

## ***Interactive comment on “A global compilation of over 13 000 dissolved iron measurements: focus on distributions and processes in the Southern Ocean” by A. Tagliabue et al.***

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Overview:

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

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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 manuscript 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.

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.

**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.

**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. **Reporting of statistics from the database:** It should be clearly stated

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in the text that the values presented there are  $\pm 1$  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.

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.

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].

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.

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 et

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al., 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 5°C being assumed as valid) and calculating the %saturation for dissolved iron in the water column and generating appropriate regional maps.

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  $^3\text{He}$ ) 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

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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.

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.

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.

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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].

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.

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.

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.

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  $10 \mu\text{M}$  TAC [Thuróczy et al., 2011] and a significantly lower value of  $3.5 \mu\text{M}$  [Ibisamni 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

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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.

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]?

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