

Referee #1

I thank the referee for the helpful and very constructive suggestions. The following section addresses each comment. The response is written in italics.

(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?

Response 1: The peak height ratios are now presented together with the standard deviation for all Ca-P species (see revised Table 2) to address the referee's suggestion. Further, the statistical differences between peak height ratios for all Ca-P species are now given in the revised Table 2 to present systematic statistical differences between the Ca-P species. The Table now includes a probability matrix that reports different probability levels for all possible combinations of the different Ca-P species (see revised Table 2). An important finding of this study is that apatites can be distinguished from OCP, ACP, DCPD and DCPA/MCP by their relative secondary peak heights (Figs. 3 and 4). This finding is also confirmed by statistical analysis; and related information was added in the above-mentioned section (p.18735, L14-20).

To address the last point (differences between species within libraries), the section (p.18736 L26 - p.18737 L2) was rephrased as follows: "In general, within-study differences between spectral features of two species were more pronounced than could be assumed from the peak intensity ranges shown in Figs. 3 and 4. For example, the plots for HAP and OCP show a relatively small difference between the lowest secondary peak for HAP and the highest peak for OCP. However, these two spectra were not pair-wise (collected in the same study) spectra. Each of the eight studies, which collected an OCP spectrum, also provided an HAP spectrum (see reference numbers in Fig. 3) and corresponding discrepancies in secondary peak heights between these two species were relatively large". The above-mentioned conclusion (p.18736 L26 - p.18737 L2) already considered results of several studies. As suggested by the referee, it would be useful to assess statistical differences between Ca-P species for both the complete data set and individual studies. However, the structure of the data set did not allow for an analysis of these statistical differences in individual studies. For example, individual libraries generally contained only one or two samples of a certain species (except the study of Ingall et al., 2011; Table 1) and within-

study sets of different species were frequently limited (focus on different groups of species; Table 1). This is explained by the temporary use of synchrotron facilities and indicates why the pronounced differences detected in this study were not detected in individual studies. In summary, specific spectral discrepancies between two different species should theoretically be even more pronounced in individual studies but, nevertheless, specific spectral discrepancies between two different species among studies were in good agreement (statistically significant; see revised Table 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.

Response 2: Thanks for pointing out the mistake in writing. The mistake was corrected (to substitute ‘increasing’ with ‘decreasing’; p. 18736 L2). As the referee correctly notes, the current study agrees with the cited literature. The phrase “in agreement with these observations” was substituted with “indeed” (p.18736 L5) to more clearly emphasize the latter fact.

(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 PO₄. 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 PO₄ 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.

Response 3: The specific objective was to point out that direct precipitation of poorly crystalline HAP in bone has been established. This fact was used to substantiate the conclusion (based on the criteria for Ca-P determination of the current study) that Rajendran et al. (2013) likely detected poorly crystalline HAP; and that their spectra (Fig. S2) are not spectra of potential precursors. To point out that direct precipitation of poorly crystalline HAP in bone has been established, Section 3.4 of the manuscript included the following sentence: “This assumption would be in line with the conclusion of Rey et al. (2009), who inferred from a thorough review of several studies that no substantial evidence has been established for the presence of any Ca-P

phase in bone except poorly crystalline apatite” (p.18738 L.2-5). This implies that no study was able to clearly identify precursors in bone material and, hence, poorly crystalline HAP may only form by direct precipitation in bone. Therefore, the manuscript cites earlier work (Rey et al., 2009; ‘review of several studies’) that demonstrated direct precipitation of HAP in bone. The cited review of Rey et al. (2009) even includes several related studies of the above-mentioned authors (Boskey and Posner). While direct formation of HAP has been established many decades ago, absence of step-wise formation in bone has been largely confirmed more recently (e.g. Rey et al., 2009). As sediment likely hosts both direct and successive crystallization, the true (and interesting) difference between bone and sediment appears to be the absence of successive crystallization in bone.

I revised the lines 21-25 (p.18724) to account for this specific information (“This biological apatite formation is likely opposed to that of sedimentary apatite, which apparently forms by both direct nucleation and successive crystallization.”). Further, “confirms” was substituted with “implies” (p.18724 L23) and “suggests” (p.18741 L7) to avoid the potential misinterpretation mentioned by the referee.

As the referee suggests, calcium and dissolved inorganic P concentrations could determine whether successive crystallization or direct nucleation is favoured. The pH may also be an important parameter (see e.g. Bell and Black, 1970). This subject is complex and the speciation of apatite and OCP was an example for the identification using peak height ratios. However, to consider earlier work on this subject and to include information on the strong control by formation conditions, the end of section 3.4 (p. 18739 L3-5) was revised as follows: “This study also provides evidence that authigenic apatite formation proceeds most likely via an OCP precursor pathway, in addition to direct nucleation. The numerous controls on the two pathways in sediment can be summed up by the terms ‘saturation state’ (e.g. supersaturation with respect to CFAP or precursors; Atlas, 1975; Gunnars et al., 2004; Van Cappellen and Berner, 1991), ‘kinetic factors’ (Atlas and Pytkowicz, 1977; Gulbrandsen et al., 1983; Gunnars et al., 2004, Jahnke et al., 1983; Schenau et al., 2000; Sheldon, 1981) and ‘inhibitors’ (Eanes and Rattner, 1981; Golubev et al., 1999; Gunnars et al., 2004; Martens and Harriss, 1970; Van Cappellen and Berner, 1991). In consideration of the still limited knowledge about the complex interplay of these factors in CFAP formation, Slomp (2011) recently emphasized the need for detailed studies on this subject.”

Technical corrections

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

p. 18725, L26. Add ‘dibasic calcium phosphate dihydrate’ instead of only DCPD abbreviation. *Included*

p. 18728, L11. What are “related measurements”? “*measurement reproducibility*” was substituted with “*related measurements*”

p. 18729, L16. Awkward phrasing, “who published studies already selected” *Sentence was rephrased*

p. 18729, L19. Awkward phrasing, “from the period of review until collection” *Sentence was rephrased*

p. 18730, L8. “energy normalization procedure was applied to all spectra” *corrected accordingly*

p. 18730, L19-20. Awkward phrasing, “averaged among equal species” *Sentence was rephrased*

p. 18730, L22. “energy-normalized spectra” *corrected accordingly*

p. 18735, L21. “model spectra, which were created by” *corrected accordingly*

p. 18736, L2. See specific comment 2, “decreasing” should be “increasing” (and further implications for the manuscript text). *Sentence was corrected (see Reply #2)*

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? *Yes, sentence was rephrased*

p. 18737, L22. Delete “in respect of their spectral analysis” *Deleted*

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See Table on next page

Revised Table 2. Summary of diagnostic P K-edge XANES features for various Ca-P species.

Ca-P species	Other distinctive features			Secondary peak height (%)													
	Post edge shoulder	Post edge shoulder height	Oxygen osc.	Secondary peak height ¹ % (n)	SD	CFAP CHAP	HAP Σ	HAP synth.	HAP nat.	TCP	OCP	DCPD	DCPA MCP	ACP	P on CaCO ₃	HAP p. cryst. +am.	
FAP	broad	very high	narrow	8.7 (8)	8.5	1.1	N	**	***	N	*	****	****	****	****	***	***
CFAP CHAP	broad	very high	narrow	8.1 (5)	8.0	1.3		N	**	N	N	****	****	***	**	**	**
HAP Σ	broad	high	narrow	7.1 (17)	7.0	1.4			N	N	N	****	****	****	****	***	**
HAP synth.	broad	high	narrow	6.6 (7)	6.3	0.7			**	N	**	****	****	****	**	***	***
HAP nat.	broad	high	narrow	8.6 (5)	8.5	1.3				N	****	***	***	**	**	*	*
TCP	broad	medium	medium	6.3 (4)	5.9	1.6					**	*	*	*	N	N	
OCP	broad	medium	narrow	4.2 (8)	4.0	0.5						N $\sqrt{}$	N $\sqrt{}$	****	*	N $\sqrt{}$	
DCPD	mixed	low	medium	3.8 (7) ²	3.7	1.0							N $\sqrt{}$?	*	N $\sqrt{}$?	N $\sqrt{}$?	
DCPA MCP	missing	n/a	broad	2.6 (16) ³	2.5	2.8								N $\sqrt{}$	N	N	
ACP	narrow	medium	broad	1.6 (2)	1.6	0.1									N	**	
P on CaCO ₃	mixed	low	broad	2.4 (2)	2.4	1.5										N	
HAP p. cryst.	narrow	low	broad	4.2 (1)	n/a	n/a											
HAP am.	broad	low	narrow	3.8 (1) ²	n/a	n/a											

¹ Averaged relative secondary peak height (% of white-line peak height). Left column: averaged secondary peak height (%) of individual spectra and number of averaged spectra in parentheses. Right column: secondary peak height (%) of model spectra (averages for multiple curves; Figure 4)

² Secondary peak shifted towards main peak.

³ Includes four spectra, which lacked a secondary peak (see high standard deviation).

N: Difference of secondary peak heights (%; population means) is non-significant (Two Sample Independent t-Test)

*: Difference of secondary peak heights (%) is significant at the 0.05 level

**: Difference of secondary peak heights (%) is significant at the 0.01 level

***: Difference of secondary peak heights (%) is significant at the 0.001 level

****: Difference of secondary peak heights (%) is significant at the 0.0001 level

N $\sqrt{}$: Denotes other distinctive features for two species, which cannot be distinguished by their secondary peak heights (note that other distinctive features are not denoted for pairs with significantly different secondary peak heights). OCP distinguishable from DCPD (secondary peak shift or missing post-edge shoulder), DCPA (missing post-edge shoulder), MCP (missing post-edge shoulder), poorly crystalline HAP (missing post-edge shoulder, broad oxygen oscillation) and amorphous HAP (secondary peak shift). ACP distinguishable from DCPD/MCP (missing post-edge shoulder).

N $\sqrt{}$?: Denotes other potentially distinctive features for two species, which cannot be distinguished by their secondary peak heights. DCPD likely (note the two atypical DCPDs in Figure 3) distinguishable from DCPA (absent secondary peak shift), P on CaCO₃ (absent secondary peak shift, broad oxygen oscillation) and poorly crystalline HAP (absent secondary peak shift)

Grey: Note that P on CaCO₃ was probably contaminated by crystalline Ca-P phases (see text) and that poorly crystalline HAP and amorphous HAP require further verification by additional spectra.

Abbreviations: n/a (not applicable); SD (standard deviation); oxygen osc. (oxygen oscillation); HAP synth. (synthetic HAP); HAP nat. (natural HAP); HAP p. cryst. (poorly crystalline HAP); HAP am. (amorphous HAP)