# **36. HIGH-RESOLUTION SILICA PORE-WATER PROFILES IN SEDIMENTS** OF THE MADEIRA ABYSSAL PLAIN, EASTERN NORTH ATLANTIC<sup>1</sup>

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#### ABSTRACT

High-resolution pore-water sampling has been undertaken to define the pore-water silica profile vs. depth for Holes 950A and 952A in the Madeira Abyssal Plain, eastern North Atlantic. The silica pore-water concentration in the upper 50 meters below seafloor (mbsf) faithfully records the presence of biogenic silica in organic-rich turbidites. Between 50 and 250 mbsf, that is, between 1 and 6.5 Ma, however, the silica pore-water concentration is low and stable, pointing to the absence of biogenic silica in the organic-rich turbidites in this interval. Such absence could indicate a change in source area, or in the north-west African upwelling system during that period.

Near 280 mbsf in Hole 950A, and below 290 mbsf in Hole 952A, enhanced levels of silica are again observed in the pore waters, which indicates that biogenic silica is present in the deep organic-rich turbidites. For Hole 952A, this coincides with the interval where enhanced levels of diatoms have been reported. The high-resolution pore-water sampling in Holes 950A and 952A has resulted in the identification of potential intervals where authigenic silica phases are likely to have formed, thus enabling future studies on the diagenetic redistribution of silica in marine sediments.

### **INTRODUCTION**

Silica concentrations in marine pore waters vary between 100 and 1000  $\mu$ m, but usually fall between 100 and 400  $\mu$ m at normal seawater temperatures (e.g., Schink et al., 1974; Jahnke et al., 1982; De Lange, 1986). Even in sediments that contain some biogenic opal (radiolarians, diatoms, etc.), the pore-water concentration of silica is mostly far below its solubility-product-controlled concentration of 1000  $\mu$ m (Hurd, 1973). Consequently, the thermodynamic-controlled dissolution of biogenic opal must be accompanied by the kinetic-controlled incorporation of silica into a less soluble authigenic solid phase. Minerals such as smectite, chamosite, and nontronite are among the phases that have been reported to result from such redistribution of silica (e.g., Harder, 1978; Hein et al., 1979; Maris and Bender, 1982; De Lange and Rispens, 1986).

Some late-Quaternary organic-rich turbidites in the Madeira Abyssal Plain have been reported to contain a small percentage of biogenic opal (Kuijpers, 1982). Corresponding distinct maxima in the silica pore-water profiles occur at the depth levels of such turbidites, whereas distinct minima occur at intervals that have a higher proportion of pelagic intervals (e.g., De Lange et al., 1992). The concentration gradients found by De Lange et al. (1992) over the top 35 m of the sediments from the Madeira Abyssal Plain could only have resulted in the accumulation of, at most, 0.1% authigenic phases in distinct intervals. If fluxes of a similar magnitude lasted not for 0.5 Ma, but rather from 5 to 10 Ma, then substantial and more easily detectable amounts could have accumulated. The recovery of older turbiditic units during Leg 157 offered the opportunity to test this hypothesis. For this purpose, pore waters have been sampled at high resolution throughout Holes 950A and 952A. The aim of this study was to detect silica pore-water gradients to identify promising intervals for future sediment sampling of authigenic silica phases.

### **METHODS**

After the pore-water extraction by hydraulic squeezing aboard ship, the samples were stored under cool conditions until their analysis 2 weeks after the cruise. Dissolved silica concentrations were measured using a Technicon TRAACS AutoAnalyzer; standards were made in "aged" seawater low in dissolved silica. Each sample was analyzed at least in duplicate in different analytical runs. Analytical errors determined on replicate analyses of a few samples are better than 3%.

## **RESULTS AND DISCUSSION**

Leg 157 recovered a large number of organic-rich turbidites from 0 to 15–20 Ma (Howe and Sblendorio-Levy, Chap. 29, this volume), that were deposited at least as abundantly as in the intervals of 0–35 meters below seafloor (mbsf) reported earlier (e.g., Schminke, Weaver, Firth, et al., 1995; De Lange et al., 1987; Weaver and Rothwell, 1987; Weaver et al., 1992; Rothwell et al., Chap. 28, this volume).

The silica pore-water data of previous investigations in the Madeira Abyssal Plain demonstrated smooth profiles with very clear maxima and minima in sediments down to 35 mbsf (e.g., De Lange et al., 1992). In the present study, however, there appears to be consistently low values below a depth of ~50-250 mbsf (Fig. 1; Tables 1, 2). It should be noted that the pore-water concentration of silica is sensitive to the temperature of squeezing. If the temperature of squeezing deviates 20°C from the in situ temperature, then deviations of 10%-60% in the silica pore-water concentration have been reported to occur (e.g., Fanning and Pilson, 1971; Mangelsdorf et al., 1969; Sayles et al., 1973, 1976; De Lange et al., 1992). This temperature effect seems to be dependent on the type of sediment involved. Clays and marly sediment are reported to be more sensitive than siliceous oozes, consequently, to give larger deviations from the in situ porewater concentration. Ocean Drilling Program (ODP) samples cannot be adequately squeezed under temperature-controlled conditions aboard the JOIDES Resolution, which most of the time is unnecessary in view of the temperature gradients found in the sediments usually recovered by ODP. All silica pore-water concentrations in this study are, therefore, likely to be somewhat higher than the in situ con-

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Figure 1. Silica pore-water concentration vs. depth for the interval of 0–400 mbsf in Holes 950A and 952A.

centrations. In addition, most of the small variations in the concentration of silica, such as observed between 50 and 250 mbsf, may be attributable to such temperature of squeezing artifacts. In summary, the temperature of squeezing may have caused minor changes in the silica pore-water profiles. The main picture of the profiles, however, is considered to be largely unaffected by such artifacts.

The silica pore-water concentration in the intervals between 50 and 250 mbsf appears to be rather low and relatively stable, with only a minor decrease with depth (Fig. 1). The occurrence of organic-rich turbidites containing some biogenic silica coincides with enhanced levels of pore-water silica in the sediments of the upper 50 mbsf (Fig. 2; compared to Schmincke, Weaver, Firth, et al., 1995). It seems, therefore, that no (biogenic) opal occurs in the interval of 50-250 mbsf, despite the repetitive occurrence of organic-rich turbidites (see Schminke, Weaver, Firth, et al., 1995). It is only below 290 mbsf in Hole 952A, and ~280 mbsf in Hole 950A, that enhanced levels of silica occur again in the pore waters. The rare occurrence of biogenic silica is reported for the interval below 100 mbsf in Hole 950A, and a rapidly increasing Si/Al ratio in unit I/4 from 270 to 295 mbsf (Jarvis et al., Chap. 31, this volume). The amount of diatoms in Hole 952A is reported to increase again below 290 mbsf, coinciding with the rapid increase in silica pore-water concentration vs. depth (Schminke, Weaver, Firth, et al., 1995).

There are two alternative explanations for the absence of biogenic silica in organic-rich turbidites deposited approximately between 1 and 10 Ma (Howe and Sblendorio-Levy, Chap. 29, this volume): (1) only minor amounts of biogenic silica were initially present and have been dissolved since deposition (about <1%), or (2) the organic-rich turbidites did not contain any biogenic silica at all upon deposition. In any case, such low or absent biogenic opal content may point to a different source area for this group of organic-rich turbidites, or to a change or shift in the northwest African upwelling system.

If studied in more detail, it is clear that the silica pore-water concentration faithfully follows the presence of organic-rich turbidites in which some biogenic silica occurs (e.g., Fig. 2). The silica pore-water gradients and related fluxes in the sediments of the upper part of these holes seems relatively small compared with those in the sediments at 280 and 290 mbsf in Holes 950A and 952A, respectively. However, the silica flux calculated from these profiles is  $4*10^{-2}$  and  $2.5*10^{-2}$  $\mu$ m/cm<sup>2</sup> per yr, respectively, for the intervals at ~30 and 290 mbsf in Hole 952A. If fluxes are assumed to have remained the same since briefly after deposition of the opal-containing organic-rich turbidite involved, then the amount of authigenic silica that has formed can be calculated. It appears that the amount formed at 290 mbsf is  $10\times$  larger than that formed at 30 mbsf in Hole 952A. Consequently, the in-

Table 1. Pore-water silica data from Hole 950A.

Core section	Si	Core section	Si
interval (cm)	(uM)	interval (cm)	
intervar (eni)	(μινι)	intervar (ciii)	(μινι)
1H 4 145 150	400	16H 3 96 102	148
2H-4, 145-150	400	16H-4 145-150	123
3H-3 14-20	164	16H-6 46-52	136
3H-4 65-70	200	17H-2 53-60	151
3H-5, 116-121	352	17H-CC 4-10	160
3H-6 145-150	433	18X-1 103-109	179
3H-7 32-38	458	18X-2, 145-150	209
4H-1 25-30	391	19X-1 42-48	134
4H-2, 64-70	636	19X-2, 91-97	136
4H-3, 133-139	632	19X-4, 2-8	173
4H-5, 42-48	651	19X-5, 65-71	
4H-5, 145-150	606	20X-1, 31-37	89
4H-6, 89-92	395	20X-2, 89-95	143
5H-1, 24-30	388	20X-3, 127-135	106
5H-2, 49-56	365	20X-4, 140-150	186
5H-3, 90-97	422	20X-6, 21-27	128
5H-5, 76-82	441	21X-1, 18-24	120
5H-5, 145-150	527	21X-2, 85-91	142
5H-6, 102-109	499	21X-4, 22-28	121
6H-1, 16-21	481	21X-5, 118-124	94
6H-2, 70-76	414	21X-7, 39-45	138
6H-4, 13-19	358	22X-1, 42-48	75
6H-4, 145-150	305	22X-2, 80-86	125
0H-5, 90-102	314	22X-4, 41-47	119
0H-0, 5-11 7H 1, 100, 100	2/1	22X-4, 140-150	185
7H-1, 100-100 7H 2 5 11	244	22X-0, 118-124 22X 1 121 127	139
7H 2 145 150	220	23A-1, 121-127 22X = 29 = 24	04
711-5, 145-150	230	23A-3, 20-34 22V 4 99 01	94
7H 5 100 106	257	23A-4, 00-91 23X 6 21 27	162
7H-7 3-9	127	23X-0, 21-27 24X-1 52-58	85
8H-1 100-106	243	24X-2 117-123	79
8H-3 10-16	202	24X-4 20-26	97
8H-4, 70-76	259	24X-5, 105-111	104
8H-5, 145-150	296	24X-7, 25-31	139
8H-7, 52-59	224	25X-1, 19-25	73
9H-2, 50-56	176	25X-2, 93-99	100
9H-3, 100-106	176	25X-3, 140-150	236
9H-4, 145-150	231	25X-5, 36-42	66
9H-5, 50-56	156	25X-6, 121-127	148
9H-7, 44-50	179	26X-1, 22-28	130
10H-2, 50-56	172	26X-2, 65-71	58
10H-4, 145-150	201	26X-3, 94-100	96
10H-6, 86-92	153	26X-5, 9-15	134
10H-7, 128-134	157	26X-6, 80-86	130
11H-1, 25-31	1/8	2/X-1, 18-24	6/
11H-2, 83-89	1/5	27X-2, 114-120	13
1111 4 77 82	145	27X-4, 54-40	123
1111-4, 77-65	204	2/A-3, 01-0/ 27X 5, 145, 150	92
11H-5,00-72	204	2/X-3, 143-130 28X 1 22 40	100
11H 7 22 28	105	28X 2 70 86	47
12H-1 98-104	182	20X-2, 79-80 20X-1, 27-33	94
12H-3 12-18	203	29X-1, 27-55 29X-2, 71-77	72
12H-4 129-135	197	29X-2, 71-77	103
12H-4, 145-150	210	29X-5, 4-10	62
12H-6, 110-116	162	29X-5, 69-75	53
13H-1, 48-54	175	30X-1, 82-88	177
13H-3, 36-42	141	30X-3, 101-107	206
13H-4, 142-148	156	30X-4, 140-150	384
14H-1, 100-106	162	30X-5, 49-55	192
14H-3, 80-86	164	30X-6, 102-108	237
14H-4, 145-150	145	31X-2, 118-124	454
14H-6, 51-57	132	31X-4, 14-20	317
15H-1, 90-96	111	31X-5, 88-91	190
15H-3, 30-36	151	36X-1, 140-150	190
15H-4, 41-47	84	36X-1, 140-150	186
15H-5, 96-102	120	39X-4, 140-150	279
16H-2, 56-62	111		

terval near 290 mbsf seems to be the most promising for continued studies on the formation of authigenic silica phases. Because of the relatively low sample resolution in the latter interval, however, it may appear difficult to determine the exact depth location of such authigenic precipitate. In contrast, the high-resolution pore-water sampling for the sediments in the upper part of the two holes would allow the more precise detection of interval(s) with authigenic silica formation in the upper 100 mbsf.

The sample resolution of the routine shipboard pore-water samples, obviously, is insufficient to detect sites of precipitation in the sediments of the upper part of these holes. Distinct precipitation in-

Table 2. Pore-water silica data from Hole 952A.

Core, section,	Si	Core, section,	Si
interval (cm)	(µM)	interval (cm)	(µM)
1H-1, 100-106	252	15H-1, 33-39	127
1H-3, 48-54	259	15H-2, 97-103	114
1H-4, 145-150	434	15H-4, 7-13	138
IH-5, 5-11	420	15H-5, 91-97	170
IH-6, 90-96	548	15H-6, 139-145	139
2H-3, 10-16	334	10X-1, 00-/1	117
2H-4, 00-00 2H 5, 145, 150	497	16X 4 22 28	142
2H-5, 145-150 2H-6, 40-46	364	16X-4, 22-28	142
2H-7, 130-136	255	16X-5 114-120	155
3H-1 91-97	348	17X-1 44-50	158
3H-2, 140-146	304	17X-2, 95-101	174
3H-4, 50-56	392	17X-3, 143-149	164
3H-4, 145-150	386	18X-1, 9-15	141
3H-6, 10-16	414	18X-2, 73-79	197
3H-7, 30-36	332	18X-4, 22-28	250
4H-1, 125-131	563	18X-4, 140-150	266
4H-4, 28-34	690	18X-5, 104-110	166
4H-4, 145-150	665	18X-6, 133-139	122
4H-4, 48-54	576	19X-1, 26-32	107
5H-1, 100-112	485	19X-2, 74-80	154
5H 4 145 150	522	19A-5, 142-146	100
5H 6 00 105	511	19A-5, 40-40 10X 7 11 17	133
6H-1 91-97	494	20X-1 93-99	158
6H-3 59-63	404	20X-3, 24-30	149
6H-4, 145-150	433	20X-4, 140-150	195
6H-5, 60-66	432	20X-5, 22-28	132
6H-6, 125-130	354	20X-6, 88-94	114
7H-1, 85-91	393	21X-3, 60-66	118
7H-3, 23-29	393	21X-4, 95-101	176
7H-4, 64-70	409	21X-5, 19-25	159
7H-4, 145-150	380	21X-6, 128-134	207
7H-6, 42-48	344	22X-1, 114-120	143
8H-1, 80-86	347	22X-3, 33-39	154
8H-5, 25-29 8H 4, 110, 116	438	22X-5, 00-00 22X 6, 114, 120	137
8H 4 145 150	304	22X-0, 114-120 23X 1 00 06	108
8H-6 37-43	344	23X-3, 81-87	148
9H-1, 67-73	318	23X-4, 132-138	88
9H-2, 138-144	306	23X-4, 140-150	152
9H-4, 84-90	194	23X-6, 88-94	139
9H-4, 145-150	278	24X-1, 23-29	121
9H-5, 135-141	219	24X-2, 121-127	87
10H-1, 88-94	160	24X-4, 46-52	140
10H-3, 7-13	186	24X-5, 92-98	93
10H-4, 68-74	123	25X-1, 22-28	110
10H-4, 145-150	227	25X-2, 86-92	152
10H-5, 109-115	201	25X-4, 42-40 25X 5, 05, 101	130
11H-2 36-42	221	25X-5, 95-101 26X-1 84-90	126
11H-4 10-16	187	26X-2, 140-146	71
11H-5, 80-86	214	27X-1, 34-40	187
11H-6, 137-143	217	27X-2, 121-127	122
12H-1, 41-47	209	27X-4, 31-37	169
12H-2, 112-118	239	27X-4, 140-150	203
12H-4, 25-31	223	27X-5, 108-114	174
12H-4, 145-150	253	28X-1, 42-50	114
12H-5, 83-89	210	28X-2, 97-103	129
12H-6, 143-149	149	28X-3, 107-112	182
15H-2, 71-77	183	29X-2, 85-91	169
13H 5 56 67	142	29A-3, 23-31 20X 4 112 110	1.39
13H-5, 30-02 13H-6, 132, 139	145	27A-4, 113-119 30X-4 140 150	140
14H-2 70-76	94	33X-4 140-150	1056
14H-4, 5-11	134	37X-4, 140-150	1119
14H-4, 145-150	190	39X-4, 140-150	944
14H-5, 116-122	102	45X-4, 140-150	860

tervals can, however, be elucidated using the high-resolution sampling data.

#### CONCLUSIONS

Silica pore-water concentrations in the top 50 mbsf faithfully record the presence of biogenic silica in organic-rich turbidites. Between 50 and 250 mbsf, that is, between 1 and 10 Ma, the silica porewater concentration is low and stable, pointing to the absence of biogenic silica in the organic-rich turbidites. Such an absence could in-



Figure 2. Silica pore-water concentration vs. depth for the interval of 0-75 mbsf at Holes 950A and 952A. Open circles = routine samples analyzed aboard ship; solid circles = high-resolution samples analyzed at Utrecht University immediately after the cruise.

dicate a change in source area, or in the northwest African upwelling system during that period.

About 280 mbsf in Hole 950A and below 290 mbsf in Hole 952A, enhanced levels of silica are observed in the pore waters, which indicates that biogenic silica is present again in the organic-rich turbidites. The high-resolution pore-water sampling in Holes 950A and 952A has resulted in the detection of potential intervals in which authigenic silica phases must have formed.

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