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Biogeosciences Discussions

Interactive comment on "Iron oxide deposits associated with the ectosymbiotic bacteria in the hydrothermal vent shrimp Rimicaris exoculata" *by* L. Corbari et al.

Anonymous Referee #2

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General comments

Corbari et al. present a study on the iron oxides formed in the gill chamber of a hydrothermal vent shrimp. They show beautiful TEM images addressing (1) the spatial distribution of iron oxides and bacteria in the oxidic crust, (2) the contact between oxides and either cell walls or secreted substances and (3) the internal layering of the oxidic concretions. A series of Mössbauer spectra taken at different temperatures suggest that nm-sized crystals of ferrihydrite are the main mineral phase. The chemical composition of the concretions was characterized by several EDX spectra. These show that minor amounts of Mg, Ca, S and P are present in addition to Fe.

The subject fits well into the scope of Biogesciences and the methodology represents the state of the art. However, I find it rather surprising that no XRD or SAED was collected to identify the oxide. Could that possibly be handed in when revising the manuscript? Furthermore, I propose to use the EDX results in a qualitative way only (see below) and to considerably revise the discussion of these data. I also differ about the importance of the fact that ferrihydrite was found here: In my opinion, neither the presence nor a certain Fe/O ratio of ferrihydrite point to its biogenic origin. Finally, I consider this paper to be an interesting contribution to the ongoing discussion about bio-induced Fe oxidation, but the main message could be told much more directly and precisely. This is why I recommend a clear reduction in text, possibly by combining the sections results and discussion.

Specific comments

Throughout the text the authors use "thin slices", I only know the term "thin section".

Figure 1, I would appreciate an additional picture of the whole animal. It is not clear to me how the dashed line in Figure 1a relates to 2b or the rest of paper. Besides, for 2b I propose to draw in the three different layers, which are distinguished in this and the previous study.

The term "mineral density" is used in a misleading way. What in fact is observed are differences in the aggregate density or the mutual dilution of mineral- and bacterial matter.

P. 1827: Line 5 (also P. 1830, line 8 and P. 1831, line 6) , "structure" is misleading, since it implies crystal structure (architecture, morphology, spatial relation to bacteria...). In Line 7 I would prefer "EDX" instead of "X-ray microanalyses". Beside I wonder if all microscopes have to be listed in the abstract, or if mentioning SEM, TEM and EDX would suffice.

Line 9, mentioning of the location is at a strange place in the abstract. Put it in the

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beginning (in that case, also note TAG) or leave it out.

Line 11, at a first reading I couldn´t understand “step-levels of mineral crust”. I would prefer terms like “layers” or “zones”.

Lines 12, delete “heavy”

Lines 12-13, the occurrence of SiO2, sulfates and phosphates was not evidenced and is even found less probable than adsorption in P.1843, lines 9ff. Separate mineral phases cannot be assumed to stabilize ferrihydrite.

Line 14, “Morphological observations…” sentence should be phrased more precisely.

Lines 16ff: this conclusion could also be explained more clearly.

Page 1834 Line 4, results should not start with the results of a previous study

Line 14ff, description of the three layers is not very clear. For example, the individual ferrihydrite crystals or particles can have a diameter of only several nm (as usually observed and as shown by Mössbauer), everything larger must thus be described as aggregates or concretions of ferrihydrite. The different types of contact between bacteria and minerals are addressed separately (line 19f, line 22f), which blurs the observation that both types do occur. Or is precipitation/deposition on exopolysaccharides much more abundant? What is meant by “the minerals are diffuse” (line 22-23)?

P. 1835 Line 16, (and later e.g., p. 1838) “Rosette-like” is used for gypsum roses and the like, the observed habit is better described by like grape-like rounded forms, botryoidal, concentrically banded…

Line 8, could the ghosts also be artefacts, e.g. produced during the polishing, or can that be excluded?

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P. 1836 Lines 1ff, I do not really understand the Mössbauer approach. Why were these two types of sample used? Why was the temperature dependence only measured on one of the samples? What can be learned from figure 5a? Do the Mössbauer results unequivocally identify ferrihydrite?

Line 13, the chemical compositions of ferrihydrite is still under discussion, it should be mentioned that this is only one of the proposed formulas

Lines 27ff, its not necessary to list all peak positions

P. 1837, Table 3 Lines 3ff, I´m in doubt about the quantitative EDX analyses: 1) because of the small particle size the EDX signal will originate from the oxide and the resin. This will affect the ZAF correction and the final composition. To correct for the latter, i.e. the additional C, O and Cl signals from the embedding resin, the authors subtracted the spectrum of the resin from that of the sample. How was that done? In addition to the carbon content of the resin the C-coating and the organic matter from the sample will add to the signals of O and C, while the Cl-signal is only very small… I assume that this will lead to a higher error of the analysis. 2) I do not concur with the interpretation of the EDX analysis, i.e. with the calculated mineral phases. Too many assumptions must have been made: the correction mentioned above, the not measurable H, the possibility of other oxidation states of Fe, the possibility of other anions like sulfides (or can they be excluded?). The calculation can only be used to check if the presence of the proposed minerals is plausible. But even then, I cannot understand why (Ca, Mg)SO4, (Ca,Mg)PO4 and SiO2 should be the most probable minerals in a shrimp or why these elements must be accommodated in separate mineral phases. Their presence can also be explained by substitution in ferrihydrite (Si, Mg), sorption to the large surface of ferrihydrite (SO4, PO4) or maybe even “shrimp-matter”. The mineral calculation is particularly strange because even the authors seem not to be convinced as they discuss surface complexation in great detail on p. 1842.

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Interactive Comment

I propose to go without Table 3 and simply discuss the possibility of additional mineral phases, adsorption and substitution. (This means that the respective parts of the abstract and the conclusions have to be changed as well).

Lines 27ff, the discussion concerning the glutaraldehyde preparation is very important for future work and the interpretation of Gloter et al., 2004. However, Mössbauer spectroscopy would have been much better suited to quantify the Fe(II)/ Fe(III) than the Fe/O measured by EDX (O is generally hard to quantify, additional error is to be expected because of the resin correction AND the correction of the presumed phosphates and sulfates). Furthermore the Fe/O will be dependent on the drying procedure. Is there a reason why glutaraldehyde treated ferrihydrite was not investigated by Mössbauer? Could that still be done?

P. 1838 Line 4f, the parallel distribution of Fe and Si is a further argument not to believe in a separate SiO2 phase

P. 1840 Line 21, Michel et al. 2007 is an odd reference, this paper doesn´t deal with beam damage or high vacuum problems

Line 22ff, I disagree: ferrihydrite can easily be formed abiotically and can show a wide range of crystallinity and composition, i.e. a wide range of Fe/O. (I´m afraid this question can only be addressed experimentally.)

P. 1842 Lines 5ff, why should a higher Fe/O indicate bacterial influence??

P. 1844 Lines 17ff, some organic matter will probably suffice to stabilize ferrihydrite. The exopolysaccharides could do the trick or something else inside the shrimp (compare Schwertmann, Inhibitory effect of soil organic matter on crystallization of amorphous ferric hydroxide. Nature 1966, 212, 645-646).

Interactive comment on Biogeosciences Discuss., 5, 1825, 2008.