

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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Review of the Technical Note: A simple method for vaterite precipitation in isotopic equilibrium: implications for bulk clumped isotope analysis.

The paper by T. Kluge and C. M. John describes a modified method for vaterite precipitation and present measured isotope data. The paper is well written and the presentation of the method and results is easy to follow.

However, I have my concerns concerning several points. 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

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don't think that it is valid not to measure the isotopic composition of the solution.

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 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=89944D5CADF>). 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 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.

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).

In the Abstract the authors write about “pure CaCO_3 exists in three different polymorphs”. What do they mean with pure? Anhydrous maybe (but than they should use

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this word)?

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?

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.

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.

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.

Best regards,

Gernot Nehrke

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