

PROSOPE

H. CLAUSTRE : head of mission and project leader

BIOGENIC & LITHOGENIC SILICA : QUEGUINER

Data set | Protocol | References

DATA SET

Station	ctd	Bottle	Profondeur	Time	BSi $\mu\text{mol L}^{-1}$	LSi $\mu\text{mol L}^{-1}$
St#1	11	18	11,0	14/09/99 16:05	0,039	0,038
St#1	11	16	20,5	14/09/99 16:04	0,116	0,124
St#1	11	14	29,3	14/09/99 16:03	0,075	0,026
St#1	11	12	38,4	14/09/99 16:03	0,089	0,024
St#1	11	10	49,0	14/09/99 16:02	0,089	0,080
St#1	11	8	59,0	14/09/99 16:01	0,129	0,022
St#1	11	6	80,5	14/09/99 16:00	0,231	0,061
St#1	11	4	100,5	14/09/99 15:59	0,193	0,055
St#2	14	20	4,7	15/09/99 12:38	0,023	0,029
St#2	14	18	15,2	15/09/99 12:37	0,025	0,024
St#2	14	16	29,4	15/09/99 12:36	0,129	0,053
St#2	14	14	39,9	15/09/99 12:36	0,265	0,043
St#2	14	12	45,3	15/09/99 12:33	0,324	0,038
St#2	14	10	59,7	15/09/99 12:32	0,382	0,133
St#2	14	8	69,4	15/09/99 12:32	0,269	0,139
St#2	14	6	89,7	15/09/99 12:31	0,329	0,067
St#2	14	4	110,3	15/09/99 12:30	0,225	0,070
St#3	17	20	4,8	16/09/99 12:37	0,015	0,043
St#3	17	18	9,8	16/09/99 12:36	0,013	0,046
St#3	17	16	25,0	16/09/99 12:36	0,011	0,012
St#3	17	14	40,2	16/09/99 12:35	0,022	0,014
St#3	17	12	54,9	16/09/99 12:34	0,042	0,040

St#3	17	10	69,7	16/09/99 12:33	0,052	0,053
St#3	17	8	80,2	16/09/99 12:32	0,047	0,028
St#3	17	6	94,2	16/09/99 12:31	0,149	0,013
St#3	17	4	109,3	16/09/99 12:31	0,068	0,020
St#3	17	2	150,7	16/09/99 12:29	0,038	0,022
St#4	20	20	7,1	17/09/99 11:41	0,020	0,084
St#4	20	18	12,6	17/09/99 11:41	0,020	0,075
St#4	20	16	27,1	17/09/99 11:40	0,014	0,024
St#4	20	14	40,5	17/09/99 11:39	0,014	0,010
St#4	20	12	60,5	17/09/99 11:38	0,014	0,012
St#4	20	10	76,9	17/09/99 11:37	0,023	0,011
St#4	20	8	90,1	17/09/99 11:36	0,028	0,022
St#4	20	6	104,6	17/09/99 11:35	0,028	0,039
St#4	20	4	121,7	17/09/99 11:34	0,027	0,037
St#4	20	2	150,1	17/09/99 11:33	0,018	0,038
St#5	23	20	6,3	18/09/99 11:55	0,021	0,067
St#5	23	17	11,2	18/09/99 11:54	0,021	0,053
St#5	23	16	23,3	18/09/99 11:54	0,012	0,022
St#5	23	14	39,9	18/09/99 11:52	0,016	0,012
St#5	23	12	54,8	18/09/99 11:52	0,022	0,041
St#5	23	10	64,8	18/09/99 11:51	0,034	0,025
St#5	23	9	64,8	18/09/99 11:51	0,030	0,034
St#5	23	8	80,0	18/09/99 11:50	0,040	0,032
St#5	23	6	94,8	18/09/99 11:49	0,038	0,040
St#5	23	4	120,1	18/09/99 11:48	0,044	0,038
St#5	23	1	149,8	18/09/99 11:47	0,043	0,038
St#6	26	20	5,8	19/09/99 11:48	0,010	0,029
St#6	26	17	10,1	19/09/99 11:47	0,010	0,028
St#6	26	16	29,2	19/09/99 11:46	0,009	0,016
St#6	26	12	70,0	19/09/99 11:43	0,012	0,007
St#6	26	10	84,8	19/09/99 11:42	0,017	0,006
St#6	26	8	97,8	19/09/99 11:41	0,017	0,010
St#6	26	6	115,1	19/09/99 11:40	0,019	0,006
St#6	26	4	140,4	19/09/99 11:39	0,023	0,009
St#6	26	2	170,1	19/09/99 11:38	0,026	0,015

St#7	63	20	3,8	26/09/99 14:47	0,015	0,028
St#7	63	18	13,9	26/09/99 14:47	0,011	0,023
St#7	63	16	29,8	26/09/99 14:46	0,015	0,021
St#7	63	14	50,0	26/09/99 14:45	0,015	0,026
St#7	63	12	69,8	26/09/99 14:44	0,017	0,013
St#7	63	10	89,9	26/09/99 14:43	0,029	0,024
St#7	63	8	110,0	26/09/99 14:43	0,027	0,048
St#7	63	6	129,9	26/09/99 14:42	0,029	0,056
St#7	63	4	150,2	26/09/99 14:41	0,028	0,070
St#7	63	2	200,5	26/09/99 14:39	0,025	0,095
St#8	68	20	4,9	27/09/99 11:55	0,010	0,036
St#8	68	18	14,8	27/09/99 11:54	0,010	0,035
St#8	68	16	29,6	27/09/99 11:53	0,008	0,009
St#8	68	14	49,9	27/09/99 11:52	0,016	0,007
St#8	68	12	70,6	27/09/99 11:51	0,018	0,006
St#8	68	4	150,4	27/09/99 11:48	0,025	0,056
St#8	68	2	200,1	27/09/99 11:46	0,042	0,080
St#9	70	20	4,7	28/09/99 12:11	0,024	0,096
St#9	70	18	15,2	28/09/99 12:10	0,024	0,094
St#9	70	16	29,8	28/09/99 12:09	0,026	0,013
St#9	70	14	50,2	28/09/99 12:08	0,031	0,015
St#9	70	12	64,1	28/09/99 12:07	0,039	0,029
St#9	70	10	75,0	28/09/99 12:06	0,042	0,076
St#9	70	8	89,8	28/09/99 12:06	0,033	0,078
St#9	70	6	110,4	28/09/99 12:04	0,043	0,052
St#9	70	4	129,2	28/09/99 12:03	0,037	0,032
St#9	70	2	150,2	28/09/99 12:03	0,031	0,088
MIO#1	28	20	7,6	20/09/99 11:18	0,013	0,023
MIO#1	28	18	17,4	20/09/99 11:17	0,006	0,010
MIO#1	28	16	32,4	20/09/99 11:16	0,011	0,009
MIO#1	28	14	50,0	20/09/99 11:15	0,013	0,008
MIO#1	28	12	70,1	20/09/99 11:14	0,012	0,000
MIO#1	28	10	89,8	20/09/99 11:13	0,014	0,001
MIO#1	28	8	110,0	20/09/99 11:12	0,124	0,002
MIO#1	28	6	130,4	20/09/99 11:11	0,067	0,002

MIO#1	28	4	149,6	20/09/99 11:11	0,057	0,001
MIO#1	28	2	200,0	20/09/99 11:08	0,047	0,008
MIO#2	36	20	6,7	21/09/99 11:21	0,016	0,021
MIO#2	36	18	16,7	21/09/99 11:20	0,014	0,018
MIO#2	36	16	31,8	21/09/99 11:20	0,012	0,006
MIO#2	36	14	50,2	21/09/99 11:19	0,012	0,002
MIO#2	36	12	70,3	21/09/99 11:18	0,016	0,001
MIO#2	36	10	90,0	21/09/99 11:17	0,028	0,004
MIO#2	36	8	109,4	21/09/99 11:16	0,109	0,004
MIO#2	36	6	130,3	21/09/99 11:15	0,061	0,006
MIO#2	36	4	149,8	21/09/99 11:14	0,056	0,005
MIO#2	36	2	200,3	21/09/99 11:12	0,048	0,007
MIO#3	44	10	90,1	22/09/99 11:04	0,015	0,009
MIO#3	44	8	109,1	22/09/99 11:03	0,085	0,011
MIO#3	44	6	130,0	22/09/99 11:02	0,066	0,008
MIO#3	44	4	149,7	22/09/99 11:01	0,055	0,010
MIO#3	44	2	199,8	22/09/99 10:59	0,045	0,013
MIO#4	52	20	7,3	23/09/99 11:15	0,008	0,017
MIO#4	52	18	17,2	23/09/99 11:14	0,009	0,008
MIO#4	52	16	32,3	23/09/99 11:13	0,011	0,011
MIO#4	52	14	50,0	23/09/99 11:12	0,010	0,007
MIO#4	52	12	69,8	23/09/99 11:12	0,014	0,007
MIO#4	52	10	90,2	23/09/99 11:11	0,021	0,008
MIO#4	52	8	110,1	23/09/99 11:10	0,060	0,005
MIO#4	52	6	129,6	23/09/99 11:09	0,050	0,010
MIO#4	52	4	150,0	23/09/99 11:08	0,057	0,012
MIO#4	52	2	200,1	23/09/99 11:06	0,037	0,013
MIO#5	60	20	7,0	24/09/99 11:13	0,009	0,023
MIO#5	60	18	16,8	24/09/99 11:13	0,008	0,019
MIO#5	60	16	32,2	24/09/99 11:12	0,008	0,006
MIO#5	60	14	50,2	24/09/99 11:11	0,011	0,006
MIO#5	60	12	75,0	24/09/99 11:10	0,014	0,005
MIO#5	60	10	89,8	24/09/99 11:09	0,013	0,004
MIO#5	60	8	110,0	24/09/99 11:08	0,018	0,004
MIO#5	60	6	129,9	24/09/99 11:07	0,026	0,005

MIO#5	60	4	150,2	24/09/99 11:06	0,051	0,006
MIO#5	60	2	200,1	24/09/99 11:04	0,039	0,010
DYF#1	73	20	4,0	29/09/99 11:39	0,019	0,057
DYF#1	73	18	15,0	29/09/99 11:39	0,020	0,058
DYF#1	73	16	24,9	29/09/99 11:38	0,015	0,027
DYF#1	73	14	39,7	29/09/99 11:37	0,018	0,007
DYF#1	73	12	44,7	29/09/99 11:36	0,024	0,006
DYF#1	73	10	60,1	29/09/99 11:35	0,054	0,014
DYF#1	73	8	75,2	29/09/99 11:34	0,046	0,015
DYF#1	73	6	90,1	29/09/99 11:33	0,044	0,014
DYF#1	73	4	109,9	29/09/99 11:32	0,025	0,042
DYF#1	73	2	150,5	29/09/99 11:30	0,026	0,039
DYF#2	81	20	3,1	30/09/99 11:43	0,020	0,057
DYF#2	81	18	13,8	30/09/99 11:42	0,019	0,048
DYF#2	81	16	23,3	30/09/99 11:41	0,018	0,030
DYF#2	81	14	40,1	30/09/99 11:40	0,023	0,009
DYF#2	81	12	49,8	30/09/99 11:39	0,030	0,010
DYF#2	81	10	60,1	30/09/99 11:39	0,043	0,008
DYF#2	81	8	75,1	30/09/99 11:38	0,055	0,009
DYF#2	81	6	89,8	30/09/99 11:37	0,044	0,019
DYF#2	81	4	109,8	30/09/99 11:36	0,033	0,024
DYF#2	81	2	149,8	30/09/99 11:34	0,023	0,041
DYF#3	89	20	6,2	01/10/99 11:50	0,014	0,041
DYF#3	89	18	16,4	01/10/99 11:49	0,018	0,042
DYF#3	89	16	25,9	01/10/99 11:49	0,021	0,014
DYF#3	89	14	39,3	01/10/99 11:48	0,029	0,009
DYF#3	89	12	46,6	01/10/99 11:47	0,046	0,008
DYF#3	89	10	60,6	01/10/99 11:46	0,049	0,024
DYF#3	89	8	74,9	01/10/99 11:45	0,031	0,023
DYF#3	89	6	89,8	01/10/99 11:45	0,026	0,028
DYF#3	89	4	109,5	01/10/99 11:44	0,025	
DYF#3	89	2	151,4	01/10/99 11:42	0,024	0,043
DYF#4	97	20	6,8	02/10/99 11:34	0,019	0,030
DYF#4	97	18	17,2	02/10/99 11:34	0,016	0,010
DYF#4	97	16	24,7	02/10/99 11:33	0,023	0,006

DYF#4	97	14	42,2	02/10/99 11:32	0,030	0,017
DYF#4	97	12	48,1	02/10/99 11:32	0,052	0,027
DYF#4	97	10	60,1	02/10/99 11:31	0,040	0,031
DYF#4	97	8	74,9	02/10/99 11:31	0,031	0,030
DYF#4	97	6	90,0	02/10/99 11:30	0,029	0,044
DYF#4	97	4	110,0	02/10/99 11:29	0,024	0,025
DYF#4	97	2	150,1	02/10/99 11:28	0,028	0,050
DYF#5	105	20	7,1	03/10/99 12:02	0,018	0,035
DYF#5	105	18	17,4	03/10/99 12:02	0,016	0,048
DYF#5	105	16	26,4	03/10/99 12:01	0,057	0,051
DYF#5	105	14	39,7	03/10/99 12:00	0,027	0,006
DYF#5	105	12	45,0	03/10/99 12:00	0,037	0,014
DYF#5	105	10	60,0	03/10/99 11:59	0,047	0,019
DYF#5	105	8	74,9	03/10/99 11:58	0,023	0,036
DYF#5	105	4	109,9	03/10/99 11:57	0,038	0,038
DYF#5	105	2	150,2	03/10/99 11:56	0,023	

PROTOCOL FOR BIOGENIC AND LITHOGENIC SILICA MEASUREMENTS

Biogenic silica (BSi) originates from siliceous phytoplankton and mainly from diatom's envelope or frustule, but is also found in silicoflagellates and radiolarians (zooplankton). Lithogenic silica (LSi) is a mineral form, issued from terrigenous particles (quartz, aluminosilicates).

Sampling protocol :

Water was collected using a CTD rosette sampler. 2 L seawater were collected at every station (except for the UPW station which could not be sampled) from the surface to 200 m. Samples were filtered on Nucleopore polycarbonate membranes (0.6 μ m, 47 mm), and stored in plastic Petri dishes. Filters were then dried 24 h at 60°C and stored at ambient temperature until laboratory analysis.

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Laboratory analysis :

BSi and LSi were measured using Paasche's method (1973) as modified by Nelson *et al.* (1989) : BSi and LSi are extracted on the same filter after successive basic and acid treatment. BSi is extracted during a hot sodium hydroxide (NaOH 0.2 N) attack (45 min), which converts BSi into the dissolved orthosilicic acid form (Si(OH)₄). Si(OH)₄ is then

quantified using Mullin and Riley's (1965) spectrophotometric method. After the first basic attack, filters are rinsed free of remaining Si(OH)_4 and dried again at 60°C. LSi, preserved in the sample, is then treated with fluorhydric acid (HF 2.9 N) for 24h. In the same way, LSi is measured through quantification of the dissolved Si(OH)_4 form.

BSi/LSi interference :

It has been demonstrated that for coastal samples, significant leaching of orthosilicic acid from LSi could occur during the first NaOH attack (up to 15%) (Ragueneau et Tréguer, 1994). This is particularly the case when high LSi concentrations are present. The Mediterranean Sea is enclosed by land, and is the site of intense Saharan dust deposition events throughout the year. Thus we may expect occasionally high LSi concentrations in the water column. BSi measurements then need to be corrected for that interference. A way to assess the amount of LSi that has leached during the first attack, is to measure dissolved aluminium in the sample. Indeed Si/Al ratio for LSi is about 2, whereas the aluminium content of the diatom frustule is several orders of magnitude lower.

The protocol described previously was as a consequence slightly modified, including a second BSi extraction preceding HF attack, and dissolved aluminium measurements in the leachate. During the first NaOH attack, all BSi with a fraction of labile LSi are dissolved. In the second alkaline extraction, only a fraction of the remaining labile LSi is dissolved. A quantitative comparison of aluminium leached during the first two extractions will allow us to correct BSi values for LSi interference.

Data availability :

Aluminium analysis remain to be done for all samples (in collaboration with the CEREGE-Aix). **BSi data are thus susceptible to be slightly modified** (but not drastically (a few nanomoles) since LSi concentrations are low).

LSi values, which are the sum of values found in the second NaOH and in the last HF extraction, **may on the other hand be considered as definitive values.**

This data set will remain as **submitted data**, until aluminium analysis and subsequent corrections are made.

References :

Mullin, J.B. and Riley, J.P. (1965). The spectrophotometric determination of silicate-silicon in natural waters with special reference to seawater. *Anal. Chim. Acta*, 46, 491-501.

Nelson, D.M., Walker, O.S.Jr., Muench, R.D., Gordon, L.I., Sullivan, C.W., Husby, D.M. (1989). Particulate matter and nutrient distributions in the ice-edge zone of the Weddell Sea : relationship to hydrography during late summer. *Deep-Sea Research*, 36, 191-209.

Paasche, E. (1973). Silicon and the ecology of marine plankton diatoms. I. *Thalassiosira pseudonana* (*Cyclotella nana*) grown in a chemostat with silicate as limiting nutrient. *Marine Biology*, 19, 117-126.

Ragueneau, O. and Tréguer P. (1994). Determination of biogenic silica in coastal waters : applicability and limits of the alkaline digestion method. *Marine Chemistry*, 45, 43-51.