Reports

In situ Sampler for Marine Sedimentary Pore Waters: Evidence for Potassium Depletion and Calcium Enrichment

Abstract. *A device for sampling the interstitial waters of deep-sea sediments in situ has been developed and tested. The sampler collects a series of samples over a depth of 1.5 meters in the sediment and thus makes possible the accurate delineation of chemical gradients existing in the pore waters. Samples collected in the North Atlantic indicate that significant gradients of* K^+ and Ca^{2+} *exist in the sediments sampled. Interstitial solutions sampled between Ireland and Cape Cod, Massachusetts, are characterized by the depletion of* K^+ *and the enrichment of* Ca^{2+}.

Many studies have shown that the pore waters of marine sediments differ significantly in composition from the overlying sea waters (*1–4*). Such differences are produced mainly by slow reactions between the solids of sediments and the trapped interstitial solutions. The chemical gradients between the pore fluids and the overlying ocean water that result from these reactions produce diffusive fluxes of constituents across the seawater-sediment interface. Even if the gradients are very small, these fluxes may be of great importance in geochemical mass balances. Average gradients of less than 0.1 percent per centimeter of depth could produce global fluxes of many constituents (Mg^{2+}, K^+, Na^+, Cl^-, SO_4^{2-}) that would be greater than the total river inputs to the sea. In order to accurately measure such small gradients, it is essential that reliable sampling be coupled with very precise chemical analysis.

All of the data collected to date on the composition of pore waters from pelagic sediments have been obtained from water samples taken from sediment cores, usually by squeezing (*5*). Mangelsdorf *et al.* have shown (*6*) that the warming of seawater-clay suspensions significantly alters the composition of the interstitial waters. This effect has subsequently been shown to occur in marine sediments (*7, 8*). Typical changes (in percent) for sediments warmed 17°C are as follows (where positive values indicate enrichment on warming and negative values indicate depletion on warming): K^+, +20; Na^+, +1; Mg^{2+}, −6; Ca^{2+}, −5; the concentrations of SO_4^{2-} and Cl^- are not significantly affected (*8*).

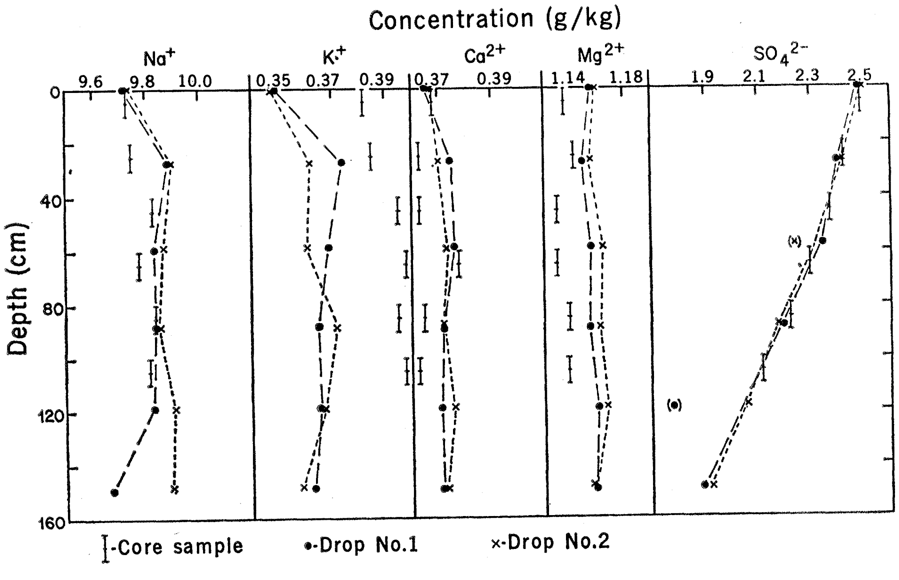

Fig. 1. Results of tests of the in situ sampler in Buzzards Bay, Massachusetts. Concentration data are presented as a function of depth in the sediment. The core sample symbol denotes the interval of sediment from which the pore fluid was extracted. Separate lowerings of the sampler are identified as drop No. 1 and drop No. 2. The data points in parentheses are suspect.

Several investigators have cooled their core samples to approximately bottom water temperatures before squeezing (*9*). Unless the bottom temperature is reproduced exactly, some residual error is likely, even if the thermal effects are fully reversible (it is not known whether this is so). Moreover, a core undergoes a large pressure change in being brought from the floor of the deep sea to the surface, and equilibrium solubilities are altered, particularly in the carbonate system.

In an effort to avoid these problems we have developed an in situ water-sampling probe which extracts samples of filtered water from the sediment at several depths simultaneously and also from the overlying bottom water. The probe is basically a 2-m length of heavy-wall stainless steel tubing, with a pointed tip for penetration and with five filter-covered sampling ports (each filter = 6 cm²) spaced 30 cm apart along the length. Above these is a broad base plate to halt penetration and above that one further port to sample overlying water.

The suction required to draw the samples into the ports is provided by a compressed heavy-duty spring working the piston of a large master cylinder (120-cm³ displacement). Aboard ship, before the probe is lowered, this master cylinder is charged with water hydraulically to a pressure of 500 pounds per square inch (34 atm) and then closed off. All the rest of the interior volume of the probe is completely filled with water and left open to ambient pressure until suction is applied.

Penetration of the probe into the sediment triggers a toggle valve, releasing the compression and permitting the piston to apply suction to the probe interior. Filtered water drawn in at each sample port is stored in a spool of capillary tubing (15-ml storage volume). To limit the volume of sample entering at any port a passive slave cylinder (20-ml volume) is interposed between each storage spool and the probe interior.

After approximately 30 minutes the probe is withdrawn from the sediment, the toggle valve trips back to its original position, and sampling ceases. Back aboard the ship, the probe interior is hydraulically pressurized; in this way the samples from the storage spools are expressed into syringes now inserted at the sample ports. As each sample is recovered, it is split into sequential aliquots of 3 to 4 ml each for separate analysis.

The sequential storage of samples in the capillary tubing is the most important single design feature of this probe. Seawater is carried into the sediment in the filters; some initial leakage of bottom water along the shaft may occur. These effects are usually eliminated entirely after the first 2 ml of sample are drawn into the sampler. Sequential storage of the sample allows us to isolate and avoid the contaminated portion (*10*).

In order to show that samples taken with our in situ sampler corresponded to the pore waters at the appropriate depths in the sediments, it was necessary to compare a chemical variable which could be determined without any temperature error in water squeezed from core samples. This variable should also be markedly depth-dependent in the sediment column. The SO_4^{2-} concentration has been shown to be insensitive to the temperature of squeezing (*8*) and is also markedly depleted in the pore fluids of anoxic sediments. Accordingly, several tests of the sampler have been carried out in Buzzards Bay, Massachusetts, an area of anoxic sediments with extensive reduction of interstitial SO_4^{2-}.

Figure 1 shows a comparison of the pore waters of Buzzards Bay sediment obtained from two trials of the in situ sampler with water squeezed from a gravity core taken at the same location. Cations were analyzed by atomic absorption; SO_4^{2-} was determined gravimetrically. Data from the two sampling techniques are in good agreement with respect to the SO_4^{2-} concentration (two aberrant points are presumably due to analytical error; they deviate in the wrong direction to be explained by seawater contamination) and demonstrate the feasibility of collecting uncontaminated samples in situ.

The differences between the cation concentrations of samples obtained by the two methods serve to emphasize the advantage of in situ sampling. The differences in Ca^{2+}, Mg^{2+}, and K^+ concentrations are about the size of the changes to be expected in core samples due to the increase of approximately 8°C from the in situ temperature to the squeezing temperature. The Na^+ values are very slightly lower in the water from the warmed core, contrary to the usual direction of the temperature effect, but the differences are, for the most part, less than the precision of the analysis (± 0.5 percent).

On a recent crossing of the North Atlantic from Ireland to Cape Cod, Massachusetts, aboard R.V. *Chain*, a series of 29 lowerings were made, of which 24 yielded usable water samples, with all but two lowerings at depths greater than 1800 m. The results of analyses by difference chromatography (*11*) of solutions from five widely spaced stations are summarized in Fig. 2. The data represent profiles from sediments of the continental slope (stations C and D), abyssal plains (stations K and T), and the eastern flank of the mid-Atlantic ridge (station H). Because of mechanical difficulties, the uppermost port (above the base plate) was sealed off, preventing the collection of bottom water samples. Bottom water concentrations presented in Fig. 2 represent typical deep-water values for the Atlantic. The use of these data as opposed to actual samples does not introduce significant uncertainty in the interpretation of the results since the variations of Ca^{2+} and K^+ in deep ocean waters is small compared to the differences between the concentrations of Ca^{2+} and K^+ in pore water and the concentrations of these ions in ocean water (*12*).

The data demonstrate that significant concentration gradients do exist in the uppermost sediments of the sea floor in a variety of environments. In the top 30 cm of sediment the Ca^{2+} enrichments reach 4.5 to 6 percent. Interestingly, at four of the five stations the Ca^{2+} concentrations decrease with depth after reaching maximum values in the interval from 30 to 90 cm.

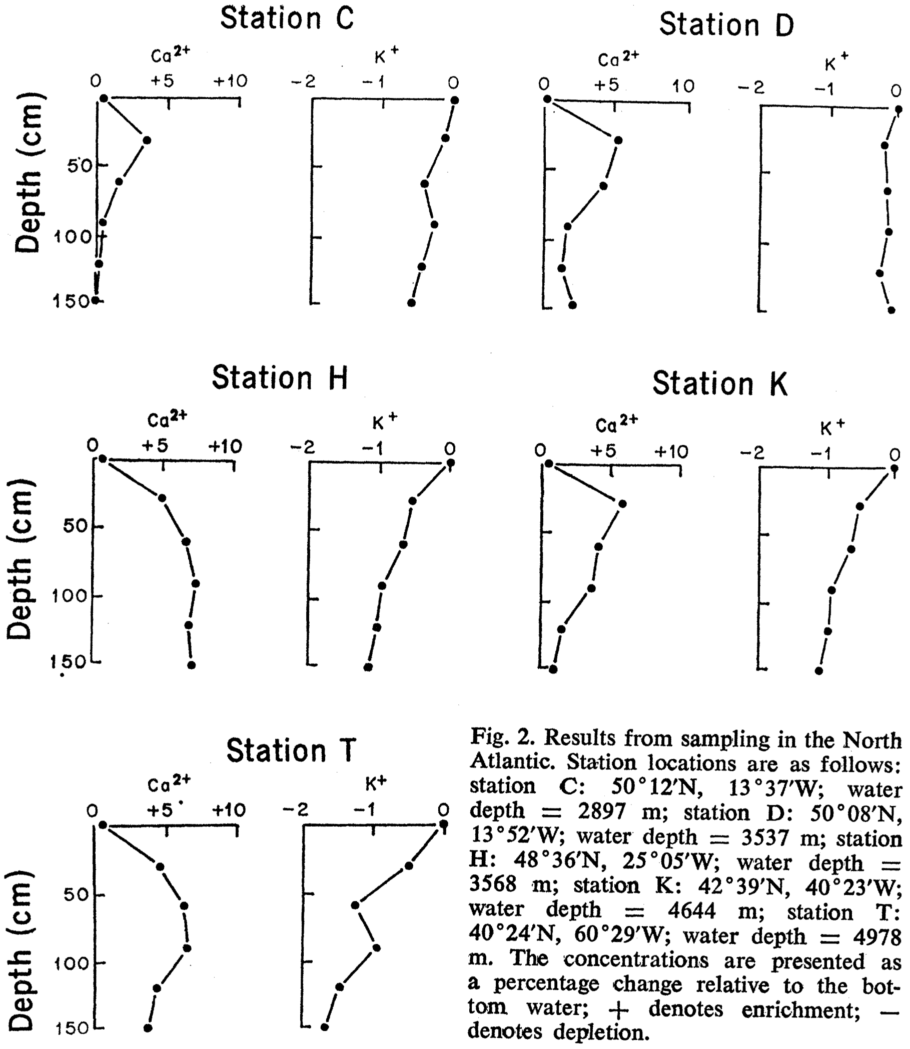

Fig. 2. Results from sampling in the North Atlantic. Station locations are as follows: station C: 50°12'N, 13°37'W; water depth = 2897 m; station D: 50°08'N, 13°52'W; water depth = 3537 m; station H: 48°36'N, 25°05'W; water depth = 3568 m; station K: 42°39'N, 40°23'W; water depth = 4644 m; station T: 40°24'N, 60°29'W; water depth = 4978 m. The concentrations are presented as a percentage change relative to the bottom water; + denotes enrichment; − denotes depletion.

Depletions of 0.2 to 0.6 percent are found at 30 cm for K^+, increasing further with depth (except at station D) (*13*).

We have also analyzed for Na^+ and Mg^{2+} but have found that NH_4^+, present in some marine sediments, affects our results. These data have not been reported in the face of this uncertainty. The Ca^{2+} and K^+ results are not subject to significant interference by NH_4^+.

These changes in interstitial K^+ differ quite markedly from those reported previously in studies of core sample extracts. Whereas earlier investigations of the upper few meters of pelagic sediments with few exceptions have shown K^+ enrichment, relative to ocean waters, in the pore fluids (*2, 3, 14*), we have found K^+ depletion in all of our in situ samples from such sediments. This difference might have been anticipated since the enrichments previously reported can, in almost all cases, be attributed to temperature-induced artifacts.

The sediments we have sampled differ widely in their environment of deposition, suggesting that K^+ depletion in interstitial solutions is widespread and perhaps generally characteristic of pelagic sediments in the North Atlantic. The pore water studies of the Deep Sea Drilling Project provide supporting evidence for the uptake of K^+ in most pelagic sediments (*15*). It was found that the K^+ concentration most commonly decreases with depth in the sediment. Those data were derived from pore water samples collected over depth intervals of several hundreds of meters in a variety of sediment types, revealing long-term trends in sedimentary reactions. The in situ data reported here indicate that this K^+ uptake is already under way even in the youngest, uppermost sediments.

The Ca^{2+} enrichments we find in the upper meter of sediment in all of the oceanic sediment profiles thus far determined are considerably larger than those previously observed in piston core studies. These enrichments probably result from the dissolution of $CaCO_3$. The bottom waters at these sites are almost certainly undersaturated with respect to skeletal calcite in the sediments, and Ca^{2+} enrichment through solution is to be expected (*16*). The decrease in Ca^{2+} with depth, seen at four of the five sites, may be the result of bacterial oxidation of organic matter and the consequent increase of interstitial HCO_3^-. However, definite conclusions regarding this hypothesis require additional data on HCO_3^- and SO_4^{2-} concentrations.

The gradients of interstitial Ca^{2+} and K^+ observed by means of in situ sampling are such that, if widespread over the rest of the world ocean, they could produce diffusive fluxes that are comparable to the annual inputs of these ions by the rivers of the world. In the case of Ca^{2+}, the upward diffusive flux merely returns a part of the great downward flux of particulate $CaCO_3$. In the case of K^+, the downward flux is in the direction required to balance river input.

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10. The sequential SO_4^{2-} data from which Fig. 1 was constructed illustrate this point. The sequential analyses (in grams per kilogram of water) by depth are: 0 cm: 2.46, 2.49*, 2.50, 2.42, 2.49, 2.49*; 30 cm: 2.40, 2.39, 3.18*, 2.40, 2.43, 2.43*; 60 cm: 2.34, 2.34, 2.48*, (2.24), 2.47, 2.43*; 90 cm: 2.19, 2.34*, 2.18, 2.57*; 120 cm: (1.78), 2.28*, 2.05, 2.07, 2.58*; 150 cm: 1.89, 2.13*, 1.92, 2.18*. The values in parentheses are those noted in Fig. 1 as being subject to suspected analytical error; the starred values are analyses of aliquots that include some or all of the first 2 ml drawn into the sampler. In only one case (60 cm) do analyses of aliquots not containing the first 2 ml differ by more than the analytical uncertainty. All aliquots are routinely analyzed to ensure the accuracy of the data.
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13. Actual sampling depths in the sediment can be less than expected, because of nonvertical penetration, or greater than expected, because of sediment compression and superpenetration. The same uncertainties afflict coring or any other remote bottom-sampling method and can probably be completely eliminated only by direct emplacement of the probe from a deep-sea submersible. For the time being, we are satisfied with the degree of reproducibility indicated by Fig. 1, where the SO_4^{2-} profiles from two probe lowerings are in good agreement with one another and with the profile obtained from a core.
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17. We thank P. Bowker and C. Olson for invaluable assistance in the development of the sampler. We thank Dr. F. T. Manheim for his instructive criticism of the manuscript. Financial support has been provided through AEC research contract AT(11)-3119 and NSF grant GA-32323. Woods Hole Oceanographic Institution contribution number 3029.

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Heavy Elements in Surface Materials: Determination by Alpha Particle Scattering

Abstract. *The backscattering of alpha particles from a radioactive source can be used to determine the amounts of heavy elements such as lead in surface materials. A light, portable instrument has been constructed that can be used as a survey meter for painted surfaces. It has a sensitivity of 0.3 percent by weight in a measurement of a few minutes.*

Concern about lead poisoning in young children has led to interest in portable instruments that can detect lead in paints used in dwellings and children's toys (*1*). Currently, most city housing and health codes limit the lead content of surface coverings to 0.5 percent by weight (*2*).

It has been shown (*3*) that the elastic scattering of alpha particles can be