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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.

**S. Frisia et al.**

silvia.frisia@newcastle.edu.au

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We are very grateful to Marc Luetscher and the anonymous referee for their comments, which will help to improve the scientific and iconographic quality of the manuscript. The revised version will incorporate most of the recommendations for rephrasing as well as technical corrections. The following points address issues raised by the two referees:

Anonymous Referee #1 Point 1.

"As so much of this study hinges on the discussion of visual patterns in crystal struc-

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Interactive Discussion
Discussion Paper

tures 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?"

Response:) We agree and will change accordingly. In the first version of the manuscript, we did not specify that the synchrotron polished section (1C) is the mirror face of the thin section (1B) and that the SEM sample is the pre-polished mirror face of the thin section, that is: the slab which was then used, once polished, for synchrotron analyses. We will include this piece of information in the caption to Fig. 1. Furthermore a new figure with four SEM picture of the P-rich layer will be included.

"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."

R) This will be done in the new version of the manuscript

"Similarly, Figure 4 would benefit from the inclusion of a micrograph of Phase 2 to allow direct comparison between crystal structure and chemical variations".

R) It is unclear what the "inclusion of a micrograph of Phase 2 to allow for direct comparison of crystal structure…" means. If our understanding is correct, we are required to provide a thin section photograph. We are, unable to provide Transmission Electron Microscope micrograph of phase 2 to illustrate microstructures, but we will provide several photos of the layer in thin section in the supplementary material.

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.

R) We agree to provide clarifying annotation in the captions to Figure 1 in the main text and we will provide additional SEM micrographs to better support the description and act as future reference for those who may find similar features in speleothems used for palaeoclimate research. We would like to stress, however, that the samples illustrated in Figure 1 and throughout the paper are not modern, actively growing surfaces. The organic matter which existed on top of past growth surface thus underwent oxidation and calcite growth has incorporated and fossilized bacteria. Consequently, we do not have the same pristine bacterial and fungal features illustrated by Jones (2009), but the result of diagenetic alteration and preservation of possible bacterial-related structures. Secondly, SC4 and, most likely, FS04 come from aphotic zones, whereas the samples illustrated in Jones (2009) may still be influenced by light, and the microbial populations may, thus, be very different.

Further imaging of Phase 2, the stromatolitic phase, in the Nullabor speleothem would also be helpful, as in Figure 3 it is only discernible that there is a zone of more finely laminated calcite.

R) We will provide as supplementary material a new plate with 6 micrographs highlighting the structure of the stromatolite-like layers in the revised manuscript.

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?

R) In the revised manuscript, we will address the issue of PCP. Unfortunately, the pCO2 of the cave was not measured, and we have no possibility to test the role of cave air pCO2 in driving calcite precipitation at Smith's Cave. Although this potential can not be directly tested, we will include in the revised manuscript time series of drip-rate, drip-water chemistry (Mg, Sr, Ca and P) as well as the rainfall amount data for the same time period which show the interplay between PCP and water-rock interaction at Smiths Cave.

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.

R) This comment is unclear as there is no data on Si/Ca and rainfall for the specimens analysed here. To date, no one knows how/if the Si/Ca ratio is modified by bacteria. The existing literature only addresses the issue hat bacteria may favor the precipitation of Si as amorphous phase. We can not provide explanation relative to processes which are still largely unexplored. Alternatively, we may only stress the lack of knowl-

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edge relative to Si incorporation in speleothem and to what Si-rich phase may develop. There is very little information relative to the significance of non-detrital Si phases in speleothems, and for the present study we had to rely on knowledge from continental chemical precipitates, such as silcretes. We are not, thus, in the position to provide a more exhaustive or clear explanation.

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.

R) This comment has been taken into account and we will discuss the PCP and periods of aquifer recharge along the scan.

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?

R) The objective of the paper is to show several different mechanisms resulting in increase in P concentration in speleothems and the fact that P may be present in the host rock, rather than in the soil as commonly assumed. One of the most important issues is that P can be incorporated as a P-rich phase in speleothems. This is true not only for Christmas Island, which is exceptionally rich in P, but also for caves where the variability of P can be considered within the “norm” for the existing body of published data (usually between 10 and 250 ppm) and there is no known P-rich phase in the host rock (or not measured, given that the host rock is not usually analysed in speleothem studies). For the published examples, only Grotta di Ernesto was tested for the presence of different P-phases in the speleothem. Obviously, the presence of phases different from pure calcite may alter the theorethical P partition coefficient, but then, this is exactly our point. If one does not check for the presence of other phases than pure calcite, then the use of the theoretical, rather than empirical partition coefficient may be inaccurate. Note that at Grotta di Ernesto the P concentration was

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between 40 and 120 ppm, much lower than at Christmas Island. Thus, if an “unknown” P-rich phase was detected at Ernesto, and “unknown”, as well as P-rich phases are detected at Christmas Island, it stands to reason that, before interpreting P variability in speleothems in terms of theoretical assumptions, we should check how P is incorporated in the stalagmite. Obviously, we should also check in which phase P is present in the host rock, because this may influence the Ksp. Thus, the answer to the Reviewer question is, in principle, yes, but our yes does not mean that one can run P time series in a speleothem without knowing what is in the rock, and then interpret P variability in terms of soil provenance and of theoretical partition coefficient for pure calcite. This may be wrong. The too common lack of supporting petrographic and mineralogic data for both host rock and speleothems in speleothem-based palaeclimate studies leads to over-semplification, which is, possibly, what we desire in palaeoclimate studies. Our study shows the complexity of the significance of P and how this element should be analized by accounting for its petrographic and “sedimentological” framework.

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.

R) In the revised version of the manuscript we present SEM pictures in a new figure which support the evidence that the P-rich phases are concentrated not only in dissolution pores, but also within the calcite. We will stress in the text that the dissolution features in SC4 are probably related to organic matter oxidation. The organic matter (bacteria) is commonly associated to high P. Thus, the P released subsequently precipitates in the bacteria-rich layers both in cavities and as co-precipitated P-rich phases. The possible association of P-rich phases, bacteria, and dissolution has been already explained by Jones (2009).

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

R) The Figure will be adjusted accordingly.

Marc Luetscher (Referee 2)

1) "Much of the paper relies on the hypothesis that P originates from the cave host-rock. This assumption is largely based on the fact that P correlates with Ca in modern drips at Smith's cave, on Christmas Island. In my understanding, this is however not sufficient to rule out other potential sources (e.g. soil microbial activity). It would therefore be nice if the authors could elaborate on this, in particular by describing the water-rock interaction more carefully. If, as suggested by the authors, P results from an increased rock/water interaction, why should it anticorrelate with Mg which most likely originates from the dolomitic host-rock? If, on the other hand PCP is invoked to explain high Mg/Ca ratios, why should P correlate with Ca? Some clarification would be appreciated here."

R) As Reviewer 1 raised the same issue, in the revised manuscript the role PCP will be more extensively addressed. In addition, to clarify P provenance, a more exhaustive description of the host rock of Smiths cave will be provided, including the fact that it contains clasts of P-rich volcanics. One of the issues raised in our manuscript is, in fact, the common assumption that P in speleothems is derived from soil and vegetation decay. This assumption is largely based on pioneering studies carried out at Grotta di Ernesto, culminating with the Borsato et al., (2007) GCA paper, a cave cut in P-poor, Mesozoic carbonates located in a mid-latitude region where the vegetation experiences autumnal to winter die-back. This is not the situation in many tropical or Southern Hemisphere regions, where vegetation has negligible seasonal die-back as it consists of evergreens. Although Treble et al. (2003) studied a mid-latitude cave in the SH, that is in Australia, they did not provide any characterization of the host rock underpinning the interpretation of P and relied on NH-based studies for their interpretation. In Treble et al. (2003) provenance of phosphorous was assumed to be from vegetation decay on the basis of the Grotta di Ernesto studies (Ref. 2 and 3 in Treble et al., 2003). We here present here the case of speleothems from tropical and mid-latitude SH caves formed in young marine limestone, which may still contain (have contained) unstable phases, are porous and reactive, and where phosphorous is (was) present ab-initio in the host rock. In both cases, the soil likely formed mostly by weathering of carbonates (residual soil) (in the wet Miocene for the Nullarbor, see. Miller et al., 2011) and the vegetation is (was) evergreen. Our case studies are unlikely to be the same as Ernesto because of the presence of P-rich minerals in the rock, whereby P derived from the rock is overwhelming relative to any vegetation die-back contribution. This is the reason why the vegetation die-back hypothesis was unexplored, because it does not pertain to the geographic and climatic setting analysed in the present study. We will, therefore, stress better in the revised manuscript that P provenance from the host rock, which has been thus far mostly neglected, may be an issue and discuss the implication of P remobilization in the epikarst. We will elaborate as requested by Luetscher on the role of PCP and water rock interaction which will become more clear with the inclusion in the revised manuscript of time series of drip-rate, drip-water chemistry (Mg, Sr, Ca and P) as well as the rainfall amount data (see the answer to comment 3, Reviewer 1).

2) "Similarly, the co-precipitation between Ca and P needs to be better explained/ demonstrated. Rather than depending on the absolute Ca concentration of the drip water (p.2566 l.18), I would expect the precipitation of calcite being related to the degassing rate (i.e. CO2 gradient or drip rate). Since “drip rate does not show a good correlation with P concentration” (p.2566 l.5) is there any change observed in the ventilation regime or is there any evidence that cave pCO2 could be higher during the wet season, when recharge is elevated?"

R) Again, this is a similar issue as that raised by Reviewer 1. We have explained that we have no pCO2 data. However, the time series of drip-water chemistry clearly document that PCP occurred seasonally and there is an inverse correlation between rainfall (=infiltration) and PCP, although the correlation between rainfall and drip rate is not always clear. There are annual cycles in PCP, related to infiltration, that influence degassing and cave calcite growth. Because at high Ca concentration the partition coefficient of P is >1, then, calcite precipitation results in over-incorporation of P and depletion of P in residual water. This situation modulates stalagmite growth, however, we document periods at multi-decadal scale when P is incorporated as P-rich phases which grow into dissolution cavities as well as in calcite, and are associated with morphologies commonly found in experiments targeted to investigate carbonate and phosphate bio-precipitation and bio-mediation. These P-rich layers are different from the annual layers possibly modulated by PCP during the recharge season. The revised text will explain in better detail the mechanisms proposed for the “supra-annual” modulation for the formation of layers which contain P-rich phases.

3) "The palaeoclimatic interpretation of the Nullarbor speleothems assumes an analogy between two study sites separated by several thousands of km and located in (present day) different climatic contexts. Since the interpretation largely relies on the rock-water interaction, a better description of the host-rock at Nullarbor would support the discussion. How does the P concentration of the carbonate compare to that at Christmas Island? Is apatite present as well?"

R) We have carried out additional X-ray investigation of the Nullarbor limestone and will provide a better description of the diagenetic history of the Nullarbor host rock which resulted in concentration of P in phosphates and carbonates. Phosphate minerals of the Apatite group are present also in the Nullarbor limestones, although not associated with volcanic rocks as at Christmas Island.

4) "Moreover, the authors suggest that some P enrichment could be related to microbial processes. Although it is hinted that microbial mats may be associated to (secondary?) micro-pores, a more detailed petrographic description would be useful here (e.g. description of microbial fabrics/mats in the old and/or modern speleothems)."

R) This is the same issue raised by Reviewer 1, and we agree with the comments. Therefore, we will provide in the new manuscript a more detailed petrographic description as requested and thin section micrographs.

5) "Finally, the authors speculate that the dry periods interpreted from Nullarbor speleothems may reflect a global climate signal associated to the closure of the Central American Seaway. A proper description of the regional climate system is however missing and the link to the “EEP” has to be described first. It is also unclear why a gradual closure of the seaway would lead to “recurrent” dry periods and not simply shift the climate system."

R) This was not the major scope of the paper, and the speculation relies on the interpretation provided by Steph et al (2010). It is not feasible to provide a proper description of the regional climate system at circa 4 MA for the Nullarbor because it is, as yet, not certain. From sedimentological data, it is known that the climate was more dry than in the Miocene, but less dry than in the Pleistocene (Miller et al., 2011). The presence of speleothems clearly indicates that the climate was wetter than today, when no speleothems grow. We just pointed out that periods when speleothems actively grew, at ca. 4 MA, may have been punctuated by a growth interruption. Hence, the climate of the Nullarbor plain in what is commonly referred to as the “warm and wet” Pliocene may have been more complex. To date, Steph et al (2010) is the reference which best explain the mechanisms for the possible climate “instability”. They suggested that the gradual closure of the seaway led to the transition to the Quaternary. We will, thus, restrict ourselves to the possible palaeoclimate significance of the bacterial laminae we have observed, and make clear that these point to possible complexities in the Nullarbor climate during the so-called wet-dry phase. The greatest issue is that the ages of these speleothems have large errors, and a refined climate reconstruction is, to date, still not feasible. Still, if our interpretation of the P-rich and bacterial-like layers holds true, it becomes clear that about 4 MA ago in the Nullarbor climate conditions may have changed towards dry spells. This is, in itself, already a new piece of information, which may be useful to unravel the Pliocene climates.

Detailed comments p.2562 l.15 “P concentration in excess of 10000 ppm relative to the parent water”. Which partitioning coefficient did you use here? p.2566 l.12 How did you determine the partition coefficient? Have you assumed an average drip discharge? p.2569 l.3 What is your “empirical enrichment factor”? The same as for Smith’s cave?

R): these comments will be addressed in a specific new paragraph dealing with the P partition coefficient and incorporation in speleothem calcite (intra and extra lattice).

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