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Using silicon isotopes to understand the role of the Southern Ocean in modern and ancient biogeochemistry and climate

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ABSTRACT

The growth of siliceous phytoplankton, mainly diatoms, in the Southern Ocean influences the preformed nutrient inventory in the ocean on a global scale. Silicic acid use by diatoms and deep circulation combine to trap dissolved Si in the Southern Ocean resulting in high levels of silica production and expansive diatom oozes in Southern Ocean sediments. The analysis of the silicon isotope composition of biogenic silica, or opal, and dissolved silicic acid provide insight into the operation of the global marine silicon cycle and the role played by the Southern Ocean in nutrient supply and carbon drawdown, both in the modern and in the past. Silicon isotope studies of diatoms have provided insight into the history of silica production in surface waters, while the analysis of spicules from deep sea sponges has defined both the spatial and the temporal variability of silicic acid concentrations in the water column; together these – and other – proxies reveal variations in the northward flow of Southern Ocean intermediate and mode waters and how changes in Southern Ocean productivity altered their preformed nutrient content. We present a new hypothesis – the "Silicic Acid Ventilation Hypothesis" (SAVH) – to explain the geographical variation of opal-based proxy records, in particular the contrasting patterns of opal burial change found in the low and high latitudes. By understanding the silicon isotope systematics of opal and silicic acid in the modern, we will be able to use opal-based proxies to reconstruct past changes in the Southern Ocean and so investigate its role in global carbon cycling and climate.

1. Introduction

1.1. Background and motivation

The Southern Ocean plays a central role in governing the inventory of preformed nutrients and carbon storage in the global ocean (Marinov et al., 2006, 2008). Of particular interest is the role of Southern Ocean circulation and biogeochemistry as a major control on the global distribution of the dissolved silicon – silicic acid or $Si(OH)_4$ – and as the single largest locus of modern opal deposition on the sea floor (Cortese et al., 2004, Fig. 1). The formation and burial of biogenic opal, amorphous silica, is the most important sink of $Si(OH)_4$ in the modern oceans, and is formed predominantly by diatoms, a diverse group of photosynthetic protists from the Class Bacillariophyceae. Diatoms have an absolute requirement for $Si(OH)_4$ and have evolved mechanisms for efficient Si uptake and metabolism (Martin-Jezequel et al., 2003). $Si(OH)_4$ uptake by diatoms severely depletes dissolved Si from surface waters (Falkowski et al., 2004). As such, diatoms rely on upwelled waters with elevated $Si(OH)_4$, thriving in ecosystems such as coastal and open ocean upwelling zones, areas of deep winter mixing (such as the Southern Ocean frontal zones), and – in the case of some giant diatoms – obtaining their requisite silicon from deep nutriclines in highly stratified waters (Kemp et al., 2006).

Diatoms contribute up to 40% of global marine primary productivity, and approximately half of the opal produced in the euphotic zone is exported to deep waters (Nelson et al., 1995; Tréguer et al., 1995). Approximately 3% of biogenic opal production is preserved in ocean floor sediments as a global average (Nelson et al., 1995), with the remainder remineralized in the water column or at the sediment–water interface (reviewed by Tréguer and De la Rocha, 2013). Although the Southern Ocean is the single largest site of opal deposition (the "opal belt") in the modern

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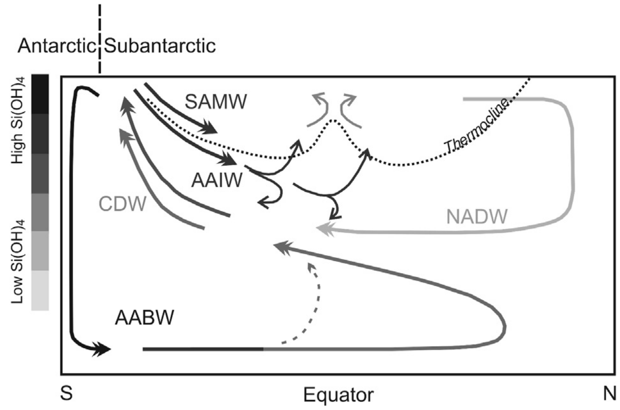

Fig. 1. Schematic of the transport of $Si(OH)_4$ in the ocean and the relationship with the MOC, after Marinov et al. (2008). The double-headed arrows show the major water masses, shaded according to $Si(OH)_4$ concentration. The dashed line shows the thermocline depth.

ocean (Cortese et al., 2004), opal preservation efficiency in the Southern Ocean is not significantly different from the global average (2–6%; DeMaster, 2002; Nelson et al., 2002; Pondaven et al., 2000) such that the high opal accumulation rates in Southern Ocean sediments is sustained by high rates of opal production rather than high preservation efficiency.

Diatom opal has received significant scrutiny over the past decades as a source of paleoceanographic information. Southern Ocean waters are often too corrosive for the preservation of traditional carbonate proxies, creating substantial interest in using opal as an indicator of past changes in southern component water. Opal accumulation rates, when ^{230}Th − normalised to account for sediment redistribution, provide an important constraint on the productivity and export of diatoms from surface waters into deep waters and sediments (Chase et al., 2003b). ^{231}Pa/^{230}Th ratios in opal-rich regions provide an additional constraint on opal production, versus preservation, due to the affinity of ^{231}Pa for opal (Chase et al., 2002). Given the dependence of diatoms on deep sources of $Si(OH)_4$, ^{230}Th-normalised opal accumulation rates, paired with ^{231}Pa/^{230}Th ratios, have been used as a proxy for wind-driven upwelling in the Southern Ocean (Anderson et al., 2009).

In addition to opal accumulation, there has been an increasing interest in the last twenty years on the use of aspects of opal chemistry as biogeochemical proxies for environmental conditions and productivity, including elemental ratios of occluded trace constituents (Ellwood and Hunter, 1999; Lal et al., 2006; Hendry and Rickaby, 2008) and stable isotopes of Si (De La Rocha et al., 1997; De La Rocha et al., 1998), O (Shemesh, 1995; Leng and Sloane, 2008), and more recently Zn (Andersen et al., 2011; Hendry and Andersen, 2013). One of the widest used applications is that of Si isotope analysis of diatom opal as a proxy for silica production. Briefly, there are three naturally occurring stable isotopes of silicon, ^{28}Si (~92 atom %), ^{29}Si (~5 atom %) and ^{30}Si (~3 atom %), and the silicon isotope composition of a material is denoted by δ^{30}Si, where:

$$\delta^{30}\mathrm{Si} = \left[\left(^{30}\mathrm{Si}/^{28}\mathrm{Si}\right)_{\mathrm{sample}}/\left(^{30}\mathrm{Si}/^{28}\mathrm{Si}\right)_{\mathrm{standard-NBS28}} - 1\right] \times 1000 \quad (1)$$

De La Rocha and co-workers first reported on the fractionation of isotopes of Si by diatoms using laboratory cultures (De La Rocha et al., 1997). That work indicated that diatoms have a constant fractionation factor (ε) favouring the lighter isotope ^{28}Si over ^{30}Si by ~1.1‰, with similar results achieved a few years later in further culture studies (Milligan et al., 2004) and field observations of water column diatoms (Varela et al., 2004; Fripiat et al., 2011, 2012), but see Sutton et al. (2013) for evidence for possible interspecific variation in ε (see below). Hence, as $Si(OH)_4$ utilization increases, both dissolved silicic acid and the opal produced from it become progressively enriched in the heavier isotopes of Si, such that the silicon isotopic composition of diatom opal extracted from dated sediment cores can be used as a measure of past surface ocean Si utilization. These concepts were first applied to downcore records of diatom δ^{30}Si from the Southern Ocean (De La Rocha et al., 1998). This progressive fractionation can be modeled as a Rayleigh-type closed distillation process, or a steady state open system, assuming a constant value of ε and a known starting isotopic composition of the nutrient substrate (De La Rocha et al., 1997; Varela et al., 2004).

The aim of this review is to bring together advances in oceanic silicon isotope studies with a focus on the role of Southern Ocean circulation and productivity in controlling the global distribution of $Si(OH)_4$ and the contribution of diatoms to global marine productivity. We will explore controls on Si isotope distribution deduced from models of modern oceanic $\delta^{30}Si(OH)_4$ distributions, the application of Si isotopes to paleoceanographic studies of Earth's climate, using the Silicic Acid Leakage Hypothesis (SALH) as a case study, and the future of opal-based multi-proxy approaches in paleoceanography.

2. Silicon isotopes as a silica production proxy

2.1. Culture experiments on diatoms

Since the original studies of De La Rocha et al. (1997) and Milligan et al. (2004), there was a considerable gap before further laboratory culture studies were carried out, which ended only recently with the publication of new culture experiments by Sutton et al. (2013). These culture experiments used the same species as the original studies (*Thalassiosira weissflogii* and *Thalassiosira pseudonana*, De La Rocha et al., 1997; Milligan et al., 2004), and some Southern Ocean species that had not been previously studied (*Porosira glacilis*, *Thalassiosira antarctica*, *Thalassiosira nordenskioeldii*, *Fragilariopsis kerguelensis*, *Chaeotceros brevis*). Most of the results were consistent with the original findings (Fig. 2), supporting the paradigm that diatom ε has a value of −1.1‰ within experimental uncertainty. However, there were some discrepancies between the different studies for different strains of the same species, *T. weissflogii*. Furthermore, two polar species had significantly different fractionation factors: *F. kerguelensis* showed a ε value of −0.54‰ (mean for two strains) and *C. brevis* showed a ε value of −2.09‰ (Sutton et al., 2013). Two major questions arising from these studies are: Do the results of culture experiments capture the range of fractionation by diatoms in the natural environment? And, is interspecific variation in ε, as represented by the extreme value for *C. brevis*, detectable in nature?

2.2. Proxy verification: core top calibrations of diatoms

2.2.1. Cleaning methods

An important aspect of paleoceanographic applications of opal composition is the effective cleaning of frustules to remove clays and fragments of other biogenic opal producers (radiolarians, sponge spicules). Heavy liquid separation has been used routinely for opal analysis for over twenty years, but there are numerous different approaches for further physical and chemical cleaning of the opal prior to analysis (Shemesh, 1989; Ellwood and Hunter, 1999; Lal et al., 2006; Hendry and Rickaby, 2008). Most studies of diatom Si isotopes have employed variants on these more