

What controls silicon isotope fractionation during dissolution of diatom opal?

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Abstract

The silicon isotope composition of opal frustules from photosynthesising diatoms is a promising tool for studying past changes in the marine silicon cycle, and indirectly that of carbon. Dissolution of this opal may be accompanied by silicon isotope fractionation that could disturb the pristine silicon isotope composition of diatom opal acquired in the surface ocean. It has previously been shown that dissolution of fresh and sediment trap diatom opal in seawater does fractionate silicon isotopes. However, as the mechanism of silicon isotope fractionation remained elusive, it is uncertain whether opal dissolution in general is associated with silicon isotope fractionation considering that opal chemistry and surface properties are spatially and temporally (i.e. opal of different age) diverse.

In this study we dissolved sediment core diatom opal in 5 mM NaOH and found that this process is not associated with significant silicon isotope fractionation. Since no variability of the isotope effect was observed over a wide range of dissolution rates, we can rule out the suggestion that back-reactions had a significant influence on the net isotope effect. Similarly, we did not observe an impact of temperature, specific surface area, or degree of undersaturation on silicon isotope partitioning during dissolution, such that these can most likely also be ruled out as controlling factors. We discuss the potential impacts of the chemical composition of the dissolution medium and age of diatom opal on silicon isotope fractionation during dissolution. It appears most likely that the controlling mechanism of silicon isotope fractionation during dissolution is related to the reactivity, or potentially, aluminium content of the opal. Such a dependency would imply that silicon isotope fractionation during dissolution of diatom opal is spatially and temporally variable. However, since the isotope effects during dissolution are small, the silicon isotope composition of diatom opal appears to be robust against dissolution in the deep sea sedimentary environment.

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1. INTRODUCTION

Diatoms are unicellular phototrophs that utilise silicon to form sophisticated opal cell walls. On a global scale, diatoms are responsible for about one-fifth of the photosynthetically

fixed carbon (Nelson et al., 1995). In the ocean, they play a major role in atmosphere–ocean CO₂ equilibrium via the biological carbon pump (Volk and Hoffert, 1985). After death, sinking diatoms efficiently transport organic carbon to the deep ocean (Buesseler, 1998), making it inaccessible to the atmosphere for hundreds to thousands of years. Changes in surface water productivity, community structure, or nutrient stocks may strongly affect the regional efficiency of the biological pump, and ultimately climate. It has been hypothesised that during glacial times the ratio of carbon export-to-supply was closer to unity than today, resulting in an efficient biological pump and hence a carbon-enriched

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deep ocean and CO₂-poorer atmosphere (Francois et al., 1997; Sigman and Boyle, 2000; Anderson et al., 2002; Kohfeld et al., 2005). A mechanistic and integrated picture of how and why the efficiency of the biological pump changes has not yet been achieved. Reliable and robust nutrient utilisation proxies are required to study past changes in nutrient dynamics.

In the oceanic water column, silicon geochemistry is relatively simple and well understood, since it exists almost entirely as silicic acid (H₄SiO₄), does not take part in redox reactions, is not transferred upward in the food chain, and has no atmospheric cycle interfering with that of the surface ocean. The discovery that diatoms fractionate silicon isotopes during uptake provided the possibility to trace both the modern marine biogeochemical cycle of silicon as well as potential changes in the past (De La Rocha et al., 1997). Silicon has three stable isotopes with atomic masses of 28, 29, and 30. During uptake by diatoms, the lighter isotopes are preferred, leaving behind an isotopically heavier dissolved Si (dSi) pool. Since the effect of isotope fractionation on stable isotope ratios is small, deviations are commonly expressed in per mil relative to an established standard reference material NBS28 quartz sand using the delta-notation:

$$\delta^{30}\text{Si} = \left[\frac{\left(\frac{^{30}\text{Si}}{^{28}\text{Si}} \right)_{\text{sample}}}{\left(\frac{^{30}\text{Si}}{^{28}\text{Si}} \right)_{\text{standard}}} - 1 \right] \times 1000$$

Early systematic studies (De La Rocha et al., 1997; Milligan et al., 2004) indicated that uptake by diatoms fractionates silicon isotopes with a constant magnitude that is independent of temperature, species, and ambient *p*CO₂. Therefore, any variability in the δ³⁰Si of recent and sediment core diatoms has been interpreted as variability in the utilised fraction of dSi (De La Rocha et al., 1998; Varela et al., 2004). This information has then been used to trace changes in nutrient limitation, efficiency of the biological pump, and water column stratification on various temporal and spatial scales (e.g. Brzezinski et al., 2002; Beucher et al., 2007; Cardinal et al., 2007; Reynolds et al., 2008; Pichevin et al., 2009; Swann et al., 2010; Fripiat et al., 2011, 2012).

The application of the diatom δ³⁰Si proxy for paleoreconstructions has recently been facilitated through several studies. First, Egan et al. (2012) showed that sedimentary core-top diatoms conserve their surface silicon isotope utilisation fingerprint within the sediment. Second, Sutton et al. (2013) found a significant dependence of the magnitude of silicon isotope fractionation on the taxonomic composition, complicating the interpretation of diatom silicon isotope variations.

A third potential issue, addressed here, is that the pristine diatom δ³⁰Si signal might be compromised by silicon isotope fractionation during dissolution. Since biogenic silica (bSi) is undersaturated throughout the entire ocean, it is constantly prone to dissolution, especially once its protective organic coating has been removed (Bidle and Azam, 1999). A study by Demarest et al. (2009) found silicon isotope fractionation during dissolution of diatom

opal collected from surface waters and sediment traps (~1000 m depth). The authors, however, point out that the observed effect is small, and that considering the excellent preservation of diatom frustules in the sediment, it is unlikely to change the diatom δ³⁰Si value significantly. While this result highlights the robustness of the diatom δ³⁰Si value against dissolution, the mechanism and controlling factors of silicon isotope fractionation remain elusive. For instance, a rather surprising feature of their dissolution experiments is the observed linear evolution of the isotope compositions of dSi and bSi during dissolution. Demarest et al. (2009) found that δ³⁰Si values of dSi are constantly lower by 0.55‰ (the isotope effect ε) than those of bSi. Such an evolution would be expected if bSi and dSi are continuously in isotopic equilibrium, or if bSi and dSi are constantly separated and removed from a continuously replenished system. While the latter is excluded by the experimental closed system setup, isotopic equilibrium throughout the reaction implies bidirectional isotope exchange, in which the back-reaction (i.e. adsorption, precipitation) might influence the net isotope fractionation. This observation raises the question to what extent – or if at all – the observed isotope fractionation is explained by dissolution only, i.e. if the results are reproducible when back-reactions are restricted. If an ε-value of –0.55‰ is characteristic for the forward (dissolution) reaction, it should be reproducible under unidirectional conditions. If the value is not reproducible, the isotope effect during dissolution might be even larger, such that the δ³⁰Si of bSi would be affected by even low degrees of dissolution.

The goal of this work is to study dissolution of diatom opal under variable boundary conditions in order to gain information on the controlling parameters of silicon isotope partitioning during dissolution of diatom opal. The main objective is to assess whether the isotope effect of –0.55‰ found by Demarest et al. (2009) is reproducible under enforced unidirectional conditions, and whether silicon isotope partitioning is sensitive to the ratio of forward and backward reaction rate. If so, then the isotope effect of –0.55‰ is likely the net fractionation effect of a forward and a backward reaction. By using a much more corrosive dissolution environment, we try to exclude competing processes in order to approximate a unidirectional dissolution reaction. Additionally, instead of fresh diatom opal we use sediment core material. It has been observed in previous studies that the reactivity of diatom opal progressively decreases with age (McManus et al., 1995; Van Cappellen and Qiu, 1997; Van Cappellen et al., 2002). As is the case for opal dissolution rates (Van Cappellen et al., 2002 and references therein; Loucaides et al., 2011), silicon isotope partitioning during dissolution might be sensitive to experimental boundary conditions, such as the age of opal surfaces or the chemical properties of the dissolution medium. Therefore, these experimental variables should allow us to get a better impression of the mechanisms and controlling parameters of dissolution, the results of which provide essential ground-truthing information about the reliability of the diatom opal δ³⁰Si proxy.

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