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Comment

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

L. Corbari et al.

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General answers:

Several points have been underlined by both referees, especially on the mineralogical interpretation of the iron oxides and also on their "biogenic" origin. That's why, we propose a general comment to discuss of the following points :

1-The difficulty to quantify light elements (O, H), the influence of the resin (C, O, Cl) and the influence of C-coating on EDX analyses (referee#2, comment 21)

Indeed, the EDX signal originates from the oxide and the resin present between the mineral particles as well from the C-coating. But all the spectra were done on large

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concretion cross-sections (at least 2 μm in diameter) with a probe size inferior of 1 μm in diameter (for quantitative analysis). The analysed volume does not exceed the size of the concretion. This limit the contribution of the resin to that present inside the concretions (between nanoparticles) and uniforms the acquisition conditions and thus reduce the ZAF corrections errors at least for comparisons between our samples. The correction of the C-coating and the resin contribution were not done by spectrum subtraction but by direct subtractions of the quantitative data. The contribution of the C-coating was estimated at 25 At% by comparison with a pure mineral sample C-coated in the same conditions. The remaining C was attributed to the resin (with the Cl) and allowed the estimation of the O due to the resin. The Cl peak is very small because the resin EPOFIX (used for thin slices) is Cl poor compared to other Epoxy resin and has been specially used for this reason. The not measurable H was considered as negligible because of its low atomic mass. It represents less than 2 Wt % of the Ferrihydrite, depending of the hydration state. In At %, it may represent about 25 % of the hydrated Ferrihydrite resulting that the evaluated % of Ferrihydrite in the concretions could be underestimated. But owing that the chemical formula of Ferrihydrite is not completely established and that the hydration state not determined, it is very difficult to estimate the contribution of H in our samples. Moreover, accounting H or not does not influence the determination of the Fe/O ratio. In the samples, H is mainly present in the resin which is disregarded for quantitative analyses of the minerals. We know that is an uncertainty about the quantification of the light elements as O even with the ZAF correction, but the different subtractions we made on each of the 14 spectra, acquired in the same conditions, allowed us to considerably reduce the variability and the standard deviation on the mean values.

2-The nature of the associated minor elements or sorbed ionic ligands (referee#2, comment 21)

Concerning the minor elements, we agree to the fact that they can be likely present as substituted elements in Ferrihydrite or as adsorbed ligands. We changed the results

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and discussion in this view. We have also modified the table 3 (not suppressed) in consequence : thus as ligands, we first consider anionic and cationic forms and Si, likely present as silicate. Indeed even if Si is substituted in Ferrihydrite, it must be limited with O and thus cannot be distinguished from silicate. We consider Si with a minimum associated O mentioned between brackets. The most probable forms of S and P are SO₄²⁻ and PO₄³⁻ and as previously shown by Châtellier et al. (2004) in biogenic iron oxides. The fact that Silicate, Mg, Ca, SO₄²⁻ and PO₄³⁻ are sorbed on the Ferrihydrite surface, substituted in the mineral or present as a separate mineral phase at the nanometric level cannot be solved by our analyses at the micrometric level (ESEM). As we explained in the results (see modifications), the proportion of Ca, Mg, S, P correspond to the stoichiometric ratio in (Ca, Mg) SO₄ and (Ca, Mg)₃ (PO₄)₂, suggesting they may be present as separate mineral intermixed with Ferrihydrite. Adsorption at the surface of the concretion is also excluded because in this case they could be visible as separate phase.

3-The Fe/O ratio (referee#2, comment 22-25 ; referee#1, comment 5)

We know that the calculated Fe/O ratio is an approximation but we think it approaches the reality in the samples also dependant of the preparation techniques. Considering these ligands and deducing their attributed O from the global O value allow reducing the variability of the O quantification attributed to Fe (reducing thus the standard error on the O). After these calculations, all the spectra from similar samples reveal approximately the same Fe/O ratio as reported in table 4. By this method, we obtain Fe/O ratios, different from that of Gloter et al. (2004). We evidenced differences between glutaraldehyde-fixed and frozen samples that are not visible otherwise. We did also the same analyses on FeO concretions from TAG shrimps and obtained a similar Fe/O ratio (0.53 ± 0.8) despite the presence of a much higher content of Si (+ O₂) in the concretions, which is inferred to compositional differences in the hydrothermal fluid (by comparison with Rainbow site). Moreover glutaraldehyde-fixed samples from TAG also show a Fe/O ratio (0.61 ± 0.1), typical of the reductive influence of glutaraldehyde.

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4-Possible presence of Fe²⁺, FeS sulfides (referee#2, comment 22; referee#1, comment 2) A large screening of the mineral concretions in the gill chamber has been performed by X-Ray microanalysis (n = 14) and the presence of such minerals has been detected but their occurrence was not considered as a direct component of the iron oxide concretions. Iron sulphides are present as large crystalline particles (2-10 μm) between the iron oxide concretions and are well separately identified by a higher electrons density in BSE images and in EDX as also shown by Zbinden et al. (2004). Their distribution was not homogeneous and their presence can be categorised as occasional. Fe-sulfide inside the concretions can be excluded because the Mössbauer analysis showed that all the Fe of the concretions is in the Fe III form.

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