

1 **A simple method for vaterite precipitation for isotopic**
2 **studies: implications for bulk and clumped isotope**
3 **analysis**

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11

12 **Abstract**

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

20 Synthetic precipitation of vaterite in the laboratory typically involves rapid processes and
21 isotopic non-equilibrium, which excludes isotope studies focused on characterization of
22 vaterite at equilibrium conditions. Here, we used a new experimental approach that enables
23 vaterite mineral formation from an isotopically equilibrated solution. The solution consists of
24 a ~0.007 mol per litre CaCO_3 solution that is saturated with NaCl at room temperature (up to
25 6.4 mol per litre). Vaterite precipitated as single phase or major phase ($\geq 94\%$) in experiments
26 performed between 23 and 91°C. Only at 80°C was vaterite a minor phase with a relative
27 abundance of 27%. The high mineral yield **per experiment** of up to 235 mg relative to the
28 **initially** dissolved CaCO_3 amount of on **average** 360 mg enables an investigation of the

1 oxygen isotope fractionation between mineral and water, and the determination of clumped
2 isotope values in vaterite.

3 **1 Introduction**

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

15 Vaterite occurrence in nature is more widespread than generally assumed. It was first
16 observed in gastropods (Mayer and Weineck, 1932), but later studies discovered vaterite also
17 related to oil field drilling (Friedman and Schultz, 1994), in Portland cement (Friedman and
18 Schultz, 1994), and as stones in the urinary system (Prien and Frondel, 1947; Sutor and
19 Wooley, 1968). Vaterite has not been found in the geologic record and is therefore suspected
20 to be metastable. The observation of vaterite in biogenic systems (Mayer and Weineck, 1932;
21 Spann et al., 2010; Nehrke et al., 2012; Kabalash-Amitai et al., 2013) gives some constraints
22 on its stability which can be on the order of years (Lowenstamm and Abbott, 1975), but not
23 geological ages.

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

1 crystals with sizes between a few 100 nm and a few μm and were mostly restricted to the
2 temperature range of 25°C-60°C.

3 As vaterite is a relevant mineral in biogenic systems (Lowenstamm and Abbott, 1975; Pouget
4 et al., 2009; Spann et al., 2010; Nehrke et al., 2012) it may provide new insights into the
5 isotope fractionation during biological carbonate formation. Vaterite was proposed as a
6 potential precursor phase in biogenic CaCO_3 precipitation, later transforming into aragonite or
7 calcite (e.g., Jacob et al., 2008). Depending on conditions prevailing during the vaterite-
8 aragonite or vaterite-calcite transformation, the original isotope signature may be inherited in
9 the final, stable CaCO_3 phase. To be able to use isotopic tools (for instance, to reconstruct
10 environmental conditions or paleoclimate) on biogenic carbonate with vaterite precursors or
11 remaining vateritic components requires the knowledge of the fractionation factor between
12 vaterite and water, and the clumped isotope $\Delta_{47}\text{-T}$ relationship of vaterite, respectively.

13 However, so far little is known about the oxygen isotope fractionation between dissolved
14 inorganic carbon and vaterite and, in particular, the clumped isotope $\Delta_{47}\text{-T}$ relationship of
15 vaterite. Whereas vaterite was reported in a few stable isotope studies aiming at determining
16 the oxygen isotope fractionation factor in the system $\text{CaCO}_3\text{-H}_2\text{O}$ (e.g., Kim and O'Neil,
17 1997), it rarely occurred as a pure phase and, thus, did not allow for a precise study focused
18 on vaterite. Based on the limited data available Tarutani et al. (1969) suggested vaterite to be
19 enriched in ^{18}O by +0.5 ‰ relative to calcite. Kim and O'Neil (1997) obtained a similar value
20 of +0.6 ‰ with respect to calcite. Both studies were limited to either one (25°C) or two
21 temperatures (25°C, 40°C), and a more comprehensive study is still lacking. In addition, the
22 clumped isotope $\Delta_{47}\text{-T}$ relationship of vaterite has not been assessed so far, but could give
23 new insights into the effect of polymorphism on isotope ratios or mineral growth related
24 isotope fractionation.

25 In this study we present a simple method that allows vaterite precipitation over a wide
26 temperature range (at least between 20 and 91°C) and that provides large quantities of the
27 mineral, enabling for example the investigation of the oxygen isotope fractionation factor
28 between vaterite and H_2O , and the $\Delta_{47}\text{-T}$ relationship of vaterite.

29 **2 Experimental setup**

30 The precipitating solution was prepared by dissolving high-purity CaCO_3 (Merck Suprapur,
31 99.95%) in de-ionized water. Light-microscopy indicates that this CaCO_3 consists of calcite.
32 The water was initially taken from the local water supply, purified with a reverse osmosis

1 technique and finally de-ionized with an UltrapureTM system with an output quality of 18 MΩ
2 cm. Trace components of the CaCO₃ used to prepare the solution are strontium (\leq 100 ppm),
3 rubidium (\leq 20 ppm), sulphate (\leq 20 ppm), and phosphate (\leq 10 ppm).

4 About 370 mg CaCO₃ was dissolved in ~500 ml de-ionized water at room temperature per
5 experiment. The water was acidified by purging of CO₂ tank gas (normal grade, BOC UK)
6 through the solution. The solution was filtered after three hours through a double layer of
7 Whatman® filter paper (grade 1, corresponding to 11 µm filtration size) to remove un-
8 dissolved CaCO₃ crystals. Optical inspection of the filtered water via light reflectance
9 confirmed no large crystals to have bypassed the filtration stage. The dissolution step
10 appeared to be quantitative as no CaCO₃ was visibly retained on the filter paper.

11 The filtered CaCO₃ solution was then thermally and isotopically equilibrated at a set
12 temperature in a temperature-controlled water bath (sketch of the experimental setup is
13 depicted in Fig. 1). The experimental temperatures ranged from 23 to 91°C. The solution was
14 enclosed in a 500 ml Erlenmeyer flask with a rubber stopper. The rubber stopper contained
15 two feed-throughs for tubes that were used to maintain a constant gas flow through the
16 solution. Humidified and thermally equilibrated CO₂ gas (same temperature as the solution)
17 was passed through the CaCO₃ solution (Table 1) at a rate of ~0.03-0.1 ml/s to prevent
18 carbonate precipitation before complete isotopic equilibrium was achieved. The CO₂ gas was
19 humidified and adjusted to the experimental temperature by bubbling it slowly through an
20 Erlenmeyer flask filled with de-ionized water and contained in the temperature-controlled
21 water bath. The equilibration period varied between 3 hours at 91°C and 23 hours at 23°C. pH
22 values during equilibration are below pH 6 due to the continuous CO₂ flux.

23 After equilibration NaCl was added, reaching concentrations between 4.2 and 6.4 mol per litre
24 (Table 1). The added NaCl (Sigma Aldrich®) has a purity of \geq 99% and contains minor traces
25 of sulphates (\leq 200 ppm), alkaline Earth metals (\leq 100 ppm) and bromides (\leq 100 ppm).
26 Carbonate precipitation was induced by slowly bubbling N₂ tank gas (BOC UK, normal
27 grade) through the solution. The N₂ gas was humidified and adjusted to the experiment
28 temperature using the same procedure as for the CO₂ gas. The bubbling rate was set to about 1
29 bubble per second (~0.03 ml/s). The gas stream was humidified to prevent water evaporation
30 and a potential change in the solution δ¹⁸O value over time. Minerals always formed on the
31 bottom or the side wall of the Erlenmeyer flask. No crystals were observed on the surface of
32 the solution. After 2-19 days the solution was passed through a double-layer of Whatman®

1 filter paper (grade 1 with a pore size of 11 μ m). Crystals on the glass walls were loosened by a
2 thin PVC plastic tube and flushed out with de-ionized water. The precipitated minerals were
3 air-dried at room temperature before microscopic and XRD analysis.

4 **3 Samples**

5 **3.1 Mineral description, microscopy and SEM**

6 Depending on the experiment temperature and duration between 5 and 235 mg CaCO₃ was
7 precipitated (Table 1, 2). Low carbonate recovery < 20 mg is linked to short experiment
8 duration (3-6 days) at lower temperatures (< 70°C, Table 2). In contrast, experiments with a
9 longer duration of 14-24 days at temperatures \leq 50°C yielded on average 135 mg. At 80-91°C
10 it was sufficient to allow two days for mineral precipitation to obtain 80-90 mg calcite. Note
11 that in all experiments the initially dissolved amount of calcite was similar at about 360 (\pm 20)
12 mg in 500 ml de-ionized water (Table 1).

13 Vaterite can be distinguished by its morphology from other CaCO₃ polymorphs. Calcite
14 rhombohedra and aragonite needles can be recognized by light microscopy (e.g., Fig 2C).
15 Vaterite crystals can be similar in size, but are more irregular and show a spherulitic shape
16 (Figs. 3, 4). Inspection of large vaterite crystals under normal and polarized light reveals a
17 complex growth history. Various globular segments of 50-100 μ m with an internal spherulitic
18 growth pattern coalesce into one larger crystal (Fig. 4). Vaterite crystals showed a typical size
19 of 50 μ m (Figs. 2, 3, 4), whereas in a few experiments crystals of up to 500 μ m were
20 observed. Experiments at 70°C and 91°C resulted also in vaterite crystals in the 50 μ m size
21 range, however, these are composed of many small (~ 10 μ m) globular sub-segments. A
22 peculiarity of vaterite crystals precipitated at 23°C is the combination of rounded, spherical
23 shapes with sharp angular forms (Fig. 3A). Together with the larger crystals sizes observed at
24 this temperature it points towards slower mineral growth. All minerals of this study were
25 investigated with XRD in addition to optical microscopy. Note, that optical microscopy alone
26 may be ambiguous and should be complemented by additional methods (e.g., XRD).

27 Scanning-electron microscope (SEM) images were made at the Institute of Earth Sciences at
28 Heidelberg University to investigate the morphology in more detail. The scanning electron
29 microscope LEO 440 was used for imaging. It has a tungsten cathode, was operated at an
30 accelerating voltage of 20 kV and enables a minimal resolution of ca. 5 nm. Samples were
31 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 was investigated using SEM images (Figs. 5, 6). The grain size decreases with increasing temperature, from about 100 µm at 23°C, 10-20 µm at 50°C, to <10 µm at 91°C. The relatively large grains detected at 23°C are internally composed of ~2 µm long elongated fibrous crystallites (Fig. 6A). The smallest grains observed at 91°C are of similar size of a few µm. Sub-µm sized crystallites and frambooidal aggregates (e.g., Nehrke and Van Cappellen, 2006) were not observed. The minerals show a radial growth pattern from a central nucleus leading to spherical conglomerate particles (Fig. 5A). The spherical shape is still dominating at 50°C (Fig. 5B), however, changes 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 dendritic crystallization (Fig. 5D).

Additional elemental analyses on carbon-sputtered vaterite grains using the energy-dispersive X-ray spectroscopy (EDS) at the SEM system at Heidelberg University revealed minor traces of sodium and chloride to be occasionally incorporated in the vaterite mineral. Quantitative analysis was not attempted due to the very sporadic and dispersed occurrence of the sodium chloride crystals.

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-K α radiation (40 kV, 35mA). 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 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)° (2 θ , Fig. 7). 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° (2 θ , Fig. 8). Thus, our laboratory CaCO₃ 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 3.63 Å, 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. 7), whereas only traces of calcite are found in the 91°C experiment. An exact quantification of this small calcite fraction was not possible due to a general uncertainty of about 3% in the phase quantification. Half of the mineral phase at 80°C consists of calcite, whereas the other half is made up of equal proportions of aragonite and vaterite (Table 2, Fig. 8). Aragonite is also a minor phase at the 91°C experiment (6 %, Fig. 7).

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 et al. (2015). In brief, per analysis ~5 mg sample was dissolved in orthophosphoric acid at 70°C to produce CO₂ for the mass spectrometric measurement. The CO₂ 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 δ¹⁸O, 0.1 ‰ for δ¹³C, and 0.03 ‰ for Δ₄₇, based on replicate analyses of standards. Samples were measured repeatedly (typically 3 times) to reduce the uncertainty.

Carbonate δ¹⁸O values follow the trend determined by the temperature-dependent isotopic fractionation between water and calcite (Fig. 9). For calculation of the expected carbonate δ¹⁸O values we used the fractionation factors of Kim and O’Neil (1997) and a water value of -6.4 ± 0.7 ‰ (-7.8 ± 0.5 ‰ for the later repeat experiments NA-4 and NA-6). The water δ¹⁸O value was not directly measured but is based on back-calculation of aragonite and calcite samples that were precipitated in close temporal connection (within 3-12 d) of the vaterite experiments using the same water source and the same precipitation technique (see Kluge et al., 2015). The back-calculated water values from the pure Ca(HCO₃)₂ solution used as reference correspond to the observed range of surface and ground water values of the London

1 Metropolitan area (Darling, 2003). For all experiments, the water was taken from the local
2 water supply. Although we have a defined water reference value based on the pure
3 $\text{Ca}(\text{HCO}_3)_2$ solution, we cannot exclude short-term fluctuations of the tap water $\delta^{18}\text{O}$.
4 However, it is unlikely that it exceeds the observed long-term variability of $\pm 0.7 \text{ ‰}$ (June-
5 October 2012) and $\pm 0.5 \text{ ‰}$ (March-April 2013) for the back-calculated solution $\delta^{18}\text{O}$ value.
6 $\delta^{13}\text{C}$ values vary between -18 and -26 ‰ and reflect the negative signature of the CO_2 tank
7 gas used during the equilibration phase (Table 2). $\delta^{13}\text{C}$ values do not show a temperature
8 dependence. Clumped isotope Δ_{47} values of vaterite samples decrease with increasing
9 temperature and are similar to calcite or aragonite-calcite mixtures precipitated at the same
10 temperature (Fig. 10). Δ_{47} values of calcite and calcite-aragonite mixtures were taken from
11 Kluge et al. (2015) for comparison.

12 4 Discussion

13 Vaterite was obtained over the entire experimental temperature range of 23-91°C. It is
14 detected either as the only phase (23, 50, 70°C) or as the major phase ($\geq 94 \text{ %}$) with minor
15 contributions from calcite or aragonite (37, 91°C). An exception is the experiment at 80°C
16 where all anhydrous CaCO_3 polymorphs were precipitated simultaneously. On average 80 mg
17 vaterite was formed per experiment. This amount may be increased by longer experiment runs
18 or by up-scaling of the setup using larger beakers with the same solution concentrations. A
19 longer experiment duration appears to be the most effective approach. Considering the
20 experiments from 23-70°C only, the yield increases exponentially with the duration, reaching
21 a recovery rate (relative to the initially dissolved CaCO_3) of 70% after $\sim 570 \text{ h}$ (Fig. 11).
22 Extrapolating the trend, about 700 h should be sufficient to recover the entire amount of
23 initially dissolved CaCO_3 . Another option of increasing the CaCO_3 super-saturation in the
24 initial solution was not tested, but has to be treated carefully. A higher initial chemical
25 potential may produce a higher yield but also lead to the precipitation of other forms of
26 CaCO_3 such as ikaite (calcium carbonate hexahydrate, $\text{CaCO}_3(\text{H}_2\text{O})_6$) or amorphous calcium
27 carbonate (Kawano et al., 2009).

28 This study shows that vaterite precipitation is not limited to a certain temperature range, e.g.,
29 to room temperature or from 10 to 48°C (Gussone et al., 2011), but can be performed at least
30 up to 91°C. A pressurized reaction vessel that prevents boiling of the solution could be used
31 to extend vaterite mineral formation to much higher temperatures (e.g., Kluge et al., 2015). A

1 thermally and isotopically equilibrated CaCO₃ super-saturated solution could be injected into
2 the thermally equilibrated and saturated NaCl solution of a pressurized reaction vessel.
3 The detection of vaterite minerals over the large temperature interval of this study and its
4 predominating character is surprising, given that many other studies emphasized the low
5 stability of vaterite (McConnel, 1959; Others). McConnel (1959) states that vaterite dissolves
6 at room temperature at contact with water. However, our precipitates were air-dried at room
7 temperature on Whatman® filter paper and stayed wet for a few hours, but did not transform
8 into calcite. Furthermore, vaterite minerals were stored for many weeks up to a year before
9 being analyzed by XRD and SEM. Despite long storage periods vaterite did not transform
10 into other CaCO₃ polymorphs and implies that vaterite can be precipitated and stored for
11 periods that are long enough to enable precise and detailed experimental analyses.
12 Independent evidence for the stability of vaterite over years comes from biogenic samples
13 such as bivalves, mollusks and other marine organism (Lowenstamm and Abbott, 1975;
14 Spann et al., 2010; Nehrke et al., 2012).

15 Isotopic analysis of vaterite

16 Our study presents a well-defined method for the isotopic study of vaterite. The technique for
17 vaterite precipitation was modified from the procedures of McCrea (1950), O’Neil et al.
18 (1969) and Kim and O’Neil (1997) that were developed for isotopic studies on calcite and
19 aragonite minerals. The values of Kim and O’Neil (1997) are commonly used as reference for
20 the oxygen isotope fractionation between calcite and water. Furthermore, for the temperature
21 calibration of clumped isotopes an analogous method was applied to precipitate calcite
22 (Ghosh et al., 2006; Zaarur et al., 2013). The closeness of the methodology for synthetic
23 vaterite and calcite precipitation ensures good comparability of the obtained results with
24 widely used calibration and fractionation data.

25 The long equilibration procedure used in our experimental approach (Table 1) enables
26 isotopic equilibration between the dissolved inorganic carbon (DIC) and water and among the
27 DIC species. 99% equilibrium between oxygen isotopes in water and DIC takes about 9 h at
28 25°C and a pH of ~8, whereas it is less than 2h at temperatures above 40°C (Beck et al.,
29 2005). For comparison, the equilibration duration was 23 h at 23°C, 14-21 h at 37.5°C, and 3-
30 17 h above 40°C (Table 1). This provides the necessary basis for a meaningful isotopic
31 analysis of the precipitated vaterite which has not been attempted in a systematic manner so
32 far.

1 Beyond the isotopic equilibration of the DIC with water, the precipitation rate and the ionic
2 concentration of the solutions can affect isotope values. The growth rate has to be considered
3 in the interpretation of isotope values as differences can be substantial between slow and
4 rapidly grown minerals (up to 2 ‰ for $\delta^{18}\text{O}$; Coplen, 2007; Dietzel et al., 2009; Gabitov et al.,
5 2012). The growth rate in our study was not precisely monitored, but can be estimated from
6 the derivative of the general relationship between experiment duration and mineral yield (Fig.
7 11). The mineral growth for temperatures below 80°C started very slowly with a value of
8 $\sim 1.4 \cdot 10^{-10}$ mol/s and increased exponentially (e.g., to $1.1 \cdot 10^{-9}$ mol/s after 350 h). Converting it
9 relative to the growth surface (using the walls of the Erlenmeyer flask as first order estimate)
10 the growth rate was about $3.7 \cdot 10^{-9}$ mol/(m²s) at the beginning of the mineral formation and
11 increased to $2.9 \cdot 10^{-8}$ mol/(m²s) at 350 h. These values only give an impression of the order of
12 magnitude due to the limitation of the assumptions, but already demonstrate that the mineral
13 formation was unlikely affected by rapid growth disequilibrium that is typically encountered
14 at values above 10^{-7} - 10^{-8} mol/(m²s) (compare e.g., Watkins et al., 2013). In contrast, in other
15 vaterite precipitation techniques two solutions were mixed leading to almost instantaneous
16 precipitation (e.g., Nebel and Epple, 2008). As rapid mineral growth may induce
17 disequilibrium fractionation related to a mineral surface effect (Watson, 2004; Dietzel et al.,
18 2009; Watson and Müller, 2009; DePaolo, 2011; Reynard et al., 2011; Gabitov et al., 2012;
19 Gabitov, 2013) experiments with quasi-instantaneous mineral growth are not suitable for
20 isotope studies. Consequently, we did not rapidly grow vaterite nor conduct isotope
21 measurements on potentially fast growth phases.

22 Traditionally, vaterite was synthesized from mixtures of CaCl₂, K₂CO₃ (Kamhi, 1963) and
23 admixtures of calgon (McConnell, 1960) or included other surfactants (Mori et al., 2009). In
24 other experiments a CaCO₃ super-saturated solution was treated with surfactants (Dupont et
25 al., 1997) or polymeric substances (Kirkboga and Oner, 2013). In few experiment Na₂CO₃
26 replaced K₂CO₃ as solution containing the carbonate ion (Nebel and Epple, 2008). The use of
27 CaCl₂ and especially K₂CO₃ could impact on the isotopic values of the forming minerals via
28 preferential fractionation related to the hydration sphere of the Ca²⁺ and K²⁺ ions (Taube,
29 1954; Sofer and Gat, 1972; O'Neil and Truesdell, 1991) and, thus, should either be restricted
30 to low concentrations or avoided. Our method uses only NaCl as additive that has been
31 confirmed not to affect the isotope values of the DIC (e.g., O'Neil and Truesdell, 1991).

1 Before discussing the measured vaterite $\delta^{18}\text{O}$ values and its implication for the oxygen isotope
2 fractionation factor $\alpha_{\text{CaCO}_3\text{-H}_2\text{O}}$ we note that we did not analyze the oxygen isotope
3 composition of the solution *per se*. However, as the solution water is ultimately taken from
4 the local water supply that reflects the London Metropolitan ground- and surface water $\delta^{18}\text{O}$
5 of -6 to -8 ‰ (Darling, 2003) and which is cross-examined by values from independent NaCl-
6 free experiments carried out in parallel, we have a defined reference water $\delta^{18}\text{O}$ value (-
7 6.4±0.7 ‰, -7.8±0.5 ‰ for the later repeat experiments NA-4 and NA-6, see section 3.3).
8 Thus, our results give a first order guideline with respect to the temperature dependence of
9 $\alpha_{\text{CaCO}_3\text{-H}_2\text{O}}$ and can provide an upper limit for the deviation of the fractionation factor of
10 vaterite compared to aragonite and calcite. We compare our values to data of Kim and O’Neil
11 (1997) due to similar experimental procedures and their universal use. Note that the exact
12 value of the equilibrium oxygen isotope fractionation factor for calcite is under debate
13 (Coplen, 2007; Dietzel et al., 2009; Gabitov et al., 2012; Kluge et al., 2014).

14 The fractionation $1000\ln\alpha_{(\text{CaCO}_3\text{-H}_2\text{O})}$ of vaterite closely follows the values of Kim and O’Neil
15 (1997) for calcite (Fig. 9). Over the entire experimental temperature range vaterite values
16 agree within uncertainty with the calcite values. Repeat experiments at 37 and 50°C confirm
17 the initial results by providing almost identical fractionation factors. The average deviation is
18 0.0±0.4 ‰ and, thus, the vaterite oxygen isotope fractionation factor $\alpha_{\text{CaCO}_3\text{-H}_2\text{O}}$ cannot be
19 distinguished from that of calcite. Tarutani et al. (1969) observed vaterite to be enriched in
20 ^{18}O by 0.5 ‰ relative to calcite at 25°C. Kim and O’Neil (1997) detected a similar difference
21 of 0.6 ‰ at 25 and 40°C. Our experiments are consistent with both studies indicating a small
22 or negligible difference of the fractionation $\alpha_{\text{CaCO}_3\text{-H}_2\text{O}}$ between vaterite and calcite. Our study
23 additionally constrains this value over the larger temperature range from 23-91°C.

24 Carbonate clumped isotope Δ_{47} values are only determined by the mineral formation
25 temperature at equilibrium conditions and are independent of the solution $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$
26 values (for reviews see e.g., Eiler, 2007, 2011). We use the Δ_{47} -T calibration of Kluge et al.
27 (2015) as reference relationship as it was determined in the same laboratory using the same
28 preparation and measurement techniques (T in K, Δ_{47} in ‰):

$$\Delta_{47}(T) = 0.98 \cdot (-3.407 \cdot 10^9 / T^4 + 2.365 \cdot 10^7 / T^3 - 2.607 \cdot 10^3 / T^2 - 5.880 / T) + 0.293 \quad (1)$$

30 Equation (1) is given in the absolute reference frame of Dennis et al. (2011). Vaterite Δ_{47}
31 values scatter around the Δ_{47} -T line of Eq. (1) with an average difference of -0.003 ± 0.013 ‰
32 and, thus, are indistinguishable from the calibration line (Fig. 10). Subtle differences in the

1 mineral structure of the CaCO₃ polymorph vaterite appear to be irrelevant for the ¹³C-¹⁸O
2 clumping.

3 **5 Conclusions**

4 Vaterite was successfully synthesized from a NaCl-saturated CaCO₃ solution. Vaterite formed
5 between 23 and 91°C and was generally the single or major phase. The precipitation
6 technique allows thermal and isotopic equilibration of the oxygen and clumped isotopes in the
7 solution. The precipitation technique fosters slow mineral formation which enables a
8 meaningful isotopic analysis of the precipitated vaterite. Recovered vaterite amounts of up to
9 235 mg also permit the precise determination of the clumped isotope value at each experiment
10 temperature which requires a relatively large sample aliquot of 5 mg per replicate
11 measurement.

12 The oxygen isotope fractionation between water and the vaterite mineral **agrees** within
13 uncertainty with calcite (**average difference 0.0±0.4 ‰**). Clumped isotope Δ_{47} values are
14 indistinguishable from calibration data (difference of -0.003 ± 0.013 ‰). The presented
15 precipitation technique for vaterite, in particular the possibility for thermal and isotopic
16 equilibration, opens research opportunities also for investigation of isotope ratios on this
17 unexplored CaCO₃ polymorph.

18 **Appendix A**

19 $\delta^{18}\text{O}$, $\delta^{13}\text{C}$ and Δ_{47} values of samples and calibration standards are provided in the
20 supplementary data file.

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29

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- 30

1 Table 1. Experimental conditions during laboratory precipitation of CaCO₃ (see section 2).

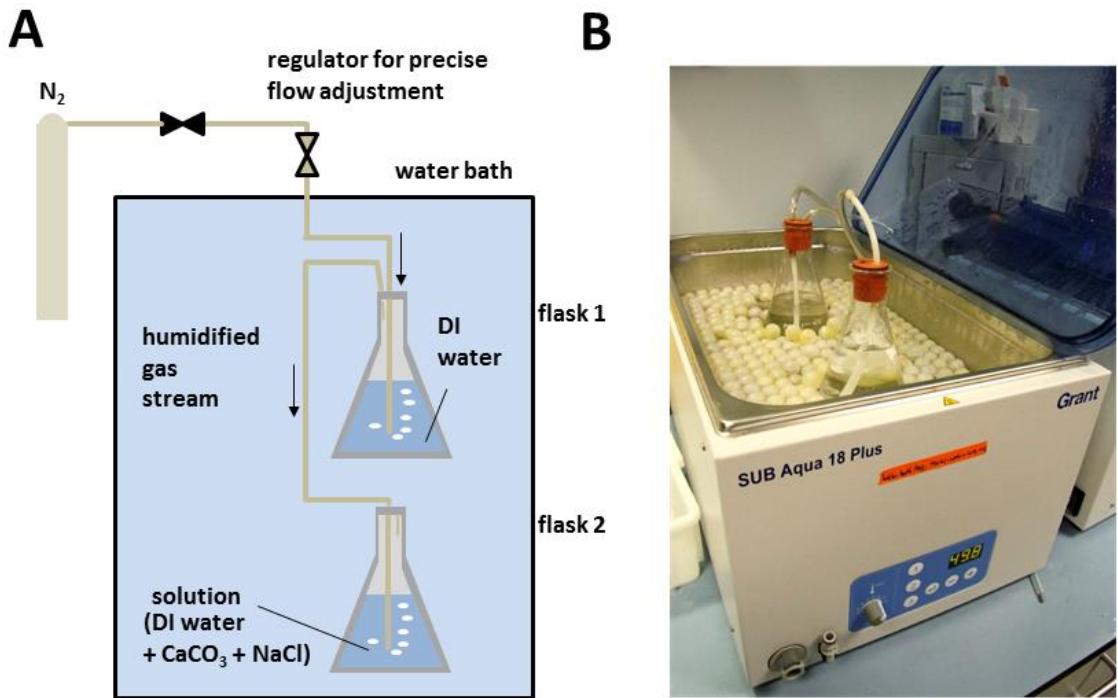
Experiment No.	T (°C)	CaCO _{3,dissolved} (g/l)	NaCl added (g/l)	equilibration (h)	precipitation (h)
NA-1	23.5±0.5	0.68	250	23	451
NA-3 ^a	37.5±0.5	0.70	260	21	72
NA-4	37.5±0.5	0.74	244	14	341
NA-5	49.6±0.5	0.70	375	16	143
NA-6	49.6±0.5	0.80	262	17	573
NA-7	69.9±0.5	0.70	325	3	69
NA-8	79.9±0.5	0.78	280	3	47
NA-9	91.0±0.5	0.70	260	3	42

2 ^aNA-2 differed in the experimental conditions and is therefore omitted

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

Experiment No.	T (°C)	CaCO ₃ precipitated (mg)	$\delta^{18}\text{O}$ (‰)	$\delta^{13}\text{C}$ (‰)	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 ^a	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 (traces)

5 ^aNA-2 differed in the experimental conditions and is therefore omitted



1
2 Figure 1. Sketch (A) and photograph (B) of the experimental setup used to precipitate vaterite.
3 In the first step CaCO₃ is dissolved in deionized (DI) water (outside the water bath), which is
4 filtered after >3h to remove any un-dissolved component. The solution is then transferred to a
5 temperature-controlled water bath for thermal and isotopic equilibration (flask 2 in A). NaCl
6 is added after the equilibration step. Mineral formation is induced by slow bubbling of N₂
7 trough the solution. The gas stream through the solution in flask 2 is humidified by passing it
8 beforehand through another flask filled with de-ionized water (flask 1).

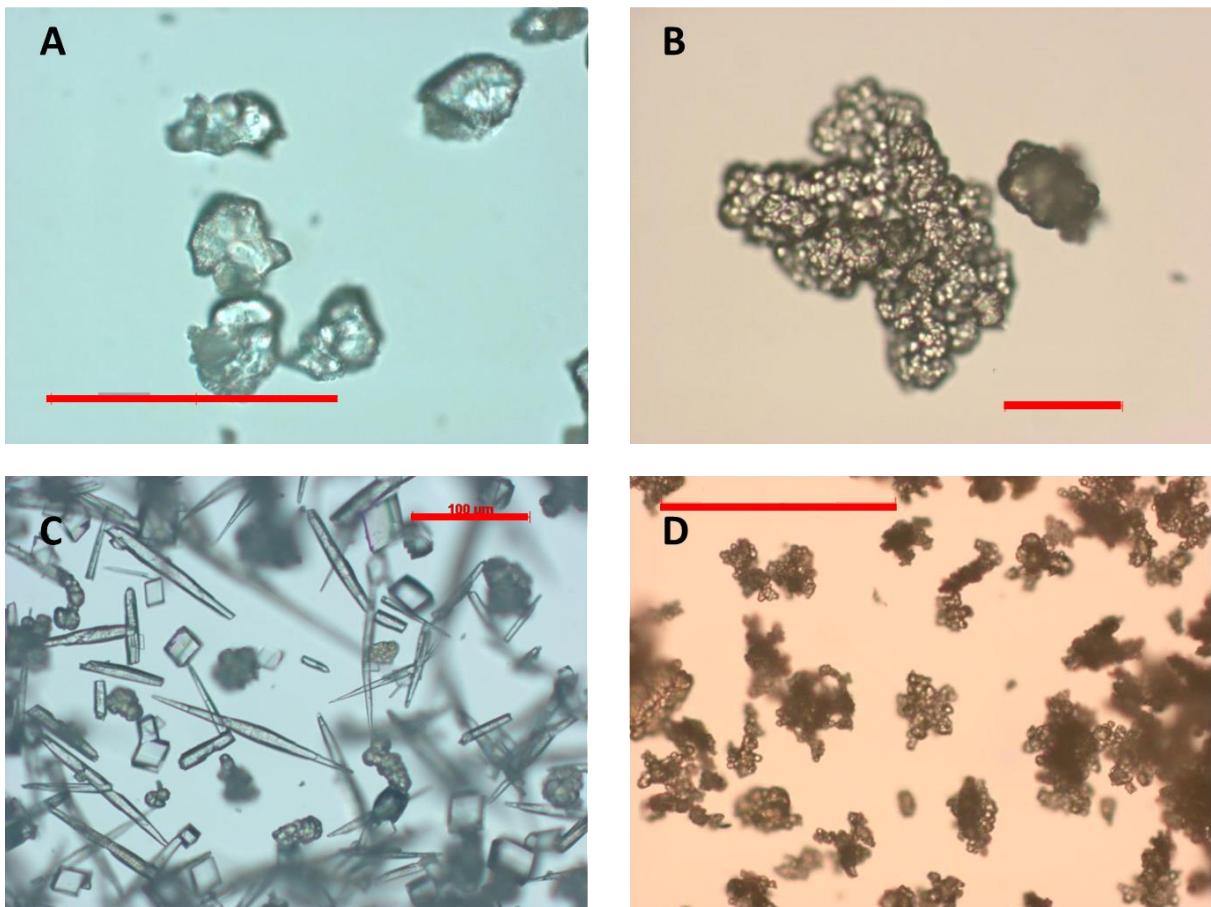
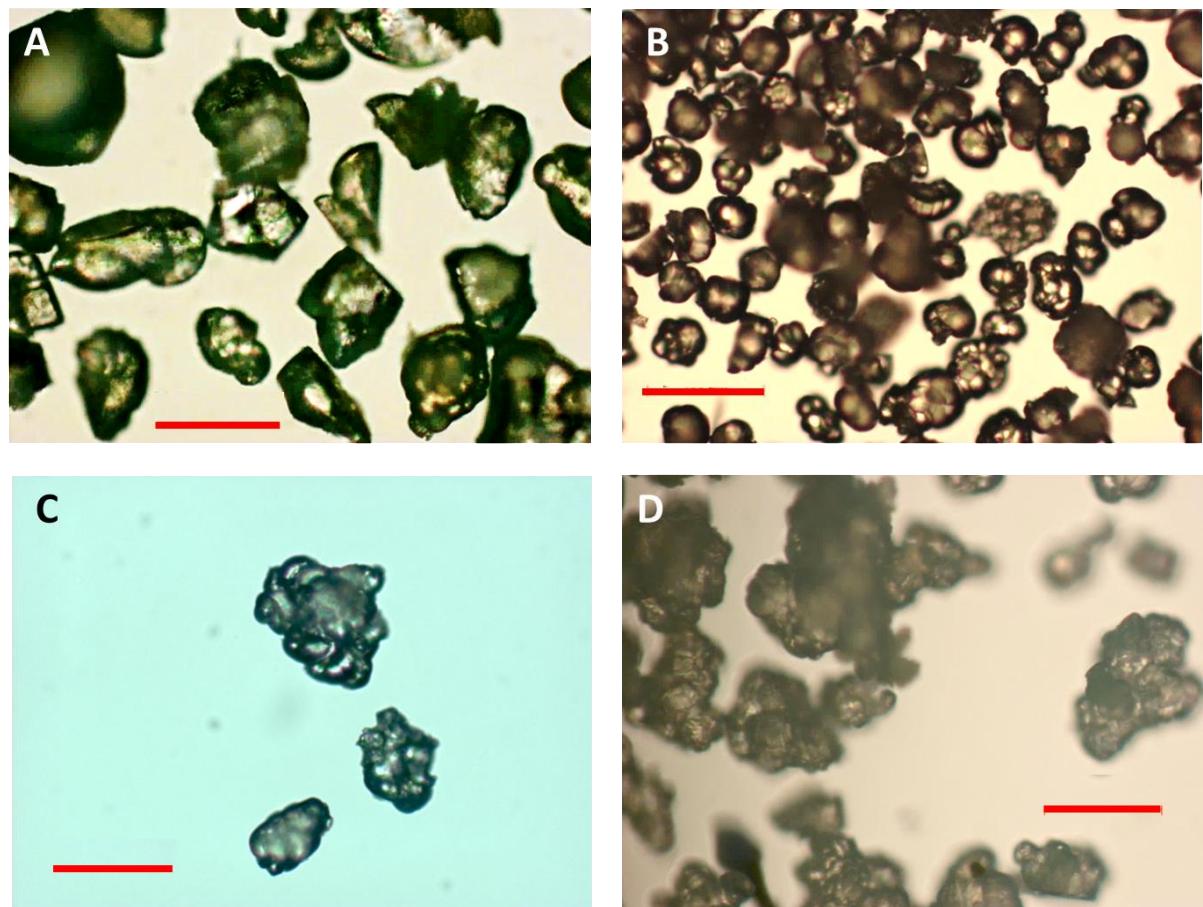
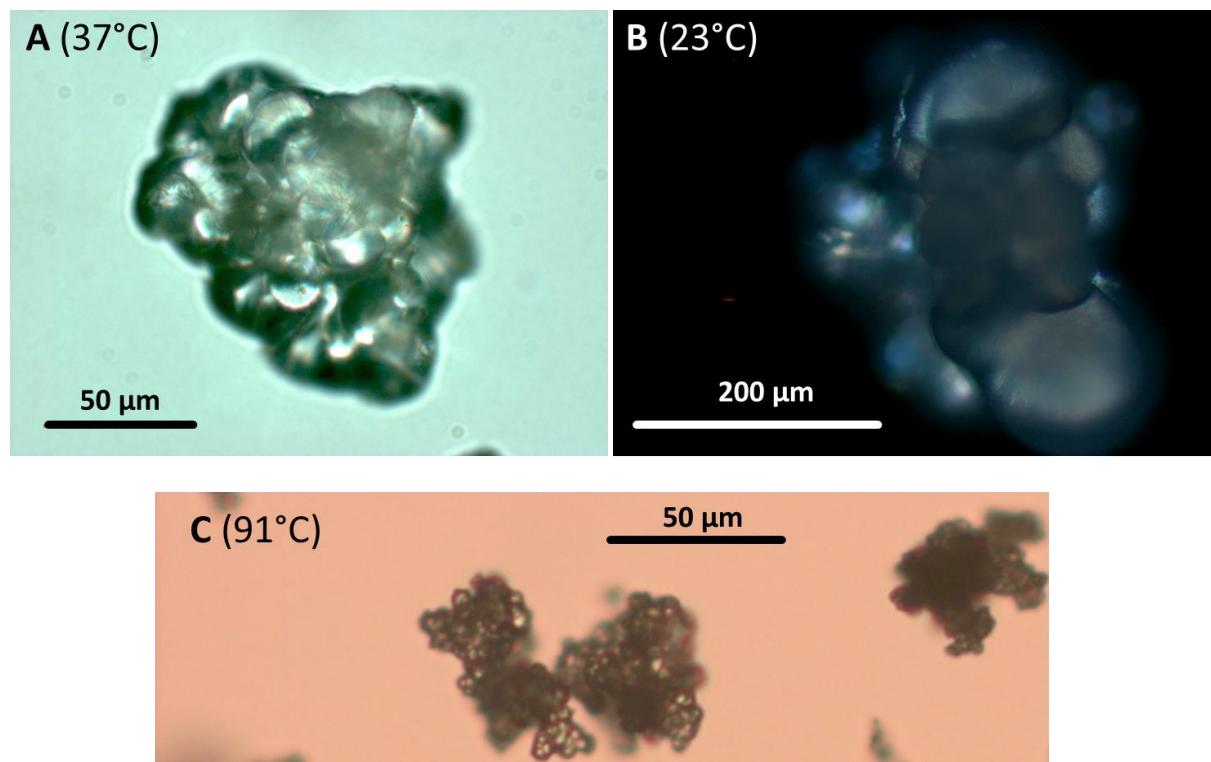


Figure 2. Photomicrographs of CaCO_3 minerals precipitated in the laboratory experiment. Scale bar is 100 μm in A-C and 200 μm in D. Vaterite crystals formed at 50°C in experiment NA-6 (**A**), at 70°C (**B**) and at 91°C (**D**). At 80°C a mixture of aragonite, calcite and vaterite was precipitated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



1
2 Figure 3. Photomicrographs of CaCO_3 minerals precipitated in the laboratory experiments.
3 Scale bar is 100 μm . Vaterite crystals formed at 23°C (A), at 37°C in experiment NA-3 (B)
4 and NA-4 (C) and 50°C (D, NA-5).



1
2 Figure 4. Close-up photomicrographs of vaterite minerals. Scale bar is 50 µm in A and C and
3 200 µm in B. B shows a vaterite crystal using polarized light.

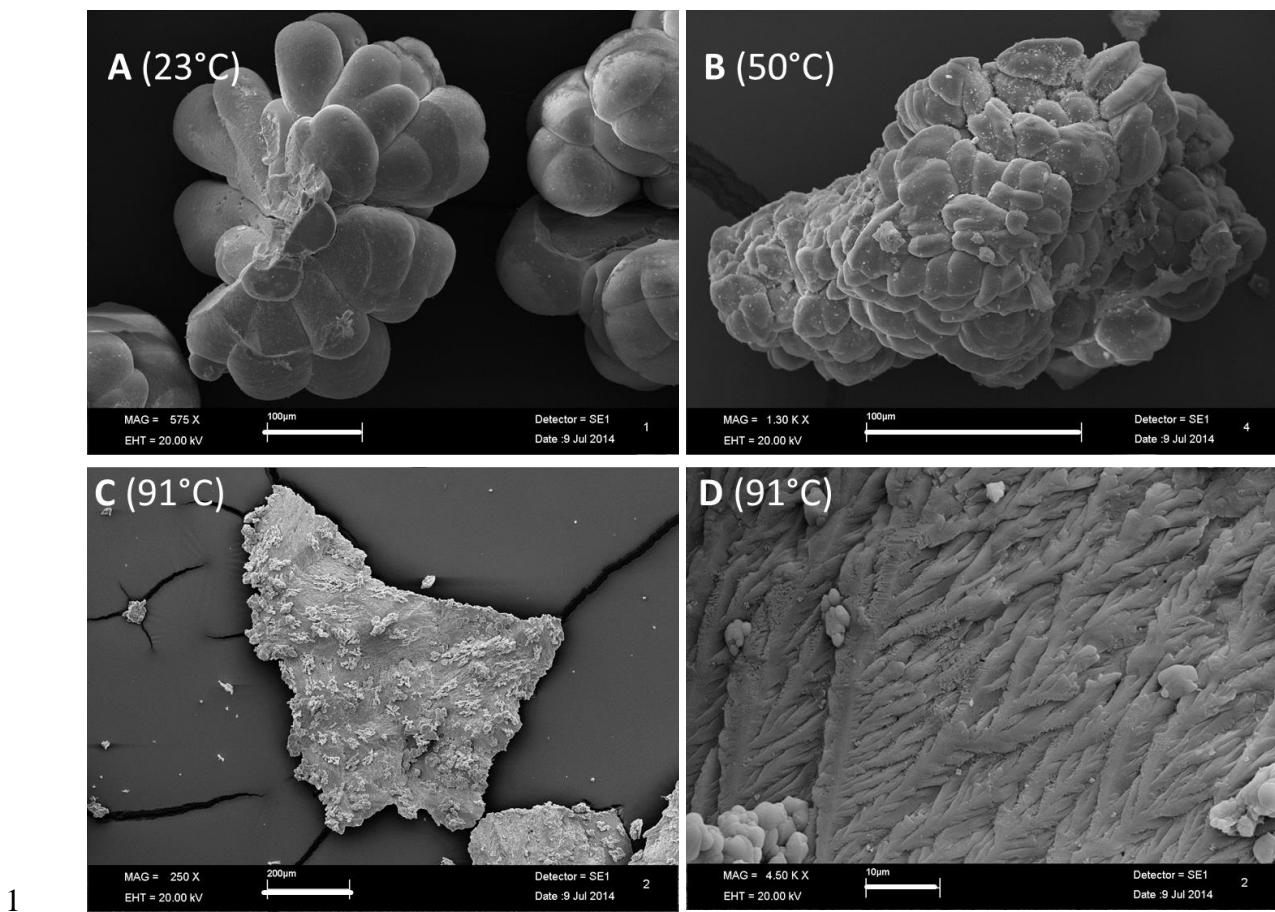
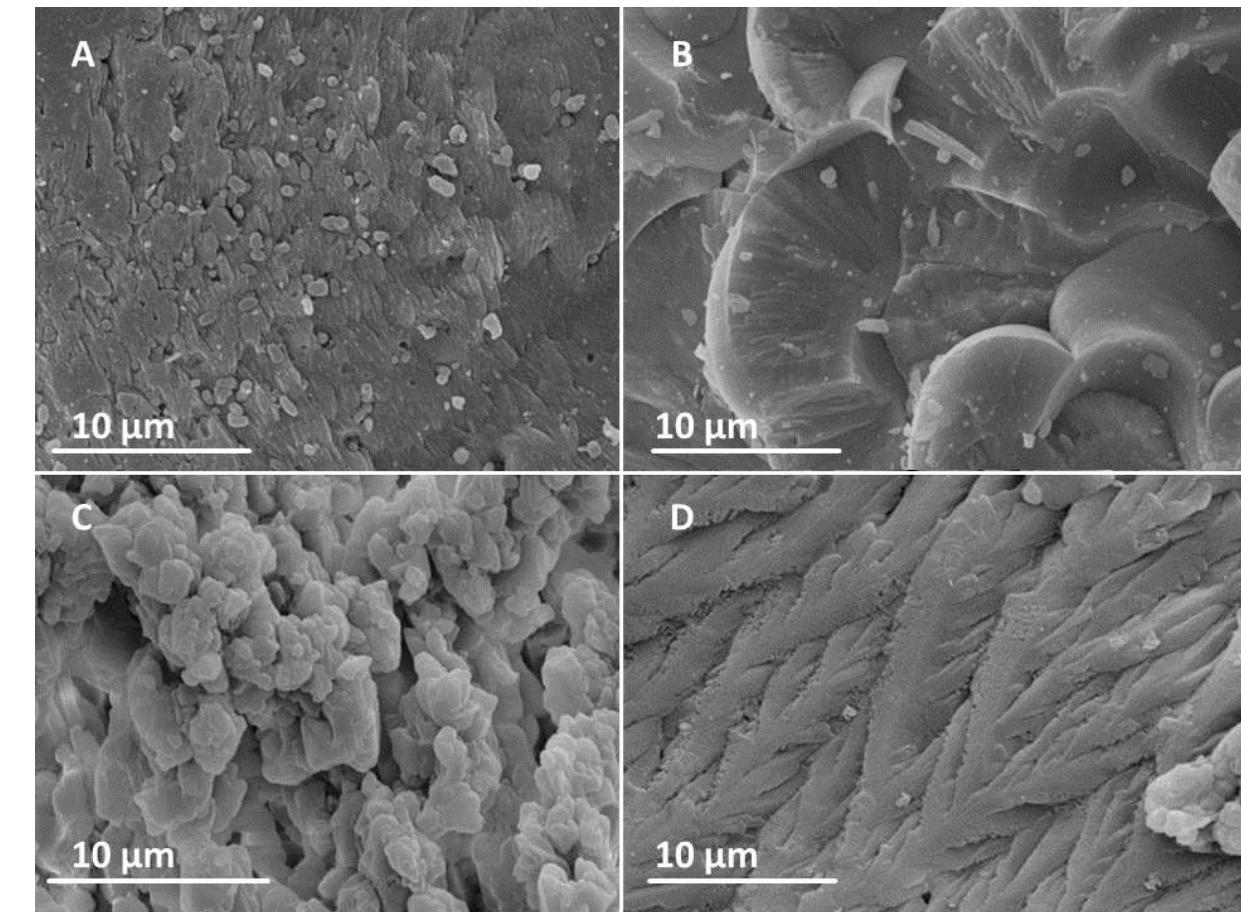
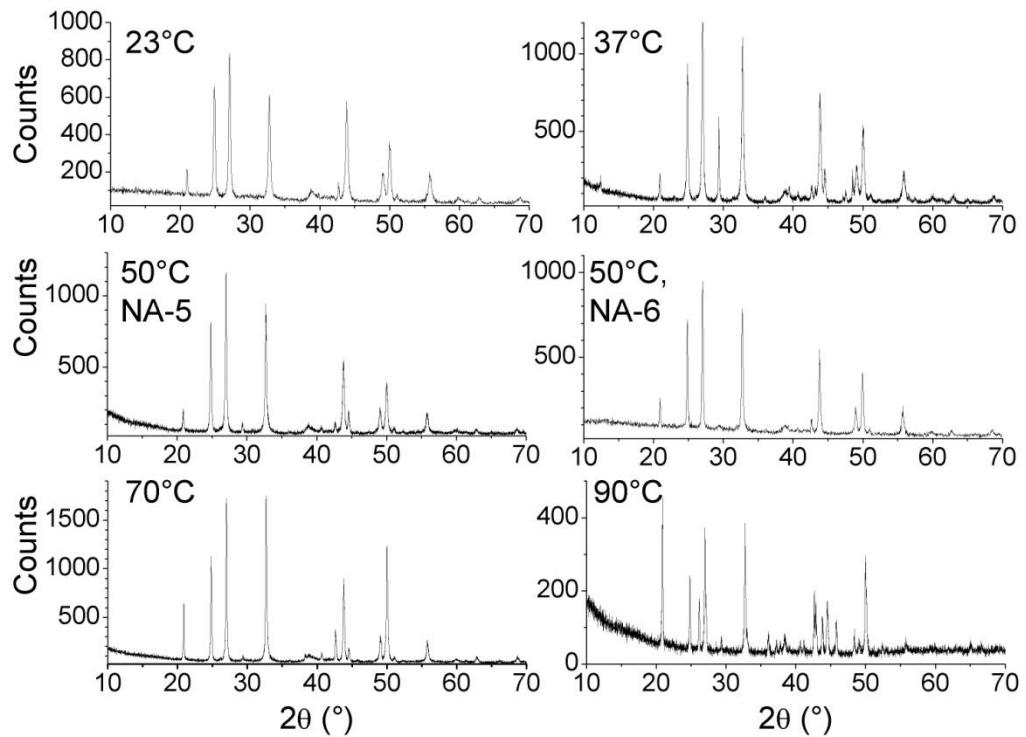


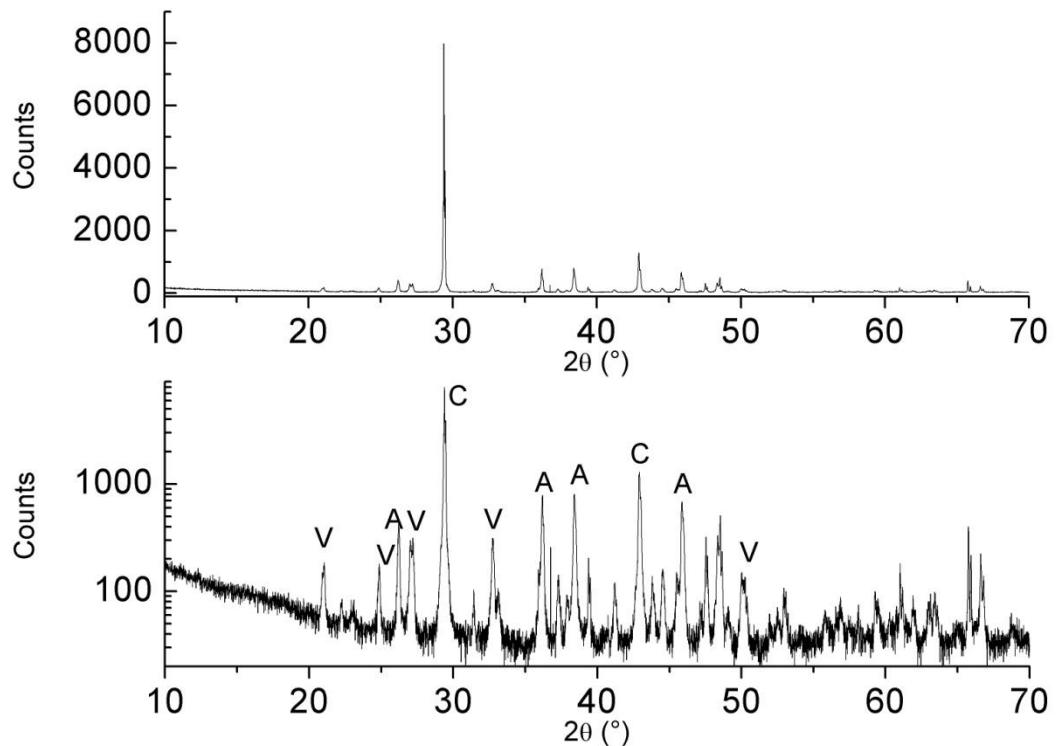
Figure 5. SEM images of vaterite aggregates in the order of increasing precipitation temperatures. Scale bars are 100 μm in A and B, 200 μm in C and 10 μm in D. Samples NA-1 (A), NA-4 (B), and NA-9 (C and D) were used for imaging.



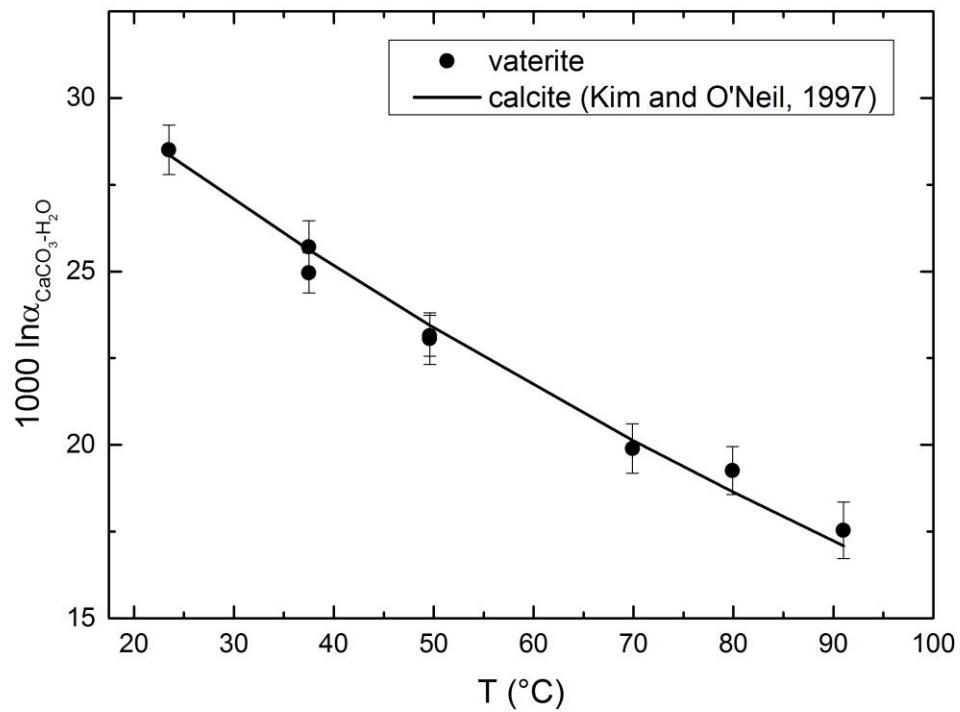
1 **Figure 6.** High-resolution SEM images of vaterite aggregates showing the internal structure in
2 the order of increasing precipitation temperatures (A: 23°C, B: 50°C, C, D: 91°C). Two
3 different growth structures are observed at 91 °C: aggregation of µm-sized flat crystallites (C)
4 and tree-like branching resulting in flat platelets (D).



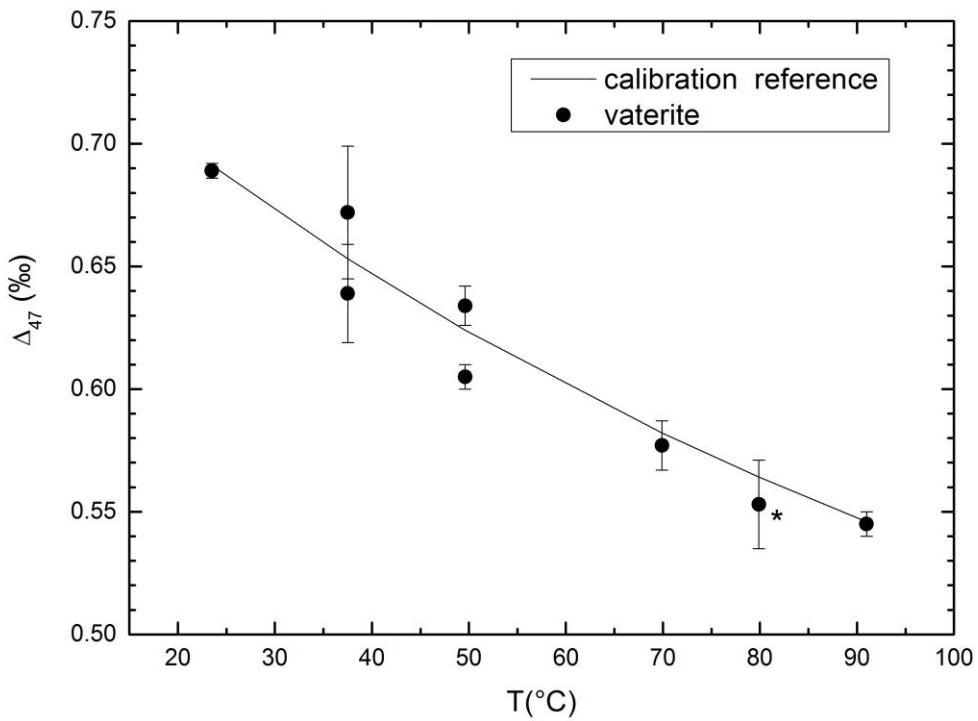
- 1
2 Figure 7. X-ray diffraction pattern of crystals from the laboratory experiments. The minerals
3 that grew at 23°C show a pure vaterite signal. Similarly, minerals formed at 50 and 70°C yield
4 an almost pure vaterite signal with a non-quantifiable fraction of calcite (**traces, \leq few %**).
5 The samples at 37 and 91°C contain a minor fraction of calcite and aragonite ($\leq 6\%$ in total).



1
2 Figure 8. X-ray diffraction pattern of crystals from laboratory experiments. The experiment at
3 80°C produced a mixture of calcite, aragonite and vaterite (lower panel). For comparison, the
4 XRD pattern of pure calcite is shown (upper panel). This example shows calcite that
5 precipitated at 25°C from a pure CaCO_3 supersaturated solution without NaCl addition. The
6 peaks in the lower panel are labeled according to the related mineral structure (A: aragonite,
7 C: calcite, V: vaterite).

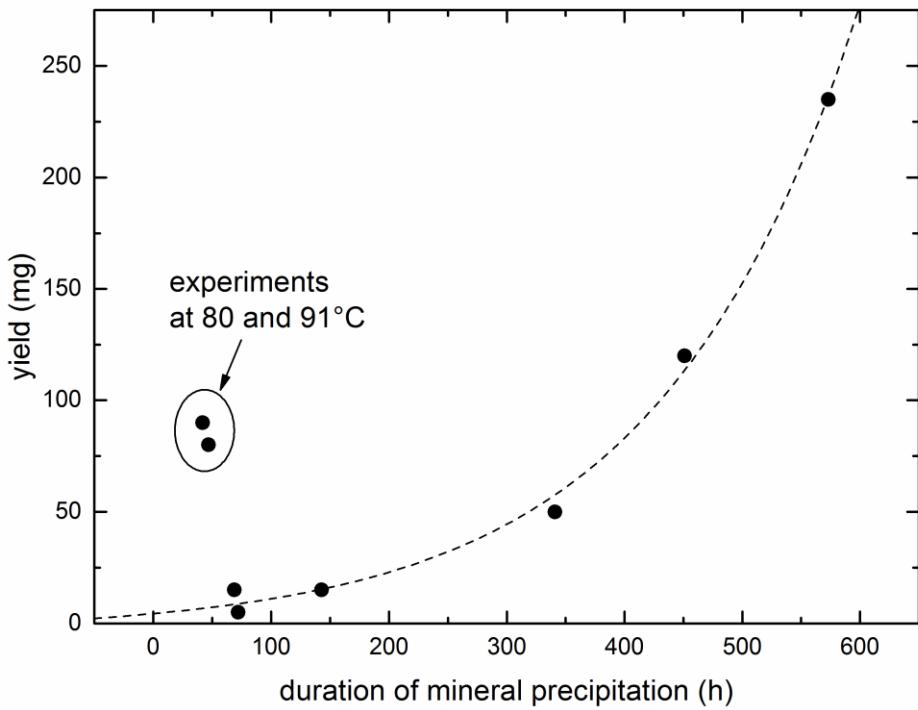


1
2 Figure 9. Oxygen isotope fractionation factor $1000\ln\alpha(\text{CaCO}_3\text{-H}_2\text{O})$ of vaterite (circles)
3 relative to expected values for calcite (Kim and O'Neil, 1997; solid line). The sample at 80°C
4 consists of a mixture of calcite, aragonite and vaterite. At 37 and 50°C repeat experiments
5 were performed yielding fractionation factors in agreement with the previous experiment at
6 the same temperature.



1

2 Figure 10. Measured Δ_{47} values of vaterite (circles) relative to expected values following the
3 calibration line of Kluge et al. (2015). The sample at 80°C (marked by an asterisk) consists of
4 a mixture of calcite, aragonite and vaterite. The calibration line of Kluge et al. (2015) was
5 mainly determined on calcite.



1

2 Figure 11. CaCO_3 formed per experiment vs. duration. The initially dissolved CaCO_3 amount
3 was identical in all experiments (about 370 mg). The yield of experiments conducted below
4 80°C follows an exponential relationship with duration.