

## ***Interactive comment on “Inputs and processes affecting the distribution of particulate iron in the North Atlantic along the GEOVIDE (GEOTRACES GA01) section” by Arthur Gourain et al.***

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Dear Dr Schlosser, We would like to thank you for your very constructive comments. All the issues you raised were carefully considered and addressed. Below are our detailed answers, including corresponding lines of text in the revised manuscript. We also took into account reviewer 2 comments, and refer to them accordingly in this response. We provide an updated manuscript with on including all modifications in track changes. We hope that you will find our answers satisfactory and our revised manuscript suitable for publication in this special issue of Biogeosciences Sincerely yours, Arthur Gourain, on behalf of all the authors

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“This manuscript presents and discusses the distribution of PFe, PAI, PMn and PP in the high latitudinal North Atlantic. The presented water column data is wonderful and I am looking forward to see the data published in the next GEOTRACES intermediate data product. We need more particulate data! And I really like their PMF calculations. However, the discussion is very detailed and long, but I am missing a straight storyline. The authors jump a lot between different topics and even present Ba data at the end of the manuscript, but a discussion is missing. The manuscript needs serious work, and I am suggesting major revision.” We thank the reviewer for his constructive remarks and his acknowledgment of performed work. Regarding the Ba data, we are not presenting them anymore, as we thought the discussion was easier to follow without remineralisation section. “My three main points are: The authors conclude that higher PFe/PAI and PMn/PAI ratios are indicative for biogenic bound particulate Fe. I am missing the discussion of scavenged and authigenic Fe, that could also cause PFe/PAI ratios higher than that of crustal ratios. For my opinion, the authors should include the PFe/PMn ratio, where biogenic ratios (phytoplankton) are available in the literature. It is true that a discussion on authigenic Fe was clearly missing, and we would like to thank you for this very constructive comment. We, unfortunately, cannot investigate specifically this important fraction of particulate iron. We are considering the PFe/PMn is having more bias than PFe/PAI due to the high kinetic of oxidation of Mn within the ocean. Kinetic wick is different than the kinetic of Fe. We now discuss more carefully on the impact of authigenic particles having on PFe/PAI. The authors include a PMF model and conclude that variances in PFe are related to changes in the content of lithogenic particles. This is in contradiction to the authors conclusion of biogenic Fe, responsible for changes in PFe/PAI. This needs to be discussed more carefully! The main lithogenic variability of the PFe is not in contradiction with the biogenic contribution to the PFe/PAI ratio. Indeed with the PMF, we describe the overall variability of PFe. The main variability of the PFe happened with inputs of PFe. These inputs are as described mainly lithogenic and imply the results observed by the PMF. Variation of PFe/PAI ratio between the basins is mainly occurring in open ocean samples where

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PFe concentrations are around 1nM. Thus, small variation of PFe at a sub-nanomolar level will highly impact the PFe/PAI elemental ratio. We add some details at the line 293 to avoid any ambiguity of the PMF interpretation. "The PMF analysis has been realised on the entire dataset, in consequence, the factors described are highly influenced by the major variations of particulate element concentrations (at the interface, i.e. margin, seafloor, surface,...)." There is an entire data set of barium excess concentrations at the end of the manuscript. I am not sure that this data is required for the conclusion of the author. If kept, please discuss the data! We removed this section following your advice. Abstract Line 32: What is meant with "At most stations over the Western" and "...relative concentration.."? I cannot see how concentrations show a ubiquitous influence of crustal particles. Ratios maybe! However, be more precise. We modified the sentence as follow: Within the Iberian Abyssal Plain, ratio of PFe over particulate aluminium (PAI) is identical to the continental crust ratio (0.21), indicating the important influence of crustal particles in the water column. Introduction Line 78: Replace to "using the distribution of particulate aluminium, manganese, and phosphorous." And remove sub-sentence ", to further..." Done. Methods Line 90: Sentence too long, please split up. Done. Line 91: Missing bracket. Corrected. Line 97: Indicate Go-Flo company. "General Oceanics". Done. Line 100: 6mm sounds a bit thin for me. Kable must be wider. Our mistake, it was 14mm. Line 111: Replace "litters" by "liters". Done. Line 111ff: Filter cleaning and what kind of filters were applied, should be stated earlier. For instance, before how much volume was passed over them. This sentence has been moved at the beginning of the paragraph (line 113). Line 113: Remove "-1" from "MΩ cm-1" Done. Line 118ff: I cannot follow, is this relevant? It is relevant, as remaining seasalts can seriously reduce the sensitivity of SF-ICP-MS analyses, so they must be reduced as much as possible. Line 120: Replace "slide" by "dish". We did not replace this, as the Millipore company sells these items as Petri dishes and not Petri dishes. They don't have the same design as standard petri dishes. Line 143: Please provide the values of blanks and limit of detection, maybe in Table 1 (Please also provide the standard deviation of your crm analysis). These have been added to

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Table 1. Results General comment 1: The result section need to be shortened. You mention in line 277 that PAI and PMn and PFe are similar in IrB, IcB, WEB and IAP (in line 270ff that the Reykjanes ridge is similar to IcB). That is the entire stretch between Spain and Greenland! Please combine results! In addition, if I look at Figure 4, the distribution of PFe in LB seems very similar to the concentrations in IcB. I am suggesting to combine the results of open ocean regions and just include separate paragraphs of results from the three margins, Iberian, Greenland and Newfoundland margin. The results have been re-arranged following your advice, with a first section regrouping all open ocean stations, then a section on margins. General comment 2: You talk about different surface currents, please include them in Fig. 1. During the preparation of the manuscript, we tried different possibility to produce a map of our section. Including some currents has been explored. But having the position of every station, their IDs and the different biogeochemical provinces, plus the current make the Figure 1 extremely unclear and difficult to understand. We reference at the beginning of the Hydrography section the paper of Garcia-Ibanez (Line 182). In this paper, the current are well explained and a really good map of the current, their figure 1, is produced.

Line 184ff: Could just find ENACW in Figure 2. Please correct text or Figure 2. The text has been corrected; the water masse is called NACW and not ENACW. Line 198: Remove "really" Done. Line 210: IB refers to IrB and IcB? Please mention that. The IB refers to the Iceland Basin. This paragraph has been deleted in light of the Reviewer comments. Line 218ff: There are five concentrations for 4 parameters! The additional concentration referring to another element finally non-discussed has been removed. It was "21.5"nM. Line 221: Please include the standard deviation of trace metals and PP hosted by small particles Done. Line 226: Please refer to transmissometry Figure. Done. Line 228ff: Sentence is hard to follow, please rephrase. The sentence has been change to: "Within the first 50m, PFe concentrations decreased towards the shelf break where PFe dropped down from 2.53 nmol L-1 (station 2) to 0.8 nmol L-1 (Station 1). Line 248. Line 233ff: Sentence "The highest. . ." does not tell anything new, remove! Since you explain results from the Iberian Margin, later referred as (IM),

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please include IM in Figure 2. The sentence has been removed. And the figure 2 has been updated, the two other shelves has been also added to keep some consistence. Line 240ff: There is something wrong with that sentence! The sentence has been completely rewritten in light of your General Comment 1. Line 242: When it is really the case at “every stations” then there are no exceptions! Please rephrase. Done. Line 244: I do not understand what is meant here: “Particulate aluminium profiles matched the PFe profiles, with low median concentrations within the first 100m of 1.77 nmol L-1 and 26 pmol L-1 respectively. Then, concentrations increased with depth to reach a maximum close to the oceanic floor.” Did you mean 1.77nM Pal and 26pM PFe? Please provide values for bottom waters. The sentence has been completely rewritten in light of your General Comment 1. Line 258: Replace “progressive” by “gradual”. Again refer to transmissometry figure. The sentence has been completely rewritten in light of your General Comment 1. Line 315: You are mentioning lithogenic elements here. How do you now? I know concentrations are high, but before introducing your tool that differentiate between biogenic and lithogenic Fe, I would leave out such terms. The word “lithogenic” elements have been removed. Discussion Line 323: I would also include run-off, which is probably similar to your “melting ice shelves” but more precise. In addition, why sea ice must have melted recently to be a source for PFe. And what do you mean with biological pool? However, please be careful what you state here as source, for instance, lateral mixing is not per se a source, just when PFe loaded waters are advected offshore. Please be more precise! The sentence has been modified to answer the comment as follows: “Possible candidate sources of PFe include lateral advection offshore from the different margins, atmospheric inputs, continental run-off, melting ice shelves and icebergs, resuspended sediments, hydrothermal inputs and biological uptake.”. Line 271. Line 350ff: How barite formation refers to remineralisation of PFe. Explain! In addition, what inputs and processes are discussed below! A sentence has been added in the previous paragraph at the line 286. The sentence on in the inputs and processes has been removed for more clarity. Line 365: Equation 2: I am pretty sure that the \* should be -. Indeed this was a mistake. It has been corrected.

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Line 367: Another possibility might be that lithogenic particles from the Iberian shelf are advected offshore. In addition, the NAC is located further west [D J Reynolds et al., 2016]. Authors need to come up with a better idea, than dust! The sentence has been re-written. The combination of the Iberian Margin input and local circulation is now discussed. Line 317. Line 375ff: This paragraph needs an overhaul! From fronts, via isobaths and isotherms (not shown) to blooms and LSW. It is really hard to follow this paragraph. In general I would have wished the authors explained differences in PFe/PAI ratio and PFe lith% over the entire transect and not just WEB and IAP. We completely rewrote this paragraph with more explanation on the front and the change of %PFelitho proxy over the section. Line 321. Line 384ff: Figure 8: The approach fingerprinting water masses with trace metals such as Fe and Mn would be nice, if it actually works. Other than NEADW and MW, other water masses have a higher Fe/Al ratio but they are very variable. In this case it is vital to check that the water mass difference is significant. I am suggesting performing a student t-test! The fingerprints analysis does not work using the Fe and Mn concentrations. We added the statistical analysis done on this. We operate a Kruskal Wallis Anova on-ranks test. This analysis demonstrates the significant difference between the different clusters of stations. We added more detail in the text, lines 330. Line 400-409: You just repeat yourself, please remove! We deleted most of this paragraph except the following sentences: “Inputs from continental shelves and margins have been demonstrated to support high productivity in shallow coastal areas. Inputs of iron from continental margin sediments supporting the high productivity found in shallow coastal regions have been demonstrated in the past (e.g. Cullen et al. (2009), Elrod et al. (2004), Jeandel et al. (2011), Ussher et al. (2007)) and sometimes, were shown to be advected at great distances from the coast (e.g. Lam et al., 2008).”. The importance of the margin inputs for biology has not been discussed previously in the paper and we consider it important to mention it. Line 414ff: I am not convinced that the different Fe/Al ratio is driven by different sediments. Where are the elemental ratios of the sediments, just because a sediment is muddy does not proof anything. Further Shelley et al. (2017) showed

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that dust particles along the GA01 section are mainly from the higher latitudes and not from North Africa. Later on you mention biogenic contribution, you have not introduced this term, and now everything higher than the 0.21 is biogenic. This is questionable, what is with scavenging, authigenic FeOOH formation etc. Throughout this paragraph, we are comparing sediment resuspension at the three different margins. The different mineralogical compositions of these sediments highly influence the composition of the resuspended particles measured. The sediment composition is thus, in our opinion, the key factor influencing the elemental ratio of particles sampled under these conditions (sedimentary resuspension). Unfortunately, we do not have sediment cores at these stations to assess by SEM or chemically their exact composition. Concerning the influence of Saharan dust over the Iberian Margin, Shelley et al. (2015) confirm their influence in the WEB. The influence of northern dust is highlighted in the northern part of the section. You are right that we now refer everything higher than 0.21 as “non-lithogenic” and not “biogenic”. Line 425: I am not convinced that using a Mn/Al ratio from the upper crust, is helpful tracking sediments. Sediments can have a much higher ratio than the upper crust (eg. Sediments on the shelf of South Georgia 0.0066, Schlosser et al 2018 ). A higher Mn/Al ratio would change your figure 10 entirely. I am suggesting to apply the Mn/Al ratio of sediments from the different regions. In addition, the transmissometry data in figure 10 need to be cited earlier! We completely agree with your comment, the ideal solution will be to have the exact composition of the sediments at our respective stations. Unfortunately as explained in the previous comment. We don't have access to this information. The different study at our margin (Iberian (Blasco et al., 2000; Merinero et al., 2008) or Greenland (Loring et al., 1996) or in the North Atlantic (Menendez et al., 2017) show important variations of ratio on small spatial range. In consequence, we decided to use a uniform reference value, the UCC value, to compare our different samples. We added a sentence to discuss about the caveats of this proxy. “This proxy assumes homogeneity of the sediment PMn/PAI ratio through the section which is maybe not completely the case at every station. In consequence, this proxy is only a tool to identify new benthic resuspension at specific

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location and inter-comparison between several locations is not possible.” Line370. Line 490: I am again not convinced that just biological uptake was responsible for elevated Fe/Al ratios. Scavenging and authigenic precipitation would do the same job. You need SEM data to convince me! The SEM picture, figure 1, was taken at Station 53, 165m depth. On this image, you can see diatom debris and lithogenic particles and no Fe oxides could be detected on these samples. Line 547ff: What do you mean with “oxido-reductive transformation”. I know this term from microbiology classes, but in sediments? I am agreeing, dead biology sinks and settles on the seafloor. However, organic material is quickly remineralised and released Fe will oxidize quickly forming oxyhydroxides. FeOOH precipitate as single particle or form a coating around sediment particles. This will increase your Fe/Al ratio too, and I think even more pronounced than biogenic Fe, which in comparison to lithogenic particles stores just a small amount of Fe. This small quantity will be strongly obscured by lithogenic Fe. Everything below line 548 is highly speculative. If you would like to track biogenic Fe, you should use the Fe/Mn ratio, ratios are provided by T-Y Ho et al. [2003]. His Fe/Mn ratio for phytoplankton is  $\approx 1.7$ , lithogenic particles have a significantly higher ratio (upper crust  $\approx 50$  and sediments  $\approx 70$ ), indicative for the formation of authigenic Fe. By “oxido-reductive transformation”, we mean any reaction of oxidation and reduction of trace element. These reactions are highly important within the sediment link to the oxygen and sulphur concentration. We agree on the plausible transformation of the biogenic PFe after burial in the sediment. But in the case of a quick oxidation of the dissolved iron from reductive sediments, the speciation of PFe is changing but not the molar ratio between PFe/PAI. Concerning the use of PFe/PMn as a proxy for the biological activity, we think using Mn and not Al brings another uncertainties. Indeed, Mn is highly affected by authigenic formation with different kinetic than iron. We agree that PFe/PAI ratio is not an idealistic proxy but we think it's the best to estimate the contribution of sources over iron cycle. Moreover, results from the PMF demonstrate the weak influence of authigenic particles over the particulate iron cycle. Line 620ff: Any explanation for Fe depleted particles and aerosols, respectively?

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Anthropogenic? Buck et al. (2010) are not giving any specific indication about reasons for these particles to be Fe-depleted. Line 636: I would check the Fe/Mn ratio too! This paragraph has been deleted. In light of the reviewers' comments, we decided it was too speculative using the current dataset at our disposition. Line 650: Now we are back to PFe/PP and not anymore PFenonlith/PP. This is all very confusing. It is an interesting approach using PP, but what are numbers actually tell us. It would be better to show first how much nonlithogenic Fe is in the top 100 m and plot PP as well in a diagram. By looking at picture 3. PP is similarly high in IrB and LB, changes in PFe/PP are then mainly driven by PFe, but what does it actually mean. Further on, you show nice plots using Ba excess data (Fig. 13 & 14), but there is not a single word towards the end of the discussion. There is more work needed!! This paragraph has been deleted. In light of the reviewers' comments, we decided it was too speculative using the current dataset

Please also note the supplement to this comment:

<https://www.biogeosciences-discuss.net/bg-2018-234/bg-2018-234-AC1-supplement.pdf>

Interactive comment on Biogeosciences Discuss., <https://doi.org/10.5194/bg-2018-234>, 2018.

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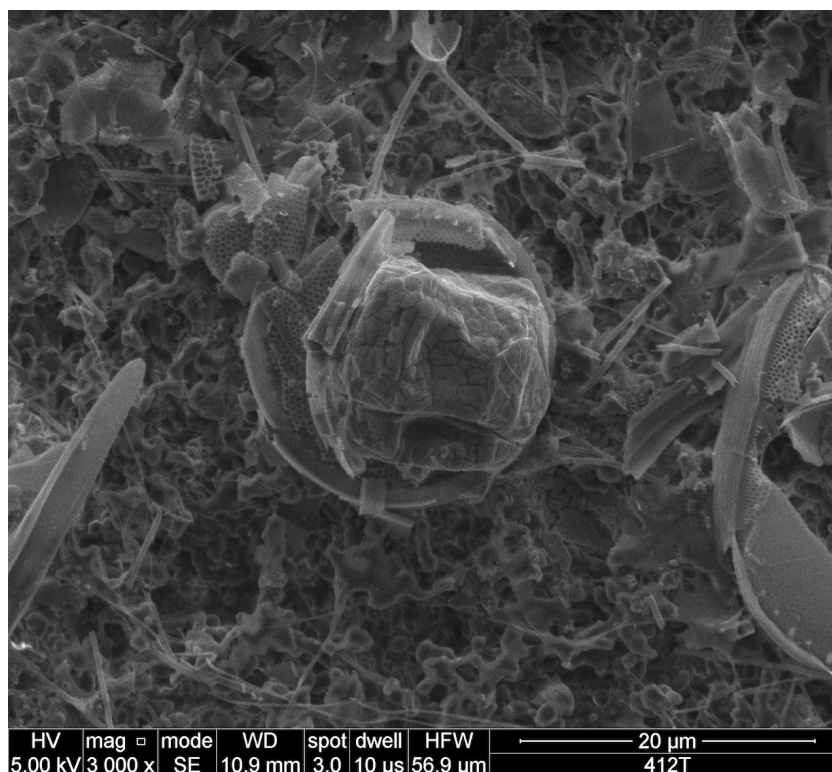


Fig. 1.

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