirical transfer function (ETF). The ETF was determined from gas line intercepts of heated and equilibrated gases that were measured via normal Dual Inlet according to Dennis et al. (2011) during the same time period. For further detail we refer to Meckler et al. (2014), which also thoroughly discuss how daily analysis of the ETH standards enables a tight monitoring of the instrument performance, corrections for changes in negative backgrounds on the minor collectors and for scale compression. We modified the analytical strategy proposed in Meckler et al. (2014) which used 10 aliquots of each sample and standard within each run of 46 samples, with the aim to improve our error determination. We now analyze one sample over multiple runs on different days with only 3-4 aliquots per run (29 to 93 aliquots per sample distributed over 5 to 12 runs) as better strategy to determine the true analytical error. We consider this an improvement over measuring more aliquots during fewer runs because the influence of one single run is less pronounced in the final Δ_{47} calculations. The isotopic data of all standards used during the period of measurements are reported in Appendix A.

Magnesite does not dissolve quantitatively at 70 °C, thus it cannot be measured on the Kiel IV carbonate device. For this reason we had to react it offline with 104 % phosphoric acid during 3 hours at 100 °C in a McCrea-type reaction vessel (Fernandez et al., 2016). The reaction vessel containing 12 mg magnesite powder was warmed for 25 min in boiling water before adding 1 ml of the phosphoric acid. During the reaction with the acid the evolved CO₂ gas is steadily removed in a LN₂ trap. After quantitative CO₂ trapping, the water was separated from the sample gas by heating the CO₂ to -80 °C with an isopropyl alcohol slush and trapping the CO₂ with LN₂. This dewatering step

was repeated 3 times before passing the water free CO₂ slowly through a Porapak QTM silver wool trap held at -40 °C by a water glycol mixture to remove eventual impurities such as sulfur and hydrocarbons/halocarbons. The CO₂ gas was cleaned two times more for residual water contamination with the isopropyl alcohol slush and then sealed in a glass vial for manual transfer to the mass spectrometer. The cleaned sample gas was measured in normal dual inlet mode with 8 reference-sample-gas cycles at constant beam pressure of 16 V for m/z 44.

In addition to the magnesite we dissolved offline at 100 °C two heated dolomite samples to determine the temperature-dependent Δ_{47} acid fractionation for dolomite and 23 ETH standards, of which we accurately know the isotopic composition for 70 °C acid digestion. The evacuated vessel containing 12 mg of dolomite and 1 ml phosphoric acid were treated the same way as the magnesite sample.

2.3. Data processing for clumped isotopes

The m/z 44 to 49 signal recorded by the Isodat software during measurement is exported as the raw beam intensities in a separate spread sheet and corrected for its mass 44 pressure dependent background noise. By doing a pressure sensitive baseline (PBL) correction using the linear regressions obtained from the correlation of m/z 44 maxima and the corresponding backgrounds of the other masses it is possible to remove non-linearity effects of the mass spectrometer (He et al., 2012; Bernasconi et al. 2013; Meckler et al., 2014; Fiebig et al., 2016). During the measuring period of this study the background of m/z 47 was selected at a narrow shoulder on the left side of the peak. The PBL corrected intensities are used to calculate the δ^{45} to δ^{48} versus the reference gas and the $\delta^{13}\text{C}_{\text{VPDB}}$ and $\delta^{18}\text{O}_{\text{VPDB}}$ of the gas are calculated with the algorithm of Brand et al. (2010) for the ¹⁷O-correction. The revised isotopic parameters recently proposed by Daëron et al. (2016) are used to calculate the raw Δ_{47} instead of those of Huntington et al., (2009) that we used in previous studies.

The use of the new parameters compared to the ones of Huntington et al. (2009), which are those commonly used by the clumped isotope community to date, leads to some differences in the calculated Δ_{47} values depending on the bulk composition of the sample (Daëron et al. 2016). These parameters also influence the slope and the intercept of the heated gas and equilibrated gas lines that are used by most laboratories to correct their data from instrumental artifacts. Because the “accepted values” of the ETH standards were determined by Meckler et al. (2014) using the Huntington et al. (2009) parameters to link the composition of the 4 ETH standards to the absolute reference frame of Dennis et al. (2011), we reevaluated all measurements used to anchor the composition of the 4 ETH standards with the new parameters. This lead to differences from the

accepted values of -0.003 ‰ for ETH 1, -0.008 ‰ for ETH 2, -0.011 ‰ for ETH 3, -0.014 ‰ for ETH 4 and -0.005 ‰ for MS 2. Because these differences are well within the current analytical reproducibility of clumped isotope measurements across laboratories, we keep our accepted values that were determined with the old parameters until the clumped isotope community agrees on a common Δ_{47} for each ETH standards.

Our data processing continues by applying an empirical transfer function (ETF) derived from plotting the raw Δ_{47} against the accepted Δ_{47} of the 4 ETH standards to transfer the Δ_{47} into the absolute reference frame. Afterwards we add a correction derived from the average offset between the measured Δ_{47} and accepted Δ_{47} of the ETH 1-4 carbonate standards with an average of a moving window consisting of 21 standards, where only standards with an offset smaller than ± 0.04 ‰ are taken into account for the calculations (Meckler et al., 2014). This moving standard average window, which smooths out minor day to day variations in the $\Delta_{47_{raw}}$, allows to correct the sample data with more robust standard averages. These steps account for fragmentation and recombination reactions of the CO_2 gas that occur in the source of the mass spectrometer and allows inter-laboratory comparison of our clumped isotope analyses (Dennis et al., 2011). In addition, we apply afterwards a secondary ETF that is derived from plotting the residual standard offsets against the accepted values for the measuring period. A new measuring period is defined when the acid reservoir in the Kiel IV is filled with fresh phosphoric acid or when a hardware modification is performed on the Kiel IV and/or MAT253 (e.g. source cleaning, filament change), all modifications that usually affect the performance of the system. The daily analyses of all 4 ETH standards and the monitoring of the offsets of the PBL corrected $\Delta_{47_{raw}}$ from the accepted values over the last few years, revealed that changes in these offsets only occurred right after such modifications. As the acid reaction and gas purification conditions in the Kiel IV carbonate device are highly reproducible the standard offsets remain on a constant level till the next modification takes place. This secondary ETF corrects for the instrument-specific stretching conditions during the measuring period and the resulting values are equal to the processed clumped isotope composition for 70°C phosphoric acid digestion or Δ_{47} (70°C). The traditional isotopes of the samples were drift corrected by using a regression line of the measured standard values against the accepted standard values of each measurement sequence. Thereby we used slightly modified values for the ETH standards vs VPDB derived from recent re-determination on our Gas Bench – DELTA V PLUS IRMS system from Thermo Scientific (ETH-1: $\delta^{13}\text{C} = 2.00$ ‰, $\delta^{18}\text{O} = -2.17$ ‰; ETH-2: $\delta^{13}\text{C} = -10.20$ ‰, $\delta^{18}\text{O} = -18.59$ ‰; ETH-3: $\delta^{13}\text{C} = 1.67$ ‰, $\delta^{18}\text{O} = -1.76$ ‰; ETH-4: $\delta^{13}\text{C} = -10.22$ ‰, $\delta^{18}\text{O} = -18.66$ ‰).

For appropriate comparison with studies that dissolve the carbonates with phosphoric acid at different temperatures we project our Δ_{47} (70°C) to 25°C acid digestion by using an acid fractionation

correction of 0.062 ‰ derived from the average of the most recent studies on the acid fractionation factor (Defliese et al., 2015; Murray et al., 2016) to obtain the final clumped isotope value Δ_{47} (25°C). Before those studies on the acid fractionation correction were published Meckler et al. (2014) used an interpolation of Henkes et al. (2013) which differed by 0.0015 ‰ from the accepted values that are in use now. The accepted Δ_{47} values that we use now for the 4 ETH standards and their original labelling of Meckler et al. (2014) are: ETH-1 = Iso A with $\Delta_{47} = 0.265$ ‰; ETH-2 = Iso B with $\Delta_{47} = 0.267$ ‰; ETH 3 = Iso C with $\Delta_{47} = 0.703$ ‰; ETH 4 = Iso R with $\Delta_{47} = 0.522$ ‰. We have to point out here that in Kele et al. (2015) the accepted Δ_{47} were unfortunately mislabeled (ETH 3 was swapped with ETH 4) and recommend to use the values above.

The external precision of the isotopic values is reported as the standard error from repeated measurements in per mill. The traditional carbon and oxygen isotopes of the carbonate minerals are presented in the conventional V-PDB scale. To correct the oxygen isotope composition for the isotope fractionation during acid digestion at 70 °C we used an acid fractionation factor of 1.00871 for calcite minerals, 1.00909 for aragonites (Kim et al., 2007) and 1.009926 for dolomites (Rosenbaum and Sheppard, 1986). For the acid fractionation correction of the samples digested offline at 100 °C we used an acid fractionation factor of 1.009178 for magnesite (Das Sharma et al., 2002), 1.007962 for calcite (Kim et al., 2007) and 1.009047 for dolomite (Rosenbaum and Sheppard, 1986).

The dual inlet analyses of carbonate samples that were digested with phosphoric acid offline at 100 °C were first PBL corrected and subsequently the raw Δ_{47} was converted into the absolute reference frame using the ETH standards that were measured before and after with our Kiel IV carbonate device. For the dolomite samples we used an extrapolation of the acid fractionation temperature dependence from Murray et al. (2016) to project the results to a 25 °C reaction temperature to enable a direct comparison to existing clumped isotope studies on other carbonate mineralogies, whereas for the magnesite we refrained to project the Δ_{47} to 25 °C as no data on the magnesite specific acid fractionation temperature dependence exist. This way of converting our DI measurements into the absolute reference frame with Kiel IV standard measurements was thoroughly examined by the analysis of ETH standards digested offline at 100 °C. Their raw values were processed the same way, PBL corrected, transferred into the ARF with Kiel IV standard measurements and projected from 100 °C to 25 °C acid fractionation by an extrapolation of Defliese et al. (2015) and Murray et al. (2016). The data of these standards with their final Δ_{47} projected to 25 °C and the comparison to the accepted standard values are listed in the Appendix C. The resulting Δ_{47} for each ETH standards reproduce nicely the accepted values and demonstrate the feasibility of

accurately correct samples measured by DI with a bigger set of all four ETH standards measured with the Kiel IV carbonate device.

3. RESULTS

The mineralogy of the various carbonates was confirmed by X-ray diffraction analysis before and after the heating experiments (Appendix B). The XRD patterns did not change after heating to approximately 1000 °C, as special care was taken to remain in the mineral specific p-T-stability field. The two calcites MS 2 (H) and ETH 4 (H) were heated during 4 hours at 1000 °C and 0.15 GPa in a Paterson apparatus to produce stochastic isotope distribution. Using a Paterson apparatus allows the production of several grams of carbonate material but has the disadvantage of a longer cooling time of approximately 45 minutes and thus with the potential of isotopic re-equilibration at lower temperatures.

The results of all the isotope analyses of MS 2 (H) and ETH 4 (H) are listed in Table 2 with the date of the measurement, the run number and number of aliquots analyzed per sample. For the average of 58 aliquots of MS 2 (H) we obtained $\delta^{13}\text{C}_{\text{V-PDB}} = 2.18 \pm 0.00$ ‰, $\delta^{18}\text{O}_{\text{V-PDB}} = -1.90 \pm 0.01$ ‰ and a clumped isotope composition in the absolute reference frame and stretching corrected with the ETH standards for 70 °C acid digestion of $\Delta_{47} (70^\circ\text{C}) = 0.196 \pm 0.004$ ‰. This clumped isotope composition projected to 25 °C acid digestion is $\Delta_{47} (25^\circ\text{C}) = 0.259 \pm 0.004$ ‰. In case of ETH 4 (H) where we analyzed more aliquots per run, we measured in total 93 aliquots and obtained $\delta^{13}\text{C}_{\text{V-PDB}} = -10.20 \pm 0.00$ ‰, $\delta^{18}\text{O}_{\text{V-PDB}} = -18.66 \pm 0.01$ ‰, $\Delta_{47} (70^\circ\text{C}) = 0.195 \pm 0.002$ ‰ and $\Delta_{47} (25^\circ\text{C}) = 0.257 \pm 0.002$ ‰. To check if MS 2 (H) and ETH 4 (H) retained their stochastic isotope distribution during their relatively long cooling phase, we heated a third calcite (Merck (H)) during 4 hours at 1000 °C, 2.5 GPa in a piston cylinder that allowed rapid cooling to room temperature within half a minute. For the average of 61 aliquots of Merck (H) we obtained $\delta^{13}\text{C}_{\text{V-PDB}} = -41.75 \pm 0.00$ ‰, $\delta^{18}\text{O}_{\text{V-PDB}} = -15.56 \pm 0.00$ ‰, $\Delta_{47} (70^\circ\text{C}) = 0.203 \pm 0.003$ ‰ and $\Delta_{47} (25^\circ\text{C}) = 0.265 \pm 0.003$ ‰ (Table 3).

The results of the heated aragonites Bilin 1 (H) and Bilin 2 (H) are listed in Table 3. For the aragonite sample Bilin 1 (H) with a bulk isotope composition of $\delta^{13}\text{C}_{\text{V-PDB}} = 3.22 \pm 0.00$ ‰, $\delta^{18}\text{O}_{\text{V-PDB}} = -8.32 \pm 0.01$ ‰ and $\delta^{47} = 8.44 \pm 0.07$ ‰ we obtained for the average of 66 aliquots $\Delta_{47} (70^\circ\text{C}) = 0.168 \pm 0.003$ ‰ and $\Delta_{47} (25^\circ\text{C}) = 0.231 \pm 0.003$ ‰. The other heated aragonite sample Bilin 2 (H) with $\delta^{13}\text{C}_{\text{V-PDB}} = -10.95 \pm 0.01$ ‰, $\delta^{18}\text{O}_{\text{V-PDB}} = -5.52 \pm 0.03$ ‰ and a negative δ^{47} of -2.43 ± 0.14 ‰ displays for the average of 36 aliquots a $\Delta_{47} (70^\circ\text{C}) = 0.179 \pm 0.005$ ‰ and $\Delta_{47} (25^\circ\text{C}) = 0.241 \pm 0.003$ ‰.

The results of all dolomite measurements are displayed in Table 4 with the average for 70 aliquots of Rodolo (H) resulting in $\delta^{13}\text{C}_{\text{V-PDB}} = -3.83 \pm 0.01 \text{ ‰}$, $\delta^{18}\text{O}_{\text{V-PDB}} = 1.75 \pm 0.01 \text{ ‰}$, $\delta^{47} = 13.12 \pm 0.02 \text{ ‰}$, $\Delta_{47} (70^\circ\text{C}) = 0.229 \pm 0.002 \text{ ‰}$ and $\Delta_{47} (25^\circ\text{C}) = 0.344 \pm 0.002 \text{ ‰}$. For the 29 aliquots of Sansa (H) we obtained $\delta^{13}\text{C}_{\text{V-PDB}} = 1.38 \pm 0.01 \text{ ‰}$, $\delta^{18}\text{O}_{\text{V-PDB}} = -3.74 \pm 0.02 \text{ ‰}$, $\delta^{47} = 12.47 \pm 0.03 \text{ ‰}$, $\Delta_{47} (70^\circ\text{C}) = 0.218 \pm 0.004 \text{ ‰}$ and $\Delta_{47} (25^\circ\text{C}) = 0.333 \pm 0.004 \text{ ‰}$. Additionally to the Kiel IV measurements at 70°C , we analyzed the two heated dolomite samples and one heated magnesite that were digested at 100°C in a manual purification line and measured them with the traditional dual inlet method (Table 5). For each dolomite we performed duplicate analyses resulting in $\delta^{13}\text{C}_{\text{V-PDB}} = -3.94 \pm 0.05 \text{ ‰}$, $\delta^{18}\text{O}_{\text{V-PDB}} = 1.45 \pm 0.10 \text{ ‰}$, $\delta^{47} = 11.31 \pm 0.15 \text{ ‰}$ and $\Delta_{47} (100^\circ\text{C}) = 0.135 \pm 0.020 \text{ ‰}$ for Rodolo (H) and in $\delta^{13}\text{C}_{\text{V-PDB}} = 1.36 \pm 0.05 \text{ ‰}$, $\delta^{18}\text{O}_{\text{V-PDB}} = -4.05 \pm 0.16 \text{ ‰}$, $\delta^{47} = 10.82 \pm 0.23 \text{ ‰}$ and $\Delta_{47} (100^\circ\text{C}) = 0.141 \pm 0.020 \text{ ‰}$ for Sansa (H). In case of magnesite (H) we performed only one analysis each and thus used the internal reproducibility as the standard error of the traditional isotopes. For magnesite (H) we measured $\delta^{13}\text{C}_{\text{V-PDB}} = -0.95 \pm 0.00 \text{ ‰}$, $\delta^{18}\text{O}_{\text{V-PDB}} = -18.33 \pm 0.01 \text{ ‰}$, $\delta^{47} = -5.96 \pm 0.02 \text{ ‰}$ and a $\Delta_{47} (100^\circ\text{C}) = 0.203 \pm 0.020 \text{ ‰}$. As we did only duplicate analyses for the dolomites digested at 100°C and only one for the magnesite, we report an analytical precision for the Δ_{47} of 0.020 ‰ that was derived from the average of the standard deviations of the 23 ETH standards (Appendix C) that were also digested at 100°C and measured via DI. For the two CaCO_3 polymorphs we used the average acid fractionation correction from Defliese et al. (2015) and Murray et al. (2016), for dolomites solely the acid fractionation correction by Murray et al. (2006) and in case of magnesite we did not project the Δ_{47} to 25°C acid digestion as there is no data on the acid fractionation available.

4. DISCUSSION

4.1. Isotope composition of calcites heated in a Paterson apparatus vs. a piston cylinder

The clumped isotope composition for Merck (H) is slightly higher, but it is statistically indistinguishable from the results of MS 2 (H) and ETH 4 (H) that were cooled over a longer time of 45 min in the Paterson apparatus. The average of all three heated calcite samples is equal to the clumped isotope fractionation for the calcite digestion with phosphoric acid at 70°C of $0.197 \pm 0.002 \text{ ‰}$ (Table 6; Fig. 2). Projecting this value to an acid digestion temperature of 25°C with an acid fractionation correction 0.062 ‰ derived from the average of the most recent studies of Defliese et al. (2015) and Murray et al. (2016), we obtain a value of $0.260 \pm 0.002 \text{ ‰}$. Although our determined acid fractionation is significantly larger than the theoretical value of 0.220 ‰ of Guo et al. (2009) it is close or even slightly smaller than the value of $0.268 \pm 0.015 \text{ ‰}$ determined experimentally for carbonates heated at about 1600°C in the same study, when converted into the absolute reference frame using the secondary reference frame transfer function from Table 4 in Dennis et al. (2011). Therefore, although the theoretical model of Guo et al. (2009) requests a heating temperature of

about 1300 °C to accomplish a random isotope distribution, we conclude that the three samples heated to 1000 °C reached a stochastic isotope distribution. Our measurements demonstrate that the determined Δ_{47} fractionation during phosphoric acid digestion of calcites at 70 °C and subsequent projection to 25 °C acid reaction temperature is within error of other existing data (see Guo et al., 2009; Dennis et al., 2011; Tripathi et al., 2015).

4.2. Cation effect on the Δ_{47} phosphoric acid fractionation

Besides our calcite measurements we also determined the acid fractionation for other carbonates such as aragonite, dolomite and magnesite. The two aragonite samples have a significantly (two tail T-test with $p < 0.0001$) lower average Δ_{47} fractionation at 70°C of 0.172 ± 0.003 ‰ than the average of the three analyzed calcites (0.197 ± 0.002 ‰). The acid fractionation for dolomites at 70°C, with Δ_{47} (70°C) = 0.226 ± 0.002 ‰ (two tail T-test with $p < 0.0001$), is 0.029 ‰ larger than the one for calcite and 0.054 ‰ larger than the one for aragonite.

A closer look at the three heated calcite samples and the two calcite standards that were heated at 600 °C (ETH-1 and ETH-2) shows that the Merck (H), which was heated in a piston cylinder followed by rapid quenching to room temperature, has a slightly higher Δ_{47} that is equal to the one of ETH-1. The Merck (H) has a strongly negative bulk isotope composition ($\delta_{47} = -42.87$ ‰) and thus is more challenging to correct for non-linearity effects in the mass spectrometer (described in more detail in section 4.4), but its Δ_{47} is statistically indistinguishable from the other four calcites. Summarizing, we obtain a sequence of increasing acid fractionations for carbonate minerals digested at 70 °C in the order aragonite-calcite-dolomite (0.172 ‰ $<$ 0.197 ‰ $<$ 0.226 ‰) and for 100 °C acid digestion the one of magnesite is much larger than the one of dolomite (0.138 ‰ $<$ 0.203 ‰).

The effect of different cations on the clumped isotope fractionation during acid digestion of carbonate minerals was calculated by Guo et al. (2009). Their theoretical predictions on the cation effect for the clumped isotopes were not as clear as for oxygen isotope fractionation, still Guo et al. (2009) suggested that the radius of the cations should be the most important factor creating the observed differences. In our study we are able to demonstrate a measurable cation effect on the Δ_{47} acid fractionation of carbonates at 70 °C acid digestion. On one side our results support the explanation of Guo et al. (2009) that cation radiuses play a crucial role and further that differences in the crystal lattice structure (calcite: trigonal; aragonite: orthorhombic) affecting the bonding strength between the cation and the carbonate molecule can also lead to small differences in the Δ_{47} acid fractionation. In the end, both cation radius and crystal structure affect the bonding strength, different cations via differences in their electronegativity and different crystal structures in affecting

the distance between the cation and the attached carbonate molecules. Combining these two factors we would expect an increasing Δ_{47} acid fractionation in the following order of more often studied carbonates:

Witherite (BaCO_3) < aragonite (CaCO_3)_{orth} < calcite (CaCO_3)_{trig} < dolomite ($\text{Ca,Mg}(\text{CO}_3)_2$) < magnesite (MgCO_3) < siderite (FeCO_3),

using the electronegativity's of the Pauling scale ($\text{Ba}^{2+} = 0.89$; $\text{Ca}^{2+} = 1.00$; $\text{Mg}^{2+} = 1.31$; $\text{Fe}^{2+} = 1.83$). Our results support only to a certain extent the theoretical predictions of Guo et al. (2009: Table 4), who observed a negative correlation between the acid fractionation of the oxygen isotopes and the acid fractionation of the Δ_{47} in different carbonates. This is correct if we compare our results to the acid fractionation of the oxygen isotopes of witherite (from Tripathi et al., 2015, with their Δ_{47} witherite projected to 70 °C acid digestion), aragonite and calcite, whereas dolomite seems to act different with the Δ_{47} acid fractionation being much larger than calcite, which is opposite to what the theoretical model by Guo et al. (2009) predicts.

4.3. Placing the Δ_{47} carbonate acid fractionation at 70 °C in the broader context of existing studies

There are only few studies that measured the absolute value of the Δ_{47} acid fractionation for the digestion of carbonate minerals. Two pioneering studies (Ghosh et al., 2006; Guo et al., 2009) attempted to determine this value for the reaction temperature of 25 °C. In both studies the authors drove calcite samples to stochastic isotope distribution by exposing them during 48 hours to temperatures of 1100 °C at 0.1 GPa confining pressure (Ghosh et al., 2006) or during 24 hours to 1550 °C or 1650 °C at 2.0 or 3.0 GPa (Guo et al., 2009). Whereas the first attempt showed an inconclusive high range in the Δ_{47} between the heated calcites (Ghosh et al., 2006), the second attempt by Guo et al. (2009) with calcites heated to about 1600 °C yielded a more narrow range from 0.245 ‰ to 0.279 ‰.

Guo et al. (2009) additionally calculated a theoretical value for the Δ_{47} acid fractionation of 0.220 ‰ and the temperature dependence of the acid fractionation factor. Later studies started to digest carbonate samples in offline purification systems at 90 °C with faster acid digestion and thus higher sample throughput. These studies added an experimentally determined acid correction factor to project their results to acid digestion temperature of 25 °C for the comparison to existing studies. To determine this acid fractionation correction factor they digested the same carbonate samples with phosphoric acid at temperatures between 25 and 90 °C and used the offset in the measured Δ_{47} as the correction factor (Passey et al., 2010; Henkes et al., 2013; Wacker et al., 2013; Defliese et al.,

2015; Murray et al., 2016). All of these studies obtained within the range of analytical precision the same acid fractionation correction factor between 90 °C to 25 °C for calcite. The acid fractionation correction factors range between 0.070 and 0.092 ‰ and are close to the theoretical acid fractionation correction of 0.069 ‰ (Guo et al., 2009).

In Fig. 3 we plotted our results together with the experimentally determined Δ_{47} acid fractionation for calcite at 25 °C by Guo et al. (2009) and its theoretical temperature dependence. Additionally, we plotted the absolute Δ_{47} acid fractionation temperature dependence of calcites using the relationships determined by Defliese et al. (2015) and Murray et al. (2016) anchored by the experimentally determined average of the Δ_{47} acid fractionation of 0.268 ‰ for 25 °C acid digestion (Guo et al., 2009; Dennis et al., 2011). Whereas the Δ_{47} of the ETH-1 and ETH-2 calcite standards and the Merck (H) fall on the experimentally determined temperature dependences (Defliese et al., 2015; Murray et al., 2016), the other two stochastic calcites fall slightly below it. Interestingly our heated aragonite samples fall on the theoretical temperature relationship, similar to witherite samples that were heated to 1650 °C at 3.0 GPa confining pressure in a piston cylinder and dissolved with phosphoric acid at 90 °C (Tripathi et al., 2015).

In our study we can clearly demonstrate that the Δ_{47} acid fractionation for 70 °C acid digestion of calcites is significantly larger relative to the heated aragonites and that the Δ_{47} acid fractionation for the heated dolomites is even larger than for the two CaCO_3 polymorphs. To our knowledge, there are no previously published attempts to estimate the absolute clumped isotope acid fractionation for dolomite. However, two studies determined the relative acid fractionation correction by digesting homogenous dolomite samples at different temperatures (Defliese et al., 2015; Murray et al., 2016). In contrast to their temperature relationships for calcite, which agree well with each other, their dolomite temperature relationships deviate strongly. Defliese et al. observed a similar dolomite Δ_{47} acid fractionation temperature dependence as for calcite, whereas Murray et al. obtained a temperature dependence that is significantly steeper.

The offset of 0.029 ‰ that we observe between the Δ_{47} of our stochastic dolomites and calcites at 70 °C acid digestion rather supports the finding of Murray et al. (2016) or would cause an offset to calcite Δ_{47} temperature calibrations. Further support for a more sensitive temperature relationship of the dolomite Δ_{47} acid fractionation comes from the results of the two heated dolomites that were digested offline at 100 °C. Although we performed only two replicate analyses per sample, the Δ_{47} of Rodolo (H) with 0.135 ± 0.020 ‰ matches nicely the Δ_{47} of the second dolomite sample Sansa (H) with 0.141 ± 0.020 ‰ resulting in a T-dependence even steeper than the one of Murray et al. (2016). However, to better constrain the T-dependence for the dolomite acid fractionation more analyses at

100 °C and lower temperatures are required. The Δ_{47} values of the heated ETH standards that were digested offline at 100 °C (Fig. 2, Appendix C) are 0.184 ± 0.008 ‰ (± 0.016 ‰ at the 95 % confidence level) for ETH-1 and 0.191 ± 0.004 ‰ (± 0.007 ‰ at the 95 % confidence level) for ETH-2. Both values match within error the extrapolated curve for calcites of Defliese et al. (2015) and Murray et al. (2016). In other words, the two ETH standards that have an isotopic composition within the error of the other stochastic calcites at 70 °C show that the Δ_{47} acid fractionation at 100 °C is clearly larger for calcites than for dolomites.

4.3.1 Recommendations for the correction of dolomite Δ_{47}

The steeper Δ_{47} acid fractionation temperature dependence of dolomite has some important implications on how to process clumped isotope measurements of dolomites. As we determined the absolute Δ_{47} acid fractionation for dolomite at 70 °C with a more accurate dataset than the 4 measurements at 100 °C we can use this former value together with the relative temperature dependence from Murray et al. (2016) to calculate the absolute temperature dependent acid fractionation for dolomite (see Fig. 3, steeper green curve). This absolute temperature relationship for dolomite displayed in Fig. 3 indicates two important aspects, first the Δ_{47} acid fractionation of dolomite is much steeper than the one of calcite and second both temperature relationships of dolomite and calcite cross each other at approximately 92 °C. This indicates that in studies using an acid digestion temperature of 90 °C the Δ_{47} acid fractionation of calcite and dolomite would be the same or within the analytical precision of each other, whereas at lower temperature the Δ_{47} acid fractionation of dolomite is progressively diverging from the one of calcite.

Before the study of Murray et al. (2016) dolomite samples were corrected the same way as calcites or aragonites. This affects the final Δ_{47} of dolomites digested at 25 °C in a significantly different way than dolomites digested at 90 °C. When expressing the data in the ARF it is common use that Δ_{47} values are projected to a digestion temperature of 25°C. However, at 25°C the acid fractionation of dolomite has been postulated to deviate from the corresponding calcite fractionation by +0.07 ‰ (Murray et al., 2016). As a consequence, the distinct temperature dependencies of the dolomite and calcite acid fractionation factors have to be taken into account when applying calcite calibrations to dolomite Δ_{47} data. Otherwise, laboratories digesting the dolomites at temperatures below 90 °C would obtain a higher Δ_{47} value and thus colder clumped isotope temperatures.

Our limited data suggest that the temperature sensitivity of the Δ_{47} acid fractionation of dolomite may be even steeper at higher temperatures because the dolomites digested at 100 °C lay below the dolomite line in Fig. 3. More measurements at these high temperature are required to confirm this observation. The best way to process dolomite samples would be to determine a dolomite specific

Δ_{47} temperature calibration with dolomite samples that formed at known temperature and use the steeper acid correction determined in Murray et al. (2016) to project the results to a 25 °C acid digestion as it is the common practice for calcites.

Recently a first dolomite-specific Δ_{47} temperature calibration was published by Winkelstern et al. (2016). For their acid fractionation correction they used the smaller value of Defliese et al. (2015), as both studies were done in the same laboratory and they did not observe a significant mineralogical effect. In the study of Winkelstern et al. (2016) dolomites were dissolved offline at 75 °C, which is close to our 70 °C. However, in contrast to these authors we find a significant difference of 0.029 ‰ between the absolute Δ_{47} acid fractionation of dolomite and calcite. Further studies are necessary to confirm the correct acid fractionation correction for dolomite. The measurement of identical dolomite samples in different laboratories would further help to constrain the dolomite Δ_{47} acid fractionation factor.

As long as laboratories do not have a dolomite-specific temperature calibration we suggest the following correction procedure: In laboratories that digest dolomite samples at 90 °C there are two ways to process Δ_{47} isotope data, as the dolomite Δ_{47} acid fractionation equals the one of calcite. First, the Δ_{47} data in the absolute reference frame can be corrected with the calcite-specific acid fractionation and temperatures calculated with a calcite-specific Δ_{47} temperature calibration. Alternatively, the Δ_{47} data can be corrected with the dolomite-specific acid fractionation. Then the temperatures can be calculated with the calcite-specific Δ_{47} temperature calibration modified by adding the difference between the Δ_{47} acid fractionation of calcite and dolomite at 25 °C (0.07 ‰) to the intercept of the $\Delta_{47} - 1/T^2$ relationship. In contrast, laboratories that digest samples at lower temperatures are recommended to apply only the second way, using the dolomite specific acid fractionation correction of Murray et al. (2016) together with the calcite Δ_{47} temperature calibration with the 0.07 ‰ acid fractionation offset added to the intercept. This is important as at digestion temperatures below 90 °C the acid fractionations of dolomite deviates from the one of calcite leading to an erroneous temperature calculation.

A study by Kluge and John (2015) could not resolve any significant differences in the acid fractionation between calcite and aragonite digested at 90 °C. Our study, in contrast, shows that the acid fractionation for aragonite at 70 °C is lower than for calcite. This difference should also be observable at 90 °C. However, because Wacker et al. (2013) obtained a slightly smaller acid fractionation dependence between 90 and 25 °C for aragonite than calcite if only samples > 7 mg are considered (Table 2 in Wacker et al. 2013), the difference will be slightly smaller for 90°C acid digestions.

Figure 3 summarizes the effect of different carbonate mineralogies on the Δ_{47} acid fractionation at different digestion temperatures, where witherite has the smallest fractionation followed by aragonite, calcite and dolomite. The magnesite (H) sample digested at 100 °C shows the largest Δ_{47} acid fractionation of 0.203 ± 0.020 ‰. This is much larger than the dolomite or calcite values (see Fig. 3 and Table 5, 6), but consists only of a single measurement and thus has a larger uncertainty. However, a recent study analyzed a set of magnesites likely formed in the temperature range of 430 to 490 °C and obtained for the hottest sample a Δ_{47} of 0.254 ‰ for a 90 °C acid digestion (García del Real et al., 2016). This finding supports the hypothesis that we reached a near-stochastic Δ_{47} distribution with our magnesite that was heated to 655 °C.

The Δ_{47} acid fractionations for the various carbonate minerals lie above (calcite by 0.022 ‰ and dolomite by 0.041 ‰ for 70 °C acid digestion) the theoretical model of Guo et al. (2009) with the exception of aragonite (-0.013 ‰) and one of the witherite samples. This is indicative that further theoretical models need to include cation specific parameters to be able to simulate more accurately the carbonate specific temperature dependent Δ_{47} acid fractionation. Other common carbonate systems that are used as an archive for the clumped isotope temperature signal and potentially biased by the cation effect are magnesite (e.g. Quesnel et al., 2016; García del Real et al., 2016) or siderite (Fernandez et al., 2014). For instance, the siderite Δ_{47} temperature calibration of Fernandez et al. (2014) with an acid digestion at 100 °C is statistically indistinguishable in slope and intercept to the existing calcite Δ_{47} temperature calibration where calcites were digested at 100 °C. Based on the cation effect we observe on the Δ_{47} acid fractionation for aragonite, calcite and dolomite, we would also expect a siderite-specific acid fractionation because iron has the strongest electronegativity compared to calcium and magnesium. We could speculate that similarly to the dolomite system, the siderite-specific Δ_{47} acid fractionation is identical or within the analytical error than the one of calcite if the mineral is digested at temperatures of 100 °C as it was done in Fernandez et al. (2014). A determination of the Δ_{47} acid fractionation of siderites with stochastic isotope distribution is necessary to clarify the T sensitivity of the Δ_{47} acid fractionation of siderites. The same is true for magnesite which is difficult to dissolve at low temperatures. Existing studies thus dissolved magnesite at 90 °C with 105 % phosphoric acid and applied a calcite specific Δ_{47} acid fractionation factor correction of 0.069 ‰ (Quesnel et al., 2016; García del Real et al., 2016). Again, the similarities that are observed in these studies to the calcite Δ_{47} temperature calibration could be explained by a Δ_{47} acid fractionation that is similar to the one of calcite at digestion at high temperatures, hiding potential cation effects.

4.4. Heated calcite standards as control for proper baseline correction

The abundance of the isotopologue of m/z 47 in CO_2 gas produced by dissolution of carbonates is in the range of 46 ppm (Eiler and Schauble, 2004) and its measurement requires very high accuracy. One major factor affecting the reproducibility and accuracy of clumped isotope analyses is the presence of negative background effects on the Faraday collectors for the minor isotopes (He et al. 2012; Bernasconi et al., 2013). A correction is carried out either by direct determination of the backgrounds (He et al. 2012; Bernasconi et al., 2013), or indirectly by measuring gases with a stochastic isotope distribution, the classic “heated gas line correction” (Huntington et al. 2009). Importantly, the error introduced by an incorrect background determination or an incorrect heated gas line is dependent on the bulk isotope composition of the sample.

The error increases with increasing difference in composition between sample and working gas, and it is of opposite sign for the samples with bulk isotope composition heavier than the working gas compared to those that are lighter than the working gas. The negative backgrounds of the minor ion beams of the CO_2 gas are likely due to secondary electrons generated from the m/z 44 beam that scatter into the cups of the other masses causing a strong dependency of the Δ_{47} on the bulk isotope composition δ^{47} . This mass spectrometer specific non-linearity effect can be corrected for by applying a so-called pressure sensitive baseline correction (PBL) on the raw beams of each mass (He et al., 2012; Bernasconi et al. 2013; Meckler et al., 2014; Fiebig et al., 2016). In our laboratory for the PBL correction we perform peak shape scans of CO_2 gas at different intensities on a daily basis and the range of beam intensities is chosen according to the expected intensity range of the carbonate samples, which is in our case between 10 and 30 V on m/z 44. The peak shape scan function of the Isodat software records in each cup the signal intensity, while the high voltage (HV) in the source is varied over a range broader than the peak width. At each intensity we select for all masses the area that we think corresponds to the right background, a task that can be difficult depending on the shape of the peaks. Identifying the right background range for m/z 47 is crucial for accurate determination of Δ_{47} .

The PBL correction is illustrated in more detail in Fig. 4 and Table 7 where the consequences of determining the backgrounds at the wrong HV range are demonstrated on the two heated calcite standards ETH-1 and ETH-2. The δ^{47} of ETH-1 and ETH-2 are strongly different with values of 13.48 ‰ and -15.30 ‰, respectively. However, as they were both heated during 10 h to 600 °C they have an almost identical near-stochastic clumped isotope composition of Δ_{47} (25°C) = 0.265 ‰ and 0.267 ‰, respectively (see also Fig. 2). The Δ_{47} values reported here are 0.0015 ‰ lower than in Meckler et al. (2014) and Kele et al. (2015) as those values were corrected with the phosphoric acid correction based on an interpolation of the data from Henkes et al. (2013). These isotopic properties of the two

standards makes them ideal candidates to monitor or check if the background determination was done at the “correct” accelerating voltage. To demonstrate the effect of incorrect background determinations we selected within the peak shape scans of m/z 47 four different areas that could potentially be the area of the background level (Fig. 4). In scenario a) the backgrounds are taken at the minima, in b) at the narrow shoulder on the left side of the peak, in d) at a range of the broader right shoulder, whereas in c) we used the mean of the backgrounds determined in scenario b) and d).

From the observed results of this background area determination exercise listed in Table 7, it becomes clear that the scenario b), the area at the narrow shoulder left of the peak, is the proper way to correct our data as the final Δ_{47} of both standards have the same Δ_{47} and the dependence of the Δ_{47} on the bulk isotope composition has disappeared. In scenario a) with the background being selected at the minima, the Δ_{47} 's of both standards are offset by 0.187 ‰. In contrast the small difference in the background level of c) with respect to b) only slightly affects ETH-2, but the offset between ETH-1 and ETH-2 remaining is 0.007 ‰. However, this offset increases to 0.021 ‰ in scenario d) although the background level is only about 6 mV higher than that in scenario b). The observation that the Δ_{47} of ETH-2 is more strongly affected by selecting the background at different HV can be explained with its δ^{47} being further away from the δ^{47} of our working gas. This exercise nicely demonstrates the large impact of the high voltage at which the background is selected on the calculated Δ_{47} and how the analysis of homogenous carbonates with near stochastic or stochastic isotope distribution (e.g. ETH-1 and ETH-2) can be used as a quality control of a proper background determination. Additionally, our measurements of the heated Merck (H) calcite are an excellent demonstration that we are recording our background at the correct HV. This calcite sample has the most negative bulk isotope composition ($\delta^{47} = -42.87$ ‰) far away of the working gas δ^{47} and would display the biggest impact of an improper background determination on its clumped isotope composition. The Δ_{47} (70°C) of Merck (H) is 0.203 ± 0.003 ‰, thus statistically indistinguishable from the other heated calcites that have a bulk isotope composition closer to the one of the working gas (see Table 6).

5. CONCLUSIONS

Our clumped isotope measurements on carbonate minerals with stochastic isotope distributions revealed a Δ_{47} fractionation during phosphoric acid digestion of calcite at 70 °C of 0.197 ± 0.002 ‰ filling the lack of absolute Δ_{47} acid fractionations at elevated temperatures. Projecting this Δ_{47} value with existing temperature relationships to an acid digestion temperature of 25 °C, we obtain a Δ_{47} acid fractionation of 0.260 ± 0.002 ‰, matching closely the experimental determination at 25 °C (0.268 ± 0.015 ‰; Guo et al., 2009 converted to the absolute reference frame).

Our stochastic dolomite samples revealed a significantly larger Δ_{47} acid fractionation of 0.226 ± 0.002 ‰ at 70 °C and with approximately 0.139 ± 0.020 ‰ when digested at 100 °C a significantly smaller absolute Δ_{47} acid fractionation. This is an important finding that supports the determination of a steeper acid fractionation temperature relationship for dolomite than for calcite by Murray et al., (2016). Anchoring the Δ_{47} acid fractionation temperature relationship of Murray et al. (2016) with our absolute value for dolomite at 70 °C we can demonstrate that the acid fractionations of calcite and dolomite are within the analytical error of each other for carbonates digested at 90 °C, whereas the two acid fractionations progressively diverge from each other at lower acid digestion temperatures (Fig. 3). This finding implies that Δ_{47} studies on dolomites applying identical correction as for calcites, will obtain a heavier Δ_{47} or lower temperature signal if the dolomite samples were digested at 25 °C compared to studies using higher digestion temperatures.

Aragonite shows a Δ_{47} acid fractionation of 0.172 ± 0.003 ‰ at 70 °C, smaller than calcite. Because the difference of aragonite to calcite is close to the analytical error of most Δ_{47} measurements and the temperature relationship of the acid fractionation of aragonite is not significantly different to the one of calcite (Wacker et al., 2013), this small difference has a relatively minor impact on the results if not properly considered.

Our measurements of the Δ_{47} acid fractionation of calcite, aragonite, dolomite, magnesite together with the study of witherite of Tripathi et al. (2016) indicate that different cations can impact the final Δ_{47} temperature signal probably due to differences in their bond strength. Ideally the Δ_{47} signal of different carbonate minerals is determined with mineral specific Δ_{47} acid fractionation corrections and mineral specific Δ_{47} temperature calibrations to avoid inaccuracies in the interpretation of the Δ_{47} signal. Besides cation specific effects, Δ_{47} measurements still suffer from mass spectrometer specific non-linearities that bring in additional uncertainties and limit the temperature resolution of the Δ_{47} temperature proxy. Those non-linearity effects depend mainly on the background noise on the raw beam intensities and strongly affect samples that have a bulk isotope composition (δ^{47}) far away from the one of the working gas in use. We can correct for these non-linearities by performing a proper pressure baseline correction and monitor the quality of this background correction with daily measurements of calcite standards with strongly different δ^{47} that have stochastic or near stochastic isotope composition.

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Figure Caption:

Figure 1. Description of the two heating devices. a) Paterson apparatus on the left side with the sample capsule held between alumina and zirconia pistons in an iron jacket inside the internal furnace. The temperature is controlled and monitored with a thermocouple K (± 2 °C). b) Piston cylinder on the right side is comprised by a talc cylinder with a graphite furnace and the sample capsule in an MgO assembly. The temperature is controlled by a thermocouple reaching just next to the capsule, thereof the sample capsule has an outer diameter of approximately 3 mm and a length of 7 mm.

Figure 2. On this graph we plotted the Δ_{47} of the analyzed calcites and aragonites for 70 °C phosphoric acid digestion against their bulk isotope composition (δ_{47}). The heated calcite samples (filled circles) average in a Δ_{47} of 0.197 ‰ whereas the two aragonites (squares) average in a Δ_{47} of 0.172 ‰. Additionally we plotted the two calcite ETH standards that were heated to 600 °C and reveal a near stochastic isotope distribution.

Figure 3. Plot of the Δ_{47} acid fractionation versus the phosphoric acid digestion temperature. The green line corresponds to the dolomite temperature relationship from Murray et al. (2016). The blue line corresponds to the calcite temperature relationship from Defliese et al. (2015) and Murray et al. (2016). The golden line is the theoretical temperature relationship for carbonates determined by Guo et al. (2009). The crosses at 25 °C correspond to the heated calcites from Guo et al. (2009) in the absolute reference frame and the diamonds at 70 °C to our heated calcites plus the ETH-1 and ETH-2 standards. The filled circles are the heated dolomites, the filled squares the heated aragonite samples and the filled triangles correspond to heated witherite samples from Tripathi et al. (2015). The grey trapezoid corresponds to the heated magnesite sample.

Figure 4. Peakshape scans of m/z 47 of different intensity scans ranging from 30 V to 10 V on m/z 44. The plot focus on the negative background area at the base of the m/z 47 peaks with four different areas (a, b, c, d) where the background level could be selected.

a) Paterson apparatus

b) Piston cylinder
Talc-Pyrex-MgO assembly

modified after Kägi et al., 2005

Table 1: Heated Carbonates

Sample Material	Heating Device	Temperature (°C)	Pressure (GPa)	Heating Time (hours)	Quench Time (min)	Capsule Material
<i>Calcites (CaCO₃)</i>						
<i>MS 2 (H)</i>	Paterson	1000	0.15	4	45	Steel
<i>ETH 4 (H)</i>	Paterson	1000	0.15	4	45	Steel
<i>Merck (H)</i>	Piston Cyl.	1000	2.5	4	0.5	Au ₅₀ Pd ₅₀
<i>Aragonite (CaCO₃)</i>						
<i>Bilin 1 (H)</i>	Piston Cyl.	850	3.5	4	0.5	Au ₅₀ Pd ₅₀
<i>Bilin 2 (H)</i>	Piston Cyl.	850	3.5	4	0.5	Au ₅₀ Pd ₅₀
<i>Dolomite (CaMg(CO₃)₂)</i>						
<i>Rodolo (H)</i>	Piston Cyl.	1100	2.5	4	0.5	Au ₅₀ Pd ₅₀
<i>Sansa (H)</i>	Piston Cyl.	1100	2.5	4	0.5	Au ₅₀ Pd ₅₀
<i>Magnesite (MgCO₃)</i>						
<i>Magnesite (H)</i>	Paterson	655	0.12	4	45	Steel

Table 2. Stable isotope data (in ‰) of calcites heated in a Paterson apparatus

Date of analysis	Run	$\delta^{13}\text{C}$ (V-PDB)	$\delta^{18}\text{O}$ (V-PDB)	δ^{47}	Δ_{47} raw	Δ_{47} (70°C)	Δ_{47} (25°C)	#
MS 2 (H)								
02/11/2015	1706	2.18±0.02	-1.93±0.06	13.67±0.10	-0.631±0.028	0.244	0.306	3
02/11/2015	1706	2.17±0.01	-1.91±0.04	13.66±0.07	-0.654±0.035	0.218	0.280	3
02/13/2015	1707	2.16±0.02	-1.98±0.01	13.67±0.02	-0.691±0.026	0.170	0.233	3
02/13/2015	1707	2.15±0.05	-1.95±0.09	13.73±0.14	-0.655±0.008	0.210	0.272	3
02/20/2015	1710	2.12±0.01	-2.03±0.02	13.49±0.03	-0.700±0.007	0.149	0.211	3
02/21/2015	1710	2.14±0.02	-2.00±0.01	13.61±0.04	-0.626±0.007	0.231	0.294	3
03/07/2015	1717	2.16±0.00	-1.91±0.01	13.59±0.03	-0.585±0.027	0.226	0.289	2
03/07/2015	1717	2.22±0.04	-1.80±0.06	13.71±0.11	-0.626±0.016	0.179	0.242	3
03/08/2015	1718	2.16±0.01	-1.93±0.01	13.60±0.02	-0.597±0.014	0.216	0.278	3
03/08/2015	1718	2.19±0.01	-1.86±0.02	13.70±0.03	-0.603±0.020	0.208	0.270	3
04/09/2015	1742	2.21±0.01	-1.86±0.02	14.00±0.04	-0.613±0.010	0.199	0.262	3
04/09/2015	1742	2.19±0.02	-1.89±0.05	13.96±0.08	-0.615±0.012	0.196	0.259	3
04/30/2015	1756	2.22±0.00	-1.82±0.01	14.07±0.01	-0.621±0.010	0.199	0.262	3
04/30/2015	1756	2.20±0.02	-1.78±0.02	14.09±0.02	-0.619±0.011	0.202	0.265	4
05/18/2015	1767	2.19±0.01	-1.88±0.02	14.11±0.04	-0.611±0.008	0.198	0.261	4
05/18/2015	1767	2.16±0.01	-1.92±0.02	14.03±0.03	-0.624±0.008	0.184	0.246	4
05/20/2015	1769	2.21±0.01	-1.88±0.02	14.08±0.03	-0.646±0.006	0.155	0.217	4
05/20/2015	1769	2.19±0.00	-1.90±0.01	14.04±0.02	-0.649±0.010	0.150	0.213	4
Average		2.18±0.00	-1.90±0.01	13.82±0.03		0.196±004	0.259±004	58
ETH 4 (H)								
10/28/2014	1648	-10.17±0.01	-18.78±0.03	-15.46±0.04	-0.646±0.008	0.207	0.269	12
10/28/2014	1648	-10.14±0.01	-18.72±0.03	-15.39±0.04	-0.657±0.009	0.195	0.257	12
10/29/2014	1649	-10.15±0.01	-18.73±0.02	-15.43±0.03	-0.679±0.008	0.168	0.231	10
10/29/2014	1649	-10.19±0.01	-18.78±0.03	-15.48±0.04	-0.642±0.012	0.209	0.272	9
11/04/2014	1654	-10.25±0.01	-18.61±0.02	-15.46±0.04	-0.671±0.025	0.184	0.246	9
11/04/2014	1654	-10.21±0.01	-18.57±0.03	-15.39±0.05	-0.673±0.011	0.181	0.243	7
11/06/2014	1655	-10.23±0.02	-18.61±0.04	-15.41±0.06	-0.637±0.017	0.218	0.280	9
11/06/2014	1655	-10.22±0.01	-18.60±0.04	-15.40±0.06	-0.652±0.023	0.202	0.264	6

11/07/2014	1656	-10.21±0.01	-18.58±0.03	-15.39±0.04	-0.668±0.011	0.184	0.246	9
11/08/2014	1656	-10.21±0.02	-18.58±0.03	-15.37±0.04	-0.652±0.014	0.201	0.264	10
Average		-10.20±0.00	-18.66±0.01	15.42±0.00		0.195±0.002	0.257±0.002	93

Table 3. Stable isotope composition (in ‰) of calcite and aragonites heated in a piston cylinder

Date of analysis	Run	$\delta^{13}\text{C}$ (V-PDB)	$\delta^{18}\text{O}$ (V-PDB)	δ^{47}	Δ_{47} raw	Δ_{47} (70°C)	Δ_{47} (25°C)	#
Merck (H) – calcite								
02/10/2016	1937	-41.79±0.01	-15.53±0.00	-42.82±0.04	-0.777±0.018	0.248	0.311	2
02/10/2016	1937	-41.79±0.02	-15.55±0.01	-42.88±0.03	-0.821±0.000	0.199	0.262	2
02/15/2016	1943	-41.81±0.02	-15.55±0.02	-42.87±0.02	-0.801±0.020	0.215	0.277	3
02/16/2016	1943	-41.80±0.02	-15.55±0.05	-42.86±0.05	-0.795±0.018	0.221	0.283	3
02/19/2016	1949	-41.79±0.01	-15.54±0.02	-42.85±0.04	-0.804±0.025	0.207	0.269	3
02/20/2016	1949	-41.76±0.01	-15.51±0.00	-42.77±0.04	-0.789±0.042	0.224	0.286	3
03/05/2016	1969	-41.76±0.03	-15.50±0.02	-42.79±0.06	-0.812±0.016	0.198	0.260	3
03/06/2016	1969	-41.78±0.01	-15.51±0.01	-42.82±0.04	-0.815±0.023	0.194	0.256	3
03/06/2016	1970	-41.76±0.01	-15.49±0.01	-42.79±0.04	-0.828±0.015	0.177	0.239	3
03/07/2016	1970	-41.77±0.01	-15.51±0.02	-42.79±0.02	-0.797±0.027	0.212	0.274	3
03/17/2016	1979	-41.74±0.04	-15.58±0.03	-42.93±0.05	-0.896±0.016	0.212	0.274	3
03/18/2016	1979	-41.66±0.01	-15.58±0.02	-42.86±0.11	-0.903±0.003	0.204	0.267	3
03/24/2016	1989	-41.73±0.02	-15.57±0.03	-42.90±0.04	-0.880±0.023	0.226	0.288	3
03/25/2016	1989	-41.75±0.01	-15.61±0.03	-43.01±0.03	-0.939±0.019	0.161	0.223	3
03/25/2016	1990	-41.72±0.01	-15.56±0.01	-42.88±0.03	-0.880±0.022	0.202	0.265	3
03/26/2016	1990	-41.74	-15.59	-42.90	-0.854	0.231	0.293	1
03/27/2016	1991	-41.73±0.02	-15.59±0.03	-42.94±0.04	-0.909±0.009	0.172	0.235	3
04/14/2016	2008	-41.77±0.00	-15.62±0.01	-42.95±0.03	-0.843±0.024	0.187	0.250	2
04/15/2016	2008	-41.76±0.02	-15.63±0.02	-42.93±0.04	-0.821±0.002	0.212	0.274	3
04/16/2016	2009	-41.73±0.02	-15.56±0.02	-42.85±0.05	-0.841±0.021	0.188	0.250	3
04/17/2016	2009	-41.72±0.01	-15.57±0.01	-42.84±0.02	-0.838±0.023	0.191	0.254	3
04/18/2016	2010	-41.73±0.01	-15.56±0.01	-42.87±0.03	-0.857±0.017	0.180	0.242	3
Average		-41.76±0.01	-15.56±0.00	-42.87±0.01		0.203±0.003	0.265±0.003	61
Bilin 1 (H) – aragonite								
02/09/2016	1937	3.24±0.01	-8.33±0.01	8.49±0.04	-0.858±0.033	0.157	0.220	3
02/10/2016	1937	3.23±0.02	-8.34±0.03	8.51±0.08	-0.822±0.031	0.198	0.260	3
02/15/2016	1943	3.24±0.01	-8.37±0.02	8.50±0.03	-0.833±0.015	0.179	0.241	3
02/16/2016	1943	3.13±0.11	-8.30±0.08	8.43±0.00	-0.855±0.021	0.154	0.217	2

02/19/2016	1949	3.23±0.01	-8.37±0.02	8.49±0.03	-0.840±0.016	0.167	0.229	3
02/20/2016	1949	3.19±0.03	-8.40±0.06	8.40±0.11	-0.846±0.014	0.160	0.222	3
03/05/2016	1969	3.23±0.01	-8.34±0.01	8.54±0.01	-0.825±0.018	0.183	0.245	3
03/06/2016	1969	3.22±0.01	-8.35±0.01	8.51±0.02	-0.829±0.010	0.178	0.240	3
03/06/2016	1970	3.23±0.01	-8.32±0.01	8.58±0.02	-0.814±0.004	0.193	0.255	3
03/07/2016	1970	3.25±0.01	-8.36±0.00	8.51±0.00	-0.850±0.014	0.152	0.215	2
03/17/2016	1979	3.20±0.02	-8.35±0.01	8.34±0.02	-0.947±0.018	0.156	0.219	3
03/18/2016	1979	3.23±0.01	-8.32±0.02	8.44±0.03	-0.915±0.019	0.191	0.253	3
03/24/2016	1989	3.23±0.02	-8.37±0.05	8.35±0.06	-0.903±0.015	0.201	0.263	3
03/24/2016	1989	3.20±0.02	-8.41±0.06	8.30±0.09	-0.886±0.013	0.219	0.281	3
03/25/2016	1990	3.24±0.01	-8.33±0.00	8.40±0.01	-0.918±0.007	0.161	0.223	4
03/26/2016	1990	3.25±0.00	-8.33±0.01	8.40±0.01	-0.930±0.000	0.147	0.210	2
03/27/2016	1991	3.22±0.01	-8.39±0.02	8.29±0.03	-0.955±0.005	0.121	0.184	3
04/14/2016	2008	3.21±0.02	-8.38±0.00	8.41±0.02	-0.844±0.017	0.186	0.248	3
04/15/2016	2008	3.23±0.01	-8.39±0.00	8.39±0.02	-0.861±0.029	0.167	0.229	2
04/16/2016	2009	3.21±0.01	-7.97±0.03	8.45±0.04	-0.872±0.016	0.152	0.215	3
04/17/2016	2009	3.21±0.01	-7.98±0.02	8.43±0.04	-0.873±0.022	0.152	0.214	3
04/18/2016	2010	3.20±0.01	-8.37±0.01	8.43±0.02	-0.877±0.016	0.158	0.220	3
04/19/2016	2010	3.23±0.01	-8.35±0.02	8.46±0.04	-0.893±0.015	0.140	0.202	3
Average		3.22±0.00	-8.32±0.01	8.44±0.01		0.168±0.003	0.231±0.003	66

Bilin 2 (H) – aragonite

03/17/2016	1979	-10.89±0.06	-5.53±0.02	-2.36±0.09	-0.917±0.014	0.189	0.251	3
03/18/2016	1979	-10.90±0.09	-5.58±0.05	-2.39±0.04	-0.878±0.007	0.232	0.294	3
03/24/2016	1989	-10.99±0.03	-5.64±0.02	-2.57±0.00	-0.935±0.009	0.165	0.228	3
03/25/2016	1989	-11.01±0.08	-5.71±0.09	-2.66±0.17	-0.928±0.011	0.173	0.236	3
03/25/2016	1990	-10.91±0.05	-5.62±0.03	-2.45±0.07	-0.918±0.028	0.160	0.223	3
03/27/2016	1991	-10.91±0.11	-5.58±0.02	-2.42±0.12	-0.901±0.012	0.182	0.244	4
04/15/2016	2008	-10.95±0.09	-5.61±0.05	-2.41±0.13	-0.834±0.030	0.197	0.260	3
04/15/2016	2008	-10.95±0.08	-5.41±0.23	-2.24±0.33	-0.879±0.029	0.146	0.208	3
04/17/2016	2009	-10.92±0.08	-5.17±0.04	-2.27±0.13	-0.822±0.026	0.209	0.271	3
04/17/2016	2009	-10.89±0.12	-5.18±0.07	-2.27±0.18	-0.833±0.002	0.197	0.259	3
04/18/2016	2010	-10.97±0.25	-5.61±0.10	-2.41±0.34	-0.854±0.008	0.184	0.246	3

04/19/2016	2010	-11.13±0.04	-5.66±0.00	-2.68±0.06	-0.916±0.022	0.114	0.176	2
Average		-10.95±0.01	-5.52±0.03	-2.43±0.02		0.179±0.005	0.241±0.005	36

Table 4. Stable isotope composition (in ‰) of dolomites heated in a piston cylinder

Date of analysis	Run	$\delta^{13}\text{C}$ (V-PDB)	$\delta^{18}\text{O}$ (V-PDB)	δ^{47}	Δ_{47} raw	Δ_{47} (70°C)	Δ_{47} (25°C)	#
<i>Rodolo (H) – dolomite</i>								
09/24/2015	1843	-3.78±0.01	1.89±0.07	13.29±0.08	-0.644±0.013	0.238	0.353	4
09/25/2015	1843	-3.79±0.02	1.82±0.08	13.19±0.10	-0.654±0.006	0.227	0.342	4
09/27/2015	1845	-3.78±0.01	1.84±0.05	13.23±0.05	-0.653±0.013	0.229	0.344	4
09/28/2015	1845	-3.84±0.02	1.65±0.05	12.97±0.06	-0.660±0.016	0.221	0.336	4
09/29/2015	1847	-3.76±0.05	1.77±0.07	13.32±0.12	-0.643±0.030	0.244	0.359	3
09/30/2015	1847	-3.83±0.01	1.69±0.04	13.16±0.05	-0.643±0.015	0.243	0.359	4
10/01/2015	1848	-3.83±0.02	1.78±0.06	13.21±0.08	-0.663±0.026	0.211	0.326	4
10/02/2015	1848	-3.87±0.02	1.65±0.07	13.02±0.10	-0.680±0.019	0.192	0.307	4
10/16/2015	1857	-3.82±0.01	1.77±0.05	12.97±0.06	-0.673±0.023	0.198	0.313	4
10/17/2015	1857	-3.79±0.02	1.83±0.13	13.06±0.15	-0.663±0.008	0.208	0.323	4
10/18/2015	1858	-3.79±0.00	1.84±0.02	13.37±0.03	-0.626±0.019	0.250	0.365	4
10/19/2015	1858	-3.78±0.01	1.84±0.04	13.34±0.05	-0.653±0.016	0.219	0.334	4
11/23/2015	1874	-3.84±0.02	1.71±0.08	13.03±0.10	-0.646±0.007	0.257	0.372	4
11/24/2015	1874	-3.81±0.01	1.86±0.05	13.21±0.08	-0.641±0.027	0.263	0.378	4
12/23/2015	1895	-3.87±0.05	1.80±0.22	13.19±0.28	-0.650±0.029	0.235	0.351	3
12/23/2015	1895	-3.98±0.05	1.46±0.11	12.73±0.14	-0.655±0.020	0.231	0.346	4
12/27/2015	1897	-3.86±0.04	1.83±0.08	13.08±0.11	-0.675±0.012	0.220	0.335	4
12/28/2015	1897	-3.94±0.09	1.55±0.18	12.73±0.23	-0.659±0.047	0.238	0.353	4
Average		-3.83±0.01	1.75±0.01	13.12±0.02		0.229±0.002	0.344±0.002	70
<i>Sansa (H) – dolomite</i>								
11/23/2015	1874	1.40±0.02	-3.64±0.05	12.59±0.07	-0.640±0.016	0.199	0.314	4
11/24/2015	1874	1.42±0.00	-3.63±0.02	12.62±0.02	-0.650±0.015	0.188	0.303	4
12/02/2015	1877	1.40±0.01	-3.68±0.05	12.53±0.08	-0.653±0.018	0.249	0.364	4
12/03/2015	1877	1.43±0.02	-3.60±0.06	12.63±0.08	-0.671±0.009	0.229	0.344	4
12/22/2015	1895	1.43±0.03	-3.74±0.04	12.58±0.08	-0.660±0.012	0.225	0.340	2
12/23/2015	1895	1.36±0.03	-3.94±0.06	12.31±0.07	-0.652±0.012	0.234	0.349	3
12/27/2015	1897	1.31±0.07	-3.86±0.15	12.21±0.22	-0.675±0.008	0.221	0.336	4
12/28/2015	1897	1.33±0.08	-3.82±0.17	12.25±0.25	-0.696±0.029	0.197	0.312	4

Average	1.38 ± 0.01	-3.74 ± 0.02	12.47 ± 0.03	0.218 ± 0.004	0.333 ± 0.004	29
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Table 5. Stable isotope composition (in ‰) of carbonates offline digested at 100 °C

Date of analysis	Run	$\delta^{13}\text{C}$ (V-PDB)	$\delta^{18}\text{O}$ (V-PDB)	δ^{47}	Δ_{47} raw	Δ_{47} (100°C)	Δ_{47} (25°C)	#
<i>Rodolo (H) – dolomite</i>								
06/08/2016	2034	-3.99±0.00	1.35±0.01	11.16±0.02	-0.921±0.007	0.132	0.302	1
06/20/2016	2042	-3.89±0.00	1.56±0.00	11.45±0.01	-0.922±0.008	0.139	0.309	1
Average		-3.94±0.05	1.45±0.10	11.31±0.15		0.135±0.020	0.305±0.020	2
<i>Sansa (H) – dolomite</i>								
06/08/2016	2034	1.41±0.00	-3.89±0.02	11.05±0.01	-0.906±0.009	0.148	0.318	1
06/20/2016	2042	1.31±0.00	-4.21±0.00	10.59±0.00	-0.927±0.006	0.134	0.304	1
Average		1.36±0.05	-4.05±0.16	10.82±0.23		0.141±0.020	0.311±0.020	2
<i>Magnesite (H)</i>								
06/19/2016	2040	-0.95±0.00	-18.33±0.01	-5.96±0.02	-0.864±0.013	0.203		1
Average		1.36±0.05	-4.05±0.16	10.82±0.23		0.203±0.020		1

Due to the lack or the small number of replicates we use the average standard deviation from the 100 °C standard measurements (Appendix C) as our analytical precision of the final Δ_{47} values for the 100 °C offline measurements listed above.

Table 6. Stable isotope data of the heated carbonate samples (in ‰)

Identifier	$\delta^{13}\text{C}$ (V-PDB)	$\delta^{18}\text{O}$ (V-PDB)	δ^{47}	Δ_{47} (100°C)	Δ_{47} (70°C)	Δ_{47} (25°C)	#
Calcites (CaCO_3)							
MS 2 (H)	2.18±0.00	-1.90±0.01	13.82±0.03		0.196±0.004	0.259	58
ETH 4 (H)	-10.20±0.00	-18.66±0.01	-15.42±0.00		0.195±0.002	0.257	93
Merck (H)	-41.75±0.00	-15.56±0.00	-42.87±0.01		0.203±0.003	0.265	61
Average calcite:					0.197±0.002	0.260±0.002	212
ETH 1	2.00±0.03	-2.17±0.03	13.48±0.01		0.203±0.005	0.265	
ETH 2	-10.20±0.01	-18.59±0.03	-15.30±0.01		0.205±0.003	0.267	
Aragonites (CaCO_3)							
Bilin 1 (H)	3.22±0.00	-8.32±0.01	8.44±0.01		0.168±0.003	0.231	66
Bilin 2 (H)	-10.95±0.01	-5.52±0.03	-2.43±0.02		0.179±0.005	0.241	36
Average aragonite:					0.172±0.003	0.234±0.003	102
Dolomites ($\text{Ca,Mg}(\text{CO}_3)_2$)							
Rodolo (H)	-3.83±0.01	1.75±0.01	13.12±0.02		0.229±0.002	0.344	70
Sansa (H)	1.38±0.01	-3.74±0.02	12.47±0.03		0.218±0.004	0.333	29
Average dolomite:					0.226±0.002	0.341±0.002	99
Dual Inlet Measurements of Samples digested Offline at 100 °C:							
Dolomites:							
Rodolo (H)	-3.94±0.05	1.45±0.10	11.31±0.15	0.135±0.020		0.305	2
Sansa (H)	1.36±0.05	-4.05±0.16	10.82±0.23	0.141±0.020		0.313	2
Magnesite (MgCO_3)							
Magnesite (H)	-0.95±0.00	-18.33±0.01	-5.96±0.02	0.203±0.020			1

–For dolomite samples we applied a Δ_{47} acid fractionation correction of Murray et al., 2016. –We did not apply a Δ_{47} acid fractionation correction on the magnesite as there is none available.

Table 7. Effect of different BG ranges on Δ_{47} (in ‰) of the calcite standards ETH 1 and ETH 2

Identifier	BG area a)	BG area b)	BG area c)	BG area d)
ETH 1	0.180	0.262	0.262	0.268
ETH 2	0.367	0.267	0.255	0.247

BG range selection a), b), c) and d) are according to the illustration in Fig. 4