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Research report

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Project: Southern Ocean Oxygenation During Last Deglaciation: insights from I/Ca ratio in deep sea corals

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Overview

Oceanic dissolved oxygen (DO) levels have been declining over the past few decades, and models predict this deoxygenation will accelerate with global warming (Keeling et al., 2010). DO content in the ocean is supplied through air-sea exchange and photosynthesis, and it is consumed throughout the water column by carbon respiration. This process is linked with the storage of marine respired carbon and is mainly controlled by atmospheric CO_2 over glacial-interglacial timescales (Jaccard et al., 2016).

During the last deglaciation (18-11.5 thousand years ago), the Southern Ocean played a significant role in the rise of atmospheric CO_2 through deep ocean ventilation (Jaccard & Galbraith, 2012). Notably, during this period, the release of CO2 from the ocean and the cooling of Antarctic temperatures experienced a sudden pause between 14.7-13 thousand years ago, known as the Antarctic Cold Reversal (ACR) (Parrenin et al., 2013). This rapid event is stated owing to the reexpansion of sea ice and a northward shift in the position of the westerly winds in the Southern Ocean (Anderson et al., 2009). This event is thought to have caused a change in benthic ecology, where deep-sea corals are absent in the deeper Antarctic Zone (Stewart et al., 2021). One hypothesis is a regional increase in seawater stratification that made the Southern Ocean more prone to widespread oxygen depletion at depth during the ACR. Studies also show that this Southern Ocean deoxygenation event could have further influenced the decrease in DO content on a global scale via ocean circulation (Wang et al., 2024). Despite the importance of DO reconstruction in the Southern Ocean, there are limited oceanic archives that could capture rapid events, and limited paleo proxies for DO.

Deep-sea corals have shown their advantage in recording sudden events and offer a variety of paleoceanographic proxy potentials (Robinson et al., 2014). One novel redox (oxygenation) proxy for marine carbonate is the iodine/calcium ratios (I/Ca), which show low carbonate I/Ca values in low oxygen content regions below a certain threshold (proxy reviewed in Z. Lu et al. (2020)). Iodine in seawater has two species: the oxidized form iodate ($[IO_3^-]$) and the reduced form iodide ($[I^-]$), and the equilibration between the two species is highly redox-sensitive. Iodate is the only species incorporated into carbonate by replacing carbonate ion, suggesting low I/Ca values indicate oxygen-depleted conditions (W. Lu et al., 2020). Despite the high potential as a DO proxy, there is limited study on I/Ca in deep-sea corals. The aim of this project is to first attempt to measure the I/Ca in deep-sea corals and further evaluate its potential to record DO variations during the last deglaciation in the Southern Ocean.

Results and discussions

New I/Ca data from modern deep-sea scleractinian coral skeletons from across the Atlantic (n=63), together with a set of deglacial fossil coral samples from the Southern Ocean (n=5), have been measured*. Modern coral samples cover a wide range of DO in order to establish the correlation between DO, seawater iodate concentration, and coral I/Ca ratios. This study shows that only coral samples from low-latitude regions faithfully recorded the seawater iodate concentration. In contrast, corals from high-latitude regions (North Atlantic and Southern Ocean) showed that coral I/Ca could potentially be influenced by secondary environmental controls (e.g., seawater temperature and salinity) and/or seasonal variation of seawater iodate concentration. For those low-latitude corals, the I/Ca ratios show an apparent "step change" at DO ≈ 160 mmol/kg, after which the ratio remains elevated at high oxygen levels. This indicates the need for further investigation of iodine incorporation into deep-sea coral from high-latitude regions. The modern coral results have been published in *Frontiers in Marine Science* (doi: 10.3389/fmars.2023.1264380).

A pilot deglacial study was also carried out. The selected, well-dated coral samples from the Southern Ocean spread across ACR events (Burdwood Bank, water depth 334 m) (fossil sample details in Stewart et al. (2021)). These samples show a large Ba/Ca ratio variation (Fig 2), indicating an increase of Ba-rich water associated with upwelling of nutrients around sub-Antarctic Zones, while potentially leaving the Antarctic Zone occupied by depleted DO water mass. Unfortunately, the coral I/Ca showed no significant change during the ACR (Fig 2). This could be related to the complex iodate incorporation in corals from high-latitude regions that shown in modern calibration study. For example, a negative correlation between I/Ca and temperature has also been reported in synthetic calcite experiments (Zhou et al., 2014), and if that is the case, the potential low I/Ca from depleted DO could then be cancelled out. Another possibility is that the Southern Ocean is well ventilated, with seawater generally showing a DO ≥ 250 mmol/kg (Reagan et al., 2023), but the DO threshold for coral is around 160 mmol/kg. This means the coral I/Ca would only vary when the intermediate Southern Ocean experienced a large deoxygenation event during the ACR. Nevertheless, the deglacial coral I/Ca results suggest a more complex geochemical process in the Southern Ocean.

*A modified work plan from original proposal.

Next steps

Our findings underscore the potential of applying I/Ca ratios in deep-sea corals as an indicator to track water mass DO content, as evidenced by a significant I/Ca "step change" occurring at oxygen concentrations around 160 mmol/kg. The next step of this project is to further understand the DO variation in the Southern Ocean during deglaciation, particularly the potential changes during the ACR. Furthermore, the study highlights the importance of the biogeochemical process of iodine in the Southern Ocean and its influence on coral iodine incorporation. The results of this study will contribute to future collaborative science proposals, enhance high-latitude deep-sea coral studies, and support the development of advanced analytical techniques.

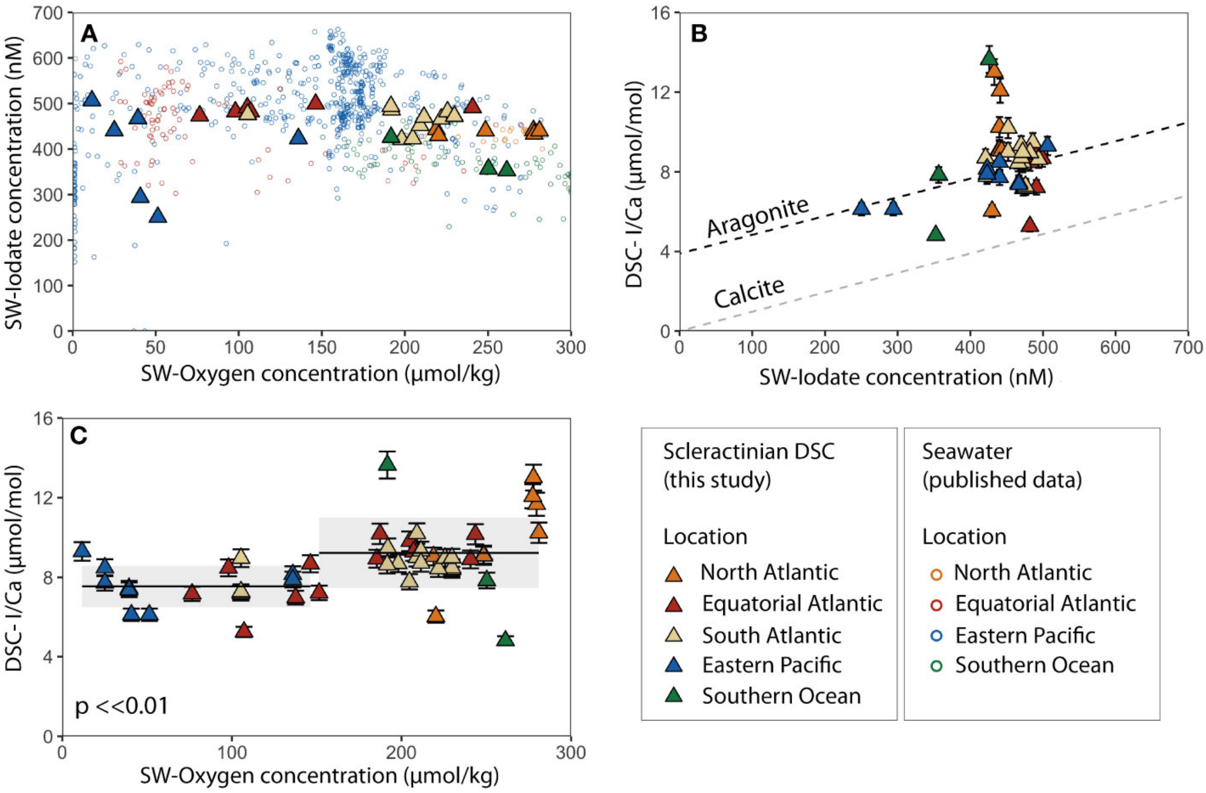

Figure 1. Cross-plots for deep-sea coral (DSC) I/Ca ratios, ambient seawater iodate concentration and seawater oxygen concentration. The detail for the coral samples and published seawater are available through Sun et al. (2023).

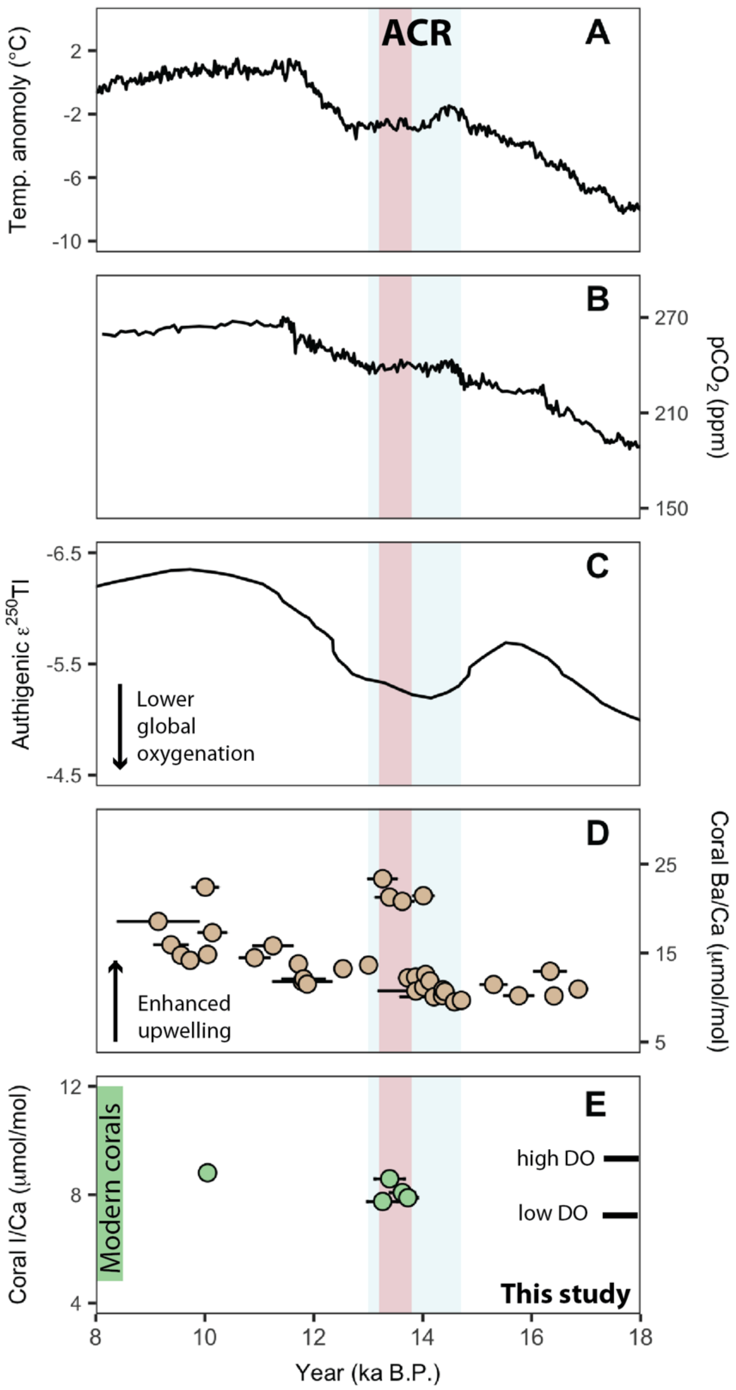

Figure 2. Deglacial deep-sea coral data from the Southern Ocean. (A) Antarctic temperature change relative to modern from the stacked ice core records (Parrenin et al., 2013). (B) Atmospheric pCO_2 concentrations from the Antarctic stacked ice core records (Bereiter et al., 2015). (C) Authigenic sedimentary ε205Tl records (smoothed) from Arabian Sea, indicating oceanic oxygenation in global scale (Wang et al., 2024). (D) Deep-sea coral Ba/Ca ratios, indicating the enhanced upwelling, Ba-rich water (Stewart et al., 2021). (E) Deep-sea coral I/Ca ratios (this study), along with the I/Ca ratios variation in modern Southern Ocean deep-sea corals and potential I/Ca step-change from Sun et al. (2023). The ACR is shaded in light blue, and the “Deep coral gap” identified by Stewart et al. (2021) is shaded in red.

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