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Silicon isotopes in spring Southern Ocean diatoms: Large zonal changes despite homogeneity among size fractions ☆

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Abstract

We determine Southern Ocean diatom silicon isotopic signatures and compare them with the previously published data for dissolved silicic acid from the same locations. Five stations distributed along the WOCE SR-3 transect (Australian Sector of the Southern Ocean) in different biogeochemical provinces are presented: Polar Front and Inter-Polar Front Zones (PFZ–IPFZ), Southern Antarctic Zone (AZ-S), Seasonal Ice Zone (SIZ). Total (>0.4 μm), medium-sized (20–70 μm), and large diatoms (>70 μm) were sampled at 2–4 depths in the upper 150 m. Silicon isotopic compositions of biogenic silica (diatoms) and seawater were then measured by MC-ICP-MS, in dry plasma mode using external Mg doping. Results are expressed as δ^{29}Si relative to the NBS28 standard. The isotopic composition of diatoms ($\delta^{29}\mathrm{Si}_{\mathrm{BSi}}$) is generally homogeneous in the mixed layer and does not exhibit a systematic isotopic fractionation linked to a size effect. $\delta^{29}\mathrm{Si}_{\mathrm{BSi}}$ are always lighter than the ambient dissolved silicic acid signatures ($\delta^{29}\mathrm{Si}_{\mathrm{DSi}}$), reflecting the preferential uptake of light isotopes by diatoms. A trend of lighter isotopic signatures southward is observed both in diatoms and seawater samples but the $\delta^{29}\mathrm{Si}_{\mathrm{BSi}}$ latitudinal gradient is much steeper. A diatom signature as low as −0.26‰ in the southernmost SIZ station strongly contrasts with the +0.65‰ signature measured on PFZ diatoms. The difference between the ambient dissolved silicic acid and diatom isotopic signatures, Δ^{29}Si, strongly increases southward: from 0.4 in the PFZ up to 1.08‰ in the SIZ. This points toward occurrence of mixing events in the PFZ–IPFZ with diatoms not being under equilibrium with their surrounding water and/or, possible variation of the diatom–seawater equilibrium fractionation factor, $^{29}\varepsilon$. Apart from mixing, we found that the other parameters likely responsible of such variation are temperature, dissolved Si contents and, Si specific uptake and dissolution rates although at this stage none of these could be clearly recognized as the leading cause. Thorough examination of these parameters through in vitro experiments reflecting the extreme Southern Ocean conditions is needed to determine whether the observed latitudinal variation of Δ^{29}Si reflects real variable fractionation or results from non-equilibrium or different time-scales recorded between dissolved and biogenic Si isotopic signatures. Our results also call for the development of more realistic models for describing short-term isotopic composition changes due to e.g. Si consumption, export

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☆ This work is gratefully dedicated to the memory of Roland Wollast as a special recognition of the excellence of his pioneer work on the silicon cycle. His brilliance, intuitive insights, kindness and zest for life are sadly missed.

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and resupply via mixing. Finally, by comparing $\delta^{29}Si_{BSi}$ within and below the mixed layer, we could identify a two-step history of the PFZ–IPFZ bloom in contrast to the recently started diatom bloom in the SIZ.

Keywords: Diatoms; Silicon isotopes; Silicon cycle; Isotope fractionation; Nutrient cycles; Southern Ocean

1. Introduction

The Southern Ocean is a major carbon sink owing to its large physical and biological C uptake capacity (Takahashi et al., 2002; Sabine et al., 2004). Diatoms have a key role in this biological carbon pump because they often dominate the phytoplankton biomass from the Polar Front Zone southward (Kopczynska et al., 2001, submitted for publication) and are prone to be easily exported from the mixed layer because of their opal frustules. Indeed due to the near absence of coccolithophorids south of the Polar Front, they are the leading Antarctic phytoplankton group accountable for this so-called ballast effect (François et al., 2002; Klaas and Archer, 2002). Therefore the silicon cycle in the Southern Ocean and its close link to that of carbon is being increasingly scrutinised (e.g. Ragueneau et al., 2002).

The strong South–North dissolved silicon (also referred to as silicates or silicic acid, H_4SiO_4) gradient from replete conditions in the Seasonal Ice Zone to depleted conditions in the Subantarctic Zone is a prominent feature of the Southern Ocean. It can be explained by the progressive diatom-controlled Si drawdown and export to the intermediate ocean in the course of northward transport of surface waters by Ekman drift (e.g., Trull et al., 2001; Brzezinski et al., 2002; Sarmiento et al., 2004) along with diapycnic mixing (Pollard et al., 2002). While the high-nutrient low chlorophyll (HNLC) modern Southern Ocean, appears to be non-limited in macro-nutrients such as phosphate and nitrate, this is not the case for the micronutrient iron (Martin et al., 1990; Boyd et al., 2000). Some uncertainty remains about the relative importance of other limiting factors such as grazing pressure (Becquevort, 1997; Smetacek et al., 2004), light (Lancelot et al., 2000), and Si availability (Nelson et al., 2001; Trull et al., 2001), in comparison to Fe-limitation. Nonetheless, it is clear that Fe stress not only limits phytoplankton growth, but also affects the diatom $Si:NO_3$ uptake ratio, leading to increased Si-uptake relative to NO_3-uptake (Takeda, 1998; Hutchins and Bruland, 1998). For that reason considerable attention has been paid to the understanding of processes influencing Si:N ratios in solution and diatoms, both in the natural environment and in laboratory experiments (e.g., Claquin et al., 2002; Brzezinski et al., 2003; Wang et al., 2003; Sarmiento et al., 2004).

Variations of the diatom Si:N ratio through time have been proposed as a possible contributor to changes in global ocean production and ocean–atmosphere partitioning of carbon dioxide. In this “silica leakage hypothesis” iron control of the Si:N ratio supports higher silicate:nitrate ratio of subducting Antarctic Intermediate Waters (AAIW) and Subantarctic Mode Waters (SAMW) during glacial stages (Brzezinski et al., 2002; Matsumoto et al., 2002; Sarmiento et al., 2004). Such changed nutrient ratios would then change the carbonate rain ratio at lower latitude by favouring diatom over coccolithophorid predominance. The N and Si isotopic signatures of diatoms in the Southern Ocean sediments, which are proxies of relative N and Si utilisation, have provided major support to this view (e.g. François et al., 1997; De La Rocha et al., 1998; Sigman et al., 1999a; Brzezinski et al., 2002; Crosta et al., 2005), despite the fact that processes acting on the isotopic signatures of Si and N are far from being constrained, especially as concerns the fractionation factor.

Several studies on seawater and, suspended and sinking particles have addressed controls on N isotope variations in a very thorough way recently, gradually building a more constrained but also a more complex picture of N isotopic fractionation in the ocean, in particular in the Southern Ocean (Sigman et al., 1999b; Altabet and François, 2001; Lourey et al., 2003; Karsh et al., 2003; Needoba and Harrison, 2004; Needoba et al., 2004). The marine isotopic system for Si should be simpler compared to N, because silicon is taken up only as silicic acid (mainly the H_4SiO_4 form; Del Amo and Brzezinski, 1999; Wischmeyer et al., 2003) and mostly by one phytoplankton group (diatoms), while N occurs as different chemical species and is utilised by all phytoplankton groups. Yet, the marine studies on Si isotopes are particularly scarce and the results are sometimes conflicting. This is especially the case for the fractionation factor between diatoms and seawater as well as the assessment of parameters and accurate models to describe the Si isotopic system at the local to ocean basin scale (De La Rocha et al., 1997, 2000; Varela et al., 2004; Milligan et al., 2004; Cardinal et al., 2005a).