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# The combined use of $^{87}Sr/^{86}Sr$ and carbon and water isotopes to study the hydrochemical interaction between groundwater and lakewater in mantled karst

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**Abstract**—The hydrochemical interaction between groundwater and lakewater influences the composition of water that percolates downward from the surficial aquifer system through the underlying intermediate confining unit and recharges the Upper Floridan aquifer along highlands in Florida. The $^{87}Sr/^{86}Sr$ ratio along with the stable isotopes, D, $^{18}O$, and $^{13}C$ were used as tracers to study the interaction between groundwater, lakewater, and aquifer minerals near Lake Barco, a seepage lake in the mantled karst terrane of northern Florida. Upgradient from the lake, the $^{87}Sr/^{86}Sr$ ratio of groundwater decreases with depth (mean values of 0.71004, 0.70890, and 0.70852 for water from the surficial aquifer system, intermediate confining unit, and Upper Floridan aquifer, respectively), resulting from the interaction of dilute oxygenated recharge water with aquifer minerals that are less radiogenic with depth. The concentrations of $Sr^{2+}$ generally increase with depth, and higher concentrations of $Sr^{2+}$ in water from the Upper Floridan aquifer (20–35 $\mu g/L$), relative to water from the surficial aquifer system and the intermediate confining unit, result from the dissolution of Sr-bearing calcite and dolomite in the Eocene limestone. Dissolution of calcite [$\delta^{13}C = -1.6$ permil (‰)] is also indicated by an enriched $\delta^{13}C_{DIC}$ (−8.8 to −11.4‰) in water from the Upper Floridan aquifer, relative to the overlying hydrogeologic units ($\delta^{13}C_{DIC} < -16$‰).

Groundwater downgradient from Lake Barco was enriched in $^{18}O$ and D relative to groundwater upgradient from the lake, indicating mixing of lakewater leakage and groundwater. Downgradient from the lake, the $^{87}Sr/^{86}Sr$ ratio of groundwater and aquifer material become less radiogenic and the $Sr^{2+}$ concentrations generally increase with depth. However, $Sr^{2+}$ concentrations are substantially less than in upgradient groundwaters at similar depths. The lower $Sr^{2+}$ concentrations result from the influence of anoxic lakewater leakage on the mobility of $Sr^{2+}$ from clays. Based on results from mass-balance modeling, it is probable that cation exchange plays the dominant role in controlling the $^{87}Sr/^{86}Sr$ ratio of groundwater, both upgradient and downgradient from Lake Barco. Even though groundwater from the three distinct hydrogeologic units displays considerable variability in Sr concentration and isotopic composition, the dominant processes associated with the mixing of lakewater leakage with groundwater, as well as the effects of mineral-water interaction, can be ascertained by integrating the use of stable and radiogenic isotopic measurements of groundwater, lakewater, and aquifer minerals.

## 1. INTRODUCTION

The isotopic composition and concentrations of strontium in groundwaters and surface waters have been used as tracers of hydrochemical processes (e.g., mineral weathering reactions) in a variety of geologic settings primarily because patterns in strontium isotope ratios in waters can reflect variations in the $^{87}Sr/^{86}Sr$ ratios of the host rocks (e.g., Faure, 1986; Aberg et al., 1989). Recently, the $^{87}Sr/^{86}Sr$ ratio has been used effectively to discriminate the relative contribution of reactive phases, such as feldspars and ferromagnesian minerals, to the chemistry of water in silicate aquifers (Bullen et al., 1996); as well as the importance of cation-exchange reactions in determining solute flux within and from watersheds (Bullen et al., 1997; Izbicki et al., 1994; Johnson and DePaolo, 1994).

This study presents an evaluation of the use of $^{87}Sr/^{86}Sr$ ratios in a mantled karst system where groundwater and lakewater constitute a dynamic interconnected flow system. In northern Florida, the quality of groundwater and its flow patterns are profoundly influenced by lakewater leakage from sinkhole lakes (Katz et al., 1995a,b; Lee, 1996). The Lake Barco study area was chosen for this study because the work of previous investigators provides a well-defined hydrogeologic base (Pollman et al., 1991; Sacks et al., 1992; Lee, 1996). Also, detailed information exists on the mineralogy of aquifer material and on the chemical composition of groundwater, lakewater, and rainfall in this area (Katz et al., 1995b). The presence of three distinct hydrogeologic units that have different depositional histories and mineralogy provides an excellent opportunity to use $^{87}Sr/^{86}Sr$ as a discriminant of the relative contribution of aquifer mineralogy to the solute chemistry of groundwater that is influenced by leakage from a sinkhole lake. A comparison of $^{87}Sr/^{86}Sr$ ratios between the aqueous phase (lakewater and groundwater) with the $^{87}Sr/^{86}Sr$ ratio of exchangeable Sr from aquifer material can give detailed information on the hydrochemical processes that contribute solutes to the water. Furthermore, the combination of $^{87}Sr/^{86}Sr$ ratios with information on flow patterns deduced from other isotopes ($^{18}O/^{16}O$, D/H, and $^{13}C/^{12}C$) and geochemical modeling of the cycling of major ions in lakewater and groundwater provides an effective

multitracer approach that can significantly add to our understanding of complex hydrologic systems.

## 2. HYDROGEOLOGY AND GROUNDWATER FLOW PATTERNS

The Lake Barco basin is located within a nature preserve in the Interlachen Sand Hills, which is part of the Central Lake physiographic district (Brooks, 1981). This district is characterized by the formation of active sinkholes. Lake Barco has been identified as a cover-collapse sinkhole, typical of many of the lakes in the Central Lake District (Sinclair and Stewart, 1985; Arrington and Lindquist, 1987). The numerous lakes and other surficial depressions in this region have formed as the result of the filling of solution voids in the underlying limestone by unconsolidated sediments (Lane, 1986). The infilling material can be highly conductive hydraulically (Lee and Swancar, 1995) and can serve as an effective conduit for direct recharge to the Upper Floridan aquifer, which is the source of public-water supply in most of the northern peninsula of Florida. Lake Barco is an acidic seepage lake typical of other seepage lakes along ridges, uplands, and highlands in Florida having no surface-water inflow or outflow.

The hydrogeologic framework of the Lake Barco study area is shown in a cross section through the basin (Fig. 1). The Ocala Limestone of Upper Eocene age is unconformably overlain by 15–30 m of the Hawthorn Group of Miocene age, which consists of a variable mixture of sand, gravel, clay, phosphate, and carbonate sediments (Scott, 1988). The sediments of the Hawthorn Group comprise the intermediate confining unit. Undifferentiated surficial deposits of Holocene to Pliocene Age lie above the Hawthorn Group and consist of poorly to well sorted sands with variable amounts of silt and clay. These sands and clays comprise the surficial aquifer system. Seismic-reflection data indicated that the Hawthorn Group and surficial deposits below the lake do not consist of coherent, continuous beds (Sacks et al., 1992). Most likely, these beds are broken up because of subsidence activity with subsequent infilling of solution voids in the limestone by overlying sediments.

Groundwater inflow occurs only along the northeastern perimeter of the lake (near the 1PNB site), over approximately 12% of the total circumference of the lake (Pollman et al., 1991). The remaining groundwater that moves laterally toward the lake, but does not contribute inflow, flows laterally around and beneath Lake Barco where it mixes with leakage that moves downward through the lake bottom. North of the lake near the 1PNB site the direction of groundwater flow is predominantly downward, with shallow groundwater contributing about 1–10% (approximately 1,090–11,700 $m^3$/month during April 1989 through December 1990) of the total inflow to the lake, which includes groundwater plus direct rainfall on the lake surface (Lee, 1996). Upgradient from Lake Barco, groundwater was aerobic and travel times ranged from 5 years at a depth about 1 m below water table to about 17 years for water collected at a depth of 30 m below the water table, based on CFC-12 age-dating techniques (Katz et al., 1995a).

Lake Barco loses water to the surficial aquifer system along its southern side as evidenced by the lower elevation of the water table along the entire southern perimeter of the lake, especially in the vicinity of well nest 2PNB (Fig. 1). Prior to entering the underlying hydrogeologic units, the lakewater passes through about 3 m of soft, organic-rich sediments at the bottom of the central part of the lake (Sacks et al., 1992). As a result, groundwater downgradient from the lake evolves under anoxic conditions (Katz et al., 1995b). Groundwater flow is downward at the 2PNB site as a result of the strong downward head gradient. The residence time of groundwater increased with depth and ranged from about 19–30 years (Katz et al., 1995a).

Leakage from Lake Barco to the underlying surficial aquifer system and the Upper Floridan aquifer contributes significantly to the total lake outflow. Hydrologic budget measurements (during April 1989 through December 1990) indicated that lakewater leakage contributed about 30% of the total outflow (leakage plus evapotranspiration averaged 18,800 $m^3$/month) and exceeded groundwater inflow to the lake every month during the budget period by 70–8,500 $m^3$/month (Lee, 1996). During 1991–92, leakage from the lake resulted from a relatively constant downward head difference (1.07–1.28 m) between the lake and the Upper Floridan aquifer, as measured in well 1PNB-FL. Water levels for the in-lake wells (MLW-2, MLW-4, and MLW-6) were virtually equal to the lake level during the sampling period (May 1991 to September 1992) and during 1988 through 1990 (Sacks et al., 1992). In-lake well 4 (MLW-4) generally had a measurable head difference, usually less than 3.5 cm lower than the lake stage. However, there is some uncertainty as to the reliability of the head measurement from the in-lake wells because of possible leakage of lakewater at casing joints (Sacks et al., 1992).

## 3. METHODS

The location of lakewater and groundwater samples collected for strontium isotopic composition are shown in the cross-section of Fig. 1. The wells sampled in this study were originally installed as part of an investigation to determine the influence of groundwater inflow on the regulation of the acid neutralizing capacity of Lake Barco (Pollman et al., 1991; Sacks et al., 1992; Lee, 1996). Groundwater and lakewater were sampled as follows: two aliquots were filtered using a 0.10 $\mu$m nucleopore filter and subsequently acidified for the analysis of strontium isotopic composition and $Sr^{2+}$ concentration. Additional aliquots were collected for a companion study that included stable isotope analyses, dissolved gases, and major and minor constituents (for methods of sample collection and analysis, see Katz et al., 1995a,b).

The isotopic composition of water and acid exchangeable $Sr^{2+}$ was determined in clay-size material from the undifferentiated sands and clays of the surficial aquifer system, the Hawthorn Group (intermediate confining unit), and the Ocala Limestone (Upper Floridan aquifer). Water leachates were obtained by reacting 1 g of pulverized material (<2 $\mu$m, to homogenize the sample) in 10 mL of deionized water at 50°C for 48 h. The slurry was filtered through an acid-rinsed 0.45 $\mu$m syringe unit and the Sr extracted from the water leachate. Acid leachates were obtained by reacting 1 g of material with 10 mL of 0.5 N HCl at 35°C for 24 h, filtering as above, and extracting the Sr from the acid leachate (Bullen et al., 1996).

Samples of groundwater and lakewater were analyzed for $Sr^{2+}$ concentration using inductively coupled plasma spectroscopic methods, with an analytical detection limit of 2 $\mu$g/L. Groundwater sam-

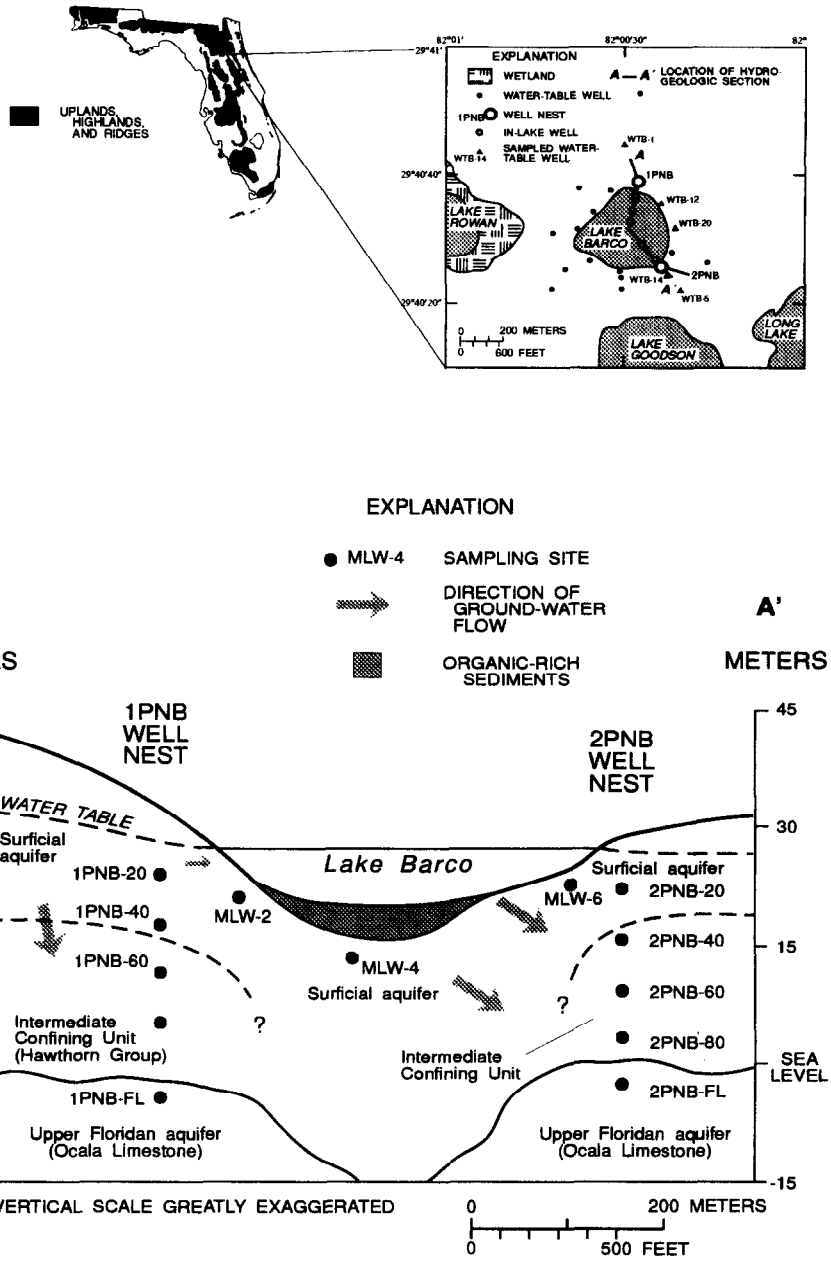


FIG. 1. Location map of study area and cross section showing hydrogeologic framework, location of sampling sites, and direction of groundwater flow.

ples that contained $Sr^{2+}$ concentrations $<2\mu g/L$ were analyzed by isotope dilution using an enriched $^{84}Sr$ spike. The analytical detection limit using this method was 0.02 $\mu g/L$. Approximately 50 mL of each of the acidified samples was passed through a cation exchange column and eluted with HCl to separate Sr for isotopic analysis. Isotopic compositions were measured on a Finnigan MAT 261 solid-source mass spectrometer at the U.S. Geological Survey (USGS) Water Resources Division Laboratory in Menlo Park, CA. (The use of trade names does not constitute endorsement by the USGS.) The reported $^{87}Sr/^{86}Sr$ ratios for groundwater, lakewater, and leachates have a precision of 0.00002 at the 95% confidence level. The long-term average value for a $SrCO_3$ standard (NIST 987) at the USGS isotope laboratory is $0.71024 \pm 0.00001$ ($\pm 2\sigma$).

Mineralogic analyses were performed on nine representative sediment samples from the surficial aquifer system, intermediate confining unit, and the top of the Upper Floridan aquifer (Ocala Limestone). Bulk mineralogy and clay-sized particles ($<1$ and $<0.03$ $\mu m$) were analyzed using standard X-ray diffraction techniques (XRD; Brindley and Brown, 1980; Moore and Reynolds, 1989). The finer fraction ($<0.03$ $\mu m$) was also analyzed by direct coupled plasma spectroscopic (DCP) methods in addition to XRD to characterize the chemical composition of smectite minerals in clays from the intermediate confining unit (Katz, 1993).

The stable isotopes, ($^{18}O/^{16}O$, D/H, and $^{13}C/^{12}C$) were determined in precipitation, groundwater and lakewater to identify water sources and quantify mixing proportions (Katz et al., 1995a,b). Standard $\delta$ (delta) notation for these isotopes is used (Gonfiantini, 1981). The analysis of $\delta^{13}C$ of dissolved inorganic carbon (DIC) in groundwater and lakewater involved the precipitation of the DIC using $NH_4OH$-$SrCl_2$, followed by filtering, drying, and acidifying the $SrCO_3$ precip-

Table 1: $Sr^{2+}$ concentrations and $^{87}Sr/^{86}Sr$ ratios for groundwater and lakewater samples.

[m denotes meters; groundwater travel time is based on CFC-12 modeled recharge dates (Katz et al., 1995a); µg/L denotes micrograms per liter; NA denotes not applicable; NS denotes not sampled; $\delta^{13}C_{DIC}$ denotes delta carbon-13 of dissolved inorganic carbon; site information and the variability in $\delta^{13}C_{DIC}$ values are described in detail by Katz et al., 1995b.]

| Site Name | Depth below land surface (m) | Groundwater travel time, in years | | $Sr^{2+}$ (µg/L) | $^{87}Sr/^{86}Sr$ (May 1991) | $^{87}Sr/^{86}Sr$ (Sept 1992) | $^{87}Sr/^{86}Sr$ (mean) | $\delta^{13}C_{DIC}$ (per mil) |
|---|---|---|---|---|---|---|---|---|
| 1PNB-20 | 6.5 | 3.3 | ±1.8 | 2.0 | NS | 0.71004 | 0.71004 | -22.75 |
| 1PNB-40 | 12.1 | 9.0 | ±0.9 | 9.0 | NS | 0.70863 | 0.70863 | -17.75 |
| 1PNB-60 | 19.3 | 14 | ±1.1 | 7.0 | 0.70913 | 0.70920 | 0.70917 | -18.45 |
| 1PNB-FL | 37.2 | 14.4 | ±1.4 | 24.0 | 0.70845 | 0.70859 | 0.70852 | -11.35 |
| Lake Barco | NA | 2.0 | ±1.9 | 6.0 | NS | 0.70997 | 0.70997 | -14.95 |
| MLW-2 | 2.9 | 4.1 | ±1.4 | 2.0 | NS | 0.71041 | 0.71041 | -17.25 |
| MLW-4 | 4.1 | 34 | ±1.9 | 7.0 | NS | 0.71052 | 0.71052 | -4.30 |
| MLW-6 | 2.3 | 3.3 | ±0.8 | 22.0 | NS | 0.71025 | 0.71025 | -26.50 |
| 2PNB-20 | 6.4 | 19 | ±2.4 | 0.66 | 0.71120 | 0.71143 | 0.71132 | -16.00 |
| 2PNB-40 | 12.3 | 23 | ±0.9 | 0.83 | 0.71042 | 0.71068 | 0.71055 | -18.00 |
| 2PNB-60 | 18.6 | 21 | ±1.8 | 0.67 | NS | 0.71044 | 0.71044 | -20.05 |
| 2PNB-80 | 24.9 | 21 | ±0.6 | 1.21 | 0.70882 | 0.70881 | 0.70882 | -16.15 |
| 2PNB-FL | 31.4 | 36 | ±1.6 | 35.0 | 0.70809 | 0.70806 | 0.70808 | -8.80 |

itate to produce $CO_2$, which was analyzed by mass spectrometric methods (Gleason et al., 1969). The $2\sigma$ precision for the analytical procedure is 0.2‰ (Coplen, 1994). Carbon isotope analyses of both water samples and aquifer material were performed by the U.S. Geological Survey Isotope Geochemistry Laboratory, Reston, Virginia. Values of $\delta^{13}C$ are reported relative to the Vienna Pee Dee Belemnite (VPDB) standard. Oxygen- and hydrogen-isotope results are reported in permil (‰) relative to VSMOW (Vienna Standard Mean Ocean Water) and normalized on scales such that the oxygen and hydrogen isotopic values of SLAP (Standard Light Antarctic Precipitation) are −55.5‰ and −428‰, respectively (Coplen, 1988; Coplen et al., 1991). The $2\sigma$ precision of oxygen and hydrogen isotope results is 0.2 and 1.5‰, respectively.

## 4. RESULTS

The $Sr^{2+}$ concentrations of groundwater and lakewater tend to follow the concentrations of major dissolved species. In this system, where the downward flow velocity of groundwater is about 0.5–1.0 m/yr and recharge is relatively high (approximately 25 cm/yr), lakewater and groundwater are characterized by very low concentrations of dissolved solids (DS): lakewater averages 8 mg/L DS, waters from the silicate surficial aquifer system and intermediate confining unit have DS ranging from 15–35 mg/L, and water from the Upper Floridan aquifer has DS ranging from 54 (1PNB-FL) to 141 mg/L (2PNB-FL). Water from well MLW-4, screened beneath the lake, has relatively high dissolved solids, 105 mg/L; however, dissolved $SiO_2$ from biogenic sources in lakewater comprised more than 50% of this value (Katz et al., 1995b). Rainwater collected during June 1990 through June 1991 had a mean volume-weighted dissolved-solids concentration of 2.6 mg/L (Katz et al., 1995b). Upgradient from the lake, groundwater moves downward from the water table to the top of the Upper Floridan aquifer under oxic conditions. The $Sr^{2+}$ concentration increases with depth in water from 1PNB-20 to 1PNB-40 (Table 1), corresponding to the increase in the concentration of $Ca^{2+}$ and $Mg^{2+}$ (Table 2). The dominant ions in water from 1PNB-20 are $Na^+$ and $Cl^-$, but $Ca^{2+}$, $Mg^{2+}$, and $HCO_3^-$ predominate at 1PNB-40. The $Sr^{2+}$ concentration decreases slightly from 9–7 µg/L in water from 1PNB-40 to 1PNB-60, even though the concentration of Ca and Mg both increase, and $Ca^{2+}$, $Mg^{2+}$, and $HCO_3^-$ remain the dominant ions (Table 2). There is a large increase in the concentration of $Sr^{2+}$ in water, from 7 µg/L (1PNB-60) to 24 µg/L (1PNB-FL), which is indicative of the dissolution of soluble calcite [$CaCO_3$] and dolomite [$CaMg(CO_3)_2$] in the Ocala Limestone at the top of the Upper Floridan aquifer. The saturation index (SI) of groundwater with respect to calcite also shows a corresponding increase with depth, from −3.06 (1PNB-60) to −1.07 (1PNB-FL).

The concentration of $Sr^{2+}$ in lakewater is higher (6.0 µg/L) than the concentration of $Sr^{2+}$ in groundwater inflow to the lake (2.0 µg/L at 1PNB-20) and in rainfall (<2.0 µg/L). The higher $Sr^{2+}$ in lakewater results from an evapoconcentration factor of approximately 3 (Lee, 1996). The concentration of $Ca^{2+}$ also shows a similar threefold increase in lakewater compared to groundwater inflow and precipitation, although $Na^+$, $SO_4^{2-}$, and $Cl^-$ are the dominant ions in lakewater (Table 2). Evaporation contributed about 70% of the total outflow of the lake, represented by evaporation plus lakewater leakage (Lee, 1996).

Downgradient from the lake, groundwater is anoxic, and the $Sr^{2+}$ concentrations are less than 2 µg/L for water near the water table (2PNB-20) downward to a depth of 24 m (2PNB-80). $Na^+$ and $Cl^-$ are the dominant ions in water from 2PNB-20, 2PNB-40, and 2PNB-60 and the concentrations of $Ca^{2+}$ and $Mg^{2+}$ both remain constant at less than 0.20 mg/L (Table 2). $Ca^{2+}$ and $Mg^{2+}$ increase substantially from 2PNB-60 to 2PNB-80 and a corresponding increase in

**Table 2. Concentrations of major elements, chemical species, delta oxygen-18, and delta deuterium in rainfall, groundwater and lakewater.**

[All concentrations of elements and species are in millimoles per kilogram of water; $\delta^{18}O$ (delta oxygen-18) and $\delta D$ (delta deuterium) are expressed as per mil; DO denotes dissolved oxygen. Based on water samples collected during August 31 to September 4, 1992, except for rainfall, which was a composite sample collected from June 30 to September 29, 1992. Chemical composition of rainfall corrected for dry deposition (see Katz et al., 1995a). $C_{DIC}$ denotes dissolved inorganic carbon.]

| SITE | Temp °C | pH | DO | Ca | Mg | Na | K | Cl | $SO_4$ | $C_{DIC}$ | $SiO_2$ | $\delta^{18}O$ | $\delta D$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| RAINFALL | 21. | 4.36 | 0.275 | 0.007 | 0.003 | 0.016 | 0.002 | 0.019 | 0.020 | 0.012 | 0.00 | -3.35 | -15.5 |
| 1PNB-20 | 23. | 5.49 | 0.181 | 0.018 | 0.021 | 0.128 | 0.001 | 0.133 | 0.004 | 0.043 | 0.090 | -4.40 | -24.5 |
| 1PNB-40 | 24. | 6.16 | 0.194 | 0.083 | 0.058 | 0.089 | 0.004 | 0.096 | 0.008 | 0.071 | 0.118 | -4.10 | -21.0 |
| 1PNB-60 | 24. | 6.34 | 0.194 | 0.100 | 0.086 | 0.090 | 0.005 | 0.096 | 0.008 | 0.681 | 0.131 | -3.95 | -19.5 |
| 1PNB-FL | 24. | 7.51 | 0.203 | 0.285 | 0.111 | 0.094 | 0.006 | 0.0828 | 0.010 | 0.891 | 0.112 | -3.95 | -20.0 |
| 2PNB-20 | 24. | 5.13 | 0.009 | 0.005 | 0.008 | 0.112 | 0.003 | 0.130 | 0.002 | 0.527 | 0.108 | -2.25 | -11.0 |
| 2PNB-40 | 23. | 5.11 | 0.006 | 0.003 | 0.008 | 0.135 | 0.003 | 0.147 | 0.006 | 0.162 | 0.126 | -1.00 | -5.5 |
| 2PNB-60 | 24. | 5.25 | 0.009 | 0.005 | 0.008 | 0.132 | 0.006 | 0.104 | 0.005 | 0.705 | 0.117 | +0.25 | -2.5 |
| 2PNB-80 | 22. | 6.03 | 0.000 | 0.130 | 0.066 | 0.125 | 0.008 | 0.093 | 0.003 | 1.37 | 0.122 | +0.50 | +2.0 |
| 2PNB-FL | 24. | 7.35 | 0.000 | 1.10 | 0.148 | 0.135 | 0.017 | 0.141 | 0.002 | 2.81 | 0.166 | +0.85 | +2.0 |
| L BARCO | 29. | 4.66 | 0.181 | 0.031 | 0.033 | 0.169 | 0.007 | 0.152 | 0.084 | 0.216 | 0.010 | +3.60 | +16.5 |
| MLW-2 | 24. | 5.11 | 0.156 | 0.016 | 0.012 | 0.081 | 0.003 | 0.087 | 0.017 | 0.090 | 0.117 | -3.85 | -19.0 |
| MLW-4 | 24. | 6.03 | 0.000 | 0.037 | 0.029 | 0.222 | 0.013 | 0.141 | 0.0000 | 0.372 | 0.915 | +0.95 | +2.5 |
| MLW-6 | 24. | 5.63 | 0.016 | 0.098 | 0.086 | 0.068 | 0.001 | 0.045 | 0.079 | 1.08 | 0.067 | -3.35 | -15.5 |

the $Sr^{2+}$ concentration is also observed. The $Sr^{2+}$ concentration increases sharply to 35 $\mu$g/L in water from 2PNB-FL, following the large increase in $Ca^{2+}$ and $Mg^{2+}$, resulting from the dissolution of calcite and dolomite at the top of the Upper Floridan aquifer (Ocala Limestone). A greater amount of dissolution of carbonate minerals, which is observed in the Upper Floridan aquifer downgradient from the lake as opposed to upgradient (1PNB-FL), is indicated by the much higher concentrations of DIC (factor of 3), Ca, and Mg, greater $\delta^{13}C$ (−8.80‰ for 2PNB-FL compared to −11.35‰ for 1PNB-FL), and a SI with respect to calcite of 0.0 (Katz et al., 1995b). The longer residence time of water in the aquifer at this location, compared to 1PNB-FL, and the increased amount of $CO_2$ generated from microbially mediated oxidation-reduction reactions probably account for this increased dissolution of calcite and dolomite (Katz et al., 1995b).

Water collected from the surficial aquifer system and the intermediate confining unit is more radiogenic (higher $^{87}Sr/^{86}Sr$ ratios) than groundwater from the Ocala Limestone (Table 1). Lakewater has a $^{87}Sr/^{86}Sr$ ratio (0.70997) that is similar to water from the surficial aquifer system (0.71004 at 1PNB-20). The $^{87}Sr/^{86}Sr$ ratios for groundwater and lakewater are inversely related to the $\delta^{13}C$ composition of the DIC (Table 1). Water from the surficial aquifer system and the intermediate confining unit is highly depleted in $^{13}C$ ($\delta^{13}C$ = −16.0 to −22.8‰) and its $^{87}Sr/^{86}Sr$ ratio is more radiogenic (0.7113–0.7088) compared to water from the top of the Ocala Limestone (1PNB-FL and 2PNB-FL), which is more enriched in $^{13}C$ ($\delta^{13}C$ = −8.8 to −11.4‰) and has $^{87}Sr/^{86}Sr$ ratios of 0.70852 to 0.70808 (Table 1).

The $^{87}Sr/^{86}Sr$ ratios for extracted Sr in water and acid leachates of sediments from the three hydrogeologic units are given in Table 3. The $^{87}Sr/^{86}Sr$ ratios of the water and acid leachates of aquifer material become less radiogenic with depth, reflecting the mineralogy and age of the sediments (the time of deposition). The values for the two treatments were similar, with a difference of less than ±0.09%. Other studies have also reported similar strontium isotope values in water and acetic acid leachates, such as for soils from coral-reef terraces on Barbados (Banner et al., 1994). With the exception of two samples (1PN9 and 1PN60), the water leachates were slightly more radiogenic (higher $^{87}Sr/^{86}Sr$ ratios) than the acid leachates of aquifer sediments. The close agreement between the two treatments in this study indicates that the $Sr^{2+}$ is in a highly exchangeable form, most likely occurring on exchange sites of clay minerals present in the sediments from the surficial aquifer system and the intermediate confining unit (Table 3). The possibility of a rapid geochemical process, such as cation exchange, that could be providing $Sr^{2+}$ to the dissolved phase, is discussed in the following section.

## 5. DISCUSSION

The variations in the strontium isotopic composition of groundwater with depth as well as between groundwater

Table 3. $^{87}Sr/^{86}Sr$ ratios of water and acid leachates of sediments from the undifferentiated surficial deposits (USD, surficial aquifer system), the Hawthorn Group (HG, intermediate confining unit), and the Ocala Limestone (OL, Upper Floridan aquifer).

[rep denotes replicate analysis; minerals in aquifer sediments were analyzed by X-ray diffraction techniques, listed for each sample in decreasing order of abundance, and abbreviated as follows: quartz, Q; kaolinite, K; fluorapatite, F; K-feldspar, Ks; calcite, C; dolomite, D; smectite, S; chlorite, Chl; illite, I; sepiolite, Se; palygorskite, P; and traces of other clays, T.]

| Aquifer material designation | Sample depth below land surface (m) | Hydrogeologic unit | $^{87}Sr/^{86}Sr$ DI water leachate | $^{87}Sr/^{86}Sr$ 0.5N HCl leachate | Mineralogy of <1μm size fraction |
|---|---|---|---|---|---|
| 1PN9 | 3-4 | USD | 0.71003 | 0.71061 | Q,K,T,Chl,S |
| 1PN60 | 18. | HG | 0.70931 | 0.70971 | Q,K,T |
| 1PN73 | 22. | HG | 0.70905 | 0.70901 | Q,F,Ks |
| 1PN77 | 23.5 | HG | 0.70925 | 0.70893 | Q,F,Ks,T |
| 1PN120 | 36.6 | OL | 0.70799 | 0.70788 | C,F,T |
| 2PN40 | 12. | USD | 0.71062 | 0.71016 | Q,K,I,S,D |
| 2PN80 | 24.4 | HG | 0.70950 | 0.70886 | Q,D,F,S,Se,P,K,I |
| 2PN110 | 33.5 | OL | 0.70855 | 0.70837 | F,Q,D,Ks,T |
| 2PN110 (rep) | 33.5 | OL | 0.70838 | 0.70838 | F,Q,D,Ks,T |

and water from Lake Barco are related to differences in mineralogy among the three hydrogeologic units, hydrochemical conditions at upgradient and downgradient sites, patterns of groundwater flow, and residence time of groundwater in the three hydrogeologic units. These factors are discussed with respect to their influence on the strontium isotopic composition and the concentration of $Sr^{2+}$ in water from the silicate material comprising the surficial aquifer system and the intermediate confining unit, the carbonate rocks comprising the Upper Floridan aquifer, and in lakewater.

### 5.1. Cation Exchange Reactions in Silicate Aquifer Material

The silicate material that comprises the surficial aquifer system and intermediate confining unit is predominantly fine sands that contain low amounts of silt and clay-sized particles (see Table 3 for clay mineralogy). Furthermore, sandy soils in the study area typically have low amounts of extractable bases ($Ca^{2+}$, $Mg^{2+}$, $Na^{+}$, and $K^{+}$), 0.04–0.27 meq/100 g soil with a base saturation of 4–9% (Readle, 1990). Yet, reactions involving clay minerals, in particular the incongruent dissolution of smectite minerals to form kaolinite, and cation exchange had a dominant role in the evolution of major-ion chemistry in this dilute system, based on geochemical modeling (Katz et al., 1995b) and petrographic evidence (Kane, 1984). In most cases, the strontium isotopic composition of the groundwater upgradient from Lake Barco was found to be in isotopic equilibrium with the exchangeable Sr from the surficial material and the clays from the intermediate confining unit (Fig. 2). In this dynamic flow system where the residence time of groundwater is on the order of years to tens of years, the strontium isotopic ratio of groundwater appears to be buffered by exchangeable Sr from clays, as is the case for systems where the residence time of waters is on a timescale of hundreds to thousands of years (Johnson and DePaolo, 1994). In other groundwater systems, a rapid equilibration of $^{87}Sr/^{86}Sr$ between the aqueous and solid phases indicated that cation-exchange reactions provide $Sr^{2+}$ to the dissolved (aqueous) phase as groundwater is recharged or moves from one type of geologic material to another (Hunt et al., 1994; Izbicki et al., 1994).

Water samples from the surficial aquifer system and the intermediate confining unit at the 2PNB well nest do not appear to be in isotopic equilibrium with their host sediments; that is, the water is more radiogenic than the aquifer material at the depth of water sampling. The more radiogenic Sr ratios and lower $Sr^{2+}$ concentrations at a given depth of groundwater in the 2PNB profile relative to the comparable depth in the 1PNB profile are most likely related to differences in redox conditions and residence times between the downgradient and upgradient groundwater. The anoxic conditions downgradient from the lake (2PNB profile) could enhance the dissolution of ferromagnesian clay minerals, such as chlorite. Chlorite could have been formed from the hydration of mica minerals with a more radiogenic strontium isotopic ratio. In fact, micas and heavy minerals in sand deposits near the study area (along Trail Ridge) have been derived directly or indirectly from granites, quartzofeldspathic gneisses, and or schists from the Piedmont and Blue Ridge physiographic regions of the southern Appalachians (Pirkle et al., 1974; Kane, 1984). The chlorite appears to be stable under aerobic conditions at the 1PNB site, as it was observed in the 1PN9 sample (Table 3), collected at a depth of 3–4 m below land surface. No chlorite was present in samples of surficial aquifer system material downgradient from the lake. A possible scenario for the absence of chlorite in these sediments is that the longer residence time of waters at the 2PNB site (as determined from CFC-12 modeled re-

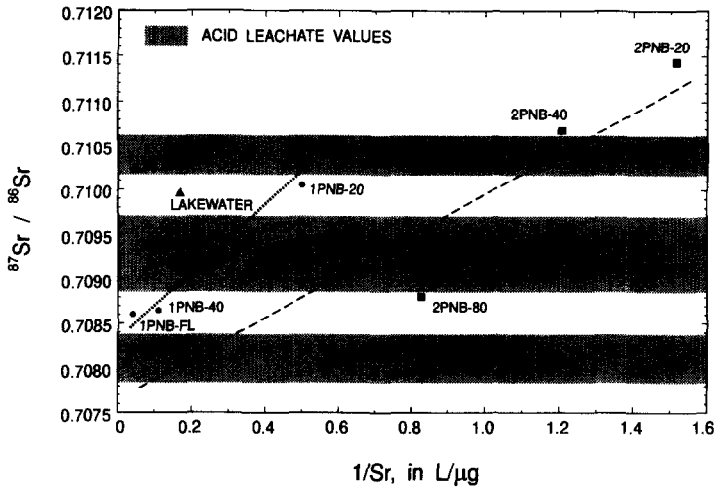


FIG. 2. Diagram showing the relation between $^{87}Sr/^{86}Sr$ and 1/Sr in groundwater and lakewater, and the range in $^{87}Sr/^{86}Sr$ for acid leachates of samples of aquifer material. The dotted line represents a mixing line for water samples from the 1PNB well nest (filled circles). The dashed line represents a mixing line for water samples from the 2PNB well nest (filled squares). Water samples from in-lake wells and Lake Barco are denoted by the filled triangles.

charge dates) could lead to protracted dissolution of the ferromagnesian minerals relative to some other phase that might quickly reach saturation. The strontium isotopic ratio of exchangeable $Sr^{2+}$, therefore, reflects the transient balance between the mineral source of radiogenic Sr to the cation exchange pool, redox conditions, and the strontium isotopic composition of the water derived from overlying units that reacts with the clay minerals in the aquifer material (Bullen et al., 1994).

### 5.2. Dissolution of Carbonate Minerals in the Ocala Limestone

Water from the upper part of the Ocala Limestone (Upper Floridan aquifer) upgradient from the lake (1PNB-FL) is more radiogenic ($^{87}Sr/^{86}Sr$ = 0.70852) than the isotopic composition of the exchangeable Sr, as determined from the water (0.70799) of acid (0.70788) leachates of the Ocala Limestone (1PN120 sample; Table 3). The higher $^{87}Sr/^{86}Sr$ ratio in water from 1PNB-FL could be indicative of an insufficient amount of time for equilibration to occur between the water and rock. The observed strontium isotopic ratio is close to the value that would result from a 50/50 mixture of the Sr in the water leachates of the intermediate confining unit (sample 1PN77, 0.70925) and the water from the top of the Upper Floridan aquifer (sample 1PN120, 0.70788). In contrast, the strontium isotopic ratio of water from the top of the Upper Floridan aquifer downgradient from the lake at 2PNB-FL (0.70808) is less radiogenic than that of water or acid leachates of rock with which it is in contact (sample 2PN110, $^{87}Sr/^{86}Sr$ = 0.70837–0.70855) and less radiogenic than water from the 1PNB-FL site. The Sr ratio of water from 2PNB-FL could not result from a simple mixture of water from the upgradient side of the lake with lakewater leakage. Based on mass-balance modeling of major dissolved constituents (Katz et al., 1995b) and using $\delta^{18}O$ and $\delta D$ to determine the mixing ratio of upgradient groundwater with lakewater leakage (Table 2), a mixing scenario that involved 37% water from 1PNB-FL and 63% lakewater leakage produced the observed chemical and isotopic composition of water from 2PNB-FL (Katz et al., 1995b). However, lakewater leakage, water from 1PNB-FL, and water and acid leachates of 2PN110 are all more radiogenic than the $^{87}Sr/^{86}Sr$ ratio of water from 2PNB-FL. Two possible explanations for this low $^{87}Sr/^{86}Sr$ ratio are related to (1) the longer residence time of water at 2PNB-FL compared to 1PNB-FL, and (2) the relatively nonreactive nature of the rock at that site (see below). Thus, the strontium isotopic signature of water from 2PNB-FL is probably determined from the dissolution and equilibration of upgradient water with more soluble rock from upgradient of the lake (1PN120) that has a less radiogenic strontium isotopic composition.

The more radiogenic strontium isotopic composition of rock (water leachate) from the top of the Upper Floridan aquifer on the downgradient side of the lake (0.70837–0.70855) compared to water leachate of rock from the top of the Upper Floridan aquifer on the upgradient side of the lake (0.70788) is probably related to difference in mineralogy between the two locations. Based on XRD analysis, calcite and fluorapatite were the dominant minerals in the 1PN120 sample, whereas the 2PN110 sample contained fluorapatite, quartz, dolomite, and some K-feldspar (Table 3). The higher strontium isotopic ratio in the water and acid leachates could result from the reaction of other minerals with a more radiogenic composition, such as K-feldspar. Differences in mineralogy between these two sites were corroborated by other physical properties. For example, cuttings of limestone from well drilling at the 1PN120 location (upgradient from the lake) had a yellowish tint, which most likely was an iron oxyhydroxide coating. These samples effervesced vigorously, liberating $CO_2$ when HCl solution was

added dropwise. In contrast, the 2PN110 samples (collected downgradient from the lake) did not have any noticeable coating and did not effervesce when HCl was added dropwise to the rock. These differences in mineralogy, combined with a longer residence time for water and the anaerobic conditions at the 2PNB-FL site compared to the 1PNB-FL site, could account for the observed strontium isotopic patterns at the two sites.

The water and acid leachate values for exchangeable Sr from samples of the Ocala Limestone (1PN120 and 2PN110) are more radiogenic than the value for Eocene seawater of 0.7077–0.7079 (Veizer, 1989). The $^{87}Sr/^{86}Sr$ ratio of ancient seawater is determined from the $^{87}Sr/^{86}Sr$ ratio that is incorporated into authigenic minerals such as carbonates, sulfates, and phosphates. However, the $^{87}Sr/^{86}Sr$ ratio in sediments can change over time as diagenesis proceeds and a more stable assemblage evolves (Veizer, 1989). In fact, the lower $\delta^{13}C$ value of calcite (−1.55‰) from the 1PN120 site, compared to the typical range of $\delta^{13}C$ for calcite of −0.5 to +0.5‰ for the Upper Floridan aquifer (Sprinkle, 1989), indicates that calcite and dolomite most likely formed in a groundwater environment during the last diagenetic episode that contained isotopically-light $HCO_3^-$ ions (Hanshaw and Back, 1972; Sprinkle, 1989). Furthermore, much lower $Sr^{2+}$ concentrations in dolomite from the Ocala Limestone than in modern dolomite (Randazzo and Hickey, 1978) possibly indicate successive recrystallization of dolomite in waters that were substantially less saline than seawater (Hanshaw et al., 1971). Successive episodes of alteration of calcite and dolomite would lead to lower values of $Sr^{2+}$ in the rock (Randazzo and Bloom, 1985) and the remaining $Sr^{2+}$ could possibly have a more radiogenic strontium isotopic composition.

To reiterate, there is an inverse relation between $^{87}Sr/^{86}Sr$ and $\delta^{13}C$ values in water samples from the three hydrogeologic units in the study area. Water collected from sediments that comprise the surficial aquifer system and the intermediate confining unit, which typically do not contain carbonates, have $^{87}Sr/^{86}Sr$ ratios that are greater than 0.70863 and values of $\delta^{13}C$ that are less than −16.0‰. In contrast, water from the Ocala Limestone has lower $^{87}Sr/^{86}Sr$ ratios (0.70806–0.70859) and higher $\delta^{13}C$ values (−8.80 to −11.35‰). On a plot of $\delta^{13}C$ against $^{87}Sr/^{86}Sr$ (Fig. 3), these waters form a hyperbolic array between the silicate material of the surficial aquifer system and the intermediate confining unit, and the calcite and dolomite of the Ocala Limestone (Upper Floridan aquifer). The anomalously high $\delta^{13}C$ value of −4.3‰ for MLW-4 (Fig. 3) results from methanogenesis reactions where microorganisms preferentially utilize $^{12}C$ in the production of methane gas resulting in an enrichment in of $^{13}C$ of the DIC in the water (Katz et al., 1995b). The reaction of groundwater with carbonate minerals is shown trending toward the strontium and carbon isotopic composition of calcite in the upper lefthand corner of Fig. 3, whereas the weathering of aluminosilicate minerals in the overlying hydrogeologic units can be represented by a horizontal line (Fig. 3).

### 5.3. Comparison of $^{87}Sr/^{86}Sr$ with $^{18}O$ and D in Groundwater

The combined use of strontium isotopes and the stable isotopes of water provide complementary information on the hydrochemical interaction between groundwater and lakewater in this system. Stable isotopes ($^{18}O/^{16}O$ and D/H) are commonly used to determine the origin of waters, flow patterns, and mixing of waters, whereas the strontium isotopes are useful in describing the reactions between the water and the solid phase material along known pathways of flow. The composition of $^{18}O$ and D in lakewater, groundwater, and rainfall indicates that rainfall is the dominant source of water in the three hydrogeologic units upgradient from the lake (Katz et al., 1995a). The $\delta^{18}O$ and $\delta D$ values for rainfall and groundwater upgradient from Lake Barco (sampled near the water table and at several depths below it) plot in close proximity along the global meteoric water line (Fig. 4). In contrast, the $\delta^{18}O$ and $\delta D$ values for lakewater and groundwater downgradient from the lake were enriched relative to meteoric water (or upgradient groundwater) as a result of evaporation of lakewater and subsequent mixing of lakewater leakage with groundwater. The relation between $\delta D$ and $\delta^{18}O$ in groundwater downgradient from the lake was described by the expression $\delta D(‰) = 4.76\delta^{18}O(‰) - 0.41$ ($r^2 = 0.992$). A two-component mixing model, which accounted for the enriched isotopic composition of groundwater downgradient from the lake, indicated that the amount of lakewater leakage that mixed with infiltrating meteoric water or groundwater ranged from 11–67% (Katz et al., 1995a), with a limit of detection of lakewater in groundwater of 4.3% (confirmed independently by using data for both $\delta^{18}O$ and $\delta D$).

The flow patterns, which were delineated from stable isotopes and vertical-head gradients, partly influence the strontium isotopic composition of groundwater and lakewater due to mixing processes; however, the strontium isotopic composition is controlled to a greater extent by the interaction between the water and the minerals present in the aquifer material. Mixing of waters and reactions between groundwater and aquifer material can be elucidated by comparing the $^{87}Sr/^{86}Sr$ of groundwater, lakewater, and exchangeable Sr from aquifer sediments against the reciprocal of the $Sr^{2+}$ concentration, 1/Sr (Fig. 2). Some distinct patterns can be discerned from the apparent scatter. For example, waters from both the 1PNB and 2PNB sites fall along approximate lines or bands that could be interpreted as mixing lines, which represent mixing between dilute recharge water with low concentrations of $Sr^{2+}$ near the water table (e.g., 1PNB-20 and 2PNB-20) and higher concentrations of $Sr^{2+}$ in water derived from the dissolution of carbonate minerals in the lower part of the intermediate confining unit and the top of the Upper Floridan aquifer (Ocala Limestone). The major differences in the two profiles are that the 2PNB samples are much more radiogenic and contain less $Sr^{2+}$ than samples collected at similar depths from the 1PNB profile. Overall, similar reactions must be occurring in aquifer material located upgradient and downgradient from the lake because the $^{87}Sr/^{86}Sr$ ratios decrease with depth for the 1PNB and 2PNB profiles. However, the differences between the two profiles are related, in part, to the contribution from lakewater leakage, longer residence time of water at the 2PNB sites, and differences in mineralogy between sites upgradient and downgradient from the lake (Table 3). The anoxic con-

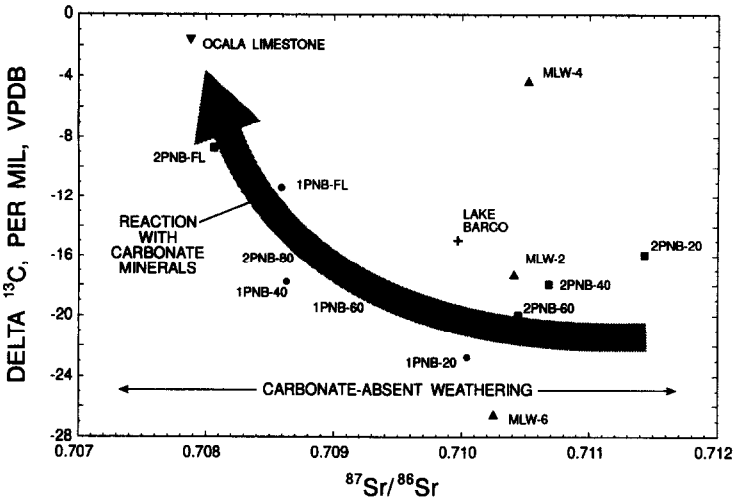


FIG. 3. $^{87}Sr/^{86}Sr$ vs. delta $^{13}C$ for groundwater, lakewater, and Ocala limestone leached phase.

ditions downgradient from the lake at the 2PNB profile are controlling some undetermined precipitation/exchange reaction that keeps Sr buffered near 1 μg/L, even though some dissolution of carbonate minerals is occurring at 2PNB-80.

The flow and mixing patterns determined using $\delta^{18}O$ and $\delta D$ can be used to assess the effectiveness of mass-balance mixing models determined by Katz et al. (1995b) to predict $^{87}Sr/^{86}Sr$ ratios along downgradient flow paths. The calculated $^{87}Sr/^{86}Sr$ ratios shown in Fig. 5 were determined using mixing proportions of lakewater leakage and groundwater based on $\delta^{18}O$ and $\delta D$ values (Table 2). For example, the two-component mixing model indicated that water from 2PNB-40 was a mixture of 21% lakewater leakage and 79% groundwater from 2PNB-20. The measured $Sr^{2+}$ concentrations and the $^{87}Sr/^{86}Sr$ ratios were used for lakewater leakage (0.70997, 6.0 μg/L) and groundwater from 2PNB-20 (0.71132, 0.66 μg/L) to obtain the calculated $^{87}Sr/^{86}Sr$ ratio of 0.71070 for groundwater at 2PNB-40. The mass-balance mixing models calculate a more radiogenic $^{87}Sr/^{86}Sr$ ratio for 2PNB-FL and 2PNB-80 than the observed ratio, and a less radiogenic $^{87}Sr/^{86}Sr$ ratio for 2PNB-20, 2PNB-40, and 2PNB-60 than the observed ratios. This lack of agreement indicates that the strontium isotopic composition of groundwater downgradient from the lake cannot be accounted for solely by a two endmember model involving a mixture of lakewater leakage and upgradient groundwater. Another component, namely the contribution of $Sr^{2+}$ from a cation-exchange pool or from dissolution of a Sr-bearing mineral (e.g., calcite or dolomite), needs to be included to more accurately predict the strontium isotopic composition of groundwater.

### 5.4. Modeling Strontium Isotopic Composition from the Cation-Exchange Pool

The cation-exchange pool reflects the contributions from mineral weathering reactions and atmospheric inputs along

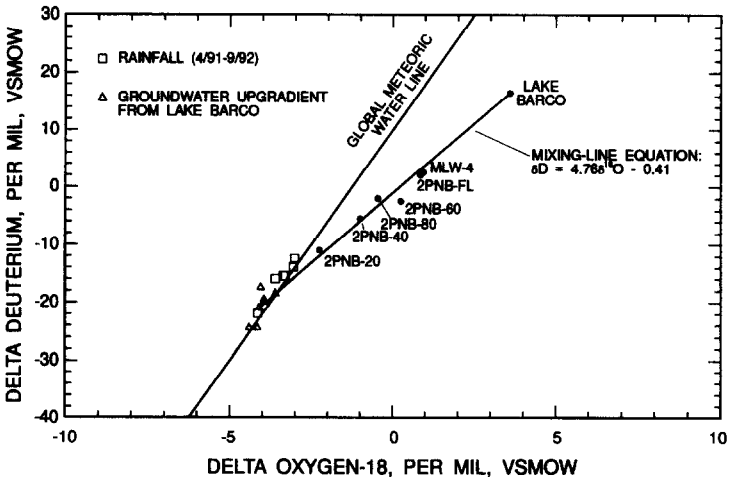


FIG. 4. Deuterium and oxygen-18 values for rainfall, groundwater, and lakewater (September 1992) in comparison to the global meteoric water (MWL) line.

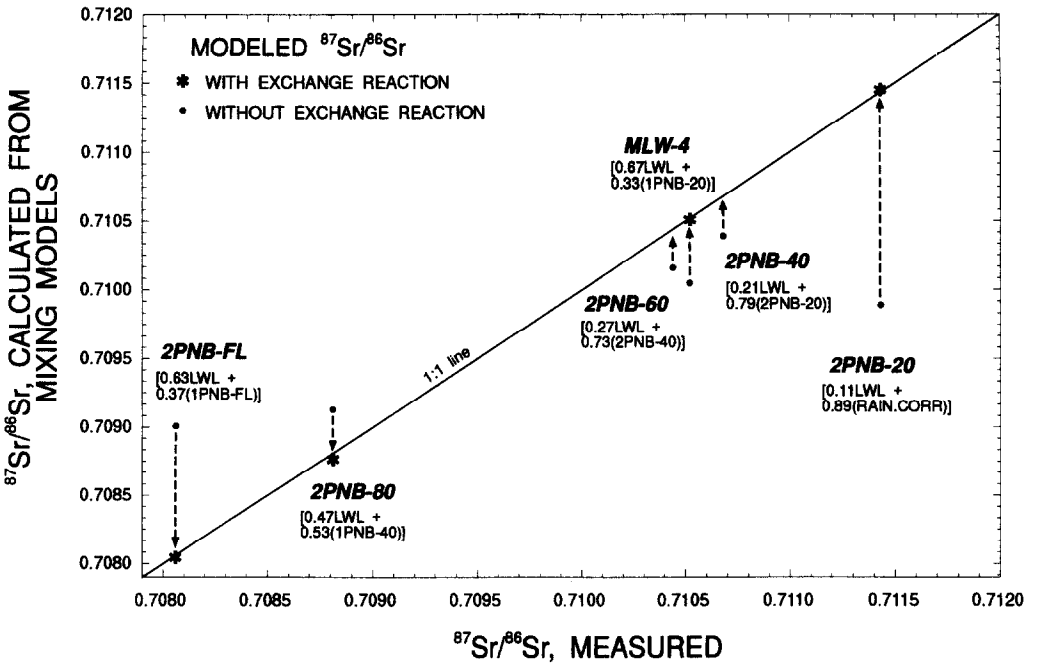


FIG. 5. Comparison of observed and computed $^{87}Sr/^{86}Sr$ in groundwater downgradient from Lake Barco. Computed $^{87}Sr/^{86}Sr$ values were determined from two endmember mixing models, shown in brackets, of lakewater leakage (LWL) and upgradient groundwater or meteoric water (RAIN.CORR) from Katz et al. (1995b). Dashed arrows show the direction toward the $^{87}Sr/^{86}Sr$ of exchangeable $Sr^{2+}$ that is necessary for the modeled reaction to predict the measured $^{87}Sr/^{86}Sr$ ratio.

a flow path. As a first approximation, it is assumed that Sr is efficiently exchanged at mineral surfaces, and the ratio of Sr to other exchangeable cations (e.g., Sr/Ca, Sr/Na, Sr/Mg) remains relatively constant for a given clay mineralogy, water pH, and water composition (Bullen and Kendall, 1997). A second assumption is that the amount of Sr in the exchange pool is much greater than that in solution. A new phase, referred to as Sr-exchange, was added to the mass-balance models presented in Katz et al. (1995b) to simulate the exchange of $Sr^{2+}$ for $Ca^{2+}$, $Na^+$, or $K^+$. This new phase defines the exchange of $Ca^{2+}$ or $Na^+$ for $Sr^{2+}$ on an exchanger according to the following reactions:

$$SrX + Ca^{2+} \rightarrow CaX + Sr^{2+}$$

or

$$SrX + 2Na^+ \rightarrow Na_2X + Sr^{2+}.$$

An inverse modeling approach, NETPATH (Plummer et al., 1994), was used to calculate the $^{87}Sr/^{86}Sr$ ratio for $Sr^{2+}$ contributed from the exchange pool that is necessary to match the measured isotopic ratio for the downgradient groundwater sample. Detailed information is presented by Katz et al. (1995b) regarding the assumptions inherent in modeling mass transfer in this system, the use of NETPATH, reactant and product minerals, saturation indices, and testing the sensitivity of the reaction models to uncertainties in data. The reactive clay minerals exert a strong influence on the evolution of major ion chemistry in this dilute system. Therefore, a cation exchange pool could represent a net source or sink for $Sr^{2+}$. Small amounts of exchange involving $Sr^{2+}$ were modeled (0.0–0.26 $\mu$mol/L; Table 4) and these small quantities do not appreciably affect the mass transfer coefficients of the other phases that are dissolving or precipitating.

In water from the surficial aquifer system (e.g., from sites MLW-4, 2PNB-20, 1PNB-20), the $^{87}Sr/^{86}Sr$ ratio of exchangeable $Sr^{2+}$ needed to obtain a match between calculated (modeled) and measured $^{87}Sr/^{86}Sr$ ratios is more radiogenic than the $^{87}Sr/^{86}Sr$ ratio of the acid and water leachates of the aquifer material. The $^{87}Sr/^{86}Sr$ ratio has to be greater than 0.7108 for $Sr^{2+}$ contributed from the exchange pool (Table 4). For these cases, the strontium isotopic composition of the water or acid leachates determined in the laboratory for surficial aquifer material ranged from 0.7100–0.71006 (Table 4). The $^{87}Sr/^{86}Sr$ ratios of the exchangeable $Sr^{2+}$ determined from acid and water leachates of aquifer material in laboratory experiments might not be representative of the actual isotopic composition of $Sr^{2+}$ in the effective exchange pool in the aquifer. The laboratory technique is probably more effective in removing all potentially exchangeable $Sr^{2+}$ from the aquifer material, whereas groundwater may only remove a small proportion of the total exchangeable Sr (Bullen et al., 1997).

Where water is moving fairly rapidly downward through the top of the Upper Floridan aquifer, the isotopic ratio for exchangeable $Sr^{2+}$ from dissolution of calcite or dolomite near 1PNB-FL falls within the range of $^{87}Sr/^{86}Sr$ ratios for water leachates for samples from the Upper Floridan aquifer. However, to predict the observed $^{87}Sr/^{86}Sr$ ratio at 2PNB-

Table 4. Mass transfer coefficients for an exchangeable-Sr phase, the $^{87}Sr/^{86}Sr$ ratio of exchangeable $Sr^{2+}$, and calculated and observed $^{87}Sr/^{86}Sr$ ratios in groundwater downgradient and upgradient from Lake Barco.

[units of mass-transfer coefficients are μmol/L; Sr/Ca denotes $Ca^{2+}$ is replacing $Sr^{2+}$ on exchange sites; Sr/Na denotes $2Na^{+}$ is replacing $Sr^{2+}$ on exchange sites; LWL denotes lakewater leakage; Rain.corr denotes rainfall corrected for dry deposition, based on data in Katz et al. (1995b); $^{87}Sr/^{86}Sr$ ratio of 0.70926 for rainfall based on seawater ratio (Veizer, 1989); obs denotes observed value; calc denotes value calculated from model]

| Reaction path | Mass transfer coeff. for exchangeable-Sr phase and exchange reaction | $^{87}Sr/^{86}Sr$ of exchangeable $Sr^{2+}$ | $^{87}Sr/^{86}Sr$ calc | $^{87}Sr/^{86}Sr$ obs |
|---|---|---|---|---|
| **Groundwater Downgradient from Lake Barco** | | | | |
| 0.67 LWL + 0.33(1PNB-20) to MLW-4 | 0.03 Sr/Ca | 0.7116 | 0.71052 | 0.71052 |
| 0.11 LWL + 0.89(Rain.corr) to 2PNB-20 | 0.00 Sr/Na | 0.7175 | 0.71144 | 0.71143 |
| 0.63 LWL + 0.37(1PNB-FL) to 2PNB-FL | 0.26 Sr/Ca | 0.7075 | 0.70804 | 0.70806 |
| **Groundwater Upgradient from Lake Barco** | | | | |
| Rain.corr to 1PNB-20 | 0.01 Sr/Na | 0.7108 | 0.71002 | 0.71004 |
| 1PNB-20 to 1PNB-40 | 0.08 Sr/Na | 0.7083 | 0.70865 | 0.70863 |
| 1PNB-60 to 1PNB-FL | 0.19 Sr/Ca | 0.7083 | 0.70857 | 0.70859 |

FL, the modeled $^{87}Sr/^{86}Sr$ ratio of exchangeable $Sr^{2+}$ needs to be approximately 0.7075. This $^{87}Sr/^{86}Sr$ ratio is lower than what was obtained from the acid or water leachates of limestone (Table 4) and could be indicative of differences in groundwater residence time and mineralogy (Katz et al., 1995b), or the inability of strontium isotopic ratios determined in the laboratory to represent actual values of exchangeable $Sr^{2+}$ in the aquifer system.

Where water is moving along flow paths in the intermediate confining unit (for example from 2PNB-20 to 2PNB-40, 2PNB-40 to 2PNB-60, and 2PNB-60 to 2PNB-80) there was typically a net mass transfer of $Sr^{2+}$ to the exchange sites, based on the lower concentration of $Sr^{2+}$ in the final water compared to the mixture of initial waters. As a result, the water from 2PNB-40, 2PNB-60, and 2PNB-80 could not be modeled using a simplified two-element exchange reaction as for waters from the surficial aquifer system and the Upper Floridan aquifer (Table 4). The exact mechanism(s) of ion exchange is not known, but may involve more than a two-element exchange with $Sr^{2+}$ contributed to and from an exchange pool by several minerals at varying rates. The sediments from the Hawthorn Group have the most varied mineralogy of the three hydrogeologic units and this mineralogic heterogeneity is indicated by the wider range of $^{87}Sr/^{86}Sr$ ratios obtained for the acid leachates compared to the range in values for the water leachates (Table 3).

Based on the results from the mass-balance models, it is probable that exchangeable $Sr^{2+}$ from a cation exchange pool plays a dominant role in controlling the $^{87}Sr/^{86}Sr$ ratio of groundwater both upgradient and downgradient from Lake Barco. However, even though the cation-exchange models determine realistic values of $^{87}Sr/^{86}Sr$ ratios that closely match observed values, unique processes have not necessarily been constrained. Exchange reactions involving $Sr^{2+}$ may not be the only process controlling the $^{87}Sr/^{86}Sr$ ratios. Other possible reactions could involve isotopic equilibration between $Sr^{2+}$ in solution with that in the exchange pool. Also, in places where carbonate dissolution is occurring, such as the Upper Floridan aquifer, a constant source of $Sr^{2+}$ with a less radiogenic $^{87}Sr/^{86}Sr$ ratio is probably being added continually to the aqueous phase.

## 6. SUMMARY AND CONCLUSIONS

Distinct differences in the $^{87}Sr/^{86}Sr$ ratio in groundwater with depth and between lakewater and groundwater were useful in studying the hydrochemical interaction between groundwater and lakewater in a mantled karst area of northern Florida. The trends of strontium isotopic profiles were similar in groundwater from sites both upgradient and downgradient from Lake Barco, despite differences in water sources, ion chemistry, redox conditions, and mineralogy. The $^{87}Sr/^{86}Sr$ ratio of groundwater becomes less radiogenic with depth and age, which is related to differences in mineralogy, hydrochemical conditions, flow patterns, and the residence time of groundwater in the three hydrogeologic units. The similarity in the strontium isotopic profiles appears to result from a kinetically fast process, such as cation exchange of $Sr^{2+}$ on clays. Based on results from mass-balance modeling techniques, it is likely that $Sr^{2+}$ from a cation exchange

pool plays a dominant role in controlling the $^{87}Sr/^{86}Sr$ ratio of groundwater both upgradient and downgradient from Lake Barco. Laboratory techniques that involve leaching of aquifer material for estimating the $^{87}Sr/^{86}Sr$ ratio of $Sr^{2+}$ in the exchange pool, however, may not provide realistic estimates of the actual isotopic composition of $Sr^{2+}$ in the exchange pool in the aquifer. The strontium isotopic composition of rainwater becomes more radiogenic as it moves downward through the unsaturated zone, although the exact nature of this interaction between rainfall and surficial material is not known. Lysimeters placed at several depths in the unsaturated zone would be very useful to measure any changes in the strontium isotopic ratios as rainwater infiltrates downward to the water table. The strontium isotopic ratio of groundwater becomes less radiogenic as it reacts with calcite and dolomite in the Ocala Limestone. The lack of strontium isotopic equilibrium between groundwater and the Ocala Limestone is related to differences in mineralogy, residence times between upgradient and downgradient sites, and variations in Sr concentrations in the rock due to post-depositional diagenetic alteration of calcite and dolomite.

The results of this study clearly demonstrate that $Sr^{2+}$ and $^{87}Sr/^{86}Sr$ ratios of groundwater and lakewater are important tracers of the hydrochemical interaction between groundwater and lakewater. In combination with stable isotopes, such as $^{18}O$, D, and $^{13}C$, these tracers provide invaluable information about geochemical processes, such as dissolution of aquifer minerals and cation-exchange reactions, flow and mixing patterns in dynamic hydrologic flow systems, and sources of dissolved solutes in groundwater that control the chemical evolution of groundwater in a mantled karst setting.

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