Supplementary online material for Frings et al. *The continental Si cycle and its impact on the ocean Si isotope budget*

Description and parameterisation of ocean box model

The ocean comprises an upper euphotic box (2.6% of ocean volume) and a deep ocean box (97.4% of ocean volume). Water and DSi are exchanged between these two boxes by physical mixing of 1.37×10^{18} l yr^{-1} (De La Rocha and Bickle 2005). DSi is converted into BSi in the upper box with a fractionation $^{30}\varepsilon_{BSi/DSi}$ of -1.1‰ (De La Rocha et al. 1997) and remineralised to DSi in both boxes with no associated fractionation (Wetzel et al. 2014). Model inputs are prescribed separately for river DSi, DSi from dissolution of river SPM, DSi from submarine groundwater discharge and DSi from dissolution of aeolian dust (into the upper box) and DSi from hydrothermal fluid recirculation (into the lower box). Values for the modern DSi inputs follow those given in Table 1 (main text).

The model incorporates a DSi concentration dependency of both BSi production and dissolution, counter to De La Rocha and Bickle (2005) who held these constant. BSi production (assumed to be entirely diatoms) is related to the concentration of dissolved Si in the euphotic zone following Michaelis-Menten kinetics:

$$\text{PROD} = d\text{BSi}/dt = \text{V}_{max} * \text{C}/(\text{K}_M + \text{C})$$

where C is the ambient DSi concentration (in µM), V_{max} is the maximum production rate (in mol yr^{-1}) under ideal conditions and K_M is the half-saturation constant, the DSi concentration at which production is half of V_{max}. The isotopic composition of the produced BSi is derived from the f_{Si} fraction utilised according to a Rayleigh fractionation model:

$$\delta^{30}Si_{BSi} = \delta^{30}Si_{initial} - \left({f_{Si}}/{1 - f_{Si}} \right) \cdot {}^{30}\varepsilon_{BSi} \cdot \ln(f_{Si})$$

Where f_{Si} is calculated as the total production per timestep over the total mass of DSi in the surface box. Because the timestep used is <1 yr, this is equivalent to a scenario intermediate between DSi utilisation in open and closed systems.

The BSi dissolution rate ($d\mathrm{BSi}/dt$) is assumed to scale linearly as a function of the degree of undersaturation (Loucaides et al. 2012):

$R_{\mathrm{DIS}} = d\mathrm{BSi}/dt = -k(1-\mathrm{C}/\mathrm{C}_{\mathrm{EQ}})$

where k is a fitted constant that incorporates reactive surface area and intrinsic reactivity, C is the ambient DSi concentration and C_{EQ} is the apparent solubility of BSi in seawater. The total dissolution of BSi in a given box x, i.e. $\mathrm{DIS}_{\mathrm{surface}}$ or $\mathrm{DIS}_{\mathrm{deep}}$, is calculated as the product of the dissolution rate and the residence time of BSi in the box, i.e. the quotient of the mean depth of the box (D_x; in m) and the sinking velocity (V_x; in m yr^{-1}) of the particles:

$\mathrm{DISx} = \mathrm{R}_{\mathrm{DIS}} * \mathrm{PROD} * \mathrm{D}_x/\mathrm{V}_x$

Different k values are prescribed to account for an observed higher reactivity of 'fresh' BSi in the upper box (Loucaides et al. 2012), and the implicit inclusion of sediment dissolution in the lower box. These k values are tuned to fit observations that only ~3% of BSi production is preserved in marine sediments, and about 50% of dissolution occurs in the euphotic zone (De La Rocha and Bickle 2005; Nelson et al. 1995).

The model functions by calculating, in tandem, a mass balance for ^{28}Si and ^{30}Si in the surface and deep ocean, for each successive timestep t:

$\mathrm{Si}_{\mathrm{surface},t+1} = \mathrm{Si}_{\mathrm{surface},t} + \mathrm{UP}_t - \mathrm{DOWN}_t - \mathrm{EX}_t + \Sigma\mathrm{inputs}_{\mathrm{surface},t+1}$

$\mathrm{Si}_{\mathrm{deep},t+1} = \mathrm{Si}_{\mathrm{deep},t} - \mathrm{UP}_t - \mathrm{DOWN}_t + \mathrm{DIS}_t + \Sigma\mathrm{inputs}_{\mathrm{deep},t+1}$

where $\Sigma\mathrm{inputs}_{\mathrm{surface}}$ is the sum of DSi inputs from river DSi, dissolution of river SPM, dissolution of aeolian dust and submarine groundwater discharge, while $\Sigma\mathrm{inputs}_{\mathrm{deep}}$ is the input of DSi from alteration of the oceanic crust. EX is the export of BSi from the surface box (i.e. PROD – $\mathrm{DIS}_{\mathrm{surface}}$). Numerical stability is achieved by decreasing the timestep to 1/32 yrs. The values taken for the constants are given in Table A-1; the values for the variables (i.e. the input fluxes) are given in Tables 1 and 2 in the main text.

Sensitivity tests

We assessed the sensitivity of this model set-up to the parameterisation by systematically halving and doubling the parameters which are taken as constant in the model-run reported in the main text. These sensitivity tests tend to change the absolute values of the resulting δ^{30}Si of DSi or BSi, but not the relative trends from LGM to modern day. The results are shown in table A-2

Constant	Value	Units	Description	Reference/Notes
$^{30}\varepsilon_{BSi/DSi}$	-1.1	‰	Fractionation during diatom BSi production	De La Rocha et al. (1997)
$^{30}\varepsilon_{DSi/BSi}$	0.0	‰	Fractionation during dissolution of BSi	Wetzel et al. (2014); Panizzo et al. (2015)
R_{NBS28}	0.0335320	-	^{30}Si/^{28}Si ratio of the NBS28 standard	Ding et al. (2005)
V_{MAX}	500	x10^{12} mol yr^{-1}	Maximum production rate of diatom BSi	Sarmiento and Gruber (2006)
K_{M}	9	µM	Half saturation constant	Nelson et al. (1995); Amo and Brzezinski (1999)
C_{eq}	350	µM	Apparent solubility	Loucaides et al. (2012)
V_{ocean}	1.35x10^{21}	m^3	Total volume of the ocean	De La Rocha and Bickle (2005)
A_{ocean}	3.6x10^{14}	m^2	Surface area of the ocean	
$F_{EUPHOTIC}$	0.0263	unitless	Fraction of the ocean where production occurs	
V_{EXC}	1.37x10^{18}	m^3 yr-1	Water mass mixing rate between upper and lower ocean boxes	De La Rocha and Bickle (2005)
Vel$_{SURF}$	1800	m yr^{-1}	Sinking velocity, euphotic zone	Unaggregated; Passow et al. (2011)
Vel$_{DEEP}$	73000	m yr^{-1}	Sinking velocity, deep ocean	Aggregates; Passow et al. (2011)
K_{SURF}	9	mol/mol yr^{-1}	Dissolution constant, euphotic zone	Fitted parameter
K_{DEEP}	24	mol/mol yr^{-1}	Dissolution constant, deep ocean	Fitted parameter

Table A.1: Parameters used in the ocean two-box model. Variables (input fluxes) are given as displayed in Tables 1 and 2, main text.

Parameter	New value	Mean LGM-modern $\Delta\delta^{30}$Si
Control	Table 1, main text	0.34
$\varepsilon^{30}_{DSi\text{-}BSi}$	0.9979	0.35
	0.9999	0.31
V_{MAX}	1000	0.33
	750	0.31
K_{M}	18	0.33
	4.5	0.33
C_{eq}	700	0.30
	175	0.38
$F_{EUPHOTIC}$	0.0526	0.33
	0.01315	0.33
V_{EXC}	2.74	0.36
	0.685	0.33
Vel_{SURF}	2000	0.32
	500	0.31
Vel_{DEEP}	146000	0.44
	36500	0.30
K_{SURF}	18	0.33
	4.5	0.33
K_{DEEP}	48	0.29
	12	0.40

Table A.2: Results of model sensitivity analysis. Each model parameter was varied by 0.5x and 2.0x relative to the control run, and iterated for 100 times, randomly selecting the input variables from Table 1, main text (see main text for more details)

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