Clim. Past Discuss., 8, C1371–C1375, 2012
www.clim-past-discuss.net/8/C1371/2012/

Climate of the Past Discussions

Interactive comment on "A re-evaluation of the palaeoclimatic significance of phosphorus variability in speleothems revealed by high-resolution synchrotron micro XRF mapping" *by* S. Frisia et al.

Anonymous Referee #1

Received and published: 30 August 2012

General Comments:

This study aims to shed light on the relationship between phosphorus incorporation into speleothem calcite and the role that bacteria may play in calcite precipitation including their potential to influence isotopic and geochemical variations that have been used to interpret paleoenvironmental changes. P variations in speleothems have been linked to changes in infiltration - and thus water supply – to caves. But, P has also been associated with microbial structures in speleothems, generating controversy about the use of P variability as a straightforward proxy of water availability. With an eye toward

resolving this controversy, the authors investigate P variability in speleothems using synchrotron mapping coupled with petrographic and SEM observations of speleothem structure. They first apply these techniques to a modern speleothem from Christmas Island and use the observations from this specimen to interpret P variability and speleothem structures in a Pliocene speleothem from Australia.

Overall, this work represents a valuable contribution to speleothem science in the investigation of a potentially useful but not-well-understood proxy as well as the coupling of fine-scale chemical and physical observations of speleothem calcite. P variability presents a potentially useful, but underutilized tool for paleoclimate reconstructions from speleothems. Additionally, as the authors point out, microbial involvement in speleothem precipitation is a potentially important consideration in speleothem studies that is not often discussed. For these reasons, I support the publication of this work. However, I will suggest a few clarifications that should be addressed before final publication.

Specific Comments:

1. As so much of this study hinges on the discussion of visual patterns in crystal structures and elemental mapping, I believe that the paper would greatly benefit from more clearly constructed and annotated figures. Figure 1, for example, is difficult to interpret. It is not clear how (or if) the three panels of this figure relate to one another and to the speleothem as a whole. Are these images of the same features in the stalagmite? Could nested boxes or arrows be used to show, for example, if the corroded surface visible in 1b is also noticeable in the synchrotron maps of 1c? This is a bit easier to follow in Figure 6, as the caption notes that the two panels of the figure are "in the same region". However, in this figure as well, it would improve the clarity of the relationships between these crystallographic and chemical features if the micrographs and element maps covered the same areas and if notable features in each could be pointed out to allow the reader to directly compare the images. Similarly, Figure 4 would benefit from the inclusion of a micrograph of Phase 2 to allow direct comparison between crystal

structure and chemical variations. 2. Along the same lines, better imagery should be provided of the potential bacterial structures that the authors describe in these stalagmites. The SEM image in Figure 1 is difficult to interpret and would benefit from some annotation, as it is unclear if the "globular, tabular, and lamellar P-rich phases" are visible in this photograph, or if only the cavities that host these phases are visible. Further SEM imaging of the potential bacterial structures would be illuminating and allow better comparison with the structures noted in the Cayman speleothems by Jones (2009) – where ample imagery is provided. Further imaging of Phase 2, the stromatolitic phase, in the Nullabor speleothem would also be helpful, as in Figure 3 it is only discernable that there is a zone of more finely laminated calcite. 3. The discussion of P variability in Christmas Island drip waters merits elaboration. The authors should be more explicit in describing how the co-variation of P and Mg/Ca may suggest PCP or water-rock interactions, and clarify what is meant by "water-rock interactions". Furthermore, recent literature has called into question the assumption that PCP is only related to infiltration and drip rate, but rather suggests a role for cave air pCO2 in driving calcite precipitation. This is mentioned only briefly later in the discussion. The lack of a correlation between drip rate and P and Ca concentrations may not be grounds to reject a relationship between PCP and P and Ca concentrations, as PCP may be controlled by cave air pCO2 rather than drip rate. This potential control should be addressed. Has cave air pCO2 been investigated in this cave? Does it vary? Are there reasons to favor water-rock interaction control on P besides the lack of correlation with drip rate? Additionally, could rainfall be added to Figure 2 b along with P and drip rate variability? This would be helpful, as there is a hypothesized link between P and infiltration that is not evident when looking at drip rate. Is there a more direct way to relate P to infiltration? 4. It would be helpful to expand the discussion of Si variability and how it supports the hypothesis of water-rock interaction control on P. What is the relationship that has been noted between Si/Ca and rainfall and how might this be modified by bacterial precipitation? This is not clearly explained. 5. In the discussion of the Nullabor speleothem, and also on Figure 3, it would be helpful to designate the depths in the

stalagmite at which the suggested periods of dryness, recharge and aquifer discharge occurred. 6. How applicable are these results to other cave settings given the high presence of phosphate phases in the host limestone of the Christmas Island Cave? Would the absence of such phases alter the proposed mechanism for P variability in speleothems? 7. In the end, it is not entirely clear what the proposed relationship between P and bacterial structures in these stalagmites is. Is the assertion that the association between high P concentrations and microbial structures is a function of decreased infiltration that allows bacterial growth as well as high P concentrations? Why do P-rich phases preferentially precipitate in corrosion pores? The relationship could be made more explicit.

Technical Corrections:

-Page 2558, line 19: "trace elements incorporation" should be "trace element incorporation".

-Page 2560, line 3: "the" or "a" should be added between became and subject in, "which became subject of controversy"

-Page 2560, line 6: "Great Cayman" should be "Grand Cayman"

-Page 2561, line 7: "to" should be added between not and be in, "appear not be related".

-Page 2561, line 11: "Chrismas" should be "Christmas".

-Page 2563, line 8: change "other 50" to "50 other".

-Page 2565, line 17: change "show that P highest concentration" to "show that the highest P concentration"

-Page 2565, line 25: change "from which P transported" to "from which P is transported".

-Page 2566, line 6: should be "air filled voids".

-Page 2566, line 21: should “suspect” instead be “suspected”?

-Page 2567, line 6: I don’t believe that “Tropical” should be capitalized in this instance. This also applies on line 22 on this page.

-Page 2567, line 18: should be “although”.

-Page 2568, line 11: “riminescent” should be “reminiscent”.

-Page 2568, line 13: “show” should be “shows”

-Page 2570, line 25: should be “Pliocene”

-Figure 5: It is not clear from the figure if the first row of data refers to U or to Y concentrations.

Interactive comment on Clim. Past Discuss., 8, 2557, 2012.