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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 R. Gabitov. They help to improve the manuscript. The detailed response and intended changes to the manuscript are given below.

*‘The only problem is disequilibrium isotopic fractionation could occur because of the lack of knowledge on vaterite precipitation rate.’*

Although we did not monitor the actual growth rate as precisely as it was done e.g., in the experiments of Gabitov et al. (2012) and Gabitov (2013) we can

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calculate growth rates for each precipitation experiment. Growth rate estimates (e.g., based on the general relationship of experiment duration and mineral yield, Fig. 10) and its potential influence on the isotope fractionation will be included in the discussion.

*'Authors suggested achievement of isotopic equilibrium between water and carbonate aqueous species. However the discussion on kinetic aspects of fractionation at mineral surface is too short. My understanding that vaterite growth rate was not evaluated in those experiments and authors consider that Kim and O'Neil (1997) data represent equilibrium fractionation. There was further research on this subject which demonstrated that slow growing calcite could be enriched in oxygen-18 by up to 2 permil (e.g. Coplen 2007; Gabitov et al 2012). Therefore, I would hesitate to state that vaterite precipitation occurred at isotopic equilibrium in this work (especially in the title). The authors may see Watkins et al. (2014) for comparison of fractionation factors from different experiments'*

A section discussing the influence on growth rate will be included in the revised version. As mineral surface effects can induce isotopic disequilibrium we'll carefully consider this aspect in the data interpretation taking into account the growth rates of our experiments.

The data of Kim and O'Neil (1997) are often taken as equilibrium reference, however, we acknowledge that a growing number of studies is questioning this assumption. We did use Kim and O'Neil as the de-facto accepted study, and in lack of a new accepted equilibrium oxygen isotope fractionation curve. We'll discuss the importance of growth rate and change the title accordingly to 'Technical note: A simple method for vaterite precipitation for isotopic studies – implications for bulk and clumped isotope analysis'.

*'Also, it would be very helpful if fractionation factors[1000ln(alpha18O)] are plotted in-*

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stead of delta values because a lot of experimental data are reported this way and it will be easier to compare different datasets.'

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'Authors did not analyze experimental fluids for d18O, but used d18O of surface and ground water values of the London Metropolitan area from (Darling, 2003). I think it is important to measure d18O in the solutions from which vaterite precipitated to confirm the value reported by Darling (2003).'

Unfortunately, this is a certain limitation to the direct evaluation of water  $\delta^{18}\text{O}$  values. No solution aliquot was stored from the original experiments and therefore no direct measurement of the water  $\delta^{18}\text{O}$  version is possible. However, in close temporal connection to the vaterite experiment  $\text{CaCO}_3$  was typically precipitated from a pure  $\text{Ca}(\text{HCO}_3)_2$  solution. 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. We include additional comments for clarification and for remarking the limitation of data interpretation with regard to  $\delta^{18}\text{O}$ .

Further comments regarding the annotated pdf:

'page 17362, lines 17-19: This sentence is not fully clear for me. Do authors mean that 235 mg of vaterite was precipitated from solution where 370 mg of  $\text{CaCO}_3$  was dissolved? Clarification would be helpful.'

We dissolved on average 370 mg  $\text{CaCO}_3$  whereof a maximum of 235 mg was recovered.

'page 17364, lines 9-11: Do authors mean that vaterite is enriched in  $^{18}\text{O}$  by +0.5 permil relative to calcite or some other phase?'

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Enrichment is given relative to calcite. Will be clarified in the revised version.

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'page 17364, line 21: What is the mineralogy of this  $\text{CaCO}_3$  ?'

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'page 17365, line 4: why two different sizes were used? Have filtering been done in two stages: first with 11 micron paper and after with 1 micron paper?'

The filter paper has a pore size of  $11\mu\text{m}$  (identical to grade 1).

'page 17365, line 5: How much of  $\text{CaCO}_3$  was dissolved?'

The amount of the undissolved fraction was not quantified, but appears to be negligible. In none of the experiments un-dissolved  $\text{CaCO}_3$  was visibly retained on the filter paper after the filtration step.

'page 17365, line 14: Please specify the concentration of  $\text{CaCO}_3$  in this solution.'

The corresponding concentrations can be taken from Table 1 and are 0.70-0.80 g  $\text{CaCO}_3$  per litre.

'page 17365, line 23: Why the concentration error is so high? Did you use the different concentration NaCl in purpose?'

NaCl concentrations in the individual experiments reached values of 200-300 g/l and are precisely known (table 1). The variation is due to the intention of having a range of concentrations at the upper limit close to the saturation level.

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*'page 17366, line 3: Please specify the pore size of the filter paper.'*

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Pore size of the grade 1 filter paper is 11  $\mu\text{m}$ .

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*'page 17367, lines 18-20: Was EDS detector used in evaluation of Na and Cl concentrations? What exact concentrations were?'*

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The EDS detector was used to evaluate the occurrence of Na and Cl, however, no exact concentrations were determined.

*'page 17368, lines 16-17: Why calcite is the dominant phase if similar proportions of aragonite and vaterite were detected.'*

Sentence will be rewritten indicating that about half is made up by calcite and a quarter by each vaterite and aragonite.

*'page 17369, lines 14-16: My impression was that vaterite was presented in all of the experiments. How did you manage to separate vaterite from calcite/aragonite mixture? If you used calcite/aragonite data from the other studies then please mention it.'*

Vaterite was not separated from the other  $\text{CaCO}_3$  polymorphs in this study. Instead data from additional studies with calcite or calcite/aragonite mixtures were taken for comparison (Kluge and John, 2014).

*'page 17371, lines 13-16: So, no isotopic analyses were conducted on rapidly precipitated vaterite. If it is correct then please confirm it in the text. Vaterite growth rate was not addressed in this manuscript. How authors can be sure that isotopic equilibrium at the mineral surface was achieved?'*

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No isotopic analyses were conducted on rapidly precipitated vaterite. The average growth rate for experiments below 80°C can be inferred from Fig. 10 and will be added to Table 2. In the first few hours precipitation rates are only about  $1.4 \times 10^{-10}$  mol/s. Using the bottom of the Erlenmeyer flask as first-order estimate of the related growth surface we get a growth rate of about  $1.8 \times 10^{-8}$  mol/(s m<sup>2</sup>) for the first few hours. The growth rate increases to  $1 \times 10^{-7}$  mol/(s m<sup>2</sup>) after 300 h and peaking at 600 h with  $6 \times 10^{-7}$  mol/(s m<sup>2</sup>). Although we ensured to obtain isotopic equilibrium between water and DIC, we do not claim to have reached or maintained isotopic equilibrium at the mineral surface. Rapid mineral formation was found to cause oxygen isotope disequilibrium and cannot be excluded for the higher rates of the experiments (compare e.g., with rates in Watkins et al., 2014). Our experimental procedure and growth rates are similar to those of Kim and O'Neil (1997) and are therefore a valid comparison study. The importance of growth rate for attaining isotopic equilibrium with regard to oxygen isotope will be included in the revision of the manuscript.

'page 17384, Fig. 4: 50 micron scale bar is shown on (b) image. Please clarify'

Mislabeled. Should be 200 μm.

'page 17388, Fig. 8: I recommend to measure fluid samples for their isotopic composition.'

Unfortunately, no fluid aliquots were stored for isotopic analysis. See also above the related main comment.

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