

## ***Interactive comment on “Trace metal evidence for a poorly ventilated glacial Southern Ocean” by M. Wagner and I. L. Hendy***

**Anonymous Referee #1**

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Meghan Wagner and Ingrid Hendy present new trace metal records from two well-documented sedimentary archives retrieved from the South Atlantic Ocean. The authors reconstruct changes in sedimentary redox conditions across the last 30 kyr. They follow an original approach using a set of trace metals characterized by different delivery pathways to separate the typically obfuscating influences of changes in deep water oxygen concentration and sedimentary organic matter remineralization. Ag and Cd are both enriched under oxygen-depleted conditions and are primarily supplied to the sediment along with sinking organic detritus. Re and Mo, on the other hand, directly diffuse into the sediment when conditions become reducing enough. Both records indicate generally more reducing conditions during the last ice age, which is interpreted as illustrating increased sequestration of remineralized carbon in the deep Southern Ocean, corroborating previous evidence. Conditions became more oxygenated during

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the second half of the glacial termination, accompanying the release of deeply sequestered CO<sub>2</sub> to the atmosphere. The detailed evolution of the two cores is however more complicated (and more confusing, I find). The two records document millennial changes in both export production and sedimentary redox conditions that are difficult to reconcile with existing data (see below). In particular, it is not straightforward to derive common patterns related to changes in deep ocean circulation at locations characterized by opposite trends in export production (and by inference organic matter respiration). The discussion should be more integrative with respect to the observations available from the literature, in particular regarding changes in export production through time.

In summary, I cannot recommend this manuscript to be accepted for publication in Climate of the Past at this stage. The data presented is certainly valuable and of interest to the paleoceanographic community. The authors will find my comments below, which I hope will prove to be helpful and constructive as they intended to be.

### **General comments**

- Both sites are currently bathed by LCDW. According the authors' interpretation site TN057-13PC would have been bathed by a well-oxygenated water mass during the LGM (p. 13, l. 3), whereas site RC13-253 would have been bathed by a poorly ventilated water mass (p. 12, l. 13). This water-mass geometry outlined in §4.3 seems very difficult to fathom given the expected tilting of the isopycnals if the ACC continued to flow during the past ice age.
- The inferred export production patterns based on the sedimentary distribution of Ag, Cd and Corg are at odds with previously published records from the Atlantic sector of the Southern Ocean (e.g. Francois et al., 1997; Frank et al., 2000; Kohfeld et al., 2005; Anderson et al., 2009; Jaccard et al., 2013; Anderson et al., 2014; Martinez-Garcia et al., 2014), which warrants a much more thorough treatment. In addition, I would encourage the authors to normalize their trace metal records to Al, Ti or Fe to

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ascertain that their downcore patterns are not driven primarily by sedimentary dilution.

-  $^{230}\text{Th}$ -normalization allows quantifying the vertical flux of a given sedimentary component through the water-column (e.g. Francois et al., 2004). In suboxic environments, redox-sensitive trace metal enrichments occur through diffusion of trace elements from the water column across the sediment-water interface (or through remobilization and repartitioning along redox gradient within the sediment). As such, it is erroneous to derive the accumulation of redox-sensitive trace metals using Th-normalization as the process is largely authigenic (although the situation may be somewhat different for Ag and Cd, which are delivered, in part, in association with sinking organic particles). Now, the sedimentary distribution of metals is dependent on the total sediment mass accumulation rate (sedimentary dilution). However, determining bulk sedimentary mass accumulation rates is heavily dependent on the age model. In addition, piston cores are often characterized by differential stretching. As such, I would recommend determining the total vertical flux (using  $^{230}\text{Th}$ -normalisation) as well as the sediment focusing to determine whether the observed downcore patterns are driven by changes in sediment accumulation rates (for a detailed methodological description please refer to Hayes et al., 2014 and its supplementary materials).

#### Specific comments

p. 2, l. 3 – “Enhanced storage of REMINERALIZED CO<sub>2</sub> in the . . . “ Storage of excess CO<sub>2</sub> via the solubility- or carbonate pumps alone will not affect O<sub>2</sub> concentrations p. 2, l. 5 – requires seems more adequate than predicts p. 2, l. 16 – geometry would be more appropriate than arrangement p. 2, l. 21 – several studies have attempted to quantify the “excess” deep ocean carbon storage, both from a modeling (e.g. Hain et al., 2010) and an observational (e.g. Yu et al., 2010; Skinner et al., 2015) perspective. p. 3, l. 10 – I agree with the statement, but the authors should keep in mind that extended se-ice coverage could theoretically alter the air-sea exchange (and equilibration) of oxygen. p. 5, l. 13 - p. 6, l. 2. Enhanced preservation of Ag and Cd, indicates oxygen-depleted conditions caused by a high flux of organic matter, but the

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opposite is not necessarily true. The absence of Ag or Cd enrichments above background cannot be uniquely related to low export production as these metals may not have been precipitated/preserved under oxygenated conditions. p. 10, l. 2 – I find it a bit awkward to begin the discussion part with the burndown paragraph. I would suggest the authors to possibly invert parts 4.1 and 4.2. p. 11, l. 10 – Sedimentary Corg concentrations are primarily controlled by oxygen exposure time, which is ultimately modulated by (i) the oxygen concentration at the sediment-water interface and (ii) the bulk sediment accumulation. It is thus not surprising to see increased Corg concentration during the LGM when the inferred oxygenation was lowest, signaling enhanced preservation. Corg concentrations alone cannot be used as an export production indicator under these conditions. p. 11, l. 15 – Oxidative burndown usually does not affect rapidly (i.e. > 10 cm/kyr) accumulating sediments. I would not worry too much about post-depositional patterns in the sediments investigated here. p. 12, l. 3-22 – Export production patterns suggest a typical SAZ-type behavior, with high opal- and Corg fluxes during the last ice age as a result of enhanced Fe-fertilization, declining into the Holocene (e.g. Martinez-Garcia et al., 2014; Anderson et al., 2014). Enhanced Corg remineralization would have contributed to consume oxygen regionally, which could explain the downcore trace metal observed in core RC13-254. p. 14, l. 12 – the correlation between Re concentration at site RC13-254 and apparent ventilation ages determined in core MD07-3076 is an interesting conjecture. It would be interesting to see whether Re concentrations at site TN057-13PC also show a positive correlation. p. 15, l. 10 – Re concentrations at site PS2489-2 have been interpreted as illustrating changes in export production/Corg remineralization (Martinez-Garcia et al., 2009). The separation between changes in ventilation and changes in organic matter respiration cannot be made at this site based on the data in hand. p. 16 – the discussion related to <sup>14</sup>C seems out of place here and remains largely speculative. I would recommend removing it altogether and concentrate on describing the outcome provided by the newly generated records. p. 16, l. 24 – increased upwelling alone cannot account for the net transfer of deeply sequestered CO<sub>2</sub> back to the atmosphere. The net transfer of CO<sub>2</sub>

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from the ocean interior to the atmosphere requires changes in deep ocean ventilation or more specifically a change in the relative dominance of northern- versus southern sourced deep water masses in ventilating the global ocean (e.g. Sigman et al., 2010). p. 17, l. 16-20 – bulk accumulation rate/sediment focusing, organic carbon rain rate and bottom water O<sub>2</sub> concentration also affect the sedimentary distribution of Ag, Cd, Re and Mo just like it influences U. suppl., l. 15-16 –  $^{230}\text{Th}_{\text{xs},0}$  is the measured sedimentary  $^{230}\text{Th}$  not associated with the detrital and authigenic components

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