

# Geochemistry and Origins of Mineralized Waters in the Floridan Aquifer System, Northeastern Florida

By G.G. Phelps

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## CONVERSION FACTORS, VERTICAL DATUM, ABBREVIATIONS AND ACRONYMS

Multiply	By	To obtain
<i>Length</i>		
foot (ft)	0.3048	meter
inch (in.)	25.4	millimeter
<i>Flow</i>		
foot per year (ft/yr)	0.3048	meter per year
gallon per minute (gal/min)	0.06309	liter per second
million gallons per day (Mgal/d)	0.04381	cubic meter per second
cubic feet per second (ft <sup>3</sup> /s)	0.02832	cubic meter per second
<i>Transmissivity</i>		
foot squared per day (ft <sup>2</sup> /d)	0.0929	meter squared per day

Temperature in degrees Fahrenheit (°F) may be converted to degrees Celsius (°C) as follows:  
 $^{\circ}\text{C}=(^{\circ}\text{F}-32)/1.8.$

**Sea level:** In this report, sea level refers to the National Geodetic Vertical Datum of 1929 (NGVD of 1929)--a geodetic datum derived from a general adjustment of the first-order level nets of both the United States and Canada, formerly called Sea Level Datum of 1929.

Horizontal coordinate information is referenced to the North American Datum of 1983 (NAD83).

Acronyms and additional abbreviations used in report:

AMS	accelerator mass spectrometry
FPZ	Fernandina permeable zone
GML	Global Meteoric Line
JEA	Jacksonville Electric Authority
LFA	Lower Floridan aquifer
µg	microgram
µL	microliter
µm	micrometer
mg/L	milligrams per liter
mL	milliliter
ng	nanogram
NIST	National Institute of Standards and Technology
NWIS	National Water Data Information System
RASA	Regional Aquifer-System Analysis
SJRWMD	St. Johns River Water Management District
SI	saturation index
SLAP	Standard Light Antarctic Precipitation
SMOC	Standard Mean Ocean Chloride
UFA	Upper Floridan aquifer
UZLF	Upper zone of the Lower Floridan aquifer
USGS	U.S. Geological Survey
VPDB	Vienna PeeDee Belemnite
VSMOW	Vienna Standard Mean Ocean Water



# Geochemistry and Origins of Mineralized Waters in the Floridan Aquifer System, Northeastern Florida

By G. G. Phelps

## ABSTRACT

Increases in chloride concentration have been observed in water from numerous wells tapping the Floridan aquifer system in northeastern Florida. Although most increases have been in the eastern part of Duval County, Florida, no spatial pattern in elevated chloride concentrations is discernible. Possible sources of the mineralized water include modern seawater intrusion; unflushed Miocene-to-Pleistocene-age seawater or connate water in aquifer sediments; or mineralized water from deeper zones of the aquifer system or from formations beneath the Floridan aquifer system. The purpose of this study was to document the chemical and isotopic characteristics of water samples from various aquifer zones, and from geochemical and hydrogeologic data, to infer the source of the increased mineralization.

Water samples were collected from 53 wells in northeastern Florida during 1997-1999. Wells tapped various zones of the aquifer including: the Fernandina permeable zone (FPZ), the upper zone of the Lower Floridan aquifer (UZLF), the Upper Floridan aquifer (UFA), and both the UFA and the UZLF. Water samples were analyzed for major ions and trace constituents and for isotopes of carbon, oxygen, hydrogen, sulfur, strontium, chlorine, and boron. Samples of rock from the aquifer were analyzed for isotopes of oxygen, carbon, and strontium.

In general, water from various aquifer zones cannot be differentiated based on chemistry, except for water from FPZ wells. Major-ion concentrations vary as much within the upper zone of the Lower Floridan aquifer and the Upper

Floridan aquifer as between these two zones. Simple models of mixing between fresh ground water and either modern seawater or water from the FPZ as a mineralized end member show that many water samples from the UZLF aquifer and the UFA are enriched in bicarbonate, calcium, magnesium, sulfate, fluoride, and silica and are depleted in sodium and potassium (as compared to concentrations predicted by simple mixing). Chemical mass-balance models of mixing and reactions between a hypothetical initial seawater and aquifer minerals cannot account for the observed water chemistry in a few wells, implying a source other than seawater, either ancient or modern, or the occurrence of other more complex rock-water reactions.

Hydrogeologic and geochemical data from water and aquifer samples indicate that the most likely source of mineralized water in some wells yielding water with increasing chloride concentrations is water from the FPZ. In other wells, the flushing of Miocene-to-Pleistocene-age seawater can account for the observed chloride concentrations. The fact that most of the water samples collected are a mixture of less than one percent of mineralized water with more than 99 percent fresh or recharge water makes identifying the source of the mineralized water difficult. Differences in carbon-14 and sulfur-34 values probably reflect areal differences in aquifer mineralogy and distribution of organic carbon related to paleokarst features. Geochemical mass-balance models of seawater-rock interaction are unable to account for the chemical and isotopic composition of mineralized water from the FPZ,

which implies another source of mineralized water, such as a brine, or the occurrence of more complex water-rock reactions.

## INTRODUCTION

The Floridan aquifer system is the major source of water supply in northeastern Florida. Ground-water withdrawals in Duval County have increased from about 127 million gallons per day (Mgal/d) in 1965 to about 145 Mgal/d in 1995 (Marella, 1999, table 2). As a result, the altitude of the potentiometric surface of the Floridan aquifer system has gradually declined at a rate of about 0.3 to 0.75 foot per year (ft/yr) (Spechler, 1994). Concomitant with declines in the potentiometric surface have been increases in chloride concentrations in water from numerous wells (figs. 1 and 2). Most of the observed increases are in the eastern part of Duval County, but a pattern in the locations of wells yielding water with chloride concentrations higher than background values (greater than about 20-30 milligrams per liter (mg/L)) is not discernible (fig. 3) and wells as far as 14 miles inland have been affected (Spechler, 1994). In contrast, chloride concentrations in water from other wells near the center of pumping have remained less than 20 mg/L (Phelps and Spechler, 1997, fig. 7.).

Background ground-water quality primarily reflects the chemistry of local precipitation and aquifer mineralogy. The mean chloride concentration of bulk precipitation at 24 sites throughout Florida was 3.2 mg/L with a standard deviation of 2.0 mg/L (Irwin and Kirkland, 1980). Davis and others (2000) estimated that the chloride concentration of precipitation probably increases by a factor of 10 due to the combined effects of evapotranspiration and dissolution of dry fallout before the water is recharged into an aquifer. Thus, the assumption of a background chloride concentration of about 20 mg/L is reasonable. Leve (1966) reported that of the 26 samples collected in Duval County between the 1940s and 1960s, only 2 had chloride concentrations greater than 30 mg/L. Another constituent to consider is sulfate. Dissolution of sulfur-bearing minerals is the primary source of sulfate in water from the Floridan aquifer system. A sulfate concentration of 5 mg/L was reported by Spechler (1994) for a well in Clay County, Fla., and median sulfate concentrations less than 7 mg/L were reported for about 40 wells tapping the surficial aquifer system in central and north-central Florida (Adamski and Knowles, 2001). A number of wells tapping the Floridan aquifer system in northeastern Florida have chloride concentrations less than 30 mg/L and sulfate concentrations

less than 100 mg/L (Spechler, 1994; Phelps and Spechler, 1997). The term mineralized water is used in this report to describe water with chloride concentrations greater than 30 mg/L and sulfate concentrations greater than 100 mg/L.

Previous investigations (Spechler, 1994; Phelps and Spechler, 1997) indicate that the most likely source of mineralized water to the upper zone of the Lower Floridan aquifer is the deepest zone of the aquifer system, the Fernandina permeable zone (FPZ), which contains freshwater in the western part of the county but saline water in the eastern part. The ultimate source of mineralized water in the FPZ, however, has not been determined. Possible sources of mineralized water include intrusion of modern seawater, entrapped connate water in the aquifer, unflushed seawater from higher stands of seas level during Miocene to Pleistocene time, and upconing of highly mineralized water (brine) from formations beneath the aquifer. For example, a water sample from a depth of about 5,000 ft below land surface in an oil test well drilled near Fernandina Beach in 1970 had a chloride concentration of about 55,700 mg/L (R.E. Faye, U.S. Geological Survey (USGS), written commun., 1997) compared to about 19,000 mg/L for seawater. Another possible source of brackish water is unflushed relict seawater in the upper, freshwater-producing zones of the Floridan aquifer system. In some areas, zones bearing brackish water are underlain by zones of freshwater, whereas in other areas, freshwater is absent beneath the brackish water.

The pathways for saline water movement are interconnecting vertical and horizontal fracture or solution zones probably developed along paleokarst features (fig. 3; Phelps and Spechler, 1997). A single fracture or solution feature was the source of brackish water found in several wells in Duval County (Phelps and Spechler, 1997). These pathways for upward movement cannot be delineated from land surface by using observational or geophysical methods, making monitoring of existing well fields and development of new well field sites difficult. Geochemical analysis of water from saline parts of the FPZ, from wells that yield water with increased chloride concentrations, and from wells in which chloride concentrations have not increased may help determine whether the source of the mineralized water is the same throughout Duval County, or if more than one source exists.

Analysis of water samples for isotopes of hydrogen, oxygen, sulfur, strontium, and carbon is commonly used to help determine the origin of waters in many hydrogeologic settings, to identify and quantify dominant geochemical processes that occur along



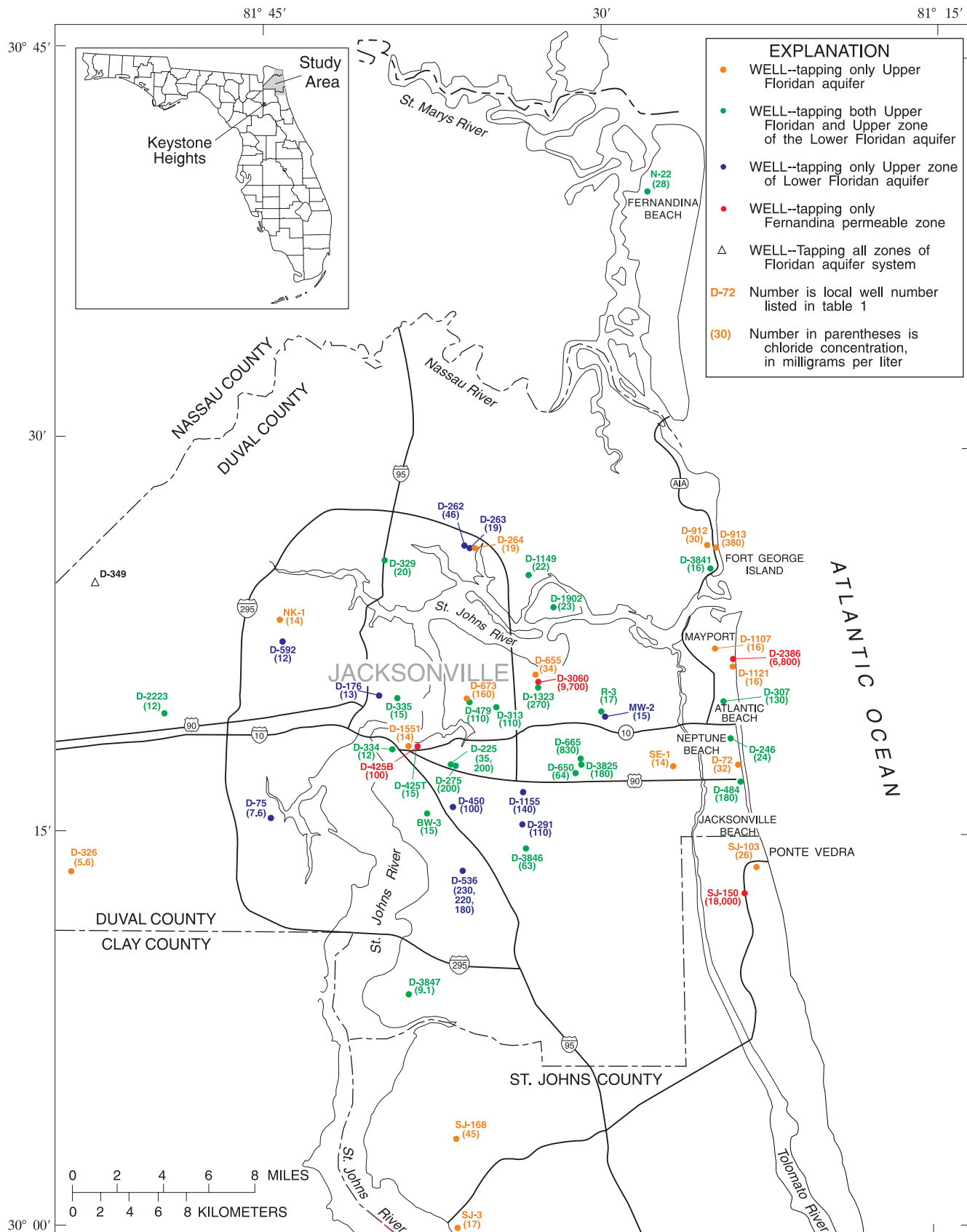


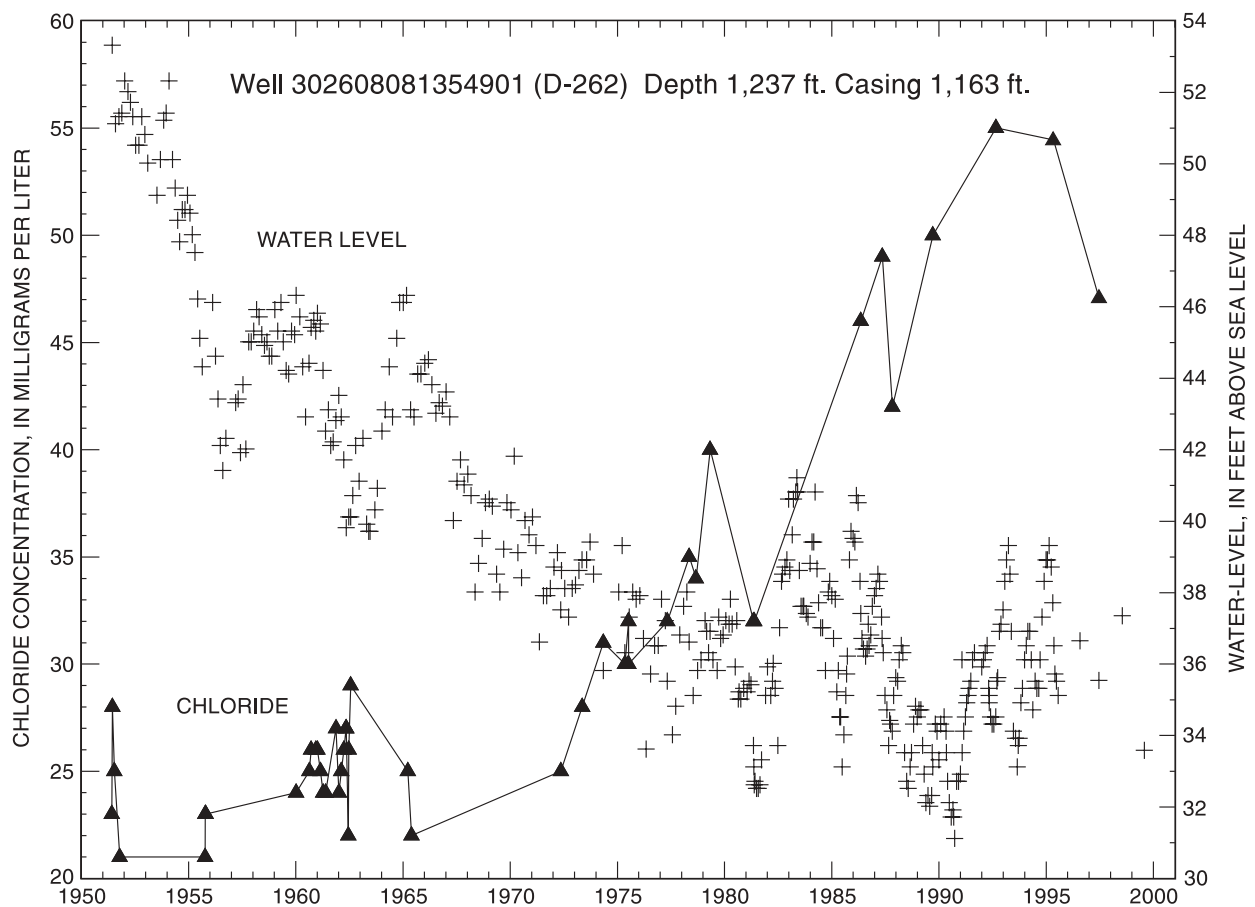
Figure 1. Selected wells in northeastern Florida.

flow paths, and (for strontium and carbon) to determine the age of ground water. Boron and chlorine isotopes are less widely used in ground-water geochemical investigations because the analytical methods used to determine the abundance of these isotopes are performed by only a few researchers. The hypothesis was made that saline water in the Floridan aquifer system would have chemical and isotopic characteristics that would be dependent upon the age and origin of the water. For example, relict seawater would have a chemical composition similar to seawater but its isotopic composition would indicate an age older than modern seawater. Entrapped seawater from previous higher stands of sea level also would show the effects of some chemical interaction with the aquifer matrix, as well as having isotopic compositions that would indicate an age that is not modern. Brines would be expected to have undergone extensive chem-

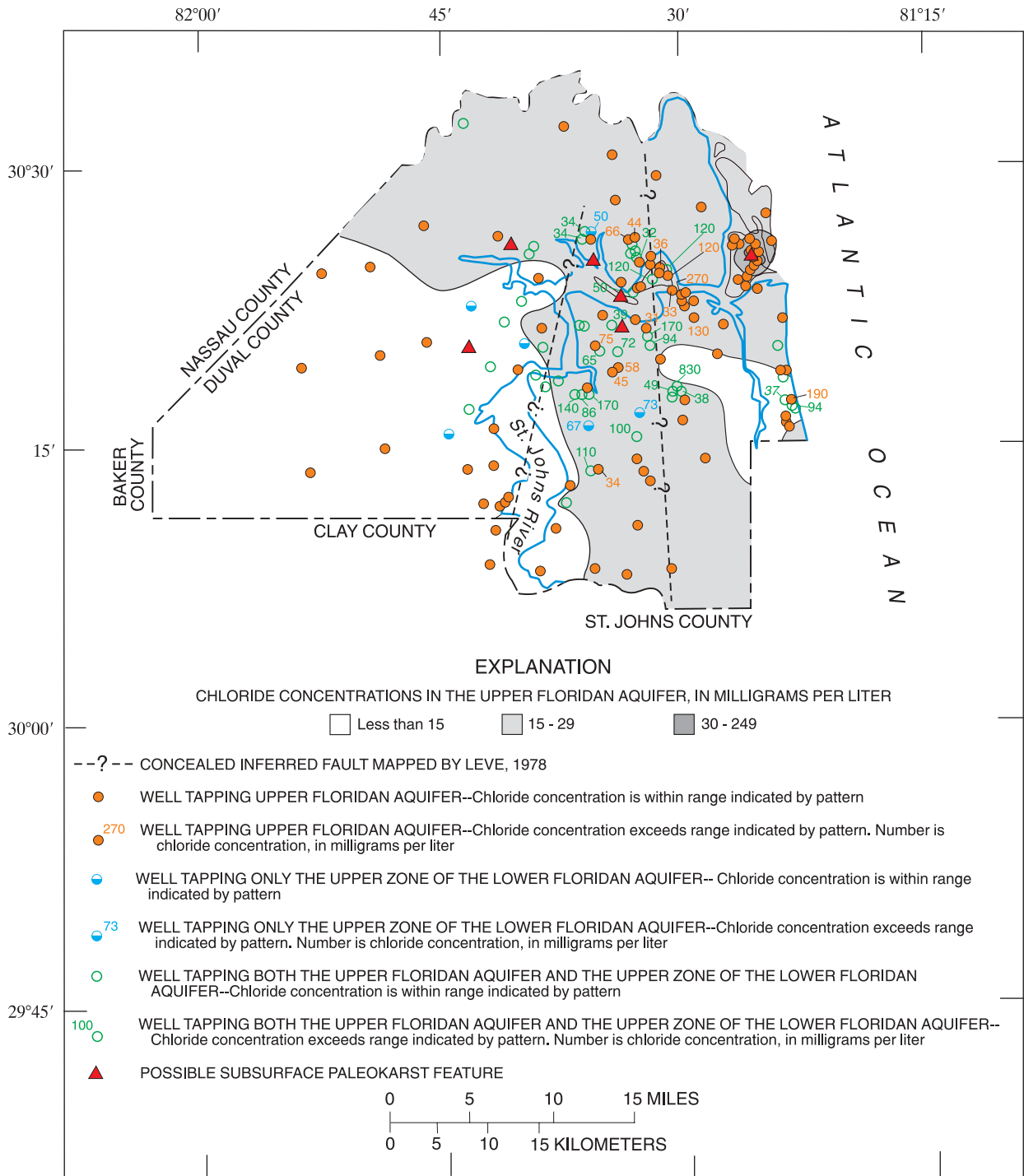
ical modification and have isotopic compositions that indicate very old ages. To test this hypothesis, the USGS, in cooperation with the City of Jacksonville, the Jacksonville Electric Authority (JEA), and the St Johns River Water Management District (SJRWMD), began a 4-year study in 1996 to characterize the geochemical and isotopic composition of water from the Floridan aquifer system and to evaluate the possible sources of mineralized waters that have resulted in the degradation of water quality in northeastern Florida, and particularly in Duval County.

## Purpose and Scope

This report presents a summary and interpretation of the chemical analysis of water from 53 wells in northeastern Florida (fig. 1, table 1). The water was analyzed for major and trace ions and for isotopes of



**Figure 2.** Chloride concentrations of water and water levels from well D-262 in Duval County, Florida, 1950-2000 (modified from Phelps and Spechler, 1997, fig. 2).



**Figure 3.** Chloride concentrations in water from the Upper Floridan aquifer and the upper zone of the Lower Floridan aquifer and locations of inferred faults and paleokarst features in Duval County, Florida (modified from Phelps and Spechler, 1997, fig. 8).

hydrogen, oxygen, sulfur, strontium, carbon, chlorine, and boron. The wells sampled were selected so that most areas of Duval County and all zones of the Floridan aquifer system are represented. Wells that yield water with increasing chloride concentrations and wells that do not were sampled. A sample of modern seawater was collected to provide a chemical end-member for seawater-freshwater mixing models. Samples of rock from wells penetrating various depths of the Floridan aquifer system were analyzed for isotopes of oxygen, strontium, and carbon. A geochemical modeling program, NETPATH (Plummer and others, 1994), was used to calculate carbon-14 age dates and to provide insight into possible models of ground-water mixing and potential flow paths in the Duval County area. The hydrogeologic and geochemical data were used to draw conclusions about the source or sources of mineralized waters in northeastern Florida.

The data and analyses presented in this report are relevant to the goals of the USGS. Specifically, these data help to better define the quality of drinking water in a coastal area where saltwater intrusion may be occurring. Also, this coastal area is one where existing sources of water are being stressed by increasing withdrawals. Understanding the possible sources of mineralized waters can help local and state water managers plan for the use of existing or alternative water-supply sources. Similar conditions occur in the Floridan aquifer system in adjacent states, and the methods used in this study could, therefore, be applicable to other areas.

## Previous Investigations

The geology and hydrology of Duval County and adjacent areas of northeastern Florida have been discussed in numerous reports. The geology of northeastern Florida was described by Puri (1957), Puri and Vernon (1964), and Miller (1986). The ground-water resources of Duval County were described by Leve (1966), Leve and Goolsby (1966), Fairchild (1972 and 1977), and Causey and Phelps (1978). Water quality in Duval County was described by Thompson (1982), and the intrusion of saline water into the Floridan aquifer system in northeastern Florida has been documented by Fairchild and Bentley (1977), Leve (1983), Toth (1990), and Spechler (1994). The relation between hydrogeology and water quality in the Lower Floridan aquifer has been described by Phelps and Spechler (1997). Data from test wells drilled into

the Lower Floridan aquifer in northeastern Florida have been described by Brown (1980), Brown and others (1984), Brown and others (1985), and Brown and others (1986).

In addition to the numerous interpretive reports describing the hydrogeology of the Duval County area, a data-collection network is operated cooperatively by the USGS, the SJRWMD, and the City of Jacksonville. Water levels are collected in about 30 wells and water samples from 24 wells are analyzed yearly for major ions and quarterly for chloride concentration. Data from the network are published annually by the USGS (U.S. Geological Survey, 2000).

## Well-Numbering System

Two well-numbering systems are used in this report. The first is a 15-digit site identification number (Site ID) based on latitude and longitude, used to identify wells in the USGS National Water Data Information System (NWIS). The first six digits denote the degrees, minutes, and seconds of latitude; the next seven digits denote degrees, minutes, and seconds of longitude; and the last two digits denote a sequential number for a site within a 1-second grid. For example, well 302538081253101 is the first well inventoried at latitude 30°25'38" N, longitude 081°25'31" W.

The second well-numbering system consists of shortened, local identifiers used in place of the longer, 15-digit site identification numbers. Local numbers were assigned by the USGS to wells in each county in northeastern Florida as the wells were inventoried. The prefixes D, N, SJ, and C denote wells in Duval, Nassau, St. Johns and Clay Counties, respectively. The sequence number denotes the order in which the well was inventoried. For example, well D-164 is the 164th well inventoried in Duval County. Other government agencies also have local well-numbering systems. For example, the City of Jacksonville Department of Regulatory and Environmental Services assigns local well numbers beginning with a J, and the JEA Water Production Division assigns numbers to its water-supply wells that denote the pumping station number and sequence number. For example, well 0502 designates the number 2 well at the number 5 well field. The SJRWMD also uses local well numbers that begin with the letter D for wells in Duval County. The local numbers used by the SJRWMD may not correspond with the local numbers used by the USGS. In this report, USGS local well numbers are used. A few wells

**Table 1. Well information**

[Aquifer: UFA, Upper Floridan aquifer; B, both Upper Floridan and upper zone of Lower Floridan aquifers; UZLF, Upper zone of Lower Floridan aquifer; FPZ, Fernandina permeable zone; --, no information; na, not applicable]

Site identification number	Local number	Aquifer	Depth (feet)	Casing (feet)	Sample date	Remarks
300019081363301	SJ-3	UFA	500		07/15/97	
300347081363701	SJ-168	UFA	630	590	07/15/97	
301304081222701	SJ-103	UFA	857	385	03/19/98	
301339081531201	D-326	UFA	887	400	01/28/99	
301547081271901	SE-1	UFA	870	349	01/28/99	
301714081233301	D-72	UFA	850	350	01/21/98	
301830081375501	D-1551	UFA	660	540	01/27/99	
302013081353801	D-673	UFA	814	578	01/21/98	
302058081244101	D-1107	UFA	1,011	395	01/27/99	
302113081322301	D-655	UFA	750	--	10/29/98	
302140081235501	D-1121	UFA	518	--	10/28/98	
302239081434401	NK-1	UFA	600	500	10/29/98	Well and casing depth estimated
302557081253101	D-913	UFA	556	435	07/15/97	
302608081354903	D-264	UFA	700	--	10/27/98	
302609081260601	D-912	UFA	484	431	10/27/98	
300856081382401	D-3847	B	1,220	470	03/18/98	
301405081325601	D-3846	B	1,198	578	01/20/98	
301407081324101	Deer3-03	B	1,180	578	01/20/98	
301508081364601	BW-3	B	1,102	510	02/23/99	
301704081233401	D-484	B	1,220	357	02/04/97	
301725081305002	D-650	B	1,276	424	01/20/98	
301740081361001	D-275	B	1,230	515	01/28/97	
301743081303501	D-3825	B	1,093	440	01/20/98	
301743081362301	D-225	B	1,277	547	01/28/97	High chloride
301743081362301	D-225	B	1,277	547	07/14/97	Low chloride
301748081383401	D-334	B	1,500	535	01/21/98	
301758081303901	D-665	B	1,185	417	01/31/97	
301817081374901	D-425T	B	1,895	752	03/18/98	
301846081240201	D-246	B	1,210	388	01/22/98	
301934081292301	R-3	B	920	425	01/28/99	
301937081471401	D-2223	B	1,315	553	01/28/99	
301957081342301	D-313	B	1,150	576	01/22/98	
302007081353201	D-479	B	1,350	606	03/18/98	
302008081242101	D-307	B	1,300	407	01/27/99	
302015081384501	D-335	B	1,290	531	03/18/98	
302045081323101	D-1323	B	1,170	580	04/06/98	
302342081320601	D-1902	B	1,209	515	03/17/98	
302503081332001	D-1149	B	1,104	520	03/17/98	
302510081260201	D-3841	B	1,311	771	04/08/98	
302538081392501	D-329	B	1,210	545	01/21/98	
303940081281801	N-22	B	1,000	--	05/18/99	
301335081355001	D-536-1	UZLF	1,140	372	02/04/97	Sample depth 1,042 ft
301335081355001	D-536-2	UZLF	1,140	372	02/04/97	Sample depth 1,059 ft
301335081355001	D-536-3	UZLF	1,140	372	02/04/97	Sample depth 1,078 ft
301522081331301	D-291	UZLF	1,237	537	01/31/97	Sample depth 1,213 ft
301537081441901	D-75	UZLF	1,290	970	01/29/97	
301604081361501	D-450	UZLF	1,300	1,100	01/29/97	
301639081330802	D-1155	UZLF	1,170	1,080	01/28/97	
301936081292401	MW-2	UZLF	1,121	1,010	03/19/98	
302022081393501	D-176	UZLF	1,270	800	01/29/97	
302227081435001	D-592	UZLF	1,330	1,150	01/29/97	
302608081354901	D-262	UZLF	1,237	1,163	01/29/97	
302608081354902	D-263	UZLF	1,020	850	01/22/98	
301132081225801	SJ-150	FPZ	2,035	1,980	01/30/97	
301405081325601	D-425B	FPZ	2,486	2,055	01/28/97	
301725081305002	D-3060	FPZ	2,112	2,050	01/30/97	
301743081303501	D-2386	FPZ	2,026	1,892	01/27/97	
302737080571801	Seawater	na	na	na	04/07/98	

inventoried during this study were given local numbers based on nearby features, such as NK-1 and R-3.

## Acknowledgments

The author would like to thank the staff of the JEA Water Production Division for their assistance and cooperation in providing access to wells for collection of water samples. Personnel of the City of Jacksonville, Department of Regulatory and Environmental Services also provided help in locating wells to sample. Thanks also to United Water of Florida, Inc., for access to selected wells and to private property owners for permission to sample their wells. Ratios of  $^{36}\text{Cl}/\text{Cl}^-$  were determined by P. Sharma, Purdue University, and strontium and boron isotopes of water samples and strontium isotopes of aquifer samples were determined by Thomas D. Bullen, USGS, Menlo Park, Calif., Thomas D. Bullen and L. Neil Plummer (USGS, Reston, Va.) and Stanley N. Davis (University of Arizona) provided helpful advice and discussions. The author also is grateful to technical reviewers Laura Sacks (USGS, Tampa, Fla.) and Peter McMahon (USGS, Denver, Colo.).

## METHODS OF SAMPLING AND CHEMICAL ANALYSIS

Water samples were collected from 53 wells in northeastern Florida. Many of the wells sampled for this study have large open-hole intervals, although a few are open to a relatively short aquifer interval (table 1). The large open-hole intervals sampled in many of the wells complicated the interpretation of water-chemistry data. For example, many of the wells are open to both the Upper Floridan aquifer (UFA) and the upper zone of the Lower Floridan aquifer (UZLF). This makes comparison of water chemistry from the two aquifers difficult. In two wells (D-291 and D-536), samples were collected by using a down-hole thief sampler, so although the wells are open to both aquifers, the samples analyzed represent only the UZLF. One well (D-225) produces water with varying water chemistry. The chloride concentration fluctuates from about 60 to 200 mg/L, depending on whether the well is allowed to flow naturally or is pumped (Phelps and Spechler, 1997). For this study, well D-225 was sampled twice so water of both high and low chloride compositions could be analyzed.

Samples of aquifer material from four wells in Duval County were analyzed for isotopes of oxygen, carbon, and strontium. The rocks analyzed include samples of limestone and dolomite that represent rocks of the UFA (Ocala Limestone), the UZLF, and the FPZ (Avon Park Formation). Also analyzed were two samples of organic carbon (peat) probably from cavity-fill in the Avon Park Formation.

For most isotope determinations, standard  $\delta$  (delta) notation (Gonfiantini, 1981) is used in units of parts per thousand (per mil), and is expressed by the equation:

$$\delta_{\text{sample}} = \left[ \frac{R_{\text{sample}}}{R_{\text{standard}}} - 1 \right] \times 1,000, \quad (1)$$

where

R is the ratio of heavy to light isotope.

More information about standards and reporting units for various environmental isotopes is given in a later section of this report.

## Water Samples

Both public-supply and monitor wells were sampled for this study. Many of the wells sampled are public-supply wells that are in nearly continuous use. Some of the wells flow naturally, but in most public-supply wells, the flow rates are augmented by deep-well turbine pumps. All public-supply wells were sampled after at least three casing volumes had been pumped. Other wells were pumped by using a submersible electric pump. Those wells were sampled after at least three casing volumes had been pumped and after field measurements of water temperature, pH, and specific conductance had stabilized.

Samples were collected following a standard USGS protocol described by Wood (1976). Water temperature, pH, and specific conductance were determined in the field. For most samples, alkalinity was determined in the field by titration with sulfuric acid. Sulfide was measured in the field for many samples using the methylene blue method and a field spectrophotometer (Hach Company, 1989). The detection limit for sulfide is 0.01 mg/L. Many of the samples contained sulfide concentrations in excess of 0.6 mg/L, in which case the samples were diluted with deionized

water in a volumetric flask, which may have oxidized some of the sulfide in the sample, thereby resulting in a lower apparent sulfide concentration (C.J. Patton, USGS, oral commun., 1998). As a comparison, sulfide was precipitated in the field for some samples using sodium hydroxide and zinc acetate and the resulting precipitate was analyzed at the USGS laboratory in Ocala, Fla.

Water samples for anion and cation analysis were filtered using 0.45 micrometer ( $\mu\text{m}$ ) Gelman capsule filters. Cation, trace metal, and  $^{87}\text{Sr}/^{86}\text{Sr}$  samples were collected in acid-washed bottles and acidified with 70 percent nitric acid. Major ion and trace constituent samples were analyzed at the USGS laboratory in Ocala, Fla.

The minimum reporting level for bromide determined by ion chromatography is 0.01 mg/L. For this study, more accurate determinations were desired, so low-level bromide determinations were made at the USGS laboratory in Denver, Colorado. The method involved spiking the samples with 10-microliter ( $\mu\text{L}$ ), 30- $\mu\text{L}$ , 50- $\mu\text{L}$ , or 100- $\mu\text{L}$  volumes of a bromide standard solution (0.01 mg Br/milliliter (mL)) depending on the unspiked concentrations. Then addition of aliquots of the spike solution (10  $\mu\text{L}$ , 30  $\mu\text{L}$ , 50  $\mu\text{L}$ , or 100  $\mu\text{L}$ ) to 10-mL volumes of sample resulted in increased bromide concentration in the samples by 10  $\mu\text{g}/\text{L}$ , 30  $\mu\text{g}/\text{L}$ , 50  $\mu\text{g}/\text{L}$ , and 100  $\mu\text{g}/\text{L}$ , respectively. Dilution of the sample by the spike solution was 1 percent or less (worst case, 100  $\mu\text{L}$  spike in 10 mL of sample = 1 percent). A colorimetric method was then used to determine bromide concentrations, after correction for iodide concentrations. Relatively high and variable concentrations of chloride and sulfate in the samples could interfere with the bromide recovery. During the first round of sampling, this custom procedure had bromide recovery rates ranging from 15 to 188 percent (the extremes representing two samples with very low bromide concentrations). In later sampling, the recovery rates ranged from 44 to 111 percent. The median recovery rate for all samples was 92 percent.

Ratios of  $^{87}\text{Sr}/^{86}\text{Sr}$  (on filtered, acidified samples) and  $^{11}\text{B}/^{10}\text{B}$  (on filtered, unacidified samples) were determined at the USGS research laboratory in Menlo Park, Calif., using a Finnigan MAT 261 solid source mass spectrometer. Strontium isotopes were analyzed by the positive ion thermal mass spectrometry technique. For each analysis, sufficient fluid sample containing approximately 1 microgram ( $\mu\text{g}$ ) of stron-

tium was loaded onto a pre-cleaned cation exchange column, and strontium was separated from other cations and anions by using 2N hydrochloric acid as the eluent. The strontium fraction was evaporated to dryness with 40  $\mu\text{L}$  of 0.5N phosphoric acid and converted to a nitrate. The sample was then loaded onto a tantalum ribbon filament and placed in the mass spectrometer. Samples were analyzed for isotopic composition using a double collector dynamic data acquisition approach. Measured  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios were corrected for all stable isotope fractionation by simultaneously measuring  $^{88}\text{Sr}/^{86}\text{Sr}$ , correcting this ratio to a value of 8.37521, and then correcting the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio by using an exponential mass-dependent fractionation relation. NIST 987, a widely-used standard reference material, routinely gives a value of 0.71024 on the Finnigan MAT 261 instrument. Reported  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios are precise to 0.00002 at the 95-percent confidence level.

Boron isotopes were analyzed by the negative ion thermal mass spectrometry technique. For each analysis, sufficient sample containing approximately 2 nanograms (ng) of boron was evaporated in a Teflon beaker and treated with 100  $\mu\text{L}$   $\text{H}_2\text{O}_2$  to eradicate organics. The dried sample was loaded onto a rhenium filament ribbon and placed into the high vacuum source of the mass spectrometer. Filaments were heated to approximately 950  $^\circ\text{C}$ , and data were collected when ion beams stabilized in their growth characteristics. Ion beams were measured simultaneously at mass 42 ( $^{10}\text{BO}_2$ ) and 43 ( $^{11}\text{BO}_2$ ) for approximately 30 minutes. The reported  $\delta^{11}\text{B}$  is the per mil difference of the ratio of the measured  $^{11}\text{BO}_2$  to  $^{10}\text{BO}_2$  beams, relative to the reference standard NIST 951 boric acid. The correction for oxygen isotope composition is negligible. On this mass spectrometer, NIST 951 gives a  $^{11}\text{B}/^{10}\text{B}$  value of 4.004; seawater gives a value of 4.161, which corresponds to a  $\delta^{11}\text{B}$  of +39.2 relative to NIST 951. Precision is  $\pm 0.5$  per mil.

For analysis of  $^{36}\text{Cl}$  and ratios of  $^{35}\text{Cl}/^{37}\text{Cl}$ , filtered, unacidified samples were collected in plastic bottles secured with polyseal caps. Targets were prepared by using ion exchange techniques at the Purdue Rare Isotope Measurement Laboratory, Purdue University; the ratios of  $^{36}\text{Cl}/\text{Cl}^-$  were determined by using accelerator mass spectrometry (AMS). The ratios of  $^{35}\text{Cl}/^{37}\text{Cl}$  were determined at the Environmental Isotope Laboratory, University of Waterloo Ontario, Canada. The chloride ion was precipitated as silver chloride by addition of silver nitrate to an acidified

solution. Methyl iodide was added to the dried silver chloride and reacted for approximately 48 hours at 85 °C in a vacuum to produce methyl chloride. The methyl chloride was then isolated and purified by gas chromatography and cryogenics, and then analyzed on a mass spectrometer. Ratios of  $^{35}\text{Cl}/^{37}\text{Cl}$  were calculated relative to SMOC (Standard Mean Ocean Chloride). Precision is  $\pm 0.15$  per mil.

Unfiltered samples were collected in glass bottles secured with polyseal caps for deuterium ( $\delta\text{D}$ ) and oxygen-18 ( $\delta^{18}\text{O}$ ) analysis of the water and carbon-14 ( $^{14}\text{C}$ ) and carbon-13 ( $\delta^{13}\text{C}$ ) analysis of total inorganic carbon. Concentration ratios of deuterium and hydrogen isotopes (D/H) and oxygen-18 and oxygen-16 isotopes ( $^{18}\text{O}/^{16}\text{O}$ ) were determined by the USGS Isotope Fractionation Laboratory in Reston, Va., using techniques described by Coplen (1988 and 1994). Analytical determinations of  $^{14}\text{C}$  and  $^{13}\text{C}/^{12}\text{C}$  were made by contract laboratories using AMS. Oxygen and hydrogen isotopic results are reported in per mil relative to VSMOW (Vienna Standard Mean Ocean Water), and are normalized on scales such that the oxygen and hydrogen isotopic values of SLAP (Standard Light Antarctic Precipitation) are -55.5 per mil and -428 per mil, respectively. Carbon isotopic results are reported in per mil relative to VPDB (Vienna PeeDee belemnite). The uncertainties of both carbon and oxygen isotopic results are  $\pm 0.2$  per mil; the uncertainty for hydrogen results is 2 per mil.

Samples also were collected for analysis of sulfur-34 ( $^{34}\text{S}$ ) of sulfate. Previous studies in Duval County have shown that the sulfate concentrations in nearly all ground water are much greater than 20 mg/L and nearly all water contains substantial concentrations of sulfide. Samples for sulfate analysis were collected in 1-L plastic bottles and then immediately acidified to a pH between 3 and 4 by using 1N hydrochloric acid. The samples were stripped of  $\text{H}_2\text{S}$  by bubbling  $\text{N}_2$  gas through the sample for at least 30 minutes, until there was no discernible  $\text{H}_2\text{S}$  odor. Samples were then shipped to the USGS Isotope Fractionation Laboratory in Reston, VA, where  $\text{BaSO}_4$  was precipitated for isotopic analysis (Carmody and others, 1998). The uncertainty associated with these data is  $\pm 0.3$  per mil.

## Quality Assurance Samples

For quality assurance purposes, various duplicate samples were collected from some wells and three equipment blanks were collected by using laboratory-

prepared inorganic blank water. Because nearly all of the wells had been sampled previously for major ions and trace metals (and some are sampled for major ions on a regular basis), duplicate samples for those constituents were not collected. Ionic charge balances for all analyses were within 10 percent, with the majority within 5 percent. The three equipment blanks all had concentrations of major ions and trace metals near or below detection limits, indicating that negligible contamination was introduced by the sampling or analytical processes.

A duplicate pair of samples for chlorine isotopes indicated a  $^{36}\text{Cl}/\text{Cl}$  ratio of 59 with a 7.8 percent error and 55.9 with a 9.1 percent error for water with a relatively low chloride concentration of 12 mg/L. The ratios of  $^{35}\text{Cl}/^{37}\text{Cl}$  for that pair of duplicates were 0.04 and 0.08, respectively, with a precision of  $\pm 0.4$  per mil. In general, errors in the determination of the  $^{36}\text{Cl}/\text{Cl}$  ratio tended to increase as chloride concentration increased, but there was considerable scatter in the trend. Duplicate samples were analyzed for  $^{14}\text{C}$  at two wells. For one well, the percent modern carbon values were  $1.37 \pm 0.06$  percent and  $1.33 \pm 0.05$  percent. For the other well, the values were 2.9 percent  $\pm 0.09$  percent and 1.04 percent  $\pm 0.05$  percent. The effects of analytical errors on the calculated  $^{14}\text{C}$  ages of water samples is discussed in a later section of this report. For a duplicate pair of samples analyzed for low-level bromide concentrations, the results were 61  $\mu\text{g}/\text{L}$  and 45  $\mu\text{g}/\text{L}$ , a 30 percent difference. The mean of the two values (53), is estimated to be the actual value,  $\pm 15$  percent.

## Analysis of Aquifer Materials

Samples of cuttings from four wells in Duval County were analyzed for  $\delta^{13}\text{C}$ ,  $\delta^{18}\text{O}$ , and the ratio of  $^{87}\text{Sr}/^{86}\text{Sr}$  to provide information about the isotopic composition of aquifer materials that contain and interact with the ground water in northeastern Florida. Washed cuttings were selected from depth intervals corresponding to the UFA and the UZLF from well MW-2 (drilled in 1995) and the UZLF from well D-3846 (drilled in 1994). Samples of cores from wells D-349 and D-425 that correspond to the FPZ also were analyzed. Bulk samples identified as limestone or dolomite in geologists' logs were analyzed. In addition to samples of limestone and dolomite, two samples of peat and several tests of the foraminifera *Lepidocyclina ocalana* and *Dictyoconus americanus* collected from



well D-3846 were analyzed. The  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  samples were analyzed at the USGS Isotope Fractionation Laboratory at Reston, Va. Analyses for  $^{87}\text{Sr}/^{86}\text{Sr}$  were done at the USGS research laboratory, Menlo Park, Calif.

## HYDROGEOLOGIC FRAMEWORK

Northeastern Florida is underlain by a thick sequence of marine sedimentary rocks that overlie a basement complex of metamorphic strata. Geologic formations and hydrogeologic units penetrated by wells in the Jacksonville area are described in figure 4. Rocks of the Cedar Keys Formation of late Paleocene age underlie all of northeastern Florida. They are overlain, in ascending order, by the Oldsmar Formation of early Eocene age, the Avon Park Formation of middle Eocene age, the Ocala Limestone of late Eocene age, the Hawthorn Formation of Miocene age, and undifferentiated deposits of late Miocene to Holocene age.

### Surficial Aquifer System and Intermediate Confining Unit

The sediments of late Miocene to Holocene age generally consist of interbedded sand, shell, and clay with some dolomitic limestone. These sediments together make up the surficial aquifer system, which in most areas of Duval County has two water-producing zones separated by beds of lower permeability. The surficial aquifer system usually is unconfined, but may be semiconfined where overlying beds of lower permeability are sufficiently thick and continuous. The thickness of the surficial aquifer system is variable, ranging from about 20 to 120 feet (ft) in Duval County and vicinity.

The Hawthorn Formation of Miocene age underlies the surficial sediments and consists of interbedded clay, silt, sand, dolomite, and limestone that contain abundant phosphate pebbles and granules and phosphatic sand. Throughout most of northeastern Florida the clays and silts of the Hawthorn Formation serve as an effective confining unit. This intermediate confining unit retards the movement of water between the overlying surficial aquifer system and the underlying Floridan aquifer system.

## Floridan Aquifer System

The Floridan aquifer system underlies all of the Florida peninsula, as well as parts of Alabama, Georgia, and South Carolina. It is the principal source of water-supply for the study area. The aquifer system ranges in thickness from about 1,600 to 1,900 ft in the study area and includes the Ocala Limestone, the Avon Park Formation, the Oldsmar Formation, and locally, the upper part of the Cedar Keys Formation. The beds range in age from Paleocene (Cedar Keys Formation) to Eocene (Oldsmar and Avon Park Formations and Ocala Limestone). In northeastern Florida, sediments of Oligocene age are absent (Miller, 1986; Stringfield, 1966). Miller (1986) definitively described the various water-bearing zones of the Floridan aquifer system as part of the Regional Aquifer-System Analysis (RASA) study. The Floridan aquifer system is divided into two aquifers of relatively high permeability, referred to as the Upper Floridan and the Lower Floridan aquifers. The Lower Floridan aquifer (LFA) can be subdivided into two principal water-bearing zones, the UZLF and the FPZ, separated by a less permeable unit. The aquifer layers are delineated on the basis of rock permeability, not on the basis of lithology, formation, or time-stratigraphic boundaries (Miller, 1986, p. B54). In general, the upper zones of the aquifer system produce freshwater, but mineralization increases with depth. For example, some wells completed into the UFA yield water with chloride concentrations less than 10 mg/L. In contrast, Leve (1966, p. 91) reported a chloride concentration of about 33,000 mg/L in a water sample from a depth of about 2,220 ft below land surface (FPZ) in an oil test well in northwestern Nassau County.

### Upper Floridan Aquifer

The UFA generally corresponds to the Ocala Limestone, and in some areas includes the upper part of the Avon Park Formation. The UFA is about 300 to 500 ft thick in Duval County. The Ocala Limestone is fossiliferous and characterized by high permeability and high effective porosity. Permeability has been enhanced by dissolution of the rock along bedding planes, joints, and fractures. The surface of the Ocala Limestone is a paleokarst plain that exhibits erosional and collapse features that developed before the deposition of the overlying Hawthorn Formation. Leve (1983, p. 251) attributed some of the abrupt variations in the altitude of the surface of the Ocala Limestone to faults.

SERIES	STRATIGRAPHIC UNIT	APPROXIMATE THICKNESS (FT)	GENERAL LITHOLOGY	HYDROGEOLOGIC UNIT	HYDROGEOLOGIC PROPERTIES	
Holocene to Upper Miocene	Undifferentiated surficial deposits	20-120	Discontinuous sand, clay, shell beds, and limestone	Surficial aquifer system	Sand, shell, limestone, and coquina deposits provide local water supplies.	
Miocene	Hawthorn Formation	100-500	Interbedded phosphatic sand, clay, limestone, and dolomite	Intermediate confining unit	Sand, shell, and carbonate deposits provide limited local water supplies. Low permeability clays serve as the principle confining beds for the Floridan aquifer system below.	
Eocene	Ocala Limestone	100-350	Massive fossiliferous chalky to granular marine limestone	Floridan aquifer system	Upper Floridan aquifer	Principal source of ground water. High permeability overall.
	Avon Park Formation	700-1,100	Alternating beds of massive granular and chalky limestone, and dense dolomite		Middle semiconfining unit	Low permeability limestone and dolomite.
	Oldsmar Formation	300-500			Lower Floridan aquifer	Upper zone
Semiconfining unit			Low permeability limestone and dolomite.			
				Fernandina permeable zone	High permeability; salinity increases with depth.	
Paleocene	Cedar Keys Formation	about-500	Uppermost appearance of evaporites; dense limestones	Sub-Floridan confining unit	Low permeability; contains highly saline water.	

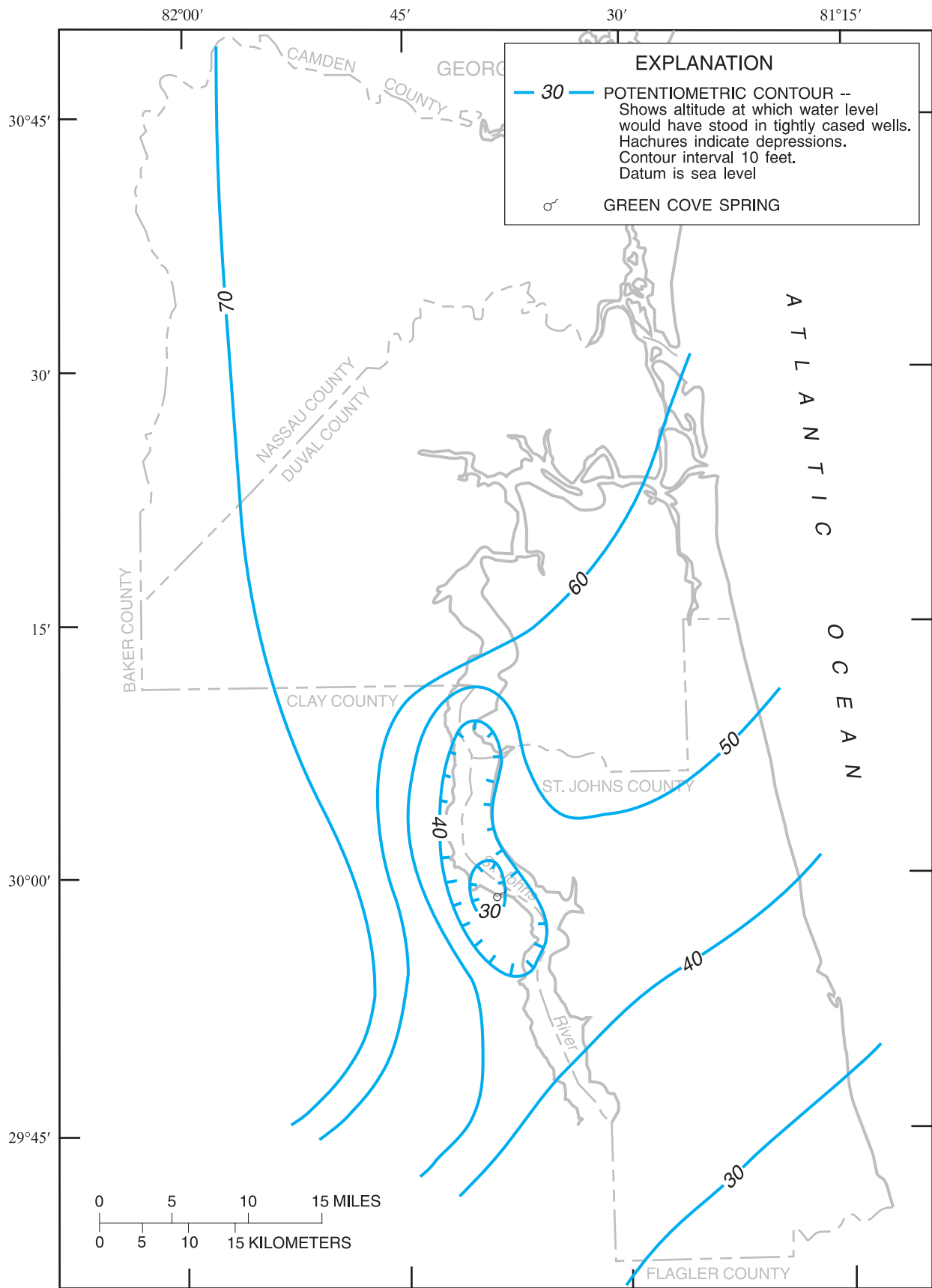
**Figure 4.** Generalized geology and hydrogeology of northeastern Florida (from Phelps and Spechler, 1997).

Using additional data collected since 1983, Spechler (1994, pl. 1) compiled a more detailed map of the top of the Ocala Limestone, which indicates the presence of numerous closed-contour depressions in the surface of the unit. The observed configuration of the top of the Ocala Limestone could be the result solely of paleo-karst processes, rather than movement along faults.

The transmissivity of the UFA varies considerably throughout the study area. Transmissivity values for six wells that penetrated 50 to 500 ft of the Floridan aquifer system, corresponding to the UFA and the middle semi-confining unit, ranged from 20,000 to 50,000 feet squared per day (ft<sup>2</sup>/d) (Franks and Phelps, 1979, p. 7). At Ft. George Island, in eastern Duval County, transmissivity values of 31,000 and 49,000 ft<sup>2</sup>/d were determined (Environmental Science and Engineering, Inc., 1985, p. 3-36). Brown (1984, p. 27) reported transmissivity values ranging from about 20,000 to 50,000 ft<sup>2</sup>/d for the UFA in Nassau County and adjacent Camden Country, Ga. Transmissivity values in Duval County from modeling simulations

range from 50,000 to 250,000 ft<sup>2</sup>/d (Bush and Johnston, 1988, pl. 2). Bush and Johnston (1988) noted that a contrast between field and model-derived transmissivity data was evident in the Jacksonville area, perhaps because model-derived values were averaged for large grid blocks and, therefore, did not reflect local variation.

Flow in the UFA is generally from west to east (figs. 5a and 5b). The major recharge area in northeastern Florida is in the vicinity of Keystone Heights (fig. 1), southwest of the study area. A deep cone of depression has formed in Nassau County as a result of heavy industrial pumping. In Duval County, a broad cone of depression probably is due to a combination of municipal and industrial pumping and natural discharge by diffuse upward leakage or through springs in the St. Johns River (Spechler, 1995). Green Cove Spring, at the southern end of the study area (fig. 5a), discharges about 3 cubic feet per second (ft<sup>3</sup>/s) (about 2 million gallons per day) (Rosenau and others, 1977).



**Figure 5a.** Estimated pre-development potentiometric surface of the Upper Floridan aquifer (from Johnston and others, 1980).



## Middle Semi-Confining Unit and Lower Floridan Aquifer

The middle semi-confining unit separates the Upper and Lower Floridan aquifers and usually is composed of beds of hard, less permeable limestone and dolomite. In Duval County, this unit generally occurs in the upper part of the Avon Park Formation and ranges in thickness from about 100 to 150 ft (Phelps and Spechler, 1997). Miller (1986) noted that the contrast in permeability between rocks of the middle semi-confining unit in northeastern Florida relative to the rocks above and below this unit is less than that of any other confining unit mapped during the RASA study. Also, the lithology of this unit does not differ much from that of the permeable zones above and below it. This interval usually is observed to contribute little or no flow to wells during flow logging.

The LFA underlies the middle semi-confining unit. Most wells in the Jacksonville area deeper than 900 ft penetrate the Lower Floridan aquifer. The LFA contains two main water-bearing zones, the UZLF and the FPZ, which are separated by a less-permeable semi-confining unit (Brown, 1984). In some parts of Duval County the UZLF may have two sub-zones. The top of the UZLF usually can be identified on flow logs as an interval contributing a noticeable increase in flow to the well.

The UZLF consists of approximately the lower two-thirds of the Avon Park Formation and is composed of alternating beds of limestone and dolomite. The top of the unit is about 850 to 950 ft below sea level in Duval County (Phelps and Spechler, 1997, p. 9). In some parts of Duval County, the UZLF has a single flow zone and a maximum thickness of about 300 ft. In other areas, less permeable strata separate two distinct flow zones. At test well D-3060, flow-meter traverses indicate that the altitude of the top of the UZLF is about 870 ft below sea level. A second highly productive zone was penetrated about 1,200 ft below sea level (Brown and others, 1985, fig. 15). A flow zone at 950 ft below land surface and others at about 1,150 and 1,250 ft below land surface were observed at test well D-2386 (Brown and others 1984, figs. 15-16). Test well D-425 also has two flow zones, one about 880 ft below sea level and another, more productive zone at about 1,080 to 1,280 ft below sea level. At other sites in Duval County, the UZLF has only one flow zone (Phelps and Spechler, 1997, p. 9).

The LFA, like the UFA, also exhibits evidence of paleokarst development. Miller (1986) described a high-permeability cavernous zone in the lower part of

the rocks of middle Eocene age. The zone is a fairly thick horizon of large-scale solution features representing a period when paleowater tables were at a level that permitted karstification of the carbonate rocks at or near land surface (Miller, 1986, p. B69). Borehole televiewer surveys of wells penetrating a similar zone in southern Florida show that the paleokarst levels, separated by intervals of undissolved rock, commonly are connected by vertical fractures, which can be enlarged by solution into vertical "pipes" that connect the horizontal cavernous levels (Miller, 1986, p. B66).

The permeability, and thus the transmissivity, of the UZLF is strongly related to secondary porosity developed along bedding planes, joints, and fractures (Phelps and Spechler, 1997, p. 9). The transmissivity of the zone has not been determined by aquifer tests of wells open only to that zone. Transmissivity values derived from digital model simulations of the Jacksonville area range from 17,000 to 320,000 ft<sup>2</sup>/d (R.E. Krause, USGS, written commun., 1991). Transmissivity estimates based on specific capacity tests range from 2,000 to about 194,000 ft<sup>2</sup>/d, with a median of 24,000 ft<sup>2</sup>/d for 50 tests analyzed by Phelps and Spechler (1997, table 2).

Hydraulic heads generally increase with depth in the Floridan aquifer system in northeastern Florida. In some areas, however, where the potentiometric surface of the UZLF is lowered by pumping, the head may be higher in the overlying UFA than in the LFA (Phelps and Spechler, 1997, p. 12). About half of the water pumped by large municipal and industrial wells in the Jacksonville area is withdrawn from the UZLF (Spechler, 1994, p. 16). Many wells are open to both the UFA and the UZLF, resulting in local equalization of heads in the two aquifer zones.

The FPZ is a high-permeability unit that lies at the base of the Floridan aquifer system in parts of southeastern Georgia and northeastern Florida (Miller, 1986, p. B70). The FPZ was first tapped by a 2,130-ft deep test well at Fernandina Beach (fig. 1) in 1945 (Brown, 1984, p. 39). Little is known about the extent or thickness of the FPZ because of the sparsity of data. Only four wells in Duval County and one test well each in Fernandina Beach, Nassau County, and Ponte Vedra, St. Johns County (fig. 1) penetrate the FPZ. The thickness of the zone is estimated to range from about 100 ft in the Jacksonville area to about 500 ft in southeastern Georgia (Krause and Randolph, 1989, p. D23). No aquifer test data are available to estimate the transmissivity of the FPZ.

The base of the Floridan aquifer system (the top of the sub-Floridan confining unit) represents a composite surface that crosses formation and time boundaries (Miller, 1986, p. B73). Below the top of this surface there are no high-permeability carbonate rocks. The top of the sub-Floridan confining unit generally corresponds with the top of the Cedar Keys Formation in northeastern Florida.

## Isotopic Data from Aquifers

Information about the chemical and isotopic composition of the Floridan aquifer system sediments can aid in understanding the chemical and isotopic composition of the ground water. The aquifer system is composed primarily of limestone and dolomite, as indicated by the lithologic logs of deep test wells in northeastern Florida (Brown, 1980; Brown and others, 1984; Brown and others, 1986). Most of the limestone ranges from pure calcite (CaCO<sub>3</sub>) to low-magnesium calcite (less than 2 percent magnesium on a molar basis; Han-

shaw, Back and Deike, 1971). The dolomites of the Avon Park Formation probably formed relatively soon after deposition; however, multiple episodes of dolomitization probably occurred (Cander, 1994). Some of the dolomites may have formed at later times in saltwater mixing zones (Hanshaw and Back, 1972; Randazzo and Hickey, 1978). Gypsum and anhydrite occur in the Avon Park Formation and deeper deposits in much of the Florida peninsula (Miller, 1986), although neither was noted in the three deep test wells in northeastern Florida. Localized carbonaceous materials also occur in the aquifer system as thin beds of peat, particularly in the Avon Park Formation, and as cavity fill. Appreciable amounts of quartz sand (SiO<sub>2</sub>) also are found in the aquifer, but because quartz has a low solubility, the δ<sup>18</sup>O of oxygen in the quartz would have little effect on ground-water chemistry and was, therefore, not analyzed. The isotopic data for 14 samples of aquifer materials are given in table 2.

**Table 2.** Lithology and isotopic content of aquifer samples

[Aquifer: UFA, Upper Floridan aquifer; UZLF, upper zone of Lower Floridan aquifer; FPZ, Fernandina permeable zone. δ<sup>13</sup>C, delta carbon-13; δ<sup>18</sup>O, delta oxygen-18; LS, limestone; na, not analyzed. Well locations shown in figure 1]

Site identification number	Local number	Lithology	Depth (feet)	Aquifer	δ <sup>13</sup> C (per mil) <sup>a</sup>	δ <sup>18</sup> O (per mil) <sup>b</sup>	<sup>87</sup> Sr/ <sup>86</sup> Sr ratio <sup>c</sup>
301405081325601	D-3846	Peat	1,110-1,120	UZLF	-22.74	na	0.70796
301405081325601	D-3846	Very hard gray LS	1,110-1,120	UZLF	1.15	29.62	.70788
301405081325601	D-3846	White LS	1,180-1,190	UZLF	1.40	29.62	.70784
301405081325601	D-3846	<i>Lepidocyclina ocalana</i>	1,180-1,190	UZLF	na	na	.70781
301405081325601	D-3846	<i>Dictyoconus americanus</i>	1,180-1,190	UZLF	na	na	.70783
301405081325601	D-3846	Peat	1,180-1,190	UZLF	-22.24	na	.70800
301817081374901	D-425	Gray dolomite	2,075-2,080	FPZ	2.02	33.42	.70790
301817081374901	D-425	Light gray dolomite	2,105	FPZ	2.40	33.39	.70809
301936081292401	MW-2	White fossiliferous LS	670-680	UFA	0.39	30.41	.70782
301936081292401	MW-2	White fossiliferous LS	1,102-1,112	UZLF	.89	29.90	.70777
301936081292401	MW-2	White LS	1,112-1,121	UZLF	1.23	29.90	.70781
301936081292401	MW-2	Tan to gray dolomite	1,112-1,121	UZLF	1.69	32.53	.70789
302416081522601	D-349	Very hard gray dolomite	1,893-1,894	FPZ	-1.66	31.28	.70778
302416081522601	D-349	Soft white LS	1,991-1,992	FPZ	1.75	33.91	.70794

<sup>a</sup>Isotope standard for analyses is Pee Dee belemnite (PDB).

<sup>b</sup>Isotope standard for analyses is Vienna Standard Mean Ocean Water (VSMOW).

<sup>c</sup>All data have been normalized to <sup>88</sup>Sr/<sup>86</sup>Sr = 0.1194. National Institute of Standards and Technology (NIST) 987 is measured as 0.71024.

The values of  $\delta^{13}\text{C}$  for the limestone and dolomite samples range from -1.66 to 2.40 per mil. Values for the peat samples (which are interpreted to be cavity fill and, therefore, younger than the limestone) are much lighter (about -22 per mil). Values near 0 per mil indicate little change from seawater composition (Sacks and Tihansky, 1996). The limestone samples analyzed in this study have values similar to those reported for calcite by Hanshaw and Back (1972) and Cander (1994), whereas the dolomite samples have a narrower range (-1.66 to 2.40) than those reported in the previous studies (-7.5 to 1.0). The dolomites analyzed in this study were nearly contemporaneous in origin, which could explain the narrower range of values.

The  $\delta^{18}\text{O}$  values for the limestone and dolomite samples ranged from 29.62 to 33.91 per mil. Oxygen is present in  $\text{CaCO}_3$  or  $\text{CaMg}(\text{CO}_3)_2$ , which presumably precipitated from ancient seawater at the time of deposition. In general, the  $\delta^{18}\text{O}$  values for limestones were isotopically lighter than the dolomites. This variation may reflect the fact that dolomites formed in a more

saline (compared to the environment of limestone deposition) sabka environment, or could be due to diagenetic changes after deposition. Values of  $\delta^{18}\text{O}$  were not analyzed for the peat and foraminifera samples.

Samples of aquifer materials also were analyzed for the ratio of  $^{87}\text{Sr}/^{86}\text{Sr}$ , which has varied in seawater over geologic time (DePaolo and Ingram, 1985; Elderfield, 1986; Hess, Bender, and Schilling, 1986). Because of later diagenesis, the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of rocks may differ from the ratio of the seawater in which the rocks were deposited (Sacks and Tihansky, 1996). Most of the limestone samples from the study area (from the Avon Park Formation and the lower part of the Ocala Limestone) had ratios indicating an Eocene age, concordant with the time of deposition (fig. 6). One sample from well D-349, however, had a ratio indicating an Oligocene age. This sample was taken from a core (not cuttings) from a depth of 1,991 ft below land surface and could have been affected by recrystallization in Oligocene seawater, thus incorporating the Oligocene-age strontium isotope ratio.

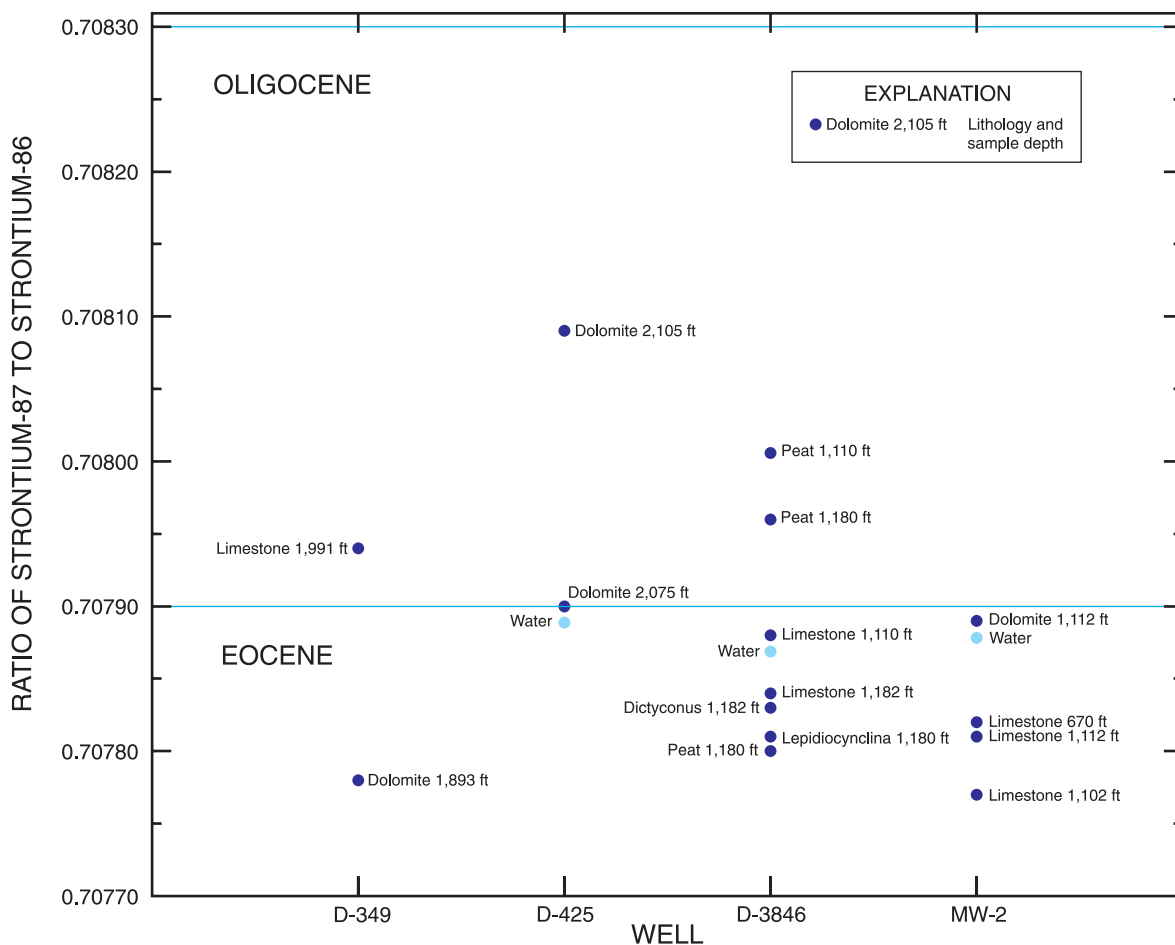


Figure 6. Comparison of strontium-87 to strontium-86 ratio for rock samples from four wells in northeastern Florida.

Strontium isotope ratios for dolomite samples were more diverse. A dolomite sample from a depth of 2,075 ft below land surface in well D-425 (Oldsmar Formation) had the same ratio as a sample from 1,112 ft below land surface in well MW-2 (Avon Park Formation). Another dolomite sample from a depth of 2,105 ft in well D-425 had an even younger ratio, indicating an apparent middle-Oligocene age. The diverse isotope ratios for dolomites tend to confirm the hypothesis that at least some episodes of dolomitization occurred later than during Eocene time (Sacks and Tihansky, 1996).

The two peat samples, both from the Avon Park Formation, had slightly different  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios, which are, nevertheless, significant based on the analytical precision of the method. This variation for the peat samples could reflect the fact that peat easily adsorbs ions from circulating water and the two samples could represent the effects of two episodes of dolomitization. Neither the peat sample from a depth of 1,180 ft nor the sample from 1,110 ft had the same ratio as the carbonate rocks from the same depth intervals.

## CHEMICAL AND ISOTOPIC COMPOSITION OF GROUND WATER

During 1997-99, water samples were collected from 53 wells in Duval County and vicinity, and a sample of seawater was collected about 25 miles off the coast of Duval County. Four of the wells sampled tap only the Fernandina permeable zone (referred to as FPZ wells), 10 tap only the upper zone of the Lower Floridan aquifer (UZLF wells), 24 tap both the UFA and the UZLF (i both wells), and 15 tap only the Upper Floridan aquifer (UFA wells). One well (D-225), which has a wide fluctuation in chloride concentration, was sampled under both free-flowing, low chloride concentration (35 mg/L) and pumped, high chloride concentration (200 mg/L) conditions. In another well (D-536), three samples were collected from different depths by using a down-hole thief sampler.

### Major Ions and Trace Constituents

Water samples were analyzed for major ions and trace constituents of iron, barium, boron, manganese, strontium, lithium, iodide, and bromide. During the first round of sampling, aluminum also was analyzed but results were inconsistent, possibly because high

strontium concentrations interfered with the method of analysis for aluminum, so those data are not reported. Water chemistry varied within the aquifer zones as well as among the various zones (table 3). Of the major ions, chloride and sulfate are important because the U.S. Environmental Protection Agency (U.S. Environmental Protection Agency, 2000) has established secondary recommended limits of 250 mg/L for both constituents in water used for public supply. Increasing chloride concentrations have received the most attention from water managers, but in some areas, sulfate concentrations are more of a concern than chloride because they exceed the recommended limits.

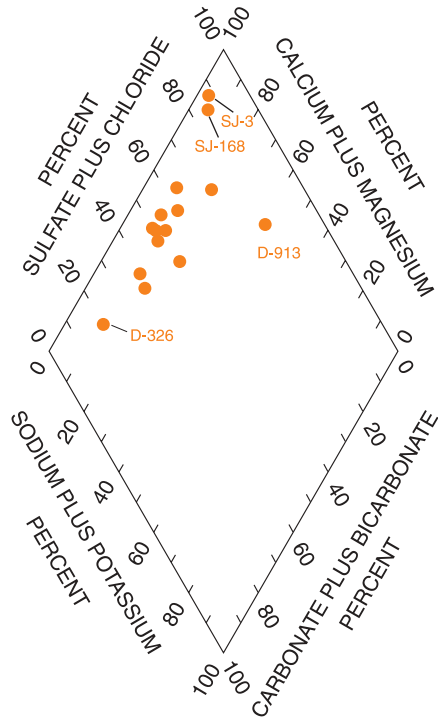
Three of the four FPZ wells yield sodium-chloride type water (fig. 7). The water from well SJ-150 is chemically similar to modern seawater except for having higher concentrations of calcium and strontium and a slightly higher sulfate concentration. Well D-425B yields calcium-sulfate type water that is much lower in chloride concentration than the other FPZ wells (100 mg/L compared to greater than 6,000 mg/L in the other three wells tapping the FPZ). On the basis of these data, the lateral interface between fresh and saline water in the FPZ probably occurs within the approximately 6-mile distance between wells D-425B and D-3060 (fig. 1).

Some questions exist about the integrity of the well completion in well D-425, a multizone monitor well. The bottom zone, D-425B, was designed to tap the FPZ and the upper zone, D-425T, taps both the UZLF and the UFA. When the wellhead was being reworked during the summer of 2000, there was some indication that the separation between the two zones in the well may have been breached and the well might be open to both the FPZ and the UZLF. The major ion data do not indicate conclusively whether or not the well is open to both zones, but saturation index and isotopic data, discussed in later sections of this report, may be more useful.

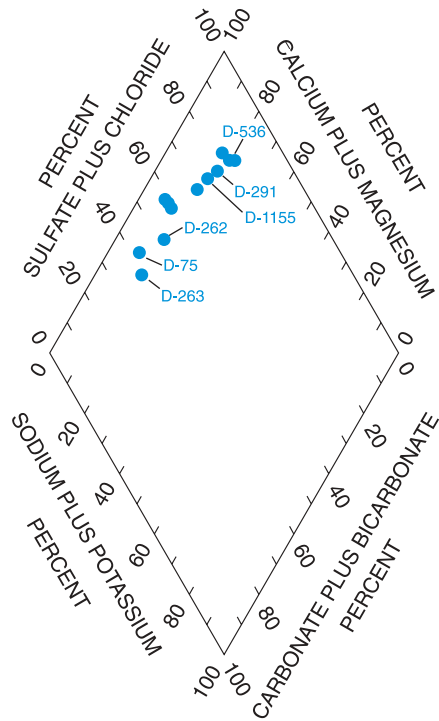
Twelve water samples were collected from the UZLF. Of these, three were collected from different zones of one well, D-536. The sample collected by using a thief sampler just above a fracture at a depth of 1,042 ft in well D-536 had the highest chloride concentration (230 mg/L) of all wells tapping only the UZLF. A sample from a depth of 1,059 ft had water with chemical characteristics very similar to the first sample (table 3). A third sample from a depth of 1,078 ft had a slightly lower chloride concentration (180 mg/L) but slightly higher sulfate concentration (340 mg/L).



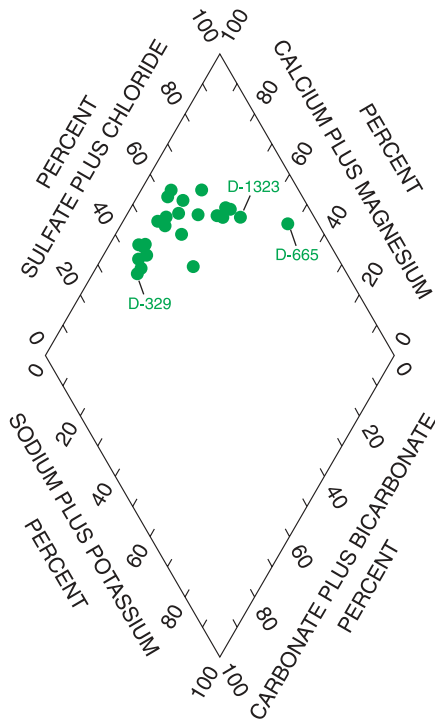
UPPER FLORIDAN AQUIFER



LOWER FLORIDAN AQUIFER



BOTH UPPER ZONE OF LOWER FLORIDAN AND UPPER FLORIDAN AQUIFERS



FERNANDINA PERMEABLE ZONE

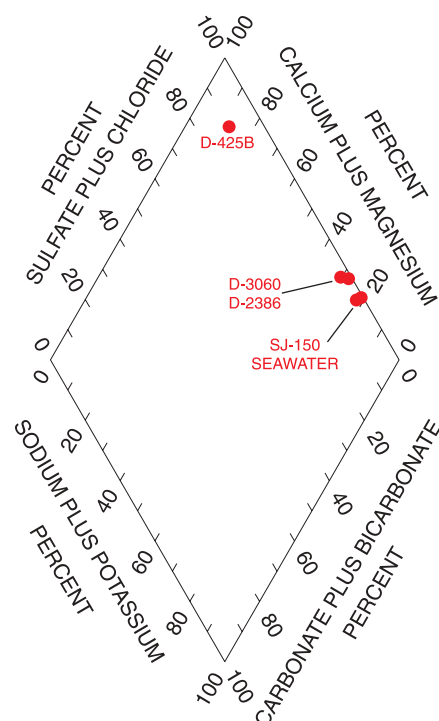


Figure 7. Trilinear diagrams for water from wells tapping various aquifer zones.

**Table 3.** Chemical and physical data for water samples

[°C, degrees Celsius; µS/cm, microsiemens per centimeter at 25 °C; mg/L, milligrams per liter; µg/L, micrograms per liter; --, no data. Aquifer: UFA, Upper Floridan aquifer; B, both Upper Floridan and upper zone of Lower Floridan aquifers; UZLF, upper zone of Lower Floridan aquifer; FPZ, Fernandina permeable zone. All constituents are dissolved]

Site identification number	Local number	Aquifer	Date	Water temperature (°C)	Specific conductance (µS/cm)	pH (standard units field)	Calcium (mg/L as Ca)	Magnesium (mg/L as Mg)	Sodium (mg/L as Na)	Potassium (mg/L as K)	Chloride (mg/L as Cl)	Sulfate (mg/L as SO <sub>4</sub> )	Fluoride (mg/L as F)	Silica (mg/L as Si)
300019081363301	SJ-3	UFA	07/15/97	29.1	1,330	7.44	180	68	11	3.1	17	660	0.9	17
300347081363701	SJ-168	UFA	07/15/97	29.6	1,350	7.52	180	63	18	3.2	45	600	.7	17
301304081222701	SJ-103	UFA	03/19/98	23.0	557	7.18	62	29	18	2.2	26	140	.8	27
301339081531201	D-326	UFA	01/28/99	22.8	241	7.87	26	11	5.5	1.5	5.6	20	.34	15
301547081271901	SE-1	UFA	01/28/99	23.0	650	7.60	66	33	13	2.3	14	190	.8	22
301714081233301	D-72	UFA	01/21/98	21.2	676	7.33	64	36	21	2.3	32	160	.76	26
301830081375501	D-1551	UFA	01/27/99	23.4	569	7.51	65	24	12	1.9	14	140	.69	24
302013081353801	D-673	UFA	01/21/98	27.2	1,040	7.10	100	39	45	2.2	160	140	.55	27
302058081244101	D-1107	UFA	01/27/99	24.1	584	7.56	62	28	12	1.7	16	140	.7	25
302113081322301	D-655	UFA	10/29/98	24.0	600	7.62	65	24	17	1.7	34	110	.65	26
302140081235501	D-1121	UFA	10/28/98	23.0	587	7.44	66	24	13	2.1	16	130	.68	25
302239081434401	NK-1	UFA	10/29/98	23.0	646	7.60	55	29	33	2.7	14	160	.75	20
302557081253101	D-913	UFA	07/15/97	26.1	1,830	7.24	110	57	160	3.6	380	200	.5	30
302608081354903	D-264	UFA	10/27/98	24.0	500	7.45	53	22	15	1.5	19	72	.56	30
302609081260601	D-912	UFA	10/27/98	23.0	506	7.53	48	22	19	2.1	30	58	.63	28
300856081382401	D-3847	B	03/18/98	23.3	367	7.52	39	21	8.4	2.4	9.1	86	.71	17
301405081325601	D-3846	B	01/20/98	26.4	797	7.37	81	39	25	2.8	63	180	.81	24
301508081364601	BW-3	B	02/23/99	26.5	650	7.70	69	32	12	2.4	15	180	.75	23
301704081233401	D-484	B	02/04/97	28.0	1,000	7.24	95	40	66	2.6	180	140	.3	30
301725081305002	D-650	B	01/20/98	25.3	711	7.14	78	31	24	2.1	64	140	.69	25
301740081361001	D-275	B	01/28/97	28.1	1,150	7.00	100	39	70	2.3	200	140	.6	26
301743081303501	D-3825	B	01/20/98	26.0	1,200	7.44	96	40	70	2.4	180	160	.6	26
301743081362301	D-225	B	01/28/97	28.0	1,160	7.27	100	39	71	2.3	200	150	.6	26
301743081362301	D-225	B	07/14/97	28.8	650	7.47	69	28	16	2.1	35	160	.7	23
301748081383401	D-334	B	01/21/98	25.3	600	7.42	73	29	12	2.3	12	180	.61	22
301758081303901	D-665	B	01/31/97	26.8	3,140	7.85	180	78	320	4.1	830	250	.6	26
301817081374901	D-425T	B	03/18/98	25.0	535	7.29	68	25	12	1.9	15	140	.68	23
301846081240201	D-246	B	01/22/98	26.0	599	7.30	63	31	16	1.9	24	140	.73	26
301934081292301	R-3	B	01/28/99	23.5	495	7.78	68	26	13	1.8	17	140	.69	25
301937081471401	D-2223	B	01/28/99	27.0	550	7.43	64	24	11	1.9	12	140	.6	21
301957081342301	D-313	B	01/22/98	23.1	902	7.18	83	32	39	2	110	120	.58	27
302007081353201	D-479	B	03/18/98	26.3	750	7.18	82	30	34	1.9	110	120	.59	26
302008081242101	D-307	B	01/27/99	26.0	930	7.40	73	35	56	2.2	130	140	.63	27
302015081384501	D-335	B	03/18/98	26.0	490	7.22	63	22	13	1.8	15	110	.71	25
302045081323101	D-1323	B	04/06/98	26.6	1,200	7.21	110	42	100	2.4	270	150	.55	27
302342081320601	D-1902	B	03/17/98	25.0	474	7.32	59	24	15	1.7	23	91	.64	26
302503081332001	D-1149	B	03/17/98	21.0	464	7.22	55	23	15	1.5	22	79	.58	29
302510081260201	D-3841	B	04/08/98	22.3	435	7.55	56	22	11	1.5	16	94	.63	26
302538081392501	D-329	B	01/21/98	23.3	530	7.32	58	24	15	1.6	20	74	.56	31
303940081281801	N-22	B	05/18/99	24.0	650	6.50	64	33	19	1.8	28	150	.6	34
301335081355001	D-536-1 <sup>a</sup>	UZLF	02/04/97	30.0	1,400	7.76	150	57	69	3.1	230	330	.8	24
301335081355001	D-536-2 <sup>b</sup>	UZLF	02/04/97	30.0	1,430	7.60	150	57	68	3.1	220	320	.8	24
301335081355001	D-536-3 <sup>c</sup>	UZLF	02/04/97	30.0	1,200	7.50	150	52	50	3.1	180	340	.4	24
301522081331301	D-291 <sup>d</sup>	UZLF	01/31/97	--	884	7.80	86	33	34	2.2	110	160	.7	25
301537081441901	D-75	UZLF	01/29/97	24.5	349	7.90	41	16	6.5	1.8	7.6	65	.4	17
301604081361501	D-450	UZLF	01/29/97	24.1	879	7.78	92	37	30	2.3	100	170	.7	24
301639081330802	D-1155	UZLF	01/28/97	--	1,030	7.08	110	41	39	2.4	140	180	.7	25
301936081292401	MW-2	UZLF	03/19/98	22.6	560	7.53	72	29	15	1.8	15	160	.69	23
302022081393501	D-176	UZLF	01/29/97	24.1	591	7.66	73	27	11	1.9	13	160	.7	22
302227081435001	D-592	UZLF	01/29/97	23.5	585	7.70	75	26	9.8	1.6	12	160	.6	23
302608081354901	D-262	UZLF	01/29/97	26.1	620	7.60	68	28	20	1.6	46	98	.6	31
302608081354902	D-263	UZLF	01/22/98	22.6	500	7.43	56	24	16	1.6	19	73	.6	31
301132081225801	SJ-150	FPZ	01/30/97	29.7	47,100	7.40	760	940	9,700	290	18,000	2,600	.4	19
301405081325601	D-425B	FPZ	01/28/97	27.7	1,860	7.65	290	60	63	4.4	100	850	.9	24
301725081305002	D-3060	FPZ	01/30/97	28.7	27,200	7.40	800	540	4,900	70	9,700	1,500	.3	23
301743081303501	D-2386	FPZ	01/27/97	27.0	20,400	7.50	540	390	3,400	62	6,800	1,100	.4	25
302737080571801	Seawater		04/07/98	--	41,800	7.76	370	1,200	10,400	360	19,000	2,500	.49	3.4

<sup>a</sup>Sampling depth 1,042 ft below land surface.

<sup>b</sup>Sampling depth 1,059 ft below land surface.

<sup>c</sup>Sampling depth 1,078 ft below land surface.

<sup>d</sup>Sampling depth 1,210 ft below land surface.

**Table 3.** Chemical and physical data for water samples--Continued

[°C, degrees Celsius;  $\mu\text{S}/\text{cm}$ , microsiemens per centimeter at 25 °C; mg/L, milligrams per liter;  $\mu\text{g}/\text{L}$ , micrograms per liter; --, no data. Aquifer: UFA, Upper Floridan aquifer; B, both Upper Floridan and upper zone of Lower Floridan aquifers; UZLF, upper zone of Lower Floridan aquifer; FPZ, Fernandina permeable zone. All constituents are dissolved]

Site identification number	Local number	Aquifer	Barium ( $\mu\text{g}/\text{L}$ as Ba)	Boron ( $\mu\text{g}/\text{L}$ as B)	Iron ( $\mu\text{g}/\text{L}$ as Fe)	Manganese ( $\mu\text{g}/\text{L}$ as Mn)	Strontium ( $\mu\text{g}/\text{L}$ as Sr)	Lithium ( $\mu\text{g}/\text{L}$ as Li)	Iodide (mg/L as I)	Bromide (mg/L as Br)	Field alkalinity as $\text{CaCO}_3$	Lab alkalinity as $\text{CaCO}_3$	Field sulfide (mg/L)	Lab sulfide (mg/L)
300019081363301	SJ-3	UFA	20	24	6	0.4	7,800	6	0.015	0.066	96	93	--	--
300347081363701	SJ-168	UFA	22	22	3	.5	8,200	8	.017	.163	116	105	--	--
301304081222701	SJ-103	UFA	25	37	3	.3	2,400	4	.021	.085	160	150	1.7	--
301339081531201	D-326	UFA	14	28	16	1.1	1,200	4	.009	.045	118	99	.5	1.6
301547081271901	SE-1	UFA	25	40	15	.5	2,700	6	.019	.062	125	128	1.6	4.6
301714081233301	D-72	UFA	24	26	20	2.8	2,100	6	.017	.109	142	133	1.5	--
301830081375501	D-1551	UFA	21	35	4.6	.3	3,000	6	.017	.062	140	138	1.3	4.6
302013081353801	D-673	UFA	31	19	110	1.3	3,000	7	.024	.378	137	141	1.5	--
302058081244101	D-1107	UFA	25	34	2.6	.4	2,100	5	.018	.036	--	140	1.9	5.8
302113081322301	D-655	UFA	19	35	82	10	2,200	6	.022	.122	--	133	1.3	2.6
302140081235501	D-1121	UFA	28	36	11	1.4	2,300	7	.02	.059	--	144	2.4	3
302239081434401	NK-1	UFA	16	43	4.2	3.9	1,500	9	.015	.04	--	159	1.8	2.4
302557081253101	D-913	UFA	60	49	310	2.9	1,800	10	.031	1.32	153	145	--	--
302608081354903	D-264	UFA	26	34	53	4.7	500	5	.021	.037	162	162	1.1	1.9
302609081260601	D-912	UFA	24	33	37	9.7	560	6	.023	.12	--	154	1.2	2.6
300856081382401	D-3847	B	18	29	50	.7	3,600	4	.01	.012	122	106	.7	--
301405081325601	D-3846	B	30	16	20	.6	4,300	7	.018	.213	149	130	1.5	--
301508081364601	BW-3	B	24	33	19	.8	4,200	5	.021	.061	122	131	1.5	1.8
301704081233401	D-484	B	38	52	6	.9	2,500	10	.022	.538	--	149	--	--
301725081305002	D-650	B	26	16	7	.5	3,200	7	.02	.217	148	138	1.7	--
301740081361001	D-275	B	33	36	40	1.2	3,700	10	.022	.689	--	138	--	--
301743081303501	D-3825	B	34	20	40	1.5	3,700	7	.023	.405	150	140	1.2	--
301743081362301	D-225	B	33	37	50	1.3	3,700	20	.022	.682	--	139	--	--
301743081362301	D-225	B	23	32	40	2.5	3,300	5	.019	.119	121	138	--	--
301748081383401	D-334	B	20	12	30	7	4,000	6	.018	.033	130	127	1.2	--
301758081303901	D-665	B	77	93	150	5.8	6,300	20	.028	2.879	--	137	--	--
301817081374901	D-425T	B	19	29	7	.7	3,300	4	.018	.049	198	139	1.1	--
301846081240201	D-246	B	27	24	5	.8	2,100	5	.017	.06	135	143	1.8	--
301934081292301	R-3	B	22	36	13	.7	2,800	6	.021	.073	144	143	1.9	3.7
301934081471801	D-2223	B	18	36	14	.6	3,300	6	.013	.02	--	130	1.2	4.2
301957081342301	D-313	B	26	22	20	.7	2,400	6	.019	.328	138	146	1.5	--
302007081353201	D-479	B	25	34	20	1.1	2,500	4	.021	.357	196	145	1.3	--
302008081242101	D-307	B	36	43	16	.9	2,000	7	.023	.405	--	149	2.06	5.8
302015081384501	D-335	B	19	32	3	.4	2,500	4	.018	.051	185	147	.9	--
302045081323101	D-1323	B	40	42	40	5.6	2,800	5	.03	.996	144	147	1.5	2.2
302342081320601	D-1902	B	24	33	60	5.4	1,800	4	.022	.087	154	157	1.7	--
302503081332001	D-1149	B	24	39	9	.5	880	4	.022	.066	160	157	1.9	--
302510081260201	D-3841	B	28	37	100	10	1,300	4	.019	.061	138	149	1.4	1.8
302538081392501	D-329	B	27	28	50	1.5	560	5	.019	.056	161	160	1.5	--
303940081281801	N-22	B	28	40	5.1	.3	590	8.1		.084	--	156	--	3.8
301335081355001	D-536-1	UZLF	35	50	10	1	8,400	10	.024	.738	--	127	--	--
301335081355001	D-536-2	UZLF	35	51	20	.9	8,300	10	.023	.747	--	126	--	--
301335081355001	D-536-3	UZLF	29	53	20	.9	7,800	10	.023	.555	--	125	--	--
301522081331301	D-291	UZLF	26	46	20	3.5	3,800	10	.021	.369	--	91	--	--
301537081441901	D-75	UZLF	22	39	160	1.6	3,300	9	.01	.028	--	108	--	--
301604081361501	D-450	UZLF	33	29	660	13	4,300	10	.021	.365	--	141	--	--
301639081330802	D-1155	UZLF	29	28	220	5	4,800	8	.019	.465	--	137	--	--
301936081292401	MW-2	UZLF	28	32	730	15	2,900	4	.02	.06	133	145	.3	--
302022081393501	D-176	UZLF	41	28	530	7.1	3,900	8	.017	.051	--	134	--	--
302227081435001	D-592	UZLF	42	41	270	3.1	2,800	8	.012	.03	--	132	--	--
302608081354901	D-262	UZLF	35	30	20	3	630	10	.025	.146	--	158	--	--
302608081354902	D-263	UZLF	27	27	30	3.1	730	5	.022	.058	160	164	1	--
301132081225801	SJ-150	FPZ	88	3,600	1,200	38	14,100	200	.121	81	--	120	--	--
301405081325601	D-425B	FPZ	19	76	130	5.2	8,900	10	.015	.34	--	118	--	--
301725081305002	D-3060	FPZ	170	1,300	1,500	59	21,800	100	.082	58	--	130	--	--
301743081303501	D-2386	FPZ	160	910	50	6.3	11,400	100	.07	27	--	136	--	--
302737080571801	Seawater		25	4,300	20	25	650	120	.105	62	--	113	--	--

Well D-536 had the warmest water temperature (32.5 °C) measured during geophysical logging of numerous wells in Duval County (Phelps and Spechler, 1997). The sample collected during the present study had a lower temperature because the water cooled as the sampler was being raised to the land surface. These samples and the sample from well D-291 (also a thief sample from near the bottom of the well) were calcium-magnesium sulfate-chloride type water.

Most of the other samples from UZLF wells were identified as calcium-magnesium sulfate-bicarbonate type water (fig. 7). Wells with the lower chloride concentrations are generally west (or north) of the St. Johns River (fig. 1), except for MW-2. Chloride concentrations do not show an increasing trend with depth; wells D-450 and D-592 both are about 1,300 ft deep, but the chloride concentration is 100 mg/L in D-450 and only 12 mg/L in D-592. These wells are located about 10 miles apart in central Duval County (fig. 1).

Twenty-five water samples were collected from wells tapping both the UZLF and the UFA. Many public supply wells in northeastern Florida have been drilled to penetrate both zones to take advantage of the increased yield of water from the UZLF. The chemistry of water from wells open to both zones varies greatly, from calcium-magnesium-bicarbonate type water (wells D-329 and D-334) with relatively low specific conductance (about 360-500  $\mu\text{S}/\text{cm}$ ) to calcium-sodium-magnesium chloride-sulfate type water (wells D-665 and D-225) with much higher specific conductance (about 1,000-3,000  $\mu\text{S}/\text{cm}$ ) (figs. 7 and 8).

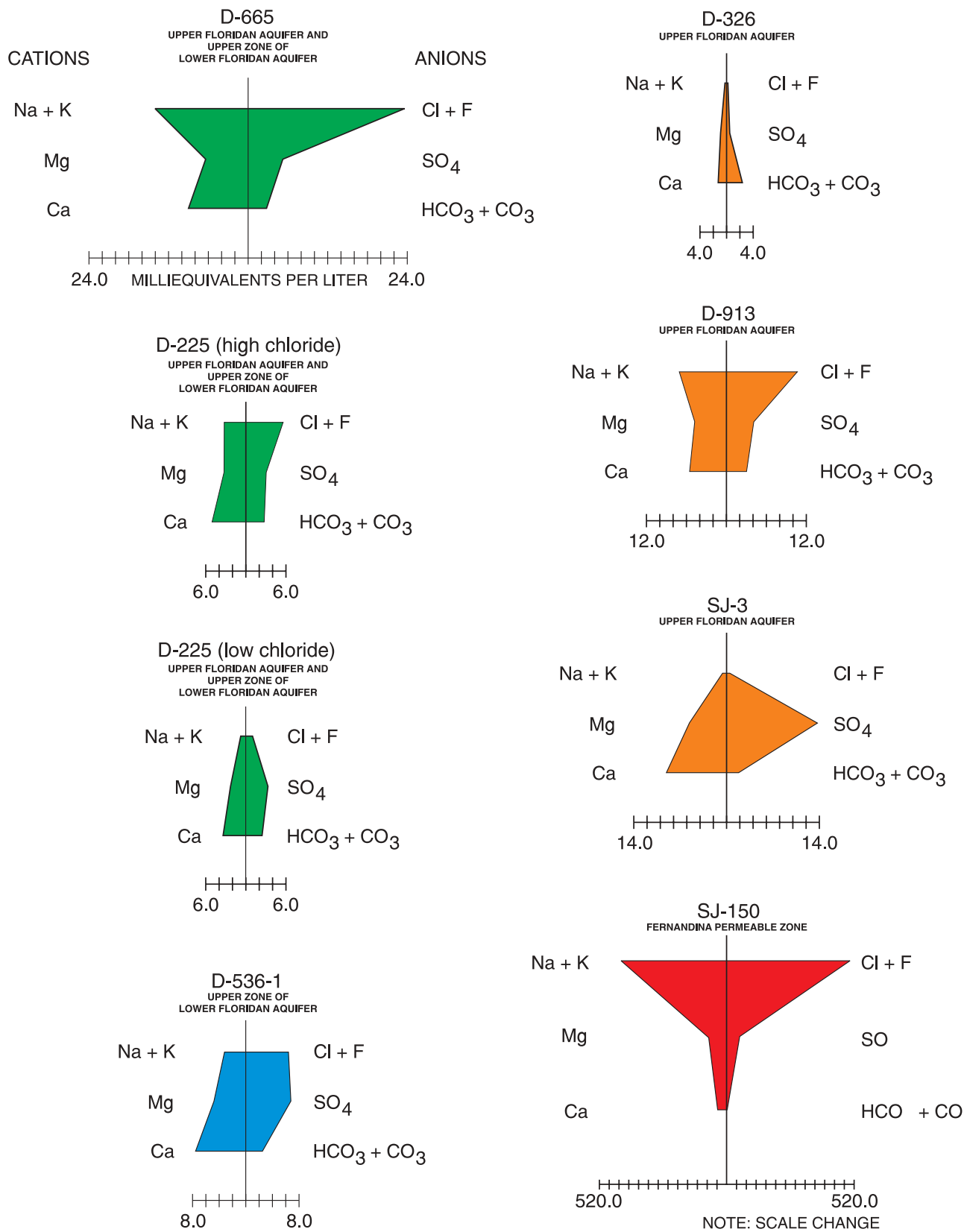
Water from well D-665 is chemically more similar to the high chloride water from the FPZ wells than to water from wells tapping the UZLF (fig. 7). Most of the water produced from well D-665 apparently comes from a single fracture at a depth of about 1,080 ft below land surface (1,040 ft below sea level) (Phelps and Spechler, 1997). High-resolution seismic reflection surveys near this well (Odum and others, 1997) indicate the presence of a paleokarst feature that possibly breaches the semi-confining unit separating the UZLF from the FPZ. This feature could provide a pathway for mineralized water to move from the FPZ to the UZLF. When the well is not allowed to flow, water from the UZLF moves up the wellbore and flows into the UFA, thus introducing high chloride water into the UFA. This type of situation probably accounts for some of the variability in water quality observed in wells tapping both zones and also in the UFA.

Well D-225 also is finished in both aquifers, and the water chemistry reflects this construction. This well is sampled regularly and chloride concentrations

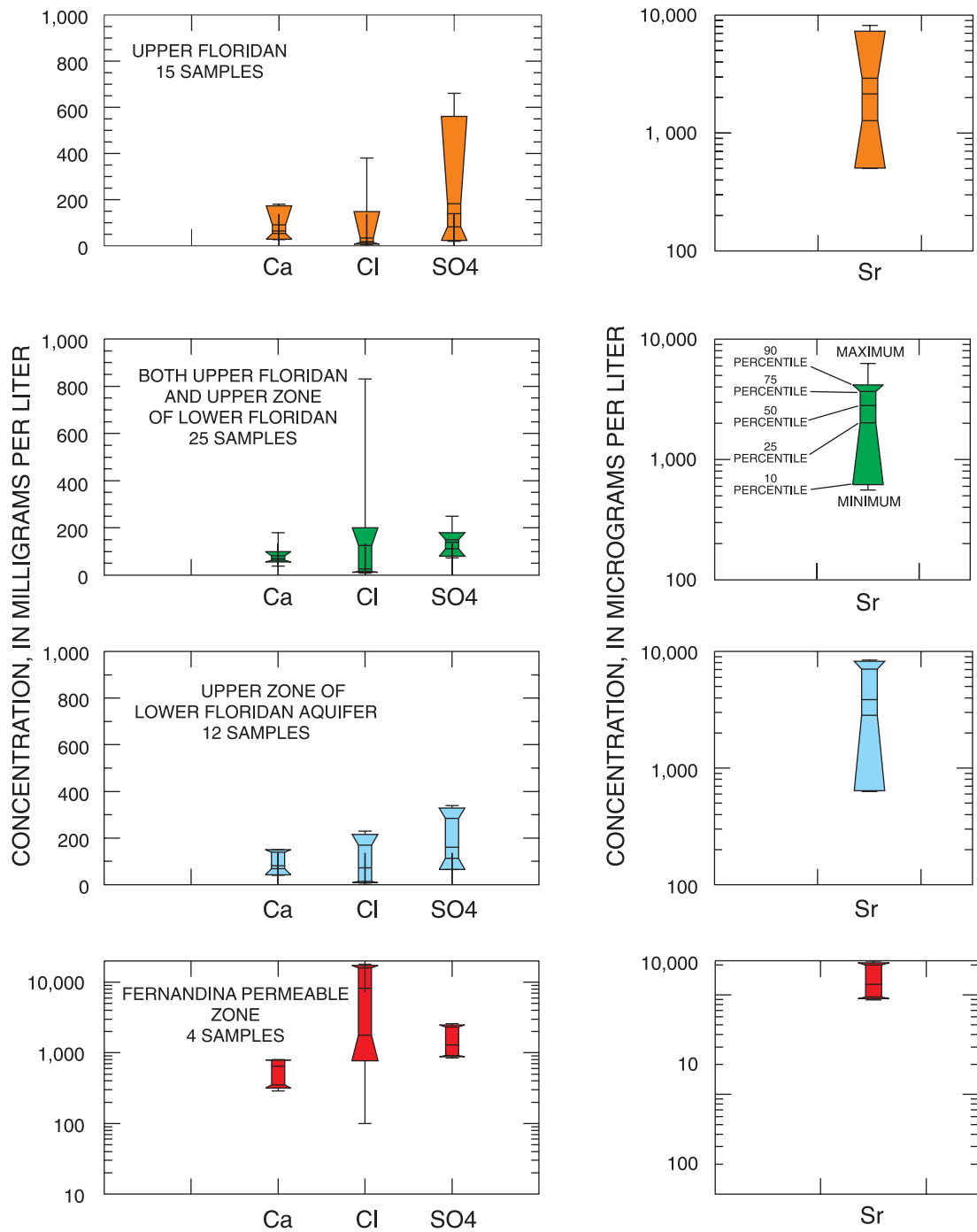
fluctuate between about 35 and 200 mg/L (Phelps and Spechler, 1997). When the well is flowing naturally (flow rate about 1,000 gallons per minute (gal/min)), the water at the wellhead and from a zone of fractures or solution features at a depth of about 1,225 to 1,245 ft below land surface are nearly identical (Phelps and Spechler, 1997, table 3), indicating that most of the flow comes from that zone. Non-pumped conditions represent low chloride conditions. A sample collected when the well was being pumped at about 2,000 gal/min had a different chemistry, however, including a higher chloride concentration (table 3, fig. 8). When the well was pumped, concentrations of chloride, calcium, magnesium, and sodium were much higher than under non-pumped conditions, but the sulfate concentration was about the same (150-160 mg/L). Other water samples collected monthly from this well had chloride concentrations intermediate between the values sampled during this study. Although the well has been geophysically logged, the source of the higher chloride water is unclear, but may be related to whether or not other nearby wells are being pumped.

Water chemistry of the 15 samples collected from the UFA wells varied considerably (figs. 7 and 8). Well D-326 yielded calcium-magnesium bicarbonate type water with a low specific conductance (241  $\mu\text{S}/\text{cm}$ ) and low chloride (5.6 mg/L) and sulfate (20 mg/L) concentrations. Well SJ-3 also had a relatively low chloride concentration (17 mg/L) but was much higher in sulfate (660 mg/L) (a calcium-magnesium sulfate type water). Well D-913 had the highest chloride concentration of the UFA wells sampled (380 mg/L). The major-ion diagram of water from this well more closely resembles that of water from well D-665 than water from other wells tapping the UFA. Both wells are located near paleokarst collapse features (fig. 3).

Except for water from the FPZ, water from the various aquifer zones cannot be differentiated based on chemistry; major-ion concentrations vary as much within a particular zone as among zones (fig. 9). The UZLF wells showed the least variability. Wells tapping both the UFA and the UZLF had a wider range in chloride concentration than wells tapping just the UFA or just the UZLF. Water from the UFA had the widest range of sulfate concentrations (58-660 mg/L). A Kruskal-Wallis test of the means of chemical constituents also confirms the similarity of water chemistry among the various aquifer zones. Only the trace constituents barium, iron, strontium, and lithium were significantly different (at a probability level of 0.05) in samples from the UFA, the UZLF, and wells completed in both aquifer zones. Means for FPZ wells were not included because there were so few data available.



**Figure 8.** Major ion diagrams for selected wells.



**Figure 9.** Box plots of calcium, chloride, sulfate, and strontium concentrations.

In general, water samples collected in northeastern Florida show a trend similar to the dilution of seawater with freshwater (fig. 10) for the relation between chloride and sodium. The data, however, cannot indicate the age of a possible seawater end member. Water from UFA well D-326 could represent the freshwater recharge end member, and water from FPZ well SJ-150 could represent a saline-water end member. Samples with chloride concentrations ranging between about 20-1,000 mg/L have excess chloride, possibly indicating loss of sodium by ion exchange. Water from well NK-1 (UFA well) departs slightly from the mixing line, indicating the presence of excess sodium. This well may be open to the overlying surficial aquifer system and would, thus, have different water chemistry from UFA wells. Although figure 10 implies slightly different trends for lower and higher chloride samples, the relation between chloride and sodium cannot definitely indicate the source of the mineralized water.

### Halogens

More insight into the possible sources of mineralized ground water that mixes with fresher water can be gained by comparing the ratio of chloride to bromide ( $\text{Cl}^-/\text{Br}^-$ ) in the water. Seawater has a mass ratio of chloride to bromide ranging between 288 and 292 (Davis and others, 1998a). In most ground-water samples in the United States reported by Davis and others (1998a), water with chloride concentrations less than 200 mg/L had  $\text{Cl}^-/\text{Br}^-$  ratios less than 200, and the  $\text{Cl}^-/\text{Br}^-$  ratios increased as chloride concentrations increased within a given area. Those trends generally could be attributed to a source of mineralized water such as an oil-field brine or treated wastewater. In coastal areas, however, Davis and others (1998a) suggested that  $\text{Cl}^-/\text{Br}^-$  ratios would likely be affected by the flushing of small amounts of residual Cenozoic seawater and by sea salt in the atmosphere, which affects the  $\text{Cl}^-/\text{Br}^-$  ratio in precipitation. The ratio generally is less than 200 in inland areas.

Water samples collected in northeastern Florida (fig. 10) generally support the conclusion of dilution of seawater, although the ground-water samples with the highest chloride concentrations tended to have excess bromide. Among the low chloride samples ( $\text{Cl}^-$  less than 100 mg/L), well D-3847 had excess chloride, whereas well D-326 had excess bromide. Excess bromide in ground water has been attributed to the diagenesis of organic material (such as peat) in the aquifer

material (Davis and others, 1998a). Peat commonly is observed in the Floridan aquifer system.

Possible errors in the determination of low-level concentrations of bromide could affect the calculated ratios of bromide to chloride. Based on a sample split, an estimated error for the low-level bromide determinations is about 15 percent. A few examples of how this error affects the calculated chloride-to-bromide ratio are given in the following table:

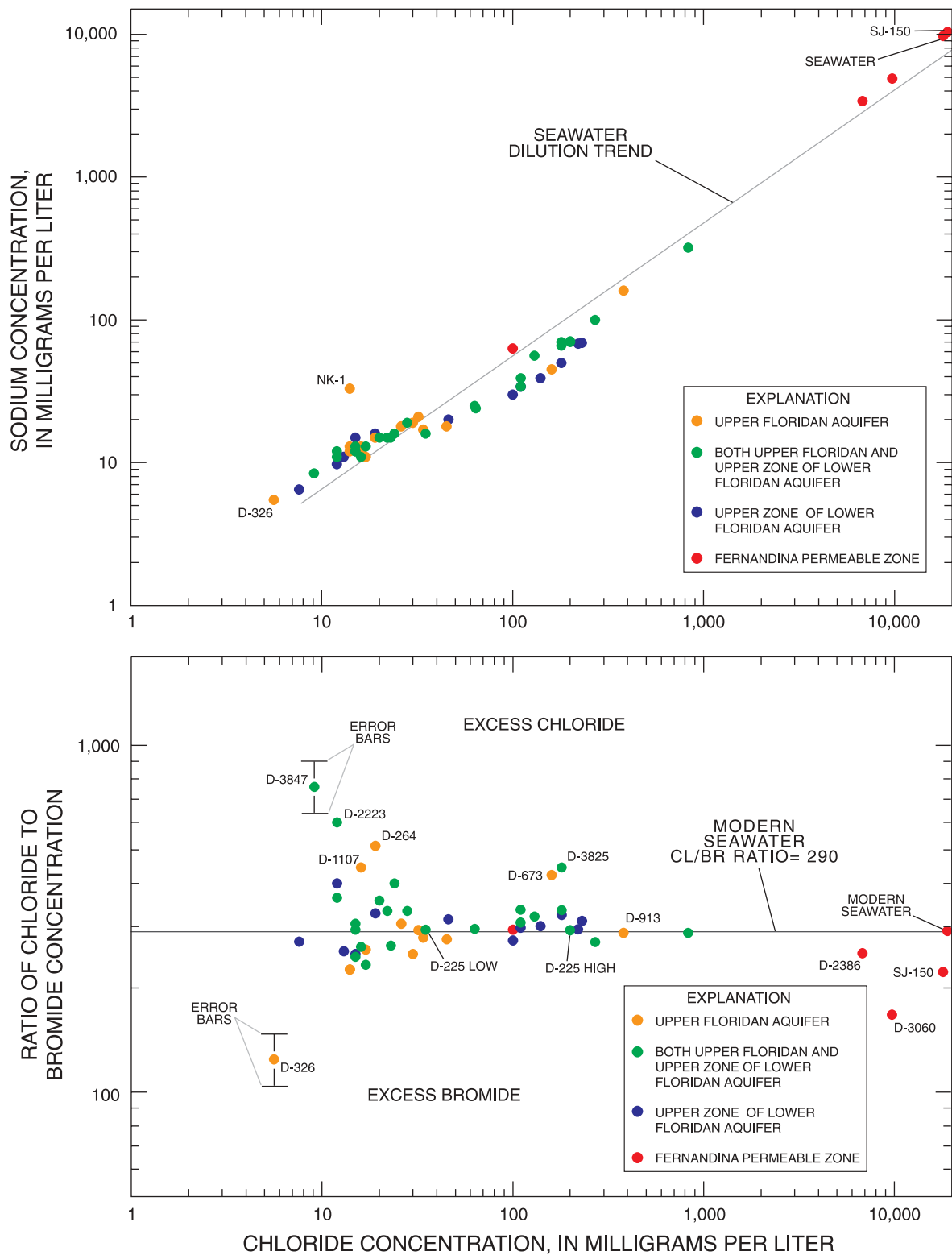
Well	Cl	Br	$\text{Cl}^-/\text{Br}^-$ ratio	Br error	Ratio range with error
D-326	5.6	0.045	124	0.0068	108-147
D-3847	9.1	.012	758	.0018	650-910
D-225 (low)	35	.119	294	.0178	255-346
D-225 (high)	200	.682	293	.102	255-344

For most wells, although the ratio may change slightly because of errors in bromide determinations, the range of  $\text{Cl}^-/\text{Br}^-$  still is indicative of whether or not the ratio is consistent with seawater dilution (the range for seawater dilution is 247 to 334).

Thus, for some wells, such as D-225, the  $\text{Cl}^-/\text{Br}^-$  ratio implies dilution of seawater but for wells such as D-3847 and D-326, this is clearly not the case. For other wells, however, possible errors in bromide determinations can obscure any conclusions based on the  $\text{Cl}^-/\text{Br}^-$  ratio. The dilution trend (fig. 10) showing the gradual flushing of seawater out of the aquifer probably accounts for background chloride concentrations in the Floridan aquifer system, but probably does not explain increasing chloride concentrations. If unflushed pockets of relict seawater from higher stands of sea level were the source of the increased chloride concentrations, such pockets would be expected to occur in strata of low permeability; however, geophysical logging has shown that fracture flow zones are the sources of high chloride water in numerous wells (Phelps and Spechler, 1997).

### Sulfur

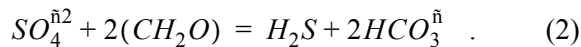
Sources of sulfur in the ground water include atmospheric precipitation, dissolution of gypsum or sulfide minerals from deeper zones of the aquifer, and mixing with saline waters (Sacks and Tihansky, 1996).



**Figure 10.** Relations between sodium and chloride concentration, and between the mass ratio of chloride-to-bromide and chloride concentration.



Two common forms of sulfur are the oxidized sulfate ( $\text{SO}_4^{\text{n}2}$ ) ion and the reduced sulfide ( $\text{S}^{-2}$ ) ion (Hem, 1985). High sulfate concentrations in ground water contribute to high dissolved solids and the gaseous sulfide, hydrogen sulfide, which produces the unpleasant rotten egg smell in water. In anoxic ground-water systems, bacteria may metabolize sulfate, reducing it to sulfide (Long and others, 1988). A representative equation for the process from Berner (1971) is:



Sulfate concentrations in water from FPZ wells ranged from 850 mg/L at well D-425B to 2,600 mg/L at well SJ-150 (table 3), of which the latter was slightly higher than the sulfate concentration in the seawater sample (2,500 mg/L). For wells tapping all other aquifer zones, the highest concentrations were from UFA wells SJ-3 (660 mg/L) and SJ-168 (600 mg/L). In well D-665 (completed in both the UFA and the UZLF), which had a chloride concentration of 830 mg/L, the sulfate concentration was only 250 mg/L. All three samples from well D-536 (UZLF) had relatively high sulfate concentrations of about 330 mg/L. The lowest sulfate concentration measured was 20 mg/L in well D-326, which taps the UFA.

Nearly all of the water samples collected in northeastern Florida have the characteristic smell of hydrogen sulfide. Sulfide concentrations measured in the field ranged from 0.3 mg/L at well MW-2 to 2.4 mg/L at well D-1121 (table 3). As discussed previously, the field technique for determining sulfide concentrations probably aerates the sample, resulting in some loss of hydrogen sulfide gas, so for a number of samples, both field and laboratory determinations were made. Field and laboratory determinations were similar for well BW-3 (1.5 and 1.8 mg/L, respectively). For wells with higher concentrations, however, the field procedure apparently allowed significant loss. At well D-1107, the field value was 1.9 mg/L, whereas the lab value was 5.8 mg/L; and at well D-307 the field value was about 2.1 mg/L, whereas the lab value also was 5.8 mg/L.

Sources of sulfur in the ground water include dissolution of sulfur-bearing minerals in the aquifer and mixing with water having a chemical composition similar to that of seawater. Dissolution of gypsum and dilution of seawater have distinct trends on a plot of the relation of the mass ratio of sulfate to chloride and the sulfate concentration of water samples (Rightmire and others, 1974). Water samples from the high chloride FPZ wells follow a trend similar to that for seawater mixing with water from well D-326 (fig. 11). Other

samples follow a trend similar to that for gypsum dissolution. In many of the samples, sulfate reduction probably has affected sulfate concentrations. The dominant chemical processes involving sulfur in northeastern Florida ground water apparently are varying degrees of freshwater-seawater mixing, gypsum dissolution, and sulfate reduction.

### Ion Enrichment

Additional insight into possible geochemical reactions and the source of mineralized water that mixes with fresh ground water in northeastern Florida can be gained by comparing observed ground-water chemistry with hypothetical mixing using various saline waters. Water from UFA well D-326 was selected to represent the chemistry of ambient fresh ground water. A spreadsheet was made to tabulate mixing of D-326 water with water from well SJ-150 and with modern seawater (based on chloride concentration as the mixing variable). Compared to simple mixing with water either from well SJ-150 or modern seawater, the samples generally are enriched in bicarbonate, calcium, magnesium, sulfate, fluoride and silica, and depleted in sodium and potassium (table 4). The fraction of saline water ( $x$ ) was computed using the following equation:

$$x = (Cl_w - Cl_{fw}) / (Cl_{sw} - Cl_{fw}), \quad (3)$$

where

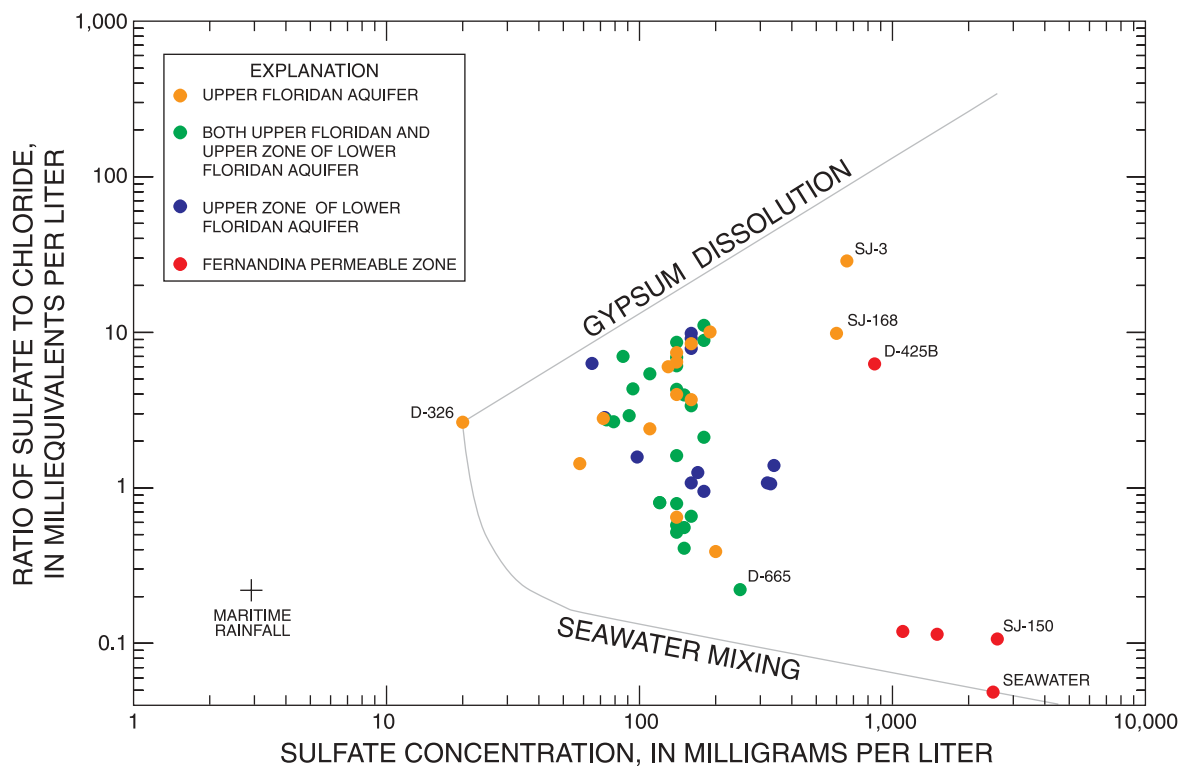
$Cl$  is the chloride concentration, in milligrams per liter, and  
 $w$ ,  $fw$ , and  $sw$  refer to the sample from a well, freshwater end member (D-326) or saline water end member, respectively.

The ion concentrations observed in each sample were then compared to the expected concentrations based on the relation:

$$i_e = i_{obs} - [(i_{sw}x) + (i_{fw}(1 - x))] \quad (4)$$

where

$i_e$  is ion enrichment if positive and ion depletion if negative,  
 $i_{obs}$  is the observed ion concentration in the well, and  
 $i_{sw}$  and  $i_{fw}$  are the ion concentrations in the saline water and freshwater end members, respectively.



**Figure 11.** Relation between sulfate-chloride ratio and sulfate concentration (Maritime rainfall data from Rightmire and others, 1974).

Sulfate is enriched in all samples compared to conservative mixing. The low chloride waters were most enriched and the high chloride waters least enriched, which agrees with observations in west-central Florida by Sacks and Tihansky (1996). In northeastern Florida, however, sulfate enrichment was related more to chloride concentrations than to aquifer zone sampled; the high chloride samples from the UFA had sulfate enrichment similar to that for high chloride waters from the LFA and the FPZ. For low chloride waters, the sulfate enrichment is indicative of gypsum dissolution (Sacks and Tihansky, 1996).

Calcium is enriched in all samples compared to conservative mixing, and is more enriched in high chloride waters. If conservative mixing with modern seawater is assumed, calcium enrichment for some of the high chloride waters is related to sulfate enrichment, indicating that dissolution of gypsum is the source of both calcium and sulfate (fig. 12). For other samples, such as that from D-665, there must be another source of calcium. Cation exchange (of calcium for sodium) could be a mechanism for calcium enrichment. As sodium-rich seawater moves through an aquifer, two sodium ions can replace one calcium

ion at exchange sites (probably in the minor amounts of clay minerals that occur in the aquifer) (Sacks and Tihansky, 1996). This cation exchange results in ground water that is enriched in calcium and depleted in sodium. In northeastern Florida, water samples from the FPZ were slightly depleted in sodium, whereas the other high chloride samples were more depleted. For the high chloride waters, calcium enrichment is linearly related to sodium depletion, supporting cation exchange as a mechanism for reducing the sodium and increasing the calcium concentrations in the ground water. The low chloride samples were slightly enriched in sodium compared to conservative mixing.

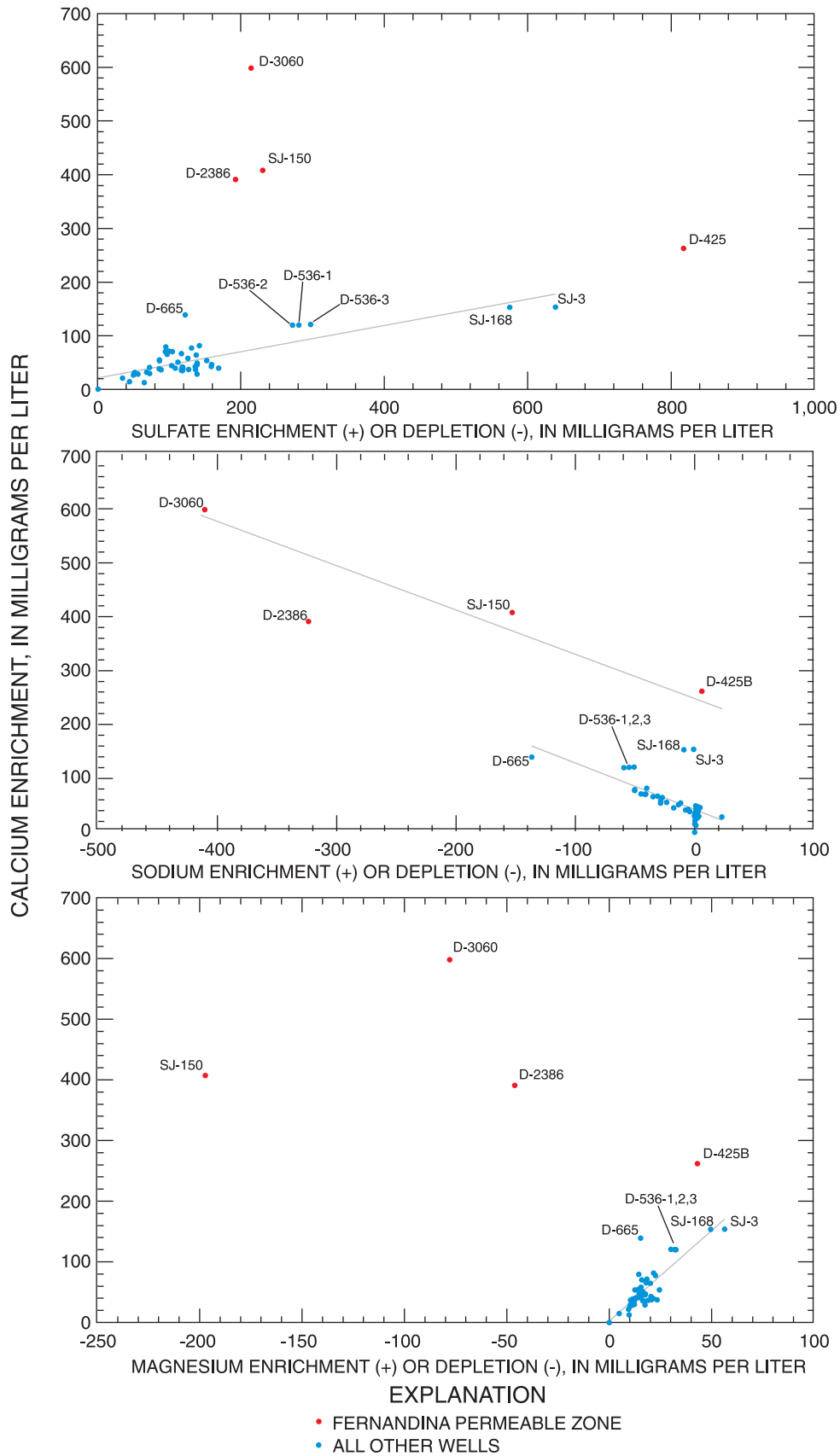
Other ions, such as magnesium, potassium, and silica, also show enrichment or depletion (table 4). Magnesium generally was enriched compared to conservative mixing with seawater for all samples except those from the FPZ, which were depleted. The sample from well D-665 was about 20 percent enriched, compared to about 45 to 50 percent for the other high chloride samples. These data indicate that the source of mineralized water in well D-665 could be the FPZ. The low chloride samples generally were more enriched in magnesium (50 to 60 percent) than the higher chloride samples.

**Table 4.** Percent excess of some constituents for selected wells

[Aquifer: UFA, Upper Floridan aquifer; B, both Upper Floridan and upper zone of Lower Floridan aquifers; UZLF, upper zone of Lower Floridan aquifer; FPZ, Fernandina permeable zone. mg/L, milligrams per liter. First number is percent excess over conservative mixing of water from well D-326 with water from well SJ-150. Second number is mixing of water from well D-326 with modern seawater sample. Positive numbers indicate enrichment, negative numbers indicate depletion]

Local No.	Aquifer	Chloride concentration, mg/L	Percent saline water		Bicarbonate		Calcium		Magnesium		Sodium		Potassium		Sulfate		Fluoride		Silica		Bromide	
D-673	UFA	160	0.8	0.9	30	30	71	68	47	51	-100	-97	-101	-81	71	70	38	38	45	44	-45	-96
D-913	UFA	380	2.0	2.1	32	31	70	62	40	47	-32	-30	-138	-108	66	63	31	32	51	50	4	-31
D-225 (high)	B	200	1.0	1.1	29	29	70	66	41	46	-57	55	-125	-101	70	68	43	43	43	42	0	-35
D-665	B	830	4.3	4.6	27	27	77	70	20	31	-43	-41	-316	-259	49	45	42	43	44	42	5	-30
D-536-1	UZLF	230	1.2	1.2	22	22	80	77	56	60	-86	-83	-85	-64	85	84	57	57	38	37	-5.3	-43
D-1155	UZLF	140	0.7	0.7	28	28	74	71	53	56	-103	-100	68	-52	79	78	51	51	40	40	-4	-40
D-3060	FPZ	9,700	51.0	54.0	18	15	75	47	-14	5	-8	-7	-164	-124	14	6	-39	-24	61	25	45	25
D-2386	FPZ	6,800	35.8	37.8	24	21	72	44	-12	7	-10	-8	-109	-78	18	10	2	9	57	34	18	-13
SE-1	UFA	14	<0.1	<0.1	23	23	60	60	65	65	23	22	29	28	89	89	58	58	32	32	-34	-17
D-1551	UFA	14	<0.1	<0.1	28	28	60	60	52	52	16	16	14	13	85	85	51	51	38	38	-34	-17
NK-1	UFA	14	<0.1	<0.1	38	38	52	52	61	60	70	69	40	39	87	87	55	55	25	25	-107	-81
D-3847	B	9	<0.1	<0.1	7	7	33	33	47	47	12	12	35	35	76	76	52	52	12	12	-406	-370
BW-3	B	15	0.1	<0.1	24	24	62	62	64	64	12	11	31	30	88	88	55	55	35	35	-43	-24
D-334	B	12	<0.1	<0.1	22	22	64	64	61	61	25	25	30	30	88	88	44	44	32	32	-124	-100
D-2223	B	12	<0.1	<0.1	24	24	59	59	53	52	19	18	16	15	85	85	43	43	29	29	-269	-229
D-335	B	15	0.1	<0.1	33	33	58	58	48	47	19	18	8	7	81	81	52	52	40	40	-71	-48
D-75	UZLF	7.6	<0.1	<0.1	8	8	36	36	31	30	-1	-2	15	15	69	69	15	15	12	12	-92	-84
MW-2	UZLF	15	0.1	<0.1	32	32	63	64	60	60	30	29	8	7	87	87	51	51	35	35	-46	-26
D-176	UZLF	13	<0.1	<0.1	26	26	64	64	58	58	14	14	15	14	87	87	51	51	32	32	-54	-36
D-592	UZLF	12	<0.1	<0.1	25	25	65	65	56	56	9	8	0	-1	87	87	43	43	35	35	-146	-120

Chemical and Isotopic Composition of Ground Water



**Figure 12.** Enrichment of calcium compared to enrichment or depletion of sulfate, sodium, and magnesium for mixing with seawater.

These data agree with observations in west-central Florida (Sacks and Tihansky, 1996), and are consistent with dedolomitization reactions (dolomite and gypsum dissolution and calcite precipitation) in the freshwater-bearing zones of the aquifer and either calcium/magnesium exchange or dolomitization of calcite in the saline water-bearing zones. Potassium was depleted for all the high chloride samples and enriched for all the low chloride samples. Silica also is enriched in all samples, with those from the FPZ wells showing the greatest enrichment.

Comparisons of ion enrichment or depletion based on simple mixing models indicate that water from the FPZ could be the source of the mineralized water in well D-665 (fig. 12). For water from the FPZ wells and from well D-665, however, the data are not consistent with simple mixing of seawater, either ancient or modern. This could imply that mixing with water of a different (but as yet unknown) chemical type, or more complex reactions with aquifer materials, may have been involved in the increased mineralization of water in northeastern Florida. For the low chloride samples, common reactions with aquifer materials and simple mixing (dilution) during the process of flushing after the last retreat of Pleistocene seas could account for the observed chemical composition of the water samples.

### Saturation State with Respect to Minerals

To better understand the chemical changes that can occur in water as it moves through the ground, the chemistry of the water and aquifer materials and the interactions between them can be examined. One aspect of such geochemical interactions is the dissolution or precipitation of minerals along flow paths in the ground-water system. The saturation index (SI) is a measure of the departure from equilibrium of the water with respect to various mineral phases. An SI value of zero indicates that the water is at equilibrium (saturated) with respect to the mineral phase. A negative value indicates undersaturation (dissolution of the mineral is possible), and a positive value indicates supersaturation (precipitation is possible). SIs for the water samples were calculated using the aqueous speciation model WATEQ4F (Ball and Nordstrom, 1991):

$$SI = \log(IAP/K_T), \quad (5)$$

where

$IAP$  is the ion activity product of the components of the mineral phase, and

$K_T$  is the solid phase solubility equilibrium product at the specified temperature.

The determination of whether or not carbonate minerals are at equilibrium is dependent upon the accuracy of the chemical analysis and pH and water temperature measurements (Sacks and Tihansky, 1996), so equilibrium is defined to occur within a range of SI values and not at a single specific value. For calcite, equilibrium is assumed for SI values between -0.15 and 0.15 and for dolomite the range is -0.30 to 0.30 (Sacks and Tihansky, 1996). For dolomite, the value is uncertain because the exact value of the equilibrium reaction constant is uncertain (Hsu, 1963); therefore, SI values are given (table 5) for both "crystalline" and "disordered" dolomite (Nordstrom and others, 1990). Comparing saturation indexes among various wells can show which geochemical reactions can or cannot occur as water moves along a flow path between a pair of wells, assuming the reactions are controlled by thermodynamic equilibrium. For example, if a possible model indicates that calcite is dissolving at a particular well, but the saturation index calculated for water from that well shows calcite supersaturation, then the model must be rejected.

All water samples from the FPZ were supersaturated with respect to calcite ( $\text{CaCO}_3$ ), and both crystalline and disordered dolomite ( $\text{CaMg}(\text{CO}_3)_2$ ) (table 5). This is consistent with long residence times in the aquifer. The samples were undersaturated with respect to gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) and celestite ( $\text{SrSO}_4$ ), although water from the FPZ was closer to saturation for those minerals than samples from other zones.

Mineral saturation data also may be useful for evaluating the integrity of well D-425, a multi-zone monitor well. The SI data for well D-425B are more similar to those from the other FPZ wells than to the UZLF wells. The water from well D-425B is supersaturated with respect to calcite and to both crystalline and disordered dolomite, as are the other samples from the FPZ. The only other sample that was supersaturated with respect to all three minerals was the sample from well D-665, which has a much higher chloride concentration. Further field investigation of well D-425 is needed to evaluate whether or not the sampling zones are adequately separated.

**Table 5.** Calculated partial pressure of carbon dioxide and saturation indexes of water with respect to selected minerals

[Aquifer: UFA, Upper Floridan aquifer; B, both Upper Floridan and upper zone of Lower Floridan aquifers; UZLF, upper zone/upper zone of Lower Floridan aquifer; FPZ, Fernandina permeable zone; CO<sub>2</sub>, carbon dioxide; atm, atmospheres; for calcite, equilibrium is assumed in the saturation index range between -0.15 and 0.15; for dolomite, equilibrium is assumed in the saturation index range between -0.30 and 0.30]

Site identification number	Local number	Aquifer	Log partial pressure of CO <sub>2</sub> (atm)	Calcite <sup>a</sup>	Crystalline dolomite <sup>a</sup>	Disordered dolomite <sup>a</sup>	Gypsum <sup>a</sup>	Celestite <sup>a</sup>
300019081363301	SJ-3	UFA	-2.35	0.09	0.13	-0.42	-0.69	-0.33
300347081363701	SJ-168	UFA	-2.37	.28	.49	-.05	-.72	-.34
301304081222701	SJ-103	UFA	-1.94	-.27	-.54	-1.08	-1.55	-1.26
301339081531201	D-326	UFA	-2.82	-.08	-.22	-.76	-2.59	-2.22
301547081271901	SE-1	UFA	-2.46	.03	.07	-.47	-1.42	-1.10
301714081233301	D-72	UFA	-2.11	-.24	-.44	-.98	-1.50	-1.28
301830081375501	D-1551	UFA	-2.33	-.00	-.11	-.65	-1.52	-1.15
302013081353801	D-673	UFA	-1.8	-.30	-.64	-1.18	-1.43	-1.24
302058081244101	D-1107	UFA	-2.38	.04	.06	-.48	-1.55	-1.31
302113081322301	D-655	UFA	-2.45	.11	.13	-.41	-1.62	-1.38
302140081235501	D-1121	UFA	-2.24	-.04	-.21	-.75	-1.54	-1.29
302239081434401	NK-1	UFA	-2.36	.06	.17	-.37	-1.55	-1.41
302557081253101	D-913	UFA	-1.97	-.08	-.09	-.63	-1.33	-1.40
302608081354903	D-264	UFA	-2.18	-.00	-.11	-.65	-1.85	-2.17
302609081260601	D-912	UFA	-2.29	-.02	-.06	-.61	-1.98	-2.20
300856081382401	D-3847	B	-2.35	-.23	-.40	-.94	-1.88	-1.21
301405081325601	D-3846	B	-2.16	.03	.11	-.43	-1.39	-.95
301508081364601	BW-3	B	-2.52	.22	.46	-.08	-1.43	-.93
301704081233401	D-484	B	-1.95	-.08	-.15	-.69	-1.46	-1.32
301725081305002	D-650	B	-1.87	-.28	-.61	-1.15	-1.49	-1.16
301740081361001	D-275	B	-1.79	-.29	-.61	-1.15	-1.44	-1.16
301743081303501	D-3825	B	-2.17	.08	.14	-.40	-1.40	-1.10
301743081362301	D-225 (high)	B	-2.09	.01	-.02	-.56	-1.42	-1.13
301743081362301	D-225 (low)	B	-2.33	.04	.06	-.48	-1.47	-1.07
301748081383401	D-334	B	-2.22	-.07	-.20	-.74	-1.40	-.94
301758081303901	D-665	B	-2.74	.71	1.43	.89	-1.15	-.88
301817081374901	D-425T	B	-1.94	-.02	-.13	-.67	-1.52	-1.12
301846081240201	D-246	B	-2.1	-.19	-.34	-.88	-1.55	-1.32
301934081292301	R-3	B	-2.59	.30	.50	-.04	-1.51	-1.19
301937081471401	D-2223	B	-2.25	-.06	-.19	-.73	-1.53	-1.10
301957081342301	D-313	B	-2.02	-.21	-.52	-1.06	-1.53	-1.36
302007081353201	D-479	B	-1.84	-.02	-.12	-.66	-1.54	-1.35
302008081242101	D-307	B	-2.18	-.03	-.02	-.56	-1.54	-1.38
302015081384501	D-335	B	-1.86	-.13	-.36	-.90	-1.63	-1.32
302045081323101	D-1323	B	-1.99	-.08	-.21	-.74	-1.40	-1.28
302342081320601	D-1902	B	-2.05	-.15	-.35	-.89	-1.73	-1.53
302503081332001	D-1149	B	-1.65	-.31	-.71	-1.25	-1.80	-1.89
302510081260201	D-3841	B	-2.41	.04	-.00	-.54	-1.72	-1.65
302538081392501	D-329	B	-2.04	-.16	-.37	-.91	-1.81	-2.12
303940081281801	N-22	B	-1.25	-.95	-1.86	-2.40	-1.52	-1.85
301335081355001	D-536-1	UZLF	-2.65	.56	1.07	.53	-1.01	-.54
301335081355001	D-536-2	UZLF	-2.45	.36	.66	.12	-1.02	-.55
301335081355001	D-536-3	UZLF	-2.35	.26	.42	-.12	-.98	-.55
301522081331301	D-291	UZLF	-2.79	.24	.41	-.13	-1.41	-1.05
301537081441901	D-75	UZLF	-2.8	.16	.26	-.28	-1.96	-1.34
301604081361501	D-450	UZLF	-2.6	.43	.79	.25	-1.37	-.99
301639081330802	D-1155	UZLF	-1.91	-.20	-.48	-1.02	-1.30	-.95
301936081292401	MW-2	UZLF	-2.33	.01	-.07	-.61	-1.44	-1.13
302022081393501	D-176	UZLF	-2.5	.24	.37	-.17	-1.44	-1.00
302227081435001	D-592	UZLF	-2.53	.23	.33	-.21	-1.42	-1.14
302608081354901	D-262	UZLF	-2.33	.22	.42	-.12	-1.67	-1.98
302608081354902	D-263	UZLF	-2.14	-.08	-.21	-.75	-1.83	-2.01
301132081225801	SJ-150	FPZ	-2.45	.34	1.20	.66	-.38	-.38
301405081325601	D-425B	FPZ	-2.59	.61	.88	.34	-.46	-.25
301725081305002	D-3060	FPZ	-2.38	.48	1.19	.65	-.42	-.25
301743081303501	D-2386	FPZ	-2.44	.47	1.20	.66	-.59	-.54

<sup>a</sup>Values in black are at equilibrium with respect to the mineral. Values in red are undersaturated and those in blue are supersaturated.

With respect to calcite, most water samples from the UZLF were supersaturated. The exceptions were water samples from wells D-1155, which was slightly undersaturated, and MW-2 and D-263, which were at equilibrium. Water from most of the wells tapping this zone was at equilibrium with respect to disordered dolomite, except for the first sample from D-536 (supersaturated) and samples from wells D-1155, MW-2, and D-263 (undersaturated). With respect to crystalline dolomite, the water was supersaturated except at wells D-1155 (undersaturated) and D-75, MW-2, and D-263 (equilibrium). All the samples from the UZLF were undersaturated with respect to gypsum and celestite. The three samples from D-536, along with the samples from the FPZ, were closer to celestite saturation than any other samples. Those three samples were from fracture flow zones and the chemical similarity between those samples and water from the FPZ tends to confirm the FPZ as the source of mineralized water in at least some of the UZLF wells.

Samples from wells tapping both the UZLF and the UFA had more diverse saturation indexes than wells tapping only the UZLF or only the FPZ. For calcite, the majority of the water samples were at equilibrium and nearly all of the rest were undersaturated; however, water from wells D-665, BW-3 and R-3 was supersaturated. The same distribution was calculated for crystalline dolomite, with D-665, BW-3 and R-3 again the exceptions (supersaturated). For disordered dolomite, all samples were undersaturated, except D-665 (supersaturated), and BW-3 and R-3 (equilibrium). All samples were undersaturated with respect to gypsum and celestite.

Nearly all of the water samples from wells tapping only the UFA were at equilibrium with respect to calcite, except SJ-168 (supersaturated); and SJ-103, D-72, and D-673 (undersaturated). All samples also were at equilibrium with respect to crystalline dolomite, with the same exceptions: SJ-168 (supersaturated); SJ-103, D-72, and D-673 (undersaturated). All the samples from the UFA also were undersaturated with respect to gypsum and celestite, although the samples from wells SJ-3 and SJ-168 were closest to saturation. These two wells, although yielding water with relatively low chloride concentrations, have high sulfate concentrations and are more similar with respect to celestite saturation to wells tapping the FPZ than to other UFA wells (fig. 13), possibly suggesting a different source of water to these wells. The water from these wells also had the highest temperature (29°C) (table 3)

of all the UFA wells, possibly indicating a deeper source of water. There is a strong relation between gypsum saturation index and sulfate concentration, implying that gypsum dissolution is the primary source of sulfate in most wells (fig. 13). The relation, however, is not as clear for the more highly mineralized FPZ samples (D-3060, D-2386, and SJ-150).

## Isotopic Analyses

Another technique to better understand the sources of mineralized water in northeastern Florida is the use of environmental isotopes in water. Stable isotopes of oxygen-18, deuterium, carbon-13, sulfur-34, and boron-11, as well as radiogenic isotopes carbon-14, chlorine-36, and the ratio of strontium-87 to strontium-86 were analyzed in most of the water samples from northeastern Florida (table 6). Isotopic similarities or differences among waters from the various aquifer zones can help differentiate the source or sources of mineralized waters.

### Oxygen and Deuterium

The oxygen and hydrogen that make up water molecules contain a mixture of isotopes of both elements, including the stable isotopes oxygen-18 and deuterium. These isotopes can be fractionated by hydrologic processes such as evaporation. The abundance of these isotopes can help researchers to understand the movement or evolution of ground water, including processes such as recharge and mixing. Deuterium and oxygen-18 do not evaporate as readily as their lighter isotopes, so they are concentrated in seawater relative to atmospheric water vapor. Conversely, when it rains, deuterium and oxygen-18 are more easily condensed, so precipitation becomes isotopically lighter and lighter as it continuously condenses from clouds (Coplen, 1993). Thus, rain that falls inland will be isotopically lighter than rain that falls along the coast. Both oxygen-18 and deuterium are reported in delta ( $\delta$ ) units of parts per thousand (per mil) relative to an arbitrary standard, VSMOW. The Global Meteoric Line (GML) (Craig, 1961) is an average of  $\delta D$  and  $\delta^{18}O$  values for precipitation and freshwater worldwide.

**Table 6.** Isotopic data for water samples

[ $\delta$  D, delta deuterium;  $\delta^{18}\text{O}$ , delta oxygen-18;  $\delta^{34}\text{S}$ , delta sulfur-34;  $\delta^{37}\text{Cl}$ , delta chlorine-37;  $^{36}\text{Cl}$ , chlorine-36;  $^{14}\text{C}$ , carbon-14;  $\delta^{13}\text{C}$ , delta carbon-13;  $^{87}\text{Sr}$ , strontium-87;  $^{86}\text{Sr}$ , strontium-86;  $\delta^{11}\text{B}$ , delta boron-11; na, not analyzed; --, no data. Aquifer: UFA, Upper Floridan aquifer; B, both Upper Floridan and upper zone of Lower Floridan aquifers; UZLF, upper zone of Lower Floridan aquifer; FPZ, Fernandina permeable zone]

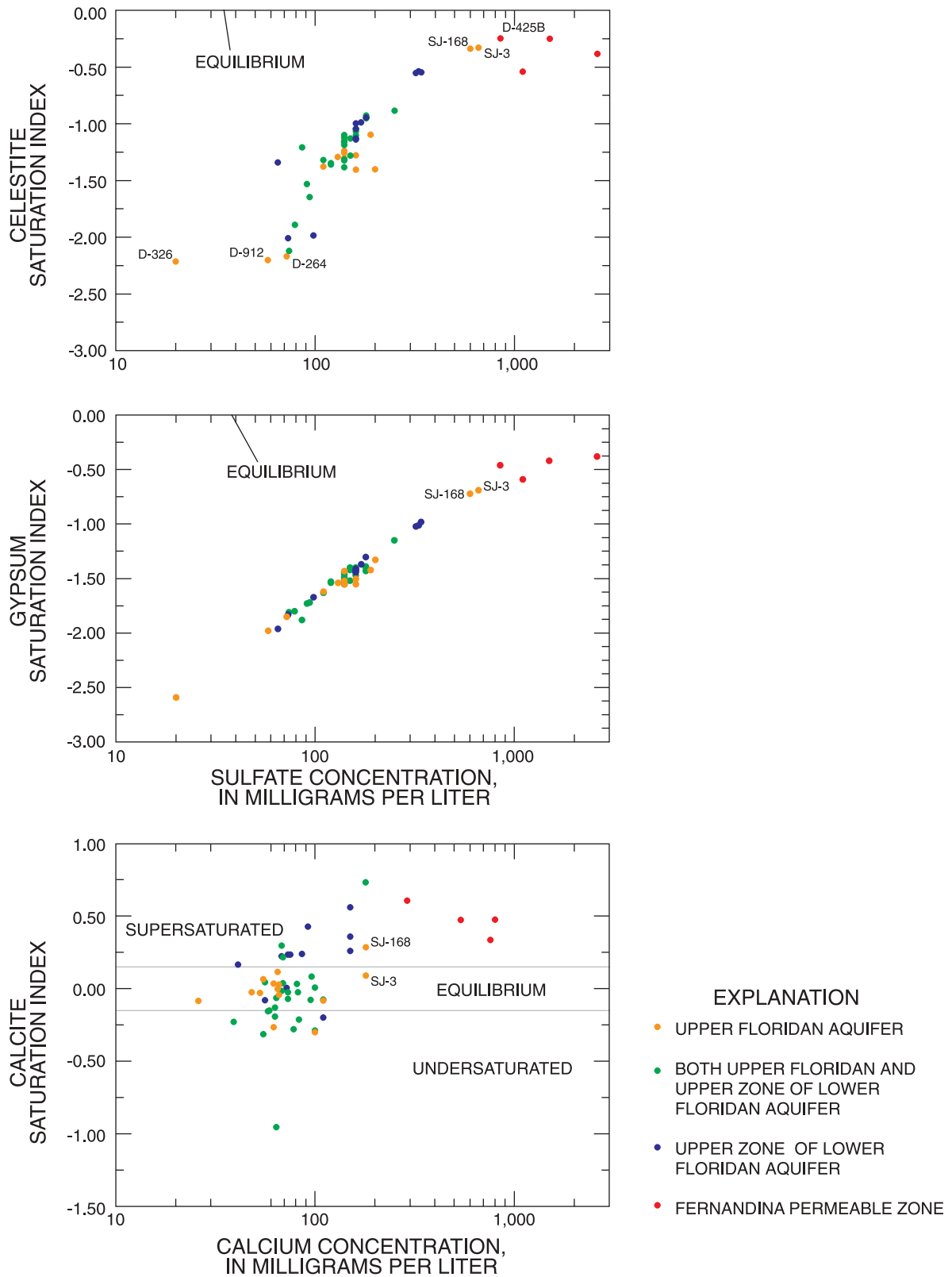
Site identification number	Local number	Aquifer	$\delta$ D (per mil)	$\delta^{18}\text{O}$ (per mil)	$\delta^{34}\text{S}$ of sulfate (per mil)	$\delta^{37}\text{Cl}$ (per mil)	$\delta^{37}\text{Cl}$ , repeat (per mil)	$^{36}\text{Cl}/\text{Cl}$ ratio ( $\times 10^{-15}$ )	Error, $\pm$ ( $\times 10^{-15}$ )	$^{14}\text{C}$ , percent modern	$^{14}\text{C}$ error (percent)	$\delta^{13}\text{C}$ (per mil)	$^{87}\text{Sr}/^{86}\text{Sr}$ ratio	$\delta^{11}\text{B}$ (per mil)
300019081363301	SJ-3	UFA	-8.9	-2.42	20.9	-0.52	-0.35	37.1	5.7	3.37	0.11	-3.48	0.70783	na
300347081363701	SJ-168	UFA	-10.9	-2.42	20.9	.24	.19	17.4	5.8	3.5	.12	-3.82	.70783	na
301304081222701	SJ-103	UFA	-9.9	-2.51	21.7	.23	--	48	7	0.56	.05	-6.98	.70789	17.2
301339081531201	D-326	UFA	-10	-2.35	27.6	-.14	-.17	38.1	5	2.9	.09	-9.22	.70788	19.7
301547081271901	SE-1	UFA	-8.8	-2.47	22.2	na	--	na	na	1.47	.06	-11.02	.70788	12.7
301714081233301	D-72	UFA	-9.5	-2.51	24.3	.15	--	23	13	2.12	.05	-7.26	.7079	17
301830081375501	D-1551	UFA	-8.3	-2.31	23.4	.29	.18	52.4	4.7	1.23	.05	-7.9	.70783	18.5
302013081353801	D-673	UFA	-10	-2.43	25.2	.08	--	8	8	1.3	.06	-9.4	.70788	22.5
302058081244101	D-1107	UFA	-9.9	-2.48	24.1	na	--	na	na	1.79	.07	-7.97	.70787	20.7
302113081322301	D-655	UFA	-8.8	-2.4	24.2	na	--	na	na	1.86	.07	-8.96	.70789	18.5
302140081235501	D-1121	UFA	-6.9	-2.25	23.5	.22	.15	94	9	1.48	.06	-9.24	.70788	13.7
302239081434401	NK-1	UFA	-7.7	-2.48	26	na	--	na	na	1.24	.05	-7.82	.70801	9
302557081253101	D-913	UFA	-11.9	-2.58	24.9	-.07	-.39	9.6	5.9	1.34	.08	-10.3	.70797	28.2
302608081354903	D-264	UFA	-10.2	-2.49	28.2	na	--	na	na	2.35	.08	-7.3	.70803	17
302609081260601	D-912	UFA	-8.5	-2.38	16.9	.06	--	50	6	2	.07	-10.66	.70803	12.2
300856081382401	D-3847	B	-9.4	-2.34	22.8	-.02	--	66.5	5.5	4.59	.10	-4.87	.70785	13.5
301405081325601	D-3846	B	-10.4	-2.37	22.2	.41	.13	10.2	4.8	.68	.05	-6.79	.70787	18.7
301508081364601	BW-3	B	-8.2	-2.4	22.5	na	--	na	na	1.56	.09	-6.04	.70783	14.2
301704081233401	D-484	B	-10.9	-2.5	25.3	.28	--	10.4	2.5	2.28	.09	-9.37	.7079	na
301725081305002	D-650	B	-9.1	-2.44	22.9	.09	--	16.9	2.8	.83	.06	-8.48	.70788	22.2
301740081361001	D-275	B	-9.5	-2.39	23.7	.61	--	7	2.1	1.95	.08	-9.09	.70783	na
301743081303501	D-3825	B	-8.2	-2.36	23.8	.35	--	5	4.7	2.46	.07	-8.37	.70788	27.7
301743081362301	D-225	B	-7.3	-2.4	23.5	-.07	-.31	9.9	2.3	2.19	.08	-9.29	.70784	na
301743081362301	D-225	B	-8.8	-2.4	23	.65	.33	30	11	1.81	.09	-8.22	.70786	na
301748081383401	D-334	B	-9.9	-2.27	21.6	.04	.08	59	4.6	.97	.06	-7.95	.70786	15.5
301758081303901	D-665	B	-10.4	-2.31	22.6	.34	--	3.6	2.1	3.64	.13	-9.01	.7079	na
301817081374901	D-425T	B	-10.3	-2.48	22.9	.07	--	55.8	4	.88	.06	-8.12	.70786	17.2
301846081240201	D-246	B	-9.8	-2.54	21.7	-.38	-.33	60	80	2.96	.08	-7.67	.70788	16.2
301934081292301	R-3	B	-9.5	-2.34	23	na	--	na	na	1.54	.06	-8.64	.70786	13.5
301937081471401	D-2223	B	-8.1	-2.36	23.4	na	--	na	na	1.41	.06	-8.62	.70786	18



**Table 6.** Isotopic data for water samples (Continued)

[ $\delta$  D, delta deuterium;  $\delta^{18}\text{O}$ , delta oxygen-18;  $\delta^{34}\text{S}$ , delta sulfur-34;  $\delta^{37}\text{Cl}$ , delta chlorine-37;  $^{36}\text{Cl}$ , chlorine-36;  $^{14}\text{C}$ , carbon-14;  $\delta^{13}\text{C}$ , delta carbon-13;  $^{87}\text{Sr}$ , strontium-87;  $^{86}\text{Sr}$ , strontium-86;  $\delta^{11}\text{B}$ , delta boron-11; na, not analyzed; --, no data. Aquifer: UFA, Upper Floridan aquifer; B, both Upper Floridan and upper zone of Lower Floridan aquifers; UZLF, upper zone of Lower Floridan aquifer; FPZ, Fernandina permeable zone]

Site identification number	Local number	Aquifer	$\delta$ D (per mil)	$\delta^{18}\text{O}$ (per mil)	$\delta^{34}\text{S}$ of sulfate (per mil)	$\delta^{37}\text{Cl}$ (per mil)	$\delta^{37}\text{Cl}$ , repeat (per mil)	$^{36}\text{Cl}/\text{Cl}$ ratio ( $\times 10^{-15}$ )	Error, $\pm$ ( $\times 10^{-15}$ )	$^{14}\text{C}$ , percent modern	$^{14}\text{C}$ error (percent)	$\delta^{13}\text{C}$ (per mil)	$^{87}\text{Sr}/^{86}\text{Sr}$ ratio	$\delta^{11}\text{B}$ (per mil)
301957081342301	D-313	B	-10.3	-2.49	25.9	-.06	--	7.5	4.8	1.99	.08	-10.12	.70789	21.5
302007081353201	D-479	B	-9.1	-2.35	25.3	.49	--	11.7	2.7	1.12	.08	-9.88	.70788	20.5
302008081242101	D-307	B	-9.3	-2.53	24.5	.14	--	3	12	1.33	.05	-9.02	.7079	23.7
302015081384501	D-335	B	-10.4	-2.38	23.1	-.21	--	56.6	4.1	.98	.06	-9.08	.70785	17
302045081323101	D-1323	B	-9.2	-2.47	23.8	.37	--	370	240	.91	.05	-10.11	.70789	22.7
302342081320601	D-1902	B	-10.5	-2.45	26.9	.66	--	47	9	2.02	.07	-9.56	.70787	19
302503081332001	D-1149	B	-9.6	-2.4	29.5	-.24	--	55.5	4.1	.62	.05	-11.22	.70794	17
302510081260201	D-3841	B	-10.1	-2.32	22.7	.05	--	75.3	4.2	.53	.05	-10.05	.70789	17.7
302538081392501	D-329	B	-9.1	-2.49	27.1	-.12	-.26	51.5	4.1	1.37	.07	-11.57	.70801	21.2
303940081281801	N-22	B	-12.6	-2.68	27.5	na	na	na	na	9.96	.19	-8.23	.70808	na
301335081355001	D-536-1	UZLF	-9.7	-2.34	21.7	.34	.45	2	13	2.2	.08	-5.98	.70785	na
301335081355001	D-536-2	UZLF	-8.9	-2.38	21.8	.11	-.12	7.5	1.9	2.32	.09	-6.38	.70785	na
301335081355001	D-536-3	UZLF	-9.4	-2.36	21.5	.3	.15	3.6	5.5	4.07	.11	-5.35	.70783	na
301522081331301	D-291	UZLF	-8.8	-2.27	21.9	.54	--	13.5	1.4	3.05	.10	-8.6	.70783	na
301537081441901	D-75	UZLF	-9	-2.35	23.4	.24	--	.5	3.3	3.09	.10	-8.53	.70789	na
301604081361501	D-450	UZLF	-8.1	-2.4	23.2	.29	--	10	12	1.54	.07	-7.99	.70787	na
301639081330802	D-1155	UZLF	-7.2	-2.35	22.6	.73	--	14.6	2.9	1.95	.08	-8.11	.70786	na
301936081292401	MW-2	UZLF	-8.8	-2.44	23	.33	.33	76.2	4.3	.96	.05	-8.28	.70787	16.5
302022081393501	D-176	UZLF	-9.5	-2.39	22.7	.02	--	57.1	2.9	3.07	.10	-7.79	.70785	na
302227081435001	D-592	UZLF	-9.4	-2.3	22.4	.16	--	51.2	2.5	2.47	.09	-8.99	.70789	na
302608081354901	D-262	UZLF	-8.6	-2.57	27.2	-.03	--	29.3	3.3	2.48	.09	-11.96	.70801	na
302608081354902	D-263	UZLF	-10.8	-2.49	25.8	.02	--	67	33	.88	.06	-11.22	.70798	23
301132081225801	SJ-150	FPZ	2.6	.12	20.9	-.03	--	.8	2.3	1.31	.07	-6.3	.7083	na
301405081325601	D-425B	FPZ	-10.6	-2.38	21.5	-.44	-.42	20.7	2.4	1.27	.07	-7.19	.70787	na
301725081305002	D-3060	FPZ	-4	-1.18	21	.25	--	4	2.4	1.63	.07	-9.28	.70798	na
301743081303501	D-2386	FPZ	-4.7	-1.66	21.3	.07	--	11.5	1.7	1.68	.08	-9.83	.70802	na
302737080571801	Seawater		6.2	.66	20.6	.52	.52	1.1	3.7	109.96	.55	-1.75	.70916	na

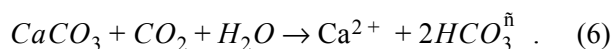


**Figure 13.** Relations between celestite and gypsum saturation indexes and sulfate concentration, and between calcite saturation index and calcium concentration.

Most of the water samples from the study area plot near the GML (fig. 14). Except for the high chloride samples from the FPZ, no trend by aquifer zone is apparent. This indicates that climatic conditions probably did not vary substantially during the time period that the water was recharged to the aquifer. The regression line for the water samples (fig. 14) is similar to that for water from the UFA in west-central Florida (Swancar and Hutchinson, 1992). The samples that depart from the GML (that is, are enriched in oxygen-18) have higher chloride concentrations and are indicative of freshwater-salt water mixing. The deuterium and oxygen-18 values for the water from well SJ-150 are similar to those of seawater. These data, however, cannot indicate whether the seawater is ancient or modern.

### Carbon

Two isotopes of carbon in dissolved inorganic carbon were analyzed in the samples from the Duval County area: the stable isotope carbon-13 ( $^{13}\text{C}$ ) and the radiogenic isotope carbon-14 ( $^{14}\text{C}$ ). Values of delta carbon-13 ( $\delta^{13}\text{C}$ ) for dissolved inorganic carbon also are needed to correct the calculations of water age using carbon-14. Processes affecting the stable carbon isotope composition ( $\delta^{13}\text{C}$ ) of inorganic carbon in ground water include carbonate mineral dissolution and precipitation, microbially mediated processes that oxidize organic carbon and generate carbon dioxide ( $\text{CO}_2$ ), and mixing of waters (Sacks and Tihansky, 1996). A general equation for carbonate dissolution driven by  $\text{CO}_2$  is:



Values of  $\delta^{13}\text{C}$  depend on the source of the carbon. For example, most vegetation and atmospheric  $\text{CO}_2$  have  $\delta^{13}\text{C}$  values averaging about -25 per mil (Deines and others, 1974), so organically derived carbon tends to add lighter  $^{13}\text{C}$  to the system. On the other hand, dissolution of calcium carbonate adds heavier  $^{13}\text{C}$ . According to equation 6, calcite having a  $\delta^{13}\text{C}$  value of 1 per mil (table 2) reacting with  $\text{CO}_2$  having a  $\delta^{13}\text{C}$  value -22 per mil (table 2) would produce dissolved inorganic carbon with a  $\delta^{13}\text{C}$  value of -11.5 per mil.  $\delta^{13}\text{C}$  values ranged from -3.48 to -11.96 per mil in the study area (table 6). The generally heavier  $\delta^{13}\text{C}$  values measured in the study area indicate that a larger proportion of the dissolved inorganic carbon in those samples was derived from carbonate minerals.

Delta  $^{13}\text{C}$  values do not seem to be related to aquifer zones (figs. 15 and 16). In the UFA,  $\delta^{13}\text{C}$  was heaviest (-3.48 and -3.82) in the high-sulfate waters from wells SJ-3 and SJ-168, respectively. The lightest value was at well SE-1 (-11.02). In wells tapping both the UFA and the UZLF, the heaviest value (-4.87) was at well D-3847 in southern Duval County (a low chloride water). The lightest values were north of the St. Johns River at wells D-329 (-11.57) and D-1149 (-11.22). In samples from the UZLF, the heaviest values (-5.35 to -6.38) were from well D-536 in southern Duval County and the lightest from D-262 (-11.96). The samples from the FPZ ranged from -6.3 at well SJ-150 to -9.83 at well D-2386. These data show that the water from well SJ-150, although chemically almost identical to modern seawater, is isotopically different with respect to  $\delta^{13}\text{C}$  (fig. 15, table 6), as are the other high chloride water samples from the FPZ. The  $\delta^{13}\text{C}$  for the dolomite sample from a depth of 1,893 ft in well D-349 was similar to that for modern seawater, whereas the other samples of aquifer material had heavier values.

In general, in all aquifer zones, water with the heaviest  $\delta^{13}\text{C}$  values was found in the southern part of the study area and water with the lightest values was in the northern part (fig. 16). This is somewhat inconsistent with the fact that all of northeastern Florida is a discharge area and the principal recharge area for the study area is to the southwest. Data from west-central Florida showed that  $\delta^{13}\text{C}$  in the UFA was lightest in the recharge area (less than -8 per mil) and heaviest in the discharge areas (greater than -5 per mil) and generally increased with depth in the UFA (Sacks and Tihansky, 1996). In the Keystone Heights recharge area, Plummer (1997) reported a value of -12 per mil. In northeastern Florida, however, each aquifer zone except the FPZ had at least one well with a  $\delta^{13}\text{C}$  value of -11 per mil or lighter. Light values could be related to the presence of buried organic materials associated with paleokarst features.

The mean value of  $\delta^{13}\text{C}$  for all wells sampled ranged from -8.09 per mil for wells tapping only the UFA to -8.79 for wells tapping both the UFA and the UZLF. This is heavier than the average value (-13 per mil) reported by Deines and others (1974) for a closed ground-water system in contact with carbonates in Pennsylvania. The heavier values could result from dissolution of isotopically heavier marine carbonates in northeastern Florida (Long and others, 1988). Sacks and Tihansky (1996) reported an average  $\delta^{13}\text{C}$  value for marine dolomites in southwestern Florida of 1.7 per mil. In northeastern Florida, the values ranged from -1.66 to 2.4 per mil (table 2).

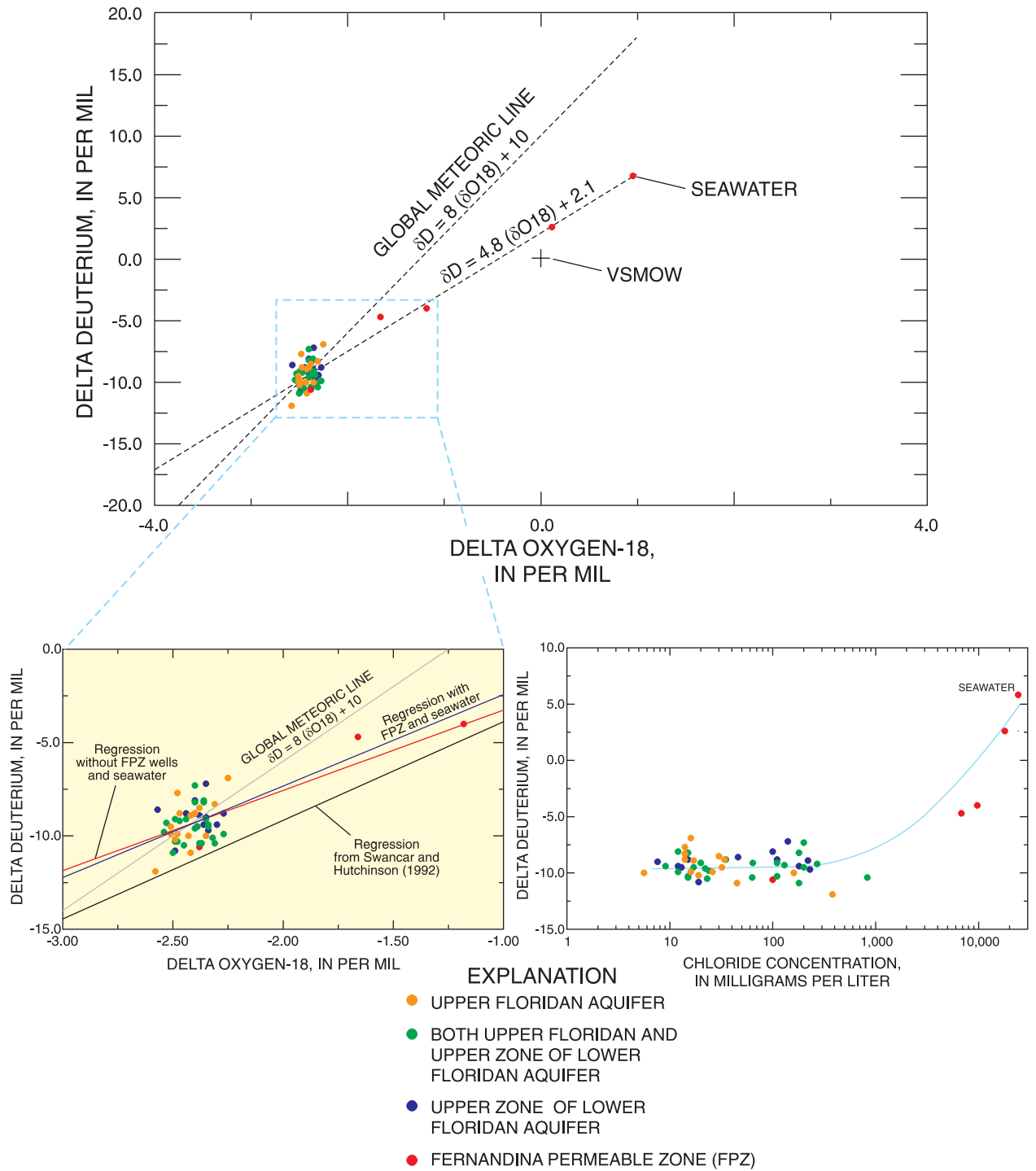


Figure 14. Relations between delta deuterium and delta oxygen-18 and between delta deuterium and chloride concentration.

Heavier  $\delta^{13}\text{C}$  values also could result from recrystallization of unstable carbonate phases such as aragonite or high-magnesium calcite, which also would enrich the dissolved inorganic carbon in  $^{13}\text{C}$  without increasing the dissolved inorganic carbon concentration.

In contrast, the light values of  $\delta^{13}\text{C}$  can result from sulfate reduction, which produces isotopically light  $\text{CO}_2$  (Long and others, 1988) from the oxidation of organic carbon, such as the peat found in the aquifer (table 2). If values of  $\delta^{13}\text{C}$  were strongly related to sulfate reduction, then  $\delta^{13}\text{C}$  values should be lighter in waters with lower sulfate concentrations. There is a general trend for lighter  $\delta^{13}\text{C}$  values where sulfate concentrations are lower (fig. 17), although the data show considerable scatter. Water samples from the FPZ do not show such a trend. Also, the delta sulfur-34 ( $\delta^{34}\text{S}$ ) values of dissolved sulfide become more positive as sulfide reduction progresses. Therefore,  $\delta^{13}\text{C}$  values should become more negative as  $\delta^{34}\text{S}$  values become more positive, if sulfate reduction is occurring. That trend in carbon and sulfur isotopes was observed in the aquifer system (fig. 17). The trend of increased sulfate enrichment and heavier  $\delta^{13}\text{C}$  values (fig. 17) is indicative of the occurrence of dedolomitization reactions

(gypsum and dolomite dissolution and calcite precipitation). Apparently, in northeastern Florida the competing processes of sulfate reduction and dissolution of isotopically heavier marine carbonates both influence the  $^{13}\text{C}$  isotopic content of the ground water, as does the areal distribution of gypsum in the aquifer.

The percent modern carbon ( $^{14}\text{C}$ ) for dissolved inorganic carbon also was determined for the samples. Percent modern carbon values ranged from 0.53 in well D-3841 to 9.96 in well N-22 (table 6). Radiogenic  $^{14}\text{C}$  can be used to age-date waters, although in a carbonate aquifer dissolution of carbon from the aquifer matrix (which contains zero percent modern carbon) can complicate the calculations (Wigley, 1975), as can dissolved inorganic carbon derived from the oxidation of buried peat. Another difficulty in calculating radiocarbon ages is defining the initial carbon activity of the sample. A geochemical modeling program, NETPATH (Plummer and others, 1994), was used to correct the measured  $^{14}\text{C}$  activity values for water samples from the study area. A complete discussion of this process is given in a later section of this report.

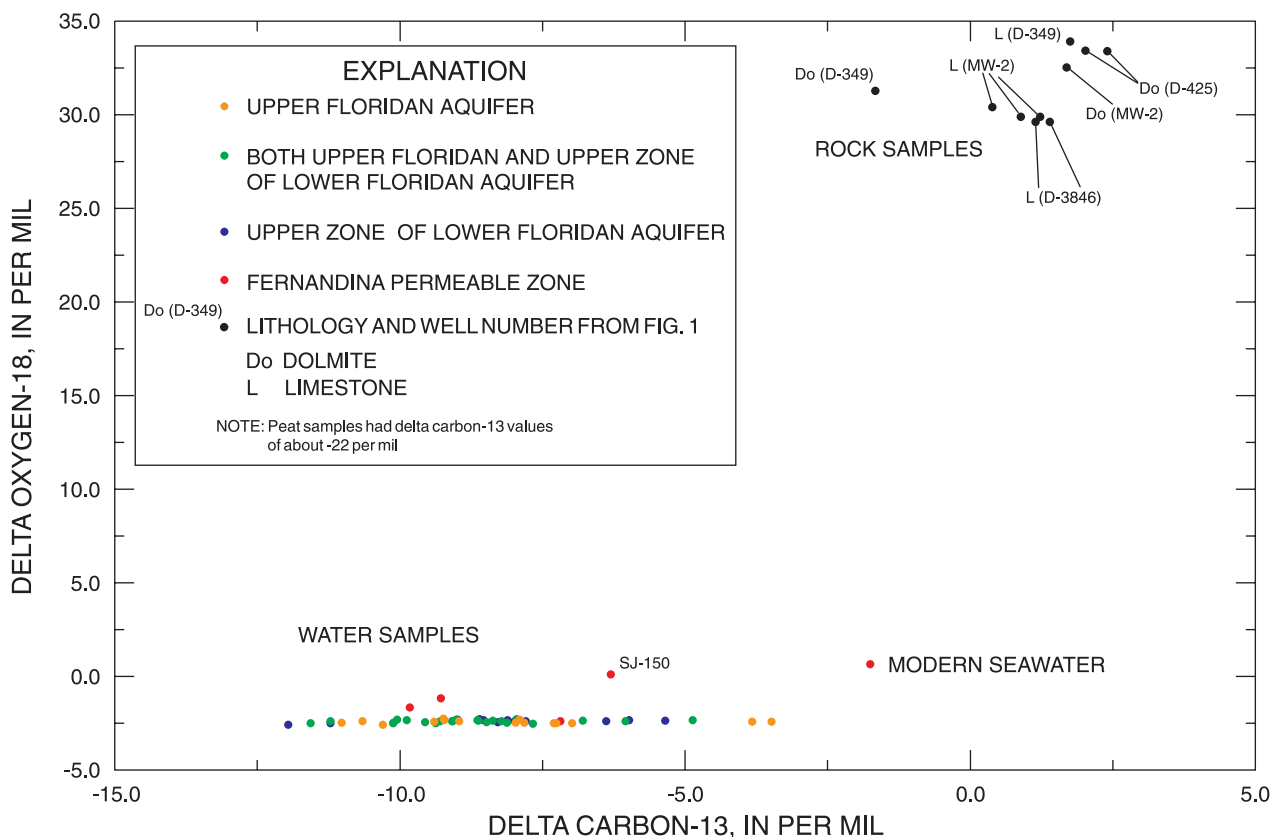


Figure 15. Relation between delta oxygen-18 and delta carbon-13 for rock and water samples.

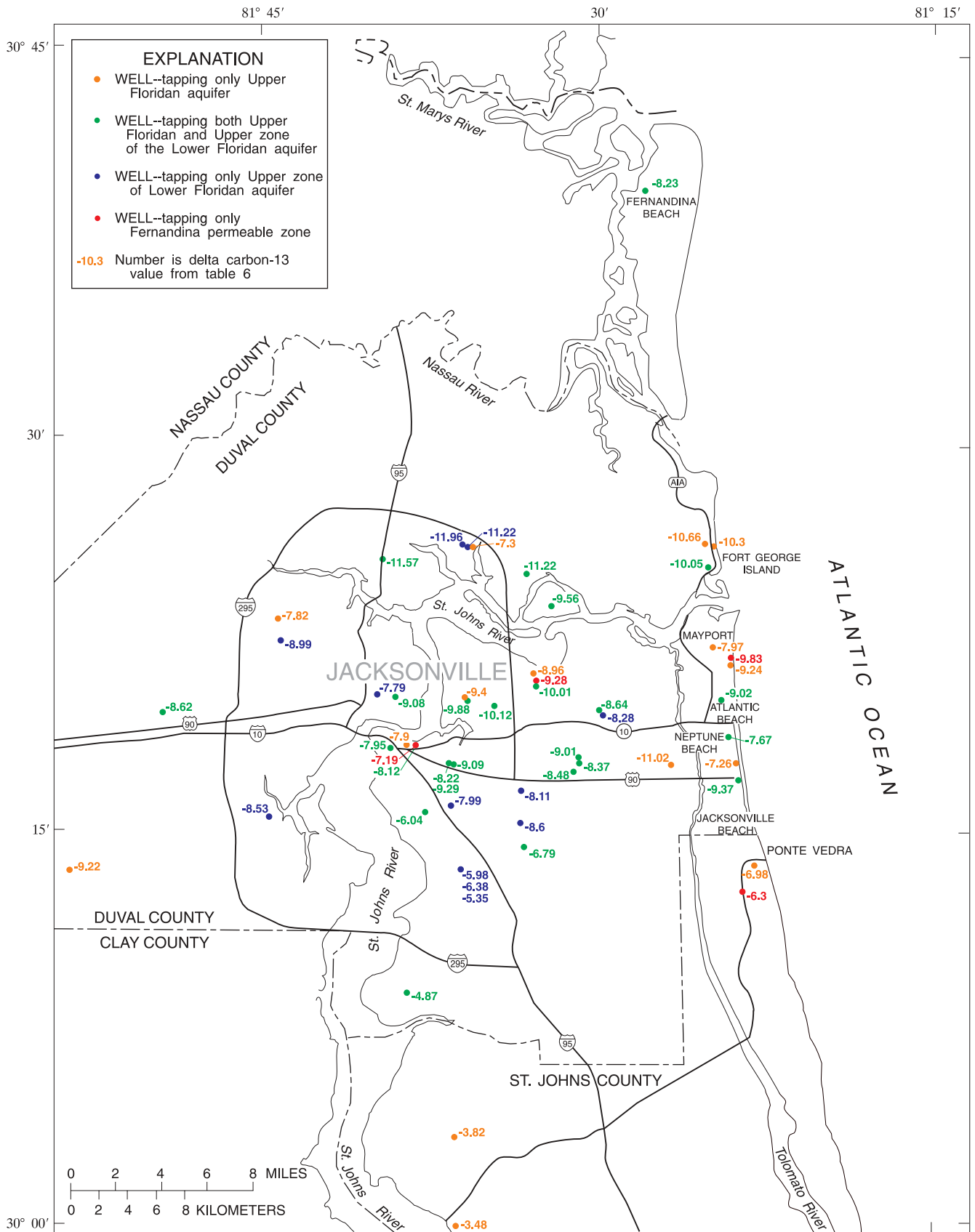
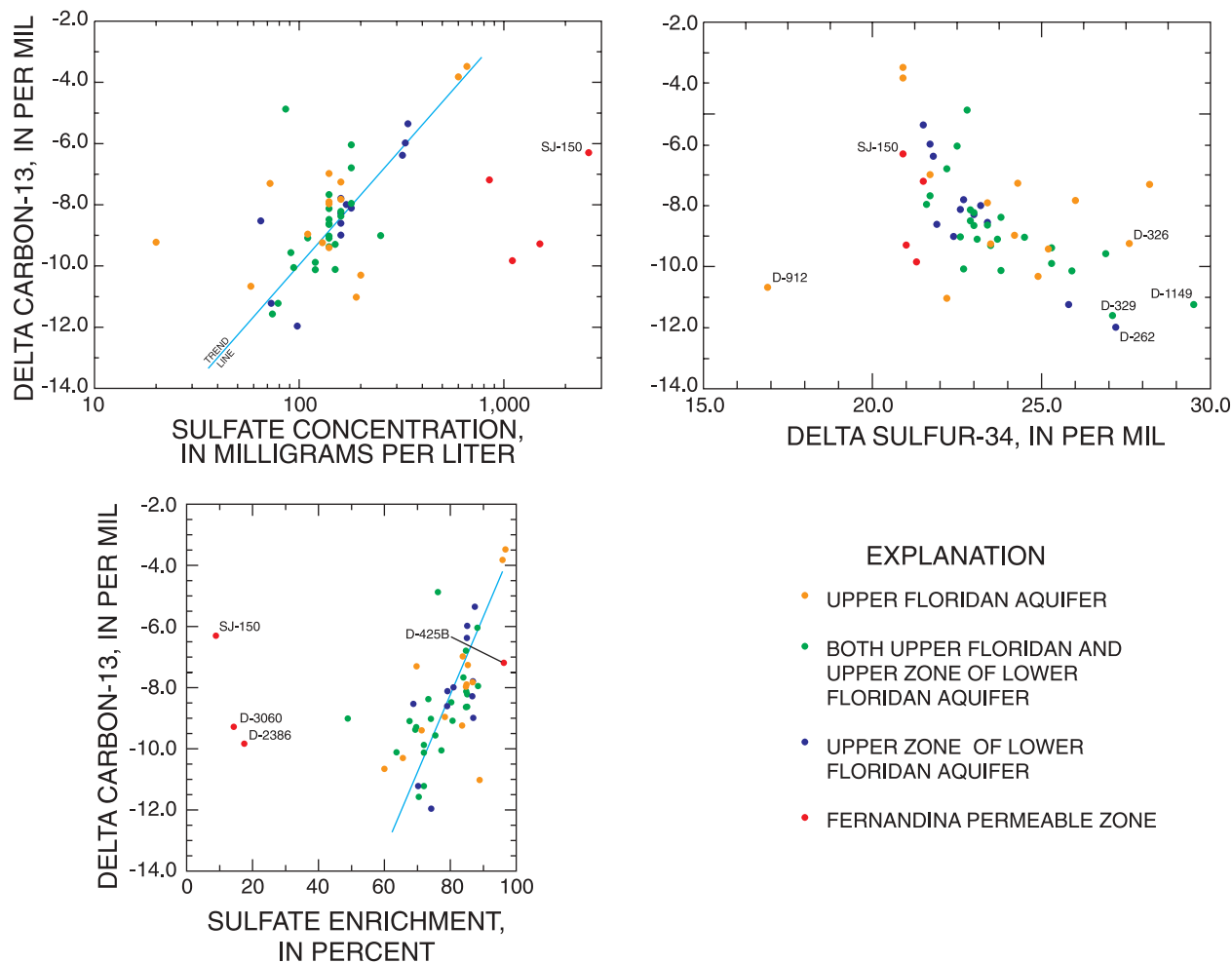


Figure 16. Distribution of delta carbon-13 in ground water.



**Figure 17.** Relations between delta carbon-13 and (a) sulfate concentration, (b) delta sulfur-34, and (c) sulfate enrichment.

## Sulfur

The stable isotope of sulfur,  $^{34}\text{S}$ , can be used to evaluate the sources of sulfur in ground water and to test geochemical models by calculating the  $\delta^{34}\text{S}$  balance of chemical reactions along flow paths (Coplen, 1993). Sulfur sources such as atmospheric precipitation, gypsum, and seawater all can have different sulfur isotope signatures. Atmospheric sulfur and most fresh waters have sulfur isotopic compositions ranging from 0 to about +15 per mil (Long and others, 1988). This agrees with data from rain water in north-central Florida that ranged from 3.4 to 5.9 per mil (Katz and others, 1995). A water sample from the surficial aquifer system in central Florida had a sulfur isotopic composition of 8.3 per mil (Sacks and Tihansky, 1996).

If the source of sulfur in ground water is from dissolution of sulfate minerals in the aquifer, the isoto-

pic composition would reflect the composition of the various minerals. In southwestern Florida, evaporites from the Avon Park Formation (the middle semi-confining unit of the Floridan aquifer system) had an average  $\delta^{34}\text{S}$  value of 23.4 per mil. In the same area, gypsum from the Lower Floridan aquifer and the lower confining unit (Oldsmar and Cedar Keys Formations) had lighter values, averaging 20.1 per mil (Sacks and Tihansky, 1996).

The modern seawater sample collected during this study had a  $\delta^{34}\text{S}$  value of 20.6 per mil (table 6), almost identical to that of the sample from well SJ-150 (20.9 per mil). The sulfur isotopic composition cannot be used to differentiate ancient from modern seawater. In fact, the  $\delta^{34}\text{S}$  of seawater probably has not changed substantially since the middle Miocene, about 15 million years ago (Claypool and others, 1980).

The sulfur isotopic composition of ground water can be altered by biological processes. Bacterial reduction of sulfate to sulfide fractionates sulfur by preferentially using isotopically lighter sulfur-32, causing the remaining sulfate to be isotopically enriched in sulfur-34. As mentioned previously, the sulfate reduction process also results in ground water with a lighter  $\delta^{13}\text{C}$  composition and a lower sulfate concentration. Some water samples from the study area show a sulfate reduction trend (figs. 17 and 18).

The  $\delta^{34}\text{S}$  values for the samples collected varied somewhat from one aquifer zone to another. For wells tapping the FPZ,  $\delta^{34}\text{S}$  values ranged from 20.9 to 21.5 per mil. This corresponds to the values from Sacks and Tihansky (1996) for evaporites from the Oldsmar and Cedar Keys Formations and to post-mid-Miocene seawater. Samples from the UZLF had values ranging from 21.5 per mil to 27.2 per mil, with a median of about 22.5. Wells tapping both the UZLF and the UFA had  $\delta^{34}\text{S}$  values ranging from 21.6 per mil to 29.5 per mil, with a median value of about 23.2 per mil. The median for samples from the UFA was 23.5 per mil, with values ranging from 16.9 to 28.2 per mil.

If the concentration of sulfate in ground water were altered by bacterial reduction of sulfate to sulfide, then samples with lower sulfate concentrations should have heavier values of  $\delta^{34}\text{S}$ . For some wells, this trend was observed (fig. 18). For example, water from well D-1149 had the heaviest  $\delta^{34}\text{S}$  value, a light  $\delta^{13}\text{C}$  value, and a relatively low sulfate concentration (79 mg/L). The sulfide concentration from that sample (1.9 mg/L), as measured in the field, was not among the highest values, which could have been because sulfide was released during the field analysis or because sulfide precipitation is occurring in the aquifer. Other samples that fit this general trend are those from wells D-329 and D-262. The low sulfate concentration in water from well D-912, accompanied by the lightest  $\delta^{34}\text{S}$  value and a relatively light  $\delta^{13}\text{C}$  value, is more difficult to explain. That sample may show the effects of more recent recharge water. The UFA wells with the highest sulfate concentrations (SJ-3 and SJ-168) have light  $\delta^{34}\text{S}$  values, similar to Oldsmar and Cedar Keys evaporites, and heavy  $\delta^{13}\text{C}$  values, possibly indicating the influence of water from another source, or the effects of more extensive dedolomitization reactions.

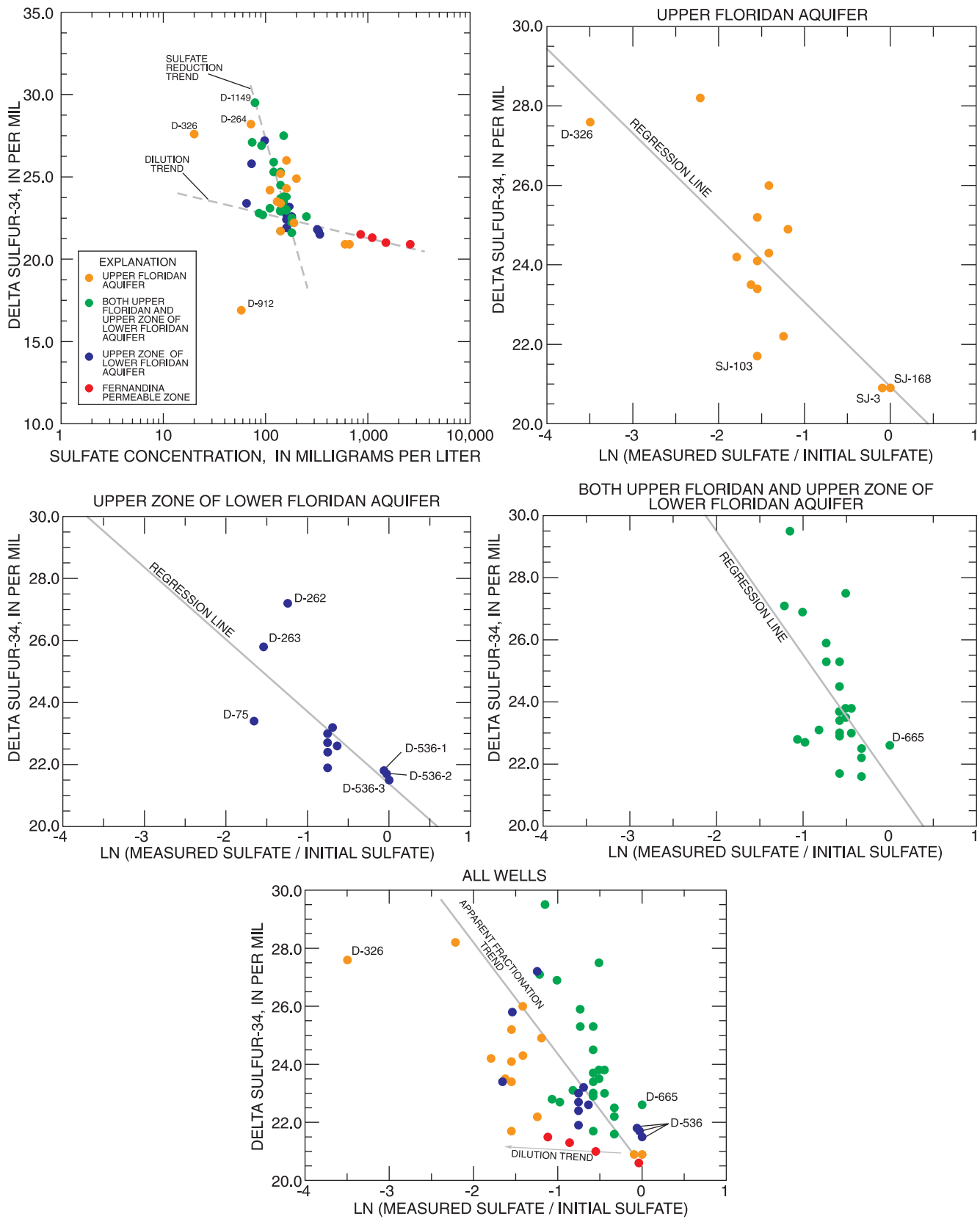
The extent to which sulfate reduction increases the abundance of  $^{34}\text{S}$  in a ground-water system can be quantified, assuming that no other processes such as gypsum dissolution or pyrite oxidation are occurring,

by calculating the enrichment factor. This can be done by plotting the relation between  $\delta^{34}\text{S}$  of sulfate and the natural logarithm of the ratio of measured sulfate concentration to an assumed initial (unreacted) sulfate concentration (fig. 18). The slope of the best-fit (regression) line is the enrichment factor. For each group of wells, the highest measured sulfate value was used as the initial value; for UFA wells this was the sulfate concentration from well SJ-3 (660 mg/L), for UZLF wells the value from D-536-3 (340 mg/L) was used, and for wells tapping the UFA and the UZLF, the value from D-665 (250 mg/L) was used. The enrichment factors were -2.1 per mil for UFA wells, -2.3 per mil for UZLF wells, and -4.0 per mil for wells tapping both the UFA and the UZLF. For all three groups plotted together (excluding FPZ wells and seawater) the factor is -3.1 per mil. The plot of all wells, adding FPZ wells and seawater (fig. 18) shows two trends: a trend for possible dilution of seawater that includes the FPZ wells and UFA wells SJ-3 and SJ-168; and an apparent fractionation trend for most of the other wells, along which  $\delta^{34}\text{S}$  increases as sulfate decreases. The trend for decreasing sulfate concentration and increasing  $\delta^{34}\text{S}$  content could represent changes down a flow path. Long and others (1988) reached a different conclusion, however, for aquifers they studied in Michigan. Long and others (1988) concluded that sulfate reduction had been occurring for different lengths of time in different parts of the aquifers. This also could be the case in northeastern Florida. Other processes such as gypsum dissolution or pyrite oxidation also are likely occurring. Thus, the isotopic content of water samples from northeastern Florida indicate that two chemical processes probably are occurring, but the sulfur isotope data cannot be used to help determine the origin of mineralized water affecting wells such as D-665.

## Strontium

The aqueous chemistry of strontium is similar to that of calcium because of a similar ionic size and valence. The minerals strontium carbonate (strontianite) and strontium sulfate (celestite) are common in sediments (Hem, 1985). Fossils in limestone tend to be enriched in strontium, relative to an overall ratio of strontium-to-calcium in massive limestone (Kulp and others, 1952). The ratio of radiogenic strontium-87 ( $^{87}\text{Sr}$ ) to stable strontium-86 ( $^{86}\text{Sr}$ ) in marine carbonates is presumed to have been the same as that in the oceans at the time of deposition.





**Figure 18.** Relation between delta sulfur-34 and sulfate concentration, and calculation of enrichment factors for delta sulfur-34 of sulfate.

That ratio persists in calcite and gypsum, but in dolomite may be changed by diagenetic processes during dolomitization (Sacks and Tihansky, 1996). The variations in the ratio of  $^{87}\text{Sr}$  to  $^{86}\text{Sr}$  in seawater over geologic time have been well-documented (DePaolo and Ingram, 1985; Elderfield, 1986; Hess and others, 1986), so the ratio measured in rock or water samples may help in interpretation of the relative ages of various samples.

Strontium concentrations in ground-water samples ranged from 500  $\mu\text{g/L}$  at well D-264 (UFA) to 21,800  $\mu\text{g/L}$  in well D-3060 (FPZ) (table 3). The modern seawater sample had a strontium concentration of 650  $\mu\text{g/L}$ , much lower than the high chloride samples from the FPZ (range 11,400 to 21,800  $\mu\text{g/L}$ ) and lower than the 8 mg/L (8,000  $\mu\text{g/L}$ ) reported by Hem (1985). If mixing between seawater (using the strontium concentration from Hem) and water from well D-326 is assumed, most of the samples are enriched in strontium, compared to the mixing trend (fig. 19). This probably is the result of dissolution of strontium from the aquifer matrix. Areal variations in strontium

enrichment may be related to the distribution of strontium-rich minerals in the aquifer. Another possibility is that strontium concentrations are related to aquifer residence time (and, thus, ground-water age); this is discussed in a later section of this report. Another trend, with water from well SJ-150 as the mineralized end member, includes wells D-665, D-536, SJ-168, and SJ-3. A third group of samples (wells north of the St. Johns River) have low strontium and chloride concentrations, and plot in a group below the trend line. The strontium data, therefore, seem to indicate that dilution of at least two different mineralized end members probably is occurring.

Ratios of  $^{87}\text{Sr}$  to  $^{86}\text{Sr}$  for most of the samples are in the range of Eocene-age (approximately 37-58 million years before present) seawater, as a result of dissolution of the Eocene-age rocks of the aquifer matrix (fig. 20). The exceptions include the samples from the FPZ with high strontium concentrations and high chloride concentrations (SJ-150, D-2386, and D-3060) and samples from several wells north of the St. Johns River with relatively low strontium concentrations. The

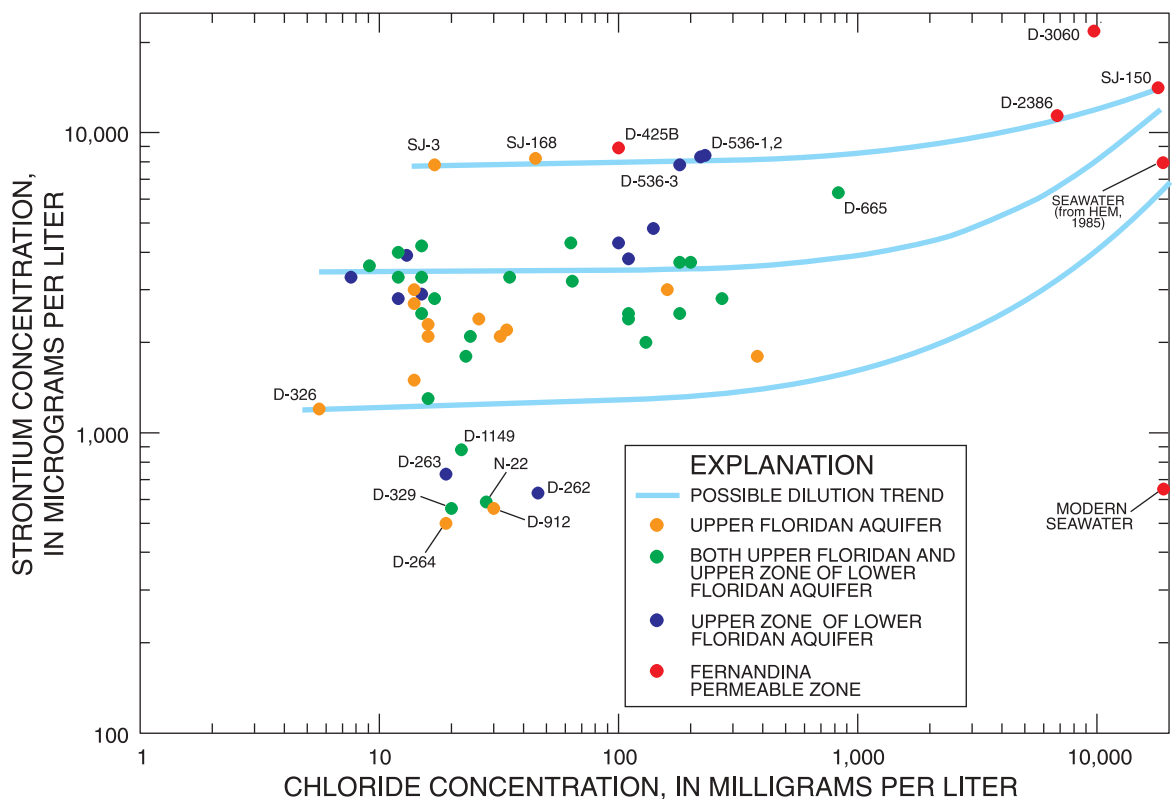
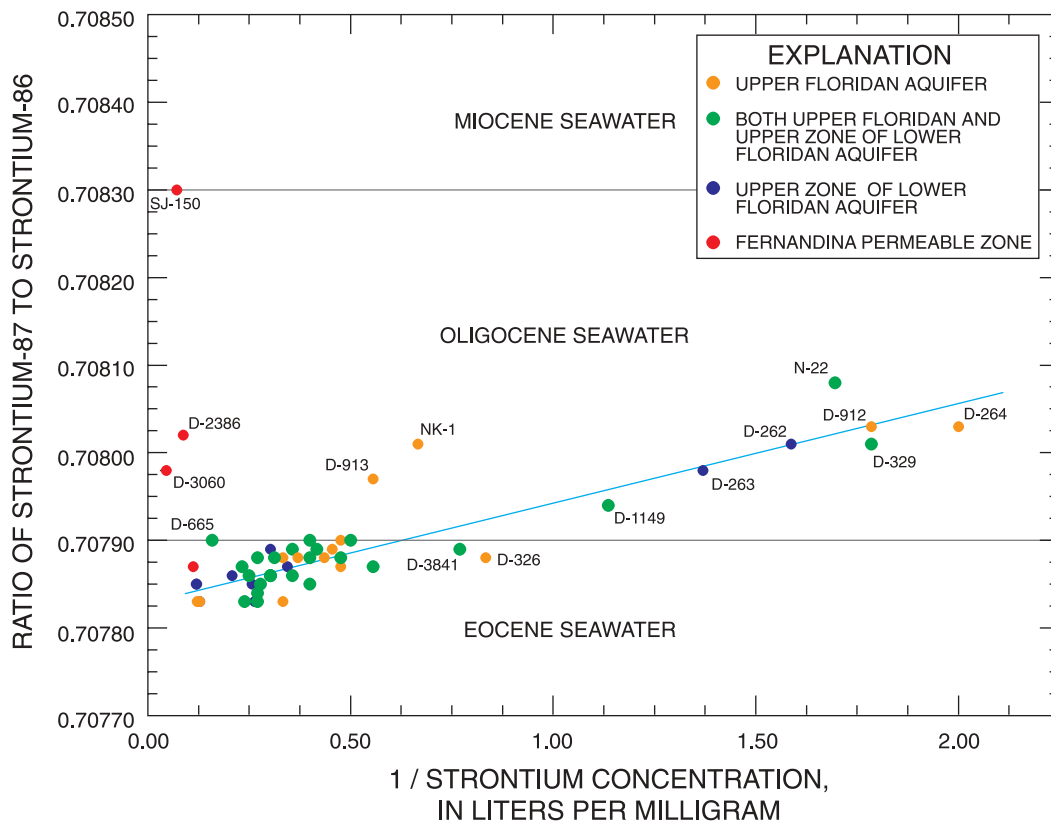


Figure 19. Relation between strontium concentration and chloride concentration.

strontium-depleted samples have the strontium isotope ratio of Oligocene-age (approximately 24-37 million years before present) seawater. There are no Oligocene-age rocks present in northeastern Florida, so non-Eocene strontium isotope ratios must be the result either of diagenetic changes during dolomitization or waters of different ages mixing, or both. Possibly, contact with dolomites could explain the Oligocene ages for water samples from the UZLF, but is unlikely for wells tapping the UFA because of the absence of dolomite. If chemical changes during dolomitization were the cause of non-Eocene ratios, then considerable scatter might be expected in the plot of strontium isotope ratios as a function of inverse strontium concentration (fig. 20). Instead, the plot in figure 20 clearly shows a mixing trend. For the wells north of the St. Johns River that have low strontium concentrations and strontium isotope ratios of Oligocene age, it is possible that water from this group of wells was recharged from a different, closer recharge area than that for the wells south of the St. Johns River. The source of increasing chloride

concentrations in some of these wells (for example, D-262; fig. 2) could be seawater of an age different from the water from well SJ-150.

Water from well SJ-150 has a strontium isotope ratio between that of Oligocene and Miocene age (approximately 5-24 million years before present); water from wells D-3060 and D-2386 (the other high chloride waters from the FPZ) have ratios consistent with Oligocene-age waters. The dolomite samples analyzed in this study had strontium isotope ratios ranging from Eocene-to-Oligocene-age (fig. 6), so it is unlikely that dissolution of dolomite from the aquifer matrix is the major factor controlling the strontium isotope ratio in the sample from well SJ-150. Instead, the water from well SJ-150 could contain a mixture of strontium from younger seawater (with a higher strontium isotope ratio) and strontium dissolved from Eocene-age rocks. Strontium isotope data point to mixing of waters of different ages, but do not conclusively indicate the age of mineralized waters involved in the mixing process.



**Figure 20.** Relation between inverse of strontium concentration and ratio of strontium-87 to strontium-86.

## Boron

Boron is chemically and physically similar to silicon, although it is less abundant. Boron is not found free in nature, occurring only in oxy-compounds. The most common forms are boric acid ( $\text{H}_3\text{BO}_3$ ) and borax (hydrated sodium borate,  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ ), an evaporite deposit. Boric acid in seawater is ingested by foraminifera and incorporated into their tests. Comparing the delta boron-11 ( $\delta^{11}\text{B}$ ) content of foraminifera from different formations has been used to assess the pH of the ocean, and thus the atmospheric carbon dioxide concentration through geologic time (Ramesh and Krishnamurthy, 1998; Pearson and Palmer, 1999). Also, the  $\delta^{11}\text{B}$  content of fertilizers and detergents, the source of which is evaporite deposits, generally has a different boron-11 ( $^{11}\text{B}$ ) content from that metabolized by marine foraminifera. Thus, the influence of relatively recent recharge water affected by anthropogenic activities can be observed. The worldwide  $\delta^{11}\text{B}$  content for modern seawater is about 40 per mil (Barth, 1998).

Values of  $\delta^{11}\text{B}$  were measured for 34 of the samples collected during this study; however, samples collected during the first round of data collection, including those from the FPZ and the UZLF, were not analyzed for  $\delta^{11}\text{B}$ . Water samples with higher chloride concentrations tend to have heavier values of  $\delta^{11}\text{B}$ , whereas samples with lower chloride concentrations show more scatter in the boron-chloride relation (fig. 21). The relation between  $\delta^{11}\text{B}$  and chloride concentration does not help to clarify the source of the high chloride water. The lack of a relation between  $\delta^{11}\text{B}$  and boron concentration, however, indicates that dilution of modern seawater is not the source of boron in most of the samples. Additional sampling of wells from the Lower Floridan aquifer and from the FPZ could confirm this conclusion. The low  $\delta^{11}\text{B}$  content of water from some UFA wells (NK-1 and D-912) could be the result of anthropogenic influences.

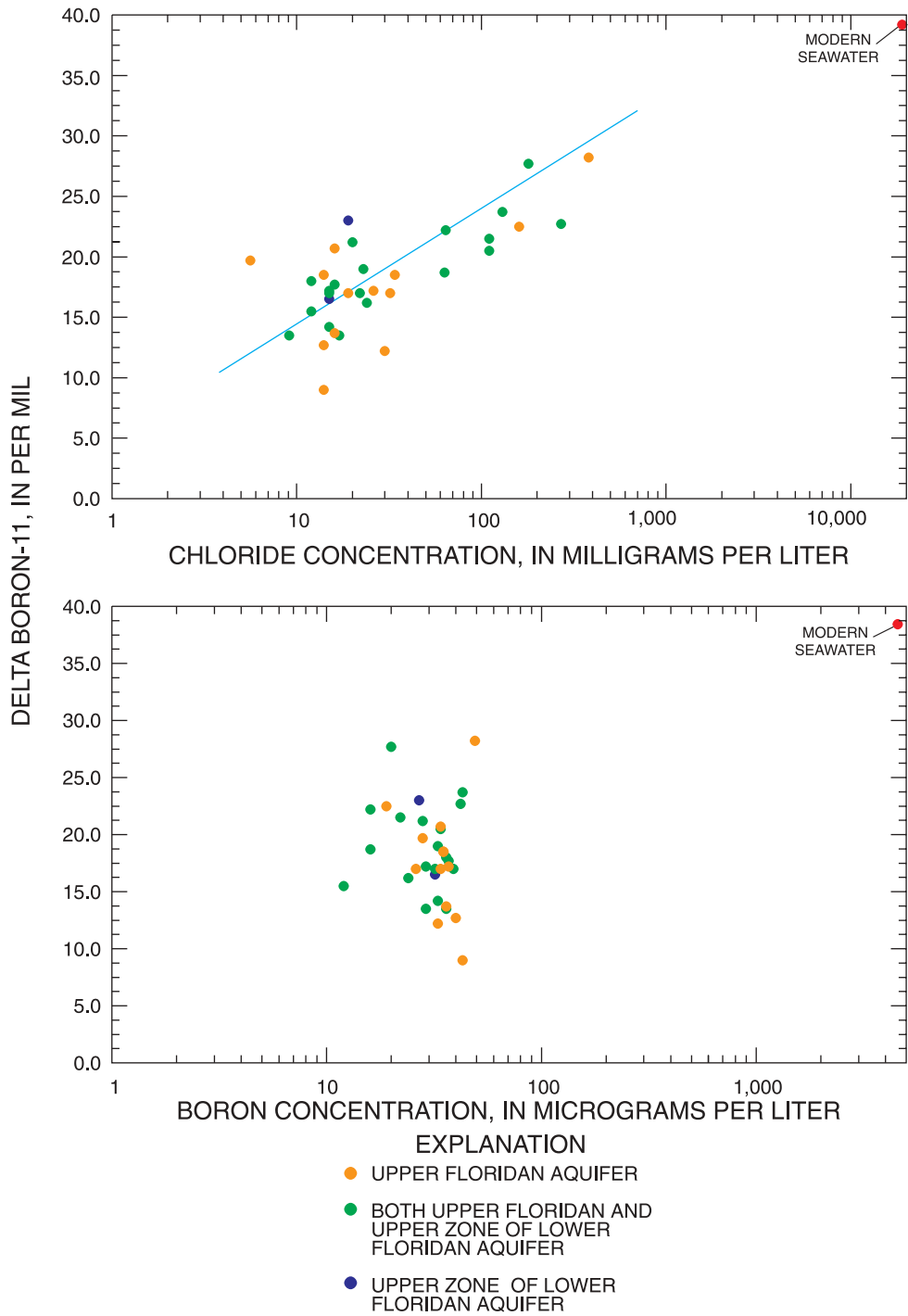
## Chlorine

The long half-life of chlorine-36 ( $^{36}\text{Cl}$ ) (about  $3 \times 10^5$  years) and its low chemical activity make  $^{36}\text{Cl}$  suitable for establishing model dates for some old ground-water systems (Bentley and others, 1986a). However, radioactive  $^{36}\text{Cl}$  is a relatively scarce isotope and, therefore, difficult to analyze. The scarcity of  $^{36}\text{Cl}$  has limited use of this isotope in ground-water investigations until recently, when more laboratories began to offer analysis for  $^{36}\text{C}$  by AMS. Chlorine-36 is formed naturally in the atmosphere by cosmic ray spallation of argon-40 ( $^{40}\text{Ar}$ ) (meteoric  $^{36}\text{Cl}$ ); in the shallow zones

of the Earth's crust by the interaction of cosmic rays and chlorine-35 ( $^{35}\text{Cl}$ ) in near-surface rocks (epigene  $^{36}\text{Cl}$ ); and in deeper rocks by the activation of  $^{35}\text{Cl}$  by neutrons resulting from alpha particle emission during the decay of uranium and thorium (hypogene  $^{36}\text{Cl}$ ) (Bentley and others, 1986a; Fontes and Andrews, 1994). Anthropogenic sources of  $^{36}\text{Cl}$  include atmospheric testing of nuclear weapons (Bentley and others, 1986b) and disposal of waste from nuclear facilities (Cecil and others, 1992). For example, Davis and others (1998b) attributed a ratio of  $^{36}\text{Cl}$  to total chlorine of  $377 \times 10^{-15}$  in water from a well in Tallahassee, Fla., to the presence of bomb-produced  $^{36}\text{Cl}$ . At the Savannah River Site nuclear fuel reprocessing facility in South Carolina, Beasley and others (1992) reported ratios in shallow ground water as high as  $4,400 \times 10^{-15}$ .

Ideally, the ratio of  $^{36}\text{Cl}$  to total chlorine in ground water can be determined by the initial meteoric  $^{36}\text{Cl}$  of recharge water and a "background" value (secular equilibrium) for the aquifer based on location and lithology. When recharge water enters the aquifer, the radiometric "clock" is set; the decay of  $^{36}\text{Cl}$  gradually decreases the ratio unless chlorine is added to the system by dissolution of evaporites or mixing with water from other aquifers. Thus, the time since recharge can be calculated. This method works best for ground water isolated from the atmosphere for 50,000 years or longer (Bentley and others, 1986a). The analysis made during the present study is likely the first attempt to use the  $^{36}\text{Cl}$  method to study water from the Floridan aquifer system.

Water from 49 of the wells sampled during this study was analyzed for the ratio of  $^{36}\text{Cl}$  to total chlorine. Ratios ranged from  $0.5 \times 10^{-15}$  for well D-75 to  $370 \times 10^{-15}$  for well D-1323 (table 6). The anomalously high value for well D-1323 probably results from contamination of the sample by water from the surficial aquifer system; geophysical logs of the well indicate that the casing is leaking at a depth of 120 ft below land surface where the casing reduces from 12 to 6 inches in diameter. This ratio ( $370 \times 10^{-15}$ ) is, therefore, not considered to be representative of the Floridan aquifer system and is not included in the data analysis. Ratios of  $^{36}\text{Cl}$  to total chlorine vary both by aquifer and by location (fig. 22). Ratios for the FPZ ranged from  $0.8 \times 10^{-15}$  to  $20.7 \times 10^{-15}$ . For wells tapping only the UZLF, the range was  $0.5 \times 10^{-15}$  to  $76.2 \times 10^{-15}$ , with a median of about  $15 \times 10^{-15}$ . Wells tapping both the UZLF and the UFA had ratios ranging from  $3 \times 10^{-15}$  to  $75.3 \times 10^{-15}$ , with a median of about  $20 \times 10^{-15}$ . For wells tapping only the UFA, the range was from  $8 \times 10^{-15}$  to  $94 \times 10^{-15}$ , with a median of  $37 \times 10^{-15}$ .



**Figure 21.** Relations between delta boron-11 and chloride and boron concentrations.

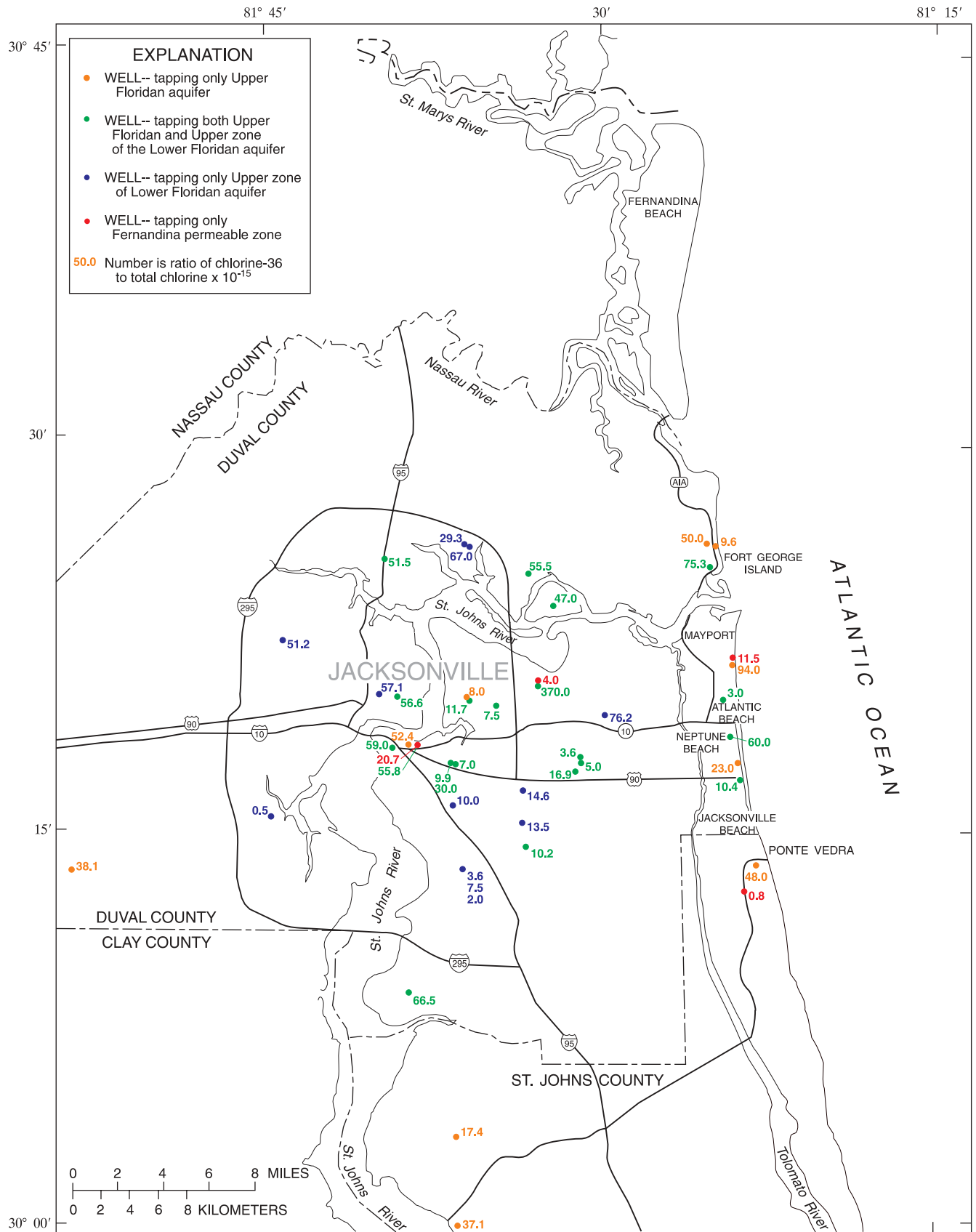


Figure 22. Ratio of chlorine-36 to total chlorine in water from wells in northeastern Florida.

The natural (pre-bomb) ratio of  $^{36}\text{Cl}$  to total chlorine in Florida ground water has been estimated to be  $20 \times 10^{-15}$  or less (Bentley and others, 1986a). However, Davis and others (1998b) concluded that during the time interval 12,000-40,000 years before present, the average production rate of meteoric  $^{36}\text{Cl}$  was higher than the present-day rate by more than 33 percent. Based on this, an initial value of at least  $27 \times 10^{-15}$  is estimated. Even for water samples with low chloride concentrations (20 mg/L or less), many of the ratios are larger than this estimated initial ratio. Therefore, there must be another source of  $^{36}\text{Cl}$  to the ground water, and as a result, the decay of  $^{36}\text{Cl}$  from an initial value cannot be used to date the water. The  $^{36}\text{Cl}$  data may, however, still be useful in understanding flow systems in northeastern Florida.

The chemical evolution of ground water in a region sometimes can be evaluated by looking at the relation between the ratio of  $^{36}\text{Cl}$  to total chlorine and the number of  $^{36}\text{Cl}$  atoms in the water samples (Bentley and others, 1986b). The ratio of  $^{36}\text{Cl}$  to total chlorine for water samples that have evolved from a common initial composition by evaporation or ion filtration will plot on a horizontal line. Samples that have evolved by addition of "dead" chlorine (having little or no  $^{36}\text{Cl}$ , such as from evaporite deposits) will plot on a vertical line. Low chloride waters that have evolved from an initial composition by aging alone will plot on a straight line between the initial composition and the origin of the plot.

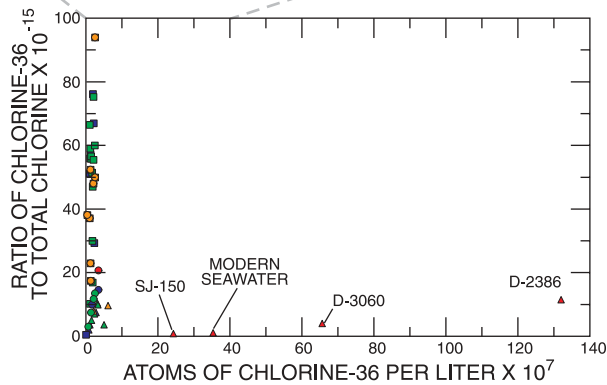
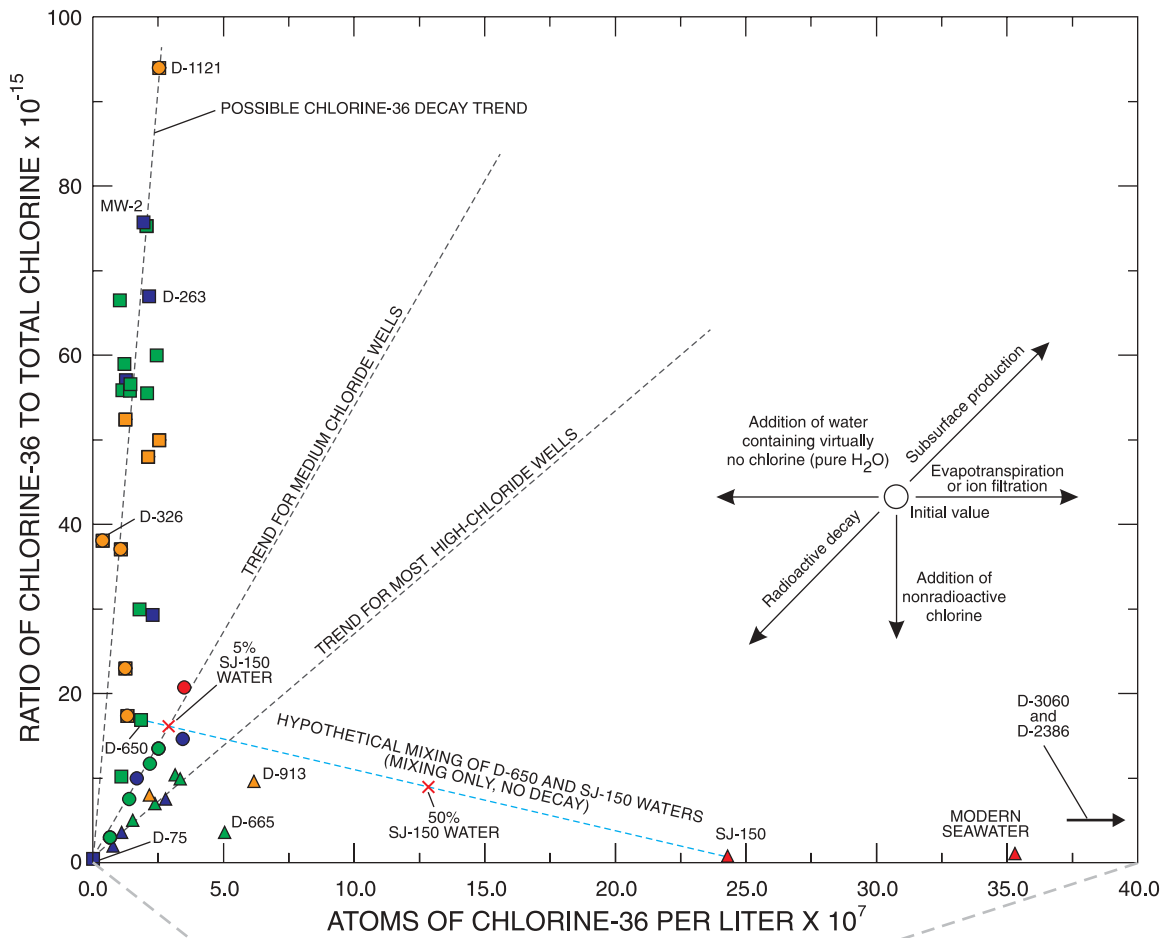
The plot of the relation between the ratio of  $^{36}\text{Cl}$  to total chlorine and  $^{36}\text{Cl}$  concentration for waters from the Duval County area shows several trends (fig. 23). The low chloride samples (chloride concentration less than 100 mg/L) plot on a steeply sloping line possibly indicating a  $^{36}\text{Cl}$  decay trend. Along such a trend, both the number of  $^{36}\text{Cl}$  atoms and the ratio of  $^{36}\text{Cl}$  to total chlorine should decrease along flow lines as water flows from recharge to discharge areas. In northeastern Florida, however, this is not always the case. The sample with the lowest ratio of  $^{36}\text{Cl}$  to total chlorine, UZLF well D-75, is closer to the present-day recharge area than the sample from the same aquifer zone with the highest ratio (well MW-2). The same trend is apparent for low chloride samples from wells tapping the UFA; well D-326, closer to the present-day recharge area, has a lower ratio than well D-1121, which is located downgradient. This could indicate that water in the Floridan aquifer system in the Jacksonville area did not recharge the aquifer at modern-day recharge areas,

or that the wells sampled do not lie along the same flow paths. Another possible conclusion is that these data indicate a higher initial  $^{36}\text{Cl}$  concentration for water recharged during the last approximately 10,000 to 30,000 years than previously estimated. For all of the samples (except well D-75, which could be anomalous) with chloride concentrations less than 15 mg/L, the  $^{36}\text{Cl}$  to total chlorine ratio was in the range 50 to  $66 \times 10^{-15}$ .

Samples with higher chloride concentrations follow trends that are different from the trend for low chloride waters. The high chloride samples from the FPZ (wells SJ-150, D-3060, and D-2386) form a nearly horizontal trend (fig. 23, inset). The water samples with chloride concentrations between 100 and 150 mg/L form a trend, as do most of the samples with chloride concentrations greater than 150 mg/L. These trends could represent the superposition of the effects of mixing with high chloride concentration water from the FPZ (such as from well SJ-150) on a simple decay trend.

To illustrate the possible effects of mixing, values of the ratio of  $^{36}\text{Cl}$  to total chlorine and the number of atoms of  $^{36}\text{Cl}$  were calculated for the mixing of various percentages of water from well D-650 (chloride concentration 64 mg/L) with water from well SJ-150. The plotted points (fig. 23) show how mixing could cause trends that depart from a simple decay trend. This hypothetical mixing, however, does not explain the values for samples from well D-665 (chloride concentration 830 mg/L) and well D-913 (chloride concentration 380 mg/L). According to the calculations, a mixture of about 5 percent water from well SJ-150 with 95 percent water from well D-650 should plot along one of the trend lines shown in figure 23. However, water from well D-665, which according to mass-balance mixing contains about 5 percent water similar to SJ-150 water, does not plot along any of the other trends. Likewise, the sample from well D-913 does not plot on a trend. Thus the source of chlorine to water from wells D-665 and D-913 could be different from the source to the other wells sampled.

The fact that, in general, the ratio of  $^{36}\text{Cl}$  to total chlorine decreases as chlorine concentration increases probably indicates that old chloride from a source deep in the aquifer (or from formations beneath the aquifer) is mixing with fresher water in the upper zones of the aquifer (S. Davis, University of Arizona, written commun., 2000). Analysis of additional water samples in northeastern Florida would be useful for understanding this complex problem.



**EXPLANATION**

- ▲ FERNANDINA PERMEABLE ZONE WELL, CL > 150 MG/L
- FERNANDINA PERMEABLE ZONE WELL, 100 ≤ CL ≤ 150 MG/L
- LOWER FLORIDAN WELL, CL < 100 MG/L
- ▲ LOWER FLORIDAN WELL, CL > 150 MG/L
- LOWER FLORIDAN WELL, 100 ≤ CL ≤ 150 MG/L
- WELL TAPPING BOTH UPPER AND LOWER FLORIDAN, CL < 100 MG/L
- ▲ WELL TAPPING BOTH UPPER AND LOWER FLORIDAN, CL > 150 MG/L
- WELL TAPPING BOTH UPPER AND LOWER FLORIDAN, 100 ≤ CL ≤ 150 MG/L
- UPPER FLORIDAN WELL, CL < 100 MG/L
- ▲ UPPER FLORIDAN WELL, CL > 150 MG/L
- UPPER FLORIDAN WELL, 100 ≤ CL ≤ 150 MG/L

**Figure 23.** Relation between ratio of chlorine-36 to total chlorine and chlorine-36 concentration.



## ORIGINS OF MINERALIZED WATERS

The chemical and isotopic data discussed in previous sections have shown that there are several possible sources of mineralized water, including unflushed Miocene-to-Pleistocene-age seawater, modern seawater, or brine. However, differentiating among the possible sources is difficult. To aid in this task, the geochemical modeling program NETPATH (Plummer and others, 1994) was used to investigate possible mixing scenarios that could yield the chemical and isotopic composition observed in the waters at some of the wells sampled. NETPATH can calculate the mixing proportions of two or more initial waters and the net geochemical mass-balance reactions that can account for the observed composition of a final water. The program also was used to evaluate possible flow paths in the aquifer system and to correct initial  $^{14}\text{C}$  values for age-dating the water samples. Finally, hydrogeologic and geochemical evidence can be evaluated together to provide conclusions about the source or sources of mineralized water.

### Mass-Balance Models

A series of NETPATH runs was made to investigate possible mixing of an initial water that represents ambient ground water with the highly mineralized waters from the FPZ and with the modern seawater sample. Water from D-326, a UFA well yielding water with a chloride concentration of 5.6 mg/L and a sulfate concentration of 20 mg/L, was selected as the ambient (freshwater) end member for wells tapping the UFA and both the UFA and the UZLF. The ambient initial water was mixed with mineralized initial water from well SJ-150 and with modern seawater to simulate water samples from wells with elevated chloride concentrations such as D-665, D-673, D-913, D-275, D-479, D-307, D-3846, and D-225 (both low and high chloride conditions), and wells N-22 and SE-1 which have a low chloride concentration. Mixing models also were created for UZLF wells using the chemical composition of water from well D-75 (chloride concentration 7.6 mg/L and sulfate concentration 65 mg/L; table 3) as the ambient initial water and with water from well SJ-150 and modern seawater as the mineralized initial water. Mixing scenarios were simulated for wells D-450, D-291, D-1155, and for the three samples from D-536 (table 7). Simulations also were made for wells MW-2, D-262, and D-263, which have chloride concentrations of 15 mg/L, 46 mg/L and 19 mg/L, respectively.

The geochemical modeling program NETPATH (Plummer and others, 1994) computes sets of possible reactions (including mineral dissolution or precipitation, ion exchange, and gas exchange) based on the net mass transfer of elements, given a set of constraints and plausible mineral phases. Possible constraints include available elements and concentrations, isotopic data, and electron balance. The model also can compute an isotopic composition for the final water based on the isotopic compositions of the initial waters, calculated mass transfer of elements, and fractionation factors for precipitating mineral phases. The models are not unique but do indicate possible reactions that could result in an observed final water.

The models used in this study were constrained by carbon, calcium, chloride, sodium, sulfur, magnesium, iron, and electron balance (redox state). Chloride was used as the constraint for mixing of fresh and mineralized waters. Electron balance was needed for modeling redox reactions such as oxidation of organic matter. Reaction phases included in the models were calcite, dolomite, gypsum,  $\text{CO}_2$  gas, organic material (represented as  $\text{CH}_2\text{O}$  and constrained to dissolve only), pyrite ( $\text{FeS}_2$ , constrained to precipitate only), goethite ( $\text{FeOOH}$ , constrained to dissolve only), and both calcium/sodium and magnesium/sodium exchange. Trace amounts of clay minerals in the aquifer could serve as ion-exchange sites (Sacks and Tihansky, 1996). Although the aquifer system is expected to be closed to  $\text{CO}_2$  gas mass transfer, chemical reactions (such as oxidation of organic matter accompanying sulfate reduction, methanogenesis, or carbonate mineral dissolution or precipitation) can produce or consume  $\text{CO}_2$  within the aquifer (Plummer and others, 1990).

The observed final-water chemistry could be simulated with either of the mineralized initial waters. Furthermore, the isotopic compositions of the final waters also could be simulated using either FPZ water or modern seawater. This is because the fraction of mineralized water needed to produce the final water in most of the samples was so small that the major-ion composition and isotopic signature of the ambient (freshwater) end member dominated the modeled chemical and isotopic composition of the final water. For the sample from well D-665 (chloride concentration 830 mg/L), the proportions were about 95.5 percent ambient water and 4.5 percent mineralized water (table 4). For samples from the other UFA and from both the UFA and UZLF, the proportions were 97 to 98 percent ambient water.

**Table 7.** NETPATH models for selected wells

[Units in millimoles per liter (mmol/L) unless otherwise noted; positive mass transfer indicates dissolution or ingassing; negative mass transfer indicates precipitation or outgassing. Aquifer: UFA, Upper Floridan aquifer; B, both Upper Floridan and upper zone of Lower Floridan aquifers; UZLF, upper zone of Lower Floridan aquifer.  $\delta^{34}\text{S}$ , delta sulfur-34;  $\delta^{13}\text{C}$ , delta carbon-13; calc, calculated; obs, observed; --, not modeled; na, not analyzed. Isotopic data used in models unless otherwise specified:  $\delta^{13}\text{C}$  of  $\text{CH}_2\text{O}$  and  $\text{CO}_2 = -25.0$  per mil. For dissolving phases:  $\delta^{34}\text{S}$  of gypsum = 22.0 per mil;  $\delta^{13}\text{C}$  of calcite = 1 per mil;  $\delta^{13}\text{C}$  of dolomite = 2 per mil. For precipitating phases,  $\delta^{13}\text{C}$  or  $\delta^{34}\text{S}$  computed by model based on Rayleigh calculations and additive fractionation factors defined at the final water composition;  $\delta^{34}\text{S}$  of pyrite = -30.0 per mil;  $\delta^{34}\text{S}$  (observed) based on measured  $\delta^{34}\text{S}$  of sulfate. Remarks give more information about phases: X, calcium-sodium exchange modeled; MX, magnesium-sodium exchange modeled; P, pyrite not modeled; G, goethite not modeled; C, all models included  $\text{CO}_2$  outgassing]

Final well	Initial well 1	Initial well 2	Aquifer	Gypsum	Dolomite	Calcite	$\text{CH}_2\text{O}$	$\text{CO}_2$	$\delta^{34}\text{S}$ (total S), per mil		$\delta^{13}\text{C}$ (total C), per mil		Carbon-14, percent modern		$^{87}\text{Sr}/^{86}\text{Sr}$		Remarks
									calc	obs	calc	obs	calc	obs	calc	obs	
SE-1	D-326	SJ-150	UFA	1.94	--	--	0.36	0.22	23.9	19.2	-12.8	-11.0	32.7	1.47	0.70788	0.70788	X, MX
SE-1	D-326	Seawater	UFA	1.85	--	0.09	.19	.30	22.1	19.2	-11.9	-11.0	32.9	1.47	.70788	.70788	MX,G
D-673	D-326	SJ-150	UFA	1.02	0.82	-1.10	--	.70	22.1	23.9	-8.2	-9.4	17.4	1.30	.70792	.70788	X,
D-673	D-326	Seawater	UFA	1.04	.75	-.99	--	.73	22.1	23.9	-8.6	-9.4	18.1	1.30	.70789	.70788	X
D-913	D-326	SJ-150	UFA	1.32	1.10	-1.73	--	.93	22.2	24.2	-8.1	-10.3	13.5	1.34	.70796	.70797	X
D-913	D-326	Seawater	UFA	1.37	.93	-1.46	--	1.01	22.2	24.2	-9.0	-10.3	14.8	1.34	.70789	.70797	X
D-3846	D-326	SJ-150	B	1.58	1.03	-1.54	--	.66	22.2	21.1	-7.1	-6.8	14.9	.68	.70790	.70787	X
D-3846	D-326	Seawater	B	1.59	1.00	-1.51	--	.67	22.2	21.1	-7.2	-6.8	15.1	.68	.70789	.70787	X
D-275	D-326	SJ-150	B	1.81	.74	-1.77	1.58	--	22.0	23.7	-12.4	-9.1	12.5	1.95	.70793	.70783	X
D-275	D-326	Seawater	B	1.88	.65	-1.68	1.67	--	22.0	23.7	-13.2	-9.1	12.9	1.95	.70789	.70783	X
D-225 (high)	D-326	SJ-150	B	1.73	.74	-1.67	1.24	.58	22.0	23.5	-11.0	-9.3	13.7	2.19	.70793	.70784	X
D-225 (high)	D-326	Seawater	B	1.80	.65	-1.58	1.33	--	22.0	23.5	-11.8	-9.3	14.1	2.19	.70789	.70784	X
D-225 (low)	D-326	SJ-150	B	1.91	.64	-1.62	.92	--	22.1	23.0	-10.4	-8.2	15.7	1.81	.70789	.70786	X
D-225 (low)	D-326	Seawater	B	1.92	.62	-1.60	.93	--	22.1	23.0	-10.5	-8.2	15.8	1.81	.70788	.70786	X
D-665	D-326	SJ-150	B	1.18	1.01	-2.00	.02	.65	21.5	21.6	-7.2	-9.0	13.6	3.64	.70803	.70790	X, P
D-665	D-326	Seawater	B	1.29	.63	-1.43	.03	.82	21.5	21.6	-9.7	-9.0	17.2	3.64	.70791	.70790	X, P
D-479	D-326	SJ-150	B	.89	.56	-.76	--	2.01	22.5	23.6	-15.6	-9.9	16.7	1.12	.70791	.70788	X
D-479	D-326	Seawater	B	.90	.51	-.69	--	2.04	22.5	23.6	-13.9	-9.9	17.1	1.12	.70788	.70788	X
D-307	D-326	SJ-150	B	1.20	.72	-1.23	.26	.59	22.0	19.7	-9.3	-9.0	17.1	1.33	.70791	.70790	X, G
D-307	D-326	Seawater	B	1.21	.67	-1.14	.26	.62	22.0	19.7	-9.7	-9.0	17.7	1.33	.70789	.70790	X, G
N-22	D-326	SJ-150	B	1.39	.89	-1.35	.14	2.51	22.2	24.4	-14.1	-8.2	12.8	9.96	.70787	na	MX, G
N-22	D-326	Seawater	B	1.39	.88	-1.32	.14	2.52	22.2	24.4	-14.1	-8.2	12.9	9.96	.70788	na	MX, G
D-536-1	D-75	SJ-150	UZLF	2.82	1.22	-2.78	.72	--	22.1	21.7	-6.8	-6.0	10.1	2.20	.70791	.70785	X
D-536-1	D-75	Seawater	UZLF	2.91	1.12	-2.68	.83	--	22.1	21.7	-7.6	-6.0	10.5	2.20	.70789	.70785	X
D-536-2	D-75	SJ-150	UZLF	2.53	1.23	-2.41	.35	.16	22.1	21.8	-4.9	-6.4	11.74	2.23	.70791	.70785	X
D-536-2	D-75	Seawater	UZLF	2.61	1.14	-2.31	.44	--	22.1	21.8	-5.7	-6.4	12.2	2.32	.70789	.70785	X
D-536-3	D-75	SJ-150	UZLF	2.62	1.12	-2.26	.01	.45	22.2	21.5	-5.9	-5.4	13.0	4.07	.70791	.70783	X, G
D-536-3	D-75	Seawater	UZLF	2.64	1.04	-2.14	.01	.48	22.2	21.5	-6.3	-5.4	13.7	4.07	.70789	.70783	X, G
D-291	D-75	SJ-150	UZLF	.90	--	--	.12	-.46	22.4	21.9	-7.8	-8.6	36.4	3.05	.70790	.70783	X, MX, C
D-291	D-75	Seawater	UZLF	.90	--	--	.08	-.42	22.4	21.9	-7.6	-8.6	37.0	3.05	.70789	.70783	X, MX, C
D-450	D-75	SJ-150	UZLF	1.36	.67	-1.42	.76	--	22.4	23.2	-9.0	-8.0	16.6	1.54	.70790	.70787	X
D-450	D-75	Seawater	UZLF	1.40	.63	-1.38	.81	--	22.3	23.2	-9.4	-8.0	16.9	1.54	.70789	.70787	X
D-1155	D-75	SJ-150	UZLF	1.54	.75	-1.54	1.00	--	22.2	22.6	-9.9	-8.1	14.9	1.95	.70790	.70786	X
D-1155	D-75	Seawater	UZLF	1.59	.69	-1.48	1.06	--	22.2	22.6	-10.4	-8.1	15.2	1.95	.70789	.70786	X
MW-2	D-75	SJ-150	UZLF	.99	.20	--	.02	.20	22.5	22.7	-8.3	-8.3	2.76	.96	.70789	.70787	X, MX, P
MW-2	D-75	Seawater	UZLF	1.22	.62	-1.06	.45	--	28.2	22.7	-7.7	-8.3	19.6	.96	.70789	.70787	MX
D-262	D-75	SJ-150	UZLF	.85	.41	-.78	1.06	--	22.4	27.2	-11.3	-12.0	19.2	2.48	.70789	.70801	X
D-262	D-75	Seawater	UZLF	.87	.40	-.76	1.07	--	22.4	27.2	-11.5	-12.0	19.3	2.48	.70789	.70801	X
D-263	D-75	SJ-150	UZLF	.13	.31	--	.13	.50	25.5	23.6	-9.7	-11.2	25.4	.88	.70789	.70798	X
D-263	D-75	Seawater	UZLF	.10	.32	--	.07	.53	23.5	23.6	-9.4	-11.2	25.4	.88	.70789	.70798	X, MX, G

For wells tapping only the UZLF, the mixtures were 98.8 to 99.9 percent ambient water. The only apparent exception to this generalization is well MW-2, where the water from SJ-150 more accurately simulated the observed  $^{14}\text{C}$  value than did modern seawater.

The dominant reaction simulated is dedolomitization (dolomite dissolution and calcite precipitation) driven by gypsum dissolution. This generally is consistent with the chemical reactions that would be expected to occur as ground water flows through the Floridan aquifer system. For some wells, however, this reaction may not be realistic. The samples from wells D-673 (UFA), D-275 and N-22 (both UFA and UZLF), and D-1155 (UZLF) are undersaturated with respect to calcite, precluding the precipitation of calcite. This could be because water from well D-326 does not represent the initial freshwater end member for water from wells D-673, D-275, and N-22 (and, similarly, that well D-75 is not the initial freshwater end member for water from well D-1155). Alternatively, there could be another initial water involved in the evolution of the observed final water but not simulated in these models. This possibility is especially likely for the wells with large open-hole intervals.

Some other discrepancies exist between the simulated and observed water chemistry. For example, simulated values for  $^{14}\text{C}$  for wells SE-1 and D-291 are poor regardless of which mineralized end member is used. This also is true for water from wells D-262 and D-263. Finally, many of the models include  $\text{CO}_2$  ingassing. Models with  $\text{CO}_2$  ingassing are considered to be unrealistic in an aquifer discharge area (Sacks and Tihansky, 1996). Small amounts of  $\text{CO}_2$  (a few tenths of a millimole per liter) could be explained by uncertainties in the analytical data; however, larger values can be attributed to uncertainties in the sulfur isotopic composition of gypsum in the aquifer (Plummer and others, 1990), which could, in turn, affect the models for sulfur isotopic composition.

## Ground-Water Ages

Ground-water ages were estimated based on the carbon-14 composition of total inorganic carbon in the water samples. For most samples, the ages were estimated with NETPATH using the Fontes and Garnier (1979) model, which assumes a simple mixing of the three carbon phases (gaseous  $\text{CO}_2$  and solid and aqueous carbonate) in the ground-water system. The Fontes and Garnier model is applicable to

present-day recharge in the karst of the Floridan aquifer system; it, therefore, is assumed that the model is applicable to past conditions. In the models, the following  $\delta^{13}\text{C}$  values were assumed: soil gas  $\text{CO}_2$  of -23 per mil; carbonate minerals in the aquifer of 1.0 per mil;  $\text{CO}_2$  gas at all wells of -23 per mil; and water at each well was given the measured value.

The calculated  $^{14}\text{C}$  ages, using the Fontes and Garnier model, ranged from about 9,500 years at well N-22 to about 35,700 years at well D-3841 (table 8, fig. 24). Both wells tap both the UFA and the UZLF. For wells tapping the UFA only, ages ranged from about 10,500 at well SJ-3 to 32,000 at well SJ-103. Wells tapping the UZLF only had ages ranging from about 13,200 years for the sample from a depth of 1,078 ft in well D-536 to 32,400 years for the sample from well D-263.

Errors in the determination of  $^{14}\text{C}$  values will affect the ages calculated. In addition to possible sample variability, two processes are subject to error: the laboratory preparation of targets and the AMS analysis. Of the two, the target preparation probably has more potential for the introduction of error. The AMS determinations of percent modern carbon had errors ranging from 0.05 to 0.19 percent. The effects of AMS errors on age determinations were negligible. To determine the effect of target preparation errors, two duplicate samples were analyzed for  $^{14}\text{C}$ . The duplicates were collected at wells D-326 (chloride concentration 5.6 mg/L and lab alkalinity 99 mg/L) and D-307 (chloride concentration 130 mg/L and lab alkalinity 149 mg/L). For well D-307 the percent modern carbon values were 1.37 and 1.33, resulting in calculated ages of 26,700 and 27,100 years, respectively (a difference of about 400 years). The differences were greater for well D-326: 1.04 and 2.90 percent modern carbon, with calculated ages of 29,200 and 20,900 years, respectively (a difference of about 8,300 years). To be conservative,  $^{14}\text{C}$  ages could be considered to be accurate to  $\pm 4,000$  years.

Trends in the areal distribution of  $^{14}\text{C}$  ages are difficult to discern. Relatively young waters were found in wells SJ-3, SJ-168, and D-3847, in the southern part of the study area, suggesting the presence of a different flow path than that supplying most of the water to wells in Duval County (figs. 1, 5b, and 24). The youngest age calculated was for water from well N-22, located in an area of heavy industrial pumping just to the north of the study area.

**Table 8.** Carbon-14 ages for ground-water samples

[<sup>14</sup>C, carbon-14; δ <sup>13</sup>C, delta carbon-13; dup, duplicate; na, not analyzed. Aquifer: UFA, Upper Floridan aquifer; B, both Upper Floridan and upper zone of Lower Floridan aquifers; UZLF, upper zone of Lower Floridan aquifer; FPZ, Fernandina permeable zone. FG, Fontes and Garnier (1979) model; T, Tamers (1975) model; uncertainty in <sup>14</sup>C ages is ± 4,000 years]

Site identification number	Local number	Aquifer	<sup>14</sup> C (percent modern)	<sup>14</sup> C error (percent)	δ <sup>13</sup> C (per mil)	<sup>14</sup> C FG age (years)	<sup>14</sup> C T age (years)
300019081363301	SJ-3	UFA	3.37	0.11	-3.48	10,500	22,800
300347081363701	SJ-168	UFA	3.5	.12	-3.82	11,100	22,400
301304081222701	SJ-103	UFA	0.56	.05	-6.98	32,000	38,000
301339081531201	D-326	UFA	2.90	.09	-9.22	20,900	23,800
301339081531201	D-326dup	UFA	1.04	.05	-9.02	29,200	32,200
301547081271901	SE-1	UFA	1.47	.06	-11.02	28,100	29,600
301714081233301	D-72	UFA	2.12	.05	-7.26	21,400	26,900
301830081375501	D-1551	UFA	1.23	.05	-7.9	26,600	31,100
302013081353801	D-673	UFA	1.30	.06	-9.4	27,600	31,400
302058081244101	D-1107	UFA	1.79	.07	-7.97	23,600	28,000
302113081322301	D-655	UFA	1.86	.07	-8.96	24,300	27,600
302140081235501	D-1121	UFA	1.48	.06	-9.24	26,500	29,700
302239081434401	NK-1	UFA	1.24	.05	-7.82	26,500	31,000
302557081253101	D-913	UFA	1.34	.08	-10.3	28,200	31,000
302608081354903	D-264	UFA	2.35	.08	-7.3	20,600	25,800
302609081260601	D-912	UFA	2.0	.07	-10.66	25,200	27,100
300856081382401	D-3847	B	4.59	.10	-4.87	11,400	20,200
301405081325601	D-3846	B	.68	.05	-6.79	30,100	36,100
301508081364601	BW-3	B	1.56	.09	-6.04	22,200	29,000
301704081233401	D-484	B	2.28	.09	-9.37	23,000	26,400
301725081305002	D-650	B	.83	.06	-8.48	30,400	34,900
301740081361001	D-275	B	1.95	.08	-9.09	24,000	28,000
301743081303501	D-3825	B	2.46	.07	-8.37	21,400	25,500
301743081362301	D-225	B	2.19	.08	-9.29	23,200	26,500
301743081362301	D-225	B	1.81	.09	-8.22	23,700	27,900
301748081383401	D-334	B	.97	.06	-7.95	28,600	33,200
301758081303901	D-665	B	3.64	.13	-9.01	18,800	21,800
301817081374901	D-425T	B	.88	.06	-8.12	29,600	34,100
301846081240201	D-246	B	2.96	.08	-7.67	19,100	24,100
301934081292301	R-3	B	1.54	.06	-8.64	25,600	29,000
301937081471401	D-2223	B	1.41	.06	-8.62	26,200	30,000
301957081342301	D-313	B	1.99	.08	-10.12	24,800	27,500
302007081353201	D-479	B	1.12	.08	-9.88	29,300	32,300
302008081242101	D-307	B	1.33	.05	-9.02	27,100	30,600
302008081242101	D-307dup	B	1.37	.06	-8.80	26,700	30,300
302015081384501	D-335	B	.98	.06	-9.08	29,700	33,400
302045081323101	D-1323	B	.91	.05	-10.11	31,200	34,000
302342081320601	D-1902	B	2.02	.07	-9.56	24,200	27,200
302503081332001	D-1149	B	.62	.05	-11.22	35,300	37,200
302510081260201	D-3841	B	.53	.05	-10.05	35,700	38,000
302538081392501	D-329	B	1.37	.07	-11.57	29,000	30,500
303940081281801	N-22	B	9.96	.19	-8.23	9,500	16,100
301335081355001	D-536-1 <sup>a</sup>	UZLF	2.2	.08	-5.98	19,300	26,000
301335081355001	D-536-2 <sup>b</sup>	UZLF	2.32	.09	-6.38	19,400	25,700
301335081355001	D-536-3 <sup>c</sup>	UZLF	4.07	.11	-5.35	13,200	21,200
301522081331301	D-291 <sup>d</sup>	UZLF	3.05	.10	-8.6	19,900	23,400
301537081441901	D-75	UZLF	3.09	.10	-8.53	19,700	23,200
301604081361501	D-450	UZLF	1.54	.07	-7.99	24,900	29,000
301639081330802	D-1155	UZLF	1.95	.08	-8.11	23,000	27,900
301936081292401	MW-2	UZLF	.96	.05	-8.28	29,100	32,200
302022081393501	D-176	UZLF	3.07	.10	-7.79	19,000	23,400
302227081435001	D-592	UZLF	2.47	.09	-8.99	22,000	25,200
302608081354901	D-262	UZLF	2.48	.09	-11.96	24,400	25,200
302608081354902	D-263	UZLF	.88	.06	-11.22	32,400	34,000
301132081225801	SJ-150	FPZ	1.31	.07	-6.3	na	na
301405081325601	D-425B	FPZ	1.27	.07	-7.19	25,500	30,600
301725081305002	D-3060	FPZ	1.63	.07	-9.28	na	na
301743081303501	D-2386	FPZ	1.68	.08	-9.83	na	na
302737080571801	Seawater		109.96	.55	-1.75	na	na

<sup>a</sup>Sampling depth 1,042 ft below land surface.

<sup>b</sup>Sampling depth 1,059 ft below land surface.

<sup>c</sup>Sampling depth 1,078 ft below land surface.

<sup>d</sup>Sampling depth 1,210 ft below land surface.

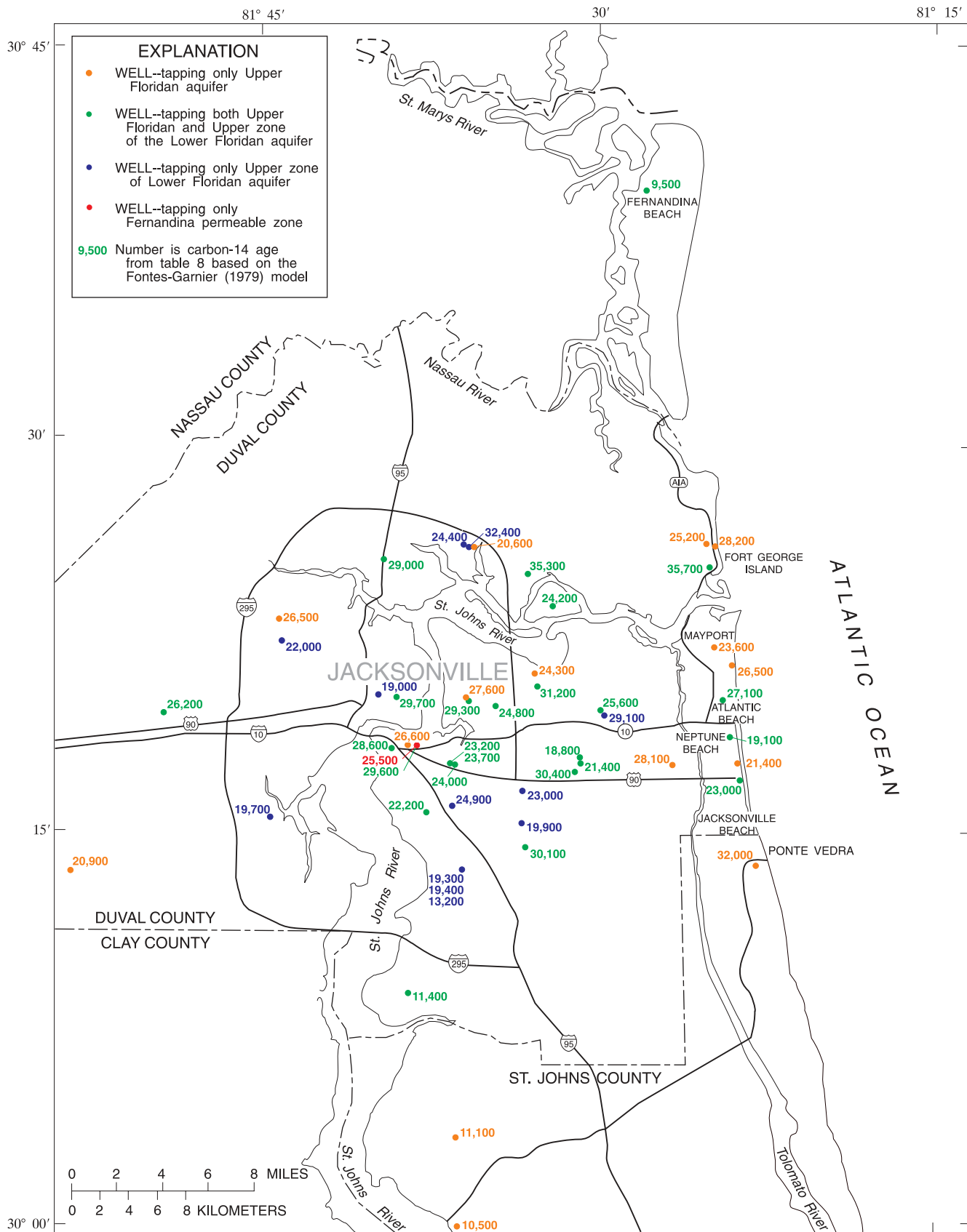


Figure 24. Carbon-14 ages of ground-water samples.

Much of the water discharged from well N-22 possibly follows flow paths from recharge areas in southeastern Georgia rather than from the Keystone Heights recharge area. Carbon-14 ages also are apparently not related to chloride concentration (fig. 25). In general, water samples from wells in the southern part of the study area have younger ages, heavier  $\delta^{13}\text{C}$  values, and have undergone more extensive dedolomitization reactions; however, this could be related to the distribution of gypsum in the aquifer, rather than to residence time in the aquifer.

The simulated ages for most samples ranged from about 20,000 to about 30,000 years, regardless of chloride concentration. The samples having the oldest simulated ages, from wells D-3841 and D-1149, were north of the St. Johns River and could represent a flow divide between pumping centers in Nassau and Duval Counties, along which older water has not been intercepted by pumping. Because the ages calculated are approaching the upper limits of the  $^{14}\text{C}$  age dating technique, the water could in fact be older than estimated.

At Ft. George Island and in the area of well D-665, waters with the lowest chloride concentrations have the oldest calculated  $^{14}\text{C}$  ages. For example, at Ft. George, water from wells D-3841 (chloride 16 mg/L) and D-1149 (chloride 22 mg/L), a few miles to the west, both have ages of about 35,000 years. Water from well D-913 (chloride 380 mg/L) has an apparent age of about 28,000 years. Similarly, water from well D-665 (chloride concentration 830 mg/L) has an apparent age of about 19,000 years, but water from nearby well D-650 (chloride 64 mg/L) has an apparent age of about 30,000 years. In other areas, water with a higher chloride concentration has an older age. Water from well D-1323 (chloride 270 mg/L), about 3.5 miles north of well D-665, has an apparent age of about 30,000 years; whereas, water from the nearby UFA well D-655 (chloride 34 mg/L) has an age of about 24,000 years (although given the error range, this difference may not be significant).

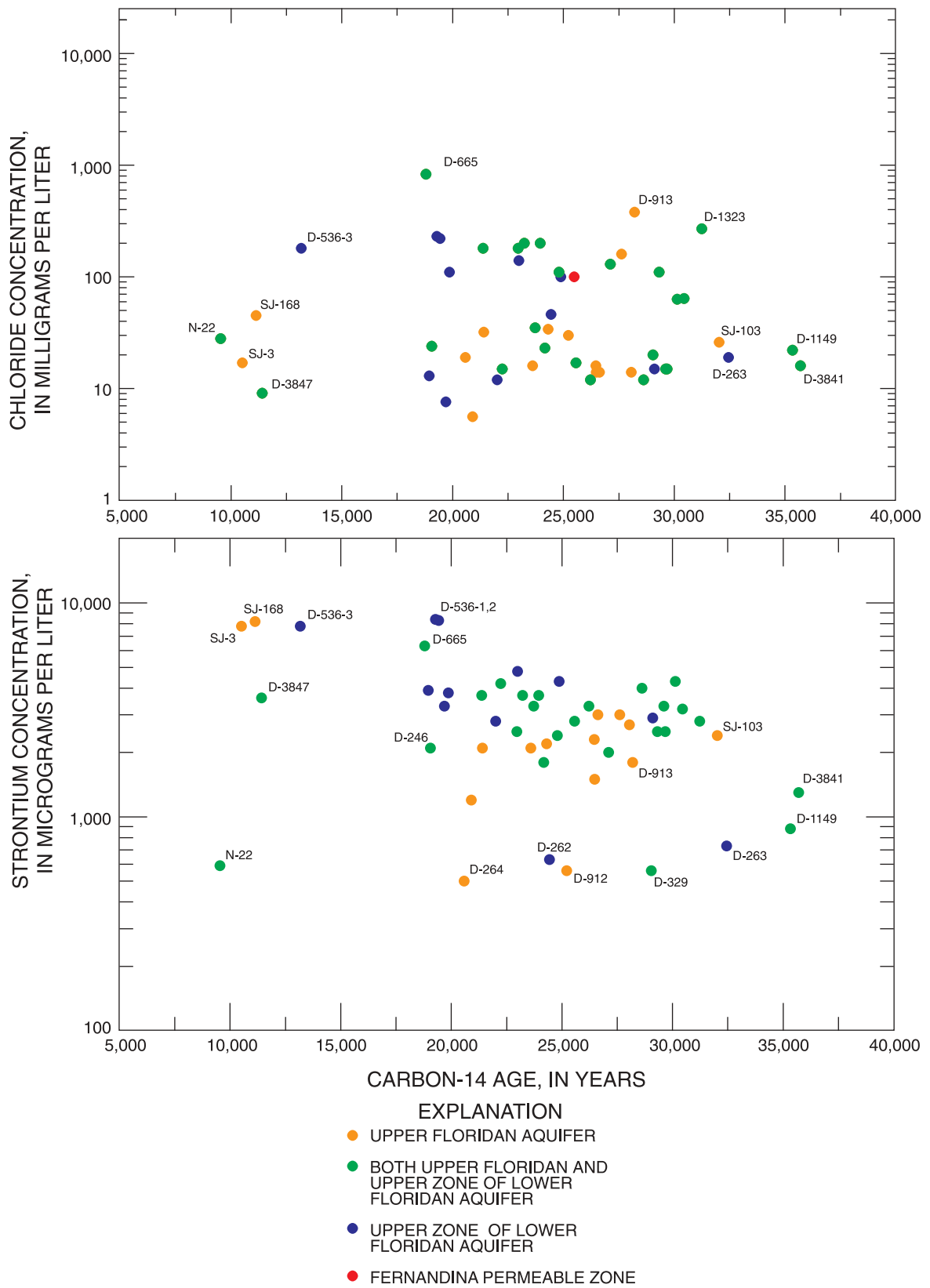
The relation between  $^{14}\text{C}$  age and strontium concentration also was considered (fig. 25). Apparently, residence time in the aquifer (i age) is not related to strontium concentration; the wells with water having the youngest apparent ages (N-22, SJ-3, and SJ-168) had a variation of more than an order of magnitude in strontium concentration. Also, other wells with relatively low strontium concentrations (D-264, D-262, D-912, D-329, D-263, and D-1149) had ages ranging from about 20,000 to more than 35,000 years.

Thus, the strontium concentrations probably relate to aquifer mineralogy.

Carbon-14 ages for the mineralized samples from the FPZ are more difficult to calculate because the initial  $^{14}\text{C}$  activity at the time the water entered the aquifer is unknown. If it is assumed that the FPZ water began as seawater left from a higher stand of sea level, then NETPATH could be used to simulate reactions between seawater and aquifer materials that could result in the observed water in the FPZ. Several models were found but none was entirely satisfactory in simulating the water from well SJ-150, particularly with regard to carbon isotope values (L.N. Plummer, USGS, written commun., 2000). Reasons for the discrepancy could include errors in the chemical analysis or the possibility that the sample has mixed with saline water that differs in chemical and isotopic composition from seawater. Attempts to simulate mineralized water in the LFA in southwestern Florida also have been problematic (L.A. Sacks, USGS, written commun., 2001). This suggests that saline water underlying both northeastern and southwestern Florida may have had a similar chemical history; however, a solution to this problem is beyond the scope of the present study.

Based on the low values of percent modern carbon (less than 2 percent) and the light values of  $\delta^{13}\text{C}$  (-6 to -9 per mil), the FPZ waters are old. It is likely that the mineralized waters from the FPZ are too old to be dated using  $^{14}\text{C}$ . Sea level has not been higher than at present during approximately the last 125,000 years (Chappell and Shackleton, 1986). According to their data, during the period 25,000-30,000 years ago, sea level was about 150 feet lower than at present.

In summary,  $^{14}\text{C}$  data indicate that most ground water in northeastern Florida was recharged to the aquifer about 25,000-30,000 years ago, although some samples indicate recharge about 10,000 years ago. Mineralized water from the FPZ is old (probably greater than 25,000 years). Water samples from wells D-665 and D-913, which had the highest chloride concentrations of all non-FPZ wells, had slightly younger ages than samples from nearby wells having lower chloride concentrations. In well D-536, however, the sample with the highest chloride water had the youngest age. These data could indicate at least two different sources of mineralized water in northeastern Florida.



**Figure 25.** Relations between chloride concentration and carbon-14 age, and between strontium concentration and carbon-14 age.

## Reconciling Hydrogeologic and Geochemical Evidence

Previous investigations (Spechler, 1994; Phelps and Spechler, 1997) have documented the distribution of increasing chloride concentrations in ground water in northeastern Florida. Several sources of the mineralized water and mechanisms of movement have been postulated: lateral movement of the freshwater-salt-water interface from the Atlantic Ocean (modern seawater intrusion); unflushed connate water (from the time of sediment deposition) or relict seawater from high sea level stands in the geologic past that was trapped in the upper, freshwater-bearing zones of the aquifer; or upconing of mineralized water from deeper zones of the aquifer or from underlying formations. In northeastern Florida, upward movement of mineralized water from deeper aquifer zones probably occurs through preferential structural pathways such as joints, fractures, faults, or paleokarst features rather than on a regional scale in response to lowering of the potentiometric surface.

Modern seawater, if intruding into the aquifer from the Atlantic Ocean, would be found in most or all wells near the coast and in few or no wells farther inland. This is not the case in northeastern Florida. Unflushed connate or relict seawater in upper, freshwater-bearing zones would be expected to be found in zones of low transmissivity. In northeastern Florida, mineralized water was more likely to be found in high transmissivity or fracture flow zones than in low transmissivity zones (Spechler, 1994; Phelps and Spechler, 1997). Connate water would be expected to have major ion concentrations similar to or higher than seawater, strontium isotope data indicating an Eocene age, and  $^{14}\text{C}$  activity near zero. The most mineralized water sampled during the study, however, had major ion concentrations that could not be accounted for by model reactions of seawater with aquifer rock, strontium isotope ratios generally in the Oligocene-age range, and measurable  $^{14}\text{C}$  activity. It is possible that upconing of mineralized water through thin or permeable confining layers in response to increased pumping is the source of the observed chloride increases in some wells in Duval County; information is sparse about the thickness and vertical hydraulic conductivity of the semi-confining layers separating the upper, freshwater-bearing zones of the Floridan aquifer system from deeper zones. Many wells in the Jacksonville area, however, have been pumped for as long as 60 years with no increase in chloride concentration (Phelps and Spechler, 1997,

p. 41-42), whereas others have increasing chloride concentrations after only a few years.

The geochemical and isotopic data indicate that the likely source of increased mineralization in some water samples from the upper zones of the Floridan aquifer system is mineralized water from the FPZ. The assumption is that mineralized water moves upward in response to decreased heads through interconnecting vertical and horizontal fracture or solution zones probably developed along deep, subsurface paleokarst features. Geophysical logging and surface geophysical investigations have described the occurrence of fracture flow zones in wells and subsurface paleokarst features near several wells that have increasing chloride concentrations. This mineralized water could be relict seawater that was not flushed from the aquifer during lower stands of sea level, perhaps because the thick sequence of overlying carbonates and confining units prevented flushing during the peak of Pleistocene glaciation, when the sea level was much lower than present day. However, the fact that the chemical and isotopic composition of the FPZ water cannot be simulated by simple reactions of seawater with aquifer rocks indicates that either some other, more complex, rock-water reactions are occurring, or that the water could be affected by a brine, probably from formations beneath the FPZ.

Water from well SJ-150 probably represents, both chemically and isotopically, the mineralized water end member affecting water from some wells with increasing chloride concentrations (such as well D-665). Both the  $\delta^{13}\text{C}$  and strontium data (figs. 17 and 20) indicate that although water from well SJ-150 is chemically similar to modern seawater, it is isotopically different, precluding the possibility that the source of mineralized water is modern seawater intrusion. The  $^{14}\text{C}$  data also point to old, rather than modern, seawater as the source of mineralized water. Waters from the other two high chloride FPZ wells (D-3060 and D-2386) also are isotopically different from modern seawater. All of the samples from the FPZ are saturated with respect to calcite and both crystalline and disordered dolomite, indicative of long residence time in the aquifer. For example, the chemistry of water samples with low chloride and strontium concentrations, such as those from wells D-329, D-264, and D-1149, could result from the residual effects of gradual flushing of seawater from the aquifer system by freshwater (figs. 19 and 20). Thus, it is likely that there are at least two sources of mineralization for ground-water samples in northeastern Florida.



The water sampled from well D-326, in western Duval County, probably most nearly represents the chemistry of ambient ground water in the Floridan aquifer system. The water has very low concentrations of dissolved constituents and is at equilibrium with respect to calcite and crystalline dolomite, probably indicating a shorter residence time in the aquifer (because the area is closer to the recharge area), but perhaps also indicating a difference in aquifer mineralogy in that area.

The geochemical modeling program NETPATH was used to calculate proportions of the respective end members that would produce water of the composition found in the water samples analyzed. Water from most of the wells sampled is a mixture of about 99 percent recharge water and less than 1 percent water with the chemical composition of water from well SJ-150. The sample with the highest chloride concentration (from well D-665) is about 95.5 percent recharge water and about 4.5 percent water chemically similar to that from well SJ-150. The small percentage of mineralized water present in most samples makes it difficult to find a unique solution to the problem of estimating the chemical and isotopic composition, and thus, the source of the mineralized water.

Based on the potentiometric surface (figs. 5a and 5b) and on the chemical and isotopic data, there may be at least two different flow systems in northeastern Florida. For example, wells north of the St. Johns River have relatively low sulfate and strontium concentrations, heavy  $\delta^{34}\text{S}$  content, and light values of  $\delta^{13}\text{C}$ . The distribution of  $^{14}\text{C}$  ages for that area (fig. 24) apparently indicates that this may be due to areal differences in aquifer mineralogy, rather than differences in aquifer residence time. In these wells north of the St. Johns River, the data do not clearly indicate whether or not the mineralized water from the FPZ is the source of increased chloride concentrations; however, strontium data (fig. 20) indicate that waters in that area could be mixing with higher chloride water from a source geochemically different from the water from well SJ-150. The source of higher chloride water to these wells could be pockets of unflushed seawater from higher stands of sea level during Miocene to Pleistocene time.

## SUMMARY

Increases in the chloride concentration have been observed in the water from numerous wells in northeastern Florida. Most of the increases have been in the

eastern part of Duval County, but a pattern in the locations of wells with chloride increases is not readily discernible. Possible sources of the mineralized water include lateral intrusion of modern seawater; unflushed connate water in aquifer sediments or relict seawater from higher stands of sea level in the past; or upconing of mineralized water from formations beneath the Floridan aquifer system. Chemical and isotopic data were used to differentiate water samples from various wells and infer the source of the increased mineralization observed.

Water samples were collected from 53 wells in northeastern Florida during 1997-99. Wells tapped various zones of the aquifer including: the Fernandina permeable zone (FPZ), the upper zone of the Lower Floridan aquifer (UZLF), the Upper Floridan aquifer (UFA), and both the UFA and the UZLF. Some wells had large open-hole intervals, which could have complicated the analysis of the chemical data. Water samples were analyzed for major ions and trace constituents and for isotopes of carbon, oxygen, hydrogen, sulfur, strontium, chlorine, and boron. Samples of rock from the aquifer also were analyzed for isotopes of oxygen, carbon, and strontium.

In general, water from various aquifer zones cannot be differentiated based on chemistry; major-ion concentrations vary as much within a particular zone as among zones. Three of the four wells tapping the FPZ had sodium-chloride-type water. Water from well SJ-150 was chemically similar to seawater except for higher concentrations of calcium, strontium, and sulfate, which probably are the result of dissolution of aquifer materials. Most of the samples from the UZLF were calcium-magnesium sulfate-bicarbonate-type water. Chloride concentrations did not show an increasing trend with depth. The water with the highest chloride concentrations in the UZLF came from fracture flow zones and was collected by using a thief sampler at one well. Water samples from wells tapping both the UZLF and the UFA had widely varying chemistries. Some wells yielded calcium-magnesium-bicarbonate-type water with low specific conductance, whereas others were sodium-chloride type and calcium-sodium-magnesium chloride-sulfate-type waters. The water from well D-665 was chemically more similar to the high chloride water of the FPZ than to water from wells tapping the UZLF. The water chemistry from the UFA also varied widely. The sample from D-326 had very low concentrations of dissolved constituents and probably closely resembles recharge water. Other wells had low chloride concentrations but very high sulfate concentrations.

Saturation indexes calculated for various minerals based on water chemistry can give an indication of the residence time of water in the aquifer. All of the water samples from the FPZ were supersaturated with respect to calcite, and both crystalline and disordered dolomite, which is consistent with a long residence time. Most of the samples from the UZLF were supersaturated with respect to calcite and crystalline dolomite, and at equilibrium with respect to disordered dolomite. Wells tapping both the UZLF and the UFA and those tapping only the UFA had more diverse saturation indexes. Most were at equilibrium with respect to calcite, but dolomite saturation varied.

Hydrogeologic and geochemical data from water and aquifer samples indicate that the most likely source of mineralized water in some wells yielding water with increasing chloride concentrations is water from the FPZ. In other wells, flushing of Miocene-to-Pleistocene-age seawater can account for the observed chloride concentrations. The fact that most of the water samples collected are a mixture of less than 1 percent of the mineralized type water with more than 99 percent fresh or recharge water makes identifying the source of the mineralized water difficult. Differences in carbon-13 and sulfur-34 values probably reflect areal differences in aquifer mineralogy and distribution of organic carbon related to paleokarst features. Geochemical mass-balance models of seawater-rock interaction are unable to account for the chemical and isotopic composition of mineralized water from the FPZ, which implies another source of mineralized water, such as a brine, or the occurrence of more complex water-rock reactions.

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