Supplementary information: A biomimetic peptide has no effect on the isotopic fractionation during *in vitro* silica precipitation

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ABSTRACT

The stable isotopic composition of diatom silica is used as a proxy for nutrient utilisation in natural waters. This approach provides essential insight into the current and historic links between biological production, carbon cycling and climate. However, estimates of isotopic fractionation during diatom silica production from both laboratory and field studies are variable, and the biochemical pathways responsible remain unknown. Here, we investigate silicon isotopic fractionation through a series of chemical precipitation experiments that are analogous to the first stages of intracellular silica formation within the diatom silicon deposition vesicle. The novelty of our experiment is the inclusion of the R5 peptide, which is closely related to a natural biomolecule known to play a role in diatom silicification. Our results suggest that the presence of R5 induces a systematic but non-significant difference in fractionation behaviour. It thus appears that silicon isotopic fractionation *in vitro* is largely driven by an early kinetic fractionation during rapid precipitation that correlates with the initial amount of dissolved silica in the system. Our findings raise the question of how environmental changes might impact silicon isotopic fractionation in diatoms, and whether frustule archives record information in addition to silica consumption in surface water.

Introduction

The data presented in this supplementary document are the data use for all the figures in the main text. Table 1 are the data corresponding to Figure 2 and Figure 3, Table 2 to the abiotic values of Figure 4 and Figure 5, and finally Table 3 to the biomimetic (R5) values of Figure 4 and Figure 5.

Table 1. Data corresponding to the Equilibrium and Kinetic experiments of Figure 2 and Figure 3 in the main text.

Figure	Experiment	Si concentration	Time	Relative Si loss	$\Delta^{30}Si_{p-s}$	2sd	pH
2 – 3	Equilibrium	743.0	8 days	0.40	0.02	0.24	10.9
2 – 3	Equilibrium	371.5	8 days	0.73	0.46	0.28	10.62
2 – 3	Equilibrium	148.6	8 days	0.98	-0.21	0.17	8.86
2 – 3	Equilibrium	74.3	8 days	0.97	-0.41	0.11	8.41
2 – 3	Equilibrium	37.2	8 days	0.94	-0.98	0.12	8.06
2 – 3	Equilibrium	18.6	8 days	0.87	-1.86	0.30	7.68
2 – 3	Equilibrium	7.4	8 days	0.68	-1.70	0.27	7.48
2 – 3	Equilibrium	3.7	8 days	0.34	-0.77	0.24	7.37
2 – 3	Kinetic	148.6	1 h	0.93	-2.71	0.09	7.85
2 – 3	Kinetic	74.3	1 h	0.91	-3.13	0.17	7.4
2 – 3	Kinetic	37.2	1 h	0.84	-1.55	0.22	7.72
2 – 3	Kinetic	18.6	1 h	0.71	-1.38	0.12	7.75
2 – 3	Kinetic	7.4	1 h	0.55	-0.46	0.09	7.55
2 – 3	Kinetic	3.7	1 h	0.47	-0.40	0.17	7.62

Table 2. Data corresponding to the abiotic experiment of Figure 4 and Figure 5 in the main text.

Figure	Experiment	Si concentration	Day	Relative Si loss	$\Delta^{30}Si_{p-s}$	2sd
4 – 5	Abiotic	148.6	0	0.98	-3.34	0.22
4 – 5	Abiotic	148.6	1	0.98	-1.35	0.58
4 – 5	Abiotic	148.6	2	0.96	-0.72	0.21
4 – 5	Abiotic	148.6	4	0.98	-0.20	0.23
4 – 5	Abiotic	148.6	5	0.96	0.04	0.22
4 – 5	Abiotic	148.6	6	0.97	-0.01	0.26
4 – 5	Abiotic	148.6	10	0.97	0.16	0.18
4 – 5	Abiotic	74.3	0	0.96	-2.40	0.33
4 – 5	Abiotic	74.3	1	0.97	-1.20	0.10
4 – 5	Abiotic	74.3	2	0.94	-0.59	0.18
4 – 5	Abiotic	74.3	4	0.98	-0.26	0.13
4 – 5	Abiotic	74.3	5	0.93	0.02	0.19
4 – 5	Abiotic	74.3	6	0.96	-0.13	0.19
4 – 5	Abiotic	74.3	10	0.94	0.10	0.14
4 – 5	Abiotic	37.2	0	0.89	-2.01	0.26
4 – 5	Abiotic	37.2	1	0.94	-1.57	0.17
4 – 5	Abiotic	37.2	2	0.90	-0.90	0.71
4 – 5	Abiotic	37.2	4	0.87	-0.30	0.08
4 – 5	Abiotic	37.2	5	0.87	-0.15	0.11
4 – 5	Abiotic	37.2	6	0.90	-0.25	0.13
4 – 5	Abiotic	37.2	10	0.87	-0.08	0.14
4 – 5	Abiotic	18.6	0	0.88	-1.67	0.61
4 – 5	Abiotic	18.6	1	0.85	-1.45	0.34
4 – 5	Abiotic	18.6	2	0.79	-0.95	0.39
4 – 5	Abiotic	18.6	4	0.83	-0.66	0.51
4 – 5	Abiotic	18.6	5	0.72	-0.70	0.62
4 – 5	Abiotic	18.6	6	0.83	-0.41	0.40
4 – 5	Abiotic	18.6	10	0.85	-0.27	0.31

Table 3. Data corresponding to the biomimetic (R5) experiment of Figure 4 and Figure 5 in the main text.

Figure	Experiment	Si concentration	Day	Relative Si loss	$\Delta^{30}Si_{p-s}$	2sd
4 – 5	Biomimetic (R5)	148.6	0	0.99	-3.12	0.35
4 – 5	Biomimetic (R5)	148.6	1	/	-0.58	0.22
4 – 5	Biomimetic (R5)	148.6	2	0.99	-0.44	0.26
4 – 5	Biomimetic (R5)	148.6	4	0.99	-0.17	0.22
4 – 5	Biomimetic (R5)	148.6	5	0.99	0.04	0.32
4 – 5	Biomimetic (R5)	148.6	6	0.99	-0.17	0.23
4 – 5	Biomimetic (R5)	148.6	10	0.99	-0.02	0.27
4 – 5	Biomimetic (R5)	74.3	0	/	-2.45	0.15
4 – 5	Biomimetic (R5)	74.3	1	/	-1.03	0.35
4 – 5	Biomimetic (R5)	74.3	2	0.98	-0.73	0.14
4 – 5	Biomimetic (R5)	74.3	4	0.98	-0.38	0.21
4 – 5	Biomimetic (R5)	74.3	5	0.98	-0.28	0.17
4 – 5	Biomimetic (R5)	74.3	6	0.98	-0.35	0.14
4 – 5	Biomimetic (R5)	74.3	10	0.99	-0.19	0.21
4 – 5	Biomimetic (R5)	37.2	0	/	-1.83	0.12
4 – 5	Biomimetic (R5)	37.2	1	/	-1.61	0.04
4 – 5	Biomimetic (R5)	37.2	2	0.95	-1.00	0.02
4 – 5	Biomimetic (R5)	37.2	4	0.97	-0.77	0.12
4 – 5	Biomimetic (R5)	37.2	5	0.97	-0.89	0.02
4 – 5	Biomimetic (R5)	37.2	6	0.96	-0.57	0.02
4 – 5	Biomimetic (R5)	37.2	10	0.97	-0.38	0.10
4 – 5	Biomimetic (R5)	18.6	0	/	-1.45	0.26
4 – 5	Biomimetic (R5)	18.6	1	/	-1.32	0.20
4 – 5	Biomimetic (R5)	18.6	2	0.91	-1.23	0.17
4 – 5	Biomimetic (R5)	18.6	4	0.94	-0.97	0.35
4 – 5	Biomimetic (R5)	18.6	5	0.93	-0.68	0.17
4 – 5	Biomimetic (R5)	18.6	6	0.93	-0.64	0.19
4 – 5	Biomimetic (R5)	18.6	10	0.95	-0.34	0.20