

## ***Interactive comment on “Sedimentary phosphorus and iron cycling in and below the oxygen minimum zone of the northern Arabian Sea” by P. Kraal et al.***

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We thank Prof. Gabriel Filipelli for his kind words regarding this study and are very pleased to see that he appreciates the implications, specifically regarding the possible over-interpretation of reactive (Ca-)P burial based on chemical analysis of sedimentary records. We have also taken to heart his criticism that the final section (6.3) on Fe and S cycling does not seem to fit with the core topics of the paper.

We feel that this final section is an important and integral part of the paper for two reasons. Firstly, Fe cycling has a major impact on the biogeochemical P cycle and is strongly affected by its interaction with the S cycle. Iron-sulfur interactions directly affect the availability and upward dissolved Fe diffusion, thereby in part controlling Fe (oxyhydr)oxide precipitation and sedimentary P retention capacity. As such, the results

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in section 6.3 are important not only for a better understanding of Fe and S cycling, but also for understanding sedimentary P retention. Secondly, our model results provide valuable information that allow us to better identify the processes that are responsible for the limited formation of pyrite in sediments from the Arabian Sea. Because our results and conclusions regarding Fe and S cycling are for an important part based on model results, a detailed discussion of the specifics of our model runs is inevitable. We have now revised the final section to hopefully give better expression to the importance of these results in light of the general focus of the study. For convenience, the revised section 6.3 appears below:

### **6.3 Iron and sulfur cycling in the northern Arabian Sea**

Sedimentary Fe and P dynamics are strongly linked, yet the burial of these two elements across the investigated depth transect showed marked differences. While sedimentary P abundance showed a clear decrease from the OMZ to the deep sea, the Fe/Al ratio in the surface sediments along the depth transect showed little variability (Fig. 3), indicating that there are only minor changes with depth in Fe deposition and sequestration at the sediment surface. Within cores, reductive Fe (oxyhydr)oxide dissolution at depth leads to the down-core decrease in Fe at all stations. The surface enrichment in Fe (oxyhydr)oxides is likely in part caused by precipitation of upward diffusing Fe<sup>2+</sup>. At station 10, the relatively high concentrations of total Fe and Fe<sub>ox1</sub> suggest that down-slope sediment transport may have affected the Fe chemistry at the base of the Murray Ridge. Due to its location, this station may have also received some sediment from the adjacent Indus Fan. The sedimentary Fe cycle and its impact on the S cycle in the Arabian Sea have been subject to research and debate for decades. The Arabian Sea is unusual in that pyrite formation in the upper tens of centimeters of the sediment is limited, even in the OMZ which is characterized by low BWO concentrations and large depositional fluxes of OM. The very low pyrite concentrations in the sediments at stations 1B and 4 confirm the general lack of pyrite formation in the Arabian Sea OMZ. In contrast, pyrite is a significant sink for Fe at depth in the core

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from station 2, accounting for up to 40% of highly reactive Fe (Fig. 6). Such pyrite concentrations are unusual for surface sediments from the Arabian Sea and, together with the strong P enrichment between  $\sim 15$  and 26 cm core depth at station 2 and the abundance of subsurface Fe (oxyhydr)oxides at station 1B, emphasize the spatial and potentially even temporal variability in benthic conditions and sediment geochemistry associated with the OMZ.

The generally low pyrite abundance in Arabian sea sediments has been attributed to low SRRs caused by the diagenetic formation of recalcitrant organic matter through sulfurization (Passier et al., 1997) or the limited availability of reactive Fe (Schenau et al., 2002). In contrast, Law et al. (2009) hypothesize that the abundance of reactive Fe (oxyhydr)oxides in Arabian Sea surface sediments may suppress sulfate reduction and pyrite formation. These suggestions have been qualitative in nature, based on interpretation of sedimentary records. The application of the RTM to the dataset from station 4 provides a valuable opportunity to study sedimentary Fe and S dynamics on a quantitative basis. In general, the model seems to represent the role of sulfate reduction well. Earlier work has shown that there is a large variability in SRRs in the Arabian Sea (Boetius et al., 2000; Law et al., 2009). Nonetheless, the RTM gives a depth-integrated rate of  $1.2 \mu\text{mol cm}^{-2} \text{y}^{-1}$ , which is similar to the depth-integrated value (30 cm sediment depth) of  $\sim 1.3 \mu\text{mol cm}^{-2} \text{y}^{-1}$  measured in a  $^{35}\text{S}$  tracer study by Boetius et al. (2000) using sediments from the deep western Arabian Sea. With a contribution of  $\sim 10\%$  to total OM oxidation, our RTM for station 4 results also confirm that sulfate reduction is a minor OM degradation pathway in the top 30 – 40 cm of Arabian Sea sediments (Lückge et al., 2002; Law et al., 2009).

Despite its modest role in OM degradation, sulfate reduction leads to appreciable pore-water  $\text{H}_2\text{S}$  concentrations in the RTM results for station 4. In our current model the rate of reaction between  $\text{Fe}^{2+}$  and  $\text{H}_2\text{S}$  is set to such a low value that, unrealistically,  $\text{Fe}^{2+}$  and  $\text{H}_2\text{S}$  coexist in the pore-water (at concentrations of up to 15 and  $60 \mu\text{mol L}^{-1}$ , respectively). Prescribing literature-derived rate constants for the reaction between

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$\text{Fe}^{2+}$  and  $\text{H}_2\text{S}$  in the model would result in the depletion of pore-water  $\text{Fe}^{2+}$  by  $\text{FeS}_2$  formation with  $\text{H}_2\text{S}$  concentrations up to  $\sim 60 \mu\text{mol L}^{-1}$ . This contrasts with the experimental data that showed up to  $30 \mu\text{mol L}^{-1}$   $\text{Fe}^{2+}$  and negligible  $\text{H}_2\text{S}$  (not shown). Also, solid-phase  $\text{FeS}_2$  would reach concentrations (up to  $\sim 25 \mu\text{mol g}^{-1}$ ) exceeding those determined in the sequential extraction procedure ( $\sim 2 \mu\text{mol g}^{-1}$ ). This has direct consequences for the discussion on Fe and S cycling in the Arabian Sea. Our results suggest that pyrite formation is not suppressed by a limited supply of either pore-water  $\text{H}_2\text{S}$  or  $\text{Fe}^{2+}$ , but rather by a rapid removal process for pore-water  $\text{H}_2\text{S}$  not accounted for in the model. It may be crucial to obtain a better understanding of the impact of the microbial community and dissolved organic compounds on the sedimentary S cycle. The suppression of pyrite formation limits Fe sequestration at depth in the sediment, leading to stronger upward diffusion of  $\text{Fe}^{2+}$  and surface enrichment in Fe (oxy)hydroxides, which in turn impacts the P retention capacity of the sediment.

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