Contents lists available at ScienceDirect

### Earth and Planetary Science Letters

journal homepage: www.elsevier.com/locate/epsl

## Opening the gateways for diatoms primes Earth for Antarctic glaciation

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#### ARTICLE INFO

Article history: Received 18 February 2013 Received in revised form 16 April 2013 Accepted 20 April 2013 Editor: J. Lynch-Stieglitz Available online 6 June 2013

Keywords: Eocene–Oligocene diatom Antarctic circumpolar current silicon isotope Antarctic glaciation organic carbon

#### ABSTRACT

The abrupt onset of Antarctic glaciation during the Eocene–Oligocene Transition (~33.7 Ma, Oi1) is linked to declining atmospheric  $pCO_2$  levels, yet the mechanisms that forced  $pCO_2$  decline remain elusive. Biogenic silicon cycling is inextricably linked to both long and short term carbon cycling through the diatoms, siliceous walled autotrophs which today account for up to 40% of primary production. It is hypothesised that during the Late Eocene a sharp rise in diatom abundance could have contributed to  $pCO_2$  drawdown and global cooling by increasing the proportion of organic carbon buried in marine sediment. Diatom and sponge silicon isotope ratios ( $\delta^{30}$ Si) are here combined for the first time to reconstruct the late Eocene-early Oligocene ocean silicon cycle and provide new insight into the role of diatom productivity in Antarctic glaciation. At ODP site 1090 in the Southern Ocean, a 0.6‰ rise in diatom  $\delta^{30}$ Si through the late Eocene documents increasing diatom silicic acid utilisation with high, near modern values attained by the earliest Oligocene. A concomitant 1.5‰ decline in sponge  $\delta^{30}$ Si at ODP site 689 on the Maud Rise tracks an approximate doubling of intermediate depth silicic acid concentration in the high southern latitudes. Intermediate depth silicic acid concentration peaked at ~31.5 Ma, coincident with the final establishment of a deepwater pathway through the Tasman Gateway and Drake Passage. These results suggest that upwelling intensification related to the spin-up of a circum-Antarctic current may have driven late Eocene diatom proliferation. Organic carbon burial associated with higher diatom abundance and export provides a mechanism that can account for  $pCO_2$  drawdown not only at, but also prior to, Antarctic glaciation as required by a  $pCO_2$ 'threshold' mechanism for ice sheet growth.

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#### 1. Introduction

The Eocene–Oligocene Transition (EOT) marks the onset of modern icehouse conditions when continental-scale ice sheets enveloped Antarctica ('Oi1,' ~33.7 Ma, Coxall et al., 2005; Ehrmann and Mackensen, 1992). Oi1 typifies the non-linearity of global climate, with the emplacement of an ice volume between 60% and 100% of that present today on Antarctica over only ~400 ka, superimposed on a million-year timescale cooling trend (Coxall et al., 2005; Lear et al., 2008; Zachos et al., 2001). Declining atmospheric  $pCO_2$  levels are thought to have driven the accelerated onset of Antarctic glaciation during Oi1, with numerical models suggesting a 'threshold' response of the cryosphere to a

\* Corresponding author. Current address: National Oceanography Centre, Southampton, European Way, Southampton SO14 3ZH, UK. Tel.: +44 776608 4872. *E-mail address*: K.E.Egan@soton.ac.uk (K.E. Egan). long-term lowering of  $pCO_2$  (DeConto and Pollard, 2003). Recent reconstruction of  $pCO_2$  across the late Eocene and early Oligocene (Pagani et al., 2011) documents a decline that began ~2 Ma prior to geological and stable isotope evidence for Antarctic glaciation, supporting this hypothesis. However, the mechanisms responsible for this gradual  $pCO_2$  drawdown remain unclear. The biological carbon pump, in particular associated with increased diatom abundance in the Southern Ocean during the late Eocene, represents a potential candidate (Rabosky and Sorhannus, 2009; Salamy and Zachos, 1999; Scher and Martin, 2006).

Diatoms are prolific phytoplankton, today accounting for up to 40% of global primary production (Tréguer et al., 1995). The formation of opaline frustules by diatoms imposes an absolute requirement for silicon, fundamentally linking the modern marine silicon and carbon cycles. Among the phytoplankton, diatoms are notably important for the export and burial of organic carbon for a number of reasons. Firstly, diatoms efficiently export carbon from the surface ocean: their silica frustules provide ballast material, they are relatively large cells at the base of short food webs, and they form blooms that can terminate in aggregation and mass settling of cells (Baines et al., 2010; Buesseler, 1998; Ragueneau et al., 2000; Smetacek, 1999). Secondly, diatoms may contribute up to 75% of







<sup>0012-821</sup>X  $\,$  © 2013 The Authors. Published by Elsevier B.V. Open access under CC BY license. http://dx.doi.org/10.1016/j.epsl.2013.04.030

primary production in upwelling regions of the world's oceans (Nelson et al., 1995). In these areas, nutrients and  $CO_2$  sequestered in the deep ocean by the biological pump are resupplied to the surface. Diatom domination of the resident phytoplankton community makes them critical in determining the magnitude of the  $CO_2$  flux to the atmosphere and the efficiency of the biological pump (Marinov et al., 2006; Sarmiento et al., 2004).

Today, diatom production in the Southern Ocean, coupled with the unique overturning circulation of the Antarctic Circumpolar Current (ACC), plays an important role in determining the efficiency of the biological pump and in setting the oceanatmosphere CO<sub>2</sub> balance. The wind-driven ACC facilitates deep upwelling to the south of the Polar Front. These upwelled waters are advected northwards by Ekman transport and thus provide nutrients that fuel diatom (as well as other phytoplankton) production, creating marked bands of opal and carbon export (Fig. 1; Speer et al., 2000; Ito et al., 2005). These surface waters are eventually subducted to intermediate depths and supply nutrients to the lower latitude thermocline. Thus, the amount and proportion of macronutrients used in this region play a major role in determining the efficiency of the biological pump globally (Sarmiento et al., 2004). Travelling an alternative path, some of this upwelled water moves southwards, eventually forming Antarctic Bottom Water. The magnitude of phytoplankton production and export along this path relative to the degree of nutrient supply sets the degree to which CO<sub>2</sub> escapes from the ocean. Today, incomplete nutrient utilisation makes this a region of CO<sub>2</sub> venting to the atmosphere (Marinov et al., 2006).

Diatom radiation, coupled with the development of an ACCtype circulation, may have substantially increased the efficiency of the biological pump during the late Eocene and early Oligocene, facilitating organic carbon burial and contributing to the  $pCO_2$  drawdown hypothesised to have driven Antarctic Glaciation (Rabosky and Sorhannus, 2009; Scher and Martin, 2006). Diatoms originated in the Jurassic, and open ocean diatom diversity and abundance increased through the late Cretaceous and Palaeogene, pumping silicic acid to depth and driving a concomitant decrease in shelf chert abundance (Maliva et al., 1989). The late Eocene witnessed both a second diatom proliferation, culminating in an explosion of species diversity (Rabosky and Sorhannus, 2009) and enhanced Southern Ocean biogenic opal burial (Salamy and Zachos, 1999; Schumacher and Lazarus, 2004). An increase in benthic  $\delta^{13}$ C, indicative of enhanced organic carbon burial, took place concomitantly (Cramer et al., 2009), particularly in the high latitude Southern Ocean. The opening of the two tectonic gateways that allow an unimpeded current flow in the Southern Ocean also occurred gradually through the late Eocene and into the Oligocene. Initial subsidence began between 50 (Drake Passage) and 35.5 Ma (Tasman Gateway), with a deep connection completed by 33.5–30.2 Ma (Livermore et al., 2007: Mackensen, 2004: Sticklev et al., 2004). From the time when these gateways opened, even to a relatively shallow depth, a complete pathway for wind-driven currents would have begun to affect Southern Ocean circulation, gradually intensifying upwelling as subsidence progressed (Livermore et al., 2007; Sijp et al., 2011). The Late Eocene is thus hypothesised as the time when the important relationship between diatoms and the ACC developed.

Affirming the link between diatom radiation and late Eocene pCO<sub>2</sub> drawdown requires evidence that diatom diversification and opal deposition corresponded to increased diatom productivity and organic carbon burial. To this end, combined diatom and isotope records  $(\delta^{30}Si = [({}^{30}Si/{}^{28}Si)_{Sample}/$ sponge silicon  $({}^{30}\text{Si}/{}^{28}\text{Si})_{Standard}$ -1]  $\times$  10<sup>3</sup>) are used here to characterise the late Eocene–early Oligocene marine silicon cycle. Diatom  $\delta^{30}$ Si is a proxy for diatom silicic acid utilisation (Fig. 2a) because frustule growth preferentially incorporates  $^{28}\text{Si}$  over  $^{30}\text{Si}$  with  $^{30}e\text{--}1.1\%$ (De La Rocha et al., 1997). Silicic acid utilisation is determined by both diatom uptake (broadly reflecting diatom productivity) and silicic acid supply to the surface ocean. Although diatom  $\delta^{30}$ Si has previously been used to reconstruct silicic acid utilisation. efforts to convert this to productivity have been hampered by a lack of knowledge of the concentration of silicic acid supplied from depth. Benthic siliceous sponges form spicules with a silicon isotope fractionation factor dependent on ambient silicic acid concentration (Hendry et al., 2010; Hendry and Robinson, 2012; Fig. 2b). Sponge  $\delta^{30}$ Si constitutes a proxy for bottomwater silicic acid concentration and ocean circulation (Fig. 2b)



**Fig. 1.** Schematic of Southern Ocean overturning circulation (modified from Speer et al., 2000) and its relationship with diatoms, the biological pump, and atmospheric *p*CO<sub>2</sub>. Upwelling to the south of the Polar Front (PF), driven by the Antarctic Circumpolar Current (ACC), supplies nutrient–CO<sub>2</sub>-rich water to the surface. A portion of this water moves northwards via Ekman transport, where these nutrients are utilised by phytoplankton. Diatoms dominate production in the southern ACC, leading to a marked belt of opal export and deposition (yellow arrow, location based on Atlantic sector opal export in the model of Ito et al. (2005)), whilst a combination of diatoms and smaller phytoplankton contributes to a broader belt of carbon export whose locus lies a few degrees northwards (black arrow, again based on Ito et al. (2005)). A second portion of upwelled water moves southwards where it eventually cools and becomes modified to form Antarctic Bottom-Water (AABW). Along this pathway, limited primary production allows carbon dioxide venting to the atmosphere (Marinov et al., 2006). CDW=circumpolar deepwater; UCDW=upper circumpolar deepwater; AAIW=Antarctic intermediate water; SAMW=sub-Antarctic mode water; SB=southern boundary of the ACC; SACCF=southern ACC front; PF=Polar front; SAF=sub-Antarctic front; STF=sub-tropical front. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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