RESPONSE TO REVIEWER CROOT

This paper presents statistical analysis on a compilation of dissolved iron data from the Southern Ocean. The authors group their data by region and depth to examine variations around the Southern Ocean. While this approach seems a good first attempt it could be significantly improved in my opinion by placing the data in an oceanographic context rather than simply a relationship with depth, and to examine in detail key processes through comparison with ancillary data (see below for suggestions) if it is available. The paper is well written but could be shortened in a number of places and concentrate more on what has been found through this data mining exercise and how this can help to plan sampling campaigns in the future in the context of international programs such as GEOTRACES. This is a mansucript that the Southern Ocean and iron biogeochemistry communities have been waiting for in many ways and my criticisms are founded on what my own expectations for such a work are and what I believe the authors could do with the dataset they have compiled. My recommendation is that this manuscript would be suitable for publication after suitable revisions have been made.

We thank Peter Croot for his detailed and considerate review, we present our response in bold and preceded by '>' in case of formatting errors.

General Comments:

Title: The title is presently slightly misleading as it states there are 13 000+ measurements for dissolved iron but in actual fact the paper is only concerned with 3332 Southern Ocean values. I strongly suggest the number of samples is removed from the title.

> Acknowledged and addressed

Abstract: I find that the abstract presents a number of the findings of the paper in more certainty than the main text does and this is particularly the case with regard to the control of deep water iron concentrations and the statistical differences between measurement periods. Thus I would urge that the abstract be rewritten in a similar tone to the main text so that the abstract is a summary of the findings of the manuscript rather than a version with the uncertainties removed.

> Acknowledged and addressed

The database: The compilation of this dataset is an important undertaking but it needs a home, which is fully accessible for all researchers (though credit and acknowledgment to the authors of this work should be always be made) and so my strong suggestion is that the authors make this database available via a website or deposit it in a database (e.g. GEOTRACES at BODC). It should also be made clear where the data is sourced from, what ancillary data is available, and importantly a supplementary file is required with the necessary citation information for the source of the Antarctic data reported here.

> We have arranged with GEOTRACES that the database will be hosted on their website as well as being available by contacting the lead authors of this paper.

Reporting of statistics from the database: It should be clearly stated in the text that the values presented there are ±1 sigma and that the 95% confidence interval for the data lies at 2 sigma, and thus there is a great deal of variability in the data sets. Currently the table and figures have this information but not the manuscript text itself.

> Acknowledged and addressed

>> In response to the following ideas/suggestions we think we have not been clear enough that our compilation (which we state builds on previous exercises initiated by Johnson et al. 1997) only includes dissolved Fe data. To put it another way, we do not have any metadata associated to the dataset and this means no data on salinity, temperature, macronutrients etc. While it might be plausible to go back through the entire dataset of 13,000 + measurements and compile the companion T, S and macronutrient data (if available) this would be a massive undertaking and we feel, out of the scope of the already large effort we have made here. Often researchers only furnished us with dFe data and only in very rare cases were metadata supplied (actually very rarely indeed). This is not to say that the ideas below are not worth pursuing, in fact that brought a lot of interesting questions to mind, but that they are perhaps best left for individual papers, or perhaps a 'post GEOTRACES' based paper where we have a better chance to compile such a dataset. This could be possible with the intermediate data product arising from the GEOTRACES programme. Even if we were to do that, it would we feel be a separate effort to that which we have undertaken herein. We would re-iterate that with a dFe + metadata dataset, attacking the ideas outlined below would be of great interest. If we do such an undertaking we will endeavour to contact Dr. Croot to ask him to be a part of this study since he has raised a number of very interesting ideas.

Sea ice melt: Data impacted by sea ice melt could be flagged by salinity anomalies and then surface water datasets analyzed with and without them included. In this way the impact of sea ice as an iron source may be evaluated in more detail.

> Despite our caution above, we did decide in the spirit of response that we would pursue the only avenue available to obtaining this metadata in a efficient manner. That is, to extract them from climatological datasets such as the World Ocean Atlas. While, of course, this is far from ideal (very far indeed) we decided to at least explore these hypotheses. To that end we extracted salinity at the longitude, latitude, depth and month of year of the iron samples for all sampling locations south of the Polar Front and in the upper 50m. From the 490 dFe observations that remained, we obtained 470 salinity values from the WOA 2009 salinity dataset (20 were lost due to no salinity data at those extreme coastal locations). This left us with a 'synthetic' (of sorts) salinity dataset. To examine whether lower salinities were associated with higher dFe levels (and vice-versa) we examined the regression between dFe and Salinity for these 420 points. We obtained a poor regression ($R2 = 0.016$) associated to a positive slope (0.38 nM/psu). This means that salinity does not explain much of the dFe variance and if anything, higher dFe was associated with higher salinities, probably reflecting physical processes (e.g., upwelling of high salinity and high dFe UCDW) rather than ice melt/formation. But of course, it is not ideal to compare point measurements with aggregated climatologies.

Sea ice formation: The authors could explore the hypothesis that frazil ice formation leads to lower dissolved iron in coastal and open ocean waters during autumn and winter. As sea ice may be a sink for iron via the intriguing mechanism of frazil ice formation stripping iron from the water column as it rises and accumulates at the surface to form sea ice, however this is yet to be demonstrated in the open ocean and the evidence in the coastal ocean is only from studies in the Arctic [Ackermann et al., 1994; Holland and Feltham, 2005; Reimnitz et al., 1993; Smedsrud, 1998; Smedsrud and Jenkins, 2004].

> See previous response.

Biological activity and dissolved iron: Throughout the manuscript it is assumed that biological drawdown is a major control on dissolved iron, however no data is presented on this and the seasonal cycle plots from SR3 would suggest that dissolved iron is in phase with chlorophyll levels and not anti-phase as one would anticipate. It would be useful then to see some calculations indicating what the anticipated drawdown would be for the dissolved iron, based on Southern Ocean algal stoichiometry [Strzepek et al., 2011; Twining et al., 2004a; Twining et al., 2004b] plus data from other regions examining if this drawdown is directly observable or if it is always masked by other processes.

> Again, it is only at SR3 and perhaps also the Ross Sea that we have enough dFe data to begin to explore seasonal drawdown figures/calculations. And in each of these locations the lack of constraints regarding the seasonal maxima (as noted in the text) is a major problem. Even if we could to that, the C/Fe ratio is (unlike the C/N ratio) by no means fixed although we do agree that some degree of an estimate might be made using published values similar to those suggested by the reviewer. More generally, the idea of biological drawdown as a major control on dFe is we believe a reasonable starting point, although it is indeed thrown into question when examining the SR3 seasonal cycle plots. This highlights the role for other processes (including changes in the strengths of the Fe sources, and heterotrophy as suggested below) as the major driver of seasonal dFe trends (at least in the Sub-Antarctic).

Iron solubility and temperature: Comparing the low dissolved iron concentrations found in the Southern Ocean with the solubility of iron in seawater [Kitayama et al., 2009; Kuma et al., 1996; Kuma et al., 1992; Liu and Millero, 1999; 2002; Nakabayashi etal., 2001; Tani et al., 2003] at the low temperatures found throughout the water column strongly suggests that iron is under-saturated with respect to mineral phases in the Southern Ocean. Given the strong organic complexation of iron this then further suggests that removal (scavenging) processes are critically important in maintaining dissolved iron at concentrations below the solubility limit [Baker and Croot, 2010]. Thus the authors could assess differences in scavenging in the water column by applying a relevant iron solubility equation (extrapolation to temperatures below 5ËŽ C being assumed as valid) and calculating the % saturation for dissolved iron in the water column and generating appropriate regional maps.

> See previous

Total iron and iron cycling in the ocean, remineralization depth and disappearance ratios: The importance of remineralization and iron recycling in the surface waters of the Southern Ocean cannot be underestimated and this should be more thoroughly examined in the manuscript. Such an analysis should include calculation of the remineralization depth for iron [Croot et al., 2007; Frew et al., 2006] in the water column at each station to generate a regional map from which variations might be assessed in terms of physical and biological processes. Similarly calculation of the disappearance ratio [Arrigo et al., 1999] for iron relative to other nutrients (N, P) in the upper water column could provide valuable information on the stoichiometry of nutrient utilization and recycling in different parts of the Southern Ocean. Additionally comparison with the apparent oxygen utilization (AOU), or humic fluorescence, has also suggested that iron is strongly remineralized in the deep ocean [Nakabayashi et al., 2001; Nakabayashi et al., 2002; Tani et al., 2003] – comparison of DFe with AOU would also allow identification of hydrothermal inputs (in the absence of Mn or 3He) as they would presumably be present as anomalies to the general trend. That iron is important on a regional scale has been shown in a number of recent papers that have examined the shallow remineralization occurring in the Weddell Sea in the context of other elements including Th [Usbeck et al., 2002] and Zn [Croot et al., 2011], that are influenced by the iron limited primary productivity found there. Presumably these processes are also occurring in the Ross Sea. Finally it should be noted that changes in the particulate iron will also be important to the seasonal cycling of iron and that this reservoir should be included in the modelling of iron cycling in the ocean, yet currently there is even less data for particulate iron or total iron than for dissolved iron.

> As previously, the lack of metadata on nutrients etc and the lack of constraints on seasonal maxima in dFe make the calculation of budgets problemtatic (which is not to say that we do not think it a worthwhile exercise in the future with more 'complete' GEOTRACES era datasets).

The manuscript has been amended to include the noted shallow dFe recycling that may also occur in the Ross Sea, as well as to note the importance of particulate phases in the seasonal dFe cycle at all locations (even if their contribution is difficult to assess at present).

RESPONSE

Comparison of old and recent data: I am not sure what the purpose of this section is as it appears that there is too much variability in both sets to come to any firm conclusions particular in light of the very different strategies of the earlier cruises, which were predominantly process based, to the long open ocean transects of the GEOTRACES era. Temporal variations in the distribution and supply of icebergs to the open ocean may also be important in this analysis [de Baar et al., 1995; de Baar et al., 1999; Lin et al., 2011; Raiswell, 2011; Raiswell et al., 2008; Schwarz and Schodlok, 2009]. There is are also still analytical questions involved in comparing the data where the older data was run on long term strongly acidified samples, similar to the SAFe and GEOTRACES intercalibration samples, but that the at sea methods for dissolved iron, due to logistical reasons don't incorporate either such a low pH or long term storage before analysis. While the use of a low pH (< 1.7) has been shown [Lohan et al., 2006] to be effective for the recovery of dissolved iron in a flow injection analysis (FIA) method, a number of recently published studies have used FIA protocols that do not involve such low pHs in their at sea treatment. Thus any comparison of this type of data on a temporal basis needs to look at the analytical methods first to see where the analytical bias might lie. My suggestion therefore would be to significantly shorten this section so that it reflects the good agreement in the deep waters but that the differences in the upper waters may be due to temporal variations as outlined above.

> Acknowledged and addressed. The reviewer raises important points regarding 'process' versus 'section' sampling, as well as potential analytical biases in the methods used and we have shortened the section accordingly.

Specific Comments:

P11491, line 17. The statistical differences are not explained here in the abstract and so the reader skimming the abstract does not know in what way the data differ. I would suggest removal of this statement from the abstract as the main text does not present a strong case for major differences between datasets.

> Acknowledged and addressed

P11492, line 15. Biological processes also affect the cycling of iron in surface waters through zooplankton grazing [Barbeau et al., 1996; Barbeau and Moffett, 1998] and recently the role of krill and whales has also been implicated in iron cycling in the Southern Ocean [Nicol et al., 2010; Tovar-Sanchez et al., 2007].

> Acknowledged and addressed, we were indeed negligent to not mention grazing.

P11492, line 28. Sea-ice melting is more a transport mechanism for iron supplied via other sources, rather than a primary source itself, see also the section above regarding sea ice formation as a sink for dissolved iron.

> Acknowledged and addressed.

P11495, line 7. It would have been perhaps more useful to have the samples distributed by water mass properties, either a flag for the water mass type or simply the neutral density for comparison between different water masses and in the same water mass.

> This is a good point, but beyond the scope of our analysis. We have however added some comments to address this is our new discussion section.

P11496, line 4. The Boye et al. [2010] article is for an iron enrichment experiment and contains almost no intermediate or deep water samples, similarly the Ibisamni et al. [2011] work has no samples from below 1000 m. However there are two other papers with speciation data from this sector that do contain some intermediate and deep water data [Boye et al., 2001; Croot et al., 2004] that should be included. See also the comment above regarding iron solubility at low temperatures.

> Acknowledged and addressed. We thank the reviewer for drawing our attention to these two papers.

P11507 lines 1-20. Care should be taken in comparing the Ibisamni et al. [2011] work with that of Thuróczy et al. [2011] as the two studies differ slightly and this difference is important to be aware of. Whilst at face value they use the same ligand, TAC, and basic methodological approach [Croot and Johansson, 2000], they employ different detection windows; the commonly used 10 μM TAC [Thuróczy et al., 2011] and a significantly lower value of 3.5 μM [Ibisanmi et al., 2011]. While it might be expected that the lower detection window would determine a higher concentration of weaker ligands then found using a higher detection window, this is the apparent opposite in this case for what is observed – assuming no regional differences. However there are other analytical issues related to the sensitivity of the technique [Hudson et al., 2003] that will affect the determination of the ligand concentration and thus it is important that iron speciation studies also report their sensitivity data, particular in the case where a non-standard detection window is used. I raise this rather technical point here so that the authors are aware of this and that the comparison not be presented as being completely the same.

> We thank the reviewer for raising our awareness of these issues. We have added a mention of this to the manuscript as a parenthetical statement to draw caution to the direct comparison of the datasets.

P11507, line 25-29. This seems to be highly speculative as I am unaware of any definitive data from the IND basin for the presence of long range transport from hydrothermal sources as this is at present a prediction from modelling [Tagliabue et al., 2010]?

> Acknowledged and addressed. It is indeed a prediction from modelling and is based on the notion that ridge spreading rates govern the hydrothermal input of Fe at the first order.