Reports

Interstitial Silica and pH in Marine Sediments: Some Effects of Sampling Procedures

Abstract. *The temperature at which the interstitial water was squeezed from a marine sediment had a profound effect on the measured interstitial silica concentrations which showed an average increase of 51 percent after the sediment was exposed to a temperature 20°C higher than the in situ temperature. Similar effects were not found for interstitial phosphate or alkalinity, but the* pH *was slightly higher in the water squeezed at the higher temperature. These temperature-induced changes were completed in a few hours. The use of filter paper can significantly lower the* pH *of expressed pore waters. Until some important questions about temperature effects are answered, all future data on the* pH *and silica concentration of pore waters of marine sediments should be obtained from samples extracted at in situ temperatures.*

The interstitial water in marine sediments is reported to have a silica concentration which is 100 to 800 μM higher than that in the overlying bottom water (*1–3*). These concentration differences imply a flux of silica out of the sediments, and a simple calculation shows the potential importance of this flux. Of over 150 cores taken for pore-water analyses in the Atlantic and Pacific oceans, about 80 were sampled for silica at a depth of 50 cm, and the average silica concentration at this depth was 400 μM. If the overlying water has an average concentration of 100 μM, then the linear gradient is 6 μM/cm. An estimate of the diffusion constant at 2°C (*4*) allows one to calculate an average flux from the sediments of 16.5 μg cm^{-2} year^{-1}. Thus for the world oceans (3.6×10^{18} cm^2) the total flux is 0.6×10^{14} g of SiO_2 per year, or about 14 percent of the river input of 4.24×10^{14} g of SiO_2 per year (*5*). Instead of linear gradients, many of the data seem to show curved gradients (*6*) which would make the estimated flux even higher.

To the best of our knowledge, the published data on silica concentrations in interstitial water have been taken from samples of sediment processed at room temperature. Mangelsdorf *et al.* (*7*) predicted that the temperature at which a sediment was squeezed would affect the "apparent" interstitial concentrations of exchangeable cations. Both Bischoff *et al.* (*8*) and Presley (*9*) found such effects for K^+, Mg^{2+}, and Ca^{2+}, but Bischoff and Ku (*2*) speculated that silica concentrations might not be affected by temperature.

In this report we present data from experiments designed to measure ways in which sampling procedures can alter the composition of interstitial water. We have studied these effects on silica and phosphate concentrations and on pH and alkalinity.

On 12 December 1970, a gravity core, core TR-091-3, was taken from a depth of 5092 m on the Bermuda Rise at 30°51'N, 67°33'W. It was 5.7 cm in diameter and consisted of 130 cm of brown foraminiferal lutite which appeared to be homogeneous. Sediments in this region are typically 30 to 40 percent calcium carbonate (*10*). The core was capped and immediately stored upright in a walk-in refrigerator at 0° to 3°C (*11*). The temperature near the sea floor in that area is 2.2°C. After 12 hours of storage, the core liner was slit while the core was still in the refrigerator, and, during the next 28 hours, one quarter of the core was cut into segments which were squeezed at 0° to 3°C to obtain the pore waters. The rest of the core was stored under Saran Wrap in the refrigerator for an additional 14 hours, and then half of the core was removed to the warm shipboard laboratory (21° to 23°C). The remaining quarter was left in the refrigerator wrapped in Saran Wrap and aluminum foil. After 2½ hours of warming, the temperature of the sediment in the half core had reached 20°C, and it was divided into quarter core segments and squeezed. Segments in the same position along the warm half core were squeezed at different times to provide a measure of the time course of any temperature effect.

All samples of sediment were squeezed with a hydraulically driven stainless steel squeezer similar to that of Manheim (*12*). The squeezer was designed to minimize the internal air space to which the expressed water was exposed. Each sample of pore water passed through two pieces of 9-cm filter paper (Whatman No. 42) which were placed over the filter plate in the bottom of the squeezer.

Table 1. Effect of warming time on the apparent interstitial concentrations of dissolved silica for core TR-091-3 from the Bermuda Rise (30°51'N, 67°33'W).

Depth interval of segment in core (cm)	Interstitial silica concentration of quarter core squeezed at 0° to 3°C (μM)	Half core squeezed at 21° to 23°C					
		Quarter A			Quarter B		
		Warming time (hours)	Interstitial silica concentration (μM)	Percent increase in silica	Warming time (hours)	Interstitial silica concentration (μM)	Percent increase in silica
0–10	81	3.8	127	57	26.3	135	67
10–25	99	8.6	152	54	23.7	155	57
25–40	111	10.7	166	50	13.6	173	56
40–55	125	12.7	179	43	11.6	184	47
55–70	130	22.4	182	40	9.5	187	44
70–90	128	25.2	188	47	7.2	189	48
90–100	120	27.4	190	58	2.5	173	44

Table 2. Effect of warming time on the apparent interstitial salinity, inorganic phosphate concentration, and *p*H for core TR-091-3 from the Bermuda Rise (30°51′N, 67°33′W).

Depth interval of segment in core (cm)	Quarter core squeezed at 0° to 3°C			Half core squeezed at 21° to 23°C					
				Quarter A			Quarter B		
	Inorganic phosphate (*μM*)	*p*H	Salinity (‰)	Inorganic phosphate (*μM*)	*p*H	Salinity (‰)	Inorganic phosphate (*μM*)	*p*H	Salinity (‰)
0–10	0.30		35.0	2.12	7.23	35.0	1.76	7.22	35.9
10–25	1.92		35.2	1.56	7.39	35.2	1.91	7.46	35.7
25–40	1.92	7.31	35.0	1.83	7.43	35.0	1.90	7.46	35.2
40–55	1.81	7.14	35.0	1.76	7.38	35.2	1.70	7.38	35.0
55–70	1.71	7.15	35.0	1.80	7.42	35.4	1.83	7.34	35.0
70–90	1.81	7.27	35.0	3.42	7.45	35.5	2.78	7.37	35.0
90–100	1.81		35.0	2.12	7.26	35.2	2.01	7.19	35.0

The water was collected in plastic syringes which were capped and stored at 2°C until the *p*H was measured with a water-jacketed capillary electrode system (Radiometer models G297 and K497). The cap was taken off the end of the syringe, and the inlet capillary tube of the electrode chamber was inserted into the tip of the syringe. Samples of pore water (50 μl each) were sucked into the electrode chamber until a reproducible potential between glass and reference electrodes was obtained. The *p*H values reported below for cold- and warm-squeezed pore waters were obtained at a measurement temperature of 25°C and were reproducible to within ± 0.02 *p*H unit. This approach has the advantage that the *p*H is measured without the need to expose the pore water to the open air and to risk the loss of CO_2 and also without the necessity of inserting electrodes into the mud (*13*). After the *p*H measurements were made, the pore water samples were filtered through 0.45-μm Millipore membrane filters and stored in polyethylene bottles at 0° to 3°C until they were analyzed for silica, phosphate, alkalinity, and salinity.

Silica and phosphorus concentrations were measured according to the methods of Strickland and Parsons (*14*), and salinity was measured to within 0.5 part per thousand by a temperature-compensated hand-held refractometer. Total alkalinities were measured on 4-ml samples. Standardized acid (1 ml) was added, and the mixture was stirred and allowed to stand for 20 to 30 minutes with occasional swirling to allow CO_2 to escape. The *p*H was measured as before, and the total alkalinity calculated (*15*).

After 3 months of storage under Saran Wrap and aluminum foil in a refrigerator (0° to 1°C), the last quarter was cut into segments and squeezed at 0° to 3°C. The samples of pore water obtained were analyzed for salinity, silica, *p*H, and alkalinity for comparison with the earlier data for cold-squeezed water.

After the analyses on shipboard were completed, several control experiments were performed to examine the possibility of contamination from the materials used in extraction. The filter paper used in the squeezer seemed to show the greatest effects. Seawater with a known *p*H and known concentrations of silica and phosphorus was passed through fresh Whatman No. 42 filter paper inside the squeezer. The ratio of the volume of seawater passed to the pad area simulated that during sediment squeezing (20 to 50 ml of pore water to two 9-cm pads). The *p*H decreased 0.2 *p*H unit. The decrease is significant and may help to explain, for example, why Presley reported that the *p*H values of squeezed pore waters were lower than those measured by the insertion of electrodes into the mud (*9*). This release of hydrogen ions by the filter paper could reduce total alkalinities by about 0.1 meq/liter. The use of filter paper also increased the phosphorus concentration slightly (5 to 10 percent) but had no effect on the silica concentration. Cold storage of seawater in plastic syringes followed by filtration through 0.45-μm Millipore pads and then by further cold storage in polyethylene bottles did not alter the concentrations of silica and phosphate in the seawater. The cold storage of seawater in the core liner did not alter the concentrations of silica and phosphate or the *p*H during a period of at least 3 days. Exposure to Saran Wrap did not alter the *p*H of seawater.

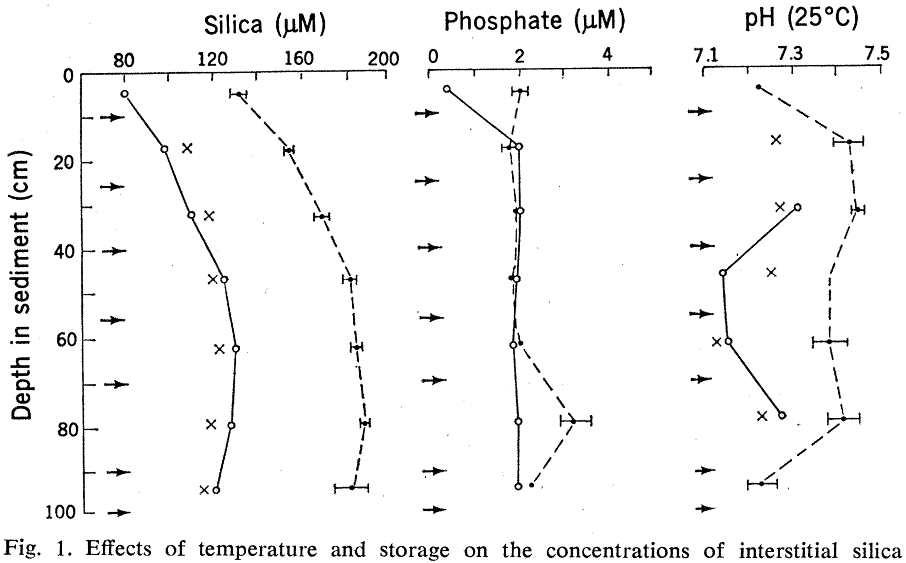

Fig. 1. Effects of temperature and storage on the concentrations of interstitial silica and phosphate, and on the *p*H in core TR-091-3. Arrows denote boundaries between segments, and each point is plotted in the center of the segment. Temperatures of squeezing were as follows: cold (solid lines), 0° to 3°C and warm (broken lines), 21° to 23°C. The lengths of the horizontal bars on the curves for sediment squeezed warm represent ranges of values for corresponding segments squeezed after different warming times. The points marked with an "X" are values for the refrigerated quarter squeezed after 3 months of storage.

Table 3. Effect of temperature on the rate of silica release from surface sediment taken near core TR-091-3 (ratio of solid to liquid = 3.5 g of sediment in 500 ml of seawater).

Time (hours)	Supernatant silica concentration (μM)		Cumulative total dissolved silica released (μg)	
	2° to 4°C	25°C	2° to 4°C	25°C
0.00	1.0	1.0	0	0
0.50	2.3	3.6	39	78
1.00	2.3	4.8	39	110
1.50	3.0	5.8	56	134
2.25	3.4	7.2	64	239
3.00	3.9	8.8	73	268

Tables 1 and 2 show the results of most of the analyses made on interstitial water squeezed from the core on shipboard, and some of the data are plotted in Fig. 1. Figure 1 also includes the silica and *p*H data obtained on water squeezed from the last quarter of core TR-091-3 after 3 months of storage.

Increased temperature caused a profound effect on the concentration of silica in the interstitial water: a 40 to 67 percent increase (average, 51 percent) was associated with a warming of approximately 20°C. This effect is much greater than any reported by Bischoff *et al.* (*8*); the maximum change they reported was for potassium which showed an average increase of 0.8 percent per degree Celsius. The average increase in interstitial silica for core TR-091-3 was 2.6 percent per degree Celsius. Neither the absolute increase nor the percentage increase varied with warming time. Therefore, the temperature effect on the concentration of interstitial silica was completed in 2½ hours or less.

The temperature-related increase in the interstitial silica concentration must have been due to the release of silica from sediment particles. The following experiment was performed to confirm the effect of temperature on the release of silica from sediments. Core TR-091-4 was taken at 30°54′N, 67°31′W, adjacent to core TR-091-3. Sediment from the top 7 cm of core TR-091-4 was exposed to 500 ml of low-silica seawater at 2° to 4°C and at 25°C, and changes in the supernatant silica concentrations were monitored during the first 3 hours of exposure. The bottles were shaken 25 to 30 minutes before each sampling, and data on the release of silica are given in Table 3. After 3 hours, the warmed sediment had released 76 μg of SiO_2 per gram of total sediment whereas the cold sediment had released only 21 μg of SiO_2 per gram. Thus the rate of release of silica was increased nearly fourfold by an increase in temperature of 20°C.

It is not known what reaction may be responsible for the temperature effect observed for silica. The temperature increase may cause a quick adjustment of solubility equilibria for the mineral phases present or perhaps the desorption of some adsorbed silica. Published data on the interactions of dissolved silica with clays or marine sediments (*3, 16, 17*) may be interpreted in terms of solubility equilibrium (*17*), as may the temperature-induced release of silica in the sediment of core TR-091-3. However, if that sediment is 50 percent water, then a release of only 3 μg of SiO_2 per gram of sediment would account for the increased concentration of silica. Such a small amount of silica could easily be adsorbed on the surfaces of clay or ferromanganese particles in the sediment and be released on warming. The release upon warming of about the same amount of silica from each segment of the core is in accord with the apparently homogeneous nature of the sediment.

The estimate of the diffusive flux presented above is therefore too large by some amount. If all warmed pelagic sediments undergo an average increase in the interstitial silica concentration of 51 percent, then the total flux, calculated as before, would decrease from 0.6×10^{14} to 0.33×10^{14} g of SiO_2 per year.

There was no effect caused by warming on the concentration of interstitial phosphate or on the salinity (Fig. 1 and Table 2).

The *p*H values in Table 2 fall within the range of other reported *p*H values for interstitial waters, namely, 7.0 to 8.6 (*9, 18*). However, if the effect of filter paper on *p*H is independent of the temperature, then warming produced an average increase of 0.13 in the *p*H of the interstitial water (Fig. 1). This change was completed in 7 hours or less. The probable reason for an increase in the *p*H of the interstitial water with temperature is a shift in the equilibria between interstitial solutes and mineral phases, but it is possible that higher temperature causes an outgassing of CO_2.

Warming caused no significant or consistent changes in alkalinity. For segments between 25 and 90 cm, the total alkalinities obtained for two cold-squeezed samples were 2.25 and 2.35 meq/liter, and the range of total alkalinities obtained for five warm-squeezed samples was 2.26 to 2.43 meq/liter. There were no trends in alkalinity with depth.

The data on pore waters from the quarter core stored for 3 months at 0° to 3°C were obtained to study the effect of the release of hydrostatic pressure. The results show that any pressure effects on interstitial silica and *p*H are probably completed in 14 hours or less. Moreover, the technique of wrapping the quarter core in Saran Wrap and aluminum foil seems to have prevented loss of CO_2 from the cold sediment. The interstitial alkalinities from the cold-stored sediment did not show a consistent change. Interstitial salinities did not change in 3 months of cold storage.

In summary, the temperature of squeezing can alter the measured interstitial silica concentration greatly and the measured interstitial *p*H slightly. Also, at least one kind of filter paper can alter the *p*H and alkalinity of pore waters. The effect of temperature on the interstitial silica concentration and *p*H in other types of marine sediment should be investigated, and, in view of the initial temperature cycle during retrieval (*11*), the reversibility of the temperature effects reported here should be examined as well. Until these questions are examined, all measurements of interstitial silica concentration and *p*H should be made on pore waters extracted at in situ temperatures.

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Infrared Rainbow

Abstract. *Radiation in the near-infrared spectral region should produce a rainbow that is not visible to the human eye. An infrared photograph is shown which displays the primary bow, the secondary bow, and two supernumerary bows inside the primary bow.*

The rainbow has long been a cause for wonder and delight to observers. The explanations of its origin and of a variety of its subtle features have paralleled the development of the principles of geometrical and physical optics. To a person who takes pleasure in contemplating the rainbow, the question "Does there exist an infrared rainbow? " would seem to be one of natural interest. I have been unable to find the question raised in any published literature and, although the subject may not be profound, it raises an interesting speculation.

For the infrared rainbow to exist, the radiation from the sun, after having traveled through a long atmospheric path, must still have an infrared component. Measurements show (*1*) that, even for long slant paths through the atmosphere, there is appreciable energy in the near-infrared region out to wavelengths of at least 2.5 μm (2500 nm). Another requirement is that raindrops must be transparent to the radiation forming the bow. For path lengths as great as a centimeter, water transmits appreciably for wavelengths out to about 1.3 μm (*2*).

The conclusion from these considerations is that there should indeed exist a rainbow of near-infrared radiation. To record this bow, I used Eastman Kodak infrared film IR 135, in conjunction with a Kodak 87C filter. This combination of film and filter made it possible to isolate a band pass, centered at 865 nm, which is separated from the visible part of the spectrum. Figure 1 shows the film sensitivity and filter transmittance along with the spectral sensitivity of the human eye, which serves to define the visible region of the spectrum.

The infrared photograph (Fig. 2) shows that the primary infrared rainbow (resulting from one internal reflection in the raindrops) is quite bright. Outside this primary arc, the secondary rainbow (resulting from the two internal reflections) is visible. Just inside the primary bow are two supernumerary bows which can be explained as an interference phenomenon arising from rays which emerge from the raindrop at the same angle but which have taken different paths through the drop [see Humphreys (*3*) for a more complete discussion of this effect].

These effects are, of course, known and understood from their occurrence in visible light (and one could predict their occurrence in the near-ultraviolet spectral region). There is, however, a

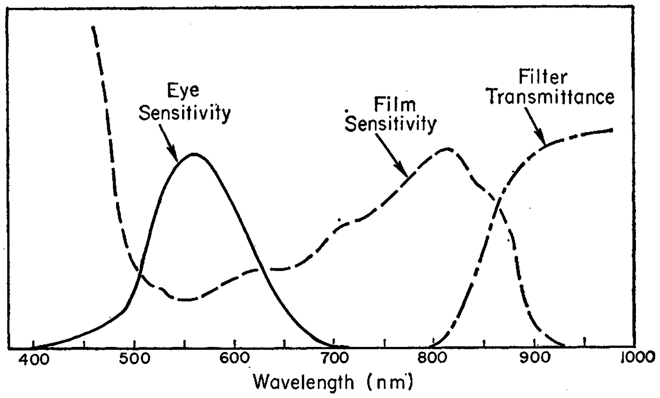

Fig. 1 (left). Relative spectral sensitivity of the human eye (——) [data for foveal cones taken from Wald (*4*)]. Relative spectral sensitivity of Eastman Kodak infrared film IR 135 (– – –) (data from Eastman Kodak Co.). Transmittance of the Eastman Kodak 87C infrared transmitting filter (-—-) (data from Eastman Kodak Co.). Fig. 2 (right). Photograph of the infrared rainbow.