Biogeosciences Discuss., 10, C8171–C8174, 2014
www.biogeosciences-discuss.net/10/C8171/2014/

Biogeosciences
Discussions
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Interactive comment on "An X-ray absorption method for the identification of calcium phosphate species using peak height ratios" *by* J. F. Oxmann

Anonymous Referee #2

Received and published: 22 January 2014

Synchrotron based X-ray absorption near edge structure spectroscopy (XANES) is becoming more available for the analysis of phosphorus composition in natural systems like soils, marine sediments and organisms. Interpretation of XANES data generated in most studies to date is typically done through comparison of unknown spectra with that of P standards. As recognized by the author of this paper, these comparisons are often confounded due to the similarity of spectra features of standard compounds and the common occurrence of natural phosphorus as a mixture of different phases. Various calcium phosphate phases are typically the most important reservoirs of phosphorus in natural systems. Unfortunately distinguishing calcium phosphates by XANES is very difficult due to spectral similarities in this class of phosphate compounds. This paper examines spectral characteristics in detail of a variety of calcium phosphates taken from a number of published studies. After data normalization procedures, differences

between spectra of different calcium phosphate phases may become more apparent. This paper represents a great effort in literature data collection and interpretation; however, the following issues complicate the overall utility of this study for interpretation of natural samples:

1) It would be difficult for readers of this manuscript to apply normalization procedures from the brief description given. For example, use of terms such as "unit edge jump" and "equal species" add confusion because they are not clearly defined. Also, when it is said that main (white line) peaks were adjusted to 2150 eV and tertiary peaks to ca. 2167 eV, it is unclear what exactly was done (Page 18730 Section 2.2). It sounds like the positions of both peaks were moved. Certainly the overall position of spectra may need to be moved due to differences in energy calibration between different studies. However, adjusting the position of multiple peaks in the same spectra to specific positions would greatly alter the original data. Subtracting multiple baseline segments from data altered to shift multiple peaks is troubling. Perhaps this is not what was done, but again the writing of this section is not detailed enough. Other examples of vague description of the method - What does "ca. 2167" specifically mean? What does "normalized to a step of one" mean?

2) It needs to be clearly demonstrated that such procedures are vastly superior to currently available spectral processing and identification routines. ATHENA and SIXPACK are powerful and freely downloadable spectral processing and comparison software for XANES spectra. In contrast, a potential user of the methods presented in this paper would be faced with writing their own code to process the data based on unclear and rather vague instructions. It may be possible to directly compare standards from a database to unknowns using ATHENA and SIXPACK to achieve nearly identical results. A direct comparison between approaches in deconvoluting mixtures of known composition (see comment 5 below) would help convince the reader that the methods presented in this paper are worth adopting.

3) Using a data set constructed from various publications is potentially problematic as it

may contain artifacts leading to erroneous conclusions. For example, white line intensities relative to tertiary peak intensities could be affected by detector response rates. Slight overload of the detector at the white line could strongly affect ratios of different peaks at different energies. Furthermore, self-adsorption can strongly affect the intensity of certain spectral regions. This concern is addressed in the manuscript by saying most studies claim to reduce self adsorption (Page 18732 Section 3.1). Even small differences in particle size used between different studies are likely to lead to spectral differences especially at higher energies in samples of the same phosphorus phase. The effect of self-adsorption is probably non-linear over the energy range of a spectrum. Finally, identification of different phosphate phases, especially different apatite minerals, is difficult. Unless the composition of the different forms of apatite used in the data compilations were independently verified, it reduces confidence in the conclusions drawn from this study. Similarity of spectra, as is invoked in the manuscript, does not prove that the standards used were of the same composition. Natural specimens of calcium phosphate minerals are often misidentified by mineral dealers and in mineral collections. Such errors can propagate through the various studies used in this compilation.

4) It seems that spectra that did fit the models were excluded from the data compilations for a particular species. “A few spectra of the reference library were excluded from the averaging in Fig. 2a due to a limited energy range (Beauchemin et al., 2003) or inconsistency with common species specific spectra.” Inconsistent spectra could be misidentified calcium phosphates in the original papers or the few samples that were dissimilar to the others could be correct ones.

5) In order to really convince a reader of the utility of the spectral normalization techniques presented in this paper, characterization of phosphorus in samples of precisely known composition is necessary. While the techniques are applied to samples of calcined bones, the wording of the section (3.4) indicates the composition of these samples was not precisely known. It would be more useful to show that the presented techniques are either superior to ATHENA and SIXPACK software in apportioning calcium phosphorus minerals in mixtures of known composition or show how these software packages can be used in tandem with the described normalization procedure. I believe one of the papers by Ajiboye cited in this manuscript contains spectra of known mixtures that would make an excellent test case.

6) The results and conclusions could also be strengthened if a theoretical basis for the difference in peak height ratios was offered.

7) Errors or ranges of values should be presented for secondary peak height % in table 2. This would give the reader a better idea of the strength of the findings.

8) The figures presenting spectra are extremely hard to read. In general there are so many overlapping spectra presented with extremely fine lines that it is impossible to readily distinguish different features or phases.

9) Much of the standard data out there in the literature is presented as figures that are not useful for spectral comparisons. The author should be commended for scanning and digitizing many of these figures. If such raw spectral data for all standards analyzed were made available as a supplement this paper would be potentially much more useful even with the problems listed above. Furthermore, if a detailed step-by-step description of their normalization procedures with a sequence of clear, simple figures would be helpful to readers as a supplement. Also inclusion of the computer code used for normalization with detailed comment lines inserted in the code may be helpful.

The techniques presented in this paper may be step forward in the interpretation of XANES spectra but the issues above need to be thoughtfully addressed to truly convince a reader that it is worthwhile to apply them. In terms of the analysis of natural samples, this method may be limited to only samples dominated by calcium phosphate phases.

Interactive comment on Biogeosciences Discuss., 10, 18723, 2013.