General comments

With great interest I have read "An X-ray absorption method for the identification of calcium phosphate species using peak height ratios" by J. Oxman, in which the author systematically analyses literature-derived XANES spectral characteristics of calcium phosphate minerals. The manuscript is well-written and focuses on a relevant topic in P geochemistry: how can XANES spectra be used for reliable (and detailed) P speciation. X-ray analysis of natural samples is widely acknowledged as a promising technique to advance our understanding of P mineral (trans)formation in soils and sediments and has been applied for several decades now, but does not seem to be able to fully shed its qualitative or at best semi-quantitative skin. The current contribution attempts to enhance our ability to quantitatively discern between different types of calcium phosphates, from amorphous calcium phosphate to crystalline apatite, based on calculated spectral parameters (peak height ratios). In my opinion, this is a worthwhile step in the overall process of elevating XANES-based P speciation to a more quantitative level. Furthermore, the study combines libraries with P XANES spectra from a variety of sources, which enables the comparison of P standard spectra that are scattered across the literature and obtained in various ways at different synchrotron facilities. The final normalized dataset also allows the author to pick out potentially contaminated standards, and back this up with known issues with the recipes for such Ca-P minerals. Because of these merits, I support publication of this manuscript in Biogeosciences, provided the author carefully considers the comments below.

Specific comments

1. (p.18735, L14-20) Here is the only statistical analysis of the results, which I think deserves more detailed attention in the manuscript. There is a contrast between the emphasis on the objective, quantitative approach of normalization and obtaining peak height ratios, and the mostly qualitative discussion of the differences between spectral parameters for the various Ca-P species. (A good example of this also is Table 2, which on its own presents little useful information to the reader because of the strictly qualitative description of spectral features.) I would propose to present the peak height ratios with standard deviation for all Ca-P species, and more systematically explore the statistical difference between the Ca-P species (and perhaps the

general spectral features of Table 2). This all would be suitable information for a table, besides being discussed in the main body of the text. In addition, the author mentions that differences between species within libraries generally were larger than the overall averages for those species. It could be useful to separately present the statistical difference between Ca-P species for the whole data set and the individual libraries?

2. (p.18736, L1-20) The author mentions that earlier work implies that XANES shoulder features become more well-defined with ***decreasing*** thermodynamic stability. It is the humble opinion of this reviewer that this is a mistake: the cited literature actually mentions that more crystalline Ca-P phases (i.e. ***increased*** thermodynamic stability) have more well-defined XANES shoulder features. This fits with the data in the current manuscript (more soluble species have more subtle shoulders, p. 18736, L9-10). The implied contrast between this work and previous studies does not exist, and the first paragraph on p.18736 should be adjusted to correct this.

3. (p. 18738, L5-13) The authors point out the difference between direct precipitation of poorly crystalline hydroxyapatite in bones, and the step-wise formation of crystalline apatite via precursor phases in sediments. The way it is written currently seems to imply that the authors are among the first to suggest direct formation (it is also mentioned explicitly in the conclusions (p. 18742, L5-9). However, direct formation of hydroxyapatite has been established many decades ago (e.g. Boskey and Posner, J. Phys. Chem., 1976, 80 (1), pp 40–45) as occurring under conditions of low supersaturation with respect to Ca and PO_4. Perhaps it is the chemical formation environment in general and not necessarily the bone-sediment contrast that determines Ca-P (trans)formation? Could marine porewater with low Ca and PO_4 concentrations also potentially host direct HAP precipitation? The manuscript would benefit from more consideration of earlier work that shows the potential of direct precipitation of (bone) hydroxyapatite, and the strong control of formation conditions on the type of Ca-P association that is (initially) formed from solution.

Technical corrections

p. 18725, L4-5. "For this reason [...] scientific fields" is a redundant sentence without information. Rephrase or delete.

p. 18725, L26. Add 'dibasic calcium phosphate dihydrate' instead of only DCPD abbreviation.

p. 18728, L11. What are "related measurements"?

p. 18729, L16. Awkward phrasing, "who published studies already selected"

p. 18729, L19. Awkward phrasing, "from the period of review until collection"

p. 18730, L8. "energy normalization procedure was applied to all spectra"

p. 18730, L19-20. Awkward phrasing, "averaged among equal species"

p. 18730, L22. "energy-normalized spectra"

p. 18735, L21. "model spectra, which were created by"

p. 18736, L2. See specific comment 2, "decreasing" should be "increasing" (and further implications for the manuscript text).

p. 18737, L9-10. Awkward phrasing "according to the reference compounds". Do you mean it was done in the same way as the HAP spectra were normalized?

p. 18737, L22. Delete "in respect of their spectral analysis"