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Technical Note: A simple method for vaterite precipitation in isotopic equilibrium: implications for bulk and clumped isotope analysis

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Abstract

Calcium carbonate ($CaCO_3$) plays an important role in the natural environment as a major constituent of the skeleton and supporting structure of marine life and has high economic importance as additive in food, chemicals and medical products. Pure $CaCO_3$ occurs in the three different polymorphs calcite, aragonite and vaterite, whereof calcite is the most abundant and best characterized mineral. In contrast, little is known about the rare polymorph vaterite, in particular with regard to the oxygen isotope fractionation between H_2O and the mineral.

Synthetic precipitation of vaterite in the laboratory typically involves rapid processes and isotopic non-equilibrium, which excludes isotope studies focused on characterization of vaterite at equilibrium conditions. Here, we used a new experimental approach that enables vaterite mineral formation from an isotopically equilibrated solution. The solution consists of a $\sim 0.007\,\mathrm{mol\,L^{-1}}$ $CaCO_3$ solution that is saturated with NaCl at room temperature (up to $6.5\,\mathrm{mol\,L^{-1}}$). Vaterite precipitated as single phase or major phase ($\geq 94\,\%$) in experiments performed between 23 and 91 °C. Only at 80 °C was vaterite a minor phase with a relative abundance of 27 %. The high mineral yield of up to 235 mg relative to a total dissolved $CaCO_3$ amount of 370 mg enables an investigation of the oxygen isotope fractionation between mineral and water, and the determination of clumped isotope values in vaterite.

1 Introduction

Vaterite is the least know polymorph of calcium carbonate and was first described by Vater in 1893 (Vater, 1893). In the 1920 and 1930s the nature and crystallographic structure of vaterite was still questioned and the occurrence of a third polymorph of $CaCO_3$ was disputed amongst various groups (Johnston et al., 1916; Spangenberg, 1921; Heide, 1924; Rinne, 1924; Gibson et al., 1925). In the following decades work focused mainly on the structure of vaterite (e.g., McConnell, 1960; Kamhi, 1963; Meyer, 1969; Mann et al., 1991; Wang and Becker, 2009) which continues to provide surprises until today (Kabalah-Amitai et al., 2013). Vaterite has a major heaxagonal structure (von Olshausen, 1925) and appears in different morphologies such as spherulitic aggregates (Han et al., 2006; Nebel and Epple, 2008; Mori et al., 2009; Hu et al., 2012) or hexagonal plates (e.g., Johnston et al., 1916; Kamhi, 1963; Dupont et al., 1997; Xu et al., 2006; Kawano et al., 2009).

Vaterite occurrence in nature is more wide-spread than generally assumed. It was first observed in gastropods (Mayer and Weineck, 1932). Later studies discovered vaterite also related to oil field drilling (Friedman and Schultz, 1994), in Portland cement (Friedman and Schultz, 1994), as stones in the urinary system (Prien and Frondel, 1947; Sutor and Wooley, 1968), and was recently postulated as a precursor $CaCO_3$ phase in the first stages of biogenic carbonate formation that later transforms into stable calcite or aragonite (Jacob et al., 2008). Vaterite has not been found in the geologic record and is therefore suspected to be metastable. The observation of vaterite in biogenic systems (Mayer and Weineck, 1932; Spann et al., 2010; Nehrke et al., 2012; Kabalah-Amitai et al., 2013) gives some constraints on its stability which can be on the order of years (Lowenstamm and Abbott, 1975), but not geological ages.

The natural occurrence of vaterite and its potential economic use due to its large specific surfaces and high porosity (Mori et al., 2009) warrants a precise investigation of this mineral. So far, most laboratory experiments were designed to precipitate relatively large single crystals of vaterite for X-ray analysis that focused on the crystal structure (e.g., Kamhi, 1963). Vaterite precipitation experiments generally used either mixtures of several solutions such as K_2CO_3, Na_2CO_3, and $CaCl_2$ (Kamhi, 1963; Easton and Claugher, 1986; Han et al., 2006; Nebel and Epple, 2008) or $CaNO_3$ (Davies et al., 1978), sometimes with added surfactants (Mann et al., 1991; Dupont et al., 1997; Mori et al., 2009) or additional organic substrates (Falini et al., 1996; Xu et al., 2006; Kirboga and Oner, 2013). These experiments provided crystals with sizes between a few 100 nm and a few µm and were mostly restricted to the temperature range of 25–60 °C.

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As vaterite is a relevant mineral in biogenic systems (Lowenstamm and Abbott, 1975; Pouget et al., 2009; Spann et al., 2010; Nehrke et al., 2012) it may provide new insights into the isotope fractionation during biological carbonate formation. However, so far little is known about the oxygen isotope fractionation between dissolved inorganic carbon and vaterite and, in particular, the clumped isotope Δ_{47}-T relationship of vaterite. Whereas vaterite was reported in a few stable isotope studies aiming at determining the oxygen isotope fractionation factor in the system $CaCO_3$-H_2O (e.g., Kim and O'Neil, 1997), it rarely occurred as a pure phase and, thus, did not allow for a precise study focused on vaterite. Based on the limited data available Tarutani et al. (1969) suggested vaterite to be enriched in ^{18}O by +0.5 ‰. Kim and O'Neil (1997) obtained a similar value of +0.6 ‰. Both studies were limited to either one (25 °C) or two temperatures (25, 40 °C), and a more comprehensive study is still lacking. In addition, the clumped isotope Δ_{47}-T relationship of vaterite has not been assessed so far, but could give new insights into the effect of polymorphism on isotope ratios or mineral growth related isotope fractionation.

In this study we present a simple method that allows vaterite precipitation over a wide temperature range (at least between 23 and 91 °C) and that provides large quantities of the mineral, enabling for example the investigation of the oxygen isotope fractionation factor between vaterite and H_2O, and the Δ_{47}-T relationship of vaterite.

2 Experimental setup

The precipitating solution was prepared by dissolving high-purity $CaCO_3$ (Merck Suprapur, 99.95 %) in de-ionized water. The water was initially taken from the local water supply, purified with a reverse osmosis technique and finally de-ionized with an Ultrapure™ system with an output quality of 18 MΩcm. Trace components of the $CaCO_3$ used to prepare the solution are strontium (≤ 100 ppm), rubidium (≤ 20 ppm), sulphate (≤ 20 ppm), and phosphate (≤ 10 ppm).

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About 370 mg $CaCO_3$ was dissolved in ∼ 500 mL de-ionized water at room temperature per experiment. The water was acidified by purging of CO_2 tank gas (normal grade, BOC UK) through the solution. The solution was filtered after three hours through a double layer of Whatman® filter paper (grade 1, 11 µm filtration size) to remove un-dissolved $CaCO_3$ crystals. Optical inspection via light reflectance confirmed no large crystals to have bypassed the filtration stage.

The filtered $CaCO_3$ solution was then thermally and isotopically equilibrated at a set temperature in a temperature-controlled water bath (sketch of the experimental setup is depicted in Fig. 1). The experimental temperatures ranged from 23 to 91 °C. The solution was enclosed in a 500 mL Erlenmeyer flask with a rubber stopper. The rubber stopper contained two feed-throughs for tubes that were used to maintain a constant gas flow through the solution. For experimental temperatures above 50 °C humidified and thermally equilibrated CO_2 gas (same temperature as the solution) was passed through the $CaCO_3$ solution at a rate of ∼ 0.03–0.1 $mL\,s^{-1}$ to prevent carbonate precipitation before complete isotopic equilibrium was achieved. The CO_2 gas was humidified and adjusted to the experimental temperature by bubbling it slowly through an Erlenmeyer flask filled with de-ionized water and contained in the temperature-controlled water bath. At temperatures below 50 °C the Erlenmeyer flask was closed for isotopic equilibration with the water and stored containing a pure CO_2 gas phase above the solution. The equilibration period varied between 3 h at 91 °C and 23 h at 23 °C. pH values during equilibration are below pH 6 in case of the continuous CO_2 bubbling.

After equilibration NaCl was added, reaching a concentration of $5.0 \pm 0.9\,mol\,L^{-1}$. The added NaCl (Sigma Aldrich®) has a purity of ≥ 99 % and contains minor traces of sulphates (≤ 200 ppm), alkaline Earth metals (≤ 100 ppm) and bromides (≤ 100 ppm). Carbonate precipitation was induced by slowly bubbling N_2 tank gas (BOC UK, normal grade) through the solution. The N_2 gas was humidified and adjusted to the experiment temperature using the same procedure as for the CO_2 gas. The bubbling rate was set to about 1 bubble per second (∼ 0.03 $mL\,s^{-1}$). Minerals always formed on the bottom or the side walls of the Erlenmeyer flask. No crystals were observed on the surface of the solution. After 2–19 days the solution was passed through a double-layer of Whatman® filter paper (grade 1). Crystals on the glass walls were loosened by a thin PVC plastic tube and flushed out with de-ionized water. The precipitated minerals were air-dried at room temperature before microscopic and XRD analysis.

3 Samples

3.1 Mineral description, microscopy and SEM

Depending on the experiment temperature and duration between 5 and 235 mg $CaCO_3$ was precipitated (Tables 1 and 2). Low carbonate recovery < 20 mg is linked to short experiment duration (3–6 days) at lower temperatures (< 70 °C, Table 2). In contrast, experiments with a longer duration of 14–24 days at temperatures ≤ 50 °C yielded on average 135 mg. At 80–90 °C it was sufficient to allow two days for mineral precipitation to obtain 80–90 mg calcite. Note that in all experiments the initially dissolved amount of calcite was similar at about 360 (±20) mg in 500 mL de-ionized water (Table 1).

Vaterite can be distinguished by its morphology from other $CaCO_3$ polymorphs. Calcite rhombohedra and aragonite needles can be easily recognized by light microscopy (e.g., Fig. 2c). Vaterite crystals can be similar in size, but are more irregular and show a spherulitic shape (Figs. 3 and 4). Inspection of large vaterite crystals under normal and polarized light reveals a complex growth history. Various globular segments of 50–100 µm with an internal spherulitic growth pattern coalesce into one larger crystal (Fig. 4). Vaterite crystals showed a typical size of 50 µm (Figs. 2–4), whereas in a few experiments crystals of up to 500 µm were observed. Experiments at 70 and 91 °C resulted also in vaterite crystals in the 50 µm size range, however, these are composed of many small (~ 10 µm) globular sub-segments. A peculiarity of vaterite crystals precipitated at 23 °C is the combination of rounded, spherical shapes

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with angular forms (Fig. 3a). Together with the larger crystals sizes observed at this temperature it points towards slower mineral growth.

Scanning-electron microscope (SEM) images were made at the Institute of Earth Sciences at Heidelberg University to investigate the morphology in more detail. The scanning electron microscope LEO 440 was used for imaging. It has a tungsten cathode, was operated at an accelerating voltage of 20 kV and enables a minimal resolution of ca. 5 nm. Samples were sputtered with a thin gold layer for imaging and with carbon for elemental analysis. A summary with characteristic vaterite aggregates is shown in Fig. 5. The size of individual grains that make up the vaterite aggregates decreases with increasing temperature, from about 100 µm at 23 °C, 10–20 µm at 50 °C, to $<$ 10 µm at 91 °C. The minerals show a radial growth pattern from a central nucleus leading to spherical conglomerate particles (Fig. 5a). This pattern gets increasingly disordered at higher temperatures with chaotic aggregation of small grains, but still spherical shape at 50 °C (Fig. 5b), eventually leading to the growth of flat platelets at 91 °C (Fig. 5c). The radiating growth pattern at 91 °C is restricted to two dimensions with a tree-like branching structure characteristic for diffusion-controlled dentritic crystallization (Fig. 5d).

Additional elemental analyses on carbon-sputtered vaterite grains using the SEM at Heidelberg University revealed minor traces of sodium and chloride to be occasionally incorporated in the vaterite mineral.

3.2 XRD analysis

The carbonate samples were analysed at the National History Museum London using an Enraf Nonius FR 590 Powder Diffractometer with Cu-Kα radiation (40 kV, 35 mA). In brief, the sample powder was placed as thin layer on a sapphire substrate and measured in a fixed beam-sample-detector geometry. Analysis times were adjusted to the counting statistics and varied between 10 and 90 min. Signals and phase fractions were evaluated by comparing measured spectra with a mineral data base using the program X'Pert Highscore (PANalytical B.V., 2009). Peak positions were calibrated with

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two standards (silver behenate and quartz). For phase quantification a pure calcite and aragonite standard was measured additionally.

For most samples the dominant XRD peaks were found at 20.98 (±0.04), 24.86 (±0.02), 27.03 (±0.03), 32.74 (±0.03), 43.79 (±0.09), and 50.0 (±0.04)° (2θ, Fig. 6). In contrast, the characteristic and dominant calcite peak of the calcite standard is observed at 29.46°; those of the aragonite calibration standard are at 26.36, 27.35, 33.25, and 46.01° (2θ, Fig. 7). Thus, our laboratory $CaCO_3$ samples are clearly different from aragonite and calcite, but coincide with the XRD data and d-spacing of vaterite. Kabalah-Amitai et al. (2013) measured vaterite d-spacing of 2.07 and 3.63Å, corresponding to 43.69 and 24.50° (2θ at Cu-Kα radiation). Earlier work of Dupont et al. (1997) determined similar d-spacing values of 4.254, 3.591, 3.307, 2.741, 2.07, and 1.826 Å, corresponding to 20.86, 24.77, 26.94, 32.64, 43.69, and 49.90° (2θ at Cu-Kα radiation). Our own results are close to these values confirming the precipitates to be composed of vaterite. In case of the 37 °C experiment additionally calcite is present as minor phase (about 5 %, visible in the peak at 29.46°, Fig. 6), whereas it is less than 1 % in the 91 °C experiment. The dominant mineral phase at 80 °C is calcite, with almost equal proportions of aragonite and vaterite (Table 2, Fig. 7). Aragonite is also a minor phase at the 91 °C experiment (6 %, Fig. 6).

3.3 Isotope analysis

Oxygen, carbon and clumped isotopes were analyzed at the Qatar Stable Isotope Laboratory at Imperial College. Details of the sample preparation and mass spectrometric procedures are given in Kluge and John (2014). In brief, per analysis ~ 5 mg sample was dissolved in ortho-phosphoric acid at 70 °C (a few samples at 90 °C) to produce CO_2 for the mass spectrometric measurement. The CO_2 is cleaned manually comprising of a step for cryogenic water separation and one for contaminant removal via porous polymers (Porapak™ Q). Analyses were done at two dual inlet isotope ratio mass spectrometers (Thermo Scientific MAT 253) that measure alternately sample and reference gas. Individual analyses have a precision of 0.2 ‰ for

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$\delta^{18}O$, 0.1 ‰ for $\delta^{13}C$, and 0.02 ‰ for Δ_{47}, based on replicate analyses of standards. Samples were measured repeatedly (typically 3 times) to reduce the uncertainty.

Carbonate $\delta^{18}O$ values follow the trend determined by the temperature-dependent isotopic fractionation between water and calcite (Fig. 8). For calculation of the expected carbonate $\delta^{18}O$ values we used a water value of -6.7 ± 0.9 ‰ and the fractionation factors of Kim and O'Neil (1997). The water $\delta^{18}O$ value corresponds to surface and ground water values of the London Metropolitan area (Darling, 2003) and was confirmed via back-calculation of aragonite and calcite samples with known fractionation factors and experimental temperature (see Kluge and John, 2014). For all experiments, the water was taken from the local water supply and therefore fluctuates slightly around the mean value (±0.9 ‰ for the back-calculated solution $\delta^{18}O$ value).

$\delta^{13}C$ values vary between −18 and −26 ‰ and reflect the negative signature of the CO_2 tank gas used during the equilibration phase (Table 2). $\delta^{13}C$ values do not show a temperature dependence. Clumped isotope Δ_{47} values of vaterite samples decrease with increasing temperature and are similar to calcite or aragonite-calcite mixtures precipitated at the same temperature (Fig. 9).

4 Discussion

Vaterite was obtained over the entire experimental temperature range of 23–91 °C. It is detected either as the only phase (23, 50, 70 °C) or as the major phase (≥ 94 %) with minor contributions from calcite or aragonite (37, 91 °C). An exception is the experiment at 80 °C where all anhydrous $CaCO_3$ polymorphs were precipitated simultaneously. On average 80 mg vaterite was formed per experiment. This amount may be increased by longer experiment runs or by up-scaling of the setup using larger beakers with the same solution concentrations. A longer experiment duration appears to be the most effective approach. Considering the experiments from 23 to 70 °C only, the yield increases exponentially with the duration, reaching a recovery rate (relative to the initially dissolved $CaCO_3$) of 70 % after ~ 570 h (Fig. 10). Extrapolating the trend, about

700 h should be sufficient to recover almost the entire amount of initially dissolved $CaCO_3$. Another option of increasing the $CaCO_3$ super-saturation in the initial solution was not tested, but has to be treated carefully. A higher initial chemical potential may produce a higher yield but also lead to the precipitation of other forms of $CaCO_3$ such as ikaite (calcium carbonate hexahydrate, $CaCO_3(H_2O)_6$) or amorphous calcium carbonate (Kawano et al., 2009).

This study shows that vaterite precipitation is not limited to a certain temperature range, e.g., to room temperature, but can be performed at least from 23 to 91 °C. A pressurized reaction vessel that prevents boiling of the solution could be used to extend vaterite mineral formation to much higher temperatures (e.g., Kluge et al., 2013). A thermally and isotopically equilibrated $CaCO_3$ super-saturated solution could be injected into the thermally equilibrated and saturated NaCl solution of a pressurized reaction vessel.

The detection of vaterite minerals over the large temperature interval of this study and its predominating character is surprising, given that many other studies emphasized the low stability of vaterite (McConnel, 1959; Others). McConnel (1959) states that vaterite dissolves at room temperature at contact with water. However, our precipitates were air-dried at room temperature on Whatman® filter paper and stayed wet for a few hours, but did not transform into calcite. Furthermore, vaterite minerals were stored for many weeks up to a year before being analyzed by XRD and SEM. Despite long storage periods vaterite did not transform into other $CaCO_3$ polymorphs and implies that vaterite can be precipitated and stored for periods that are long enough to enable precise and detailed experimental analyses. Independent evidence for the stability of vaterite over years comes from biogenic samples such as bivalves, mollusks and other marine organism (Lowenstamm and Abbott, 1975; Spann et al., 2010; Nehrke et al., 2012).

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4.1 Isotopic analysis of vaterite

The long equilibration procedure used in our experimental approach (Table 1) enables isotopic equilibration between the dissolved inorganic carbon (DIC) and water and among the DIC species. 99 % equilibrium between oxygen isotopes in water and DIC takes about 9 h at 25 °C and a pH of ~ 8, whereas it is less than 2 h at temperatures above 40 °C (Beck et al., 2005). For comparison, the equilibration duration was 23 h at 23 °C, 14–21 h at 37.5 °C, and 3–17 h above 40 °C (Table 1). This provides the necessary basis for a meaningful isotopic analysis of the precipitated vaterite which has not been attempted in a systematic manner so far.

Beyond the isotopic equilibration of the DIC with water, the precipitation rate and the ionic concentration of the solutions can affect isotope values. In some techniques two solutions are mixed leading to almost instantaneous precipitation (e.g., Nebel and Epple, 2008). As rapid mineral growth may induce disequilibrium fractionation related to a mineral surface effect (Watson, 2004; Dietzel et al., 2009; Watson and Müller, 2009; DePaolo, 2011; Reynard et al., 2011; Gabitov et al., 2012; Gabitov, 2013) these experiments are not suitable for isotope studies.

Traditionally, vaterite was synthesized from mixtures of $CaCl_2$, K_2CO_3 (Kamhi, 1963) and admixtures of calgon (McConnell, 1960) or included other surfactants (Mori et al., 2009). In other experiments a $CaCO_3$ super-saturated solution was treated with surfactants (Dupont et al., 1997) or polymeric substances (Kirboga and Oner, 2013). In few experiment Na_2CO_3 replaced K_2CO_3 as solution containing the carbonate ion (Nebel and Epple, 2008). The use of $CaCl_2$ and especially K_2CO_3 could impact on the isotopic values of the forming minerals via preferential fractionation related to the hydration sphere of the Ca^{2+} and K^+ ions (Taube, 1954; Sofer and Gat, 1972; O'Neil and Truesdell, 1991) and, thus, should either be restricted to low concentrations or avoided. Our method uses only NaCl as additive that has been confirmed not to affect the isotope values of the DIC (e.g., O'Neil and Truesdell, 1991).

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Before discussing the measured vaterite $\delta^{18}O$ values and its implication for the oxygen isotope fractionation factor $\alpha_{CaCO_3\text{-}H_2O}$ we note that we did not analyze the oxygen isotope composition of the solution per se. However, as the solution water is ultimately taken from the local water supply that reflects the London Metropolitan ground- and surface water $\delta^{18}O$ of −6 to −7‰ (Darling, 2003) and which is cross-examined by values from independent NaCl-free experiments carried out in parallel, we have a defined reference water $\delta^{18}O$ value (−6.7 ± 0.9‰, see Sect. 3.3). Thus, our results give a first order guideline with respect to the temperature dependence of $\alpha_{CaCO_3\text{-}H_2O}$ and can provide an upper limit for the deviation of the fractionation factor of vaterite compared to aragonite and calcite.

$\delta^{18}O$ values of vaterite closely follow values calculated using the fractionation factor $\alpha_{CaCO_3\text{-}H_2O}$ of Kim and O'Neil (1997) for calcite (Fig. 8). The average deviation is −0.2 ± 0.9‰ and, thus, the vaterite oxygen isotope fractionation factor $\alpha_{CaCO_3\text{-}H_2O}$ cannot be distinguished from that of calcite. Excluding two repeat experiments with slightly larger deviations (NA-4, NA-6), that were performed several months subsequent to the rest of the experiments and that were potentially influenced by isotopically different source water, the deviation between vaterite and calcite is only 0.2 ± 0.4‰ (±1.0‰ taking into account the uncertainty of the source water of ±0.9‰). Tarutani et al. (1969) observed vaterite to be enriched in ^{18}O by 0.5‰ relative to calcite at 25 °C. Kim and O'Neil (1997) detected a similar difference of 0.6‰ at 25 and 40 °C. Our experiments are consistent with both studies and constrain these values over the larger temperature range from 23–91 °C.

Carbonate clumped isotope Δ_{47} values are only determined by the mineral formation temperature at equilibrium conditions and are independent of the solution $\delta^{18}O$ and $\delta^{13}C$ values (for reviews see e.g., Eiler, 2007, 2011). We use the Δ_{47}-T calibration of Kluge et al. (2013) as reference relationship as it was determined in the same laboratory using the same preparation and measurement techniques (T in K, Δ_{47} in ‰):

$$\Delta_{47}(T) = 0.038009 \times 10^6/T^2 + 0.259 \quad (1)$$

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Equation (1) is given in the absolute reference frame of Dennis et al. (2011). Vaterite Δ_{47} values scatter around the Δ_{47}-T line of Eq. (1) with an average difference of -0.003 ± 0.013 ‰ and, thus, are indistinguishable from the calibration line (Fig. 9). Subtle differences in the mineral structure of the $CaCO_3$ polymorph vaterite appear to be irrelevant for the ^{13}C-^{18}O clumping.

5 Conclusions

Vaterite was successfully synthesized from a NaCl-saturated $CaCO_3$ solution. Vaterite formed between 23 and 91 °C and was generally the single or major phase. The precipitation technique allows thermal and isotopic equilibration of the oxygen and clumped isotopes in the solution. The precipitation technique generally fosters slow mineral formation which enables a meaningful isotopic analysis of the precipitated vaterite. Recovered vaterite amounts of up to 235 mg also permit the precise determination of the clumped isotope value at each experiment temperature which requires a relatively large sample aliquot of 5 mg per replicate measurement.

The oxygen isotope fractionation between water and the vaterite mineral follows within uncertainty the same slope as calcite, but is offset by $+0.2 \pm 1.0$ ‰. Clumped isotope Δ_{47} values are indistinguishable from calibration data (difference of -0.003 ± 0.013 ‰). The presented precipitation technique for vaterite, in particular the possibility for thermal and isotopic equilibration, opens research opportunities also for investigation of isotope ratios on this unexplored $CaCO_3$ polymorph.

Appendix

$\delta^{18}O$, $\delta^{13}C$ and Δ_{47} values of samples and calibration standards are provided in the supplementary data file.

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Table 1. Experimental conditions during laboratory precipitation of $CaCO_3$ (see Sect. 2).

Experiment No.	T (°C)	$CaCO_{3,dissolved}$ ($g\,L^{-1}$)	NaCl added ($g\,L^{-1}$)	equilibration (h)	precipitation (h)
NA-1	23.5 ± 0.5	0.68	200	23	451
NA-3*	37.5 ± 0.5	0.70	260	21	72
NA-4	37.5 ± 0.5	0.74	244	14	341
NA-5	49.6 ± 0.5	0.70	300	16	143
NA-6	49.6 ± 0.5	0.80	262	17	573
NA-7	69.9 ± 0.5	0.70	260	3	69
NA-8	79.9 ± 0.5	0.78	280	3	47
NA-9	91.0 ± 0.5	0.70	260	3	42

* NA-2 differed in the experimental conditions and is therefore omitted.

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Table 2. Mineralogical and isotopic results of the vaterite precipitation experiments. The mineralogy was determined by XRD analysis (Sect. 3.2). n gives the number of replicates measured for isotopic analysis. The Δ_{47} value is given in the absolute reference frame of Dennis et al. (2011) and is corrected for the acid digestion reaction.

Experiment No.	T (°C)	$CaCO_{3,precipitated}$ (mg)	$\delta^{18}O$ (‰)	$\delta^{13}C$ (‰)	Δ_{47} (‰)	n (–)	Mineralogy
NA-1	23.5 ± 0.5	120	−8.57 ± 0.16	−18.21 ± 0.06	0.689 ± 0.003	3	vaterite
NA-3*	37.5 ± 0.5	5	−11.29 ± 0.20	−20.39 ± 0.10	0.639 ± 0.020	1	vaterite (95 %), calcite (5 %)
NA-4	37.5 ± 0.5	50	−13.30 ± 0.37	−26.06 ± 0.18	0.672 ± 0.027	3	vaterite (> 95 %), rest: calcite
NA-5	49.6 ± 0.5	15	−13.85 ± 0.26	−21.39 ± 0.03	0.605 ± 0.005	2	vaterite
NA-6	49.6 ± 0.5	235	−15.06 ± 0.22	−25.26 ± 0.17	0.634 ± 0.008	3	vaterite
NA-7	69.9 ± 0.5	15	−16.92 ± 0.15	−21.71 ± 0.03	0.577 ± 0.010	3	vaterite
NA-8	79.9 ± 0.5	80	−17.54 ± 0.03	−25.86 ± 0.10	0.553 ± 0.018	3	calcite (49 %), aragonite (24 %), vaterite (27 %)
NA-9	91.0 ± 0.5	90	−19.21 ± 0.15	−25.00 ± 0.16	0.545 ± 0.005	5	vaterite (94 %), aragonite (6 %), calcite (< 1 %)

* NA-2 differed in the experimental conditions and is therefore omitted.

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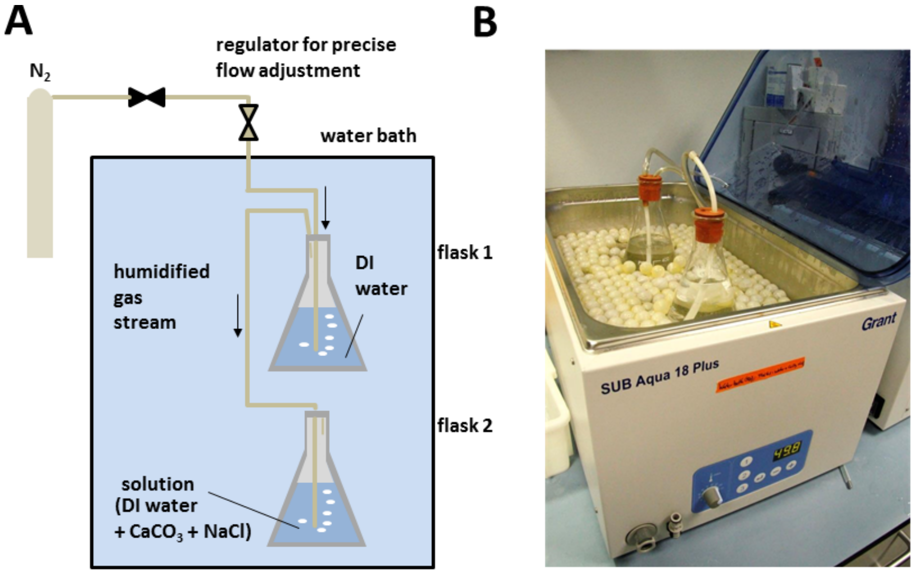

Figure 1. Sketch **(a)** and photograph **(b)** of the experimental setup used to precipitate vaterite. In the first step $CaCO_3$ is dissolved in deionized (DI) water (outside the water bath), which is filtered after > 3 h to remove any un-dissolved component. The solution is then transferred to a temperature-controlled water bath for thermal and isotopic equilibration (flask 2 in **a**). NaCl is added after the equilibration step. Mineral formation is induced by slow bubbling of N_2 trough the solution. The gas stream through the solution in flask 2 is humidified by passing it beforehand through another flask filled with de-ionized water (flask 1).

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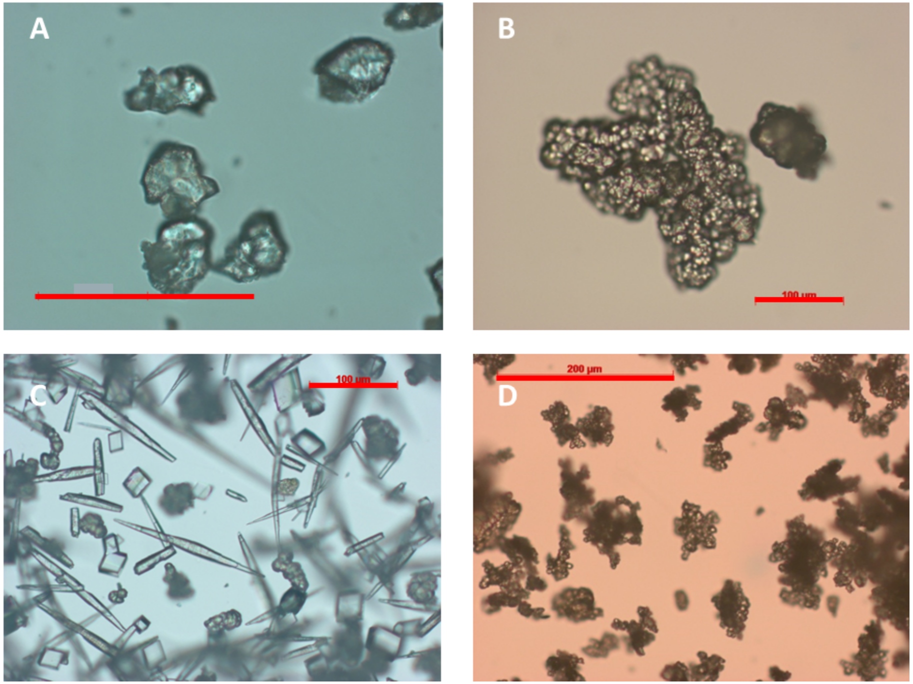

Figure 2. Photomicrographs of $CaCO_3$ minerals precipitated in the laboratory experiment. Scale bar is 100 µm in **(a–c)** and 200 µm in **(d)**. Vaterite crystals formed at 50 °C in experiment NA-6 **(a)**, at 70 °C **(b)** and at 91 °C **(d)**. At 80 °C a mixture of aragonite, calcite and vaterite was precipitated **(c)**.

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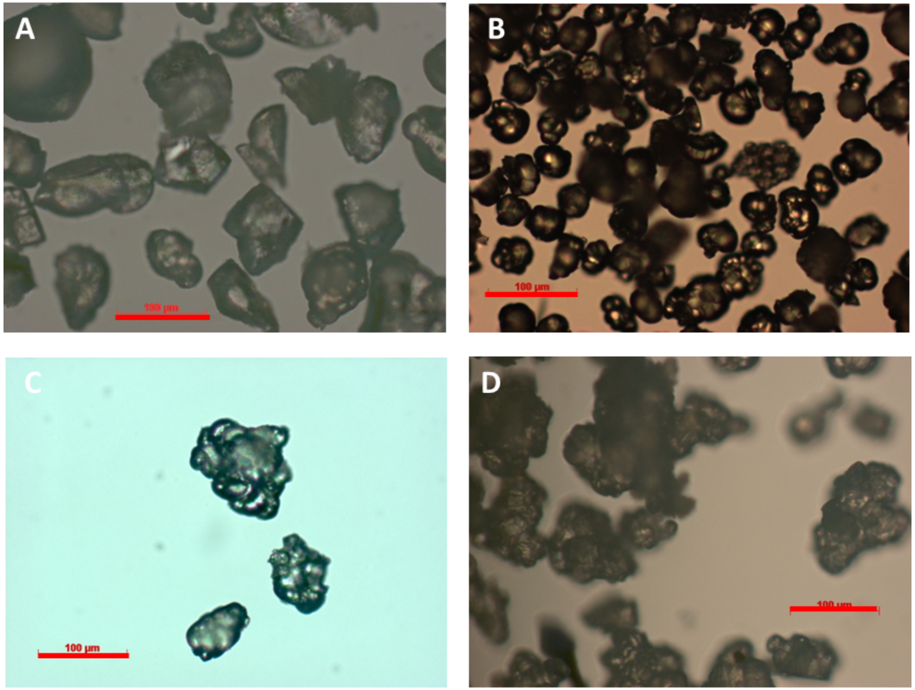

Figure 3. Photomicrographs of $CaCO_3$ minerals precipitated in the laboratory experiments. Scale bar is 100 µm. Vaterite crystals formed at 23 °C **(a)**, at 37 °C in experiment NA-3 **(b)** and NA-4 **(c)** and 50 °C (**d**, NA-5).

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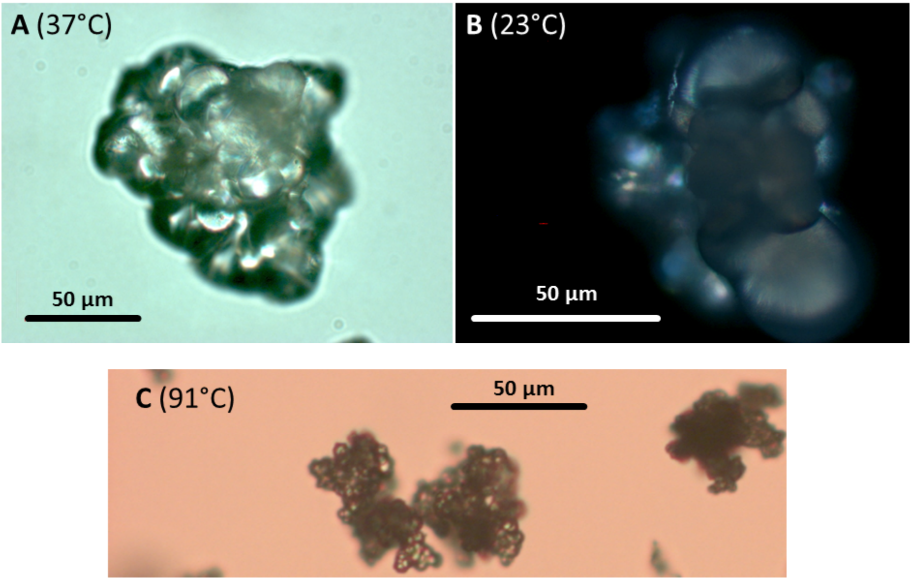

Figure 4. Close-up photomicrographs of vaterite minerals. Scale bar is 50 µm in **(a)** and **(c)** and 200 µm in (b). **(b)** shows a vaterite crystal using polarized light.

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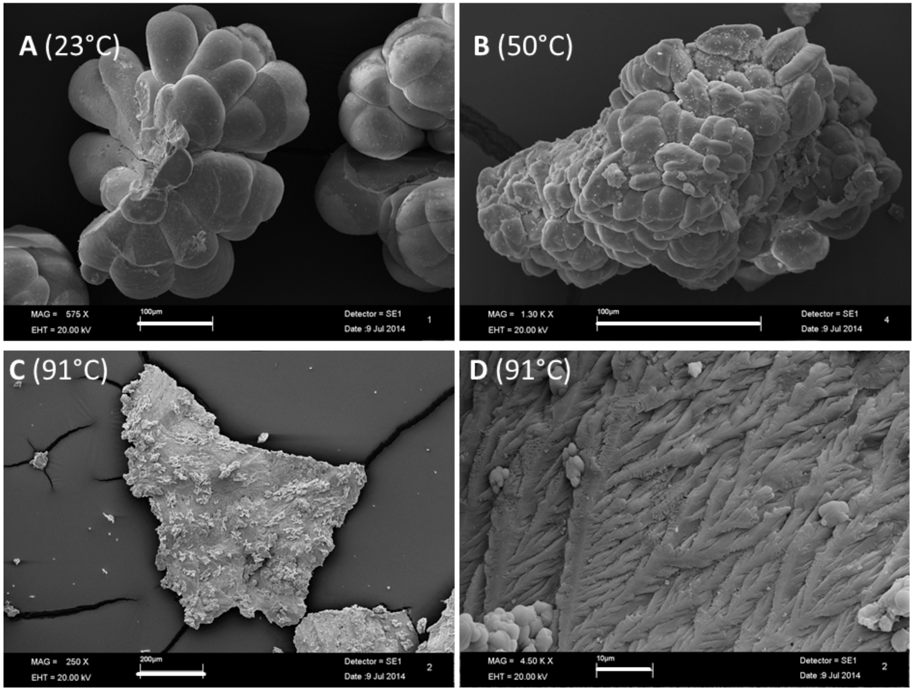

Figure 5. SEM images of vaterite aggregates in the order of increasing precipitation temperatures. Scale bars are 100 µm in (**a** and **b**), 200 µm in **(c)** and 10 µm in **(d)**. Samples NA-1 **(a)**, NA-4 **(b)**, and NA-9 (**c** and **d**) were used for imaging.

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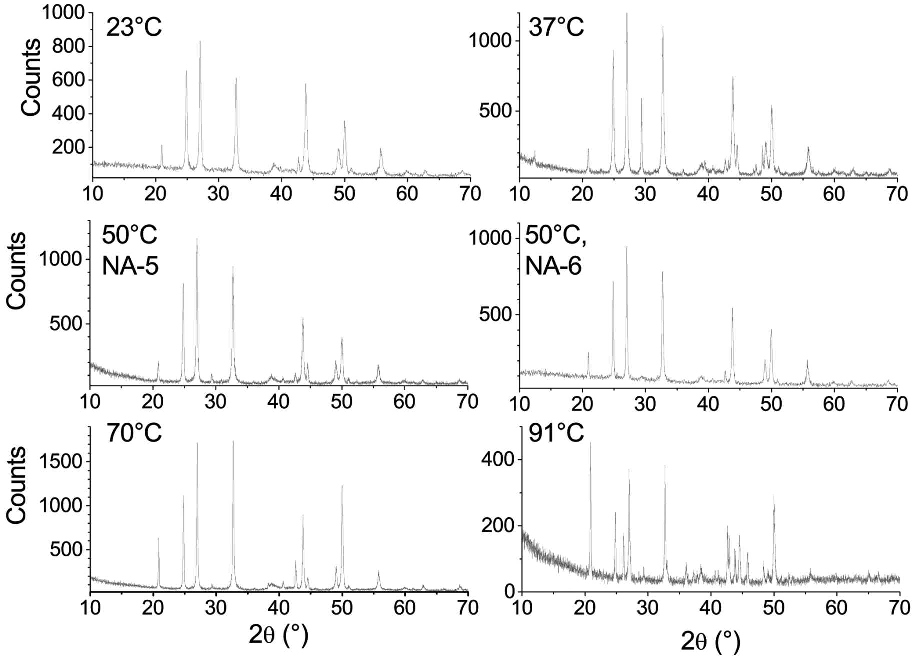

Figure 6. X-ray diffraction pattern of crystals from the laboratory experiments. The minerals that grew at 23 °C show a pure vaterite signal. Similarly, minerals formed at 50 and 70 °C yield an almost pure vaterite signal with a non-quantifiable fraction of calcite (< 1 %). The samples at 37 and 91 °C contain a minor fraction of calcite and aragonite (≤ 6 % in total).

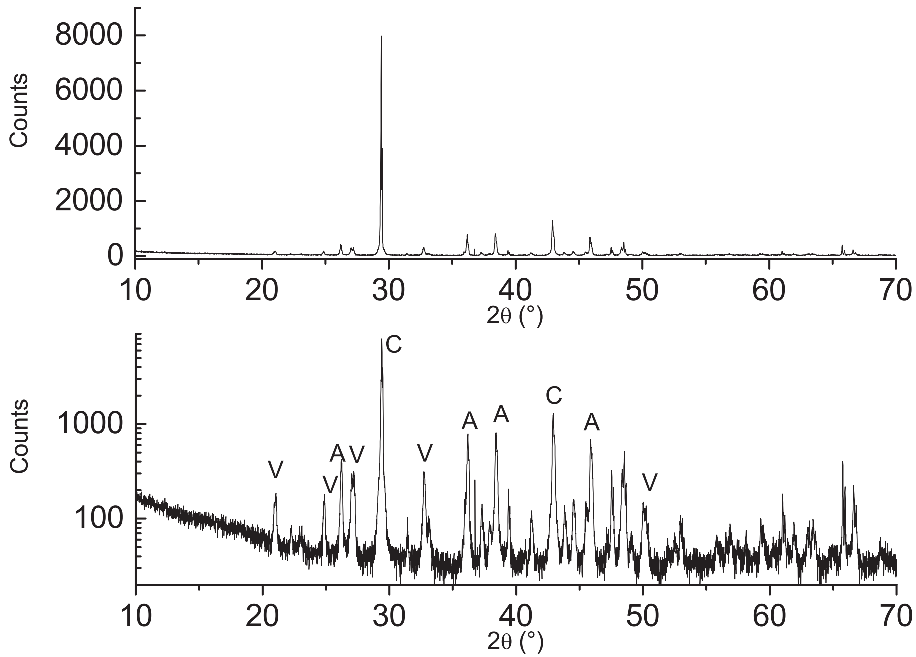

Figure 7. X-ray diffraction pattern of crystals from laboratory experiments. The experiment at 80 °C produced a mixture of calcite, aragonite and vaterite (lower panel). For comparison, the XRD pattern of pure calcite is shown (upper panel). This example shows calcite that precipitated at 25 °C from a pure $CaCO_3$ supersaturated solution without NaCl addition. The peaks in the lower panel are labeled according to the related mineral structure (A: aragonite, C: calcite, V: vaterite).

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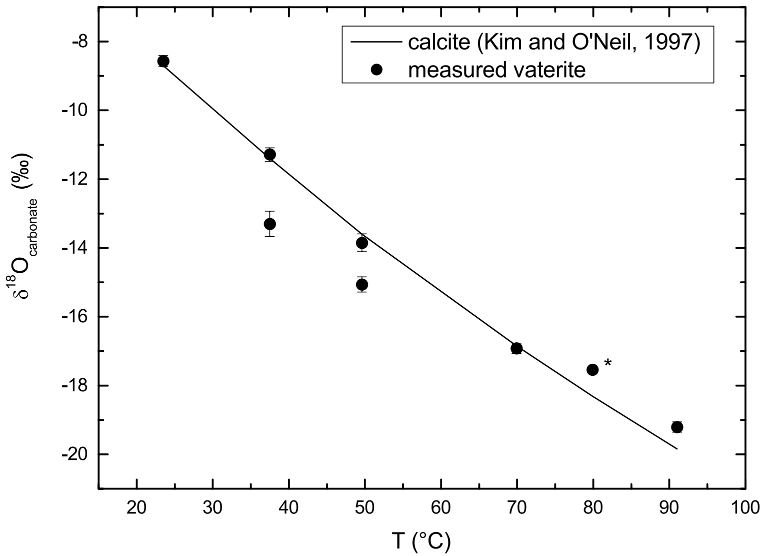

Figure 8. Measured $\delta^{18}O$ values of vaterite (circles) relative to expected values for calcite using the fractionation factor of Kim and O'Neil (1997, solid line). The sample at 80 °C (marked by an asterisk) consists of a mixture of calcite, aragonite and vaterite. The two samples that fall below the calcite reference values belong to repeat experiments and may be influenced by a shift in the solution water $\delta^{18}O$ value (see discussion).

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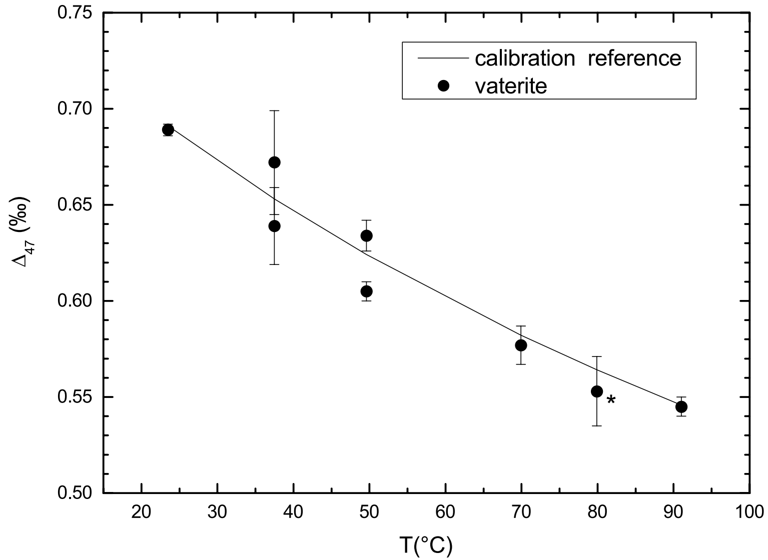

Figure 9. Measured Δ_{47} values of vaterite (circles) relative to expected values following the calibration line of Kluge et al. (2013). The sample at 80 °C (marked by an asterisk) consists of a mixture of calcite, aragonite and vaterite. The calibration line of Kluge et al. (2013) was mainly determined on calcite.

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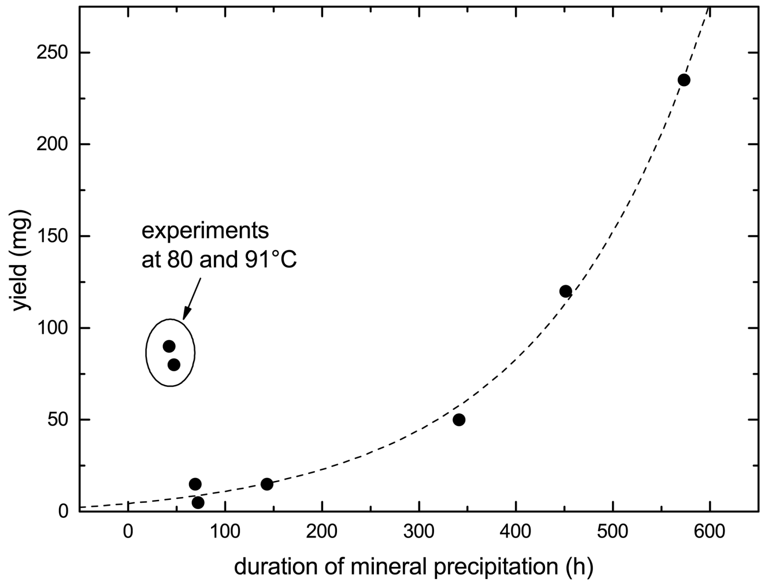

Figure 10. $CaCO_3$ formed per experiment vs. duration. The initially dissolved $CaCO_3$ amount was identical in all experiments (about 370 mg). The yield of experiments conducted below 80 °C follows an exponential relationship with duration.