

## ***Interactive comment on “Mechanisms of dissolved and labile particulate iron supply to shelf waters and phytoplankton blooms off South Georgia, Southern Ocean” by Christian Schlosser et al.***

### **Anonymous Referee #1**

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General Comments: This manuscript presents new dissolved, particulate, sediment, and porewater Fe, Mn, and Al data from the South Georgia Island region. The authors conclude that “The majority of the Fe appears to be derived from remineralisation of Fe enriched phytoplankton cells/biogenic particles that are transported with the water masses into the bloom region”. However, this conclusion is based on a Fe budget that is extremely poorly constrained, so it should be presented as a hypothesis, rather than a conclusion supported by their measurements. Overall, this is a useful dataset to add to the quickly growing datasets of Fe in naturally fertilized regions in the Southern Ocean. There are, however, many aspects in this particulate dataset that aren’t consistent, at least in the authors’ discussion of it. Sections 3.1.1 and 3.1.2 need to be overhauled

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(detailed comments below). There are several other inconsistencies: for example, assuming the region is upwelling for the calculation of benthic Fe flux, but downwelling for calculation of the Fe budget. An attempt is made at a horizontal transport term for the PFe, but then dropped from the budget. This paper needs major revisions before it can be published.

Specific comments: Methods:

-Why were sediment cores collected on the southern shelf and not the northern shelf? Given that the phytoplankton bloom appears to originate on the northern shelf, and all water column and particle samples were collected on the northern shelf, this seems like a strange decision. If this was outside of the authors' control, then this needs to at least be discussed when sediments are compared to the water column, since one would expect the stronger bloom on the northside to affect the benthic processing of Fe and Mn, so sediments on the southern shelf may not be representative of those on the northern shelf.

-Fecal pellet data are first discussed in section 3.1.3 (for data in Table 4) but without introducing the methodology for fecal pellet sampling and analysis. They are discussed again in section 3.2.3, where a reference is to the Schmidt et al papers, but this should be moved up.

Section 3.1.1

-The discussion of particulate fractions in this section is confusing. LP<sub>un</sub> is derived from acidified unfiltered seawater and defined in equation 1, but then is compared to P as if they should be the same, differing only in their sampling methods (acidified unfiltered seawater vs SAPS samples—lines 157-158). However, P is defined in section 2.2 as the sum of leachable (LP) and refractory (RP) fractions from the SAPS samples, so one wouldn't expect LP<sub>un</sub> and P to be the same. I initially read this section thinking that they were comparing LP<sub>un</sub> (from acidified unfiltered seawater) and LP (from acetic acid leach of SAPS samples), which is the more direct comparison if they want

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to isolate sampling differences (but still not perfect since acidification to pH 1.7 with HNO<sub>3</sub> is still not the same as a 25% acetic acid leach, but at least more comparable). This section needs to be clarified. It seems that they have two points in this section: 1) that pFe and pAl have a refractory component, since LP(un)/P < 100%, and 2) LP(un) scales with P, so they want to justify using LP(un) for P. For the first point, it seems that a wholly SAPS-derived assessment of LP/(LP+RP) would be the better parameter to present, because then there is no confusion of mixing sampling systems, pore sizes, and leach types. This is done in section 3.2.2 (lines 320-340), which would make more sense in this section

-For the second point, presumably, they want to use the bottle-derived leachable particulate data because of higher depth resolution than SAPS samples, so this should be a separate argument than the one about the presence of refractory Fe and Al.

-Table 2: are the LPFe, LPAI, LPMn columns derived from the SAPS LP or the bottle LPun? This should be specified in the caption. The units for the LP are specified as being in percent. But these values are all very small—mostly less than 5%, even for Mn, which contradict what was stated in the text in lines 161-163: “The LPUn corresponded to ca. 63±4% of the PFe, 83±11% of the PAI and 100±10% of the PMn fractions.” Presumably, this discrepancy arises because the Table 2 values are SAPS-based (LP/P), whereas the values in the text are mixing and matching bottle-based LPun and SAPS-based totals. Is that correct? If this is the case, then this means that the bottle-based LPun are much higher than the SAPS-based LPs. One might expect this to some degree, since the LPun is acidified to a slightly lower pH (~1.7) and for a lot longer than the SAPS-based LPs (25% acetic acid should have a pH ~ 2.1), but I wouldn’t have expected the difference to be so big. This suggests that the particle population collected by the SAPS may be a subset of the particles accessed by the LPun method, and calls into question whether normalizing or comparing the bottle based LPun by/to the SAPS-based P is appropriate or meaningful. As further detailed below, I suggest that the authors do not mix bottle-based and SAPS-based parameters (i.e.

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they should not report or interpret LPun/P).

Section 3.1.2: this section needs to be considerably revised to account for the following:

-Re. lithogenic source of suspended particles: The extremely good correlations of the PFe to PMn and PFe to PAI concentrations (Fig 3a,3b) do support their contention that the particles have a single lithogenic origin (line 197), since biogeochemical processing of the particles would be likely to affect Mn, Fe, and Al differently, and therefore cause more scatter in the data. However, the slopes of their relationships don't support this. The authors base the conclusion that the suspended particles have a lithogenic origin on the slope of the PFe to PMn data (68 mol Fe/mol Mn), which they say agrees well with a typical crustal ratio (they use 60 mol Fe/mol Mn from Wedepohl, which is close to 57 and 50 mol Fe/mol Mn for UCC and BCC crustal averages, respectively, reported by (Taylor and McLennan, 1995)). However, PMn is not usually a good crustal indicator, since Mn-oxides are frequently a large component of marine particulate Mn. For this reason, PAI or PTi are more frequently used to assess how lithogenic the PFe is. However, their PFe to PAI relationship (slope=1.251 mol Fe to mol Al) far exceeds the slope of typical crust (UCC Fe:Al=0.21; BCC Fe:Al=0.41 (Taylor and McLennan, 1995)). Since the sediment elemental ratios from the southern shelf (Table 3, line 199) are close to these crustal averages, this suggests a fairly large component of the PFe that is in excess of a lithogenic source. One can derive a PMn to PAI ratio from their data= $\text{PFe:PAI} / \text{PFe:PMn} = 0.018 \text{ mol Mn/mol Al}$ , which is also greater than typical crustal ratios (UCC Mn:Al=0.0037; BCC Mn:Al=0.0082). So just comparing their slopes to crustal ratios to Al, one would expect there to be a fair amount of non-lithogenic Fe and Mn assuming crustal averages are a reasonable approximation of the local sources (a plausible assumption given that the sediment elemental ratios are close to crustal averages). The conclusion that the suspended particles are primarily lithogenic is therefore not supported by their data.

-The slopes of Fe:Mn and Fe:Al of the LPun fractions are each about half of those for the total particulate fractions (Fig 3a-d). Comparing the leachable and total slopes,

this suggests that particulate Fe is about half as labile as particulate Mn or particulate Al. This is much more consistent with their wholly SAPS-based %leachable data from Table 2 (average %leachable Fe < average %leachable Mn ~ average %leachable Al), than with their LPun/P from lines 161-163 (Fe < Al < Mn), another reason not to mix the bottle-based (LPun) and SAPS-based (LP, P) parameters.

-To rule out data quality issues, the authors should report results from an external standard such as a standard reference material that was run alongside the digestion of the suspended particle leaches/digests. External standards in the supplements were only reported for seawater and for sediments, which used a different digestion procedure than the particles. Was there an external standard measured for the suspended particles to ensure that the digestion method was working accurately?

### Section 3.1.3

-Re. meltwater source of LPunFe: is there a relationship between LPunFe and salinity? A scatter plot of these parameters would be evidence of a meltwater source of LPunFe.

-Lines 253-256: PFe/PAI in krill fecal pellets (0.48) is much lower than PFe/PAI in suspended particles (1.25 – Fig 3b), though it is relatively close to the sediment ratios from the southern shelf. This suggests that the suspended particles have an additional source of PFe compared to krill or sediments.

### Section 3.2.1

-The authors should acknowledge that the sediment core data were taken on the non-productive, southern side of the island, whereas the water column data were taken from the productive, northern side of the island, so benthic fluxes calculated from porewater profiles could be rather disconnected to the measured DFe.

-The authors calculate a vertical supply of DFe to surface mixed layers by assuming a vertical diffusivity and vertical advection (upwelling) used by De Jong et al. 2012 for the region downstream of the Antarctic Peninsula. But later in section 3.4.2, they discuss

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a study by Tagliabue et al. 2014 modelling DFe supply for South Georgia, in which Ekman \*downwelling\* (not upwelling!) prevailed, removing DFe from the surface, rather than supplying it. I can appreciate that there's uncertainty in the estimate of vertical advection, but they should probably pick a sign and stick to it!

Section 3.3: there are some problems with the proposed flowpaths:

-Line 384: I do not understand the proposed advective pathway: the authors reference "Fig. 1; #11/12 via #13 to #14" as a NE-SW transect. First, these stations do not define a NE-SW transect. Second, what is the order of the proposed advective pathway? Is it 13 to 14 to 11/12, even though 13 is actually further from the island than 14? Is 13 shallower than 14 (Fig 4) despite being further offshore (Fig 1)?

-Presuming that the authors are assuming that #11/12 is the offshore end of the flowpath, this is inconsistent with DMn, which is higher at 11/12 compared to 13 and 14. It's no wonder that they were not able to fit an exponential function to the DFe data (lines 409-410). If this isn't an advective flowpath, the good exponential fit to the LPU<sub>n</sub>Fe data may be a coincidence, or at least unrelated to offshore transport. Further, the "exponential decrease" in PFe was based on a 2 point fit! No wonder R<sup>2</sup>=1! This should be removed.

Section 3.4: budget

-As noted above, there is a discrepancy in the manuscript about whether this region is downwelling, as assumed here for the budget, or upwelling, as assumed in section 3.2.1. The sediment DFe flux.

-In the manuscript, an overall vertical loss of DFe of -0.0025 umol DFe/m<sup>2</sup>/d is assumed (line 465), but in Figure 8, a vertical supply of +0.009 umol DFe/m<sup>2</sup>/d is indicated.

-Given the poor (lack of) constraints on both horizontal and vertical supply of DFe, the suggestion that there is a mismatch in the supply and demand that is filled by advecting biogenic Fe is a nice hypothesis, but rather speculative, both the size of the term, and

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the nature of it. The size of the flux is not constrained, since they did not have local estimates of horizontal or vertical supply. Re. the nature of their proposed flux: their PFe:PAI ratio from earlier in the manuscript does suggest excess particulate Fe over lithogenic, so this is at least consistent with an available biogenic Fe pool on the shelf, but is also consistent with Fe oxyhydroxides (i.e., authigenic, not biogenic particulate Fe).

Miscellaneous:

-Lines 104-107: I assume that unfiltered samples were also collected from the tow fish in JR247, since LPun values are plotted for this cruise in figure 6. Please add this to this section.

-Line 231-2: Fig 6a shows that surface concentrations of  $0.3 \mu\text{M}$  LPunFe are quite common on the shelf, but  $22 \mu\text{M}$  doesn't show up in this figure, so referring to it here is not that helpful.

Typos: Line 106: "cartridge filter", not "filer" Line 178: "where", not "were" Line 251: "ascent" not "ascend" Line 415: add "there was" to "...that \*there was\* a limited transfer..." Line 459: "Tagliabue" not "Tagliabu"

References

Taylor, S.R., McLennan, S.M., 1995. The Geochemical Evolution of the Continental-Crust. *Reviews of Geophysics* 33 (2), 241-265.

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