Siderite acid fractionation factors for sealed and open vessel digestions at 70°C and 100°C.

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1. Abstract

The oxygen isotope composition of siderites can be used to deduce the paleoenvironmental conditions under which the mineral formed. However, it is not clear whether the published fractionation factors ($\alpha_{\text{CO}_2\text{-siderite}}$) for the acid digestion of siderites are appropriate for modern “on-line” sample preparation techniques. This is an important source of uncertainty that has not yet been investigated. To this aim, we obtained new siderite acid fractionation factors for open and closed vessel digestions at 100°C and 70°C, respectively. We find that previous $\alpha_{\text{CO}_2\text{-siderite}}$ estimates are appropriate for GasBench-type sealed vessel digestions and propose a revised relationship between $\alpha_{\text{CO}_2\text{-siderite}}$ and temperature:

$$1000 \cdot \ln (\alpha_{\text{CO}_2\text{-siderite}}) = 4.06 \pm 0.17 (10^3/T) - 1.93 \pm 0.5 (R^2 = 0.99)$$

This relationship encompasses most practical laboratory digestion temperatures and has a temperature sensitivity of -0.032‰/°C that is similar to other carbonate minerals. The open vessel digestion $\alpha_{\text{CO}_2\text{-siderite}}$ at 100°C, on the other hand, is offset from previous estimates by 1‰, with a value of $1000 \cdot \ln \alpha = 9.79 \pm 0.23$ (0.12 se). This estimate is essential for the open vessel digestions that are needed for siderite clumped isotope analyses.

1. Introduction

The oxygen (O) isotope composition of siderites can be exploited to reconstruct the environmental conditions of carbonate formation (Ludvigson et al., 1998; Ludvigson et al., 2013). For instance, siderite $\delta^{18}\text{O}$ values have been widely used as a proxy for the oxygen isotope composition of paleoprecipitation (White et al., 2001; Ufnar et al., 2002; Suarez et al., 2009), a useful paleoenvironmental variable that can be used to estimate ancient rainfall amounts (White et al., 2001; Poulsen et al., 2007; Suarez et al., 2011). Moreover, thanks to the recent development of the clumped isotope paleothermometer (Ghosh et al., 2006), the isotopic composition of siderites can be used directly to estimate temperatures of mineral formation (Fernandez et al., 2014). In spite of that, one source of uncertainty still to be investigated is the effect of incorrect O isotope phosphoric acid fractionation factors on the accuracy of siderite based paleoclimate reconstructions.

Carbonate samples have traditionally been measured for their stable O isotope composition after digestion with anhydrous phosphoric acid. The acid reaction, however, releases only 2/3 of the available O as CO_2 and results in an O isotope fractionation that is dependent on digestion temperatures, on carbonate mineralogy, and on sample digestion techniques (McCrea, 1950; Rosenbaum and Sheppard, 1986; Swart et al., 1991; Kim et al., 2007). Consequently, mineral and method specific acid fractionation factors ($\alpha_{\text{CO}_2\text{-carbonate}}$) are needed to correctly estimate the $\delta^{18}\text{O}$ of solid samples.

Only two previous studies have attempted to estimate siderite acid fractionation factors. Rosenbaum and Sheppard (1996) determined the total oxygen isotope composition of synthetic and natural siderites using a combination of thermal decomposition and fluorination and reported $\alpha_{\text{CO}_2\text{-siderite}}$ values at 100°C and 150°C. Likewise, Carothers et al. (1988) used similar methods to report $\alpha_{\text{CO}_2\text{-siderite}}$ values at 25°C and 50°C. Both of these studies, however, utilized only a limited number of measurements for their total oxygen isotope determinations, so the uncertainties in their $\alpha_{\text{CO}_2\text{-siderite}}$ values are not well constrained. More importantly, however, both studies used the “sealed vessel” acid digestion technique, which is based on the original McCrea (1950) method. With the advent of on-line sample preparation techniques this method is no longer routinely used, and it has not yet been shown whether the published “sealed vessel” $\alpha_{\text{CO}_2\text{-siderite}}$ values are appropriate for modern sample preparation techniques.

Since the choice of incorrect siderite acid fractionation factors propagates directly into paleoclimate reconstructions, the lack of method specific $\alpha_{\text{CO}_2\text{-siderite}}$ values represents an important yet often overlooked source of uncertainty. This is especially critical for siderites because there are no international standards with agreed upon $\delta^{18}\text{O}$ values. Here, we compare the $\delta^{18}\text{O}_{\text{siderite}}$ values that result from two common acid digestion techniques: 1) an “open vessel” method that is analogous to the on-line common acid bath carbonate digestion procedure, and 2) an on-line “sealed vessel” method where samples are digested with a GasBench II (Thermo Fisher Scientific) preparation device. We find a constant

offset in the $\delta^{18}\text{O}_{\text{siderite}}$ estimates produced between both digestion styles and estimate new method specific $\alpha_{\text{CO}_2\text{-siderite}}$ values.

2. Methods

2.1 Siderite samples

Four natural siderite samples were obtained from the museum collection at ETH Zurich to calculate $\alpha_{\text{CO}_2\text{-siderite}}$ values. The samples were hand crushed with the aid of a mortar and pestle, passed through a 120 μm sieve, and stored in gas-tight Vacutainers. The mineralogy of the samples was confirmed with XRD analyses, which revealed that siderite was the only phase present in the samples. Chemical compositions were determined by ICP-MS analyses (Thermo Scientific Element XR) of homogenized sample aliquots (300 μg) after complete digestion by doubly distilled HNO_3 . The Fe content in these samples ranges from 70-90%, with varying amounts of Ca and Mg (Figure 1).

Additionally, five synthetic siderites were precipitated following the methods described in Wiesli et al. (2004) and Fernandez et al. (2014) and were used to compare the $\delta^{18}\text{O}_{\text{siderite}}$ obtained by both digestion methods. The mineralogy of these samples was also confirmed with XRD analyses prior to isotopic analyses.

2.2 Total oxygen isotope analyses

The isotope compositions of the total oxygen content of the siderite samples were determined with a high temperature pyrolysis system (TCEA) coupled to a continuous flow isotope-ratio mass spectrometer (CF-IRMS). Approximately 200 μg of carbonate was weighed into silver capsules along with 200 μg of graphite

to provide excess carbon at the site of pyrolysis (Crowley et al., 2008). Samples and standards were loaded into a zero blank autosampler and dropped into a glassy carbon pyrolysis column held at 1450°C and filled with glassy carbon chips. Samples were dropped into the furnace, and the resulting CO gas was transferred with the aid of a He carrier gas through a gas chromatography column into a Delta V Plus mass spectrometer for measurement (Thermo Fisher Scientific).

Three benzoic acid standards (IAEA 601, $\delta^{18}\text{O}_{\text{VSMOW}}=23.3\text{‰}$; IAEA 602, $\delta^{18}\text{O}_{\text{VSMOW}} = 71.4\text{‰}$; B1-internal, $\delta^{18}\text{O}_{\text{VSMOW}} = 24.5\text{‰}$;) and a cellulose standard (IAEA C3, $\delta^{18}\text{O}_{\text{VSMOW}} = 31.85\text{‰}$, Buhay et al., 1993) were used to calibrate measurements into the VSMOW scale and to correct for drift and linearity. The amount of CO produced during carbonate pyrolysis was calculated using the relationship between the weights of the three benzoic acid standards and their observed areas under the m/z 28 peaks, and yields were estimated using the expected amounts of CO based on sample stoichiometry.

2.3 Sealed Vessel digestion

Sealed vessel digestions were performed in 12 ml exetainers loaded with approximately 200 μg of carbonate (siderite and calcite standards) and flushed with helium using the procedures outlined in Breitenbach and Bernasconi (2011). Reaction temperature was controlled using the aluminum block of the Gas Bench II (Thermo Fisher Scientific), which was held at 70°C. After thermal equilibration, samples were injected with 5 drops (50 μl) of 100% phosphoric acid. In a subset of the experiments, reaction times were varied from 4 to 60

hours to investigate the time necessary to fully digest the siderite samples. Reaction products were purified with a chromatography column, and the CO₂ was measured in continuous flow mode in a Delta V Plus mass spectrometer (Thermo Fisher Scientific) as described in Breitenbach and Bernasconi (2011). Two internal calcite standards were used to correct for drift and linearity. Digestion yields were calculated in a similar manner as the TCEA data, except that in this case the mass of the calcite standards and the area under the m/z 44 peak were used to build a calibration relationship.

2.4 Open Vessel digestion

Open vessel digestions were performed at 100°C in McCrea type reaction vessels attached to a vacuum line (See Figure S1 in supplementary materials for an example of our setup). Approximately 15 mg of carbonate (standards and siderite samples) were loaded into the reactors, and the acid arm was filled with 1ml of 104% phosphoric acid. Vessels were evacuated under vacuum and placed in a 100°C boiling water bath. Enough time was allowed for thermal equilibration before tipping the acid from the side arm into the carbonate reservoir to start the reaction. As the reaction proceeded, the CO₂ was continuously trapped in a spiral trap cooled with liquid N₂. In most cases the reaction was allowed to proceed for up to three hours; although, reaction times were varied in a separate set of experiments to investigate the optimal times for complete digestions.

Gasses were cleaned cryogenically in a vacuum line. Water was removed using two spiral water traps held at approximately -80°C with an ethanol-liquid N₂

slush, and organic contaminants were removed by passing the gas through a U-shaped glass trap filled with a gas chromatography resin (Porapak Q) held at approximately -40°C. The amounts of CO₂ produced were measured manometrically and digestion yields were estimated using sample stoichiometry. The clean gases were flame sealed into pre-combusted Pyrex tubes and measured in a MAT 253 isotope ratio mass spectrometer (Thermo Fisher Scientific) operating in dual inlet mode.

2.5 Calculation of solid siderite $\delta^{18}\text{O}$ values.

Two internal calcite standards were measured along with samples digested at 70°C and four different standards were used with samples digested at 100°C. The internal standards were first calibrated using the VSMOW-SLAP scale following International Union of Pure and Applied Chemistry (IUPAC) guidelines as described by Kim et al. (2015) through repeated measurements of NBS-19 and NBS-18. These standards were then used to calibrate siderite CO₂ gas into the VSMOW-SLAP scale and were corrected for acid fractionation following the algorithm described by Kim et al. (2015). The fractionation factors of Kim et al. (2007) were used for the calcite standards. For siderite digestions at 70°C an $\alpha_{\text{CO}_2\text{-siderite}}$ value of 1.01002 was used that was estimated by extrapolation of the values reported by Carothers et al. (1988). The siderite 100°C data was corrected with an $\alpha_{\text{CO}_2\text{-siderite}}$ value of 1.00881, which is the value measured at 100°C by Rosenbaum and Sheppard (1986).

3. Results

3.1 Total Oxygen isotope composition

Quantitative conversion of siderite carbonate to CO gas was achieved with high temperature pyrolysis (Table 1). The mean recovery for the four samples is $99.26 \pm 2\%$ ($n=72$), and the yields for individual samples are all within uncertainties of expected amounts. External analytical precision in $\delta^{18}\text{O}$ values ranged from 0.13 to 0.29‰, with a mean value of 0.18‰ (See supplementary information for raw isotope data for both samples and standards)

3.2 Digestion experiments

Siderite is notoriously difficult to digest with phosphoric acid, especially at low temperatures where complete digestions can take weeks if not months (e.g., Rosenbaum and Shephard, 1986). To investigate the optimum time needed for complete digestion, we conducted several experiments where we measured yields and isotopic compositions of the acid-liberated CO₂ as a function of time. These data are presented in Figure 2.

In the closed vessel experiments at 70°C, most of the CO₂ is released within the first 700 minutes (Figure 2a), and up to 50 hours are needed for quantitative siderite digestion. The initial CO₂, however, has more negative $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values than the value measured at complete digestion. Delta values then approach --within external analytical uncertainties-- the complete digestion values once the reaction is 80% complete (Figure 2c). Digestion rates in the open vessel experiments at 100°C are much faster (Figure 2b). In this case, most of the CO₂ is released in the first 60 minutes and the reaction is completed in approximately 3 hours. Carbon and oxygen isotopes follow the same pattern as the closed vessel experiments with more negative $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values observed

in the initial CO₂ followed by a rapid convergence to their complete digestion values (Figure 2d).

At complete digestion there is no difference in the $\delta^{13}\text{C}$ values between the open and sealed vessel experiments (Figure 3a). This is not the case, however, for solid siderite oxygen isotopes where we observe a mean difference of $0.99 \pm 0.2\text{‰}$ (Figure 3b), which suggests that one or both of the $\alpha_{\text{CO}_2\text{-siderite}}$ values that were used to correct the data are inaccurate.

To investigate which of the published $\alpha_{\text{CO}_2\text{-siderite}}$ is inaccurate, we compare the $\delta^{18}\text{O}_{\text{siderite}}$ digestion data (i.e., corrected for acid fractionation) and the $\delta^{18}\text{O}_{\text{siderite}}$ total oxygen data from the TCEA measurements in Table 2. The $\delta^{18}\text{O}_{\text{siderite}}$ values for the sealed vessel experiments are indistinguishable from the values measured for the total oxygen isotope compositions by TCEA. For instance, the average difference between the TCEA and the closed vessel experiments is $0.12 \pm 0.23\text{‰}$, which is well within the average analytical uncertainty in the total oxygen measurements of 0.18‰ . On the other hand, the $\delta^{18}\text{O}_{\text{siderite}}$ values for the open vessel experiments do not match the total oxygen data (TCEA); these are offset by $0.04 \pm 0.24\text{‰}$.

4.1 Discussion

4.1 Performance of the high temperature pyrolysis system

High-temperature pyrolysis proved to be an effective alternative to the commonly used thermal decomposition/fluorination method to measure the total oxygen isotope composition of carbonate samples. We consistently

obtained quantitative decomposition yields and sufficiently precise stable oxygen isotope data ($\pm 0.18\text{‰}$) that are of comparable precision to fluorination data (e.g., approximately 0.55‰ ; Kim et al., 2007). Moreover, our results sharply contrast with previous attempts to measure carbonate minerals by high temperature pyrolysis where quantitative yields were not regularly achieved and, thus, the results were judged to be inaccurate. For instance, Crowley et al. (2008) subjected calcite and dolomite samples to both high temperature pyrolysis and conventional fluorination. They obtained low pyrolysis yields that were associated with large $\delta^{18}\text{O}$ deviations from fluorination values, and thus were judged to be inaccurate.

The low yields and variable results obtained by Crowley et al. (2008) likely result from the formation of CaO residues during pyrolysis. The metal oxide readily forms during thermal decomposition because only two out of the three oxygen atoms in the carbonate ion react with C to form CO (Boschetti and Iacumin, 2005). During siderite pyrolysis, on the other hand, Fe^{2+} can be reduced to Fe^0 , leaving all of the oxygen free to react with C. Since no metal oxide is formed, quantitative yields can be obtained even in the absence of a catalyst. This is what we observed in our experiments. Moreover, although we did not attempt to characterize the pyrolysis residues in our experiments, we note that elemental Fe has been observed as a product of thermal decomposition of siderite (Carothers et al., 1998).

For these reasons, we believe there is no oxygen isotope fractionation during siderite high temperature pyrolysis and consider the TCEA data to be an accurate

representation of the total oxygen isotope composition of the siderite samples. Our results also show that it may be possible to routinely analyze siderite samples via high temperature pyrolysis in order to avoid uncertainties associated with acid fractionation factors. Pyrolysis, however, is only a viable alternative for relatively pure siderite samples because other mineral phases present in the sample (e.g., clay minerals, oxides) would also release oxygen during thermal decomposition.

4.2. Acid digestion vs. Total Oxygen data

Open vessel $\delta^{18}\text{O}_{\text{siderite}}$ data is offset from the total oxygen data (TCEA) towards heavier isotopic compositions by approximately 1‰ (Table 2). The same is not true for the sealed vessel data, where $\delta^{18}\text{O}_{\text{siderite}}$ values closely match the TCEA data. Moreover, the carbon isotope data obtained for both techniques are identical. These observations are similar to those made for calcite by Swart et al. (1991), where they find identical carbon isotope values and an offset of 0.2-0.4‰ between open and sealed vessel techniques. These authors suggest that isotope exchange between CO_2 and extraneous O are likely behind the offset; although, they acknowledge that incomplete CO_2 removal and/or CO_2 dissolution into the acid are also possible mechanisms.

During digestion, CO_2 can exchange oxygen isotopes with water that is present in the acid or water that is produced as part of the carbonate digestion reaction. As noted by Swart et al. (1991) exchange with water should result in CO_2 that is isotopically heavier due to the large fractionation that occurs between CO_2 and water (Bottinga and Craig, 1968). Given that the residence time of CO_2 is

significantly longer in the sealed vessel experiments; CO₂ from these should be heavier. This is the opposite of what we find; although, it should be noted that this comparison is imperfect because we did not attempt to run open digestion experiments at 70°C. The comparison is made instead with the acid fractionation corrected data. Regardless of this complication, the observation that the open vessel data has more positive $\delta^{18}\text{O}_{\text{siderite}}$ values than the corresponding closed vessel data makes it unlikely that simple O exchange between CO₂ and water is behind the offset.

Another more likely possibility is that CO₂ exchanges O isotopes with the entire exchangeable O pool present in the acid and not just with water. Wachter and Hayes (1985) used ¹⁸O labeled CO₂ to investigate the ease of O isotope exchange between acid phosphate species and CO₂. They found that significant amounts of O isotope exchange could occur at high temperatures even under nominally anhydrous phosphoric acids. Moreover, they found faster rates of exchange in experiments with higher water vapor pressures because O isotope exchange occurs through the hydrolysis of phosphate species followed by O exchange between CO₂ and water. Since CO₂ is in contact with the acid for a longer time period in the sealed vessel experiments under higher water vapor pressures, this is an effect that could be invoked to explain our observations. For instance, isotopic exchange between CO₂ and the acid coupled with the preferential incorporation of ¹⁸O into the phosphate species should result in sealed vessel CO₂ that is lighter relative to the open vessel experiments (i.e., where the exchange does not take place). Regardless of the actual mechanism behind the offset

between both digestion techniques, $\delta^{18}\text{O}_{\text{CO}_2\text{-Acid}}$ data is highly reproducible and can be used to estimate method specific acid fractionation factors.

4.3. New siderite acid fractionation factors

Acid fractionation factors were calculated according to:

$$\alpha_{\text{CO}_2\text{-Siderite}} = (\delta^{18}\text{O}_{\text{CO}_2\text{-Acid}} + 1000) / (\delta^{18}\text{O}_{\text{Siderite}} + 1000)$$

where $\delta^{18}\text{O}_{\text{CO}_2\text{-Acid}}$ is the isotopic composition of the acid-liberated CO_2 calibrated into the VSMOW-SLAP scale using internal calcite standards as scale anchors, and where $\delta^{18}\text{O}_{\text{Siderite}}$ is the isotopic composition of the solid siderite sample measured by TCEA. Fractionation factors are presented in Table 3 and plotted along with previous estimates in Figure 4.

The sealed vessel $\alpha_{\text{CO}_2\text{-Siderite}}$ at 70°C is indistinguishable to the value estimated by the extrapolation of the alphas of Carothers et al. (1986) ($1000 \cdot \ln \alpha = 10.09 \pm 0.23$ vs. 10.07). The close agreement between these two is not surprising considering that Carothers et al. (1986) also used a sealed vessel digestion technique; although, the two techniques are not identical and differ in a number of important characteristics. For instance, the digestions of Carothers et al. (1986) were performed in evacuated vessels whereas the GasBench digestions were performed under helium atmospheres. Despite these differences, this observation suggests that the published $\alpha_{\text{CO}_2\text{-siderite}}$ values can be used for digestions performed in GasBench type preparation devices (Figure 4).

Moreover, the $\alpha_{\text{CO}_2\text{-siderite}}$ at 70°C can be used to fill in the gap between previous estimates and to propose a revised relationship between temperature and acid fractionation factors for sealed vessel digestions:

$$1000 \cdot \ln(\alpha_{\text{CO}_2\text{-siderite}}) = 4.06 \pm 0.17 (10^3/T) - 1.93 \pm 0.5 \quad (R^2 = 0.99)$$

This relationship encompasses most practical laboratory digestion temperatures, and it has a temperature sensitivity of -0.032‰/°C, which is similar to most carbonate minerals (see Table 4 in Kim et al., 2015). We suggest that it should be used for all sealed vessel siderite digestions.

The open vessel acid fractionation factor is offset from the corresponding sealed vessel $\alpha_{\text{CO}_2\text{-siderite}}$ value by 1‰ ($1000 \cdot \ln \alpha = 9.79 \pm 0.23$ vs. 8.77), which is consistent with the offset we observed between open and closed vessel experiments (Figure 3b). This is the first published determination of siderite acid fractionation during open vessel digestions. As a general rule, open vessel digestions are more time consuming than GasBench type reactions because reactions must be completed one at a time, so it is not particularly useful where the only variable of interest is the $\delta^{18}\text{O}$ value of a siderite sample. However, open vessel digestions are necessary for siderite clumped isotope measurements; therefore, our $\alpha_{\text{CO}_2\text{-siderite}}$ value must be used in cases where both a clumped isotope temperature estimate and the $\delta^{18}\text{O}$ value is desired for the same sample aliquot. We also note that the uncertainty in this value is well constrained as it is based on 72 independent total oxygen isotope measurements of four different siderite samples.

Our open vessel $\alpha_{\text{CO}_2\text{-Siderite}}$ estimate is also relevant for siderite digestions done via the Kiel IV carbonate preparation device (Thermo Fisher Scientific), which has been used by some workers to report siderite $\delta^{18}\text{O}$ data (e.g., Ufnar et al., 2002; Ludvigson et al., 2013). These reactions are a type of open vessel digestion where small amounts of acid are dropped into a carbonate sample and where the CO_2 is frozen as the reaction proceeds. Previous workers have used the published sealed vessel $\alpha_{\text{CO}_2\text{-Siderite}}$ values for their acid fractionation corrections. Our results, however, suggest that sealed vessel $\alpha_{\text{CO}_2\text{-Siderite}}$ values are not appropriate for open vessel digestions and as a consequence the published Kiel-derived $\delta^{18}\text{O}$ values may be biased towards positive values. It is important to note that the specific acid fractionation that occurs during Kiel digestions could be different than the fractionation observed for our set-up. This should be investigated before re-evaluating published Kiel $\delta^{18}\text{O}$ data.

4.4. Recommendations for siderite digestion

For complete siderite digestion we find that up to 50 hours are needed during closed vessel digestions at 70°C , and 3 hours are needed during open vessel digestions at 100°C . Faster or slower reactions rates, however, can occur in other laboratories due to differences in grain sizes or phosphoric acid densities. Moreover, our results also suggest that complete digestions may not be necessary for accurate $\delta^{18}\text{O}$ data since after approximately 80% digestion $\delta^{18}\text{O}$ values are within analytical uncertainty of the complete digestion values (Figure 2b). For these reasons, we suggest that the times presented above be used as

general guidelines to investigate the time required for acceptable yields in other set-ups.

4.5. Implications for other carbonate minerals

The large difference in siderite O isotope fractionations that exists between the two digestion styles has important implications for other carbonate minerals. This is particularly relevant for minerals where we do not yet have international standards with agreed upon $\delta^{18}\text{O}$ values. For instance, under the principle of equal treatment of samples and standards, differences in $\alpha_{\text{CO}_2\text{-calcite}}$ values between digestion methods should not propagate into measured solid carbonate $\delta^{18}\text{O}$ values when the mineralogy of the samples and standards is the same. In other words, for calcite $\delta^{18}\text{O}$ determinations method-specific fractionations cancel out if NBS-19 (calcite) and NBS-18 (calcite) are included as part of an analytical session (for an example of a normalization algorithm see Kim et al., 2015).

The problem with other minerals like siderite, aragonite, and dolomite is that to date there are no NBS-19 and NBS-18 equivalents that can be used to tie measurements into the VSMOW-SLAP scale. We have shown in this paper differences in siderite acid fractionation factors between techniques do not cancel out when calcite standards are used for normalization (Figure 3b). Consequently, workers should exercise caution when comparing results from different laboratories and should match the digestion style that was used when the $\alpha_{\text{CO}_2\text{-carbonate}}$ values were determined.

4.6. Implications for carbonate clumped isotope temperature calibrations

Method specific acid fractionation factors also have implications for the inter-laboratory reproducibility of carbonate clumped isotope measurements. Clumped isotopes refer to the measurement of the $^{13}\text{C}^{18}\text{O}^{16}\text{O}$ isotopologue in the CO_2 derived from the acid digestion of carbonate minerals. Measurements are reported with the Δ_{47} parameter, which is a measure of the abundance of $^{13}\text{C}^{18}\text{O}^{16}\text{O}$ relative to a random distribution of C and O isotopes among CO_2 isotopologues (Schauble et al., 2006). These measurements have attracted a lot of interest because they can be used to provide temperatures of mineral formation (Ghosh et al., 2006; Schauble et al., 2006). However, there is currently a debate about the temperature sensitivity of the clumped isotope paleothermometer that is centered around laboratories that use different digestion methods (e.g., Ghosh et al., 2006; Dennis and Schrag, 2010; Kele et al., 2015).

Much like oxygen isotopes, clumped isotopes are fractionated from the solid carbonate mineral during phosphoric acid digestion. The fractionations, which are temperature dependent (Guo et al., 2009; Henkes et al., 2013; Wacker et al., 2013; Defliese et al., 2015; Murray et al., 2016; Müller et al., in revision), must be accounted for before laboratories compare measurements; therefore, inaccurate clumped isotope acid fractionation factors can introduce uncertainties that reduce inter-laboratory reproducibility. Based on our observations for oxygen isotopes, it is possible that an analogous method-specific clumped isotope fractionation also exists. This is an important source of uncertainty that has not been properly investigated. We suggest that differences between sealed and open vessel digestions be included in future experimental designs that aim to

explain the reasons behind the disagreement in the Δ_{47} -temperature relationships.

5. Conclusions

We compared two common acid digestion techniques and found a constant 1‰ offset between $\delta^{18}\text{O}$ data generated from open vs. closed vessel digestions of siderite samples, which suggests that one of the published siderite acid fractionation factors is inaccurate. To investigate this, the total oxygen isotope composition of four natural siderite samples was measured by high temperature pyrolysis and method specific acid fractionation factors were calculated. We find that the published sealed vessel $\alpha_{\text{CO}_2\text{-siderite}}$ values are appropriate for digestions conducted in sealed vessel GasBench-type preparation devices and estimate a value of $1000 \cdot \ln \alpha = 10.09 \pm 0.23$ for digestions at 70°C. On the other hand, the estimate of $\alpha_{\text{CO}_2\text{-siderite}}$ at 100°C ($1000 \cdot \ln \alpha = 9.79 \pm 0.24$) is offset from previous estimates by 1‰. This value should be used for open vessel digestions of siderite samples.

Our observations have important implications for other carbonate minerals where there are likely analogous method specific acid fractionation factors and are especially relevant for minerals where there are no international standards that can be used to tie measurements to the VSMOW-SLAP scale. In these cases, workers should exercise caution when comparing results from different laboratories and should attempt to match the methods that were used to determine $\alpha_{\text{CO}_2\text{-carbonate}}$ values.

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Figure Captions

Figure 1. Ternary diagram showing relative Ca, Fe, and Mg compositions of the four natural siderites used to estimate the siderite acid fractionation factor. Analytical uncertainty based on the analyses of multiple replicates is approximately 5% for Fe and 3% for Ca and Mg.

Figure 2. Relationship between theoretical yields and digestion times for sealed vessel (a) and open vessel (b) digestions, c) difference between the $\delta^{13}\text{C}$ value at complete digestion vs. the $\delta^{13}\text{C}$ value for partial digestions, d) difference between the $\delta^{18}\text{O}$ value at complete digestion vs. the $\delta^{18}\text{O}$ value for partial digestions

Figure 3. a) $\delta^{13}\text{C}$ data for both sealed and open vessel digestion experiments. All of the samples fall on the 1:1 line. B) Acid fractionation corrected $\delta^{18}\text{O}_{\text{siderite}}$ data for both sealed and open vessel digestion experiments showing an offset of 1.0‰. See methods section 2.5 for details of the acid fractionation factors that were used and data normalization procedures. Data for complete digestions only.

Figure 4. Relationship between siderite acid fractionation factors and temperature for sealed and open vessel digestions. Error bars are standard deviations, and the uncertainty in the linear relationship is the 95% confidence interval on the regression coefficients. Note that error bars in previous estimates (e.g., Carothers et al., 1988; Rosenbaum and Shephard, 1986) are likely underestimated because only a limited number of total oxygen measurements were attempted (3-5 replicates); true uncertainty is likely approximately 0.5‰ (Kim et al., 2007).

Tables

Table 1. Total oxygen isotope results for the four natural siderite samples. STD is the external standard deviation and SE is the standard error.

Sample	$\delta^{18}\text{O}_{\text{Siderite}}$ VSMOW-SLAP	STD	Replicates	SE	Yield %
ES	16.86	0.22	12	0.06	101.3
Four	14.02	0.13	16	0.03	99.4
IG	6.70	0.29	22	0.06	96.8
LT	13.81	0.15	22	0.03	101.0

Table 2. Solid siderite oxygen isotope data for the sealed vessel ($\delta^{18}\text{O}_{\text{SV}}$) and open vessel ($\delta^{18}\text{O}_{\text{OV}}$) experiments (both in the VSMOW-SLAP scale), and the difference between the values for these experiments and the total oxygen isotope measurements ($\delta^{18}\text{O}_{\text{TCEA}}$). Average reproducibility of digestion experiments is 0.1‰ for carbon and 0.15‰ for oxygen. CO_2 $\delta^{18}\text{O}$ data were corrected for acid fractionation using published acid fractionation factors (see method section 2.5).

Sample	$\delta^{18}\text{O}_{\text{SV}}$ solid	$\Delta\delta^{18}\text{O}_{\text{SV}} - \delta^{18}\text{O}_{\text{TCEA}}$	$\delta^{18}\text{O}_{\text{OV}}$ solid	$\Delta\delta^{18}\text{O}_{\text{OV}} - \delta^{18}\text{O}_{\text{TCEA}}$
Sealed Vessel 70°C			Open Vessel 100°C	
ES	16.78	-0.08	17.81	0.95
Four	13.99	-0.03	14.83	0.81
IG	7.13	0.43	8.07	1.37
LT	13.96	0.15	14.82	1.01
Mean		0.12 ± 0.23‰	Mean	1.04 ± 0.24‰

Table 3. Acid fractionations for sealed vessel digestions at 70°C and open vessel digestions at 100°C. Uncertainties reflect external reproducibility reported in standard deviations and standard errors (SE).

Sample	α	$1000 \bullet \ln \alpha$		α	$1000 \bullet \ln \alpha$
	CO2-SID			CO2-SID	
Sealed Vessel 70°C			Open Vessel 100°C		
ES	1.00994	9.89		1.00974	9.70
Four	1.00999	9.94		1.00961	9.56
IG	1.01045	10.40		1.01017	10.12
LT	1.01016	10.09		1.00981	9.76
Mean	1.01014 ±0.0002	10.09 ± 0.23 (0.1 SE)	Mean	1.00983 ± 0.0002	9.79 ± 0.23 (0.12 SE)

Figure 1

Figure 2

Figure 3

Figure 4