Trace metal evidence for a poorly ventilated glacial Southern Ocean

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ABSTRACT

Glacial benthic $\delta^{13}C$ and $\Delta^{14}C$ measurements from the Atlantic Ocean have been interpreted to indicate the existence of a poorly ventilated Southern Ocean with greater CO_2 and nutrient contents compared to present. Enhanced storage of CO_2 in the deep ocean predicts that oxygen concentrations should have declined at the same time—a prediction increasingly supported by evidence for oxygen depletion in the glacial Southern Ocean. Here we take a novel approach by using a suite of redox-sensitive trace metals (Ag, Cd, Re and Mo) to show that Southern Ocean sediments from two cores in the Atlantic sector were suboxic during and prior to deglaciation, implying changes to ocean circulation and/or elevated export production that significantly altered deep water chemistry. In the Cape Basin, enrichments of the authigenically deposited trace metal Re are comparable to those found in oxygen minimum zones, pointing to substantial decreases in oxygenation. Furthermore, trace metal results suggest potential spatial heterogeneity in the glacial Southern Ocean, and a more complicated oceanographic and oxygenation history than has previously been assumed.

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1. Introduction

Ice core records demonstrate that atmospheric CO_2 concentrations (pCO_2) were 80–100 ppm lower than preindustrial levels during glacial intervals of the last ~400,000 years (Petit et al., 1999). This decrease has partly been attributed to changes in ocean temperature and salinity, terrestrial carbon storage, the biological pump, and ocean circulation (Kohfeld and Ridgwell, 2013). Of the remaining ~40–50 ppm pCO_2, the most plausible storage location for this "missing" glacial CO_2 is the deep ocean because it is the largest easily exchangeable reservoir of carbon on the planet (Sigman and Boyle, 2000). Paleoclimate studies have targeted the Southern Ocean as a primary regulator for glacial-interglacial atmospheric CO_2 changes because the CO_2 air-sea balance is set within the Antarctic Zone by gas exchange with the deep ocean and by downward CO_2 transfer via the biological pump (Marinov et al., 2006). Proposed physical mechanisms for drawing down atmospheric CO_2 during glacial intervals include increased Southern Ocean vertical stratification (Francois et al., 1997) and

(subsequently) decreased deep ocean ventilation rate (Toggweiler, 1999). If glacial Southern Ocean ventilation was reduced, continuous organic matter respiration as deep waters "aged" would cause CO_2 and nutrients to accumulate as O_2 was consumed. Because O_2 is only added at the sea surface, decreased bottom water O_2 concentrations must follow increasing CO_2 in the same water mass. Hence bottom water O_2 concentrations provide an indirect assessment of whether the biological pump and/or changes to ocean vertical water column structure enhanced deep Southern Ocean CO_2 storage during glacial intervals.

Previous work has sought to characterize global glacial-interglacial circulation and deep ocean ventilation changes using benthic $^{13}C/^{12}C$ ratios ($\delta^{13}C$) (e.g., Curry and Oppo, 2005; Herguera et al., 2010; Hodell et al., 2003; Ninnemann and Charles, 2002) or $\Delta^{14}C$ (e.g., Keigwin, 2004; Robinson et al., 2005; Skinner et al., 2010) derived from sedimentary $CaCO_3$. This work suggested that Southern Ocean bottom water O_2 concentrations may have been lower in the past. In the Atlantic Ocean, glacial $\delta^{13}C$ and $\Delta^{14}C$ data imply different Southern Ocean chemistry potentially resulting from changes to deep ocean vertical stratification and mixing. South Atlantic benthic $\delta^{13}C$ values that are more than 1‰ lower than the modern ocean support the existence of strong vertical stratification and poorer ventilation (Ninnemann and Charles, 2002). Paired benthic-planktonic ^{14}C ventilation measurements

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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 ~2.5–3 km water depth. Data from the deep Pacific Ocean additionally point to geochemical changes in Southern Ocean sourced deep water. In the western Pacific, benthic foraminiferal $\delta^{13}C$ suggest that nutrient-rich, older glacial Lower Circumpolar Deep Water upwelled only to ~2500–3000 m, in contrast to ~2000 m during the Holocene (Keigwin, 1998; Matsumoto et al., 2002). And at Chatham Rise in the southwest Pacific, apparent ventilation ages ~3600 yr older than modern values (Sikes et al., 2000; Vandergoes et al., 2013) point to inflow of old, southern-sourced water. Additionally, increased LGM benthic-planktonic age differences were observed in a core from the deep North Pacific (Galbraith et al., 2007). Despite considerable recent progress in describing glacial-interglacial changes in deep ocean oxygenation (see Section 4.3), questions remain concerning the timing and extent of changes, the mechanism(s) driving these changes, and effects on global carbon cycling. Thus, it is prudent to seek additional information from other proxies.

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 ocean Antarctic Zone (Fig. 1). By examining an expanded suite of trace metals compared to previous studies, it is possible to disentangle the relationship between low-oxygen bottom waters and intensive oxidation of organic matter in sediments that can produce reducing sedimentary pore waters. Additionally, we present new organic carbon (C_{org}) concentrations for both cores.

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 is a valuable tool for assessing bottom water oxygenation changes because it precipitates directly from seawater under suboxic conditions and is not cycled with biogenic particles (Colodner et al., 1993; Crusius et al., 1996). 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 and/or Cd indicate that low bottom water O_2 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 (MoO_4^{2-}). 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
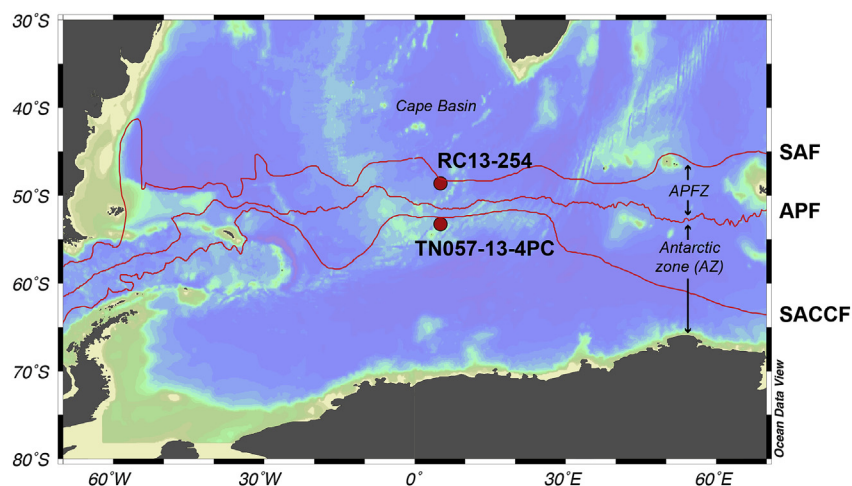

Fig. 1. Locations of cores used for this study relative to fronts of the Antarctic Circumpolar Current (after (Orsi et al., 1995)): SAF, Subantarctic Front; APF, Antarctic Polar Front; SACCF, Southern Antarctic Circumpolar Current Front; APFZ, Antarctic Polar Frontal Zone. Map created using Ocean Data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