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Trace metal evidence for a poorly ventilated glacial Southern Ocean

M. Wagner^{1,*} and I. L. Hendy¹

¹Department of Earth and Environmental Sciences, University of Michigan, 1100 N University Ave, Ann Arbor, MI 48109, USA

*now at: Department of Earth and Atmospheric Sciences, Central Michigan University, Brooks Hall 314, Mount Pleasant, MI 48859, USA

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Correspondence to: M. Wagner (wagne2me@cmich.edu)

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cannot uniquely identify whether bottom water masses were oxygen-poor and/or export productivity was high. Paired benthic-planktonic ^{14}C ventilation measurements from the northwest Atlantic Ocean (Keigwin, 2004; Keigwin and Schlegel, 2002; Robinson et al., 2005) are also consistent with an “old” Southern-sourced water mass below ~ 2.5 –
5 3 km water depth. However, $\Delta^{14}\text{C}$ is also affected by water mass mixing, and robust interpretation of this proxy requires accurate determination of surface ocean reservoir age. As an added complication, both $\delta^{13}\text{C}$ and $\Delta^{14}\text{C}$ measurements require good carbonate preservation, but CaCO_3 is poorly preserved in the CO_2 -rich waters south of the Antarctic Polar Front (Howard and Prell, 1994). Because every proxy is subject
10 to a unique set of biases, agreement among several proxies increases confidence in our interpretations. Thus, it is prudent to seek additional evidence for decreased bottom water O_2 /increased CO_2 concentrations in the glacial Southern Ocean from other proxies.

Redox-sensitive trace metals are reliable proxies for sedimentary pore water redox conditions (especially in the high latitude Southern Ocean where sediments contain primarily biogenic silica and little to no CaCO_3 ; Diekmann, 2007) and provide an alternative approach to reconstructing deep water ventilation. Additionally, by examining a suite of trace metals it is possible to disentangle the relationship between low-oxygen bottom waters and intensive oxidation of organic matter in sediments
15 that can produce reducing sedimentary pore waters. In this study we measured the redox-sensitive trace metals Ag, Cd, Re, and Mo to reconstruct deep Southern Ocean oxygenation history over the last ~ 30 kyr for two piston cores from the deep South Atlantic Ocean: RC13-254 (48.57°S , 5.127°E , 3636 m water depth), from the Cape Basin; and TN057-13-4PC (53.1728°S , 5.1275°E , 2848 m water depth), from the open
20 ocean Antarctic Zone (Fig. 1). Additionally, we present new organic carbon (C_{org}) concentrations for both cores.

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2 Background

2.1 Trace metal geochemistry

Because trace metals are supplied to sediments via a number of different delivery mechanisms, a suite of trace metals is required to differentiate the processes that produce reducing conditions in pore waters. Here we follow the definition of Berner (1981), and classify sediments whose pore waters contain no measurable dissolved oxygen or dissolved sulfide as suboxic, and those whose pore waters contain measurable dissolved sulfide as anoxic. Onset of suboxic conditions occurs between the reduction potentials of Mn and NO_3^- reduction (Froelich et al., 1979). Silver and Cd are thought to be delivered by sinking biogenic particles (Hendy and Pedersen, 2005; Wagner et al., 2013) and preserved as their respective sulfides where trace quantities of dissolved sulfide are present (Crusius and Thomson, 2003; Rosenthal et al., 1995b). Hence, enhanced preservation of these metals indicates suboxic conditions caused by a high flux of organic matter (Hendy and Pedersen, 2005). Cadmium also displays a strong tendency toward authigenic precipitation in sediments where reducing conditions occur close to the sediment–water interface (Calvert and Pedersen, 1993; Pedersen et al., 1989; Rosenthal et al., 1995b). In contrast, authigenic Ag_2S precipitation appears to be negligible except in severely anoxic sediments where sulfate reduction is occurring (McKay and Pedersen, 2008). Elevated Re concentrations also indicate pore water suboxia. Rhenium exists in seawater as the conservative perrhenate anion (ReO_4^-) (Koide et al., 1986). It diffuses into sediments along concentration gradients and precipitates directly from seawater under reducing conditions, possibly as ReO_2 (Crusius et al., 1996), although the probability for this reaction to proceed spontaneously in typical seawater has recently been questioned (Helz and Dolor, 2012; and references therein). Due to its low crustal concentrations, nearly all sedimentary Re is authigenically precipitated (Crusius et al., 1996). Hence, increases in Re accumulation without corresponding increases in Ag

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and/or Cd indicate that low bottom water O₂ concentrations were likely present, and this deficit was primarily responsible for suboxia in underlying sediments.

Molybdenum enrichment occurs under anoxic conditions and requires measurable sulfide levels to precipitate. In seawater Mo is present as the conservative molybdate anion (MoO₄²⁻). Under oxic conditions, Mo associates with Mn-oxyhydroxides (Calvert and Pedersen, 1993; Zheng et al., 2000) which produces low-level enrichments unrelated to reductive processes. When redox conditions become favorable to Mn-oxyhydroxide reduction, adsorbed Mo can be released to pore waters (Crusius et al., 1996), decreasing preserved solid-phase Mo. Significant enrichments of Mo (up to tens of ppm in non-euxinic settings (Scott and Lyons, 2012)) above lithogenic background are controlled by pore water H₂S concentrations. At sulfide concentrations below ~ 11 μM, progressive substitution of O for S atoms occurs in molybdate, leading to the formation of multiple thiomolybdate species (MoO_xS_{4-x}²⁻) that co-precipitate as a labile Mo-Fe-S phase (Erickson and Helz, 2000; Helz et al., 1996). The substitution reaction is kinetically slow, but above the threshold value of 11 μM, a “geochemical switch” (Helz et al., 1996) is flipped and complete conversion to MoS₄²⁻ (tetrathiomolybdate) occurs. Downcore measurements of Mo and H₂S in Santa Barbara Basin sediments provide empirical support for this theoretical “geochemical switch” (Zheng et al., 2000). Tetrathiomolybdate is highly particle-reactive and adsorbs to pyrite, after which it is retained in sediments as a Mo-Fe-S cubane compound (Bostick et al., 2003). Above sulfide concentrations of ~ 100 μM, direct precipitation of a discrete Mo-sulfide phase is hypothesized to occur (Zheng et al., 2000). Similar to Re, elevated Mo concentrations not coupled with increased Ag and/or Cd concentrations imply that low bottom water O₂ concentrations caused anoxic conditions in pore waters.

Because Ag and Cd delivery to sediments is associated with biogenic particles, and Cd precipitates in sediments where oxygen penetrates 0.5 cm or less (Morford and Emerson, 1999), enrichment of Ag and Cd is assumed to be approximately contemporaneous with the modelled sediment age. Under reducing conditions, Re and Mo precipitation begin within ~ 1 cm of the sediment–water interface (Crusius

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et al., 1996; Morford et al., 2009), minimizing any offset with the sediment age. A quantitative relationship has yet to be shown between sedimentary trace metal accumulation and export production or bottom water ventilation due to the combined effects of biogenic particle remineralization, sedimentation rate, dilution by other phases, and post-depositional re-oxidation of trace metals. For this reason, trace metals can provide a qualitative determination of the relative importance of export production vs. bottom water ventilation by comparing Ag and Cd (metals associated with biodebris) enrichments with Re and Mo (authigenic metals) enrichments. For this study, when Ag and/or Cd concentrations increase with increasing Re and/or Mo concentrations, we interpret this pattern as high export production that depletes sedimentary oxidants. When Ag and/or Cd concentrations decrease with increasing Re and/or Mo concentrations, we interpret this pattern as a relative decrease in export production and concomitant decrease in bottom water oxygenation. However it is important to note that export production and bottom water oxygenation may operate synergistically to produce contemporaneous trace metal enrichments.

2.2 Oceanographic setting

Core TN057-13-4PC was recovered from a small sedimentary basin northeast of Bouvet Island, at the same location as ODP Site 1094 (Kanfoush et al., 2002), so the two cores can be directly compared. Presently, TN057-13-4PC is located slightly to the south of the Southern ACC Front (Orsi et al., 1995) and $\sim 2^\circ$ north of the average winter sea ice edge (Kanfoush et al., 2002). Primary productivity in this region is high (Moore and Abbott, 2000) and dominated by the heavily-silicified diatom *Fragilariopsis kerguelensis* (Abelmann et al., 2006). Sediments are composed primarily of diatomaceous ooze and diatom mud (Shipboard Scientific Party, 1999b). Site RC13-254 is located southwest of Meteor Rise in the Cape Basin, on the northern edge of the Antarctic Polar Frontal Zone (APFZ), and within the Permanently Open Ocean Zone. Productivity within the APFZ is still high, but transitions from diatom-dominated in the south to coccolithophorid-dominated in the north (Honjo et al., 2000). Consequently,

sediments in the upper portion of the core are composed primarily of CaCO_3 and transition to diatomaceous ooze during deglaciation (Charles et al., 1991).

Today both cores are overlain by Lower Circumpolar Deep Water (LCDW) (Fig. 2), a cold, saline, recirculating water mass of the Antarctic Circumpolar Current (ACC). Modern LCDW is a mixture of North Atlantic Deep Water (NADW), Antarctic Shelf Waters, and recirculated Pacific and Indian Deep Waters (PDW and IDW) that is exported to the three major ocean basins through Deep Western Boundary Currents (Talley, 2008). LCDW is ventilated from the north by penetration of NADW into the ACC, and from the south by upward mixing of Antarctic Bottom Water (Orsi et al., 1999). (Note, however, that bottom waters overlying TN057-13-4PC receive less influence from NADW than sites further to the north (Shipboard Scientific Party, 1999a), such as RC13-254/ODP 1091.) Once LCDW enters the Indian and Pacific basins, it upwells diapycnally to form the major volume of PDW and IDW. These subsequently re-enter the Atlantic basin through Drake Passage, mix with ACC waters, and upwell isopycnally to form modern Upper Circumpolar Deep Water (UCDW) (Talley, 2008), a nutrient-rich and slightly lower-oxygen water mass. Thus in the modern ACC, waters are well ventilated but the vertical water column structure can be characterized as having a lower-oxygen water mass overlying a higher-oxygen water mass (Fig. 2b).

3 Methods and materials

3.1 Trace metal and organic carbon analysis

Cores were sampled at millennial- to submillennial-scale resolution from the core tops to ~ 30 ka. Concentrations of Ag, Cd, Re, and Mo were measured at the University of Michigan Keck Environmental Geochemistry Laboratory (KEGL) by isotope dilution inductively coupled plasma-mass spectrometry (ID ICP-MS) using a Finnigan Element mass spectrometer. Prior to analysis, samples were spiked and subjected to total microwave digestion in Teflon vessels using an acid cocktail of trace metal grade

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HF, HCl, and HNO₃ (Crusius et al., 1996). An aliquot was removed from digested samples for Cd and Ag analysis and passed through a column of Dowex 1X-8 resin to remove interfering isotopes. Working spike concentrations and ratios of ¹⁰⁹Ag/¹⁰⁷Ag, ¹¹¹Cd/¹¹³Cd, ¹⁸⁵Re/¹⁸⁷Re, and ⁹⁵Mo/⁹⁷Mo were calibrated using natural element ICP standards (Ricca Chemical Company). Errors are reported as one-sigma standard deviations for each run based on repeated analysis of the sediment standard MESS-3.

Weight percent organic carbon (C_{org}) was determined by paired analysis of acidified and unacidified bulk sediment samples using a Costech ECS4010 elemental analyzer. Relative SD is 3% based on duplicate analysis of ~ 10% of samples.

3.2 Age models

Published age models were used for both cores. The initial age model for core RC13-254 (Charles et al., 1991) was based on oxygen isotope chronostratigraphy. More recently, calibrated ¹⁴C dates have been incorporated that indicate that the core top is ~ 7 kyr younger than originally estimated, and the age model for the upper ~ 190 cm of RC13-254 has been modified accordingly (R. F. Anderson, personal communication, 2011; Anderson et al., 1998; Kumar et al., 1995). The age of the core top (0–1 cm) was set to 3500 years before present. A constant sedimentation rate was assumed between age-depth points provided by R. F. Anderson (personal communication). The age model for core TN057-13-4PC is based on a series of ¹⁴C dates (Shemesh et al., 2002) that were recalibrated using the program CALIB 6.0 and the Marine09 calibration, with an assumed 800-year reservoir effect. A constant sedimentation rate was assumed between age control points. All dates are shown in calendar kyr.

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880 cm core depth (~ 21.6–26.9 ka) indicate possible burndown. If true, co-occurring Re peaks appear to have migrated further downcore. However, U fluxes increase slightly from ~ 832 to 884 cm (~ 22.1–26.5 ka) (Anderson et al., 2009), suggesting that burndown was minimal or affected U in a similar – though less severe – manner to Ag and Cd. Changes in C_{org} flux can control the onset of burndown (Crusius and Thomson, 2000) and may help to diagnose when burndown began. Sedimentary C_{org} concentrations in TN057-13-4PC decline from a maximum of about 0.5 % to about 0.3 % from 30 ka to the end of MIS 3 (~ 22 ka), coincident with the large Ag, Cd, and Re peaks. Subsequently, agreement among Ag, Cd, Re, and C_{org} peaks between ~ 760 and 820 cm (~ 16.2–21.6 ka) suggests a true increase in export productivity. Sedimentary C_{org} concentrations in the Antarctic Zone therefore *increase* going into the LGM and a decrease in the intensity of organic matter respiration cannot be responsible for re-oxygenation of sediments. Rather, burndown appears to have occurred sometime during late MIS 3. Therefore, with the evidence at hand, we will assume that oxidative burndown has had a minimal effect on trace metal concentrations near the glacial–interglacial transition.

4.2 Glacial–interglacial changes in Southern Ocean redox conditions

Trace metal concentrations in Holocene-age sediments reported here for the Atlantic sector Southern Ocean are low, similar to those measured for Pacific sector core top sediments both within and outside the opal belt (Wagner et al., 2013). These data suggest that marine chemistry unfavorable to trace metal accumulation exists throughout the modern Southern Ocean. In contrast, trace metal concentrations at both sites are significantly higher downcore (Figs. 3a–d, 4a–d). Although both RC13-254 and TN057-13-4PC are situated in the open ocean, trace metal concentrations in deglacial- and glacial-age sediments are similar to concentrations found at modern continental margin sites (e.g., McKay and Pedersen, 2008; Morford and Emerson, 1999). These continental margin sites are often located in oxygen minimum zones

such as the eastern Pacific Ocean where dissolved oxygen concentrations are much lower than the $\sim 200\text{--}225\ \mu\text{M}$ typical of modern LCDW (Fig. 2b).

At RC13-254 (Cape Basin, modern APFZ), the obvious difference in trace metal enrichments between late MIS 2 and the late Holocene (Fig. 3a–d) indicates a significant change in deep Southern Ocean chemistry $\sim 3.6\ \text{km}$ water depth. Prior to $\sim 13.5\ \text{ka}$, the record presents a strong case for pore water suboxia near the sediment–water interface. During MIS 3, mostly elevated Ag (79–273 ppb) and Cd (0.22–1.26 ppm) concentrations coupled with a trend of relatively stable Re concentrations (average 16.3 ppb) that do not correspond to changes in Ag and Cd concentrations suggest that low bottom water O_2 concentrations acted synergistically with variations in primary productivity to produce suboxic pore waters. Transitioning into the Last Glacial Maximum ($\sim 19.1\text{--}21.1\ \text{ka}$; $\sim 181\text{--}206\ \text{cm}$), decreasing Ag and Cd and increasing Re concentrations (maximum 38.5 ppb) suggest that low bottom water O_2 concentrations became more important in controlling sedimentary redox conditions. Subsequent deglacial increases in Ag and Cd concentrations that correspond to Re concentrations from $\sim 13.5\text{--}19.1\ \text{ka}$ ($\sim 70\text{--}181\ \text{cm}$) imply that suboxic pore waters resulted primarily from high organic matter flux to sediments. After $\sim 13.5\ \text{ka}$ (above $\sim 70\ \text{cm}$), Ag, Cd, and Re concentrations greatly decrease to near or below crustal concentrations, probably due to oxidative burndown (see Sect. 4.1). The Mo record is dissimilar to the other trace metals and suggests little, if any, authigenic enrichment (Fig. 3d). A possible exception occurs $\sim 25.4\ \text{ka}$ ($\sim 309\ \text{cm}$) when a corresponding increase in Cd concentrations is observed.

Glacial- and deglacial-age Ag, Cd, and Re enrichments (Fig. 3a–c) do not likely result from lithogenic input. Estimates of terrigenous content do not exceed 35 % (Latimer and Filippelli, 2001, Fig. 3g) and Ag, Cd, and Re concentrations are nearly always greater than bulk continental crust, a purely lithogenic phase (Fig. 3a–c). Furthermore, C_{org} concentrations (Fig. 3e) correspond well to Ag and Cd concentrations, substantiating their interpretation as a record of export production.

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The pattern of trace metal enrichments at TN057-13-4PC (modern Antarctic Zone) is dissimilar to that at RC13-254. The overall record (Fig. 4a–d) suggests that bottom waters at the site have been well ventilated for approximately the last 25 kyr, with organic matter respiration mostly responsible for periods of sedimentary suboxia. Silver, Cd, and Re show large enrichments prior to ~ 16 ka (below ~ 760 cm) (Fig. 4a–c). Rhenium concentrations as high as 65 ppb (Fig. 4c) between ~ 25.2 and 30.6 ka (~ 860 –921 cm) suggest that low bottom water O_2 concentrations caused suboxic pore waters during this time. Rhenium concentrations then decrease as Ag and Cd concentrations increase to maxima of 589 ppb and 1.13 ppm, respectively, between ~ 23.4 and 25.2 ka (~ 840 –860 cm). These trends suggest increasing export production and bottom water O_2 concentrations. From ~ 16.2 –23.4 ka (~ 760 –840 cm) Re peaks show reasonable agreement with Ag and Cd, indicating a change to suboxia driven by high export production. From ~ 11 –16.2 ka (~ 560 –760 cm), relatively low Ag, Cd, and Re concentrations suggest improved bottom water ventilation at the site. Long-term increases in Ag, Cd, Re, and C_{org} concentrations between ~ 5.5 and 11 ka (~ 200 –560 cm) suggest that trace metal enrichments responded to pore water suboxia driven by high export production, but coeval opal fluxes decline. Well-oxygenated sediments similar to modern conditions appeared ~ 5.5 ka (~ 200 cm), coincident with the onset of the Neoglacial (Hodell et al., 2001) and increased sea ice presence at the site (Stuut et al., 2004, Fig. 4h). Burndown and/or a slowdown in trace metal delivery appears to be responsible for low trace metal concentrations after ~ 5.5 ka (see Sect. 4.1). Similar to site RC13-254, Mo concentrations are low throughout the core (Fig. 4d), thus indicating no authigenic enrichment.

Estimates of terrigenous content from Ti-normalization (Fig. 4g) suggest that increased lithogenic input probably contributed to high total Ag, Cd, and Re concentrations during early MIS 2 and MIS 3. However, similar to site RC13-254, estimates of terrigenous content are no more than 55% and therefore cannot be the only factor contributing to high trace metal concentrations. Sedimentary C_{org} concentrations (Fig. 4e) also correspond reasonably well to Ag and Cd concentrations

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measured benthic-atmospheric $\Delta^{14}\text{C}$ offsets of nearly 4 kyr (Fig. 6), thus supporting the conclusion of Skinner et al. (2010) that the carbon sequestration capacity of the Southern Ocean was enhanced at this time due to slower ventilation rates at the depth of modern LCDW. Overall, oxygen depletion appears to have intensified in the deep Atlantic as global climate moved into the full glacial conditions of the LGM, became less intense during deglaciation, and then Southern Ocean oxygen concentrations reset to more modern conditions sometime after ~ 13.5 ka.

A lower-resolution Re record from PS2489-2 (42.873°S , 8.973°E , 3700 m) (Martínez-García et al., 2009, Fig. 6b) corroborates the pattern from RC13-254 of lower Re concentrations/lower ventilation ages during MIS 3 and higher Re concentrations/higher ventilation ages during MIS 2. Rhenium data (this study) also support the prediction (Sarnthein et al., 2013) that oxygen-depleted conditions similar to the modern Eastern Pacific oxygen minimum zone (see Sect. 4.2) occurred in the Atlantic sector of the Southern Ocean at the LGM. Furthermore, recent deep-sea coral $\Delta\Delta^{14}\text{C}$ measurements from Drake Passage (Burke and Robinson, 2012) tentatively support better ventilation at depths corresponding to modern UCDW compared to LCDW during the LGM.

$\Delta^{14}\text{C}$ (MD07-3076) and trace metal (RC13-254) results therefore suggest that ocean circulation changes may have inhibited glacial LCDW from mixing with better ventilated waters and/or that vertical stratification increased, similar to conclusions drawn from $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ tracer data (Lund et al., 2011). Other observations further support these conclusions: (1) Glacial North Atlantic Intermediate Water (GNAIW) penetrated only to $\sim 30^\circ\text{S}$ (Curry and Oppo, 2005), reducing ventilation from the north. Lund et al. (2011) also suggest that shoaling of modern North Atlantic Deep Water to GNAIW reduced mixing by bottom topography. (2) Indian Ocean $\delta^{15}\text{N}$ measurements (Francois et al., 1997) suggest that increased Southern Ocean vertical stratification was responsible for lowered bottom water O_2 concentrations in glacial LCDW. One plausible mechanism to increase Southern Ocean vertical stratification invokes increased sea ice extent and

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distributed, “old” oceanic carbon reservoir is so far lacking. However, benthic-planktonic age differences often assume constant surface reservoir ages. If this assumption is not valid, and surface water reservoir ages are high, the “true” age of deep waters may not be apparent. Furthermore, CaCO_3 is not well preserved in the deep Pacific, and suitable samples from depths below 2.8 km are difficult to obtain (Broecker et al., 2007).

Presently, LCDW bathes site TN057-13-4PC (Antarctic Zone); however, the lack of strong Re enrichments (Fig. 4c; Table S1) suggests that a different, well-ventilated water mass (perhaps a glacial equivalent of UCDW) existed at 2.8 km. The contrast with ventilation records from RC13-254 (Cape Basin) showing older, more O_2 -depleted glacial LCDW suggests that the modern water mass arrangement in which a lower- O_2 component of CDW overlies a higher- O_2 component may have been reversed during the last glacial period. The ventilation source at TN057-13-4PC is unclear, however, and the paucity of cores from all sectors of the Antarctic Zone leaves the glacial vertical water column structure an open question.

4.4 Comparison to other trace metal records

Most other trace metal records available from the Southern Ocean utilize Cd or authigenic U as suboxic indicators, although interpreting bulk sediment U is not straightforward because its accumulation is influenced by a combination of bulk sedimentation rate/sediment focusing, organic carbon rain rate, and bottom water O_2 concentration (Frank et al., 2000). Higher Cd and U accumulation rates/concentrations in Subantarctic sediments during the last glacial period have been primarily interpreted to record suboxic conditions caused by a northward shift of the ACC high productivity zone (Anderson et al., 1998; Bareille et al., 1998; Chase et al., 2001; Frank et al., 2000; Kumar et al., 1995; Rosenthal et al., 1995a). Elevated glacial Ag, Cd, and C_{org} concentrations (Fig. 3a, b, e) concur with previous work by demonstrating strong export production north of the modern APF. In comparison, Antarctic Zone sediments from the Indian and Atlantic sectors give inconsistent results. In the Atlantic sector, some studies show minima in bulk sediment U concentrations and C_{org} and Si_{bio} (opal)

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fluxes at the LGM before increasing during deglaciation (Anderson et al., 1998; Frank et al., 2000), when the high productivity zone shifted southward again. Other studies from the Indian sector demonstrate modest increases in bulk sediment Cd and U accumulation rates during the LGM similar to deglacial accumulation rates (Rosenthal et al., 1995a). Organic carbon accumulation rates also show a modest increase during the LGM, but afterward increase rapidly during the early deglaciation, suggesting that preservation issues could have influenced proxy accumulation. South Atlantic trace metal concentrations (this study) follow the results of Anderson et al. (1998) most closely by decreasing toward the LGM and increasing through the deglacial and Holocene (Fig. 4a–d).

A simple explanation of trace metal enrichment patterns is complicated by Cd and U accumulation trends that imply decreased CDW oxygen concentrations (Bareille et al., 1998; Francois et al., 1997; Rosenthal et al., 1995a) in addition to glacial–interglacial shifts of the high productivity zone. Increasing Re concentrations coupled with decreasing Ag and Cd concentrations during the LGM (Fig. 3a–c) support this conclusion, and suggest that export production and bottom water O₂ concentrations both influenced trace metal accumulation north of the modern APF. However, available data do not provide a clear indication of oxygenation levels in the glacial Antarctic Zone, and how they may have changed over time. Further studies employing a suite of redox proxies are needed from all three sectors of the Southern Ocean to sufficiently characterize glacial deep water ventilation.

5 Conclusions

This study is the first to present a suite of trace metal (Ag, Cd, Re, and Mo) concentrations in Atlantic sector Southern Ocean sediments over the last ~30 kyr, recording substantial changes in regional ventilation and export production history. Higher concentrations of all trace metals during deglaciation and the last glacial period, compared to late Holocene sediments, reveal significantly different past

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Southern Ocean water chemistry. Cape Basin sediments (RC13-254) were suboxic from at least ~ 30 to ~ 13.5 ka due to a combination of high export production and reduced bottom water ventilation. After ~ 13.5 ka, trace metal concentrations fall to crustal levels as oxidative burndown erases the authigenic record. The presence of burndown underscores the glacial–interglacial redox shift in Southern Ocean water mass chemistry. Furthermore, during the LGM (19–23 ka) elevated Re concentrations unconnected to export production coincide with oldest $\Delta^{14}\text{C}$ apparent ventilation ages (Skinner et al., 2010, 2014).

Trace metal enrichments in the Antarctic Zone (TN057-13-4PC) are mostly weaker than those from the Cape Basin and indicate suboxic sediments due to enhanced export production from ~ 16.2 to 25.2 ka, and during the early Holocene from ~ 5.5 to 11 ka. Increased Re concentrations indicate that sedimentary suboxia due to poor bottom water ventilation may have existed from ~ 25.2 to 30.6 ka, although burndown during MIS 3 and/or at the glacial–interglacial transition cannot be entirely ruled out.

Poorer ventilation of the glacial Southern Ocean requires changes in global deep ocean circulation. We hypothesize that changes in water mass mixing and stratification altered deep water chemistry such that the model of a modified modern Southern Ocean vertical water column structure may not be appropriate. Furthermore, our work suggests that glacial CO_2 was stored within glacial LCDW and its downstream products, Indian and Pacific Deep Waters and the deep Atlantic.

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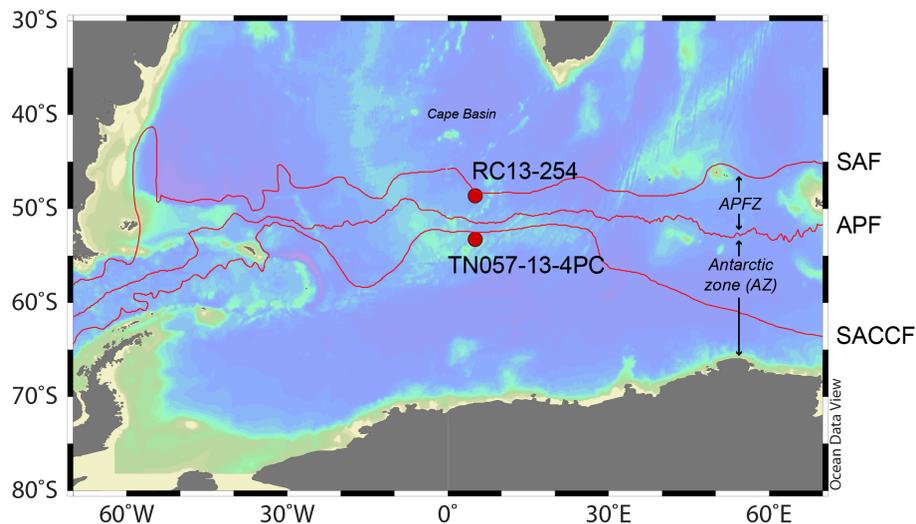


Figure 1. Locations of cores used for this study relative to fronts of the Antarctic Circumpolar Current (after Orsi et al., 1995): SAF, Subantarctic Front; APF, Antarctic Polar Front; SACCF, Southern Antarctic Circumpolar Current Front; APFZ, Antarctic Polar Frontal Zone. Map created using Ocean Data View (R. Schlitzer, Ocean Data View, <http://odv.awi.de>, 2011).

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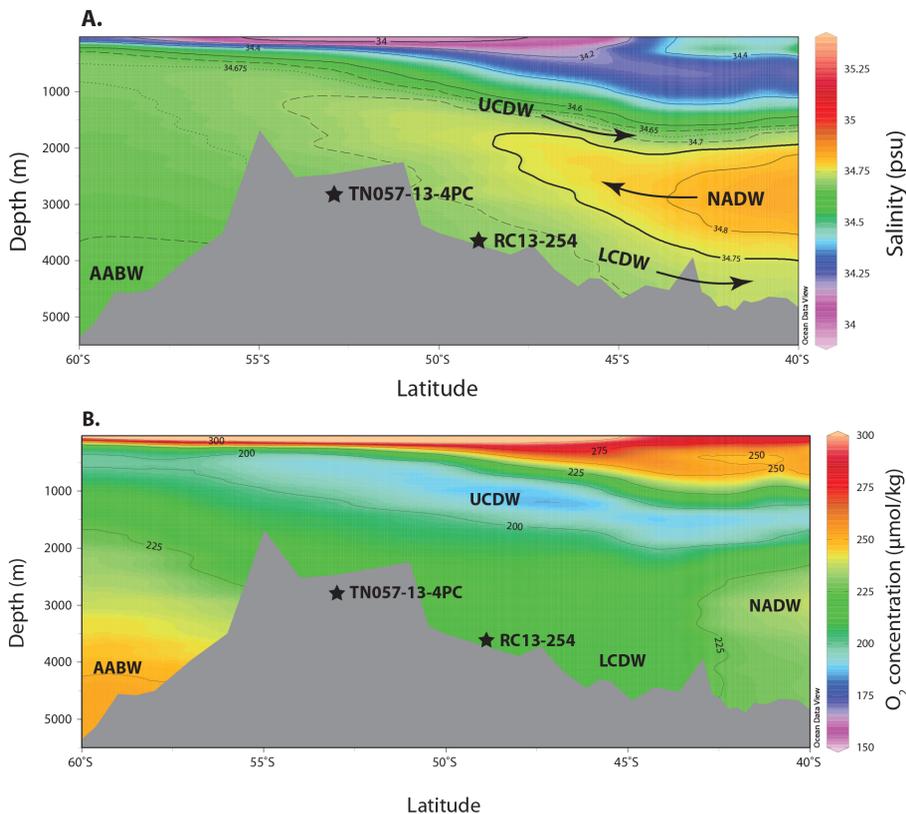
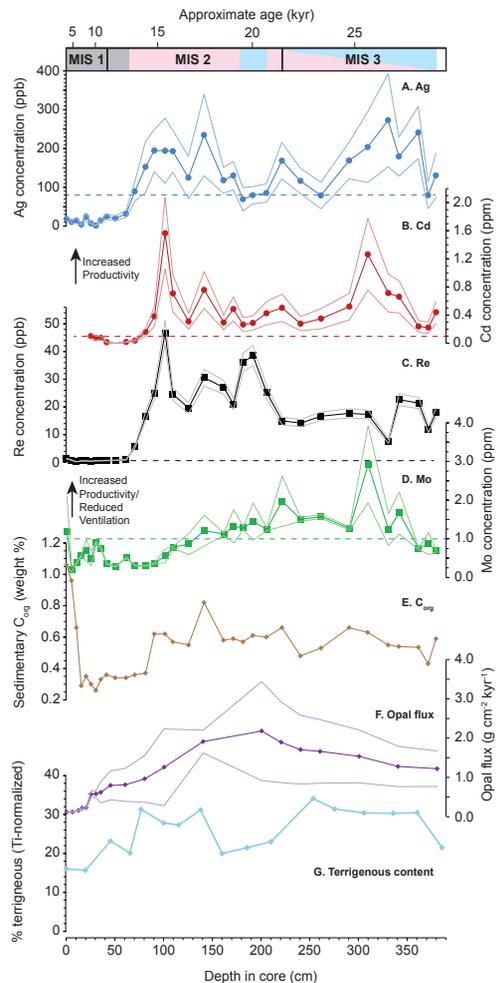


Figure 2. Locations of cores used for this study relative to water masses of the Southern Ocean. **(a)** Salinity along WOCE Line A12. **(b)** Oxygen concentration along WOCE Line A12. NADW, North Atlantic Deep Water; LCDW, Lower Circumpolar Deep Water; UCDW, Upper Circumpolar Deep Water; AABW, Antarctic Bottom Water. Map created using Ocean Data View (R. Schlitzer, Ocean Data View, <http://odv.awi.de>, 2011).

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Figure 3. RC13-254 trace metal and productivity proxy concentrations. **(a)** Blue circles, silver (Ag). **(b)** Red circles, cadmium (Cd). Cd concentration data are truncated in the Holocene due to suspected contamination in the core top (see Table S2). **(c)** Black squares, rhenium (Re). **(d)** Green squares, molybdenum (Mo). **(e)** Brown diamonds, weight percent organic carbon (C_{org}). **(f)** Purple diamonds, opal flux (opal concentration, Charles et al., 1991; $^{230}_{xs}Th_0$ values, Kumar, 1994) **(g)** Light blue diamonds, titanium (Ti)-normalized terrigenous content (Latimer and Filippelli, 2001). Lighter solid lines above and below symbols indicate measurement error. Dashed horizontal lines indicate concentrations for bulk continental crust (McLennan, 2001). Marine isotope stages (MIS) are denoted by boxes at the top of the figure. Grey shading: increasing oxygenation or burndown. Pink shading: sediments become reducing due primarily to high export production. Light blue shading: sediments become reducing due primarily to low bottom water O_2 concentrations. Pink/light blue combination shading during MIS 3: sediments become reducing due to a combination of high export production and low bottom water O_2 concentrations.

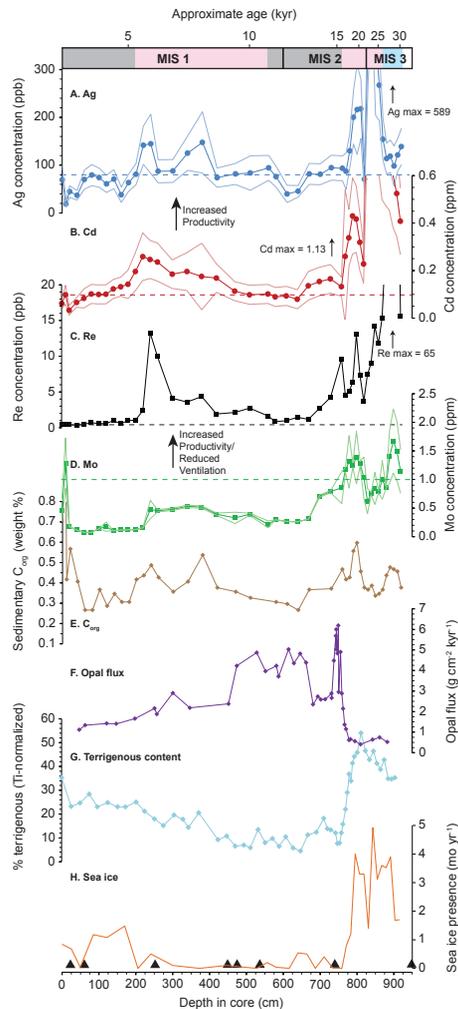
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Figure 4. TN057-13-4PC trace metal and productivity proxy concentrations. **(a)** Blue circles, silver (Ag). **(b)** Red circles, cadmium (Cd). **(c)** Black squares, rhenium (Re). **(d)** Green squares, molybdenum (Mo). **(e)** Brown diamonds, weight percent organic carbon (C_{org}). Data point at 700–701 cm was considered suspect and therefore omitted. **(f)** Purple diamonds, opal flux (Anderson et al., 2009). **(g)** Light blue diamonds, titanium (Ti)-normalized terrigenous content (S. Jaccard, unpublished data). **(h)** Orange line, sea ice presence (Stuut et al., 2004). Lighter solid lines above and below symbols indicate measurement error. Dashed horizontal lines indicate concentrations for bulk continental crust (McLennan, 2001). Black triangles at the bottom of the figure indicate calibrated, ^{14}C -dated age control points (Shemesh et al., 2002). Marine isotope stages (MIS) are denoted by boxes at the top of the figure. Grey shading: increasing oxygenation or burndown. Pink shading: sediments become reducing due primarily to high export production. Light blue shading: sediments become reducing due primarily to low bottom water O_2 concentrations.

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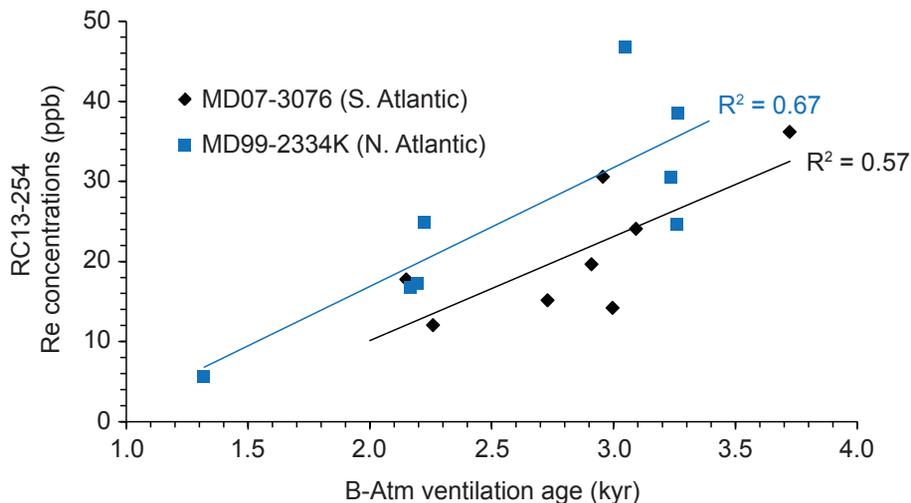


Figure 5. Crossplot of Re concentrations from RC13-254 vs. deep water ventilation age of MD07-3076 (44.074° S, 14.208° W) (Skinner et al., 2010) and MD99-2334K (37.80° N, 10.17° W) (Skinner et al., 2014). Only Re concentrations from deeper than ~ 65 cm (before ~ 13.5 ka) are used to avoid burndown.

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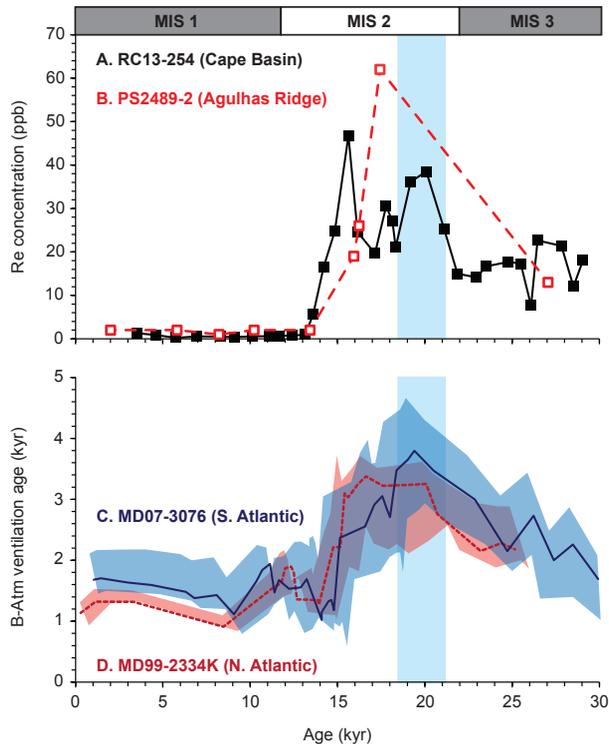


Figure 6. Comparison of Re and $\Delta^{14}\text{C}$ ventilation ages as indicators of deep Southern Ocean oxygen depletion. (A) Solid black line and filled black squares, Re concentrations for RC13-254 (this study). (B) Dashed red line and open red squares, Re concentrations for PS2489-2 (42.873° S, 8.973° E) (Martínez-García et al., 2009). (C) $\Delta^{14}\text{C}$ apparent ventilation age (B-Atm) for MD07-3076 (44.074° S, 14.208° W) (Skinner et al., 2010), plotted using original age model. (D) $\Delta^{14}\text{C}$ apparent ventilation age (B-Atm) for MD99-2334K (37.80° N, 10.17° W) (Skinner et al., 2014). Marine isotope stages (MIS) are denoted by boxes at the top of the figure. Blue boxes highlight time period of poorest ventilation in the deep Atlantic.