Chemical Geology 425 (2016) 12–36

Contents lists available at ScienceDirect

Chemical Geology

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

Invited Review Article

The continental Si cycle and its impact on the ocean Si isotope budget

Patrick J. Frings *, Wim Clymans, Guillaume Fontorbe, Christina L. De La Rocha, Daniel J. Conley

Department of Geology, Lund University, Sweden

ARTICLE INFO

Article history:
Received 16 July 2015
Received in revised form 5 January 2016
Accepted 24 January 2016
Available online 28 January 2016

Keywords:
Global silicon cycle
Biogenic silica
Silicon isotopes
LGM
Palaeoceanography
Biogeochemical cycling

ABSTRACT

The silicon isotope composition of biogenic silica ($\delta^{30}Si_{BSi}$) in the ocean is a function of the $\delta^{30}Si$ of the available dissolved Si (DSi; H_2SiO_4), the degree of utilisation of the available DSi, and, for some organisms, the concentration of DSi. This makes $\delta^{30}Si_{BSi}$ in sediment archives a promising proxy for past DSi concentrations and utilisation. At steady-state, mean $\delta^{30}Si_{BSi}$ must equal a weighted average of the inputs, the majority of which are of continental origin. Variation in the functioning of the continental Si cycle on timescales similar to the residence time of DSi in the ocean (~10 ka) may therefore contribute to downcore variability in $\delta^{30}Si_{BSi}$ on millennial or longer timescales. The direction and magnitude of change in published $\delta^{30}Si_{BSi}$ records over the last few glacial cycles is consistent among ocean basins and between groups of silicifiers. They document glacial values that are typically 0.5 to 1.0‰ lower than interglacial values and together hint at coherent and predictable glacial–interglacial variability in whole-ocean $\delta^{30}Si$ driven by a change in mean $\delta^{30}Si$ of the inputs. In this contribution, we review the modern inputs of DSi to the ocean and the controls on their isotopic composition, and assess the evidence for their variability on millennial-plus timescales.

Today, 9.55×10^{12} mol yr^{-1} DSi enters the ocean, of which roughly 64% and 25% are direct riverine inputs of DSi, and DSi from dissolution of aeolian and riverborne sediment, respectively. The remainder derives from alteration or weathering of the ocean crust. Each input has a characteristic $\delta^{30}Si$, with our current best estimate for a weighted mean being 0.74‰, although much work remains to be done to characterise the individual fluxes. Many aspects of the continental Si cycle may have differed during glacial periods that together can cumulatively substantially lower the mean $\delta^{30}Si$ of DSi entering the ocean. These changes relate to i) a cooler, drier glacial climate, ii) lowered sea level and the exposure of continental shelves, iii) the presence of large continental icesheets, and iv) altered vegetation zonation.

Using a simple box-model with a Monte-Carlo approach to parameterisation, we find that a transition from a hypothesised glacial continental Si cycle to the modern Si cycle can drive an increase in whole ocean $\delta^{30}Si$ of comparable rate and magnitude to that recorded in $\delta^{30}Si_{BSi}$. This implies that we may need to revisit our understanding of aspects of the Si cycle in the glacial ocean. Although we focus on the transition from the last glacial, our synthesis suggests that the continental Si cycle should be seen as a potential contributory factor to any variability observed in ocean $\delta^{30}Si_{BSi}$ on millennial or longer timescales.

Contents

1. Introduction . . . 13
2. Background. . . . 14
   2.1. The continental Si cycle . . . 14
   2.2. Low temperature silicon isotope geochemistry . . . 14
   2.3. Silicon isotopes in marine biogenic silica as a palaeoenvironmental proxy . . . 16
3. What controls $\delta^{30}Si$ of DSi in continental waters?. . . . 16
   3.1. Identifying incorporation of Si into secondary phases. . . . 19
      3.1.1. Heterogeneous source material . . . 20
      3.1.2. Variable fractionation factors . . . 20
      3.1.3. The manifestation of isotopic fractionation . . . 21
   3.2. Outlook: understanding and interpreting $\delta^{30}Si$ of DSi in continental waters. . . . 22

* Corresponding author.

http://dx.doi.org/10.1016/j.chemgeo.2016.01.020

4. Present-day inputs of DSi to the global ocean . . . 22
4.1. River DSi flux . . . 22
4.1.1. Magnitude of river DSi flux . . . 22
4.1.2. δ^{30}Si of river DSi flux . . . 22
4.1.3. The role of estuaries in modulating river Si fluxes . . . 22
4.1.4. Isotopic effect of estuarine Si removal . . . 23
4.2. Dissolution of river particulate matter . . . 23
4.2.1. Magnitude of DSi flux from dissolution of river particulate matter . . . 23
4.2.2. δ^{30}Si of DSi flux from dissolution of river particulate matter . . . 24
4.3. Submarine groundwater discharge (SGD) . . . 24
4.3.1. Magnitude of DSi flux from submarine groundwater discharge . . . 24
4.3.2. δ^{30}Si of DSi flux from submarine groundwater discharge . . . 24
4.4. DSi inputs from dissolution of atmospheric dust . . . 24
4.4.1. Magnitude of DSi flux from dissolution of aeolian dust . . . 24
4.4.2. δ^{30}Si of DSi flux from dissolution of aeolian dust . . . 24
4.5. Non-continental sources of DSi . . . 25
4.6. Synthesis of DSi inputs to the global ocean . . . 25
5. Potential for variability in continent-ocean Si fluxes . . . 25
5.1. Impact of glacial climate on land-to-ocean Si fluxes . . . 25
5.1.1. Impact of glacial climate on the river DSi flux and δ^{30}Si . . . 25
5.1.2. Impact of glacial climate on the dust flux and δ^{30}Si . . . 26
5.1.3. Impact of glacial climate on the river sediment flux and δ^{30}Si . . . 26
5.2. Impact of continental ice-sheets on land-to-ocean Si fluxes . . . 26
5.3. Impact of lowered sea-level on land-to-ocean Si fluxes . . . 26
5.3.1. DSi and the fluvial filter: alluvial plains, estuaries and lakes . . . 26
5.3.2. Exposure of continental shelf . . . 27
5.3.3. Potential modification of submarine groundwater discharge at the LGM . . . 27
5.4. Impact of altered vegetation zonation on land-to-ocean Si fluxes . . . 27
5.5. Synthesis of potential changes . . . 28
6. Manifestation of continental variability in the ocean Si cycle . . . 28
6.1. Box model results . . . 30
6.2. Implications of whole-ocean changes in δ^{30}Si of DSi . . . 30
7. Conclusions and future directions . . . 31
Acknowledgements . . . 31
Appendix A. Supplementary data . . . 31
References . . . 31

1. Introduction

At or near the Earth's surface silicate minerals can be chemically weathered, a process that forms soils, releases solutes and ultimately sustains life. The solutes that are released, including dissolved Si ($Si(OH)_4$; hereafter DSi), enter biogeochemical cycles – the movement of elements through the environment – that end with burial in marine sediments. The global Si cycle is characterised by one relatively discrete sub-cycle on the continents and another in the oceans (Fig. 1). The transfer of Si between the two is essentially unidirectional, so the land-to-ocean Si flux is of interest both as an integrative function of the continental Si cycle and as the chief input for the ocean Si cycle. The purpose of this contribution is (i) to review the fluxes of Si from land to ocean and the mechanisms that determine their magnitude and silicon isotopic composition (δ^{30}Si), (ii) to estimate plausible limits on the magnitude by which these fluxes can vary on millennial or longer timescales, and (iii) to assess the extent to which this variability is propagated to the ocean Si cycle and is visible in palaeoenvironmental archives.

Besides silicon's inherent interest as a major and ubiquitous element, two reasons for studying the Si cycle are commonly put forward. First, the process of chemical weathering of silicate minerals is a key step in the sequestration of atmospheric CO_2 as marine carbonates and hence is a key term in the long-term ('geological') carbon cycle (Walker et al., 1981). The rate of silicate weathering should be related to the concentration of atmospheric CO_2, *via* climatological and biological feedbacks in order to provide the negative feedback necessary to balance the continuous carbon degassing from the solid earth (Berner and Caldeira, 1997). Therefore, understanding the global Si cycle can provide insight to the functioning of Earth's thermostat. Second, DSi is a nutrient for many organisms. For some – notably the diatoms (class: Bacillariophyceae) – it is an essential nutrient. For others, including many vascular plants, DSi provides ecological, physiological or structural benefits (Epstein, 1999; Guntzer et al., 2012; Pilon-Smits et al., 2009). The availability of DSi in aquatic ecosystems controls the amount of siliceous primary productivity (mostly diatoms, which today account for 40% of ocean primary productivity) (Egge and Asknes, 1992). This siliceous production is also a key component of the ocean biological pump, which determines the partitioning of carbon between the deep ocean and the atmosphere on centennial to millennial timescales (De La Rocha, 2006).

This contribution builds on earlier reviews that have explored either the ocean Si budget, but without consideration of a Si isotope perspective (Tréguer et al., 1995; Tréguer and De La Rocha, 2013), or the continental Si isotope cycle (Opfergelt and Delmelle, 2012). It is partly motivated by the proliferation of marine biogenic silica δ^{30}Si records that are conventionally interpreted in terms of palaeonutrient utilisation or water-mass mixing (see Section 2.3). Here, we use our synthesis to advance the hypothesis that these δ^{30}Si records may also reflect changes in the continental Si cycle. This review is structured as follows: first, we provide basic background information on the continental Si cycle (Section 2.1), silicon isotope geochemistry (Section 2.2), and the use and conventional interpretation of downcore fluctuations in δ^{30}Si in marine sediments as a palaeoenvironmental proxy on millennial-plus timescales (Section 2.3). Section 3 summarises the controls on the silicon isotope composition of continental waters. We then report the current state-of-the-art of DSi inputs to the global ocean on a flux-by-flux basis (Section 4), paying close attention to the δ^{30}Si of these