# Reply to the 'Comment on “FeS colloids – formation and mobilization pathways in natural waters”' by S. Peiffer, D0EN00967A

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| Journal: | *Environmental Science: Nano* |
| Manuscript ID | EN-CMT-03-2021-000278.R1 |
| Article Type: | Comment |
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# Reply to the 'Comment on "FeS colloids – formation and mobilization pathways in natural waters"' by S. Peiffer, D0EN00967A

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## ABSTRACT

In this response to the comment by Peiffer (2021), we wish to first underline the main objective of the paper by Noël *et al.* (2020), which was to better characterize the chemical parameters controlling the generation of Fe-S-colloids under anaerobic conditions. Export of highly reactive FeS-compounds from reducing to more oxidizing environments has down-stream consequences for electron transfer and biogeochemical reactivity. Thus, detailed knowledge of formation, nature, and stability of these colloids is critical for developing conceptual models to predict Fe remobilization under sulfidic conditions in natural environments. However, our understanding of the biogeochemical behavior of Fe-S-colloids is not sufficient to develop such models. This should not be interpreted as indicating that S transformations and speciation in these systems are not important, as we have previously emphasized in several publications. Contrary, we show that detailed examination of the Fe chemistry provides clear data in terms of the Fe-S-colloid composition (*i.e.,* S-bearing colloids), as we demonstrate in this response.

# RESPONSE

At the outset, it is helpful to summarize key points relating to the literature discussed in the comment made by Peiffer[1] on Noël *et al.*[2] and in this response:

- First, we wish to thank Dr. Stephan Peiffer, University of Bayreuth, Germany for highlighting the studies by his group on the sulfidation of Fe(III)-(oxyhydr)oxides.[3-7]
- Second, we agree with Peiffer's comments concerning the importance of S-speciation in sulfidic systems; however, the focus of the work presented in Noël *et al.* [2] was not on the sulfidation mechanism but on characterizing the chemical nature of FeS-colloids generated during sulfidation. Thus, S-speciation, though very important, was not directly determined in this study. However, it was addressed in the Fe *K*-edge EXAFS spectroscopy analysis of the FeS-colloids generated by Noël *et al.*[2].
- The Noël *et al.* [2] study was a continuation of our previous study of the sulfidation mechanism of ferrihydrite.[8] However, the Noël *et al.*[2] study focused exclusively on Fe-S-colloids in the aqueous phase.
- The findings of the Kumar *et al.*[8] study are consistent with those of the Peiffer group, considering the slight differences in respective experimental setups and focus (control on pH during sulfidation mechanisms, and nature of Fe(III)-(oxyhydr)oxides of the starting material).
- Applying conclusions from experiments by the Peiffer group,[5-7] who used lepidocrocite and goethite rather than ferrihydrite at low S(-II)//Fe(III) ratio (0.25), requires additional discussion. For example, Kumar *et al.*[8] showed that crystallinity and specific surface area exert major controls over the kinetics and mechanism of sulfidation reactions.
- The conclusions of the Peiffer group are based on analysis of bulk solid-phase minerals; however, the experiments of Noël *et al.*[2] focused on the colloidal phase. These two phases do not have identical behavior
- In preparing this response, we have provided new evidence using X-ray Absorption Spectroscopy (XAS) for the Fe-S-colloidal system that confirms the long-term stability of these colloidal phases. These data clearly show only FeS phases and no transformation to pyrite even after 2 years. We also analyzed the speciation of Fe in the FeS-colloids generated using a lower S(-II)/Fe(III) ratio of 0.1 to demonstrate the presence of ferrihydrite-FeS colloids.

Peiffer suggested that investigating the S chemistry in our system would benefit the interpretation of our data and shed additional light on the mechanisms of FeS-colloid formation and their composition. Peiffer points to previous studies by his group on the sulfidation of Fe-(oxyhydr)oxides,[5-7] which are similar to our study[2] (abiotic sulfidation of same mass of Fe-(oxyhydr)oxides in presence of different amount of dissolved sulfide). They showed that low S(-II)/Fe(III) ratios (0.25) resulted in FeS formation on the rim of lepidocrocite and the ultimate release of pyrite ($FeS_2$) nanoclusters from the surface[5] – *i.e.*, these nanoclusters could nominally pass as colloids, whereas high S(-II)/Fe(III) ratios (2) resulted in full conversion of Fe-hydroxides to stable FeS in the solid phase and minimal $FeS_2$ formation.[6-7] These findings are consistent with those of our previous paper,[8] where we discussed in detail the behavior of S from the *solid*-phase perspective in a similar experiment. The Kumar *et al.*[8] study clearly showed that the reaction of ferrihydrite with dissolved sulfide leads to oxidation of sulfide ions (to zero valent sulfur, S(0)) at mineral-water interfaces resulting in solid-phase polysulfides (as also noted in the studies by Hellige *et al.*[5] and Wan *et al.*[6-7]) and elemental sulfur. The Noël *et al.*[2] study corroborates the assumption that metal-(poly)sulfides and polynuclear clusters can be stable in the *aqueous* phase,[9] based on our observations of Fe partitioning into the aqueous fraction. We therefore expect that the elemental sulfur and polysulfide, which were observed in Kumar *et al.*[8] to partition to the solid phase, could also remain stable in the aqueous phase and be transported as colloids. Indeed, our team recognizes the importance of combining Fe and S speciation to fully characterize Fe-sulfides in natural[10-12] and laboratory[8,13-15] Fe-S systems.

However, in the study by Noël *et al.*[2], the focus was to better characterize the chemical parameters controlling the generation of FeS-colloids under sulfidic conditions in order to improve predictions of when and where transport of FeS-colloids could be important. The local structural environment of Fe is significantly different between iron monosulfide (FeS) and iron disulfide ($FeS_2$),[16-17] and, thus, this difference provides a fingerprint for distinguishing FeS from $FeS_2$.[18-19] Hence, Fe *K*-edge Extended X-ray Absorption Fine Structure (EXAFS) spectroscopy in a system with a limited number of FeS-species is an efficient way to determine the identity of the main Fe-sulfide species. More specifically, Fe(II)-Fe(II) distances derived from the Fe EXAFS spectroscopy of FeS and $FeS_2$ are easily distinguished without ambiguity (**Figure 1**) and do not require reinterpretation, as suggested by Peiffer in his comment.

Nevertheless, the differences suggested by Peiffer between his group's studies[5-7] and those by Noël *et al.*[2] should not be ignored. We welcome his invitation to provide a constructive scientific discussion that will improve our understanding of the intricate Fe-S redox interactions and resulting products (such as colloids) – a discussion that remains poorly resolved even after 40 years since the first paper on this topic.[20] Consequently, here we discuss in more detail below the two points made in the comment by Peiffer and offer our perspective on the reasons for the apparent discrepancies between the results of our study and expectations of the Peiffer group.

### (1) The ferric-oxyhydroxide-surface pathway of sulfidation and consequences for the release of ferric-oxyhydroxide colloid.

The study by Noël *et al.*[2] focuses on Fe mobilization to the aqueous phase from solid phase ferrihydrite under sulfidic conditions. We show that the Fe-S and Fe-Fe pair correlations in the colloidal fraction (<20 nm) are typical of FeS,[15] and the very low coordination numbers suggest the presence of a suspended nanocluster form of FeS and not an FeS condensed phase.[2] We are not excluding the presence of other minor Fe-species in the colloids (below 10% of the total Fe content, which is the detection limit for Fe-EXAFS)[21]; however, the main colloid present in solution during sulfidation of ferrihydrite under our experimental conditions is FeS nanoclusters.

This begs the following question – why are FeS nanoclusters formed at low S(-II)/Fe(III) ratios at circumneutral pH stable to further transformations in the experiments by Noël *et al.*[2] instead of generating $FeS_x$ or $FeS_2$ colloids as might be expected based on the work by Peiffer's group[1,5-7]?

First, we note that the pyrite observed by the Peiffer group formed during sulfidation of goethite and lepidocrocite at low S(-II)/Fe(III) ratios, rather than ferrihydrite[5-7], *i.e.*, used in Noël *et al.*[2]. We previously demonstrated that the surface structure of Fe(III)-(oxyhydr)oxide nanoparticles and the degree of crystallinity and attendant differences in the local coordination environments of Fe in these nanoparticles are the primary controls on reductive transformation rates.[8] The rapid transformation rate of ferrihydrite, compared with lepidocrocite and goethite, could strongly impact the products formed in the sulfidation process. In the study highlighted by Peiffer[1], the formation of polysulfides, which are '*necessary to convert FeS ultimately into pyrite (FeS2)'* (Citation from Kumar *et al.*[8]), took 2-3 days and pyrite nanoparticles (not associated with the surface) appeared after 1 week of reactivity.[5] Kinetic of formation of pyrite can, however, proceed more quickly as noted by Wan *et al.*[7] where pyrite formation started after only 48 hours with Fe(III) concentrations in excess of sulfide. In contrast, we underline that our results demonstrated clearly that the generation of FeS-colloids from sulfidation of ferrihydrite began after the first 3 hours (for all S(-II)/Fe(III) ratios; Figure 2 of Noël *et al.*[2]). These rapid colloid formation kinetics are inconsistent with the kinetics of $FeS_2$ nanoparticle formation observed by Hellige *et al.*[5] and Wan *et al.*[7]. However, we cannot reject the possible formation of a precursor to pyrite ($FeS_x$), based on kinetics alone.

Second, we point to the importance of the ferric-(oxyhydr)oxide-surface pathway of sulfidation on surface charges. He *et al.*[22] showed that zero-valent sulfur (S(0)) and iron monosulfides produced on the surface of ferrihydrite with high hydrodynamic diameter during its sulfidation can destabilize the electrostatic effects, leading to the release of physically stable ferrihydrite colloids under anoxic conditions. In our study, we noted that '*Fe(III) concentrations measured by colorimetry (revised ferrozine method) in the aqueous phase further corroborate the assumption that Fh colloids can be released during sulfidation of Fh aggregates.'* (Fh=ferrihydrite; citation from Noël *et al.*[2]). Thus, we hypothesized that sulfidation processes could release colloids of ferrihydrite with FeS nanoclusters bound to their surface. *'The exposure of mobilized Fh-colloids to dissolved sulfide could promote rapid reductive dissolution of this phase'* (citation from Noël *et al.*[2]). This behavior could further explain the rapid kinetics observed in Noël *et al.*[2] and corroborate the hypothesis noted above that kinetics could influence the end-product. Once immersed in sulfidic solution, ferrihydrite colloids would experience a local chemical environment with higher effective S(-II)/Fe(III) ratio than at the aggregated solid-phase surface, which would increase the reduction rate of ferrihydrite colloids relative to aggregates. Additionally, the mechanisms of reduction of isolated ferrihydrite colloids could differ from those of the aggregated ferrihydrite nanoparticles, and the strong redox disequilibrium proposed by Peiffer[1] to explain the collapse of the FeS structure on the surface of lepidocrocite, would not apply to ferrihydrite colloids.

## 2) The role of S(-II)/Fe(III) ratio for Fe-colloid formation during the sulfidation process.

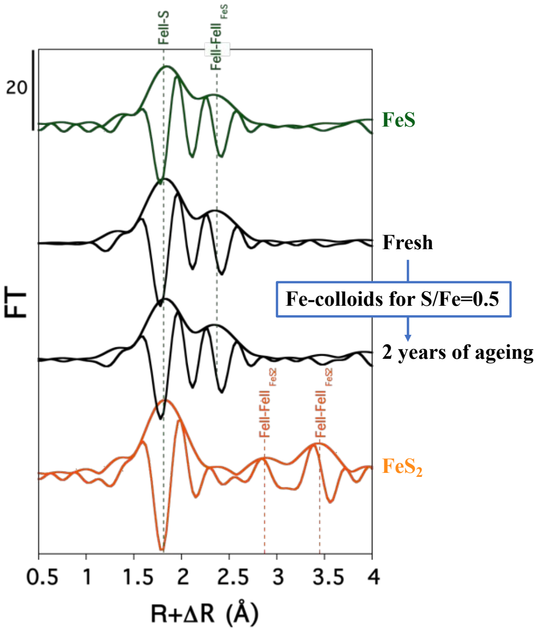

***Figure 1.*** *Fourier Transform of Fe K-edge EXAFS spectra of the aqueous fractions (<20 nm, before settling) collected from ferrihydrite sulfidation in a 0.1M NaCl-solution, after 24h of reaction (fresh) with dissolved sulfide at 0.5 S(-II)/Fe(III) ratio. FT of the fresh sample is compared with the same sample after 2 years of ageing. FeS (Kumar et al., 2018) and* $FeS_2$ *(Morin et al., 2017) references are displayed above and below for comparison. It is clear that the FeII-FeII pair correlation of* $FeS_2$ *are not representative of Fe-colloids.*

There is no controversy about the importance of the S(-II)/Fe(III) ratio for solid-phase product formation during the sulfidation process.[7] Similarly, the chemistry of Fe-colloids (*i.e.,* size, composition, stability, reaction kinetics) could indeed depend on the S(-II)/Fe(III) ratio. In the Noël *et al.*[2] study, we showed that (i) at S(-II)/Fe(III) ratios >0.5, sulfidation reaction rates were rapid and FeS cluster aggregation was accelerated compared to lower ratios; and (ii) sulfidation of ferrihydrite generated stable FeS nanoclusters (suspended in aqueous phase) at a S(-II)/Fe(III) ratio of 0.5. The structure and composition of Fe-colloids generated at a lower ratio (0.1) were not reported. Additionally, if precursors of $FeS_2$ were indeed present (as mentioned above), the FeS nanoclusters could be transformed to $FeS_2$ colloids over time. Thus, in response to the comment by Peiffer[1], we performed additional analyses of Fe-colloid speciation in the two lowest S(-II)/Fe(III) ratios (0.5 and 0.1) after two years of ageing (stored in sealed glass vials in an anoxic glove box as filtrates and kept under dark at ambient temperature). Here we summarize the results:

**S/Fe=0.5** – Fe *K*-edge EXAFS spectra of FeS nanoclusters collected after 24h of sulfidation (and presented in the original paper[2]) were analyzed again now after 2 years of ageing to confirm the long term stability. The similarity of the Fourier Transform (FT) of the Fe *K*-edge XAS spectrum to the initial one indicates that FeS nanoclusters remained stable for two years (**Figure 1**).

**S/Fe=0.1** – We performed XAS analyses on the filtered aqueous fractions (<20 nm) for a S(-II)/Fe(III) ratio of 0.1 after 2 years of ageing (**Figure 2**). The FT of the Fe *K*-edge EXAFS spectrum of these Fe-colloids shows a first Fe(III)−O pair correlation at 1.99 Å and Fe(III)−Fe(III) pair correlation at 3 Å, characteristic of Fe-(oxyhydr)oxides.[18] The FT also shows two other major pair correlations: (i) a Fe(II)−S pair at 2.35 Å and (ii) a Fe(II)−Fe(II) pair at 2.49 Å identified by shell-by-shell fitting. These two pair correlations are indicative of FeS (**Figure 1**). It is important to mention that the color of the filtrate had not changed after two years, and no aggregation was observed (**Figure 2**); the colloids thus are inferred to have persisted for two years.

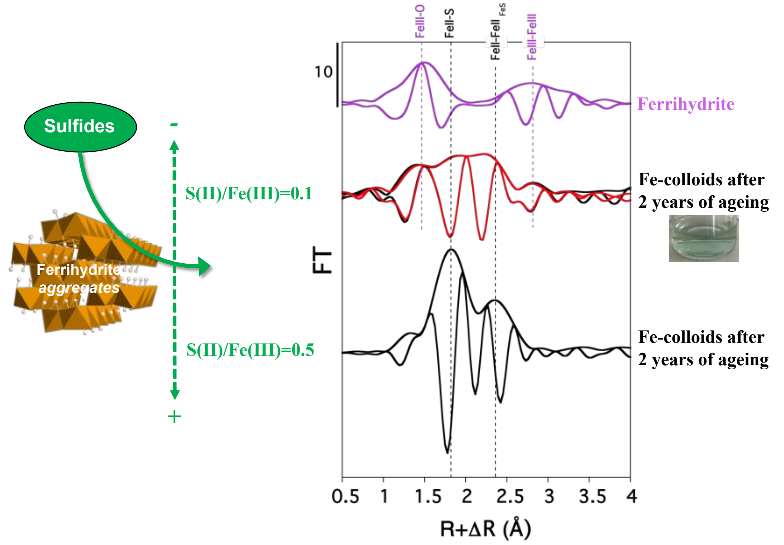

**Figure 2.** *Fourier Transform of Fe K-edge EXAFS spectra of the aqueous fractions (<20 nm, before settling) collected from ferrihydrite sulfidation in a 0.1M NaCl-solution, after reaction with dissolved sulfide at 0.1 and 0.5 S(-II)//Fe(III) ratio. Ferrihydrite is displayed above to show the FeIII-O and FeIII-FeIII pair correlation characteristics of FeIII-(oxyhydr)oxides present in FT of Fe-colloids.*

These additional results corroborate our hypothesis that sulfidation processes release colloids of ferrihydrite associated with FeS nanoclusters bound to their surface from aggregated ferrihydrite associations. However, the S(-II)/Fe(III) ratio controls the degree of reduction of ferrihydrite colloids leading either to a mixture of ferrihydrite/FeS nanoclusters at very low S(-II)/Fe(III) ratios (0.1) or complete (or almost complete) conversion to FeS nanoclusters at a S(-II)/Fe(III) ratio of 0.5. The main products of Fe-S-colloids formed under these conditions are stable (at least when separated from the solid phase) for a minimum of two years, and no conversion to $FeS_2$ is detected (**Figures 1 and 2**). This rules out the expectation of formation of $FeS_x$ and/or $FeS_2$ colloids based on the Fe mineral transformation observations for the solid fraction made by Hellige *et al.*[5] and Wan *et al.*[7], indicating that the points discussed in section (1) above are likely more relevant.

## CONCLUSION

In summary, we acknowledge the crucial role of S transformations and speciation in the reactions and fate of Fe-(oxyhydr)oxides under sulfidic conditions. We however note that constraining Fe chemistry in these systems provides clear evidence for determining the composition of Fe-S colloid products formed. We also highlight the importance of considering the specific experimental conditions and studied fractions when comparing and interpreting results from different studies and drawing conclusions about the wider implications of the findings, as exemplified by the differences in experimental materials (*i.e.*, lepidocrocite and goethite[5-7] vs. ferrihydrite[2]) and studied fractions (*i.e.*, solid phase[5-7] vs. colloidal phase[2]). Finally, we propose that the mechanisms of Fe mineral transformation of aggregated ferrihydrite associations leading to the formation of pyrite observed by the Peiffer group could differ from the sulfidation mechanism of ferrihydrite colloids released to the aqueous phase that we observed. Thus, the observations of the Pfeiffer group are not necessarily inconsistent with our observations. There is still much to learn about Fe-S redox interactions, and we are looking forward to further publications and discussions on this topic.

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