Reports

Composition of Interstitial Waters of Marine Sediments: Temperature of Squeezing Effect

Abstract. *Warming of samples of marine sediments to room temperatures prior to the extraction of interstitial water accounts for the apparent enrichments of potassium ion (13.3 percent) and chloride ion (1.4 percent) and depletions of magnesium ion (2.5 percent) and calcium ion (4.9 percent). These differences are the result of changes in ion-exchange selectivity as a function of temperature.*

In a recent study of the significance of the almost universally observed enrichments of potassium in interstitial water extracted from marine sediments, Mangelsdorf *et al.* (*1*) reported that these enrichments are due, in part, to temperature effects introduced during sampling and squeezing. Because of the shifting of ion-exchange equilibria with temperature, these investigators suggest that changes in composition will take place rapidly in the interstitial fluids as the sample approaches laboratory or shipboard temperature. Most investigators of interstitial fluids, including ourselves, have customarily squeezed the sediments at laboratory or shipboard temperatures (*2*). Therefore, until the warming effect is evaluated on natural sediments, the validity of published data on pore water geochemistry is suspect. Implications of this effect on geochemical balance calculations (*3*) are rendered even more important. Mangelsdorf *et al.* calculate, on the basis of the published data on interstitial water, that the rate at which potassium is diffusing from the sediments to seawater is approximately three to five times as great as the rate at which potassium is being introduced into seawater by the rivers. Therefore we tested the effect of sample warming by taking a series of duplicate samples from a freshly collected core and then squeezing one set at *in situ* temperature and the other at laboratory temperature.

A piston core of reducing green clayey sediment 420 cm long was taken by the University of Southern California's R.V. *Velero IV* from the San Pedro basin. Samples were taken immediately on board by sectioning the core at each sampling point and extracting two cylindrical plugs of sediment (2 cm in diameter, 4 cm in length) from the center portion of each section. The plugs were then each placed in a 2-ounce bottle with a polyethylene-sealing screw cap. In order to maintain constant water vapor pressure in the bottle, the excess space was filled with a Mylar-wrapped, seawater-dampened laboratory tissue. The bottles were placed in a portable refrigerator and transported to the laboratory the same day. A sample of bottom water was also taken.

Samples in the temperature-controlled group (set A, Fig. 1) were then squeezed at *in situ* temperature (5°C) by means of a refrigerated passivated stainless steel hydraulic squeezer (*4*). The second group of samples (set B) was removed from the refrigerator, but not from the bottles, for 1 hour prior to squeezing; the same squeezer was used for this group but this time squeezing was done at room temperature (22.5°C).

The extracted water and a sample of the bottom water were then filtered (pore size, 0.22 μ) and analyzed in triplicate for potassium, magnesium, and calcium by atomic absorption spectroscopy (1 to 2 percent precision), and for chloride by an automatic amperometric titration (Buchler Instruments, Fort Lee, N.J.; 0.1 percent precision).

The plot of the concentration as a function of depth (Fig. 1 and Table 1) clearly shows a rather constant increase of potassium, averaging 13.3 percent enrichment, in the laboratory-equilibrated samples (group B) as compared with that in the refrigerated samples (group A). Mangelsdorf *et al.*

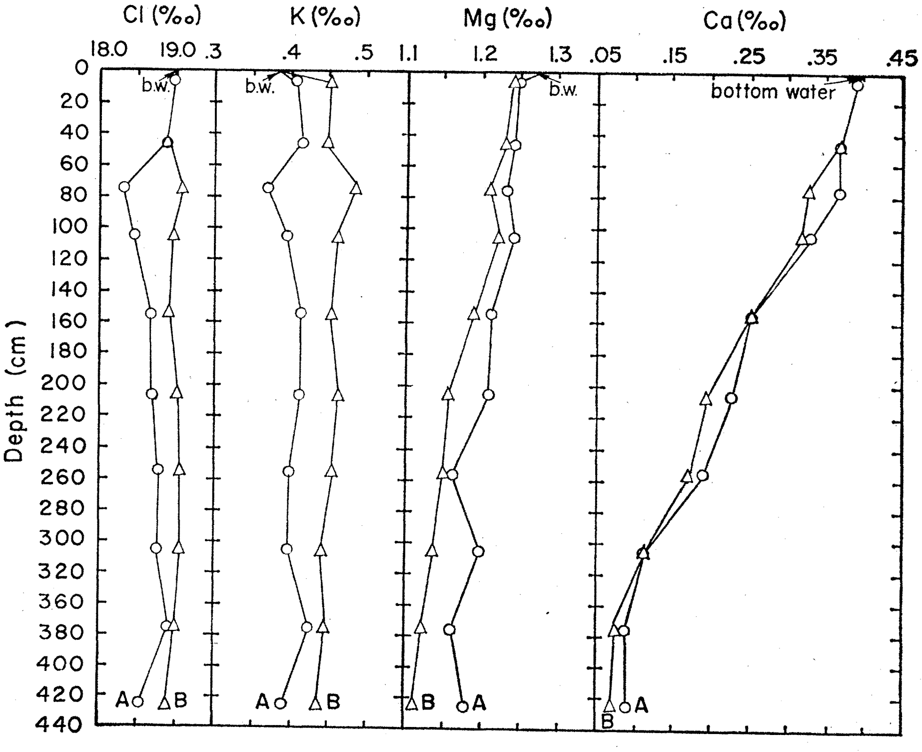

Fig. 1. Relationship of depth to concentrations (in parts per thousand) of chloride, potassium, magnesium, and calcium in interstitial water from the San Pedro basin; *A* refers to samples squeezed at *in situ* temperature (5.0°C), and *B* refers to those equilibrated to laboratory temperature (22.5°C) for 1 hour prior to squeezing. Core location, 33°28′12″N, 118°20′09″W; water depth, 950 m.

Table 1. Averaged composition and relative changes of pore water for top 4 m of sediments from the San Pedro basin.

Ion	Average composition (‰)			Changes due to temperature effect (A to B)	
	Group A	Group B	Bottom water	Change (%)	Change (meq/kg)
K	0.403	0.456	0.382	+13.3	+1.3
Mg	1.21	1.18	1.27	− 2.48	−2.4
Ca	0.24	0.23	0.40	− 4.87	−0.6
Cl	18.70	18.96	18.95	+ 1.39	+7.0

found a 1 percent enrichment of potassium per each 1.5°C temperature increase for a sediment containing equal proportions of bentonite clay and seawater (a typical average ratio for the upper few meters of deep marine clayey sediments). If we compare this to our 17°C difference (between *in situ* and laboratory temperatures) the predicted potassium enrichment would be 11.3 percent, which is rather close to our observation.

However, the samples squeezed at the *in situ* temperature display a 5.5 percent average enrichment of potassium over that of the bottom water, thus indicating there is a "true" *in situ* enrichment due to causes other than the temperature of squeezing effect. Work in progress on other cores from various locations indicates this "true" enrichment can reach 26 percent.

On the other hand, slight depletions of magnesium and calcium (Fig. 1 and Table 1) of 2.48 percent and 4.87 percent, respectively, occur during sample warming. Also, the general trend toward lower concentrations of magnesium and calcium with depth for both laboratory-equilibrated and refrigerated samples has been observed in reducing sediments (*5*) and is attributed to removal as magnesium and calcium carbonates during reduction of sulfate by bacteria. Chloride is rather strongly affected by the sample warming process, being enriched by an apparent 1.39 percent.

Ion-exchange capacities as a function of temperature have been only sketchily studied. Hofmann and Endell (*6*) found that heating montmorillonite to moderate temperatures changes the replaceability sequence of cations. The relative changes with temperature evidently depend very strongly on several variables including the type of clay mineral. Qualitatively, therefore, for sediment in the San Pedro basin, the ion-exchange capacity for K^+ decreases with temperature, thereby causing K^+ to be expelled to the pore water, whereas the ion-exchange capacities for Ca^{2+} and Mg^{2+} increase with temperature, thus allowing these ions to be taken up from the pore water. Since for K^+, Mg^{2+}, and Ca^{2+} the number of equivalents lost from the pore water is greater than the number added (Table 1), the gain in milliequivalents, to maintain electrical neutrality, is most likely provided by sodium. This would require an increase in Na^+ of 0.04 percent, which is beyond our analytical precision for Na and, therefore, difficult to test.

Changes in the concentration of chloride can be explained in terms of a similar temperature effect on anion-exchange capacities. Clay minerals exhibit considerable anion-exchange capacity, reaching 20 to 30 meq per 100 g for kaolinite and montmorillonite (*7*). Although temperature studies on anion-exchange capacities are lacking, one might expect behavior similar to that of cation-exchange materials. The observed Cl changes average 0.26 percent; if we assume a clay-water ratio of 1 to 1, this would be equivalent to a change in the exchange capacity of the sediment for Cl of only 0.7 meq per 100 g of sediment, a small change compared to the total capacity. Electrical neutrality is probably maintained by similar but opposite changes in sulfate or bicarbonate ions.

A quantitative prediction of the degree of change of pore water chemistry would be impossible, since ion-exchange capacities, and hence changes of capacities with temperature, depend on such variables as the type of clay mineral, crystal size, and the clay-to-pore water ratio. Therefore, we conclude that for an accurate analysis of pore water chemistry, extraction of the pore water must be accomplished at the *in situ* temperature of the sediment.

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Early Canid Burial from the Western Ozark Highland

Abstract. *A dog skeleton unearthed at Rodgers Shelter, Benton County, Missouri, came from a zone dating at approximately 5500 B.C. The animal, buried in a shallow pit beneath a tumulus of limestone rocks, is one of the earliest instances of canid interment to be recorded for North America.*

A few years ago the dog, *Canis familiaris*, was believed to have arrived in North America about 500 B.C. following its entry from Asia (*1*); since then, discoveries in earlier contexts have proved that both large and small varieties of *C. familiaris* were present much earlier, perhaps as early as 8400 B.C. (*2*). Evidence now suggests that the practice of interring dogs had been initiated by 5500 B.C., a trait that was later commonly performed by some American Indian groups.

This new date has been derived from the discovery of a small, adult dog, buried in a prepared grave, from the Archaic deposits of Rodgers Shelter in Benton County, Missouri (*3*). The skeleton, found during the summer of 1966, was covered by a small tumulus of dolomite stones beneath 2.7 m of later cultural deposits. The position of the rocks near the base, which were tilted down and inward, suggests that a shallow basin-shaped pit had been prepared for the burial before the rock covering was added.

The date of interment was deter-