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Interactive comment on “Technical Note: A simple method for vaterite precipitation in isotopic equilibrium: implications for bulk and clumped isotope analysis” by T. Kluge and C. M. John

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We are grateful for comments and suggestions provided by G. Nehrke. They help to improve the manuscript. The detailed response and intended changes to the manuscript are given below.

‘The preparation of purified water using a reverse osmosis system very likely alters the isotopic composition of the water (as this is often observed if diffusion via a membrane is involved). Therefore, I don’t think that it is valid not to measure the isotopic composition of the solution’

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A direct comparison with water $\delta^{18}\text{O}$ values would have been preferable. Unfortunately, no solution aliquot was stored from the original experiments and therefore no direct measurement of the water $\delta^{18}\text{O}$ is possible. However, in close temporal connection (3–12 d) to the vaterite experiments CaCO_3 was precipitated from a pure $\text{Ca}(\text{HCO}_3)_2$ solution with water taken from the same reverse osmosis (RO) system. Using the values from these experiments we have a reasonable estimate for the water $\delta^{18}\text{O}$ value (using the fractionation factors of Kim and O'Neil, 1997) and its variability. This is visible in Fig. 8 where the calcite line represents the values from the reference experiments without salt addition. However, also the limitation of this approach is visible. Repeat experiments about one year later yielded different carbonate $\delta^{18}\text{O}$ values that are due to changes in the source water value (see Fig. 8). Back-calculated water $\delta^{18}\text{O}$ values of calcite precipitated from NaCl-free solutions at the time of the repeat experiments are about 1.3 ‰ more negative. We will include additional comments for clarification in the discussion and update Fig. 8 to better illustrate this aspect.

'One point I do not understand is if up to 235 mg are precipitated (of 370 mg possible) how is dealt with Rayleigh fractionation. How is the evolution of the isotopic signature of the water known if it is not measured.'

The solution water should not show any evolution during the duration of the experiment. The gas stream that was bubbled through the solution was humidified in a container with the same RO water (page 17365, lines 12, 16, 27). Thus, no evaporation of water should take place from the solution that could potentially alter the $\delta^{18}\text{O}$ value.

'The authors state that some samples contain less than 1 % calcite. A calibration for XRD measurements using vaterite and calcite has shown that the detection limit of calcite within a vaterite sample using XRD is not better than 5 % (chapter 4 figure

4.2 in the following work <http://dspace.library.uu.nl/bitstream/handle/1874/19176/index.htm?jsessionid=89944D5CADE021D60AECC5B9DF5A8DD6?> This should be taken into account or the authors should present a calibration demonstrating that they can detect calcite down to 1 % within a vaterite matrix using XRD.'

The existence of calcite traces in the respective samples is visible by the appearance of a peak at 29.46° (2Θ) which is absent for pure vaterite (Fig. 6). We acknowledge that the precise quantification is not possible in case of a very low calcite fraction (page 17386, figure caption). The upper limit of 1% for the calcite traces was estimated based on the difference to the sum of the main CaCO_3 components. The uncertainty of the phase quantification is about 3%. In the revised version we will acknowledge the difficulties in quantification of vaterite trace fractions.

'The authors write that they showed that it is [not?] possible to precipitate vaterite at much higher temperatures than room temperatures and that this is surprising, given that many other studies emphasized the low stability of vaterite. In the study of Gussone et al. (Gussone, N., G. Nehrke, and B.M.A. Teichert, Calcium isotope fractionation in ikaite and vaterite. Chemical Geology, 2011. 285(1-4): p. 194-202.) on the Ca isotope fractionation for vaterite data in the range of 10 to 50° C have been demonstrated. Therefore this reference should not be neglected.'

Reference will be added and related sentences rephrased.

'How was the size of the "individual grains" determined? The authors write about 10 to 100 μm but do not show high resolution SEM images that confirm that smaller crystallites do not form the vaterite aggregates as for example shown by Nehrke and Van Cappellen (Nehrke, G. and P. Van Cappellen, Framboidal vaterite aggregates and their transformation into calcite: A morphological study. Journal of Crystal Growth, 2006. 287(2): p. 528-530.) (One of several studies on vaterite not cited in this study).'

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The crystallite sizes were determined on SEM images whereof a selection is shown in Fig.5. For verification we added additional SEM images to this document (Figs. R1-R5 below). A few of them may be added in the revised manuscript including a more detailed description.

The mentioned reference will be added in the corresponding section.

'In the Abstract the authors write about "pure CaCO₃ exists in three different polymorphs". What do they mean with pure? Anhydrous maybe (but than they should use this word)?'

- 'Pure' to be replaced with 'anhydrous'.

'The authors write when they describe the "conglomerate particle". "This pattern gets increasingly disordered ...with chaotic aggregation of small grains...". What type of disorder (disorder in respect to what parameter" should that be? What is "chaotic aggregation" (which parameter gets more chaotic)? How is the degree of disorder and chaotic aggregation measured?'

The corresponding paragraph will be rephrased and simplified: 'The aggregate particles are made up of increasingly smaller grains at higher temperatures.'

'Reasoning for this study is 'it may provide new insights into the isotope fractionation during biological carbonate formation'. This is very vague and undefined. The authors should give an example why this information is needed'

Vaterite was postulated to be a precursor phase in biogenic CaCO₃ precipitation, later transforming into aragonite or calcite (page 17363, lines 11-13). Depending on the transformation conditions the original isotope signature may be inherited in

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the final CaCO_3 phase. Understanding the isotope values of biogenic carbonate with such a formation history (and having in mind their potential application for reconstruction of environmental conditions or paleoclimate) requires the knowledge of the fractionation factors between vaterite and water, and the clumped isotope value of vaterite, respectively.

'I have my problems to understand why only this method should offer the possibility to perform experiments at thermal and isotopic equilibrium, when compared to some other methods used for vaterite precipitation'

The focus of our study is on the isotopic equilibration. Many methods for vaterite precipitation foster fast mineral formation, likely leading to kinetic isotope fractionation due to the rapid growth (e.g., Dietzel et al., 2009; Gabitov, 2013). Methods associated with high growth rates are thus unsuitable for isotopic studies (page 17371, lines 10–16). Other experiments use additives, surfactants or polymeric substances that potentially affect the isotope values (page 17371, lines 17–27). The relatively large amount of material required e.g., $\geq 15\text{mg}$ for clumped isotope analysis per sample (3 replicates), further limits the number of suitable methods.

The setup of our method was modified from the procedures of McCrea (1950), O'Neil et al. (1969) and Kim and O'Neil (1997) that provided important reference values for the oxygen isotope fractionation. The temperature calibration for clumped isotopes used an analogous method (Ghosh et al., 2006; Zaarur et al., 2013) and therefore provides in both cases a good comparability of the obtained results.

'Since I do calcium carbonate precipitation experiments for all possible polymorphs myself since many years I can tell that the polymorph identification using optical microscopy can often fail. Phase determination of single crystals obtained in precipitation experiments using confocal Raman microscopy sometimes can give very surprising

results. Therefore I regard phase identification by means of optical microscopy as a very unreliable method. It can be done but it is not as straight forward as stated by the authors.'

The revised manuscript will be amended by a note of caution. In addition to initial optical microscopy, the mineralogy was verified in all cases via XRD analysis.

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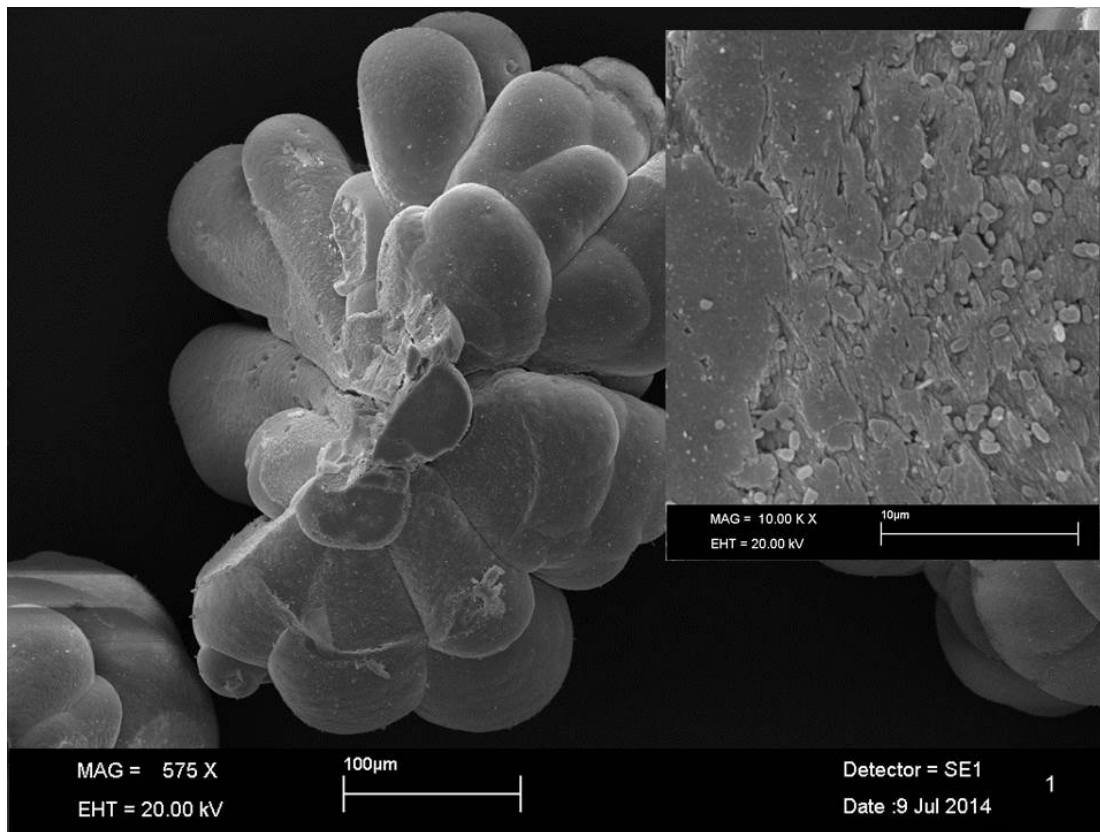


Fig. 1. SEM of a vaterite aggregate (23°C) with a higher-resolution inset (scale bar there: 10 μm). The internal structure of the globular grains is made up of small $\sim 2\mu\text{m}$ long elongated fibrous crystallites

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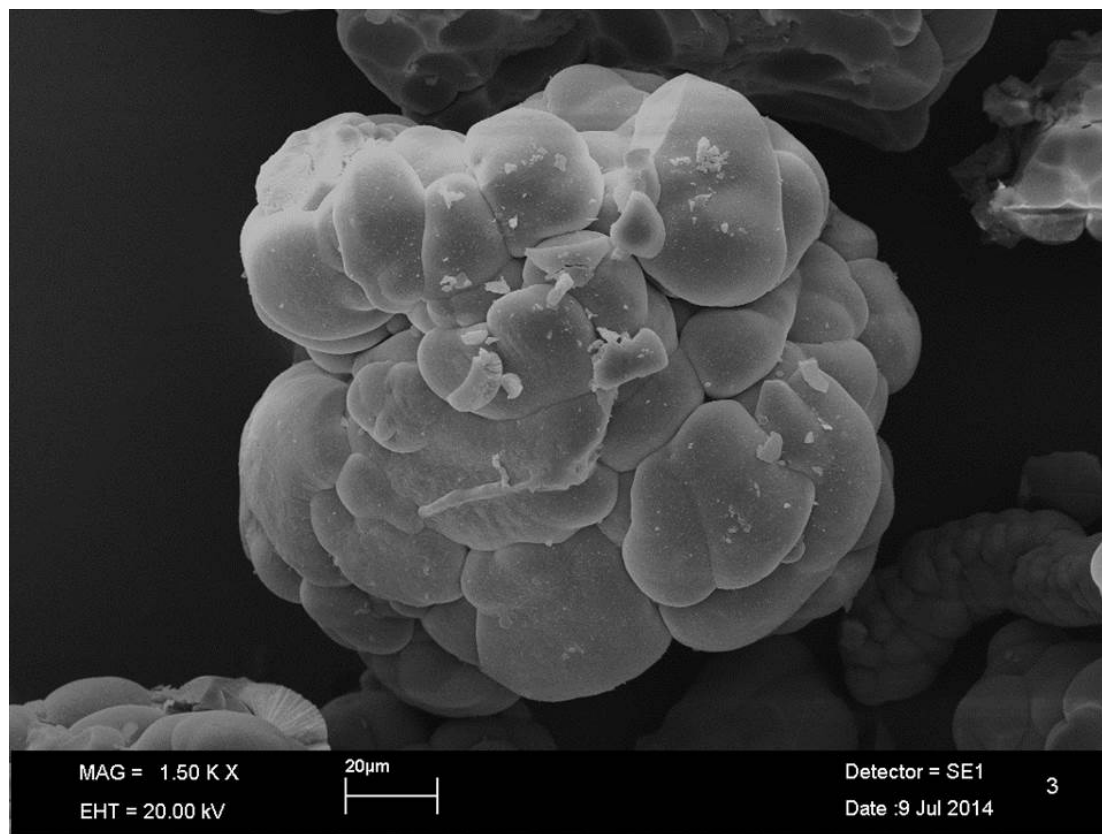
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Fig. 2. SEM image of vaterite aggregate formed at 37°C.

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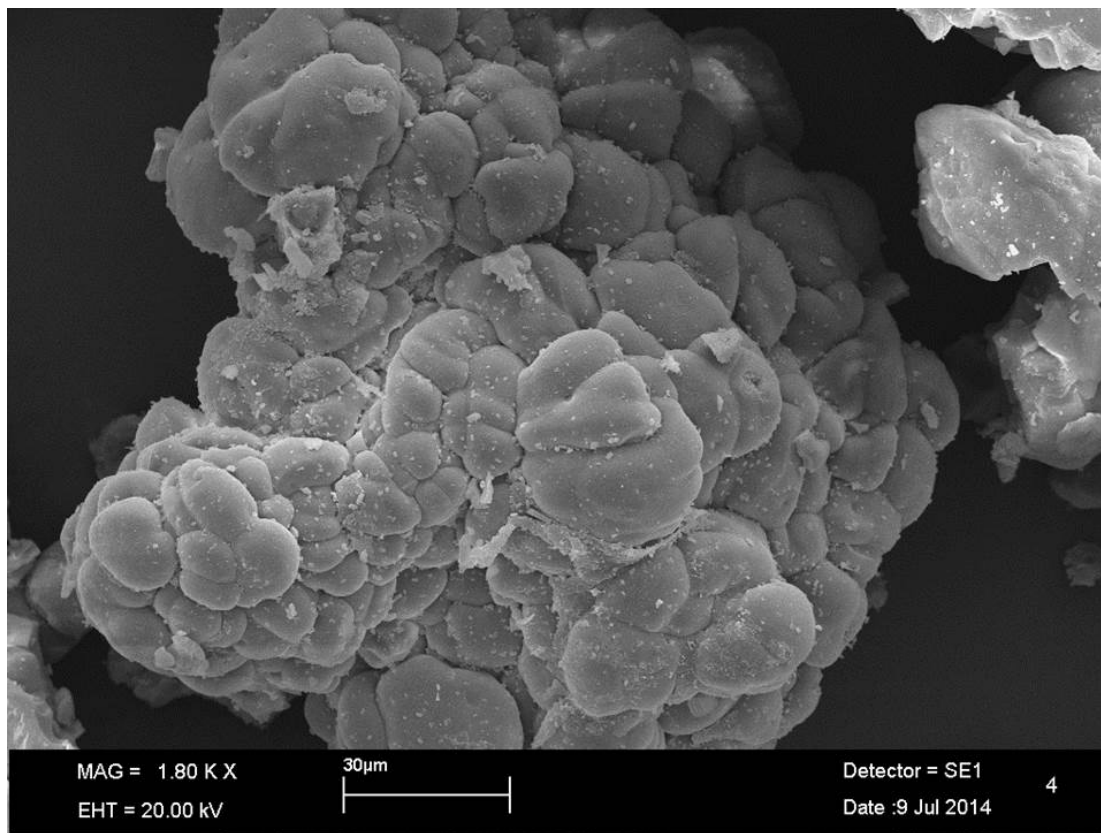
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Fig. 3. SEM image of a typical vaterite aggregate formed at 50°C.

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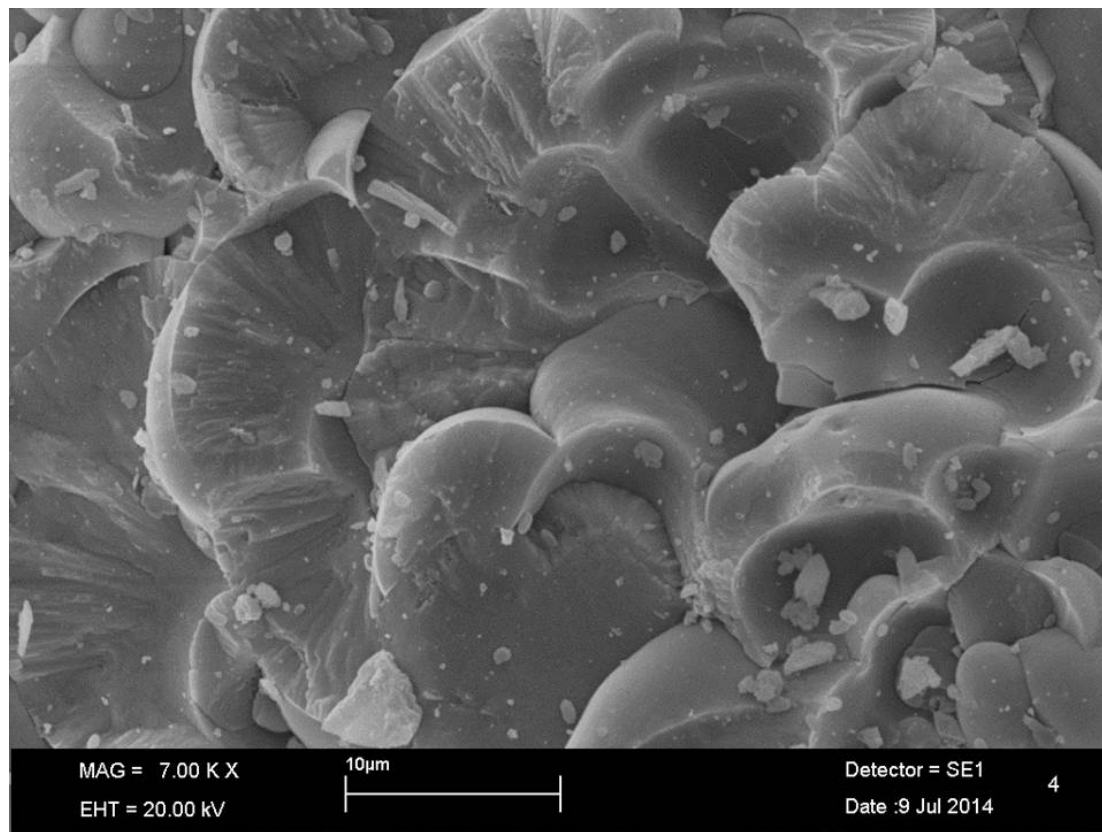
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Fig. 4. SEM image of vaterite aggregates formed at 50°C. Broken-up aggregate showing internal structure.

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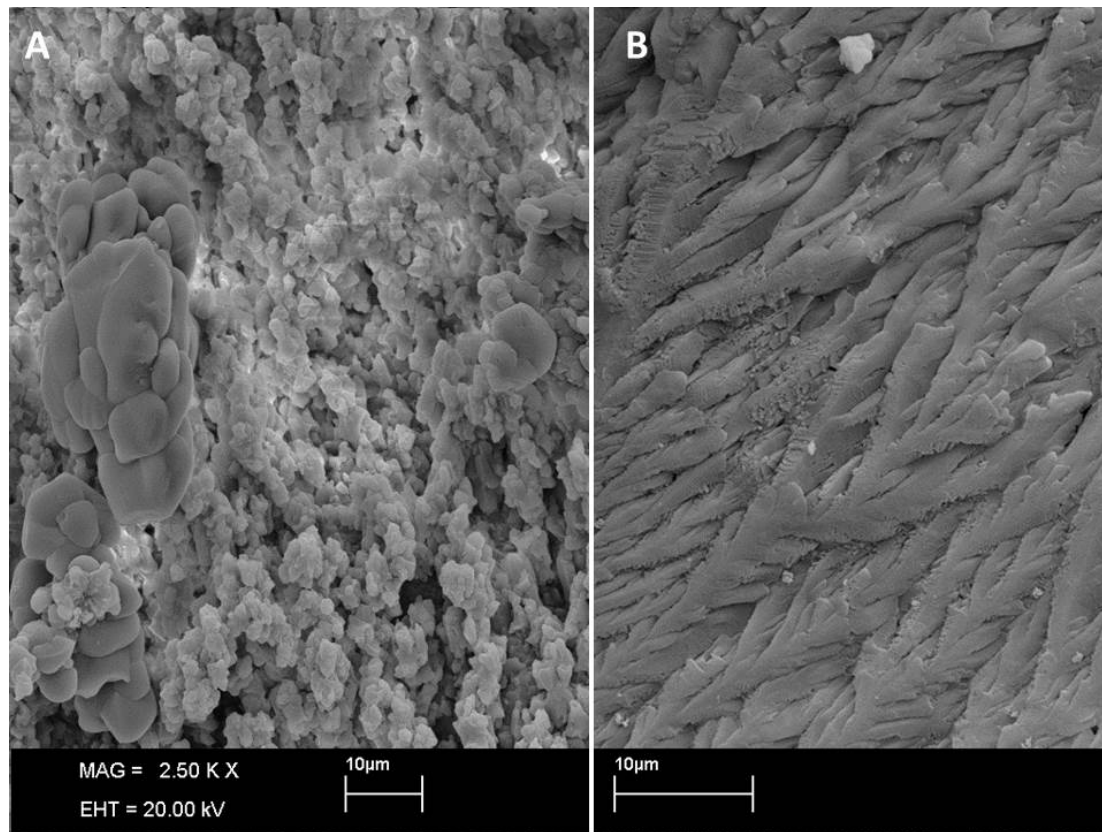


Fig. 5. High-resolution SEM of vaterite samples formed at 90°C. Two different growth pattern were distinguished: aggregation of μm -sized crystallites (A) and branch-type crystal growth in flat platelets (B).

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