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25. Sr-ISOTOPIC EVIDENCE FOR LEAKAGE OF PORE WATER FROM CLAY-SILT CONFINING UNITS TO THE ATLANTIC CITY 800-FOOT SAND, ATLANTIC CITY, NEW JERSEY[1]

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ABSTRACT

The evolution of water quality in confined aquifers in the New Jersey Coastal Plain may be affected by leakage of pore water from the adjacent confining units. We investigated the distribution and sources of solutes, particularly Sr, in pore water mechanically extracted from clay-silt core samples collected from depths of 552–840 ft (168–256 m) in the lower Miocene Kirkwood Formation at Atlantic City, New Jersey (Ocean Drilling Program Leg 150X). The sampled sediments consist of thin clay-silt stringers in the upper part of the Atlantic City 800-ft sand, a major aquifer, and the massive clay-silt units above and below it. The distribution of Sr and the ratio of ^{87}Sr to ^{86}Sr in the pore water and adjacent shell material were used to identify the possible sources of, and physical processes that may affect the distribution of, Sr in the pore water.

Concentrations of Sr in 14 pore-water samples from the clay-silt unit above the aquifer and the clay-silt interbeds in the upper part of the aquifer ranged from 2.74 to 28.19 µM/L; those in the four pore-water samples from the clay-silt unit below the aquifer ranged from 0.52 to 7.30 µM/L. Concentrations of Sr in the samples varied with depth but correlated strongly with pore-water concentrations of Ca, Mg, Na, and SO$_4$. Cation-exchange processes may be responsible, in part, for the lower concentrations of Sr, Ca, and Mg in pore water from the clay-silt unit below the aquifer than in that above the aquifer.

^{87}Sr/^{86}Sr values in 11 samples of aragonitic mollusk shells (bearing no visible evidence of recrystallization) collected from depths in the clay-silt unit similar to those from which the pore-water samples were collected ranged from 0.708468 to 0.708713, and decreased (Sr in the shells was less radiogenic) with depth. This trend is consistent with the decrease in the ^{87}Sr/^{86}Sr value in seawater through time during the early Miocene. The ^{87}Sr/^{86}Sr values in 12 pore-water samples from the studied stratigraphic interval ranged from 0.708257 to 0.708527 and also decreased with depth. The Sr-isotope ratios in the pore water were lower than those in the shell material from nearby or adjacent sediments for all samples but one. Because the only known source of Sr with an isotope ratio this low is shell material from sediments deeper than the strata from which the pore-water samples were collected (including pre-Miocene stratigraphic units), the isotope ratio in the pore-water samples from the lower Miocene clay-silt units may result from upward movement of pore water into lower Miocene strata through geologic time, which could create the observed difference in Sr isotope ratios between the pore water and shells.

INTRODUCTION

The evolution of water quality in confined aquifers of the Atlantic Coastal Plain results in the dominance of Na- and HCO$_3$-type waters downdip. It has been hypothesized that this trend may partly be the result of leakage or diffusion of SO$_4$-enriched pore water from the adjacent confining units (Chapelle and McMahon, 1991). The Atlantic Coastal Plain in the Eastern United States, of which the New Jersey Coastal Plain is a part, is a seaward-dipping wedge of unconsolidated sediments that range in age from Cretaceous to Holocene. These sediments consist of clay, silt, sand, and gravel deposited in alternating sequences of high- and low-permeability strata that represent interfingering deltaic and marine-shelf deposits. The thick sand units found between silt or clay units typically are confined aquifers. In several of these aquifers in New Jersey, such as the Piney Point aquifer (Harriman and Sargent, 1985) and the Atlantic City 800-ft sand (Barton et al., 1993), the water is increasingly dominated by Na and HCO$_3$ in the downdip direction (toward the southernmost part of New Jersey).

The Atlantic City 800-ft sand is a nearly 100-ft-thick (30 m) layer of coarse- to medium-grained sand and, in places, gravel enclosed in clay-silt units near the base of the lower Miocene Kirkwood Formation (Zapecza, 1989). The Kirkwood Formation crops out over a broad area of the southwestern New Jersey Coastal Plain (Fig. 1) and, following the regional trend, dips to the southeast. The base of the sand and gravel unit that forms the Atlantic City 800-ft sand is about 800 ft (240 m) below land surface beneath the barrier islands in eastern Atlantic County, NJ.

Results of a recent study of the quality of pore water in fine-grained sediments in the New Jersey Coastal Plain show elevated concentrations of SO$_4$, Ca, and Na (Pucci et al., 1992); these results agree with the findings of Chapelle and McMahon (1991) for clay-silt confining units in other parts of the Atlantic Coastal Plain. The chemistry of water in the confined aquifers in the New Jersey Coastal Plain, such as the Atlantic City 800-ft sand, likely is affected if leakage of mineralized pore water from the confining units occurs. The results of a computer simulation of prepumping ground-water flow in the New Jersey Coastal Plain (Martin, in press) indicates that in the Atlantic City region water from pre-Miocene strata moves upward through the Atlantic City 800-ft sand before it discharges to the Atlantic Ocean (Fig. 2).

Information on the distribution of solutes is needed to determine whether the solutes migrate within or through confining units and whether mineralogical variations in the sediments result in compositional variations in the pore water. An ongoing cooperative investigation by the U.S. Geological Survey, the New Jersey Department of Environmental Protection, Rutgers University, and Lafayette College is being conducted to evaluate the potential effects of confining-unit pore water on the quality of water in confined aquifers. The distribution and sources of solutes in the pore waters in the fine-grained units near the base of the lower Miocene Kirkwood Formation above and

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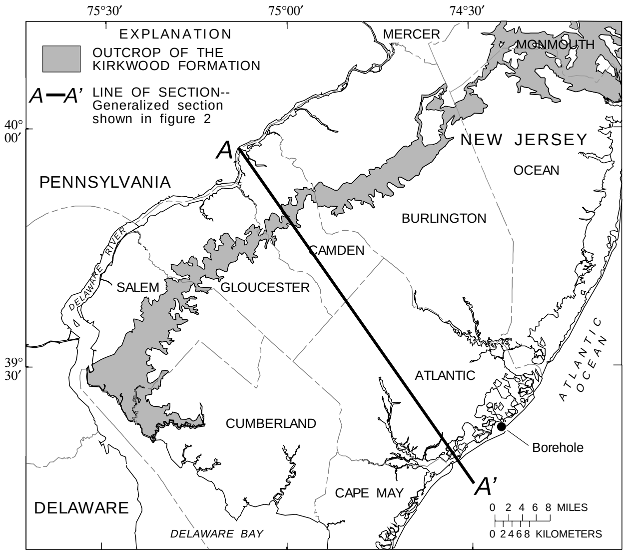

Base modified from U.S. Geological Survey digital data, 1:100,000, 1983, Universal Transverse Mercator projection, Zone 18

Figure 1. Location of the Leg 150X Atlantic City borehole; outcrop of the lower Miocene Kirkwood Formation; and generalized line of Section A–A′ through the southern Coastal Plain of New Jersey.

below the Atlantic City 800-ft sand were studied as part of this investigation.

Sr is ideal for such a study because it is abundant in most rock-forming minerals, including silicate and carbonate minerals (such as calcite or aragonite shell material), and because it is readily soluble. Furthermore, because the isotopes of Sr do not undergo observable fractionation during chemical processes (dissolution, precipitation, biologically mediated shell formation), and the ratio of two of the more common isotopes of Sr, the ^{87}Sr/^{86}Sr value, varies greatly among different geologic materials, the isotope ratio of Sr in solution is an indicator of the source of the dissolved Sr. The ^{87}Sr/^{86}Sr value has been used extensively to determine the source of Sr in pore water, the amount of water/rock interaction, and the hydrogeochemical processes in various geohydrologic environments, including shallow dilute ground water (Bishop et al., 1994; Stanley and Faure, 1979; Steuber et al., 1975), connate brines (Szabo, 1984; Stueber et al., 1984; Sunwall and Pushkar, 1979), and even pore water from deep-sea sediment (Elderfield and Gieskes, 1982; Hawkesworth and Elderfield, 1978). For example, the magnitude of the difference between the ^{87}Sr/^{86}Sr value in pore water (or carbonate minerals precipitated from pore water) and that in seawater is an indicator of the amount of chemical interaction between the pore water and silicate minerals in the sediment matrix. Determining the concentration and isotopic composition of Sr in the pore water in an individual confining unit in the Atlantic Coastal Plain and the isotopic composition of Sr in the primary Sr-bearing solid phase (sedimentary shell material) may provide similar information in this hydrogeologic setting. Therefore, an investigation was undertaken within the framework of the larger study to determine (1) the distribution of Sr in pore water in clay-silt confining units adjacent to the aquifer and (2) the possible sources of dissolved Sr from the isotopic composition of Sr, to identify the chemical and transport processes that may affect the distribution of solutes in confining units.

Pore-water and shell-material samples were collected at regular intervals at depths of 552–840 ft (168–256 m) below land surface in a continuously cored borehole (Ocean Drilling Program Leg 150X) in Atlantic City, New Jersey (Fig. 1), in the clayey silt of the "lower" confining unit overlying the Atlantic City 800-ft sand (as defined by Miller et al., 1994), the composite confining unit underlying the aquifer, and interbedded silt stringers in the upper part of the aquifer (Fig. 3). (The "lower" confining unit of Miller et al. [1994] is equivalent to the bottom half of the "confining unit above the Atlantic City 800-ft sand" as described by Zapecza [1989] and was not included as a separate confining unit in the model of Martin [in press].) Pore-water samples were mechanically extracted from the clay-silt sediments for chemical analysis (19 samples) and for determination of the ^{87}Sr/^{86}Sr values (12 samples). In addition, the ^{87}Sr/^{86}Sr values in 11 shell samples from about the same sampled interval (559–869 ft [170.4–264.9 m]) were determined. This report summarizes the variations in the concentration of Sr in the pore-water samples and the ^{87}Sr/^{86}Sr value in the pore-water and shell-material samples with depth. Possible sources of Sr and geochemical processes that affect its concentration in pore water are considered, and the relation of the ^{87}Sr/^{86}Sr value in the pore water to the regional prepumping ground-water-flow system (Fig. 2). as simulated by Martin (in press) are discussed.

Use of Strontium Isotopes as Stratigraphic Dating Tools and Indicators of Sediment-Water Interaction

Peterman et al. (1970) demonstrated the use of original, unreplaced calcium carbonate fossil shells in determining the systematic variation of the ^{87}Sr/^{86}Sr value in seawater through time. Calcium carbonate minerals in the shells of marine animals are precipitated from seawater; the Sr in these minerals is in isotopic equilibrium with that in seawater for most species, including mollusks. Unreplaced or unaltered skeletal aragonite (or, for some species, calcite) or shells of these marine animals found as fossils, therefore, contain ^{87}Sr/^{86}Sr in the same ratio as that found in the seawater from which they were precipitated. The ratio of ^{87}Sr/^{86}Sr in the ocean, and, thus, in marine shell material, is homogeneous at any given time because the residence time of Sr in the ocean is long compared to the mixing time of the ocean (Faure, 1982), and because the concentration of Sr in seawater is high relative to that in river-water input, thereby limiting local variability.

The ratio of ^{87}Sr/^{86}Sr in shell material, therefore, can be used as a dating tool in stratigraphic studies. Once the age of a reference stratigraphic section is calibrated to the time scale by paleontological, paleomagnetic, or isotopic dating techniques, the ratio of ^{87}Sr/^{86}Sr in shell material from other stratigraphic sections, representing the ratio of ^{87}Sr/^{86}Sr in the seawater from which the sediment was deposited, can be correlated to the time of deposition.

The ^{87}Sr/^{86}Sr dating technique is especially sensitive for lower to middle Miocene strata, because the rapid change of the marine ^{87}Sr/^{86}Sr value during this epoch allows for the differentiation between small intervals of time. The rate of change in the marine ^{87}Sr/^{86}Sr value was especially rapid in the Tertiary Period, rising from about 0.70760 at the beginning to the current value of 0.70906. The ratio rose most rapidly in the Oligocene and Miocene Epochs (Oslick et al., 1994; Sugarman et al., 1993; Faure, 1982). The Sr-isotope stratigraphy of the lower Miocene Kirkwood Formation in southern New Jersey has been documented by Sugarman et al. (1993), Miller and Sugarman (1995), and Sugarman et al. (Chapter 12, this volume).

If the Sr in the pore water is derived from either the original seawater entrapped, with a unique ^{87}Sr/^{86}Sr value, in the sediment, or the calcium carbonate minerals or shells precipitated from seawater during deposition of the sediment, then the isotope ratio of Sr in the pore water will reflect that in seawater at the time of deposition. Seawater entrapped in geologic strata is assumed to mix, through time, with recharging freshwater (freshwater typically contains minimal Sr and, hence, has little effect on the ^{87}Sr/^{86}Sr value in the mixture) to form the current interstitial fluid. As the pore water interacts with the silicate minerals in the sediment matrix, the ^{87}Sr/^{86}Sr value of the water generally tends to increase (Sr in the water becomes more radiogenic) because most primary felsic silicate minerals, such as K-feldspar, and

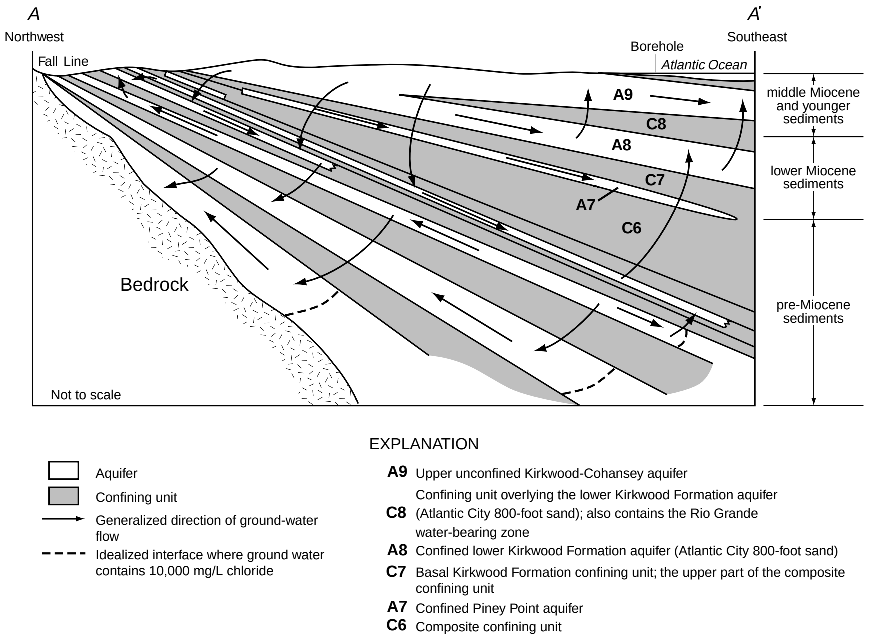

Figure 2. Generalized representation of simulated prepumping flow in a hydrogeologic section through the southern Coastal Plain of New Jersey (modified from Martin, in press, fig. 74; section-line location shown in Fig. 1).

primary (detrital) and secondary (diagenetic) clay minerals are strongly enriched in ^{87}Sr relative to seawater (Table 1). Through time, therefore, the ^{87}Sr/^{86}Sr value in the evolving pore water tends to become similar to that in the minerals in the sedimentary matrix from which the Sr in solution is primarily derived (Szabo and Faure, 1987; Stanley and Faure, 1979). The magnitude of the change in the ratio in the pore water relative to that in the primary seawater is an indicator of the degree to which the sedimentary matrix is enriched in radiogenic ^{87}Sr, the amount of chemical interaction between the pore water and mineral phases in the sediment matrix, the amount of mixing with fluids with different ^{87}Sr/^{86}Sr values, or all of the above. Some examples of reported ^{87}Sr/^{86}Sr values in excess of 0.725 in various detrital or authigenic silicate minerals or in clastic rocks are given in Table 1; these include ratios in detrital K-feldspar as high as 0.727 (Szabo and Faure, 1987), in shale as high as 0.745 (Stueber et al., 1975; Szabo and Faure, 1987), and in plagioclase-free arkose as high as 0.749 (Stanley and Faure, 1979).

Shallow ground water, deep ground water, and deep brines have all been shown to contain more radiogenic Sr than seawater at the time of deposition. Stueber et al. (1975) and Fisher and Stueber (1976) report ^{87}Sr/^{86}Sr values as high as 0.713 and 0.716 in shallow ground water from shale, whereas Sunwall and Pushkar (1979) report ratios of about 0.7103 for deep brine (Table 1).

Secondary minerals precipitated from pore water, such as calcite found as cement or grain coatings, preserve the ^{87}Sr/^{86}Sr value of the pore water at the time of secondary-mineral formation because isotopic fractionation of Sr during precipitation of secondary minerals from pore water is also negligible (Faure, 1982). The ^{87}Sr/^{86}Sr value in secondary minerals, therefore, is a function solely of that in the pore water from which the mineral precipitated (Veizer, 1983). The ^{87}Sr/^{86}Sr value in calcium carbonate–mineral cements, mineral coatings, or micritic matrix precipitated from pore water enriched in ^{87}Sr relative to seawater is higher than that in unaltered carbonate shells that still have the same ^{87}Sr/^{86}Sr value as the seawater from which they were precipitated (Popp et al., 1986). Reported ^{87}Sr/^{86}Sr values in secondary calcite cements in various clastic rocks can exceed 0.712 (Table 1). In extreme cases of silicate-mineral dissolution or replacement, such as nearly complete replacement of K-feldspar grains by carbonate cement (Szabo, 1984), both the pore water and the carbonate cement formed from it may be highly enriched in ^{87}Sr relative to seawater; the ^{87}Sr/^{86}Sr value in the secondary calcite formed in such a situation was found to be as high as 0.714 (Szabo and Faure, 1987). The magnitude of the difference between the ^{87}Sr/^{86}Sr value in pore water or carbonate minerals precipitated from pore water and that in seawater is, therefore, an indicator of the amount of chemical interaction between the pore water and the silicate minerals in the sediment matrix.

METHODS

Nineteen 1-ft (0.3 m) segments of clay-silt sediment were cut with a sharp knife from the most intact parts of core sections from the lower Miocene Kirkwood Formation collected from the borehole at Atlantic City, N.J. The sediment samples were collected at approximately 10-ft (3 m) intervals from below land surface depths of 552–651 ft (168.2–198.4 m; 11 pore-water samples analyzed for Sr concentration, ^{87}Sr/^{86}Sr determined for eight samples); 681–705 ft (207.6–214.9 m; three pore-water samples analyzed for Sr concentration, ^{87}Sr/^{86}Sr determined for one sample); and 819–840 ft (249.6–256.0 m; four pore-water samples analyzed for Sr concentration, ^{87}Sr/^{86}Sr determined for two samples; Fig. 3). The pore-water samples are representative of water in the lower confining unit overlying the Atlantic City 800-ft sand, an interbedded clay-silt unit in the uppermost part of the aquifer, and the composite confining unit underlying the aquifer, respectively. In addition, one sediment sample was collected from the isolated clay-silt stringer at a depth of 736 ft (224.3 m) in the Atlantic City 800-ft sand for pore-water extraction and determination of Sr concentration and the ^{87}Sr/^{86}Sr value.

The sediment samples were stored under an N_2 atmosphere in an anaerobic jar (Difco 1950-30-2) at a temperature of 4°C until the pore water was extracted about 1–4 weeks later. Pore-water samples were mechanically extracted from the silts at a maximum pressure of 9000 psi; details are given by Pucci et al. (Chapter 24, this volume). Deionized water was passed through the extraction equipment and used as the process blank sample. The result of the analysis of this sample indicates minimal contamination with Sr during sample processing (maximum of 0.057 μM/L). The pH of the pore water was determined in a 1- to 2-mL sample aliquot as soon as possible after extraction with a narrow-tipped glass probe.

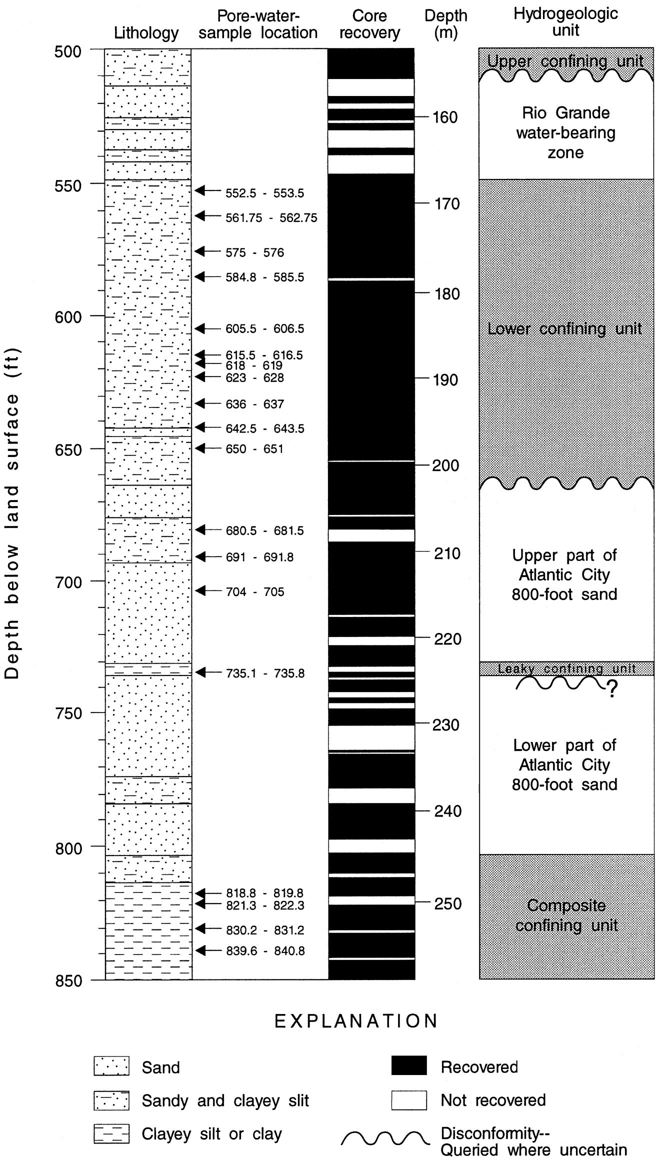

Figure 3. Lithology, pore-water sample locations, core recovery, and hydrogeologic units, lower Miocene Kirkwood Formation, Leg 150X Atlantic City borehole (modified from Miller, et al., 1994).

Concentrations of Sr and major cations (Ca, Mg, and Na) in the pore water were determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) on 5 mL of sample diluted 1:1 with deionized water. Concentrations of SO_4 were determined by ion chromatography on 1 mL of sample diluted 1:200 with deionized water. One mL of undiluted sample each was used to determine concentrations of Cl by colorimetry and of DIC (dissolved inorganic carbon) by infrared spectrometry. The $^{87}Sr/^{86}Sr$ values were determined by mass spectrometry (as described below) on 2 to 5 mL of undiluted pore-water sample.

The $^{87}Sr/^{86}Sr$ values in calcareous mollusk shells from shell beds in clay silt, silt, or silty sand collected from the Kirkwood Formation, as well as those in shells collected from pre- and post-Miocene strata cored at Atlantic City, also were determined by mass spectrometry after dissolution of the shell material. These results are described by Miller et al. (1994) and Sugarman et al. (Chapter 12, this volume). Eleven samples of shell material were collected from about the same depth intervals as the pore-water samples: four were from the lower confining unit, three were from the clay-silt unit in the upper part of the Atlantic City 800-ft sand, and four were from the composite confining unit. The depths from which the pore-water and shell-material samples were obtained did not always coincide because pore-water samples were collected only from unfractured, competent silt or clay, whereas shell beds commonly were sandy. The $^{87}Sr/^{86}Sr$ values of the silicate minerals in the clay-silt unit were not determined, but were assumed to be on the order of 0.707–0.710 on the basis of Biscaye's (1972) work on estuarine and shelf sediments and that of Dasch (1969) on shelf and deep-sea sediments.

Because Sugarman et al. (1993) found that shells from the Kirkwood Formation were completely aragonitic, the shells or shell-hash materials selected for analysis were inspected only visually for evidence of corrosion or diagenetic alteration. Neither recrystallization of shell material nor coating of shell material with a drusy or micritic crust was observed. A piece about 5 mm in diameter was taken from the most pristine part of the shell, ultrasonically cleaned in distilled water for 5–10 s, crushed, and dissolved in 1.5 N HCl.

Ion-exchange techniques were used to separate Sr for isotopic analysis. The analyses were completed on a VG Sector mass spectrometer at Rutgers University. Intrarun precision was +/-0.000008, whereas interrun precision was about +/-0.000026 to 0.000030. The $^{87}Sr/^{86}Sr$ value of reference Sample NBS 987 was determined at the Rutgers laboratory to be 0.710255 (Oslick et al., 1994).

Nonparametric Spearman rank correlation analysis was used to evaluate the relations between concentrations of Sr and those of other selected dissolved constituents in the 14 uppermost pore-water samples (11 from the lower confining unit and three from clay/silt interbeds in the Atlantic City 800-ft sand); correlations significant at a 90% confidence level are reported. Nonparametric statistics were used because the pore-water concentration data were not normally distributed. The ion-activity product of ions in solution was calculated with the geochemical speciation program SOLMINEQ.88 (Kharaka et al., 1988) to determine the degree to which pore-water samples were saturated with mineral phases, such as carbonates, present in the Kirkwood Formation.

Linear regression was completed for the relation between Sr-isotope ratios and depth in both pore water and shell material from 559 to 661 ft (170.4–201.5 m), which corresponds to the lower confining unit, and in pore water from 559 to 681 ft (170.4–207.6 m). The 95% confidence intervals were computed about the slopes (Dowdy and Wearden, 1983), which were recalculated by using standardized data, in order to evaluate with the Student's *t*-test whether the difference in the rate of change of the Sr-isotope ratios with depth between pore-water and shell-material samples was statistically significant. Linear regression also was used to describe the relation between concentrations of strongly correlated pore-water constituents.

RESULTS

Concentrations of Sr in the 14 uppermost pore-water samples ranged from 2.80 to 28.14 µM/L, whereas those in the four pore-water samples from the composite confining unit below the aquifer ranged from 1.31 to 7.27 µM/L (Table 2). The highest concentrations of dissolved Sr were in pore water extracted from sediments collected near the top of the lower confining unit. Pore-water concentrations of Sr generally decreased with depth, but were highly variable with a series of sharp peaks that increased in magnitude toward the top of the lower confining unit (Fig. 4).

The $^{87}Sr/^{86}Sr$ values in the 11 shell samples from shell-hash beds in the clay-silt sediment in the lower half of the Kirkwood Formation ranged from 0.708468 to 0.708713. The ratios decreased (the Sr in the shells was less radiogenic) relatively smoothly with depth (Fig.

Table 1. Typical ^{87}Sr/^{86}Sr values in silicate minerals, shallow ground water, deep brine, and secondary calcite cements.

^{87}Sr/^{86}Sr value, silicate mineral or matrix	^{87}Sr/^{86}Sr value, associated water	^{87}Sr/^{86}Sr value, associated secondary calcite	Source
0.7071-0.71849, shale	0.7071-0.7105*	0.7074-0.7081	Stueber et al. (1984)
ND, sandstone	0.7092-0.7143*	ND	Sunwall and Pushkar (1979)
0.7027-0.705, volcanic detritus	0.70694-0.70926	ND	Elderfield and Gieskes (1982)
0.716, continental (clayey) detritus	0.70794-0.70924		
ND, shale	0.7091-0.7166	ND	Fisher and Stueber (1976)
ND, schist	0.7099-0.7218		
0.732-0.745, shale	0.7102-0.7131	ND	Stueber et al. (1975)
ND, basaltic volcanic sediment	0.7045-0.7054	ND	Collerson et al. (1988)
ND, rhyolitic volcanic sediment	0.7060-0.7118		
0.7491, arkose	ND	0.7112	Stanley and Faure (1979)
0.7102, vitric sandstone	ND	0.7103	
0.7214-0.7271, K-feldspar	ND	0.7090-0.7144	Szabo and Faure (1987)
0.7452, shale	ND	ND	

Notes: * = brine. ND = not determined.

Table 2. Chemical composition of pore water from clay-silt and Sr-isotope ratios in pore water and shells, lower Miocene Kirkwood Formation, Atlantic City borehole.

Sample number	Sample depth (ft below land surface)	pH	Specific conductance (µS/cm)	Sulfate (mM/L)	Dissolved inorganic carbon (mM/L)	Chloride (mM/L)	Calcium (mM/L)	Magnesium (mM/L)	Sodium (mM/L)	Strontium (µM/L)	^{87}Sr/^{86}Sr, pore water	^{87}Sr/^{86}Sr, shells
Lower confining unit												
1	553	7.8	2210	9.31	0.65	2.81	6.41*	1.81	4.17	28.14	—	0.708713[†]
2	562	8.0	1710	6.63	1.17	2.04	4.99*	1.36	3.35	21.32	0.708527	0.708668[‡]
3	575	8.3	1340	5.00	0.92	1.59	3.99*	1.07	2.78	16.06	0.708508	—
4	585	8.3	1400	5.04	1.08	1.94	3.74*	1.15	3.13	17.45	0.708486	—
5	606	8.0	470	1.00	0.83	2.07	0.92	0.29	2.09	4.09	0.708491	0.708656
6	616	7.7	770	1.82	1.50	2.27	1.95*	0.62	2.48	8.43	0.708470	—
7-A1	619	8.2	440	0.59	0.78	1.90	0.80	0.26	1.83	3.56	—	—
7-B1	626	8.2	550	0.96	1.08	1.76	1.10*	0.35	2.17	4.91	0.708470	—
7-B2	626	8.2	—	1.61	0.92	1.75	1.37*	0.41	2.22	6.05	—	—
8	637	8.2	430	0.75	0.83	1.21	0.87*	0.28	1.61	3.67	0.708494	—
9	643	8.6	1500	5.78	1.08	1.88	4.07*	1.23	3.48	18.02	0.708471	0.708672
10	651	8.6	620	2.03	1.17	1.33	1.42*	0.45	2.21	6.17	—	0.708640, 0.708494**
Silt stringers, upper part of the Atlantic City 800-ft sand												
11	681	7.7	380	1.20	0.56	0.74	0.82	0.30	1.35	3.64	0.708434	—
12	691	8.1	410	0.97	0.51	1.35	0.80	0.26	1.57	3.21	—	—
13	705	8.2	320	0.75	0.72	0.57	0.65	0.20	1.30	2.80	—	0.708476[‡]
14	736	7.7	1000	4.11	0.35	0.96	2.47	0.91	2.39	10.72	0.708523	—
Composite confining unit												
15	819	8.7	860	1.67	2.08	1.34	0.27*	0.13	7.61	1.31	—	—
16	822	8.6	1630	4.90	2.25	1.94	0.95*	0.66	12.17	7.27	0.708353	0.708469
17	831	8.8	720	0.88	2.08	2.21	0.21*	0.12	6.39	1.31	—	0.708468
18	840	8.5	660	0.72	1.67	2.06	0.14	0.049	5.83	0.52	0.708527	0.708453[††]

Notes: µS/cm = microsiemens per centimeter. * = water sample saturated with respect to calcite. — = no data. [†] = analyzed shell at a depth of 519.5 ft. [‡] = analyzed shells are offset from pore-water sample by 2–3 ft; see Miller et al. (1994) for exact location. ** = analyzed shell at a depth of 661 ft. [††] = analyzed shell at a depth of 854 ft. Isotope ratios in shells from Miller et al., 1994.

5). The ^{87}Sr/^{86}Sr values determined by Miller et al. (1994) in the 12 shell samples collected below 840 ft (252 m), predominantly from pre-Miocene stratigraphic units below the Kirkwood Formation, were significantly lower than those measured in the shell samples from the Kirkwood Formation (range 0.70778-0.70844) and also decreased relatively smoothly with depth (Fig. 5). This trend is consistent with the decrease through time in the ^{87}Sr/^{86}Sr value in seawater during these epochs, as has been demonstrated by Sugarman et al. (1993), Oslick et al. (1994), and Miller and Sugarman (1995).

The ^{87}Sr/^{86}Sr values in the 12 samples of pore water from the lower part of the Kirkwood Formation ranged from 0.708257 to 0.708527 and decreased (the Sr in the water was less radiogenic) relatively smoothly with depth, as did those in the shell material (Fig. 5), with two minor exceptions: the Sr in pore-water Samples 8 and 14 was more radiogenic than that in the pore water from the immediately overlying sediment (Fig. 5). In addition, ^{87}Sr/^{86}Sr values in Samples 4 (585 ft [178.3m]) and 5 (606 ft [184.7 m]) could not be distinguished from each other within analytical uncertainty. These anomalous samples do not affect the overall trend, however. The ^{87}Sr/^{86}Sr values in the pore-water samples were lower (the Sr in the pore water was less radiogenic) than those in the shell material collected nearest the sediment from which the pore water was extracted.

Relation of Sr Concentration to Pore-Water Geochemistry

Concentrations of Sr in the 14 pore-water samples from the lower confining unit and the clay-silt in the upper part of the Atlantic City 800-ft sand correlate strongly with pore-water concentrations of Ca, Mg, Na, and SO_4 (Spearman rank correlation coefficients +0.99, +1.00, +0.97, and +0.91, respectively). The linear trend of the relation between the pore-water concentrations of Sr and Ca in these samples is illustrated by the solid symbols in Figure 6. The molar ratio of Sr to Ca is ~0.00435 (range 0.00401–0.00477), a value greater than that typical of ground water but less than that of seawater. The molar ratio of Sr to Ca in the pore water is in equilibrium in an open hydrologic environment with that in a precipitating calcite phase that contains ~400–700 ppm of Sr and a dissolving low-Sr aragonite

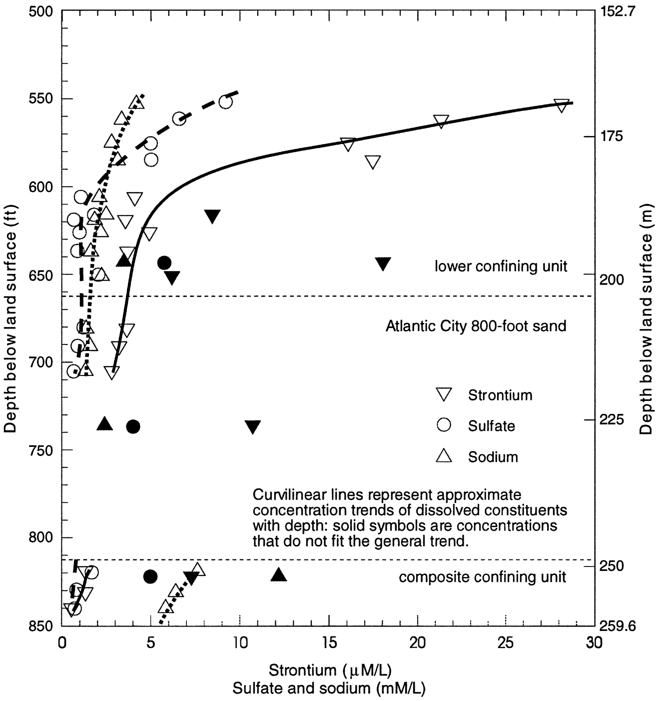

Figure 4. Variation in concentrations of strontium, sulfate, and sodium in pore water with depth below land surface, lower Miocene Kirkwood Formation, Leg 150X Atlantic City borehole.

phase that contains ~1000–4000 ppm of Sr (Kinsman, 1969). The relatively low Sr concentration of the aragonitic phase is typical of mollusks (Lowenstam, 1963). The precipitation of calcite with a much lower Sr content than that of the dissolving aragonite results in an increase in the molar ratio of Sr to Ca in the pore water relative to this ratio in typical mollusk shells (Fig. 6). Many of the pore-water samples are saturated or slightly supersaturated with respect to calcite (Table 2), indicating that calcite may precipitate from the solution. In general, the more highly mineralized pore-water samples, especially those from the uppermost part of both the lower and composite confining units, are the most likely to be saturated or slightly supersaturated with respect to calcite. The samples were undersaturated with respect to aragonite; therefore, dissolution of aragonitic shell material, the source of the dissolved Ca and Sr, is likely an ongoing chemical process. The nearly uniform linear molar ratio of Sr to Ca in these samples indicates dissolution of one or two mineral phases (one likely being the mollusk shells), which contain these two elements in fixed proportions, coupled with the precipitation of a Sr-bearing mineral (calcite) that also contains these two elements in a fixed proportion. The differences in pore-water concentrations of Sr and Ca from sample to sample indicate differences in the local chemical environment, most likely the availability of dissolving shell material, the carbonate ion, and pH. The latter two characteristics are controlled partly by the varying rates of vertical and horizontal flow and of other chemical reactions, such as metabolization of organic matter by bacteria, in each stratigraphic horizon. Substantially higher Sr concentrations in pore water from marine sediment than those found in this study have been attributed to dissolution of aragonitic shell material (Elderfield and Gieskes, 1982; Manheim et al., 1973).

The nearly linear trend of the relation between concentrations of SO_4 and Ca in the 14 pore-water samples from the lower confining unit and the clay-silt in the upper part of the Atlantic City 800-foot sand is illustrated by the open symbols in Figure 6. Unlike the molar ratio of Sr to Ca in these samples, which is exceedingly uniform, the molar ratio of SO_4 to Ca increases slightly with increasing concentrations of both Ca and SO_4. The molar ratio of SO_4 to Ca ranges from 0.74 to 1.47 in pore-water samples whose specific conductance is less than 1,000 μS/cm, but ranges from 1.25 to 1.67 in samples whose specific conductance is more than 1,000 μS/cm. Results of linear regression indicate that the molar ratio of SO_4 to Ca is about 1.04 for pore water with a specific conductance of 500 μS/cm and about 1.56 for pore water with a specific conductance of 2,200 μS/cm. This slight increase in the ratio of the concentration of SO_4 to that of Ca (Fig. 6) may indicate that, as the water becomes increasingly mineralized, concentrations of (or the rate of increase in) Ca and Sr in solution are fixed, possibly as a result of equilibrium of the mineralized solution with calcite. The concentration of SO_4, however, continues to increase strongly because equilibrium of the solution with gypsum has not yet been attained. This result is consistent with the observation that the most mineralized solutions are saturated with respect to calcite. It is also possible, however, that some other chemical process, such as ion exchange, is partly responsible for limiting the rate of increase of Sr and Ca concentrations in the most mineralized samples; evidence for ion exchange is discussed below. Understanding of the chemical processes that control the relation between dissolved Ca and SO_4 would be facilitated if the source of the dissolved SO_4 were known. Various possible sources of SO_4 in pore water from clay-silt confining units in the Atlantic Coastal Plain have been proposed, but the data collected to date are inadequate to definitively determine the source (Chapelle and McMahon, 1991; Pucci et al., 1992; Pucci et al., Chapter 24, this volume).

The composition of the pore-water samples from the composite confining unit is likely strongly affected by ion exchange, as indicated by the high ratio of the concentrations of SO_4 to Ca (Fig. 6), Na to Cl (Fig. 7), Cl to Sr (Fig. 7), Na to Ca, and Na to Sr in these samples compared with that in samples from the lower confining unit and the clay-silt sediments from the top of the Atlantic City 800-foot sand. The likelihood of a strong effect on solution chemistry as a result of ion exchange is supported by the molar ratio of SO_4 to Ca, which exceeds 4 (range 4.07–6.10) in each of the four pore-water samples from the composite confining unit, whereas the value of this ratio does not exceed 1.7 in the 14 pore-water samples from the aquifer and the overlying lower confining unit (Fig. 6). The molar ratio of Na to Cl was much higher in pore-water samples from the composite confining unit (range 2.82–6.26) than in samples from the two overlying units (range 0.96–2.49) (Fig. 7). The molar ratio of Na to Cl was highest in the samples in which Na concentrations were greatest, indicating a significant source of Na other than residual seawater or connate water. The source of this Na is likely exchangeable Na in the clay-silt. The molar ratio of Na to Cl was slightly greater than 1 in all but two of the 14 samples from the lower confining unit and the clay-silt sediments at the top of the Atlantic City 800-ft sand; the exceptions are Samples 14 and 15 from the upper part of the Atlantic City 800-ft sand (Fig. 7). This result indicates a possible minor source of exchangeable Na in the clay-silt sediments of the lower confining unit, as well as in the composite confining unit. The molar ratios of Sr and Ca to Na in the pore-water samples from the composite confining unit (range 0.00009–0.0006 and 0.025–0.078, respectively) were one-tenth or less of those in the lower confining unit and the clay-silt sediments in the Atlantic City 800-ft sand (range 0.0019–0.0067 and 0.44–1.54, respectively). The molar ratio of Sr to Cl in the composite confining unit (range 0.00026–0.00374) is much lower than that in the lower confining unit (range 0.00187–0.01116; Fig. 7). Lastly, the molar ratio of Sr to Ca in two of the pore-water samples from the composite confining unit exceeds 0.005 (maximum 0.0076), whereas no sample from the lower confining unit has a molar ratio of Sr to Ca greater than this value. Exchange substrates are more selective for Ca than Sr; therefore, pore water strongly affected by ion exchange is expected to have a higher Sr-to-Ca molar ratio than pore water that is affected only slightly or not at all. The molar ratios indicate that the composition of the pore-water samples from the composite confining unit are likely affected by ion exchange. Other possible

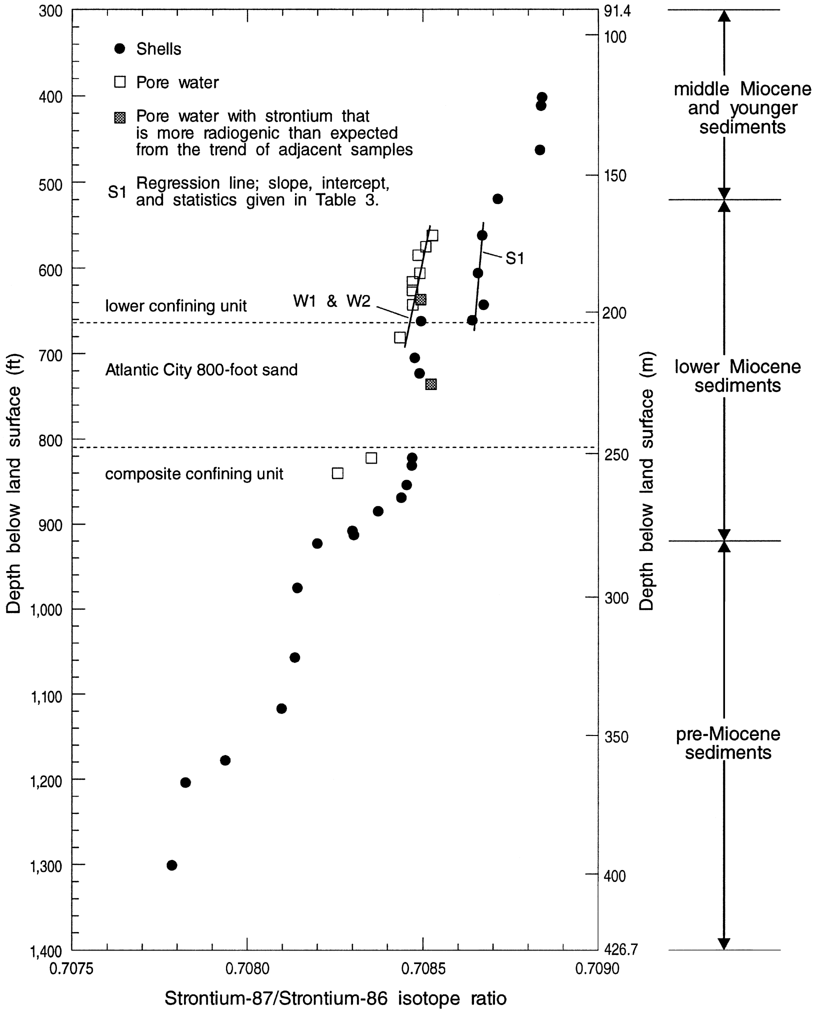

Figure 5. $^{87}Sr/^{86}Sr$ values in shells from Eocene to Pleistocene sediments and $^{87}Sr/^{86}Sr$ values in pore water from the lower Miocene Kirkwood Formation as a function of depth, Leg 150X Atlantic City borehole ($^{87}Sr/^{86}Sr$ values in shells from Miller et al., 1994).

explanations for the variable Sr-to-Ca molar ratio in pore water from the composite confining unit include the precipitation of an extremely pure, Sr-free calcite mineral phase; the presence of aragonitic shells whose Sr content varies greatly with depth; and slower flow rates in the composite confining unit than in the shallower strata, resulting in nonuniform shell dissolution (Kinsman, 1969). These possibilities cannot be evaluated without additional Sr-isotope data from shell material, carbonate cement, or other Sr-bearing minerals. The chemical composition of the pore water collected to date, however, indicates that several chemical processes likely affect the concentration of dissolved Sr.

Relation of $^{87}Sr/^{86}Sr$ Values in Pore Water and Shell Material to Depth and Sr Concentration

The $^{87}Sr/^{86}Sr$ values in the 12 pore-water samples for which this ratio was determined are inversely correlated with depth; this correlation ($r = -0.72$) is also statistically significant when only the 10 pore-water samples from the lower confining unit and the Atlantic City 800-ft sand are considered (Fig. 5). The slope of the regression line representing the rate of decrease of the $^{87}Sr/^{86}Sr$ values in shells (four samples) with depth is approximately twice that of the regression line representing the rate of decrease of the $^{87}Sr/^{86}Sr$ values in pore water (eight samples) with depth in the lower confining unit (Table 3; Fig. 5).

The slope of a line representing the decrease in the $^{87}Sr/^{86}Sr$ values of shells in the lower part of the Kirkwood Formation with depth should be steep but uniform, because the rate of increase of the $^{87}Sr/^{86}Sr$ value in seawater through time was nearly uniform and very rapid in the early Miocene Epoch when the sediments were deposited (Oslick et al., 1994; Sugarman et al., 1993; Faure, 1982). Therefore, the slope of the regression line is affected only by changes in sedimentation rates during the early Miocene, a time of rapid but variable sedimentation in the New Jersey Coastal Plain (Sugarman et al., 1993); it is not affected by changes in the rate of increase of the $^{87}Sr/^{86}Sr$ value in seawater through time, as is the case for sediments deposited in the middle Miocene and other epochs. The sedimentation rate is assumed to have increased greatly beginning with the deposition of the Atlantic City 800-ft sand; the rate of deposition likely was slower when the clay-silt confining units were deposited (Sugarman et al., 1993). The sudden increase in deposition rate significantly affects the slope of the best-fit line that describes the relation of the $^{87}Sr/^{86}Sr$ values in shell material with depth in the lower part of the Kirkwood Formation; hence, only the four shell samples from the lower confining unit were considered for regression analysis.

The difference in the rate of change of the Sr-isotope ratios with depth for the pore-water samples and the shell material from the lower confining unit was not statistically significant (Table 3) despite the apparent difference in the slopes of the respective best-fit lines (Fig. 5). The slopes, recalculated and compared by using standardized data, were not significantly different at the 95% confidence level (Dowdy and Wearden, 1983). Confidence in the slope of all the regression lines, however, is strongly limited by the small data set.

The Sr-isotope ratios in the pore water correlated only weakly with the inverse of the pore-water concentrations of Sr, and a statistically significant regression line could not be fit to the data. This result

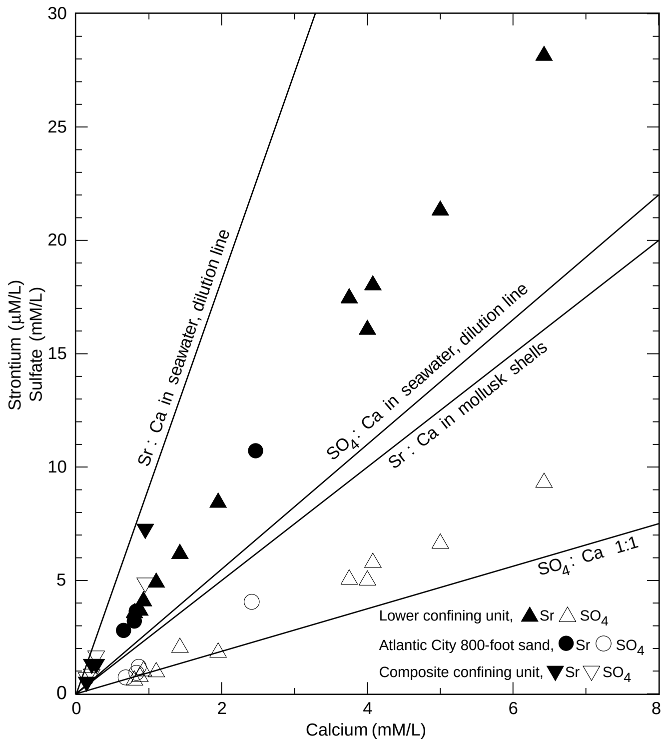

Figure 6. Concentrations of strontium and sulfate as a function of calcium concentration in pore water, lower Miocene Kirkwood Formation, Leg 150X Atlantic City borehole.

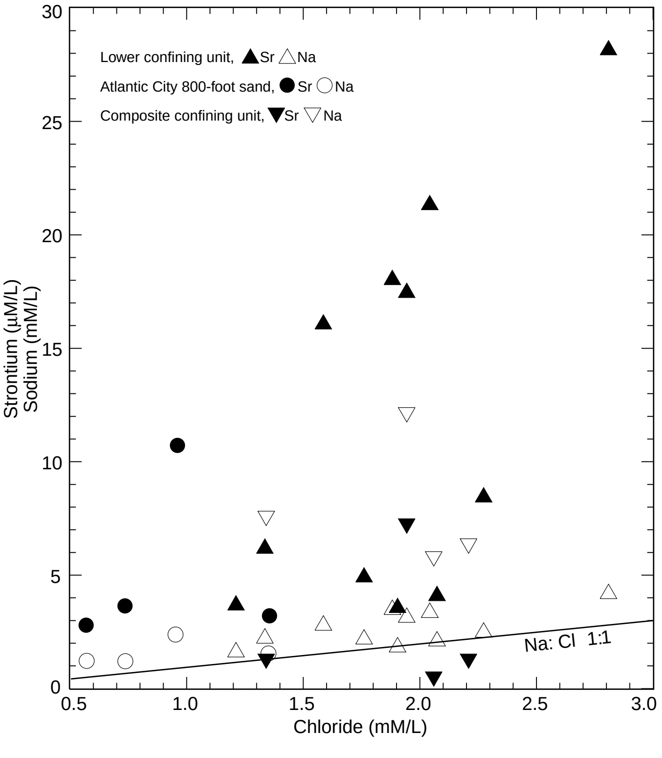

Figure 7. Concentrations of strontium and sodium as a function of chloride concentration in pore water, lower Miocene Kirkwood Formation, Leg 150X Atlantic City borehole.

indicates that the pore water cannot readily be described in terms of a simple two-component mixture by using the Sr-concentration data.

DISCUSSION

Source of Sr

The ^{87}Sr/^{86}Sr values in the pore-water samples can be used to determine the likely source(s) of Sr and the amount of interaction of pore water with carbonate minerals in shells and with silicate minerals in the sediment matrix. The ^{87}Sr/^{86}Sr values in the detrital silicate minerals in the lower part of the Kirkwood Formation, derived from the nearby continental source area, and in secondary clay minerals in the fine-grained sediment are assumed, on the basis of ^{87}Sr/^{86}Sr values determined for similar sediments by Dasch (1969), Biscaye (1972), Nardone and Faure (1978), and Elderfield and Gieskes (1982), to be greater than the ^{87}Sr/^{86}Sr values in the marine shells. Minimal or no contribution of Sr enriched in the radiogenic ^{87}Sr isotope to the pore water from primary or secondary silicate minerals is indicated in the pore-water samples; such a contribution would result in ^{87}Sr/^{86}Sr values that are greater than those observed in adjoining carbonate-shell material. Aragonitic shell material contains Sr in concentrations that are much higher than those found in typical silicate minerals; furthermore, the extreme solubility of aragonite can result in pore water with high concentrations of Sr because of partial dissolution of the aragonitic shells. Concentrations of Sr in pore water from fine-grained marine sediments containing abundant shell material have been reported by Elderfield and Gieskes (1982) and Manheim et al. (1973) to be typically as high as 600 µM/L; a maximum of 1,200 µM/L was reported by Elderfield and Gieskes (1982). Therefore, it would be reasonable to conclude that the dissolved Sr in the pore water in the lower part of the Kirkwood Formation is derived primarily from aragonitic shell material in the adjacent sediment, except that the ^{87}Sr/^{86}Sr values in the pore-water samples are lower than those in the shell material collected nearest the associated pore-water samples.

One possible source of Sr in pore water with a ^{87}Sr/^{86}Sr value lower than that of the aragonitic shell material at the same or similar depth is silicate minerals that have a low ^{87}Sr/^{86}Sr value, such as plagioclase in glass shards derived from basaltic volcanism. Pore water from deep-sea sediment interbedded with basaltic debris and glass shards or basalt flows has been shown to contain Sr with a lower ^{87}Sr/^{86}Sr value than either contemporaneous seawater or the calcite in the sediment (Elderfield and Gieskes, 1982; Hawkesworth and Elderfield, 1978). Neither basaltic debris and glass shards nor Sr-bearing, Ca-rich plagioclase from basalts, except for minor amounts of Na-rich plagioclase near the base, is known to be present in the Kirkwood Formation (Isphording, 1970). Because Kirkwood Formation sediments were deposited in the New Jersey Coastal Plain as a result of tectonic uplift of continental crust and subsequent erosion (Owens, 1985; Sugarman et al., 1993) rather than volcanism, Sr in the pore water cannot be derived from basaltic, Ca-rich plagioclase. Another possible source of Sr is a SO$_4$-bearing evaporite mineral such as gypsum; however, such a mineral is unlikely to be present in Kirkwood Formation sediments, which are marine in origin. No primary deposits of gypsum have been found in sediment from other boreholes drilled in the New Jersey Coastal Plain (Pucci et al., 1992).

The only known sources of Sr with isotope ratios lower than those in the shell material in the lower confining unit are shell material near the base of the lower confining unit, shell material from the composite confining unit near the base of the Kirkwood Formation, and shell material from pre-Miocene stratigraphic units (Fig. 5). Similarly, the only known sources of Sr with isotope ratios lower than those in the shell material in the composite confining unit are shell material from the base of the Kirkwood Formation and shell material from pre-Miocene stratigraphic units (Fig. 5). Within each of these confining

Table 3. Linear correlation of $^{87}Sr/^{86}Sr$ values in pore water and shell material with depth, lower Miocene Kirkwood Formation, Atlantic City borehole, and results of the Student's *t*-test to determine whether the slopes of the linear regressions in the lower confining unit are statistically the same or different.

Dependent Variable	Regression number	Number of samples	Depth below land surface(ft)	Slope	Intercept	F-ratio	Adjusted R^2	*t*-value	Difference in slopes
$^{87}Sr/^{86}$ Sr, shells	S1	4	559-661	2.29×10^{-7}	0.708800	3.14	0.26	1.321	None
$^{87}Sr/^{86}$ Sr, pore water	W1	8	562-643	4.95×10^{-7}	0.708794	13.76	0.61	1.321	None
$^{87}Sr/^{86}$ Sr, pore water	W2	9	562-681	5.05×10^{-7}	0.708807	48.37	0.78	No test	No test
$^{87}Sr/^{86}$ Sr, pore water	W3	12	562-840	6.63×10^{-7}	0.708918	44.99	0.68	No test	No test

Notes: Depth below land surface was treated as a negative number in the regression equations. F-ratio = mean square due to regression/mean square due to residual variation. R^2 = coefficient of determination for the regression; indicates how well the regression fits the data.

units, the $^{87}Sr/^{86}Sr$ value in shell material at the base is lower than that in shell material near the top.

Processes Affecting the Distribution of Sr Isotopes

The presence in the pore water of Sr from shells from depths greater than those from which the pore-water samples were collected could result from several processes. These processes include upward movement of Sr-bearing shells through the reworking of older shell material, and upward movement of Sr itself through diffusion and advection.

Reworking of Older Shell Material

Shells may have been reworked and redeposited in sediment younger than that in which the shells originally were deposited. Nardone and Faure (1978) document the presence of reworked Cretaceous to Oligocene coccolith shells in Quaternary sediments from the Black Sea; $^{87}Sr/^{86}Sr$ values in these older shells are lower than those in the indigenous contemporaneous species. Dissolution of similar reworked shells in the Kirkwood Formation, if present, could result in pore-water $^{87}Sr/^{86}Sr$ values that are lower than those in the adjoining contemporaneous mollusk shells. The presence of reworked pre-Miocene ^{87}Sr-depleted mollusk or other type of shell has not been demonstrated in the Kirkwood Formation, however. The shells generally are broken but, as noted by Sugarman et al. (1993), this feature may represent transport of the shells during storms into deep water before final deposition. Furthermore, no evidence is available to show that other fossil species of diatoms or foraminifers were reworked (Miller et al., 1994). Lastly, such reworked shells would have to be homogeneously distributed throughout the sediment column of the Kirkwood Formation to produce the observed smooth decrease in $^{87}Sr/^{86}Sr$ values with depth; the likelihood of such a distribution is small, especially because the sedimentation rate was variable in early the Miocene (Sugarman et al., 1993).

Upward Movement of Sr

Alternative processes that explain the low $^{87}Sr/^{86}Sr$ value in pore water, relative to that of adjoining shell material include, those that facilitate the upward movement of Sr itself. Sr in pore water that is less radiogenic than that in the adjacent shell material may, in fact, reflect upward movement of Sr-bearing pore water into the clay-silts by advective transport through geologic time from deeper sediments. Pore water at the base of the Kirkwood Formation was in contact with shell material containing Sr with a lower $^{87}Sr/^{86}Sr$ value than that in the lower confining unit. Alternatively, upward diffusive transport of Sr from depth also could result in a decrease in the $^{87}Sr/^{86}Sr$ value in pore water relative to that in the adjacent shell material through time.

Upward movement of water through the Coastal Plain sediments near the coast is consistent with the results of a computer simulation of prepumping ground-water flow in the New Jersey Coastal Plain (Martin, in press), which indicate that water from pre-Miocene strata moves upward through Miocene and younger strata before it discharges to the Atlantic Ocean (Fig. 2). Upward diffusion of Sr through the pore water in the clay-silt sediments is not consistent, however, with the observed concentration gradient of Sr in the lower confining unit. The concentration of Sr in pore water is greatest near the top of the lower confining unit and is lowest near its base (Fig. 4); diffusion of Sr as a result of the Sr-concentration gradient would therefore be expected to be downward.

Diffusion

Upward diffusion of Sr may be possible from sediments containing pore water with large concentrations of Sr to overlying strata containing pore water with small concentrations of Sr. For example, sediments at 643 ft (196 m), near the base of the lower confining unit, contain Sr-rich pore water (Sample 9, 18.0 μM/L), whereas the immediately overlying sediments (Sample 8, 637 ft [194 m]) contain Sr-poor pore water (3.67 μM/L), making upward diffusion of Sr likely. Even here, however, the $^{87}Sr/^{86}Sr$ value in the pore water at 643 ft is substantially lower (0.708471) than that in shell material (0.708672) in adjacent strata. This result indicates that, even in the Sr-rich pore water near the base of the lower confining unit, the source of the dissolved Sr must be shell material from a greater depth than that from which the pore-water sample was collected. Furthermore, both Sr concentrations and the concentration gradient decrease toward the aquifer, making upward diffusion of Sr with a low $^{87}Sr/^{86}Sr$ value unlikely. The potential for Sr diffusion downward from 643 ft cannot be adequately evaluated because the $^{87}Sr/^{86}Sr$ value was not determined for the pore-water sample from 651 ft (198.4 m; Sample 10), where downward diffusion of Sr (based on the observed Sr-concentration gradient) could be expected to affect the Sr-isotope ratio. Local downward diffusion of Sr in the lower confining unit cannot be ruled out as a mechanism that affects the $^{87}Sr/^{86}Sr$ profile with depth, especially in sections where individual pore-water samples have Sr concentrations and $^{87}Sr/^{86}Sr$ values that differ strongly from the expected value based on the general trend of the Sr concentration or isotopic ratio with depth (Fig. 5). The frequency of sample collection is insufficient, however, to evaluate this hypothesis. It is also possible that the Sr-concentration gradient has changed through time resulting in upward diffusion of Sr, but this hypothesis cannot be tested with available data.

The limited number of pore-water samples collected from the composite confining unit preclude the reconstruction of the Sr-concentration gradient through it. The concentration of Sr in the composite confining unit was greatest in Sample 16 (822 ft [251 m]), whereas the concentration was lowest in Sample 18 (840 ft [256.5 m]). This Sr-concentration distribution indicates the possibility of upward diffusion of Sr toward the Atlantic City 800-ft sand above 822 ft (251 m) and downward diffusion of Sr below this depth. As in the lower confining unit, the observed Sr-concentration gradient does not indicate that upward diffusion of Sr is the dominant process controlling the Sr-isotope ratio in pore water, except perhaps in a few selected intervals.

Advection

Upward advective transport of Sr can be considered at two scales: internal transport within an individual hydrogeologic unit, and cross-formational transport across several units. Internal transport of Sr from shell material at the base of a given confining unit toward the top can occur if the Sr is dissolved from the shell material by the pore water and at least some of this Sr is advected along the flow path without being removed immediately from solution by ion exchange or some other process, such as coprecipitation with calcite or adsorption. For the internal transport of Sr to affect the Sr isotope ratio in pore water near the top of a confining unit, the upward flux of Sr must be sufficiently large that a significant portion of the Sr in the pore water at a given point must have been derived originally from shell material near the base of the confining unit. The appreciable concentration of Sr in pore water in the lower confining unit indicates that Sr generally remains in solution after being dissolved; thus, internal advection of Sr is likely to occur. The concentration of Sr in pore water in the composite confining unit, however, is smaller than that in the lower confining unit and is limited by cation exchange. Although internal advection of Sr may occur, it may take longer to advect the same mass of Sr the same vertical distance in the composite confining unit than in the lower confining unit. Therefore, in a given period of time, internal transport of Sr likely has a smaller effect on the Sr-isotope ratio in pore water in the composite confining unit than in the lower confining unit.

If upward advection of Sr from the base to the top of each confining unit occurred, the $^{87}Sr/^{86}Sr$ values in pore water would be most similar to those in adjacent shell material at or near the base of each confining unit and least similar to those at the top of the unit. If it is assumed that the interbedded clay-silt unit at the top of the Atlantic City 800-ft sand is hydrologically the base of the lower confining unit, the $^{87}Sr/^{86}Sr$ values determined for pore water and adjacent shell material in the lower confining unit, in general, do show such a trend, but with many anomalies. The $^{87}Sr/^{86}Sr$ value in a pore-water sample from the interbedded clay-silt unit at the top of the Atlantic City 800-ft sand (Sample 11, 681 ft [207.6 m], 0.708434) is close to that in shell material collected ~14 ft (4.3 m) below the pore-water sample (0.708476). The $^{87}Sr/^{86}Sr$ value in the pore-water sample from sediment at 643 ft (196.4 m), near the base of the lower confining unit (Sample 9, 0.708471), is, however, significantly lower than that (0.708672) in the shell material collected from the same depth. The $^{87}Sr/^{86}Sr$ value in this pore-water sample is similar to that in shell material from the clay-silt unit at the top of the Atlantic City 800-ft sand (0.708476). Similarly, the pore-water samples from the middle and upper parts of the lower confining unit all contain Sr with isotopic ratios much lower than those in the adjacent shell material. These results indicate that the shell material at the top of the Atlantic City 800-ft sand and the base of the lower confining unit is likely an important source of the Sr in pore water at shallower depths in the lower confining unit. The rates of change with depth (slopes) of the $^{87}Sr/^{86}Sr$ values determined for the pore-water and shell-material samples from the lower confining unit were not significantly different, however, indicating that the ratios do not diverge toward the top of the unit. Although the $^{87}Sr/^{86}Sr$ values in pore water generally increase slowly upward from the base of the lower confining unit, the ratios in some depth intervals are nearly uniform over vertical distances of 20–30 ft (6.1–9.1 m). For example, the ratio is identical or nearly identical in pore-water samples from 616 and 626 ft (187.8 and 190.8 m; Samples 6 and 7-B) and in those from 585 and 606 ft (178.3 and 184.7 m; Samples 4 and 5). The physical significance of these results is not known. Because the sampling frequency was low, especially near the base and the top of the unit, and because the difference in the slopes of the relations between the $^{87}Sr/^{86}Sr$ values in pore water and shell material with depth was not statistically significant, the results cannot be considered conclusive evidence of internal transport through the confining unit.

The Sr-concentration and isotope-ratio data indicate that the pore water is not a simple two-component mixture; nevertheless, the concept of a simple two-component mixing curve can be used to crudely approximate the proportions of Sr in a pore-water sample that are derived from adjacent shell material and from shell material at the base of the unit. This simple approximation was made for Sample 2 from 562 ft (171.3 m) near the top of the lower confining unit. For simplification, it was assumed that the Sr concentrations in the two solutions being mixed were equal. (Because this assumption is false, the computed proportions of mixing are only gross estimates.) The simplified mixing equation, without the Sr-concentration terms, is

$$(^{87}Sr/^{86}Sr)_M = f(^{87}Sr/^{86}Sr)_A + (1 - f)(^{87}Sr/^{86}Sr)_B, \qquad (1)$$

where $(^{87}Sr/^{86}Sr)_A$, $(^{87}Sr/^{86}Sr)_B$, and $(^{87}Sr/^{86}Sr)_M$ are the Sr isotope ratios in water that is in equilibrium with adjacent shell material, in water that is in equilibrium with shell material at the base of the confining unit, and in the pore-water sample that represents the hypothetical mixture of these two end members, respectively; and f is the mixing parameter that indicates the proportion of Sr in the mixture (the pore-water sample) that originates from water that is in equilibrium with the adjacent shell material. The equation was solved for the mixing parameter, f. It was assumed that Sr in isotopic equilibrium with the shell material at 643 ft (196 m) had migrated 81 ft (24.7 m) upward to the depth from which pore-water Sample 2 was collected. The parameters used are defined in Table 2 as follows: $(^{87}Sr/^{86}Sr)_A$ = 0.708668, $(^{87}Sr/^{86}Sr)_B$ = 0.708494, and $(^{87}Sr/^{86}Sr)_M$ = 0.708527. The computed mixing parameter of 0.15 indicates that, even near the top of the lower confining unit, a large proportion of the Sr in the pore water (85%) could have originated from shell material near the base of the unit.

For large amounts of Sr to have been advectively transported from the base of the lower confining unit to near the top, many pore volumes of water must have passed through the confining unit. The residence time of a particle of water in a confining unit (the time required for the particle to move advectively from the base to the top of the unit) can be computed by using a modified version of Darcy's Law. Although some of the terms required for the computation are unknown for the lower confining unit, they are known for the upper confining unit, which lies above the Rio Grande water-bearing zone and is similar in thickness and lithology to the lower confining unit. The residence time for the upper confining unit was computed by using the formula

$$t = dAn/Q, \qquad (2)$$

where t is the residence time, d is the thickness of the upper confining unit at Atlantic City (~104 ft [31.7 m]), A is the area of the model cell (Martin, in press) that represents Atlantic City (16.2×10^6 m^2), n is the porosity (estimated minimum value of 0.35), and Q is the flow of water through the top of the model cell (1.71×10^{-4} m^3/s [Martin, in press]). The computed residence time in the upper confining unit is 33.3 ka, which is assumed to be a reasonable estimate for the lower confining unit as well. If hydrologic conditions are assumed to have been uniform through time, this result indicates that 33 pore volumes of water passed through the confining unit in the last 1 m.y., or that about 400 pore volumes passed through the unit since the emergence of the New Jersey Coastal Plain at the end of the middle Miocene Epoch (Meisler et al., 1985), when current ground-water-flow patterns were established. Depending on the concentration of Sr in the pore water through time, a large mass of Sr may have moved upward from near the base of the unit by advection; in fact, the mass of Sr that was transferred likely was sufficient to affect $^{87}Sr/^{86}Sr$ in present-day pore water near the top of the lower confining unit. Although long-term sea level has not varied significantly since the end of the middle Miocene Epoch (Kominz, 1984), short-term eustatic lowering of up to 120 m (Fairbanks, 1989) has occurred many times since then. High stands of sea level during interglacial periods would have reduced ground-water flow, whereas low stands of sea level during glacial periods would have increased it. It is not clear how these short-term changes would have affected cumulative ground-water flow through this time.

For large-scale cross-formational transport of Sr to be sufficient to affect the Sr isotope ratio in pore water in an adjacent unit, the upward flux of Sr must be sufficiently large that a significant portion of the Sr within the aquifer must be derived from the underlying confining unit. Therefore, dilution of the upward-leaking pore water must be sufficiently small that the amount of Sr contributed to the aquifer is not negligible relative to the amount of Sr in the water in the aquifer. No data on the $^{87}Sr/^{86}Sr$ values of Sr dissolved in the aquifer are available. Sr concentrations in water of the Atlantic City 800-ft sand north of Atlantic City in south-central New Jersey are low (0.38–0.71 μM/L, median 0.46 μM/L [Harriman and Sargent, 1985]). Sr concentrations in pore water from the composite confining unit underlying the Atlantic City 800-ft sand at the site of the current study were as high as 7.27 μM/L (Sample 16; Table 2), however. Because the Sr concentrations in the aquifer are low, leakage of even small amounts of confining-unit pore water could add significant amounts of Sr.

Transmissivity of the Atlantic City 800-ft sand is high (860–13,000 ft^2/d; 10,000 ft^2/d at Atlantic City); the vertical leakance of the underlying composite confining unit is low—most likely about 1×10^{-7} (ft/d)/ft at Atlantic City (see Martin, in press, table 8 and figs. 62 and 71). Therefore, vertical flow of water into the aquifer is much less than the horizontal flow of water in the aquifer, and confining-unit pore water that leaks into the aquifer is probably significantly diluted. Water budgets for individual model cells (Martin, in press) were used to estimate the dilution of pore water leaking upward from the composite confining unit through the Atlantic City 800-ft sand to the lower confining unit near Atlantic City. Calculations indicate a dilution factor (horizontal flow in the aquifer to vertical flow from the confining unit) of 20:1. With this dilution factor, the contribution of Sr from the composite confining unit to the aquifer is probably sufficient for the Sr-isotope ratio in water in the aquifer to remain similar to that in the pore water from the composite confining unit, because the pore water may contain 10 to 20 times as much Sr as the water in the aquifer. Hence, water entering the lower confining unit from the aquifer may have a Sr-isotope ratio similar to that in the pore water from the composite confining unit. This would not be true, however, if the Sr dissolved from the aquifer material were significantly more radiogenic than the Sr in the upward-leaking pore water; no data are available to evaluate this possibility. Sr-isotope data for shallow ground water in the Great Artesian Basin of Australia reported by Collerson et al. (1988) indicate, however, that the time scale at which the $^{87}Sr/^{86}Sr$ values in shallow ground water in siliciclastic sediment become strongly radiogenic is about 10^6 yr. Because the residence time of water in the Atlantic City 800-ft sand at Atlantic City is less than 10^6 yr, the $^{87}Sr/^{86}Sr$ value in the water is not expected to be controlled by radiogenic Sr derived from dissolution of Sr-bearing silicate minerals, such as K-feldspar. Another limitation of the calculation is the fact that flow paths in the aquifer are horizontal, which results in horizontal displacement of Sr from where it enters the aquifer to where it leaves the aquifer. Therefore, samples collected at the base of the lower confining unit are not on the same flow path as samples collected from the top of the composite confining unit. Whether the $^{87}Sr/^{86}Sr$ value varies horizontally or not in the confining units is unknown.

Adjacent samples of pore water in the lower confining unit commonly have great differences in concentrations of Sr but about the same $^{87}Sr/^{86}Sr$. For example, Samples 4 and 5 (585 ft [178.3 m] and 606 ft [184.7 m], respectively) have a large difference in Sr concentration (17.45 and 4.09 μM/L, respectively), but have nearly identical $^{87}Sr/^{86}Sr$ values (0.708486 and 0.708491, respectively). This result cannot be explained with the simple two-component mixing model described above. If upward-migrating pore water deposited carbonate crusts or micritic carbonate matrix throughout geologic time, the secondary calcites could contribute Sr to pore water by partial redissolution as a result of subsequent minor decreases in pore-water pH or dissolved-CO_2 concentration. Such secondary calcite crusts bear the Sr-isotopic signature of the pore water from which the crusts were precipitated, which may differ from that of the unaltered shell material they coat. Bishop et al. (1994) demonstrated that the Sr-isotope ratio of secondary calcite cement in an area underlain by carbonate rocks is significantly different from that of primary calcite in the same formation. Popp et al. (1986) found that even diagenetically altered shell material can retain the original $^{87}Sr/^{86}Sr$ values of the seawater at the time of deposition, but that $^{87}Sr/^{86}Sr$ values in diagenetically altered micritic matrix surrounding these shells are similar to those in the pore water from which the micrite was deposited. Partial redissolution of a secondary crust in the sediment of the Kirkwood Formation could contribute abundant Sr to the pore water, while the $^{87}Sr/^{86}Sr$-isotope value remains lower than that of the adjoining shell materials. No micritic cement or crusts were observed in hand samples of the sediment; however, geochemical calculations show that the pore water is saturated with respect to calcite in many of the sediment layers (Table 2). Therefore, the presence of finely disseminated secondary calcite cement is thermodynamically possible.

If the distribution of ^{87}Sr and ^{86}Sr in pore water from the confining units can be used as an indicator of flow through the New Jersey Coastal Plain sediments, it may be useful in the corroboration of the calibration of large-scale flow models, such as that of Martin (in press). First, however, the rates of the mechanisms that cause Sr-isotope ratios in the pore water to differ from those in the shell material (advection of Sr as well as geochemical reactions that affect concentrations of dissolved Sr) must be quantified.

CONCLUSIONS

The evolution of water quality in confined aquifers such as the Atlantic City 800-ft sand in the New Jersey Coastal Plain may be affected by leakage of pore water from the surrounding silty confining units; therefore, we examined the distribution and sources of solutes in the pore water in the confining units. Relations of Sr concentrations to those of other chemical constituents and the distribution of the $^{87}Sr/^{86}Sr$ value were used to determine possible sources of the solutes and identify the physical and chemical processes that may affect their distribution in the confining units above and below the Atlantic City 800-ft sand. The following conclusions were reached:

1. Concentrations of Sr in pore water in clay-silt sediments above the Atlantic City 800-ft sand varied with depth; they were highest at the top of the unit. Concentrations of Sr in pore water correlated strongly with concentrations of Ca, Mg, Na, and SO_4. The distribution of concentrations of Sr and correlated constituents indicates that diffusion of these constituents must be downward into the aquifer.
2. Concentrations of Sr and Ca in pore water from the clay-silt sediments below the sand were lower than those in the clay-silt sediments above it, possibly as a result, in part, of cation-exchange processes.
3. The $^{87}Sr/^{86}Sr$ values in the pore water were lower than those in the adjacent shell material at all depths but one. The $^{87}Sr/^{86}Sr$ values in the pore water appeared to decrease more rapidly with depth than those in the shell material, but this difference was not statistically significant. Statistical analysis was limited by the small sample size.
4. The only known source of Sr with isotope ratios lower than those in shell material in sediment from the lower Miocene Kirkwood Formation is shell material from sediment found at greater depth, including pre-Miocene stratigraphic units. Therefore, the Sr-isotope ratio in the pore water may result from upward movement of water into or through the clay-silt sediments through geologic time.

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