



Deglacial diatom production in the tropical North Atlantic driven by enhanced silicic acid supply



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ABSTRACT

Major shifts in ocean circulation are thought to be responsible for abrupt changes in temperature and atmospheric CO₂ during the last deglaciation, linked to variability in meridional heat transport and deep ocean carbon storage. There is also widespread evidence for shifts in biological production during these times of deglacial CO₂ rise, including enhanced diatom production in regions such as the tropical Atlantic. However, it remains unclear as to whether this diatom production was driven by enhanced wind-driven upwelling or density-driven vertical mixing, or by elevated thermocline concentrations of silicic acid supplied to the surface at a constant rate. Here, we demonstrate that silicic acid supply at depth in the NE Atlantic was enhanced during the abrupt climate events of the deglaciation. We use marine sediment archives to show that an increase in diatom production during abrupt climate shifts could only occur in regions of the NE Atlantic where the deep supply of silicic acid could reach the surface. The associated changes are indicative of enhanced regional wind-driven upwelling and/or weakened stratification due to circulation changes during phases of weakened Atlantic meridional overturning. Globally near-synchronous pulses of diatom production and enhanced thermocline concentrations of silicic acid suggest that widespread deglacial surface-driven breakdown of stratification, linked to changes in atmospheric circulation, had major consequences for biological productivity and carbon cycling.

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1. Introduction

Atmospheric CO₂ changes over the last glacial cycle have been associated with switches between different modes of Atlantic Meridional Overturning Circulation (AMOC): an interglacial mode with deep ventilation of North Atlantic Deep Water (NADW); a glacial mode with a shallower northern component (Glacial North Atlantic Intermediate Water, GNAIW); and a suppressed mode during Heinrich Stadials, most recently Heinrich Stadial One (HS1, 14.7–16.8 ka BP) and the Younger Dryas (YD, 11.5–12.8 ka BP), associated with iceberg rafting Heinrich Events during the last glacial termination (McManus et al., 2004). However, the change in AMOC between LGM and HS1 (Bradtmeiller et al., 2014) and the exact nature of the link between ocean circulation and atmospheric CO₂ are still under debate (Böhm et al., 2015). Early Southern Hemisphere warming as a result of AMOC slow-down and reduced inter-hemispheric heat transport, amplified by Northern Hemisphere iceberg discharge, could shift the Southern Hemisphere westerly winds southwards, promoting widespread up-

welling of CO₂-rich water and degassing of CO₂ into the atmosphere (Anderson et al., 2009). Alternatively, this early Southern Hemisphere warming could have led to shifts in oceanic circulation due to a reduction in GNAIW production resulting in changes in deep ocean density, ventilation and CO₂ release (Broecker, 1998; Meckler et al., 2013).

Silicic acid is an important nutrient for siliceous organisms such as diatoms and can be used as a water mass tracer in the modern Atlantic because there is a strong circulation driven south-north gradient in concentrations; Antarctic Bottom Water (AABW) is characterised by higher silicic acid concentrations than NADW (Fig. 1). Antarctic Intermediate Water (AAIW) and Subantarctic Mode Water (SAMW) are formed in the Southern Ocean by a combination of deep-water convection and wind-driven mixing near the Polar Front. The subducted intermediate depth water, which supplies a large area of the world's thermocline waters with nutrients, has moderate absolute concentrations of silicic acid, but low silicic acid concentration relative to other nutrients (e.g. nitrate) due to low nutrient utilisation by iron-limited diatoms (Sarmiento et al., 2004). Changes in the export of silicic acid, relative to other nutrients, in intermediate depth waters as a result of changes in iron supply to the Southern Ocean have been invoked as an expla-

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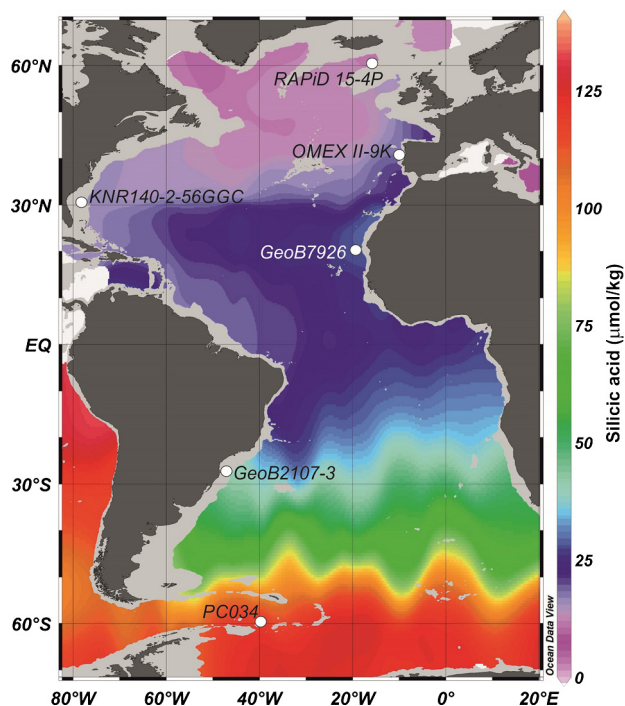


Fig. 1. Location of study sites and other cores discussed in the main text. Colour contours show silicic acid concentration at the 2000 m depth contour (Schlitzer, 2000), illustrating the low silicic acid concentrations in modern northern component waters compared to the silicic acid-rich southern component waters. Map produced using Ocean Data View.

nation for glacial–interglacial $p\text{CO}_2$ changes (the Silicic Acid Leakage Hypothesis, Brzezinski et al., 2002). However, there is arguably little evidence for either a change in the nutrient composition of AAIW or SAMW, or shifts in diatom growth relative to non-siliceous phytoplankton, over these timescales (Bradtmiller et al., 2006, 2007; Hendry and Brzezinski, 2014; Hendry et al., 2012).

The extent to which AAIW and SAMW distribution and nutrient composition changed during the climatic events of the deglaciation is also far from clear. Nutrient proxies point towards an increase in the export of nutrients from the Southern Ocean during HS1 and the YD (Came et al., 2003; Hendry et al., 2012), but it is challenging to constrain their exact nature and source (Meckler et al., 2013). Conservative tracers, such as the neodymium isotope composition of ferromanganese coatings of detrital sediments and foraminifera, provide conflicting evidence for either enhanced or reduced AAIW export into the tropical Atlantic during HS1 and the YD (Huang et al., 2014; Pahnke et al., 2008; Xie et al., 2012). Comparable sediment archives from the tropical Pacific show that there was an enhanced presence of AAIW and SAMW during the same intervals (Pena et al., 2013).

Using a different approach, the flux of diatom opal and related geochemical sedimentary properties (e.g. biogenic barium) have been used as a proxy for silicic acid supply, to trace the route of deep southern component water (SCW) into the Atlantic (e.g. Meckler et al., 2013). Pulses of diatom accumulation off the NW coast of Africa have been interpreted as indicating that the Atlantic was filled with southern sourced glacial AABW (GAABW) during glaciations. The boundary between northern and southern sourced waters shoaled further during HS1 as a result of a strong AMOC reduction which allowed density-driven mixing between surface waters and silicic acid-rich deep-waters (Meckler et al., 2013). However, the driver of these pulses of diatom production remains unclear: were nutrients brought to the surface at a greater rate as a result of stronger upwelling driven by stronger winds (Anderson et al., 2009) or vertical mixing driven by den-

sity differences (Meckler et al., 2013)? Or did supply rates stay relatively constant, with productivity enhanced by a greater concentration of the key nutrient, silicic acid, feeding from below into the thermocline and eventually into the mixed layer (Hendry et al., 2012)?

To understand the driver of pulses in diatom production we have reconstructed past changes in deep-water silicic acid concentration in the mid- and high-latitude NE Atlantic using the silicon isotope composition (denoted by $\delta^{30}\text{Si}$) of siliceous sponge spicules (Hendry and Robinson, 2012). The Iberian margin is ideally placed to investigate shifts in oceanographic processes over millennial timescales due to high sedimentation rates and a strong sensitivity to low and high latitude water exchange (Hodell et al., 2013). Furthermore, deep marine (>2500 m) sediment cores have been found to record the balance of northern component water versus SCW in planktonic and benthic geochemical archives (Hodell et al., 2013).

2. Materials and methods

2.1. Study sites

The site of sediment core OMEXII-9K (42°19.94'N, 09°41.92'W, 1833 m water depth; Hall and McCave, 2000) is bathed today in Upper Labrador Sea Water (40%), Upper Circumpolar Deep Water (20–30%) and Mediterranean Outflow Water (MOW, 30–40%) (Jenkins et al., 2015). We selected this location in order to investigate the vertical shift in the boundary between GNAIW and GAABW, which is thought to have been at approximately 2000 m water depth at the latitude of the Iberian margin during the glacial (Gebbie, 2014). Although changes in MOW inflow could potentially have changed the bottom seawater chemistry at this location, MOW today has a low dissolved silicon concentration (Schlitzer, 2000) and there is no likely mechanism by which a change in composition of this water mass could cause any significant increase in silicic acid concentration at the core site. A northern-sourced end-member record from off the south east coast of Iceland (RAPiD-15-4P, 62°17.58'N, 17°08.04'W, 2133 m water depth) was selected for comparison.

2.2. Silicon isotope measurements

Sponge spicules were hand-picked from the greater than 63 μm fraction of washed and sieved samples from sediment cores OMEXII-9K and RAPiD-15-4P and were cleaned according to published methods (Hendry and Robinson, 2012). Different spicule morphologies (megascclere types including different forms of, for example, triaenes, styles, tornotes) were monitored, to ensure that there were no biases introduced to the isotope measurements, and in order to give an indication of sponge diversity. The spicules were sonicated in methanol (Fisher), rinsed in deionised water, dried down in Teflon vials, then dried down again in 100 μL ultrapure concentrated HNO_3 (Romil) to remove any traces of organic matter. Whilst still hot, 500 μL of 0.4 M NaOH (Merck Millipore TitriPUR) were added to each sample, and dissolved over three days at 100 °C. The samples were acidified to pH \sim 2 with 8 N ultrapure HNO_3 (Romil), and purified using cation exchange resin (Bio-Rad AG50W X12) (Georg et al., 2006). Reference standards were prepared by alkaline fusion with NaOH pellets (Fisher Scientific), and processed as above (Georg et al., 2006).

The samples were analysed for silicon isotope composition (^{28}Si , ^{29}Si , ^{30}Si) using a Neptune Multi-Collector Inductively Coupled Plasma Mass Spectrometer (MC-ICP-MS) at Bristol University (operating conditions provided in Table S1). Machine blanks were monitored, and were <1% of the signal on ^{28}Si . A full procedural laboratory blank was processed and contained Si concentrations below the level of detection. Mass bias and matrix effects

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