

## ***Interactive comment on “Quantification of octacalcium phosphate, authigenic apatite and detrital apatite in coastal sediments using differential dissolution and standard addition” by J. F. Oxmann and L. Schwendenmann***

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Referee #2

*We thank the referee for the constructive suggestions. The following section addresses each comment. The response is written in italics.*

Comment 1: The standard addition experiments were performed in fairly sandy sediments. Perhaps the authors could add a sentence or two with their thoughts on the potential matrix effects of doing similar extractions in more clay rich sediments, which

C364

are often the focus of marine studies.

*Response 1: As the referee notes, the Firth of Thames sediment was sandy (clay, silt, sand: 8, 34, 58%). We referred to a study conducted in more silt- and clay-rich sediments (l. 9-14, p. 300). To provide this information directly we revised the lines 9-14 (p. 300) as follows:*

*“Results of CONVEX analysis of the sediment from the Firth of Thames were compared with those of tidal flat sediment from the Saigon River Delta, Vietnam (Ca-P: 5.36  $\mu\text{mol P g}^{-1}$ ; Al/Fe-P: 5.90  $\mu\text{mol P g}^{-1}$ ; pH: 7.47; clay: 12%, silt: 83%; sand: 5%; Oxmann et al., 2008) to test cross-regional transferability (see section 3.1).”*

*Although textural properties of the two sediments were different, we did not observe adverse matrix effects on method performance. Furthermore, the proposed method was successfully applied to different sediments from different ecosystems of the Firth of Thames (Oxmann and Schwendenmann, unpublished data), including more silt- and clay-rich sediments. A part of Sect. 4 was modified to include this information. Further, the referee acknowledged the information about solubilities of Ca-P standards, which were simultaneously gained. Section 4 was also revised to recommend modifications to the method for the analysis of solubilities under different conditions. The part of Sect. 4 is now as follows (l. 15-19, p. 314):*

*“Overall, this study demonstrated that the CONVEX method can be used for experimental evaluation of calcium phosphate solubilities in the sedimentary environment. Modifying the conversion procedure by adjusting the incubation time or varying the solution composition (e.g. different ionic strengths), could provide an understanding of dissolution kinetics and solubilities under different environmental conditions. Moreover, the method performs accurately for quantification of the most important sedimentary Ca-P species. Further analysis of sediments of different textural properties suggests that the method is robust towards differing characteristics of sample matrices (Oxmann and Schwendenmann, unpublished data). Generally, obtained results are not biased*

C365

by common matrix interferences because the method of standard addition eliminates matrix effects.”

Comment 2: The manuscript is in great shape and will be helpful to those examining phosphorus distribution in sediments. However, the text size on many of the figures is so small that it is nearly illegible. Perhaps I missed it in the text but a better description of where the thermodynamic data was obtained to create Figure 1 would be nice.

Response 2: We revised the caption of Figure 1 to better describe the data sources. Furthermore, we thought it could be useful to exemplify the uncertainties arising from  $K_{sp}$  values using hydroxylapatite as an example (see revised figure and caption). Additional colour discrimination was used to improve the clarity of Figure 1. The calculations were conducted according to Lindsay et al. (1989). For this system, results are similar to those computed by more-sophisticated algorithms (e.g. MEDUSA; Puigdomenech, 2000). This information was added to the caption of Figure 1. Additionally, we have added a reference, in which the dependence of calcium phosphate solubility on salinity is shown. The figure caption is now as follows:

“Figure 1. Apparent solubilities of calcium phosphates, strengite and variscite (in equilibrium with gibbsite or kaolinite) when  $Ca^{2+}$  is  $10^{-2}$  M or is fixed by calcite.  $CO_2(g)$ : 0.0003 atm;  $F^-$ :  $10^{-4}$  M (equilibrium level of  $CaF_2$ );  $CO_3^{2-}$  at the given  $CO_2(g)$ . Strengite and variscite are more insoluble under acidic conditions while calcium phosphate solubility decreases with increasing pH. At  $pH > 7.88$  calcium phosphate solubility may increase due to  $Ca^{2+}$  depression caused by decreasing calcite solubility (see dividing curves at this pH for  $Ca^{2+}$  depression or maintained  $Ca^{2+}$  concentration). Calculations used apparent dissociation constants and thermodynamic solubility products reported in Lindsay et al. (1989). To exemplify the inherent uncertainties arising from variability among  $K_{sp}$  measurements, hydroxylapatite (HAP) solubility was calculated using the range of corresponding  $K_{sp}$  values reported in the literature (Baker et al., 1998). The solubility of carbonate fluorapatite (CFAP) was calculated using the apparent  $K_{sp}$   $10^{-103}$  given by Perrone et al. (2002). See Lindsay et al. (1989) for details on calcu-

C366

lations. Results for this system are similar to those computed by more-sophisticated algorithms (e.g. MEDUSA; Puigdomenech, 2000). See Atlas (1975) for the theoretical dependence of calcium phosphate solubility on salinity. FAP: Fluorapatite; TCP: Tricalcium phosphate; OCP: Octacalcium phosphate.”

The body of the text was revised accordingly, where appropriate. With respect to the supplementary information about the salt effect the following text was added (l. 1, p. 306):

“When the calculation of the solubility of Ca-P phases under experimental conditions (Fig. 1) is modified to obtain solubilities for seawater of normal composition ( $5^{\circ}C$ - $25^{\circ}C$ ; see e.g. appendix in Atlas, 1975), pore-water appears to be generally undersaturated with respect to OCP. Due to widely differing solubility products (see e.g. HAP in Fig. 1) and the challenging application to multi-ion systems of high ionic strength, the uncertainty associated with such thermodynamic models is, however, relatively large. Incubations of P-spiked natural seawater on the other hand indicated that homogeneous precipitation of non-apatitic Ca-P is generally possible within some days under naturally occurring pore-water P concentrations (see kinetic considerations in Atlas, 1975).”

Please also note the supplement to this comment:

<http://www.ocean-sci-discuss.net/11/C364/2014/osd-11-C364-2014-supplement.pdf>

Interactive comment on Ocean Sci. Discuss., 11, 293, 2014.

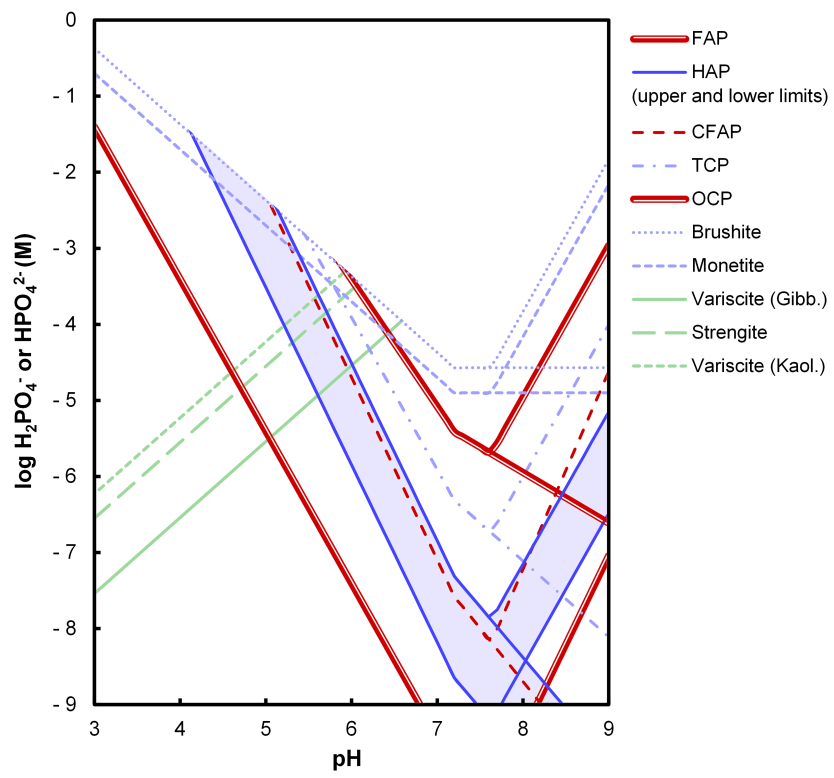


Fig. 1.

C368