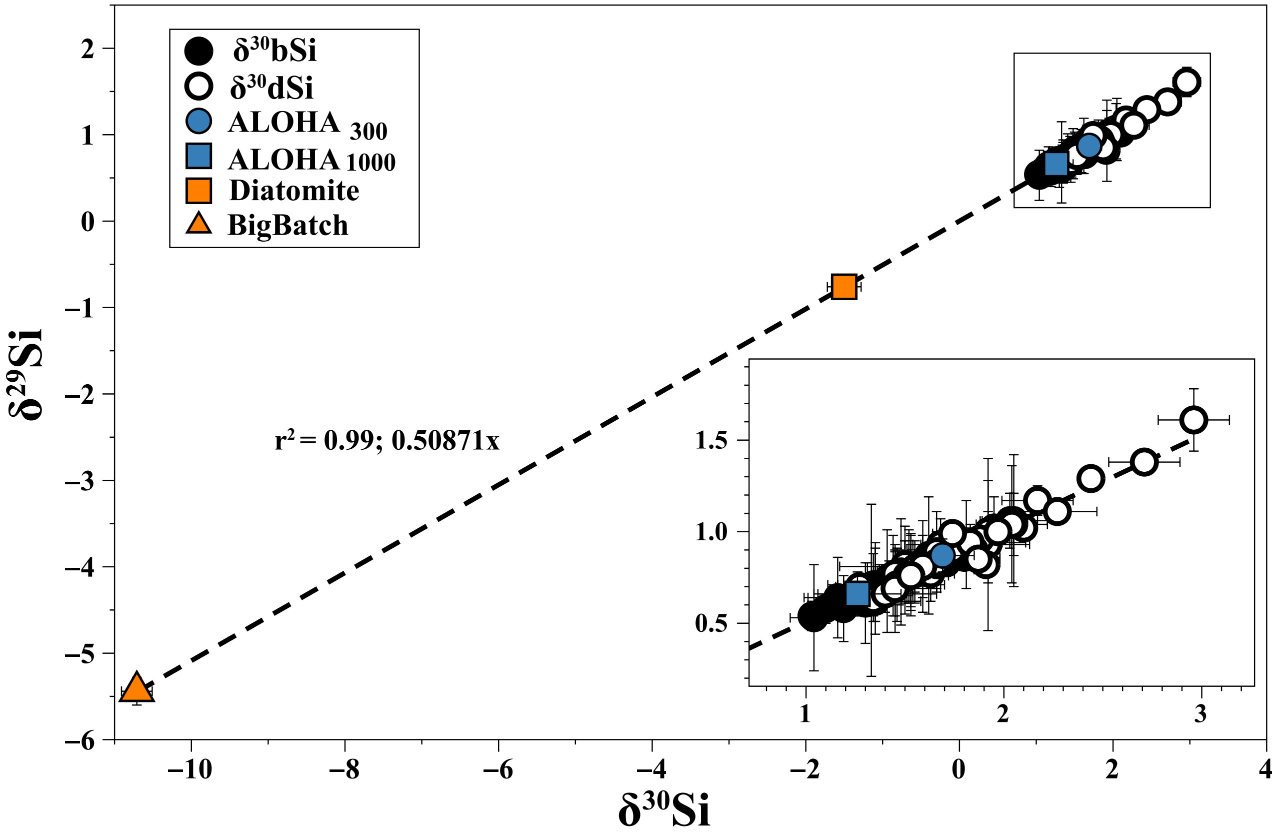
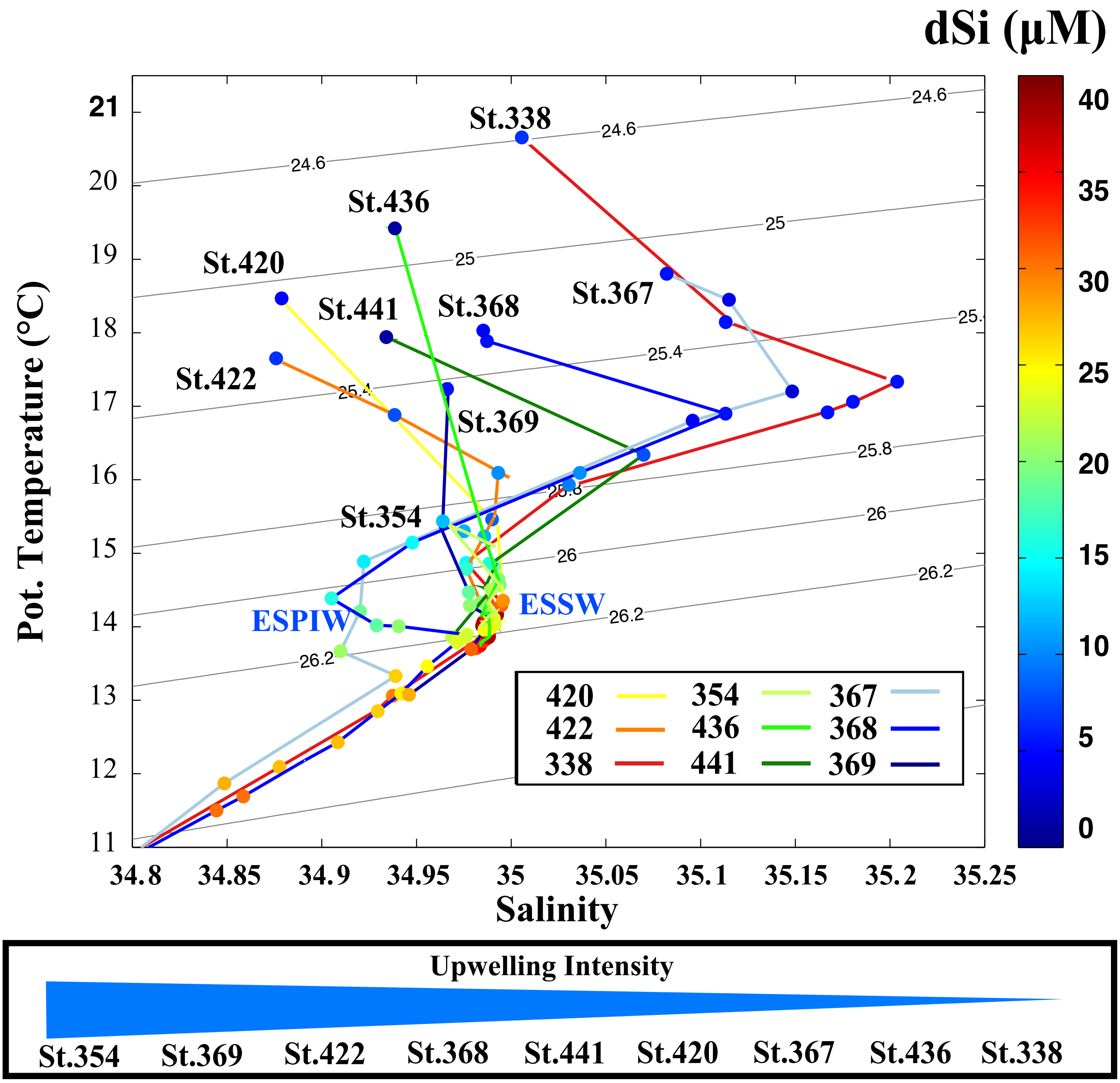
Supplementary Material

Controls on the Silicon Isotopes Composition of Diatoms in the Peruvian Upwelling

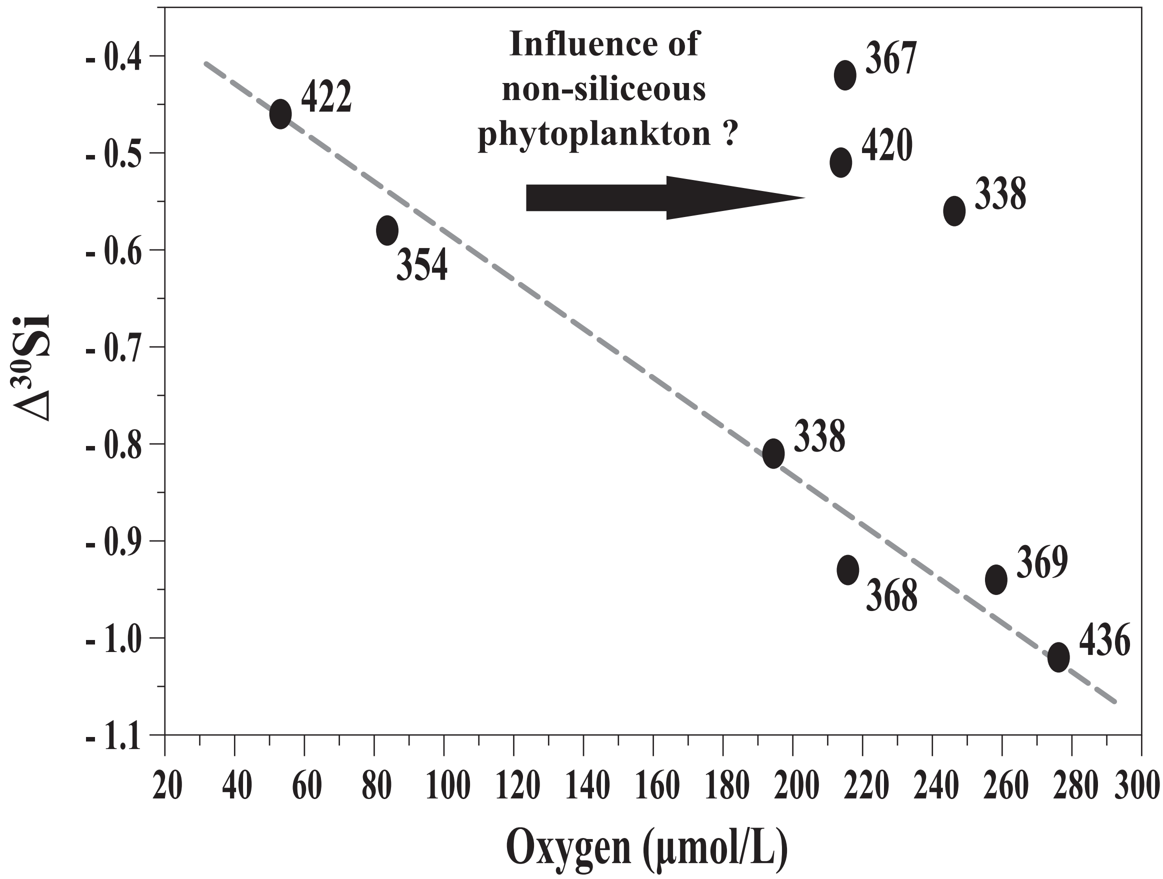
1 Supplementary Figures



Supplementary Figure 1. δ^{30}Si vs. δ^{29}Si for dissolved samples (dSi; open symbols) as well as particulate samples (bSi, black dots), means of reference materials analyzed at GEOMAR is indicated in blue and in orange. Error bars represent the average standard deviation (2 s.d.). The black dotted line is the least square linear regression between δ^{30}Si and δ^{29}Si of samples and standards ($\delta^{30}Si = 0.5087 \times \delta^{29}Si$, $R^2 = 0.9982$).



Supplementary Figure 2. Temperature-Salinity Plot for stations sampled during cruise M93 in February 2013. Colors indicate the [dSi] (µmol L^{-1}) at the corresponding depths. Upwelling intensity is derived from Sea Surface Temperature (SST), with the lowest SST at St. 354 (15°C) and the highest at Station. 338 (21°S). Most subsurface waters are influenced by Equatorial Subsurface Water (ESSW) and only Sts. 367 and 368 are influenced Equatorial South Pacific Intermediate (ESPIW) at a density of approximately 26 kg/m^3.



Supplementary Figure 3. Dependence between the apparent fractionation factor (Δ^{30}Si) and the oxygen concentration (in µmol L^{-1}) in the uppermost samples. Station numbers are indicated in the figure next to the data points. Recent upwelling events with anoxic subsurface waters (oxygen < 5 µmol L^{-1}) result in low oxygen concentrations in surface waters leading to lower Δ^{30}Si values. Surface sample deviating from the lines might be influenced by non-siliceous phytoplankton that is producing oxygen.

2 Supplementary Tables

Supplementary Table 1. Sampling locations, oxygen and dissolved and particulate Si isotope signatures ($\delta^{30}Si_{dSi}$, $\delta^{30}Si_{bSi}$ in ‰) and concentrations (in µmol L^{-1}). n denotes the number of repeated measurements on different days. For the apparent fractionation factor ($\Delta^{30}Si$) a propagated error is given. Al/Si ratios are given in mM/M.

Station	CTD	Location	depth m	DIN µmol/L	DIN/dSi M/M	Oxygen µmol/L	dSi µmol/L	δ^{30}Si(dSi) ‰	2sd ‰	δ^{29}Si(dSi) ‰	2sd ‰	n	bSi µmol/L	δ^{30}Si(bSi) ‰	2sd ‰	δ^{29}Si(bSi) ‰	2sd ‰	n	Δ^{30}Si ‰	Error ‰	Al/Si mM/M
338	49	13.13°S	1	NaN	NaN	246.32	6.64	2.03	0.14	1.06	0.15	2	0.62	1.47	0.17	0.75	0.08	2	-0.56	0.19	18.1
		76.92°W	9	NaN	NaN	194.46	5.47	2.10	0.02	1.02	0.00	2	0.95	1.29	0.16	0.67	0.03	3	-0.81	0.17	3.7
		max. depth	21	NaN	NaN	162.01	5.03	2.05	0.17	1.06	0.36	2	0.27	NaN	NaN	NaN	NaN		NaN	NaN	NaN
		360 m	41	NaN	NaN	55.83	9.86	1.81	0.07	0.89	0.03	2	0.16	1.34	0.08	0.68	0.04	2	-0.47	0.09	147.13
			59	NaN	NaN	7.35	14.97	1.82	0.07	0.91	0.03	3	0.22	1.29	0.11	0.66	0.05	4	-0.53	0.12	NaN
			81	NaN	NaN	2.99	26.21	1.47	0.20	0.74	0.10	2	0.78	1.55	0.07	0.77	0.07	3	0.08	0.10	34.3
			121	NaN	NaN	3.04	29.67	1.50	0.33	0.81	0.14	1	NaN	NaN	NaN	NaN	NaN		NaN	NaN	NaN
			202	NaN	NaN	3.29	27.03	1.57	0.09	0.82	0.03	3	NaN	NaN	NaN	NaN	NaN		NaN	NaN	NaN
			350	NaN	NaN	3.55	35.22	1.42	0.14	0.75	0.09	2	NaN	NaN	NaN	NaN	NaN		NaN	NaN	NaN
354	65	13.26°S	4	0.046	0.34	83.75	11.63	1.92	0.21	0.93	0.47	3	1.88	1.33	0.22	0.68	0.11	5	-0.58	0.24	17.72
		76.42°W	10	0.114	0.32	3.11	31.69	1.50	0.15	0.82	0.21	3	0.70	1.53	0.17	0.78	0.09	2	0.03	0.19	20.1
		max. depth	31	1.886	0.83	2.84	37.50	1.44	0.10	0.76	0.22	1	0.15	1.30	0.25	0.61	0.13	4	-0.14	0.28	18.6
		59 m	40	1.887	1.06	2.87	37.70	1.27	0.12	0.70	0.03	2	0.41	1.38	0.14	0.71	0.08	2	0.11	0.16	23.4
			57	2.964	1.42	2.93	40.18	1.34	0.04	0.63	0.12	2	1.42	1.37	0.20	0.70	0.12	4	0.03	0.23	19.02
367	76	13.99°S	3	5.74	0.57	215	5.30	2.04	0.18	1.04	0.32	2	0.23	1.62	0.03	0.87	0.23	2	-0.42	0.24	49.5
		76.74°W	20	6.21	7.89	211.34	2.53	2.44	0.03	1.29	0.03	2	0.40	1.51	0.28	0.77	0.14	2	-0.93	0.31	188.37
		max. depth	70	21.58	3.69	0	18.99	1.74	0.01	0.88	0.00	2	0.33	1.71	0.11	0.83	0.21	3	-0.03	0.23	NaN
		766 m	115	19.46	4.37	0	26.31	1.53	0.19	0.76	0.17	1	0.45	1.92	0.17	0.94	0.23	3	0.39	0.29	NaN
			200	24.72	7.12	0.22	28.09	1.66	0.14	0.89	0.22	2	NaN	NaN	NaN	NaN	NaN		NaN	NaN	NaN
			300	30.54	0.99	0.52	31.00	1.94	0.15	1.05	0.11	3	NaN	NaN	NaN	NaN	NaN		NaN	NaN	NaN
			500	42.35	0.98	6.7	43.15	1.92	0.13	0.95	0.17	2	NaN	NaN	NaN	NaN	NaN		NaN	NaN	NaN
			750	44.4	1.60	18.54	27.78	1.35	0.30	0.74	0.32	3	NaN	NaN	NaN	NaN	NaN		NaN	NaN	NaN
368	77	13.95°S	3	4.85	1.02	215.8	4.77	2.17	0.18	1.17	0.08	2	1.34	1.24	0.08	0.66	0.07	2	-0.93	0.11	18.3
		76.61°W	10	12.29	2.09	152	5.89	1.97	0.09	1.00	0.08	2	NaN	NaN	NaN	NaN	NaN		NaN	NaN	NaN
		max. depth	25	19.24	1.42	66.7	13.51	1.81	0.05	0.92	0.08	2	0.35	1.03	0.20	0.54	0.08	3	-0.78	0.21	NaN
		363 m	50	22.84	0.99	37.35	22.96	1.66	0.03	0.83	0.06	2	NaN	NaN	NaN	NaN	NaN		NaN	NaN	NaN
			80	22.55	0.86	0	26.15	1.74	0.23	0.90	0.05	2	0.96	1.35	0.18	0.62	0.18	4	-0.39	0.25	12.67
			150	23.67	0.71	0.22	33.53	1.59	0.16	0.81	0.25	2	0.14	1.35	0.27	0.69	0.10	3	-0.24	0.29	44.2
			335	31.54	0.94	1.12	33.53	1.53	0.15	0.76	0.22	2	0.16	1.16	0.06	0.64	0.05	2	-0.37	0.07	111.56
369	80	13.94°S	3	0.4	0.08	258.3	5.01	2.27	0.20	1.11	0.02	2	2.37	1.34	0.10	0.65	0.14	3	-0.94	0.17	22.67
		76.51°W	10	20.15	1.63	51.37	12.37	1.91	0.03	0.82	0.04	2	3.20	1.32	0.22	0.69	0.24	2	-0.59	0.33	2.16
		max. depth	30	24.16	1.31	2.42	18.42	1.85	0.02	0.90	0.01	2	0.38	1.34	0.08	0.68	0.04	2	-0.50	0.09	45.1
		178 m	38	22.87	1.11	1.33	20.57	1.83	0.16	0.94	0.10	3	NaN	NaN	NaN	NaN	NaN		NaN	NaN	NaN
			50	18.88	0.80	0.5	23.68	NaN	NaN	NaN	NaN		NaN	NaN	NaN	NaN	NaN		NaN	NaN	NaN
			60	23.1	0.97	0	23.85	1.87	0.11	0.85	0.08	3	0.52	1.10	0.21	0.58	0.27	4	-0.77	0.34	30.63
			100	14.57	0.47	0.14	31.06	NaN	NaN	NaN	NaN		NaN	NaN	NaN	NaN	NaN		NaN	NaN	NaN
			166	20.87	0.74	0.41	28.05	1.74	0.10	0.99	0.04	2	0.31	1.61	0.11	0.83	0.03	3	-0.14	0.11	96.07
420	120	12.87°S	8	8.7	1.01	213.78	8.66	1.92	0.04	1.00	0.28	2	1.59	1.41	0.14	0.73	0.10	3	-0.51	0.17	14.02
		76.58°W	15	3.23	0.11	51.45	29.29	1.50	0.10	0.75	0.20	1	5.63	1.52	0.17	0.81	0.11	4	0.02	0.20	13.63
		max. depth	21	2.94	0.10	2.88	30.89	1.45	0.05	0.72	0.18	2	0.26	1.19	0.14	0.58	0.07	2	NaN	0.16	NaN
		54 m	40	5.66	0.15	2.89	38.35	1.48	0.12	0.78	0.29	2	0.22	1.04	0.10	0.53	0.14	2	NaN	0.17	NaN
			50	5.76	0.15	3.08	38.39	1.40	0.26	0.66	0.10	3	0.47	1.25	0.04	0.64	0.09	2	-0.15	0.10	36.37
422	122	13.00°S	2	11.79	1.78	53.15	6.61	2.05	0.04	1.04	0.17	2	5.43	1.59	0.24	0.81	0.12	6	-0.46	0.27	6.63
		76.75°W	11	19.79	1.94	32.36	10.19	1.88	0.06	0.96	0.01	2	0.70	1.42	0.20	0.74	0.06	4	-0.46	0.21	NaN
		max. depth	51	25.23	1.07	2.98	23.52	1.63	0.01	0.77	0.15	2	4.42	1.66	0.09	0.84	0.19	3	0.02	0.21	23.03
		134 m	125	15.63	0.46	3.33	34.25	1.45	0.09	0.77	0.12	3	0.24	1.66	0.24	0.88	0.03	2	NaN	0.24	42.48
436	134	13.37°S	3	0.152	0.16	276.19	0.94	2.96	0.18	1.61	0.17	2	3.08	1.95	0.03	1.02	0.06	3	-1.02	0.07	25.20
		76.57°W	14	23.46	1.29	4.89	18.26	1.68	0.14	0.93	0.14	2	2.71	1.31	0.06	0.69	0.11	2	-0.37	0.12	6.47
		max. depth	30	23.46	1.10	2.87	21.37	1.66	0.11	0.82	0.02	2	0.48	1.68	0.12	0.85	0.06	3	0.02	0.13	NaN
		125 m	59	1.53	0.04	2.91	37.98	1.46	0.24	0.71	0.20	3	0.17	1.35	0.06	0.71	0.01	2	-0.11	0.06	102.43
			118	8.42	0.24	3.04	35.07	1.55	0.18	0.78	0.17	3	0.13	1.34	0.07	0.71	0.03	2	-0.20	0.08	54.70
441	138	13.53°S	10	2.06	1.91	238.94	1.08	2.71	0.18	1.38	0.01	2	3.94	1.80	0.11	0.86	0.13	2	-0.91	0.17	19.81
		76.79°W	36	19.53	0.90	3.11	21.73	1.55	0.10	0.80	0.05	1	1.96	1.66	0.02	0.85	0.03	2	0.11	0.03	0.00
		max. depth	53	19.33	0.82	2.93	23.46	1.51	0.02	0.76	0.08	2	1.19	1.63	0.08	0.83	0.15	2	0.12	0.17	19.72
		268 m	77	21.31	0.84	2.92	25.32	1.67	0.10	0.88	0.08	3	0.30	1.66	0.30	0.86	0.19	2	-0.01	0.35	27.10
			253	23.66	0.91	3.66	26.05	1.45	0.23	0.69	0.24	2	0.39	1.81	0.02	0.93	0.02	3	0.36	0.03	17.63

Supplementary Table 2. Relative distribution of siliceous organisms (in %) in surface samples.

	St. 338	St. 354	St. 367	St. 368	St. 369	St. 420	St. 422	St. 436	St. 441
	%	%	%	%	%	%	%	%	%
Diatoms	99	99	100	91	100	99	100	98	100
Diatom Resting Spores	1	0	0	6	0	0	0	1	0
Radiolaria	0	1	0	1	0	1	0	1	0
Silicoflagellates	0	0	0	2	0	0	0	0	0
Sponge needles	0	0	0	2	0	0	0	0	0

Supplementary Table 3. Diatom cell counts (cells L^{-1} *10,000) and the relative distribution (in %) in surface water samples.

	St. 338		St. 354		St.367		St.368		St.369		St. 420		St. 422		St. 436		St. 441	
	10^3 cell/L	%	10^3 cell/L	%	10^3 cell/L	%	10^3 cell/L	%	10^3 cell/L	%	10^3 cell/L	%	10^3 cell/L	%	10^3 cell/L	%	10^3 cell/L	%
Amphora spp.	0	0.00	0	0.00	0	0.00	0	0.00	0.48	0.60	0	0.00	0	0.00	0.06	0.66	0	0.00
Asterolampra spp.	0.1	1.25	0.04	0.11	0	0.00	0	0.00	0	0.00	0.1	0.35	0.2	0.00	0.12	1.31	0.12	0.00
Cerataulina pelagica	0	0.00	1.88	5.13	0	0.00	0	0.00	6.24	7.83	12.42	43.79	5423.76	98.44	3.32	36.32	6289.92	99.32
Chaetoceros spp.	3.52	44.11	4.44	12.10	0	0.00	1.44	29.27	0.48	0.60	0.84	2.96	13.68	0.25	1.34	14.66	4.32	0.07
Corethron criophilum	2.74	34.34	0	0.00	0	0.00	0	0.00	0	0.00	0	0.00	0	0.00	0	0.00	0	0.00
Coscinodiscus spp.	0	0.00	0.68	1.85	0.02	100.00	0	0.00	46.56	58.43	2.82	9.94	5.04	0.09	0.4	4.38	0	0.00
Cyclotella spp.	0.1	1.25	1.56	4.25	0	0.00	0	0.00	0.96	1.20	0.96	3.39	1.44	0.03	0.44	4.81	0.72	0.01
Delphineis spp.	0.2	2.51	0.04	0.11	0	0.00	0	0.00	0	0.00	0.42	1.48	2.88	0.05	0.2	2.19	0	0.00
Entomoneis alata	0	0.00	3	8.18	0	0.00	0.18	3.66	4.32	5.42	0.6	2.12	17.28	0.31	0	0.00	5.04	0.08
Fallacia spp.	0	0.00	1.24	3.38	0	0.00	0	0.00	0	0.00	0.9	3.17	0.72	0.01	0.36	3.94	2.32	0.04
Lithodesmium undulatum	0	0.00	0.2	0.55	0	0.00	0	0.00	11.52	14.46	5.4	19.04	8.64	0.16	0.2	2.19	0.08	0.00
Nitzschia spp.	0	0.00	0.16	0.44	0	0.00	0.2	4.07	0	0.00	0	0.00	3.6	0.07	0.08	0.88	1.44	0.02
Odontella spp.	0	0.00	0	0.00	0	0.00	0.04	0.81	0	0.00	0	0.00	0	0.00	0.04	0.44	0	0.00
Pleurosigma spp.	0	0.00	0	0.00	0	0.00	0	0.00	0.48	0.60	0	0.00	0	0.00	0	0.00	0	0.00
Proboscia spp.	0.34	4.26	0.16	0.44	0	0.00	0	0.00	0	0.00	0	0.00	1.44	0.03	0.2	2.19	1.44	0.02
Rhizosolenia spp.	0	0.00	0.04	0.11	0	0.00	0	0.00	0	0.00	0	0.00	0	0.00	0.14	1.53	0	0.00
Pseudo-nitzschia spp.	0.62	7.77	0.44	1.20	0	0.00	0.6	12.20	0.48	0.60	0.18	0.63	3.6	0.07	0.1	1.09	7.2	0.11
Skeletonema spp.	0	0.00	0.32	0.87	0	0.00	0.12	2.44	0	0.00	0	0.00	0	0.00	0	0.00	0	0.00
Suriella spp.	0	0.00	0	0.00	0	0.00	0	0.00	0	0.00	0	0.00	0	0.00	0.16	1.75	0	0.00
Thalassionema spp.	0	0.00	3.8	10.36	0	0.00	0.58	11.79	8.16	10.24	1.08	3.81	2.16	0.04	1.2	13.13	6.9	0.11
Thalassiosira spp.	0.36	4.51	18.64	50.82	0	0.00	1.76	35.77	0	0.00	2.64	9.31	25.2	0.46	0.78	8.53	13.68	0.22
SUM Diatoms (Cell counts)	**8**		**37**		**0**		**5**		**80**		**28**		**5510**		**9**		**6333**	

Supplementary Table 4. Comparison between relative distribution of diatoms in core-top sediment from Ehlert et al. (2012) and Doering et al. (2016) and this study

	MUC/Station	Latitude	Depth	Chaetoceros RS	Thalassionema	Skeletonema	Coscinodiscus	Thalassiosira spp.	Cyclotella	Ditylum	Rhizosolenia	Odontella	Proboscia	Actinoptycus	Actinocyclus	Cerataulina pelagica	Chaetoceros spp.	Corethron criophilum
			m	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%
Sediment	M77/1-620	-12.31	150	45	6	0	4	12	14	2	0	0	0	8	9	0	0	0
	M77/1-420	-15.19	516	36	3	1	7	18	11	2	0	0	0	9	13	0	0	0
	M772-005	-12.09	214	50	10	0	4	8	6	10	0	0	0	4	7	0	0	0
	M77/2-53	-5.48	2607	20	1	0	13	23	13	1	0	0	0	16	14	0	0	0
	M77/2-28	-9.3	1105	2	10	0	17	24	12	1	1	0	0	15	19	0	0	0
	M77/2-29	-9.3	437	10	0	0	10	17	27	1	0	1	0	29	6	0	0	0
	M77/1-543	-11	77	40	4	0	2	13	7	3	3	0	0	10	17	0	0	0
	M77/2-22	-10.89	1923	7	6	0	8	37	12	2	0	0	0	16	13	0	0	0
	M77/1-450	-11	319	53	28	0	1	4	7	1	0	0	1	1	4	0	0	0
Watercolumn	338	-13.13	160	1	0	4	0	5	1	0	0	0	5	0	0	0	47	37
	354	-13.26	59	0	12	0	2	60	5	0	0	0	0	0	0	6	14	0
	367	-13.99	178	0	0	0	100	0	0	0	0	0	0	0	0	0	0	0
	368	-13.95	363	11	19	4	0	21	0	0	0	1	0	0	0	44	0	0
	369	-13.94	766	0	13	0	75	0	2	0	0	0	0	0	0	10	1	0
	441	-13.53	268	0	0	0	0	0	0	0	0	0	0	0	0	100	0	0
	420	-12.87	54	0	5	0	13	12	5	2	0	0	0	0	0	59	4	0
	422	-13	134	0	0	0	0	0	0	0	0	0	0	0	0	99	0	0
	436	-13.37	125	2	15	0	5	10	5	2	2	0	0	0	0	41	17	0
Sediment Total		10°-15°	77 to 516	45	11	0	4	10	9	3	1	0	0	6	10	0	0	0
		All	All	33	9	0	6	16	11	3	0	0	0	11	11	0	0	0
Water Column Total		All	All	0	0	0	0	1	0	0	0	0	0	0	0	98	0	0
		All without *C.pelgica, St.367*	All	0	13	0	30	34	3	2	0	0	0	0	0	0	16	1

Compilation of water column $\delta^{30}Si_{bSi}$

The published literature on $\delta^{30}Si_{bSi}$ from the water column includes in total 10 publications listed in Table S4. Seven studies were conducted in different regions of the Southern Ocean, two in the Arctic Ocean and one in the East China Sea. After careful examination, the $\delta^{30}Si_{bSi}$ data from Cao et al. (2012) was not plotted in figure 7, as the sampling locations were close to the Pearl River and showed partly strong riverine and lithogenic influence. $\delta^{30}Si_{bSi}$ data from Fripiat et al. (2007) and Varela et al. (2016) was excluded as sample were influenced by isotopically heavier sea ice diatoms. In Figure 7, $\delta^{30}Si_{bSi}$ from the mixed layer was plotted. The Mixed Layer depth (MLD) was either directly given in the study (Cardinal et al., 2007; Fripiat et al., 2012) or it was defined by the depth, were we marked a strong increase in [dSi]. Samples that are reported in $\delta^{29}Si_{bSi}$ (Cardinal et al., 2007) were converted to $\delta^{30}Si_{bSi}$ by dividing with 0.5087, the slope obtained in Fig. S1.

Supplementary Table 5. List of references and short information on sampling location used in Fig. 7.

No.	Reference	Ocean	Location	Definition MLD	Comment
1	Varela et al. 2004	Southern Ocean	ACC region 170°W between 50°S and 71°S (AESOPS; 1996–1998) and between 60°S and 66°S (SOFeX; 2002).	Underway sampling system	Isotopically heavy Sea Icea diatoms (data excluded)
2	Fripiat et al., 2007	Southern Ocean	Ice cores (AU0301) September–October 2003; 64.5°S, 117°E	-	Isotopically heavy Sea Icea diatoms (data excluded)
3	Cardinal et al., 2007	Southern Ocean	WOCE SR-3 transect at 139 -140°E (2001)	indicated in paper	dSi published in Cardinal et al. 2005, different size fractions, used >0.4 µm
4	Cavagna et al., 2011	Southern Ocean	Antarctic Polar front (ANT-XXI/3; 2004)	upper 40 m	
5	Fripiat et al., 2011	Southern Ocean	Kerguelen Islands (KEOPS ; 2005)	Silicicline	
6	Cao et al. 2012	Pacific	East China Sea	-	Sampling location close to Pearl river (data not plotted)
7	Fripiat et al., 2012	Southern Ocean	February/March 2008, BONUS-GoodHope (BGH); transect from Cape Basin to the north of the Weddell Gyre (up to 58° S) centred around the 0° meridian	indicated in paper	
8	Varela et al. 2016	Arctic	Canada Basin	sample from 7 m depth	bSi sample are from an Underway sampling system, [dSi] was taken from nearby stations
9	Closset et al. 2016	Southern Ocean	Kerguelen Plateau (KEOPS-2; 2011)	upper 40 m	
10	Liguori et al. 2020	Arctic	Central Arctic (ARK-XXIX/3; 2015)	-	No data within the ML (data not plotted)
11	This study	Pacific	Peruvian Upwelling (2014) M93	oxygenated ML	