Geochemical and Isotopic Composition of Ground Water with Emphasis on Sources of Sulfate in the Upper Floridan Aquifer in Parts of Marion, Sumter, and Citrus Counties, Florida

By Laura A. Sacks

U.S. Geological Survey

Water-Resources Investigations Report 95–4251

Prepared in cooperation with the
SOUTHWEST FLORIDA WATER MANAGEMENT DISTRICT

U.S. DEPARTMENT OF THE INTERIOR
MARCH 3, 1849

Tallahassee, Florida
1996

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ABBREVIATIONS, ACRONYMS, and VERTICAL DATUM

ft = feet
ft^2 = square feet
ft^3 = cubic feet
in/yr = inches per year
min = minutes
ppm = parts per million
L = liter
mL = milliliter
mmol/L = millimoles per liter
mg/L = miiligrams per liter
μg/L = microgram per liter
μm = micrometer

mi = mile
P_{CO_2} = partial pressure of carbon dioxide
δ = delta
^{34}S = sulfur-34
^{13}C = carbon-13
D = deuterium
^{18}O = oxygen-18
SI = saturation index
DO = dissolved oxygen
DOC = dissolved organic carbon
SWFWMD = Southwest Florida Water Management District
USGS = United States Geological Survey

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 the United States and Canada, formerly called Sea Level Datum of 1929.

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Abstract

In inland areas of northwest central Florida, sulfate concentrations in the Upper Floridan aquifer are extremely variable and sometimes exceed drinking water standards (250 milligrams per liter). This is unusual because the aquifer is unconfined and near the surface, allowing for active recharge. The sources of sulfate and geochemical processes controlling ground-water composition were evaluated in this area. Water was sampled from thirty-three wells in parts of Marion, Sumter, and Citrus Counties, within the Southwest Florida Water Management District; these included at least a shallow and a deep well at fifteen separate locations. Ground water was analyzed for major ions, selected trace constituents, dissolved organic carbon, and stable isotopes (sulfur-34 of sulfate and sulfide, carbon-13 of inorganic carbon, deuterium, and oxygen-18).

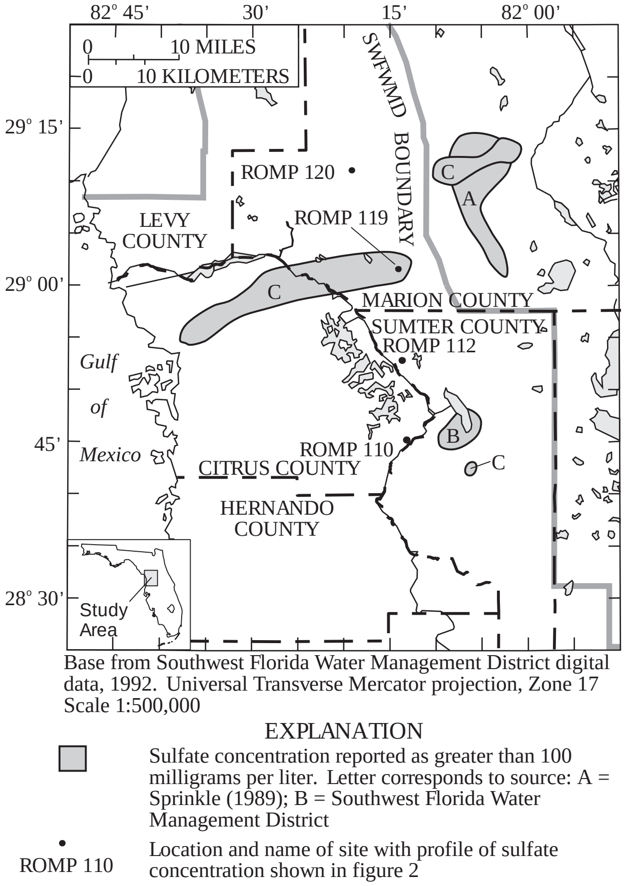
Sulfate concentrations ranged from less than 0.2 to 1,400 milligrams per liter, with higher sulfate concentrations usually in water from deeper wells. The samples can be categorized into a low sulfate group (less than 30 milligrams per liter) and a high sulfate group (greater than 30 milligrams per liter). For the high sulfate waters, concentrations of calcium and magnesium increased concurrently with sulfate. Chemical and isotopic data and mass-balance modeling indicate that the composition of high sulfate waters is controlled by dedolomitization reactions (dolomite dissolution and calcite precipitation, driven by dissolution of gypsum). Gypsum occurs deeper in the aquifer than open intervals of sampled wells. Upward flow has been documented in deeper parts of the aquifer in the study area, which may be driven by localized discharge areas or rapid flow in shallow parts of the aquifer. Mixing between shallow ground water and sulfate-rich water that dissolved gypsum at the base of the aquifer is probably responsible for the range of concentrations observed in the study area. Other solutes that increased with sulfate apparently originate from the gypsum itself, from other mineral assemblages found deeper in the aquifer in association with gypsum, and from residual seawater from less-flushed, deeper parts of the aquifer. These ions are subsequently transported with sulfate to shallower parts of the aquifer where gypsum is not present.

The composition of low sulfate ground water is controlled by differences in the extent of microbially mediated reactions, which produce carbon dioxide. This, in turn, influences the extent of calcite dissolution. Ground waters which underwent limited microbial reactions contained dissolved oxygen and were usually in ridge areas where recharge typically is rapid. Anaerobic waters were in lower lying areas of Sumter County, where soils are poorly drained and aquifer recharge is slow. Anaerobic waters had higher concentrations of calcium, bicarbonate, sulfide, dissolved organic carbon, iron, manganese, and silica, and had lower concentrations of nitrate than aerobic ground waters. For low sulfate waters,

sulfate generally originates from meteoric sources (atmospheric precipitation), with variable amounts of oxidation of reduced sulfur and sulfate reduction. Sulfide is sometimes removed from solution, probably by precipitation of a sulfide minerals such as pyrite. In areas where deep ground water has low sulfate concentrations, the shallow flow system is apparently deeper than where high sulfate concentrations occur, and upwelling of sulfate-rich water is negligible. The range of sulfate concentrations observed in the study area and differences in sulfate concentrations with depth indicate a complex interaction between shallow and deep ground-water flow systems.

INTRODUCTION

The Upper Floridan aquifer is a major source of drinking water for the state of Florida. Water in the aquifer is often nonpotable in coastal areas because sulfate concentrations exceed 250 mg/L (milligrams per liter). Sulfate concentrations are usually low in inland areas, particularly where the aquifer is unconfined. High sulfate concentrations, however, do occur in isolated locations of inland northwest central Florida (fig. 1). High concentrations in these areas are unusual because the aquifer is unconfined and near the surface and because this is primarily an aquifer recharge area. A better understanding of sulfate sources in inland areas is important because increased ground-water development could induce movement of this high sulfate water to fresher parts of the aquifer.



Base from Southwest Florida Water Management District digital data, 1992. Universal Transverse Mercator projection, Zone 17
Scale 1:500,000

EXPLANATION

▨ Sulfate concentration reported as greater than 100 milligrams per liter. Letter corresponds to source: A = Sprinkle (1989); B = Southwest Florida Water Management District

• ROMP 110 Location and name of site with profile of sulfate concentration shown in figure 2

Figure 1. Study area of northwest central Florida and inland locations where sulfate concentrations have been reported as greater than 100 milligrams per liter in water from the Upper Floridan aquifer. (Modified from Sprinkle, 1989; Southwest Florida Water Management District, 1991; and Katz, 1992.)

Several sources of sulfate exist in the aquifer. The most apparent source is dissolution of evaporite minerals (gypsum and anhydrite), which are found at the base of the Upper Floridan aquifer or in the underlying middle confining unit and Lower Floridan aquifer. This source requires an upward movement of water because the occurrence of evaporites are considerably deeper than zones in which drinking water wells are finished. Trace evaporites have not been observed in well cuttings or cores in shallow parts of the aquifer. Saltwater mixing is not a likely source of sulfate in inland areas because chloride concentrations are low (less than 50 mg/L). Other possible sources include oxidation of sulfide minerals, such as pyrite, or diffusion of sulfate from clays in overlying beds. Surficial sources of sulfate include meteoric rainwater that contains sulfate, oxidation of organic sulfur, and anthropogenic sources such as fertilizers applied in the form of sulfate salts. Sulfate in rainwater originates primarily from marine aerosols and oxidation of reduced sulfur from natural and anthropogenic sources.

Sulfur isotope data collected in a regional study of the Upper Floridan aquifer were used successfully to delineate sulfate sources on a regional scale (Rightmire and others, 1974; Rye and others, 1981). For the most part, low sulfate concentrations (less than 100 mg/L) and isotopically light sulfate were found in the aquifer recharge area and were attributed to atmospheric precipitation. Downgradient and in confined parts of the aquifer, isotopically heavier sulfate was attributed to gypsum dissolution and marine sulfate. This regional study did not examine the localized occurrences of high sulfate ground water in the recharge area or the vertical variability of sulfur sources in the aquifer.

Water from the Upper Floridan aquifer is chemically stratified in central and northwest peninsular Florida, with higher sulfate concentrations found deeper in the aquifer (Faulkner, 1973; Sprinkle, 1989; Southwest Florida Water Management District, 1991; Katz, 1992). Faulkner (1973) attributed higher sulfate concentrations in deeper ground water to an increase in gypsum and anhydrite in rocks found deeper in the aquifer. This deeper ground water is part of a slower, regional flow system with a longer aquifer residence time than the rapid, shallow flow system that discharges to springs. Southwest Florida Water Management District (1991) hypothesized that this high sulfate water moves upward in areas of low aquifer recharge, assisted by preferential flow through fractures and faults.

Although the chemical stratification of sulfate has been recognized, very little data exist on detailed chemical profiles in the aquifer in northwest central Florida. Water quality data collected during coring and drilling of several sites by Southwest Florida Water Management District (written commun., 1993) demonstrate how variable the increase in sulfate with depth is in this region (fig. 2). Sometimes sulfate concentrations increase rapidly with depth (for example, ROMP 110), but other times sulfate concentrations remain relatively low in the deeper part of the aquifer (for example, ROMP 120; fig. 2). This variability suggests that sulfate concentrations and sources vary both vertically and laterally in the aquifer.

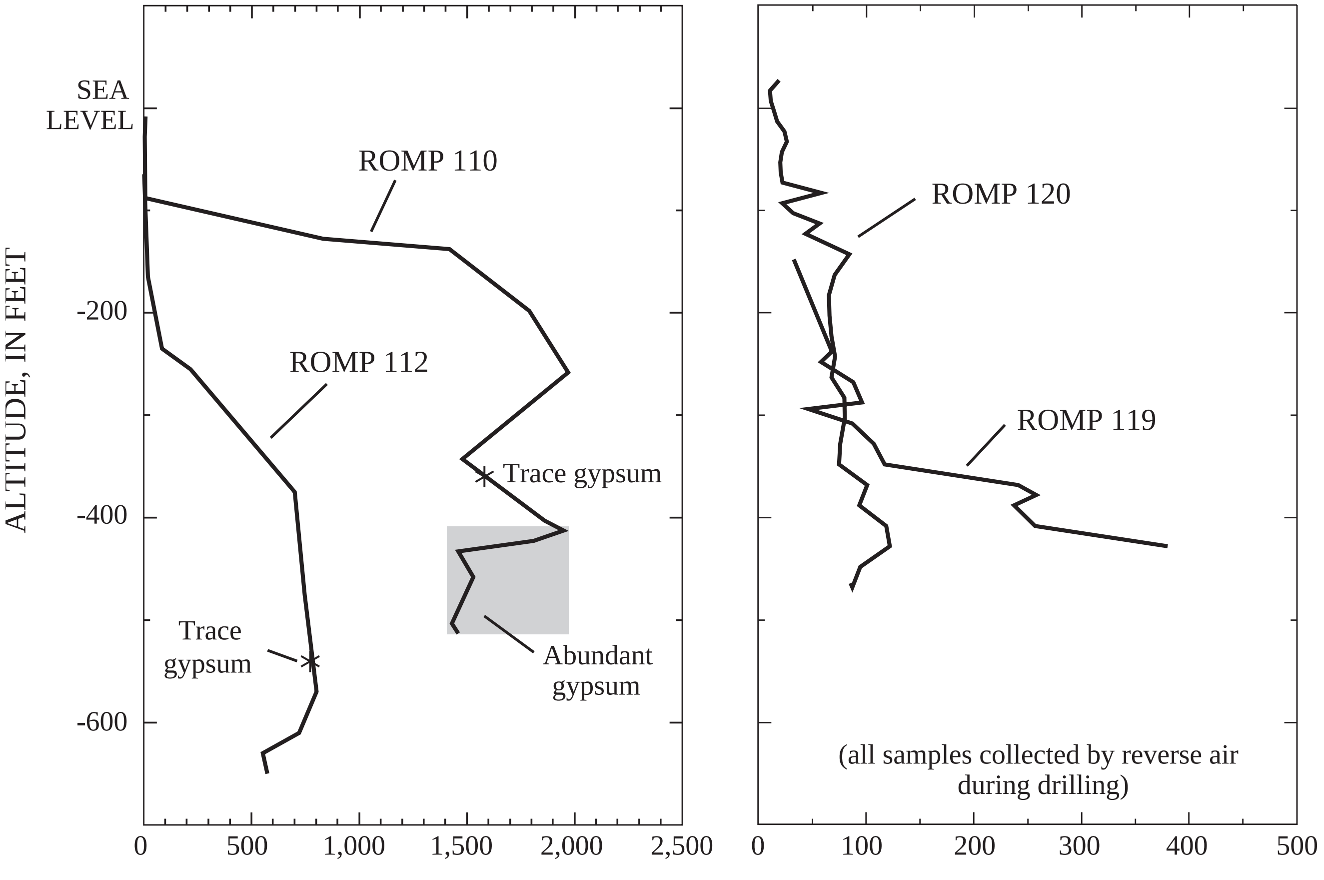


Figure 2. Profiles of sulfate concentrations in ground water from the Upper Floridan aquifer, as part of the Southwest Florida Water Management District's Regional Observation and Monitoring Program (ROMP). (Locations of sites shown in figure 1.)

The depth of freshwater resources in the unconfined aquifer is often assumed to be the thickness of the Upper Floridan aquifer (Causey and Levy, 1976; Ryder, 1985). However, the occurrence of high sulfate concentrations at relatively shallow depths results in a significantly shallower zone of potable water (Jones and Upchurch, 1994, pg. 78). Population growth in Marion and Citrus Counties will undoubtedly result in increased development of ground-water resources. In addition, fresh water resources in these counties are being considered as supplemental water supplies for water-stressed west-central Florida. A better understanding of the sources of sulfate will help water managers more judiciously develop water resources.

In 1991, the U.S. Geological Survey (USGS) began a cooperative study with the Southwest Florida Water Management District (SWFWMD) to evaluate sulfate sources in the Upper Floridan aquifer in two separate areas of the water management district. One area is in the northern part of the District, in parts of Marion, Sumter, and Citrus counties where isolated high sulfate concentrations have been observed (fig. 1). The other study area is south of Tampa Bay in the confined part of the aquifer. This report focuses on the northern study area.

Purpose and Scope

The purpose of this report is to provide additional information regarding areal and vertical distribution of sulfate in an unconfined part of the Upper Floridan aquifer, and to evaluate sources of sulfate and geochemical processes controlling ground-water composition in the aquifer. During 1992 and 1993, water was sampled from thirty-three wells in parts of Marion, Sumter, and Citrus Counties, within the SWFWMD boundaries. These included at least a shallow and deep well at fifteen separate locations. The sampling locations bracket an area where sulfate concentrations have been reported to be variable (Southwest Florida Water Management District, 1991). Ground water was sampled for major ions, selected trace elements, dissolved organic carbon, field parameters (temperature, pH, specific conductance, dissolved oxygen, alkalinity, sulfide), and stable isotopes (sulfur-34, deuterium, oxygen-18, carbon-13). The sources of sulfate and controls on chemical and isotopic composition of water were evaluated; hypotheses about reactions were examined using geochemical mass-balance modeling.

Acknowledgments

Well selection and sampling efforts depended upon the generous assistance of many individuals at the SWFWMD, including personnel from the Ambient Ground-Water Quality Monitoring Program, Regional Observation and Monitoring Program (ROMP), Resource Data Department, and Well Permitting Department. The author also would like to extend thanks to well owners, local water utility departments (Cities of Bushnell and Coleman), and local well drillers for allowing us to sample and for providing us with specific information about the wells. Rock core analyzed for this study was provided by the Florida Geological Survey. Shelley Kauffman, University of Virginia, prepared vials and provided equipment to determine presence of sulfate reducing bacteria.

GEOLOGIC AND HYDROLOGIC SETTING

The geology and hydrology of the study area are intricately associated because of the proximity of limestone to land surface and high aquifer recharge rates. Limestone in the shallow part of the Upper Floridan aquifer is highly karstified and the amount of surface-water drainage in the study area is limited. The study area falls primarily within the Withlacoochee River Basin. The hydrology and shallow geology of the study area have been studied in detail because the proposed, but now-defunct, Cross Florida Barge Canal intersected the study area (Faulkner, 1973).

Stratigraphy

The study area is underlain by approximately 4,000 ft of limestones, dolomites and evaporites (gypsum and anhydrite), ranging in age from Cretaceous to Eocene. These rocks overlie deeper volcanic, metamorphic, and Mesozoic sedimentary rocks (Vernon, 1951; Applin and Applin, 1965; Smith, 1982). Of interest in this study are the upper 2,000 ft of Tertiary age rocks, which constitute the Floridan aquifer system (table 1). The base of the Cedar Keys Formation of Paleocene age occurs at about 2,000 ft below sea level. Rocks of the Cedar Keys consist of dolomite with variable amounts of gypsum and anhydrite. The base of the Floridan aquifer system occurs in areally extensive, thick anhydrite beds in the lower two-thirds of this formation (Miller, 1986). Overlying the Cedar Keys Formation is the Oldsmar Formation of early Eocene age, which is composed of limestones, dolomites, and thin beds of evaporites and chert.

Table 1. Relation between stratagraphic and hydrogeologic units.

<table>
<tr><th>System</th><th>Series</th><th>Stratigraphic Unit</th><th>General Lithology</th><th colspan="2">Hydrogeologic Unit</th></tr>
<tr><td>Quaternary</td><td>Holocene and Pleistocene</td><td>Alluvium and terrace deposits</td><td>Sands and clays</td><td colspan="2">Surficial aquifer system</td></tr>
<tr><td rowspan="7">Tertiary</td><td>Pliocene</td><td>Alachua Formation</td><td>Phosphatic sands and clays</td><td colspan="2" rowspan="2">(Of limited areal extent in study area)</td></tr>
<tr><td>Miocene</td><td>Hawthorn Group[1]</td><td>Phosphatic sands, and clays</td></tr>
<tr><td rowspan="4">Eocene</td><td>Ocala Limestone</td><td>Limestone, fossiliferous to micritic</td><td rowspan="5">Floridan aquifer system</td><td rowspan="2">Upper S
Floridan D
aquifer</td></tr>
<tr><td rowspan="2">Avon Park Formation</td><td>Upper part, limestone and dolostone</td></tr>
<tr><td>Lower part, dolomite with intergranular gypsum; some bedded gypsum, peat and chert</td><td>Middle confining unit</td></tr>
<tr><td>Oldsmar Formation</td><td>Limestone and dolomite; some evaporites and chert</td><td rowspan="2">Lower Floridan aquifer</td></tr>
<tr><td>Paleocene</td><td>Cedar Keys Formation</td><td>Dolomite with evaporites</td></tr>
</table>

[1] Based on nomenclature of Scott (1988)

▨ Typical open intervals of shallow (S) and deep (D) wells

In the study area, water wells are drilled into the upper part of the Avon Park Formation of middle Eocene age and the Ocala Limestone of late Eocene age, which make up the Upper Floridan aquifer (table 1). The lower part of the Avon Park Formation (formerly the Lake City Limestone; Miller, 1986) consists primarily of dolomite, with intergranular gypsum and beds of anhydrite, peat, and chert occurring in some locations. The upper part of the Avon Park also is usually dolomitized, although sometimes it consists of limestone; evaporites presumably are not present.

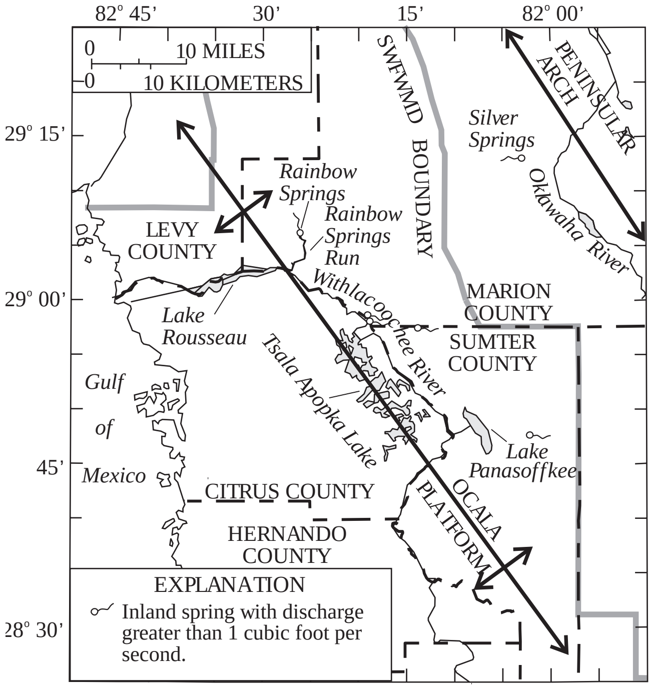
The Avon Park Formation was deposited in a peritidal warm-water carbonate bank. Evaporites were probably formed in a tidal flat or sabkha environment in an arid climate analogous to the modern Persian Gulf (Miller, 1986; Randazzo and others 1990; Cander, 1991). Sometimes evaporites are bedded, but in other places they occur as nodules or secondary infilling of preexisting pore spaces in the rock. Evaporite deposits are not continuous and probably were formed in isolated evaporative basins on a carbonate bank separated from the shallow sea. Thin evaporite beds probably fragmented when carbonate deposition resumed, and these fragments were then incorporated into the host rock as nodules. Some of these nodules have an outer core of gypsum and a central core of anhydrite (Hickey, 1990). Secondary gypsum results in significantly reduced permeability. It is generally thought that dolomitization occurred not long after deposition in the middle Eocene by a platform-wide influx of normal to hypersaline seawater (Faulkner, 1973; Cander, 1991). Multiple dolomitization episodes, however, probably occurred. Some of the dolomite probably formed in freshwater/saltwater mixing zones at later times (Hanshaw and Back, 1972; Randazzo and Hickey, 1978; Cander, 1991).

The contact between the Avon Park and the overlying Ocala Limestone is an erosional unconformity that generally occurs at an elevation between 80 ft below sea level to several feet above sea level (Faulkner, 1973; Miller, 1986; Campbell, 1989). In southwest Marion County and bordering Levy County, the Ocala Limestone has been completely removed by erosion, and the Avon Park Formation is the uppermost carbonate rock unit. The Ocala Limestone generally is composed of soft, fossiliferous to micritic limestone (Faulkner, 1973; Miller, 1986). Lower parts of the Ocala may be locally dolomitized. Thin, irregular zones of chert of limited areal extent are sometimes present. The Ocala Limestone was formed in a shallow, open to marginal marine environment (Miller, 1986; Randazzo and others, 1990). Evaporite minerals are not present in the Ocala Limestone because of better open-water circulation and possibly a more humid climate than when the Avon Park was deposited. Upper parts of the Ocala have been eroded in much of the study area, and the unit is much thinner than in other parts of Florida. The Ocala Limestone is very permeable with well developed secondary porosity and a highly irregular karstified surface.

The Ocala Limestone is overlain by clastics of Miocene to Holocene age, which range in thickness from less than 10 ft to greater than 100 ft on the ridges. Most of these deposits are undifferentiated sands; however, the Hawthorn Group and Alachua Formation are present in isolated parts of the study area. The Hawthorn Group of early Miocene age, which is present in much of peninsular Florida (Scott, 1988), is absent in the study area except for a few erosional remnants associated with ridges, usually in Marion County (Faulkner, 1973; Brooks, 1981). These deposits generally consist of phosphatic sands, clayey sands, and clays. The Alachua Formation of Miocene to Pliocene age is found beneath the Brooksville Ridge in Citrus County. This unit is composed of irregularly interbedded clays, sands, sandy clays, and phosphate (Vernon, 1951; Olson, 1972; Faulkner, 1973). The origin of the Alachua is unresolved, but it probably represents a complex depositional environment, incorporating eroded and reworked Hawthorn Group sediments (Scott, 1988).

Structure

The most significant structural feature in the study area is the Ocala Platform (also called the Ocala Uplift and the Ocala High), which is a broad structural high in rocks of middle Eocene and younger ages (fig. 3). This feature was produced by sedimentational processes, rather than tectonic processes, but the mechanisms responsible for producing this high are not understood (Winston, 1976; Miller, 1986). Because this area has been a structural high since the middle Eocene, it has undergone increased erosional activity over other parts of the Florida Peninsula. The Avon Park Formation is closer to land surface than in any other location, and the Ocala Limestone has undergone much erosion and is completely eroded in parts of southwest Marion County and neighboring Levy County. If Oligocene and Miocene age rocks were originally deposited over the study area, they have been almost completely eroded. Karst landscapes are well developed in the area of the Ocala Platform because of the presence of carbonate rocks near land surface and a poorly consolidated overburden (Schmidt and Scott, 1984).



Base from Southwest Florida Water Management District digital data, 1992. Universal Transverse Mercator projection, Zone 17
Scale 1:500,000

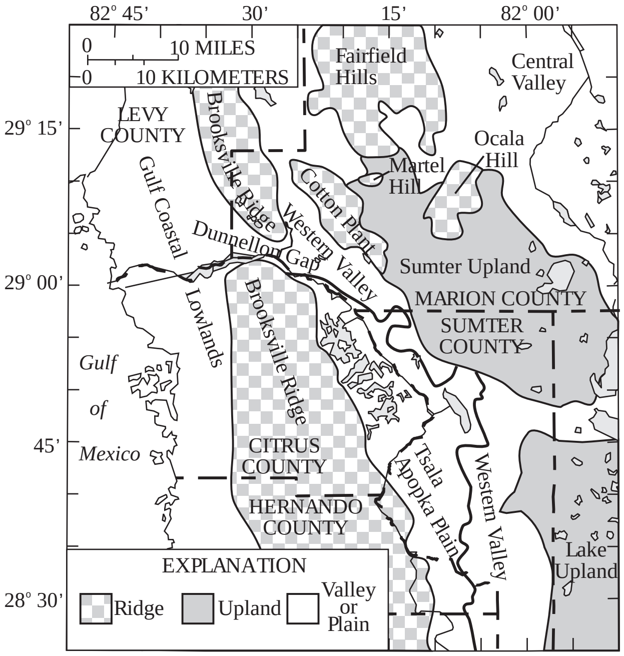
Figure 3. Large-scale structural features in the study area, and locations of major surface-water bodies and inland springs. (Modified from Faulkner, 1973; and Miller and others, 1981.)

Numerous faults and fractures have been mapped in the region of the Ocala Platform that are probably associated with this structural high (Vernon, 1951; Faulkner, 1973). These faults and fractures have trends that are parallel (northwest to southeast) and perpendicular (northeast to southwest) to the main axis of the Ocala Platform. In Marion County, cavern systems have developed in the Ocala Limestone that are oriented in these same directions, indicating preferential limestone dissolution along these fracture systems (Faulkner, 1973; Phelps, 1994). The locations of Lake Panasoffkee and the Withlacoochee River along the Citrus/Sumter County line also follow these same trends (fig. 3), and their locations may similarly be related to preferential dissolution of carbonates at fault or fracture planes (Southwest Florida Water Management District, 1991).

To the east of the Ocala Platform is the Peninsular arch, a northwest trending feature that is much older than the Ocala Platform. This feature has been intermittently positive from the Mesozoic time through the Cenozoic, and is apparently an upwarp produced by compressional tectonics (Miller, 1986). The study area is along the western flank of the Peninsular arch (fig. 3).

Physiography and Surface Water

Changing sea levels, differential erosion, and karst processes control current landform features in the study area. Topographically high areas generally correspond to erosional remnants and ancient ridges from higher sea level stands (White, 1970; Brooks, 1981). Resistant clays may be partly responsible for the preservation of these relict highlands. In the study area, upland areas consist of the Brooksville Ridge, the Sumter Upland, and, of lesser extent, the Cotton Plant Ridge, Martel Hill, and Ocala Hill in Marion County (fig. 4). The soils in these upland areas are excessively to well drained, resulting in minimal surface water other than isolated ponds (Soil Conservation Service, 1979; 1988a).



Base from Southwest Florida Water Management District digital data, 1992. Universal Transverse Mercator projection, Zone 17
Scale 1:500,000

Figure 4. Physiographic features in the study area. (Modified from White, 1970; and Miller and others, 1981.)

Lower lying areas include the Tsala Apopka Plain and the Western Valley, which cover eastern Citrus County and most of the study area in Sumter County (fig. 4). Poorly drained soils result in numerous ponds and lakes (Soil Conservation Service, 1988a; 1988b). The low elevation of the Western Valley is attributed to mature karst erosional cycles and a lack of resistant clays (White, 1970). The very flat expanse and lower elevation of the Tsala Apopka Plain probably formed from a large lake that once covered the area (White, 1958; 1970). Lake Panasoffkee, the Tsala Apopka chain of lakes, and the Withlacoochee River are in low lying areas of this plain.

The Withlacoochee River is the dominant surface drainage in the study area (fig. 3). This river originates in the Green Swamp to the southeast of the study area, in an area with low aquifer transmissivity and minimal aquifer recharge (Ryder, 1985; Swancar and Hutchinson, 1995). The Dunnellon Gap, which cuts through the Brooksville Ridge, is the outlet of the Withlacoochee River to the Gulf of Mexico (fig. 4). White (1958) concluded that this gap is relatively recent, and at one time the Withlacoochee River flowed southward toward Tampa Bay. The present course of the river probably follows solution channels in the limestone that may represent a fracture or fault trace (Faulkner, 1973). The Withlacoochee River is dammed to the west of the gap and forms Lake Rousseau, which was constructed to be part of the Cross Florida Barge Canal.

The area has several inland springs that discharge more than 1 ft^3/s (Rosenau and others, 1977; Miller and others, 1981; fig. 3). Rainbow Springs, in southwest Marion County, is the largest spring and discharges over 500 ft^3/s. Dissolved solids and tritium data from Rainbow Springs indicate that the springs discharge relatively recent ground water from shallow parts of the aquifer (Faulkner, 1973). Increased specific conductance along Rainbow Springs Run has been attributed to additional spring flow, which may have a contribution from deeper zones in the aquifer than discharge to Rainbow Springs (Jones and others, in press). Most of the other springs in the study area drain into the Withlacoochee River or Lake Panasoffkee and have not been studied in detail.

Hydrogeology

The water table usually occurs within the surficial deposits, and these saturated clastics constitute the surficial aquifer system. Clay beds generally are not thick enough to establish a confining unit, and water percolates from the surficial aquifer system into the underlying Upper Floridan aquifer. Clays of the Alachua Formation beneath the Brooksville Ridge may semiconfine the Floridan aquifer system (Miller, 1986), although variability in lithologic logs does not support a continuous confining unit.

The Floridan aquifer system is defined as a vertically continuous sequence of carbonate rocks of high permeability and regional extent (Miller, 1986). In the study area it is separated by a middle confining unit into the Upper and Lower Floridan aquifers (table 1). The middle confining unit corresponds to low permeability gypsiferous dolomite and dolomitic limestone. This unit usually is within the middle to lower part of the Avon Park Formation at an elevation between 500 and 800 ft below sea level (Miller, 1986). The hydraulic conductivity of the middle confining unit (0.01 to 0.1 ft/d; Hickey, 1990) is many orders of magnitude lower than in the overlying Upper Floridan aquifer. However, the degree of confinement is not well understood. Miller (1986) describes the middle confining unit as a “nonleaky confining bed,” whereas Hickey (1990) concludes that its confining properties may be more analogous to a fine-grained sandstone than a compact clay bed. Beneath the middle confining unit, the Lower Floridan aquifer is rarely drilled into because of its poor quality water and is not utilized in the study area.

The top of the Upper Floridan aquifer usually corresponds to the surface of the Ocala Limestone (table 1), although in places the aquifer surface is very irregular and the first carbonate rock unit encountered is the deeper Avon Park Formation. The Ocala Limestone is more permeable than the Avon Park Formation because of more extensive development of secondary porosity (Faulkner, 1973). The Upper Floridan aquifer is the principle water supply for most of the study area, and large quantities of good quality water usually can be produced at relatively shallow depths.

Shallow and deep ground-water flow systems occur in the Upper Floridan aquifer in the study area (Faulkner, 1973; Ryder, 1985; Bush and Johnston, 1988). The shallow flow system discharges to local springs and rivers. Much of this flow takes place in conduits through well-developed secondary porosity in the limestone, with a short aquifer residence time. Deeper ground water is part of a more sluggish regional flow system that bypasses local discharge areas and discharges near or offshore of the coast (fig. 5).

Maps of recharge and discharge areas and of the potentiometric surface of the Upper Floridan aquifer do not differentiate between these shallow and deep flow systems. Most of the study region is an aquifer recharge area (Anderson and Laughlin, 1982). Upland parts of Citrus and Marion Counties have somewhat higher aquifer recharge rates (10 to 20 in/yr) than lower lying parts of Sumter County (1 to 10 in/yr) (Ryder, 1985; Aucott, 1988). Discharge areas are focused in narrow areas around the Withlacoochee River and Lake Panasoffkee. Localized discharge also occurs at springs.

The direction of ground-water flow is controlled by a high in the potentiometric surface in the Green Swamp in southeast Sumter County. Ground water flows west-northwest from southern Sumter County toward the Withlacoochee River, and then flows westward in Citrus County toward the coast (fig. 6). The high in the potentiometric surface and relatively steep hydraulic gradient in Sumter County are due to relatively low aquifer transmissivity in this area (50,000 to 500,000 ft^2/d), compared to parts of Citrus and Marion Counties, where aquifer transmissivity is greater than 1,000,000 ft^2/d (Ryder, 1985). In Marion County, the potentiometric surface is very flat, and recharge dissipates rapidly because of the high aquifer transmissivity. A saddle occurs in the potentiometric surface in central Marion County, where regional ground water converges from highs in the potentiometric surface to the north and south. Flow from there is either west or southwest toward the Withlacoochee River and Rainbow Springs or eastward toward Silver Springs.

Very little information exists about head distribution with depth in this part of the Upper Floridan aquifer. It is often assumed that vertical hydraulic gradients in the aquifer are minimal (Faulkner, 1973). Head distribution data are available for three wells finished at separate depths in the aquifer near Lake Panasoffkee (ROMP LP-4; Southwest Florida Water Management District, written commun., 1994; fig. 7). At this site, an upward head gradient occurs between deeper and shallower zones in the Avon Park Formation. The head in the well finished in the Ocala Limestone, however, is usually higher than the well completed in the upper part of the Avon Park Formation, indicating recharge or downward flow.

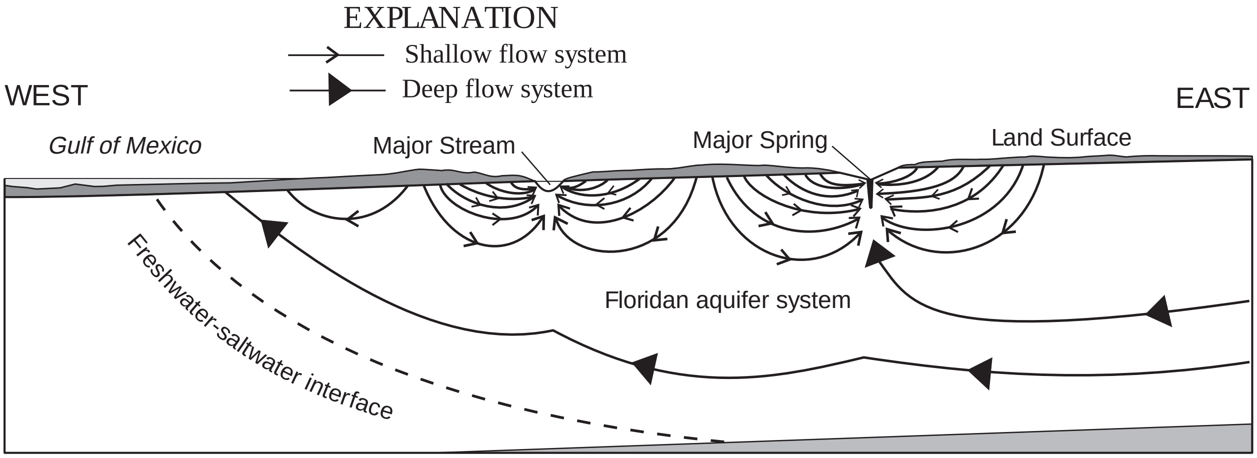
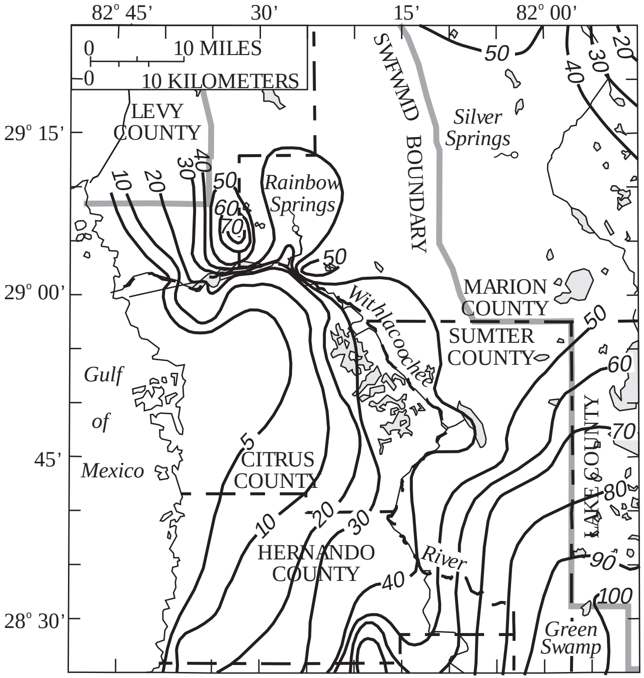


Figure 5. Idealized flow patterns in the Upper Floridan aquifer between north-central Florida and the Gulf Coast. (Modified from Bush and Johnston, 1988.)



Base from Southwest Florida Water Management District digital data, 1992. Universal Transverse Mercator projection, Zone 17
Scale 1:500,000

EXPLANATION

–10– POTENTIOMETRIC CONTOUR -- Shows altitude of potentiometric surface of Upper Floridan aquifer, May 1993. Datum is sea level. Contour interval is 5 and 10 feet.

Figure 6. Potentiometric surface of the Upper Floridan aquifer, May 1993. (Modified from Halford and others, 1993; and Mularoni, 1994.)

Mineralogical Data

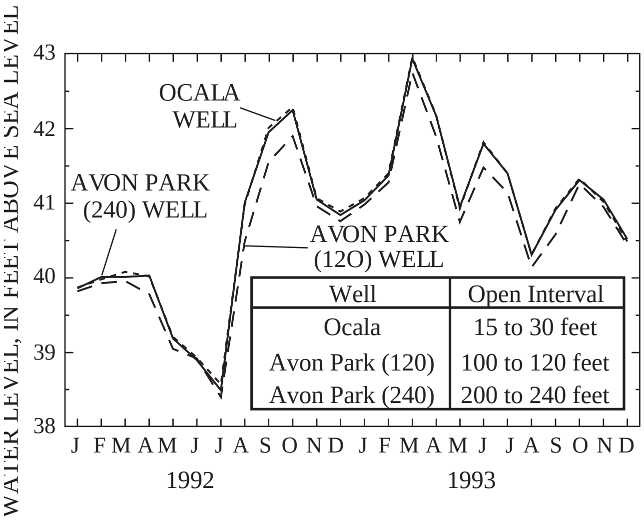
Mineralogy and the chemical and isotopic composition of major minerals in the aquifer were evaluated to assist in interpreting ground-water chemical and isotopic data. The mineralogy of the aquifer has been well defined in previous studies, with a thorough summary by Sprinkle (1989). Calcite and dolomite are, by far, the dominant minerals in the aquifer. Most of the calcite ranges from pure $CaCO_3$ to low magnesian calcite (less than 2 mole percent magnesium; Hanshaw and others, 1971). Dolomites range in composition from stoichiometric dolomite ($CaMg(CO_3)_2$) to $Ca_{1.12}Mg_{0.88}(CO_3)_2$ (Hanshaw and others, 1971; Randazzo and Hickey, 1978). This variability in dolomite composition probably influences its solubility in ground water (Sprinkle, 1989). Minor minerals in the aquifer include gypsum ($CaSO_4{\cdot}2H_2O$) and anhydrite ($CaSO_4$) in deeper zones of the aquifer, quartz and chert, apatite, clay minerals (kaolinite, glauconite, and possibly montmorillonite), potassium feldspar, and metallic oxides and sulfides (for example, goethite and pyrite); localized thin beds of peat also occur within the aquifer (Fischer, 1953; Hanshaw and others, 1971; Sprinkle, 1989; Katz and others, 1995b).

Carbonate Minerals

For mass-transfer modeling, it is necessary to define the stable carbon isotopic composition (^{13}C) of the carbonate minerals that interact with the ground water. Isotopic data are reported as ratios of the heavy to the light isotope (for example, $^{13}C/^{12}C$), relative to a standard, in delta (δ) notation:

$$\delta_{\text{sample}} = 1000\,[(R_{\text{sample}}/R_{\text{std}}) - 1], \tag{1}$$

where R_{sample} and R_{std} are the ratio of the heavy to the light isotope in the sample and in the standard, respectively. Standards used in this report are Pee Dee belemnite (PDB) for carbon ($\delta^{13}C$), Cañon Diablo troilite (CDT) for sulfur ($\delta^{34}S$), and Standard Mean Ocean Water (SMOW) for hydrogen (δD) and oxygen ($\delta^{18}O$). Units are in parts per thousand, denoted as “per mil.”



Well	Open Interval
Ocala	15 to 30 feet
Avon Park (120)	100 to 120 feet
Avon Park (240)	200 to 240 feet

Figure 7. Water levels in wells finished at different depths in the Upper Floridan at ROMP LP-4, near Lake Panasoffkee. (Data from Southwest Florida Water Management District; well locations shown in figure 8; index numbers referenced in table 3.)

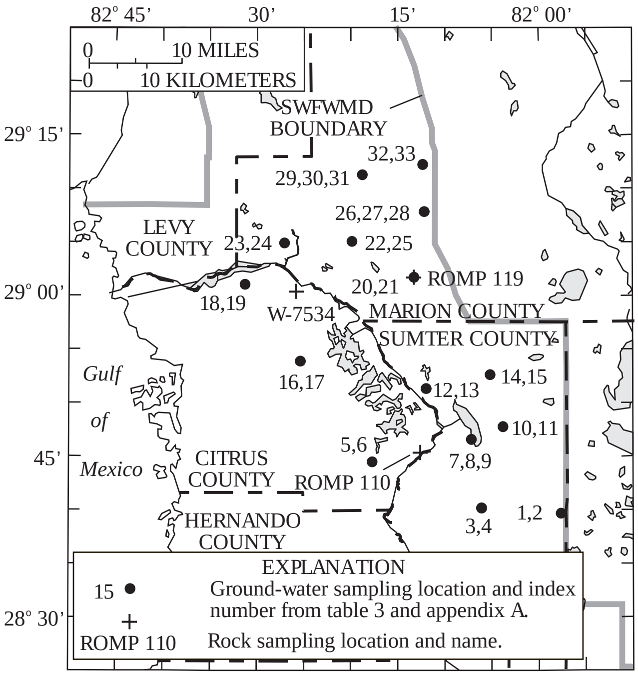
The δ^{13}C composition of calcite and dolomite from the aquifer has been determined in previous studies to evaluate water-rock interactions in the aquifer and to better understand dolomitization and diagenetic processes (Hanshaw and Back, 1972; Cander, 1991). Values near 0 per mil are typical for marine carbonates. Most reported δ^{13}C values for calcite are near 0 per mil, and range between -0.4 and 3.1 per mil in the aquifer (Hanshaw and Back 1972; Sprinkle, 1989; Cander, 1991). The range of reported δ^{13}C for dolomite is considerably greater than for calcite, between -7.5 and 1.0 per mil (Hanshaw and Back 1972; Sprinkle, 1989; Cander, 1991). Hanshaw and Back (1972) noted two groupings of dolomite based on isotopic composition, one which was near seawater composition and the other which was isotopically lighter than seawater (between -7.5 and -2.8 per mil). Lighter dolomites were hypothesized as forming in the saltwater mixing zone.

Two calcite and two dolomite samples were analyzed for this study in order to obtain specific information from the study area. The calcite samples were from the Ocala Limestone from ROMP 110 (59 ft) and ROMP 119 (70 to 75 ft; fig. 1). The δ^{13}C values for calcite were within ranges of previous work: 1.2 per mil for ROMP 110 and -0.4 per mil for ROMP 119. Dolomite samples from the Avon Park Formation at these same sites also were analyzed; x-ray diffraction analysis verified that dolomite was the only carbonate mineral present in the sample (John M. Neil, U.S. Geological Survey, written commun., 1994). The isotopic composition of carbon from the dolomite samples were very similar to each other: 0.3 per mil for ROMP 110 (469 ft) and 0.4 per mil for ROMP 119 (490 to 495 ft; within the open interval of the sampled well). These values are similar to seawater composition but differ from the isotopically light carbon observed by Hanshaw and Back (1972).

Gypsum

Gypsum and anhydrite have not been reported from the upper part of the aquifer (within the Ocala Limestone and upper part of the Avon Park Formation). However, gypsum becomes more abundant at the base of the aquifer and within the middle confining unit, which corresponds to the middle to lower part of the Avon Park Formation. Because gypsum is a probable source for sulfate in the ground water, the isotopic and trace element composition of gypsum from the middle confining unit was evaluated.

Limited data are available for the sulfur isotope composition of gypsum from the Floridan aquifer system (Rye and others, 1981; Sprinkle, 1989), and they range from 18.9 to 23.2 per mil. From within the study area, two additional gypsum samples from the Avon Park Formation (within the middle confining unit) were analyzed. These samples were both from eastern Citrus County (ROMP 110 from 486 ft and W-7534 from 795 ft) (fig. 8). The δ^{34}S values for these samples were very similar (24.5 per mil for ROMP 110 and 24.0 per mil for W-7534; analytical uncertainty is assumed to be 0.5 per mil). This is slightly heavier than previously reported $\delta^{34}S_{gypsum}$ values from the aquifer; however, these differences may be due to changes in extraction procedures and calibration standards since the early 1980's (W.C. Shanks, U.S. Geological Survey, written commun., 1995; Rees and others, 1978).



Base from Southwest Florida Water Management District digital data, 1992. Universal Transverse Mercator projection, Zone 17
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Figure 8. Ground-water and rock sampling locations.

The δ^{34}S of gypsum also is isotopically heavier than expected for evaporites deposited from Eocene seawater (about 20 per mil; Claypool and others, 1980). Gypsum that is isotopically heavier than seawater probably is the result of localized sulfate reduction in brines from which the gypsum precipitated. Sulfur is fractionated during sulfate reduction. The reduced sulfur is enriched in the lighter isotope (sulfur-32), and isotopically heavier sulfate remains in solution. In the ROMP 110 core, zones of pyrite, organics, and plant remains are reported in the same and nearby depth intervals as the gypsum sample (Southwest Florida Water Management District, written commun., 1992). This indicates that anaerobic conditions were present, although it is not known if these sediments were anaerobic at the time gypsum precipitated. Attempts to analyze the isotopic composition of sulfur in the pyrite and peat were unsuccessful because sample sizes were too small (W.C. Shanks, U.S. Geological Survey, written commun., 1994).

Gypsum samples from the Floridan aquifer system in southwest Florida were analyzed for $\delta^{34}S$, as part of a related study. Values of $\delta^{34}S_{gypsum}$ in the Avon Park Formation (within the middle confining unit) ranged from 20.0 to 24.8 per mil. Deeper samples from the underlying Oldsmar and Cedar Keys Formations (Lower Floridan aquifer and lower confining unit) also were analyzed and were slightly lighter, ranging from 19.4 to 21.2 per mil.

Gypsum often contains trace amounts of other ions that can substitute for calcium in normal lattice sites or reside in interstitial positions (Kushnir, 1980). Data were not available on trace element concentrations in gypsum and anhydrite from the Floridan aquifer system (Sprinkle, 1989). Thus, in order to estimate concentrations of other elements present in gypsum, the ROMP 110 gypsum sample from the middle confining unit was analyzed for selected trace elements. A visually pure sample of gypsum was crushed with a mortal and pestle, dried in a desiccator, and precisely weighed. Then, the gypsum was dissolved with a known volume of deionized water, acidified with 1 mL of 70 percent hydrochloric acid, and analyzed for dissolved cations and trace metals. An unacidified sample was analyzed for sulfate concentration to compare with the theoretical weight percent expected for gypsum and anhydrite. This can be used as an indicator of sample purity. The concentrations of dissolved constituents were related to ppm based on the original sample weight. Strontium was the most abundant trace element, with a concentration of 850 ppm (table 2). Other minor (less than 500 ppm) trace elements detected in the gypsum included magnesium, sodium, barium, aluminum, lithium, and iron. Data from six additional gypsum samples from the Floridan aquifer system from southwest Florida (part of a related study) also are summarized in table 2.

Table 2. Concentrations of selected constituents in gypsum

[ppm, parts per million; %, percent; concentrations determined by dissolving visually pure sample of known weight into known volume of deionized water and analyzing water sample at laboratory using standard methods of Fishman and Friedman (1989); potassium, silica, and manganese all less than detection limit of 90, 9, and 1 ppm, respectively]

Constituent	Reporting unit	ROMP 110 (486 ft)	Range of samples from southwest Florida[1]		Detection limit	Mean difference between replicate analyses[2]
			Minimum	Maximum		
Magnesium	ppm	480	120	1,400	90	28
Sodium	ppm	140	90	380	90	21
Barium	ppm	82	7	58	2	32
Iron	ppm	25	5	32	4	6
Strontium	ppm	850	480	2,000	1	310
Aluminum	ppm	59	43	200	18	51
Lithium	ppm	27	5	40	4	18
Calcium[3]	weight %	23	9	31	0.01	2.0
Sulfate[4]	weight %	55	56	75	0.01	1.6

[1] Six gypsum samples from Floridan aquifer system (unpublished data).

[2] For two sets of replicate analyses from southwest Florida (unpublished data).

[3] Theoretical weight percent is 23 for gypsum ($CaSO_4$•H_2O) and 29 for anhydrite ($CaSO_4$).

[4] Theoretical weight percent is 56 for gypsum and 71 for anhydrite.

GEOCHEMICAL AND ISOTOPIC COMPOSITION OF GROUND WATER

Water samples were collected from shallow and deep wells to assess the areal and vertical distribution of sulfate in the Upper Floridan aquifer. Chemical and isotopic data were used to evaluate geochemical and isotopic controls on ground-water composition and to assess sulfate sources in the aquifer. Well sampling locations bracketed the area where high sulfate concentrations were reported by Southwest Florida Water Management District (1991).

Sampling Methods

Well selection was based on spatial and vertical coverage within the aquifer. Although stratigraphic data were not available for most wells, shallow wells were usually finished near the top of the aquifer and are assumed to be in the Ocala Limestone; deep wells were assumed to be finished in the Avon Park Formation, based on the nearest stratigraphic control point (Southwest Florida Water Management District, written commun., 1993). Deep and shallow wells were sampled in the same general location. Because of the abundance of good quality water at shallow depths, most water wells in the study area are relatively shallow. Thus, sampling locations were limited by availability of deep wells. “Deep” wells had highly variable depths, depending upon local well availability. Consequently, it was more useful to compare deep wells to adjacent shallow wells than to other deep wells. Very few deep monitoring wells are in the study area; most sampled wells were domestic or public supply wells. Information on well and casing depths were required, particularly for deep wells. Much of this information was obtained from driller’s reports. Fourteen wells were sampled in Marion County at six separate locations; thirteen wells were sampled in Sumter County at six separate locations; and six wells were sampled in Citrus County at three separate locations (fig. 8; table 3).

Purging methods varied depending upon the type of well. Water supply wells had high yielding pumps that were used routinely. For these wells, sampling commenced after field parameters (temperature, pH, and specific conductance) stabilized. Samples were collected from as close to the well head as possible, prior to the holding tank. For monitoring wells (wells 7, 8, 9, and 20), at least three casing volumes of water were pumped prior to sampling, while monitoring field parameters. A submersible pump was used for sampling most wells. Exceptions are noted in the appendix.

Determining Flow Zones for Wells with Large Open Hole Intervals

Two monitoring wells had large open hole intervals (ROMP 119 and ROMP 120, with open hole intervals of 396 ft and 293 ft, respectively). Prior to sampling these wells, a vertical flow survey was done under static conditions to determine if distinct flow zones could be identified in the borehole. If so, a sample could be collected from a more discrete depth interval than the entire borehole. The open hole intervals of both wells were completely within the Avon Park Formation.

The heat-pulse flowmeter can detect low (0.1 ft/min) upward or downward flow within a borehole (Hess, 1990; Hess and Paillet, 1990; Crowder and others, 1994). The flow rate is determined by measuring the time for a pulse of heated borehole water to move to an upper or lower thermistor. Velocity values are determined from calibration data for tubes of similar diameter as the borehole under laboratory conditions (Hess and Paillet, 1990). A diverter was used with the meter to concentrate the flow in the borehole through the meter. Measurements were most accurate where the borehole was narrowest, allowing all of the flow to pass through the diverter to the meter.

Table 3. Information about sampled wells
[Well locations shown in figure 8; ft, feet; --, data not available]

Well number	Name	Site identification number[1]	Casing depth (ft)	Well depth (ft)	Elevation (ft above sea level)	County
1	Kellogg shallow well	283924081581501	50	60	93	Sumter
2	Kellogg deep well	283939081580701	210	250	92	Sumter
3	City of Bushnell #2 well	284002082064201	598	693	76	Sumter
4	St. Lawrence Church rectory well	284003082063201	83	105	78	Sumter
5	White well	284422082180601	252	268	65	Citrus
6	Owens well	284422082181001	62	70	60	Citrus
7	ROMP LP-4 Avon Park (240)	284628082073801	200	240	50	Sumter
8	ROMP LP-4 Avon Park (120)	284628082073802	100	120	50	Sumter
9	ROMP LP-4 Ocala	284628082073803	15	30	50	Sumter
10	City of Coleman well	284736082042301	90	200	67	Sumter
11	Rolling well	284743082041601	51	61	66	Sumter
12	Hawkins well	285055082122601	42	50	51	Sumter
13	Campers’ World well	285107082124101	130	160	52	Sumter
14	Pilot Oil well	285225082054101	84	126	56	Sumter
15	Union Oil well	285228082054301	189	253	54	Sumter
16	Lorenz well	285338082261701	475	570	125	Citrus
17	Wooten well	285340082252301	148	150	99	Citrus
18	Budd well	290053082313601	387	420	120	Citrus
19	Iacino well	290053082315101	168	170	100	Citrus
20	USGS observation well CE-78	290132082133001	61	82	89	Marion
21	ROMP 119	290133082140901	106	502	72	Marion
22	Quaglio well	290438082201501	165	167	87	Marion
23	Silver well	290438082272701	100	120	75	Marion
24	Brookshier well	290441082273301	270	360	80	Marion
25	Barton well	290506082202801	76	90	85	Marion
26	Bonnie Builders well	290736082123201	66	84	73	Marion
27	Saddle Oak deep well	290737082124601	225	282	85	Marion
28	Saddle Oak shallow well	290737082124602	86	160	85	Marion
29	ROMP 120	291059082190801	110	403	76	Marion
30	Rowland deep well	291104082191701	136	147	102	Marion
31	Rowland shallow well	291104082191702	--	69	102	Marion
32	Jones well	291157082130301	442	460	97	Marion
33	Brosky well	291201082124401	150	165	93	Marion

[1] Site identification number is composed of the latitue, longitude, and sequence number.

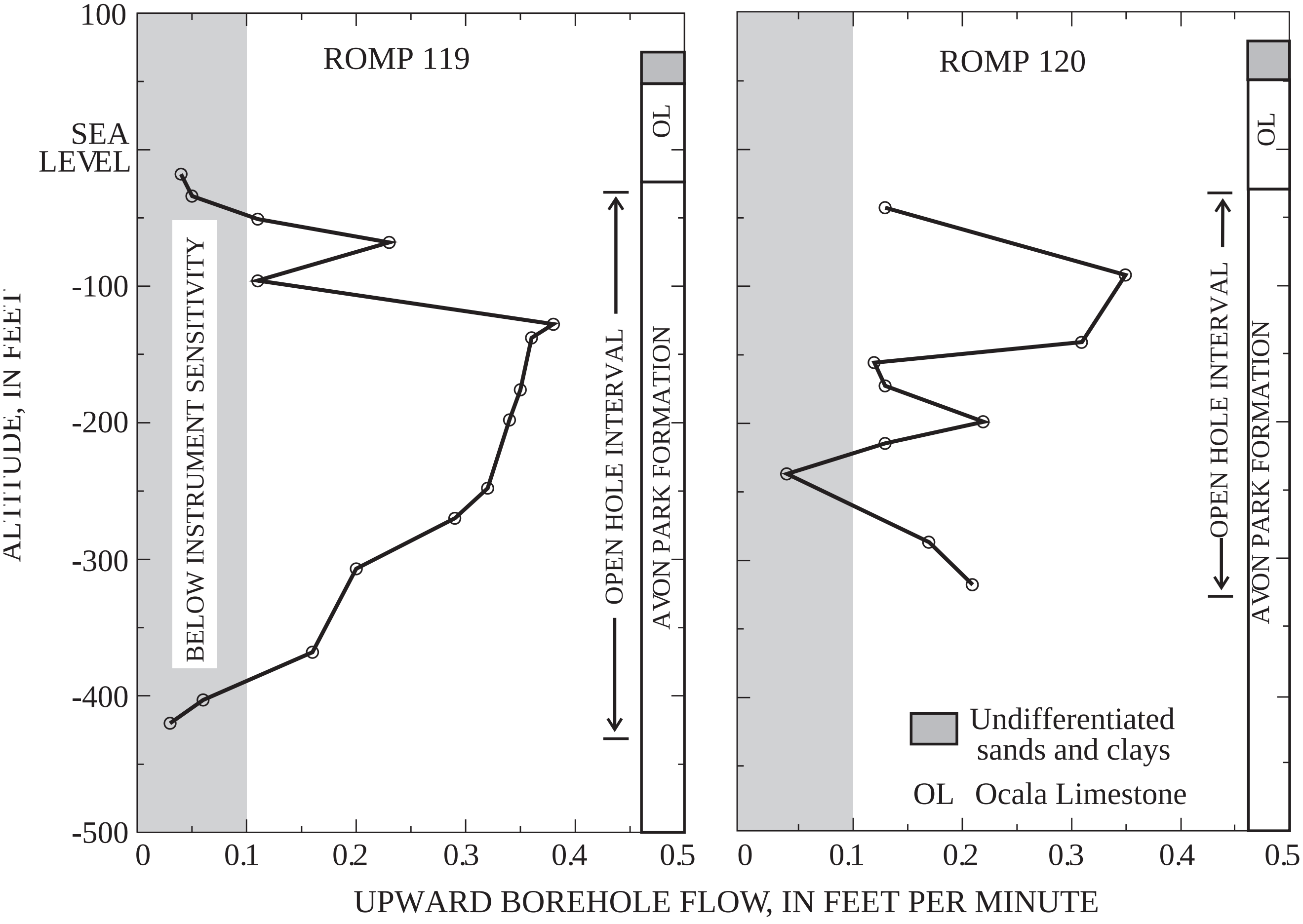


Figure 9. Profiles of upward flow using the heat-pulse flow meter in boreholes at ROMP 119 and ROMP 120, which are open exclusively to the Avon Park Formation. (Locations of wells shown on figure 1.)

Results from the flow survey are presented in figure 9. Measurable upward flow was present in both boreholes, on the order of 0.1 to 0.3 ft/min. Although this is unexpected in an aquifer recharge area, the interaction between the rapid, shallow flow system in the overlying Ocala Limestone and the deeper regional flow system in the less permeable Avon Park Formation is poorly understood.

To obtain as discrete a sample as possible, samples were collected from the deepest flow zone (near the base of the open borehole) for both wells using a drop pipe pumped with a 2-inch submersible pump. Samples also were collected for sulfate and specific conductance at several shallower intervals in the borehole using a thief sampler. Little difference was seen in water quality in the open interval of the borehole, indicating that the water in the borehole was well mixed.

Sample Collection

Standard USGS protocols were used for water-quality sampling (Wood, 1976).Temperature, pH, specific conductance, and dissolved oxygen (DO) were monitored using a flow-through chamber so that the sample was isolated from the atmosphere. Water samples were collected after field parameters stabilized and sufficient volume was cleared from the well (for monitoring wells). Alkalinity was determined in the field by titration with sulfuric acid. Sulfide was measured in the field using the methylene blue method and a field spectrophotometer (Hach, 1989). The detection limit for sulfide was typically 0.01 mg/L, although it was higher for several turbid waters. Duplicate analyses for sulfide were within 35 percent, except for one sample (well 32) that had unstable readings that varied by

85 percent; the median value was used for this sample. Sulfate concentration also was estimated in the field with the spectrophotometer (using the barium sulfate method) in order to determine the method and amount of sample necessary for sulfur isotope collection of sulfate.

Samples were filtered through a 0.45 µm filter for anion and cation analysis. Cation and trace metal samples were collected in acid-washed bottles and acidified with 1 mL of 70 percent nitric acid. Nitrate samples were preserved with mercuric chloride. Dissolved organic carbon (DOC) samples were filtered through a 0.45 µm silver filter using a stainless steel filter unit. Unfiltered samples were collected in glass bottles with polyseal caps for deuterium (δD) and oxygen-18 ($\delta^{18}O$) analysis of the water, and carbon-13 ($\delta^{13}C$) analysis of inorganic carbon. For $\delta^{13}C$, $SrCO_3$ was precipitated by adding approximately 50 mL of ammoniacal strontium chloride solution to a 500-mL unfiltered sample, minimizing exposure to the atmosphere.

Samples were collected for analysis of sulfur-34 ($\delta^{34}S$) of sulfate and sulfide (if present). (In this report, total reduced sulfur species are referred to as sulfide; $H_2S°$ and HS^- are the predominant species in the pH range of the samples). The method and amount of sample necessary for $\delta^{34}S_{sulfate}$ depended upon the sulfate concentration. If the sulfate concentration was greater than 20 mg/L, at least 250 mL of sample (depending upon sulfate concentration) was acidified to a pH of about 4 with 1N HCl, and immediately $BaCl_2$ was added to precipitate the sulfate from solution as $BaSO_4$. This precipitate was filtered and dried before sending to the laboratory. If the sulfate concentration was less than 20 mg/L, between 20 and 50 L of acidified sample were pumped through an anion exchange column that previously was flushed with KCl and deionized water, following methods described by Carmody and others (in press). In the laboratory, the sulfate was eluted from the resin by rinsing with KCl; $BaCl_2$ then was added to the sample to precipitate $BaSO_4$, as described for the high sulfate samples. When sulfate concentrations were less than 1 mg/L, insufficient sulfate was obtained for $\delta^{34}S$ analysis; insufficient sample was also obtained from well 13, which had a sulfate concentration of 4.2 mg/L.

For $\delta^{34}S_{sulfide}$, the sample was collected in a series of three 50-L carboys that were acidified with 100 mL of 6N sulfuric acid so that $H_2S°$ was the predominant reduced sulfur species. Gaseous H_2S was stripped from the sample with ultra-high purity nitrogen gas (less than 10 ppm O_2) in a system closed to the atmosphere. After leaving the carboy, the H_2S entered a solution of $AgNO_3$ and precipitated as Ag_2S. This Ag_2S was filtered and dried before sending to the laboratory. These methods closely follow those described by Carmody and others (in press). Usually if sulfide concentrations were less than 0.05 mg/L, insufficient sulfur was obtained for $\delta^{34}S$ analysis. However, sufficient sample was obtained for well 14, which had a sulfide concentration of 0.03 mg/L.

Quality Assurance Samples

For quality assurance purposes, duplicate samples were collected from two wells (wells 12 and 30; see appendix), and two deionized water equipment blanks were collected. For duplicate samples, there was generally less than seven percent difference between major ion concentrations and less than 40 percent difference between trace element concentrations (except for several analyses that had very low concentrations near the detection limit). Charge balances for all analyses were within four percent. For the isotopes, precision according to duplicate analyses was 0.1 per mil for $\delta^{18}O$, 1.1 per mil for δD, 0.4 per mil for $\delta^{13}C$, 0.2 per mil for $\delta^{34}S_{sulfate}$, and 0.5 per mil $\delta^{34}S_{sulfide}$ (see appendix).

Deionized water equipment blanks were collected through field equipment in contact with sample water (peristaltic or submersible pump, filter unit, and tubing). The deionized water was also analyzed directly from its source in the laboratory. Most constituents were below detection limits for both types of samples. There was negligible difference between water from the laboratory and water passed through field equipment, indicating that no contamination was introduced by the field equipment.

Chemical Composition of Ground Water

The chemical composition of most of the ground water was dominated by calcium and bicarbonate. Major cation and anion equivalent concentrations are illustrated on a trilinear diagram in figure 10. All shallow ground waters were dominated by calcium and bicarbonate, whereas deep waters had a wider range in composition. For some deep ground waters, the dominant anion was sulfate, and the relative proportion of magnesium increased (fig. 10).

Analytical data are presented in the appendix. Most constituents were less than primary and secondary drinking water standards, with the exception of sulfate, iron, and dissolved solids in some waters (Florida Department of State, 1993). Sulfate concentrations were greater than the secondary drinking water standard of 250 mg/L in water from four deep wells (fig. 11). Iron concentrations were greater than the secondary drinking water standard of 300 μg/L in water from 11 wells. Samples with the highest iron concentrations (greater than 1,000 μg/L) were from shallow wells in Sumter County; samples with iron concentrations between 300 and 1,000 μg/L were from deep wells in all three counties. Calculated dissolved solids concentrations ranged from 69 mg/L to 2,092 mg/L. Calculated dissolved solids concentrations were greater than the secondary drinking water standard of 500 mg/L for the same wells that had sulfate concentrations greater than 250 mg/L.

A wide range of sulfate concentrations (less than 0.2 to 1,400 mg/L) were observed in the ground water. The ground waters were grouped into two categories based on sulfate concentration: low sulfate (less than 30 mg/L) and high sulfate (greater than 30 mg/L). This was done because chemical characteristics differ between low and high sulfate waters. All low sulfate waters had concentrations less than 5 mg/L, except for water from three wells that had slightly higher sulfate concentrations, ranging between 20 and 25 mg/L. Water from most of the shallow wells had low sulfate concentrations, and only two shallow ground-water samples had sulfate concentrations greater than 30 mg/L (fig. 11). Many of the deep waters had concentrations greater than 30 mg/L; however, six deep samples had sulfate concentrations less than 5 mg/L (fig. 11). Sulfate increased between the shallow and deep ground water at nine out of the 15 sampling sites.

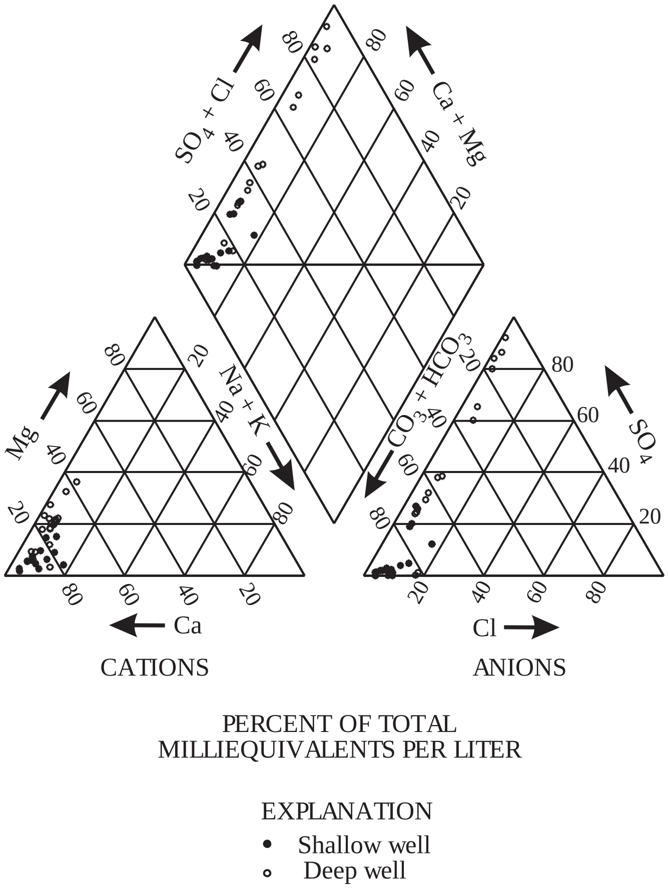
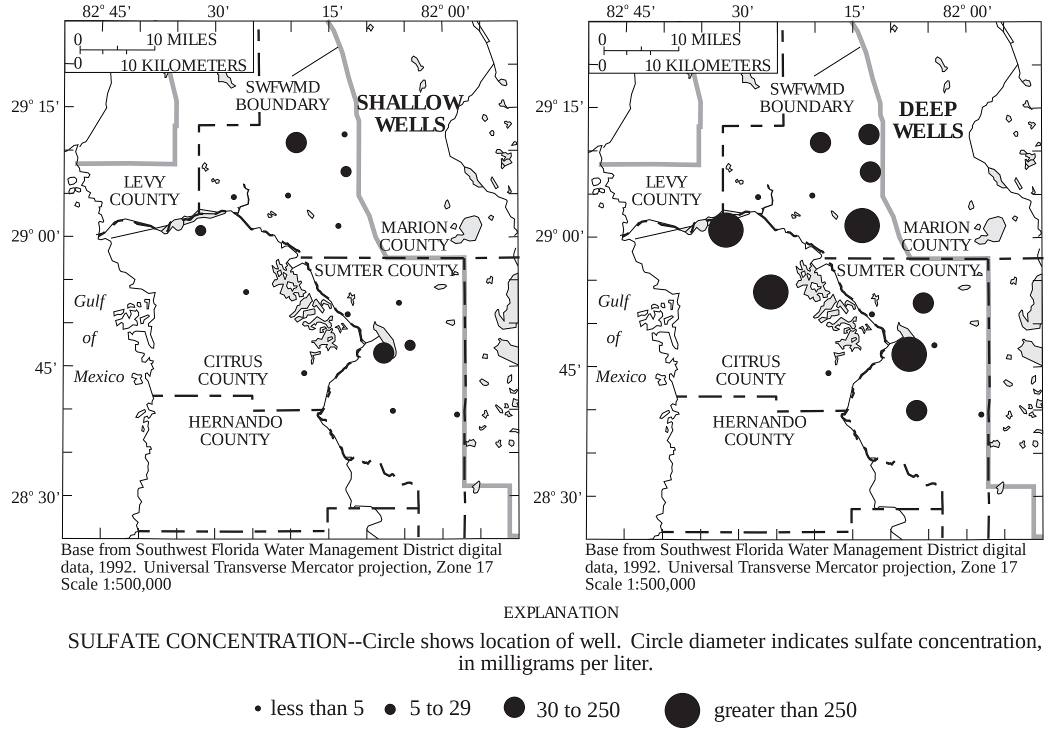


Figure 10. Chemical composition of water from shallow and deep wells from the Upper Floridan aquifer.

The deeper ground water had higher sulfide concentrations than the shallow water (fig. 12). None of the shallow ground water from Marion and Citrus Counties contained sulfide; all of these waters contained dissolved oxygen (DO). In Sumter County water from the shallow wells often contained sulfide. All deep ground water had detectable sulfide and DO below the detection limit, except for water from two wells at the same site in Marion County (wells 27 and 28), which also had relatively high DO concentrations (greater than 3 mg/L).

A number of solutes increased with sulfate at high concentrations (usually greater than 30 mg/L), but not at low sulfate concentrations (fig. 13). This indicates different controls on sulfate at low and high concentrations. At low sulfate concentrations, sulfate does not appear to be directly related to other solute concentrations. For the high sulfate waters, good relations exist between sulfate and calcium, magnesium, strontium, aluminum, and fluoride (correlation coefficient greater than 0.7). This can indicate similar sources for sulfate and these ions (for example, mineral dissolution) or similar processes responsible for the elevated concentrations (for example, upwelling of deeper ground water where other mineral assemblages may control the sources of other solutes).

Bicarbonate concentrations and pH were controlled by equilibrium with calcite. Bicarbonate concentrations ranged from 61 to 344 mg/L, and pH values ranged from 6.91 to 8.24. An inverse relation exists between bicarbonate and pH, which is expected for waters in equilibrium with calcite under a wide range of carbon dioxide partial pressures (P_{CO_2}) (Stumm and Morgan, 1981). This is because water with a higher P_{CO_2} can dissolve more calcite than water with a lower P_{CO_2}.



Base from Southwest Florida Water Management District digital data, 1992. Universal Transverse Mercator projection, Zone 17
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Base from Southwest Florida Water Management District digital data, 1992. Universal Transverse Mercator projection, Zone 17
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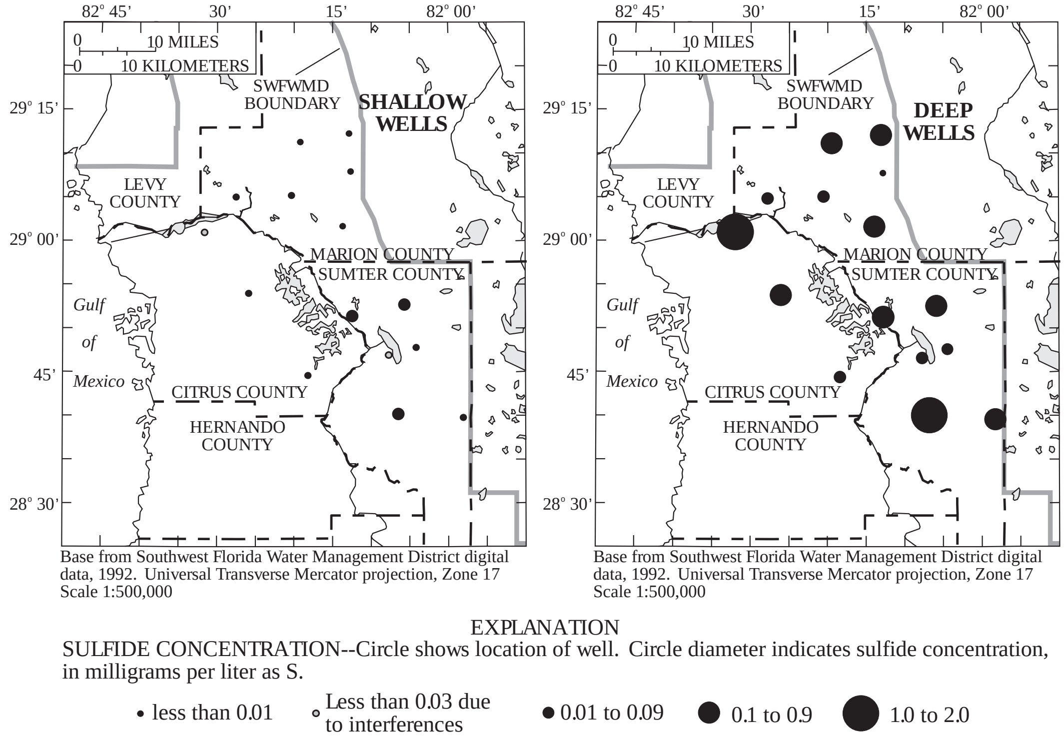
EXPLANATION

SULFATE CONCENTRATION--Circle shows location of well. Circle diameter indicates sulfate concentration, in milligrams per liter.

• less than 5 ● 5 to 29 ● 30 to 250 ● greater than 250

Figure 11. Sulfate concentrations in water from shallow and deep wells from the Upper Floridan aquifer. (Index numbers and specific information about wells shown in figure 8 and table 3.)



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EXPLANATION

SULFIDE CONCENTRATION--Circle shows location of well. Circle diameter indicates sulfide concentration, in milligrams per liter as S.

• less than 0.01 ○ Less than 0.03 due to interferences ● 0.01 to 0.09 ● 0.1 to 0.9 ● 1.0 to 2.0

Figure 12. Sulfide concentrations in water from shallow and deep wells from the Upper Floridan aquifer. (Index numbers and specific information about wells shown in figure 8 and table 3.)

Calcium and bicarbonate concentrations increased for most waters at the 1:2 molar ratio expected for dissolution of calcite by carbonic acid:

$$CaCO_3 + H_2CO_3 \rightarrow Ca^{2+} + 2HCO_3^- . \tag{2}$$

Outliers are waters from deep wells that had the highest calcium and sulfate concentrations (sulfate greater than 150 mg/L). Plotting the molar ratios of Ca/HCO_3 against Ca/SO_4 illustrates how calcium concentrations are controlled by both calcite and gypsum (fig. 14). Most waters plot along the calcite dissolution line (Ca/HCO_3 molar ratio of 0.5), with a large range in the Ca/SO_4 ratio. However, as calcium concentrations increased over bicarbonate, sulfate concentrations also increase. This other subset of data plots near to slightly below the line expected for gypsum dissolution (Ca/SO_4 ratio of 1):

$$CaSO_4 \cdot 2H_2O \rightarrow Ca^{2+} + SO_4^{2-} + 2H_2O . \tag{3}$$

This indicates that gypsum dissolution controls the elevated calcium and sulfate concentrations.

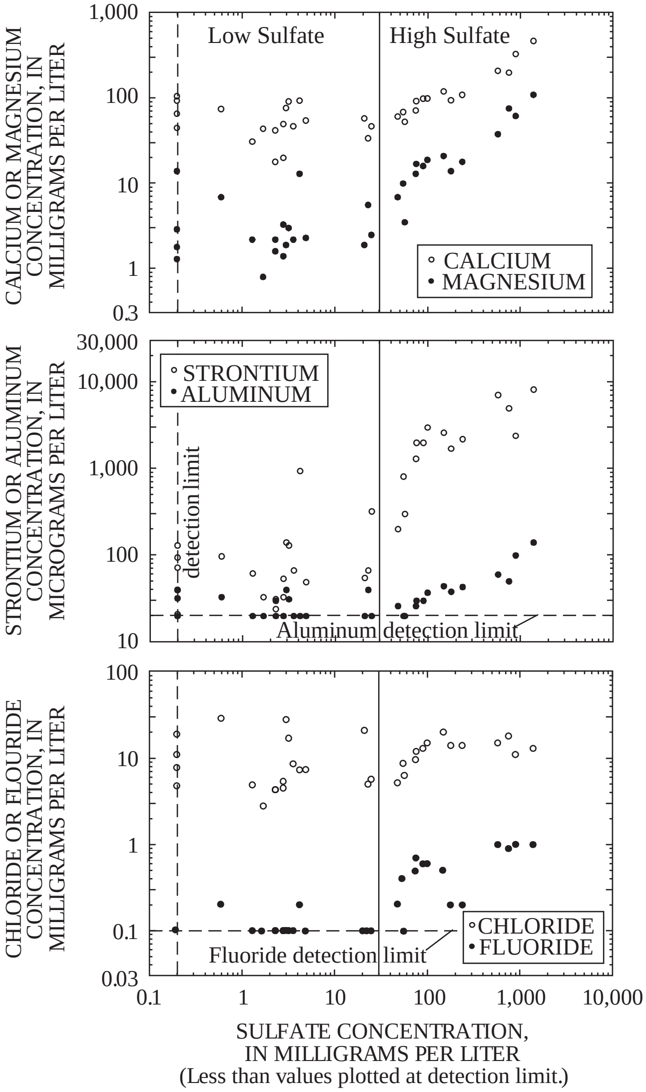


Figure 13. Relation between concentrations of sulfate and calcium, magnesium, strontium, aluminum, chloride, and fluoride in water from the Upper Floridan aquifer.

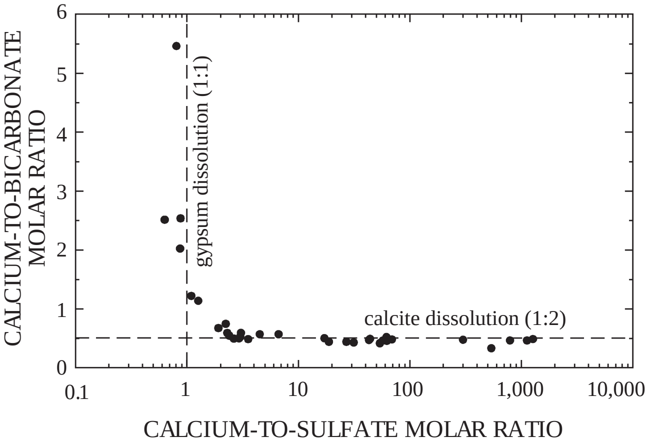


Figure 14. Relation between calcium-to-bicarbonate molar ratio and calcium-to-sulfate molar ratio in water from the Upper Floridan aquifer.

Chloride concentrations were low for all ground water (less than 30 mg/L), which is three orders of magnitude lower than seawater (19,000 mg/L). For the high sulfate waters, chloride concentrations increased from 5 to 20 mg/L as sulfate concentrations increased to 150 mg/L; above this, chloride concentrations did not increase (fig. 13). For the low sulfate waters, chloride concentrations were more widely scattered, ranging from 2.8 to 29 mg/L. Bromide and sodium concentrations increased with chloride for most waters, indicating similar sources for these ions.

Saturation State of Ground Water

The saturation state of ground water with respect to mineral phases and the P_{CO_2} were computed with the aqueous speciation model WATEQ4F (Ball and Nordstrom, 1991). Information on mineral saturation states is useful for interpreting mineral controls on ion concentrations and for hypothesizing probable reactions for mass-balance modeling. The saturation index (SI) is a measure of the departure from equilibrium of the water with respect to mineral phases.

$$SI = \log (IAP/K_T)\,, \qquad (4)$$

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. An SI value of zero, with an associated range of uncertainty, indicates the water is in equilibrium or saturated with respect to the mineral phase; a value less than zero indicates undersaturation (mineral dissolution is possible); and a value greater than zero indicates supersaturation (mineral precipitation is possible). These calculations assume that the dissolved species in the ground water are at chemical equilibrium. Distributions of species that are sensitive to redox potential were computed using the Eh value determined from sulfate and sulfide concentrations when sulfide was present in the water; otherwise dissolved oxygen was used in the calculations.

Most of the waters were saturated to supersaturated with respect to calcite (equilibrium is assumed when SI values fall between -0.15 and 0.15, given uncertainties in analytical values and pH). Water from one shallow well (well 33) was undersaturated with calcite. This water had a low concentration of dissolved solids (74 mg/L) and probably represents recent recharge with a very short residence time in the aquifer. Over half of the deep ground waters were supersaturated with calcite. In addition, waters with highest sulfate concentrations (greater than 250 mg/L) were supersaturated with respect to calcite (fig 15).

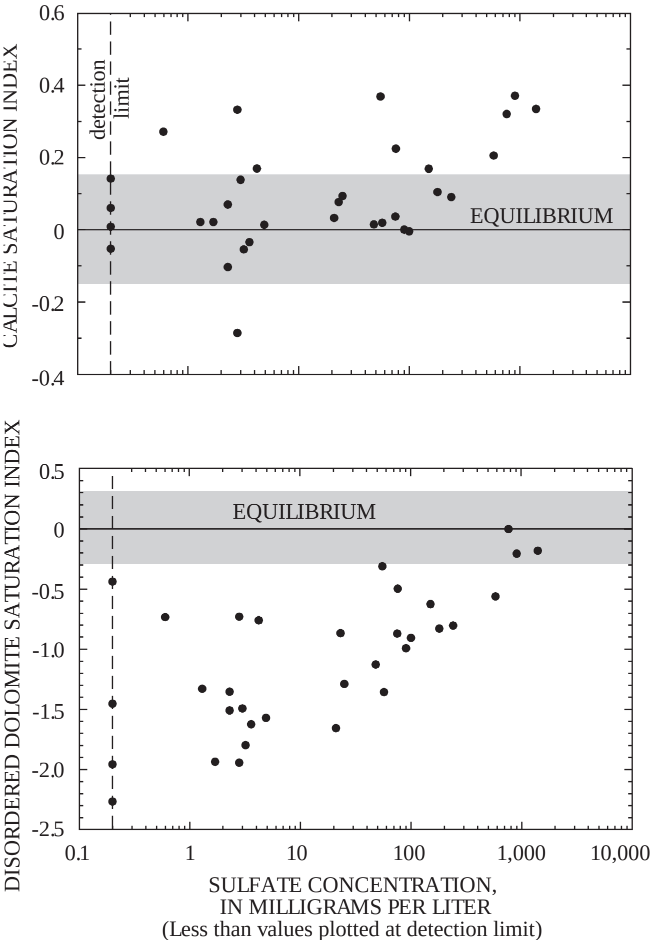


Figure 15. Relation between calcite and dolomite saturation index and sulfate concentration in water from the Upper Floridan aquifer.

Most waters were undersaturated with respect to dolomite (equilibrium is assumed for SI values between -0.3 and +0.3). The exact value for the equilibrium reaction constant (K_r) of dolomite in the aquifer is uncertain (Hsu, 1963; Hanshaw and others, 1971; Plummer, 1977); thus, SI values are reported in the appendix for both disordered (or poorly crystalline) dolomite (log K_r of -16.54) and crystalline dolomite (log K_r of -17.09; Nordstrom and others, 1990). Most waters were undersaturated with respect to disordered dolomite; however, three deep waters with the highest sulfate concentrations were in equilibrium with disordered dolomite (fig. 15). All shallow ground waters were undersaturated with respect to crystalline dolomite, but over half of the deep waters were in equilibrium or supersaturated with crystalline dolomite (see appendix).

All of the waters were undersaturated with respect to gypsum (equilibrium is assumed for SI values between -0.03 and +0.03). The water with the highest sulfate concentration approached, but did not reach, gypsum equilibrium (-0.16 for well 7; fig. 16). However, ground water collected by SWFWMD above and within depth intervals containing gypsum at ROMP 110 (located in eastern Citrus County; fig. 1) was at equilibrium with respect to gypsum (Southwest Florida Water Management District, written commun., 1993) (see appendix). All of the waters were undersaturated with celestite

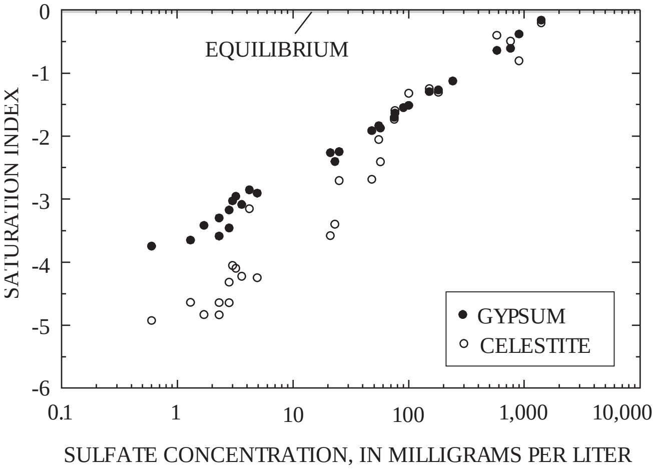


Figure 16. Relation between gypsum and celestite saturation index and sulfate concentration in water from the Upper Floridan aquifer.

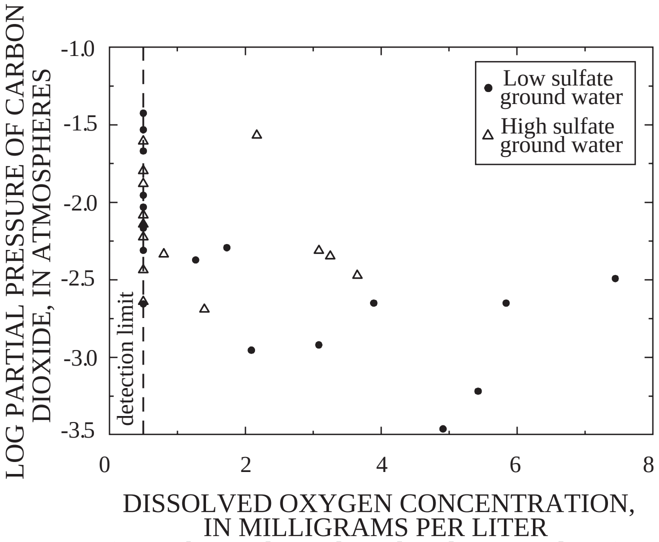
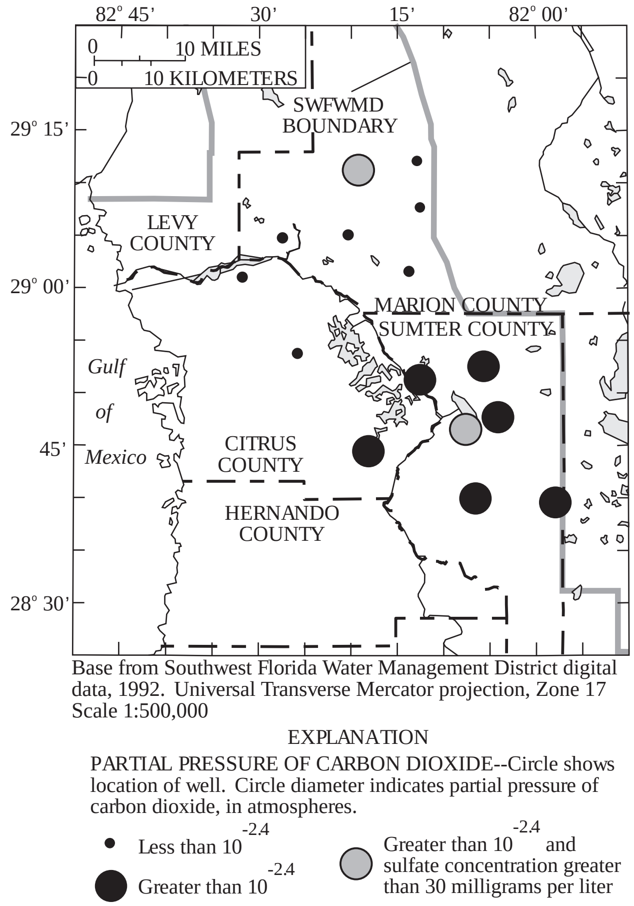


Figure 17. Relation between partial pressure of carbon dioxide and dissolved oxygen concentration for low sulfate (less than 30 milligrams per liter) and high sulfate ground water from the Upper Floridan aquifer.

($SrSO_4$), with values approaching, but not reaching, equilibrium for waters with high sulfate concentrations (fig. 16). All waters containing sulfide were supersaturated with respect to pyrite; this mineral is unstable and can be oxidized when DO is present in the water.



Base from Southwest Florida Water Management District digital data, 1992. Universal Transverse Mercator projection, Zone 17
Scale 1:500,000

Figure 18. Partial pressure of carbon dioxide in water from shallow wells from the Upper Floridan aquifer. (Index numbers and specific information about wells shown in figure 8 and table 3.)

The partial pressure of carbon dioxide (P_{CO_2}) also was calculated with WATEQ4F. The low sulfate waters had a greater range of P_{CO_2} (from $10^{-1.35}$ to $10^{-3.46}$ atm) than the high sulfate waters (between $10^{-1.57}$ to $10^{-2.69}$ atm). Low sulfate waters containing DO generally had lower P_{CO_2} values than anaerobic, low sulfate waters (fig. 17). Shallow ground water from Marion and Citrus Counties usually had low P_{CO_2} values (less than $10^{-2.4}$ atm; fig. 18), whereas shallow ground water from Sumter County generally had higher P_{CO_2} values (greater than 10-2.4 atm; fig. 18). Deeper ground water also usually had higher P_{CO_2} values. Swancar and Hutchinson (1995) found that in unconfined parts of the Upper Floridan aquifer in west-central Florida, water with high P_{CO_2} values were near swamps and river systems where recharge is reduced and soils are finer grained.

Chemical Characterization of High Sulfate Ground Water

High sulfate ground water (typically greater than 30 mg/L) was chemically distinct from low sulfate ground water. A number of ions increased in concentration along with sulfate for the high sulfate water. For example, calcium and magnesium concentrations increased with sulfate (fig. 13). Aquifer minerals that control the concentrations of these ions are calcite, dolomite, and gypsum. Calcium was slightly depleted relative to sulfate (in mmol/L) for the highest sulfate ground waters (Ca/SO_4 molar ratio less than one), compared to a Ca/SO_4 ratio of one expected if only gypsum dissolution were occurring (fig. 14). This indicates a sink for some of the calcium, such as calcite precipitation, which is possible because these ground waters were supersaturated with respect to calcite.

Dedolomitization reactions (dissolution of gypsum and dolomite and precipitation of calcite) are important in controlling the composition of ground water along regional flow paths in the confined part of the Upper Floridan aquifer in southwest Florida (Plummer, 1977; Plummer and others, 1983; Sacks and others, 1995). In the present study area, dedolomitization reactions also may be occurring. These reactions probably occur deep in the aquifer, where gypsum (which drives these reactions) is present and dolomite is more abundant. This deeper water is part of a regional, slow moving flow system with long aquifer residence times.

Strontium and aluminum concentrations also increased with increasing sulfate concentrations (fig. 13). Strontium and aluminum were observed in trace concentrations in gypsum from the Floridan aquifer system (table 2). The possibility that elevated strontium and aluminum concentrations in ground water originated from trace concentrations in gypsum was further evaluated by assuming that sulfate in excess of 30 mg/L comes from gypsum. The fraction of sulfate originating from gypsum (f_{gyp}) was computed as:

$$f_{\mathrm{gyp}} = \left(SO_{4_{\mathrm{gw}}} - 30\right) / 1800 \,, \qquad (5)$$

where $SO_{4_{gw}}$ is the sulfate concentration of the high sulfate ground water, and it was assumed that ground water in equilibrium with gypsum has a sulfate concentration of 1,800 mg/L (see appendix). Using this fraction and the ratio of strontium-to-sulfate or aluminum-to-sulfate (R_{gyp}) in gypsum from ROMP 110 (table 2), an expected strontium or aluminum concentration (i_{exp}) was computed for each of the high sulfate waters:

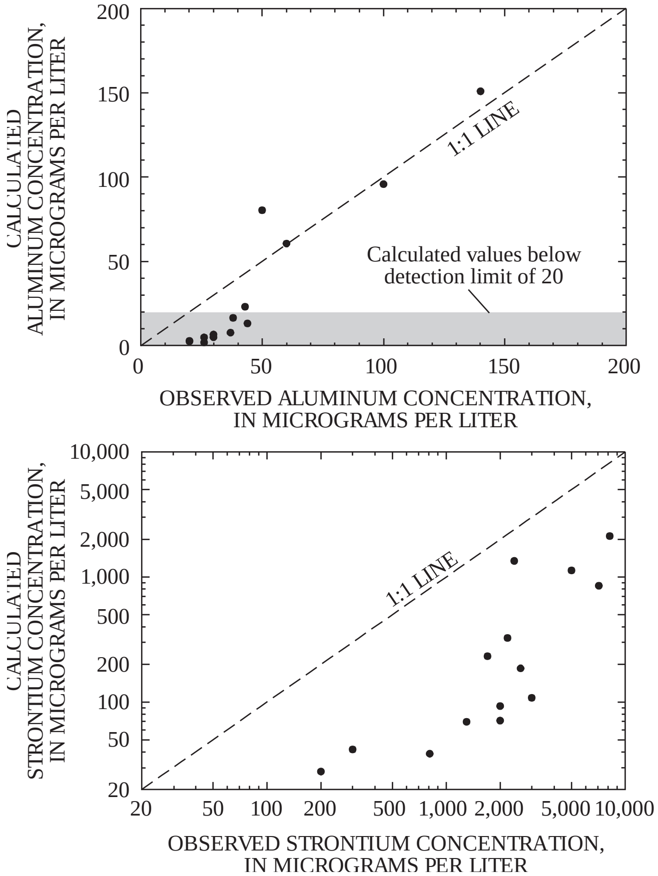


Figure 19. Relation between calculated and observed aluminum and strontium concentrations for high sulfate ground water (greater than 30 milligrams per liter) from the Upper Floridan aquifer.

$$i_{\mathrm{exp}} = f_{\mathrm{gyp}} R_{\mathrm{gyp}} \qquad (6)$$

A good relation exists (r^2 of 0.90) between calculated and observed aluminum concentrations, which implies that gypsum is the source of elevated aluminum in the ground water (fig. 19). Additional work is needed to quantify the association of aluminum with gypsum, as a source for aluminum in evaporative brines is not apparent. Possibly, aluminum could be in the form of aluminum hydroxides, rather than within the gypsum lattice or interstitial positions in an ionic form.

For strontium, the calculated concentrations were lower than observed concentrations (fig. 19), and significantly more strontium (on the order of about 3,000 ppm) would need to be present in the gypsum to explain the measured ground-water concentrations. The strontium concentration in gypsum is dependent on temperature and salinity (Kushnir, 1980). The concentration of strontium in gypsum from ROMP 110 (850 ppm; table 2) is lower than for primary gypsum formed from evaporating seawater (1,000 and 2,000 ppm; Ichikuni and Musha, 1978). Strontium concentrations in gypsum collected from the Avon Park Formation in southwest Florida had strontium concentrations ranging up to 2,000 ppm (table 2). Similarly high concentrations may occur within the study area.

An additional strontium source, such as the mineral celestite, may be present within the study area. Celestite has been observed in association with gypsum from the Avon Park Formation at a site about 30 mi southwest of the study area, in southwest Hernando County (Cook and others, 1985). It has also been observed in shallow intervals of the confined Upper Floridan aquifer in southwest Florida (McCartan and others, 1992).

Other ions (chloride, bromide, sodium, and potassium) also increased slightly with increasing sulfate concentrations for the high sulfate ground water (fig. 20). These increased concentrations may be related to water flowing through deeper, more sluggish zones in the aquifer that had less efficient flushing of seawater than the shallower more rapid-flowing ground water. Bromide concentrations increased with chloride at the same ratio as conservative saltwater mixing, which supports a residual seawater source for these ions (fig. 20). Sodium concentrations were slightly enriched relative to conservative seawater mixing, and potassium concentrations were considerably more enriched than conservative seawater mixing (fig. 20). (In contrast, strontium and aluminum concentrations were several orders of magnitude higher than conservative seawater mixing.)

Cation exchange is a possible source for sodium and potassium. Minor clay minerals present in the aquifer are possible exchange sites. At a time when saltwater was being flushed from the aquifer, calcium may have replaced sodium and potassium on exchange sites, elevating their concentrations in solution.

Alternatively, high sulfate waters could have recharged during more arid conditions than the present, resulting in more evaporative concentration of rainwater. Another possible source for potassium is weathering of silicate minerals such as potassium feldspar, which has been reported in trace quantities in the aquifer (Sprinkle, 1989; Katz and others, 1995b). Sodium and potassium do not occur in sufficient trace quantities in gypsum or carbonates to measurably influence ground-water concentrations.

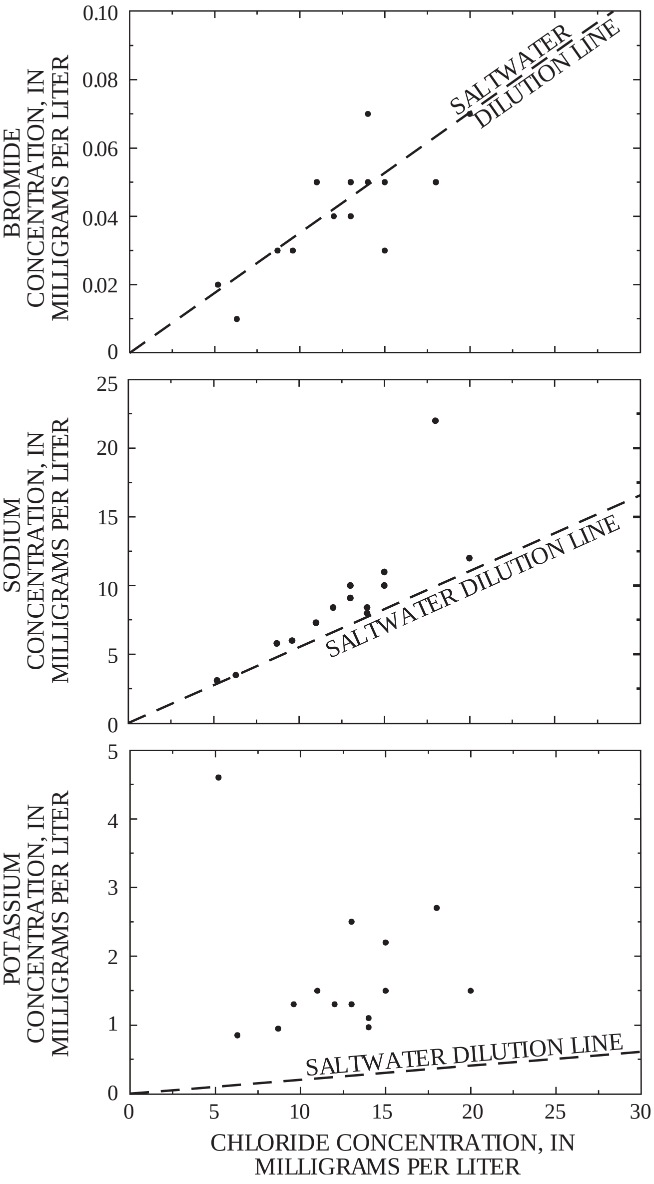


Figure 20. Relation between concentrations of chloride and bromide, sodium, and potassium for high sulfate ground water (greater than 30 milligrams per liter) from the Upper Floridan aquifer.

Fluoride concentrations also increased with sulfate (fig. 13) and was many orders of magnitude higher than conservative saltwater mixing based on chloride. Thus, residual saltwater cannot explain the elevated concentrations. The generally accepted source of fluoride in the aquifer is calcium fluoroapatite from the overlying Hawthorn Group or the Alachua Formation (Lawrence and Upchurch, 1982; Sprinkle, 1989; Katz, 1992), neither of which are continuous over the study area. Thus, a source of fluoride from overlying rock units is not likely. In addition, fluoride concentrations usually were higher in deeper ground water than in shallow ground water, which is not consistent with a shallow fluoride source. Regional ground-water flow paths could have originated far upgradient at the potentiometric high to the southeast, where the Hawthorn Group is present. The shallow flow system, on the other hand, recharges locally in the unconfined part of the aquifer where fluoride minerals are not present.

An alternative source of fluoride is trace amounts of fluoride in a mineral phase from deeper zones in the Avon Park Formation. Cook and others (1985) observed the mineral fluorite (CaF_2) in association with gypsum from the Avon Park Formation in a core from southwest Hernando County. This association of fluorite with gypsum may be fairly widespread in the Avon Park Formation, which could explain the relation between sulfate and fluoride.

The large range in sulfate concentrations observed in the high sulfate ground water (between 48 to 1,400 mg/L) indicates a range in the extent of gypsum dissolution or mixing between high and low sulfate waters. Gypsum dissolution, which is the major reaction influencing the high sulfate ground water, occurs deep in the aquifer. Other solutes that increase with sulfate apparently originate from the gypsum itself, from other mineral assemblages from deeper in the aquifer in association with gypsum, and from residual seawater from less-flushed, deeper parts of the aquifer. These ions are subsequently transported with the sulfate to shallower parts of the aquifer where gypsum is not present.

Chemical Characterization of Low Sulfate Ground Water

The chemical composition of low sulfate water is strongly controlled by the redox condition of the water (aerobic or anaerobic). This is consistent with differences in the extent of microbially mediated reactions (Chapelle, 1993). Microbial respiration initially consumes O_2 and organic matter (simplified here as CH_2O) and produces carbon dioxide (CO_2):

$$O_2 + CH_2O \rightarrow CO_2 + H_2O \quad . \qquad (7)$$

In Sumter County, where soils are organic-rich and poorly drained, shallow ground water was often anaerobic. In contrast, shallow ground water was aerobic in upland areas of Citrus and Marion Counties, where soils are well drained and sandy. The organic matter driving microbial respiration may originate in the soil horizon, resulting in anaerobic waters in shallow parts of the Upper Floridan aquifer. Dissolved organic carbon (DOC) concentrations were usually higher in the anaerobic waters (fig. 21). This is probably related to the greater amount of organic matter in the soils and the presence of intermediate fermentation reactions during the oxidation of particulate organic carbon (Chapelle, 1993). This dissolved carbon may be available for anaerobic bacteria that use mineral electron acceptors such as sulfate.

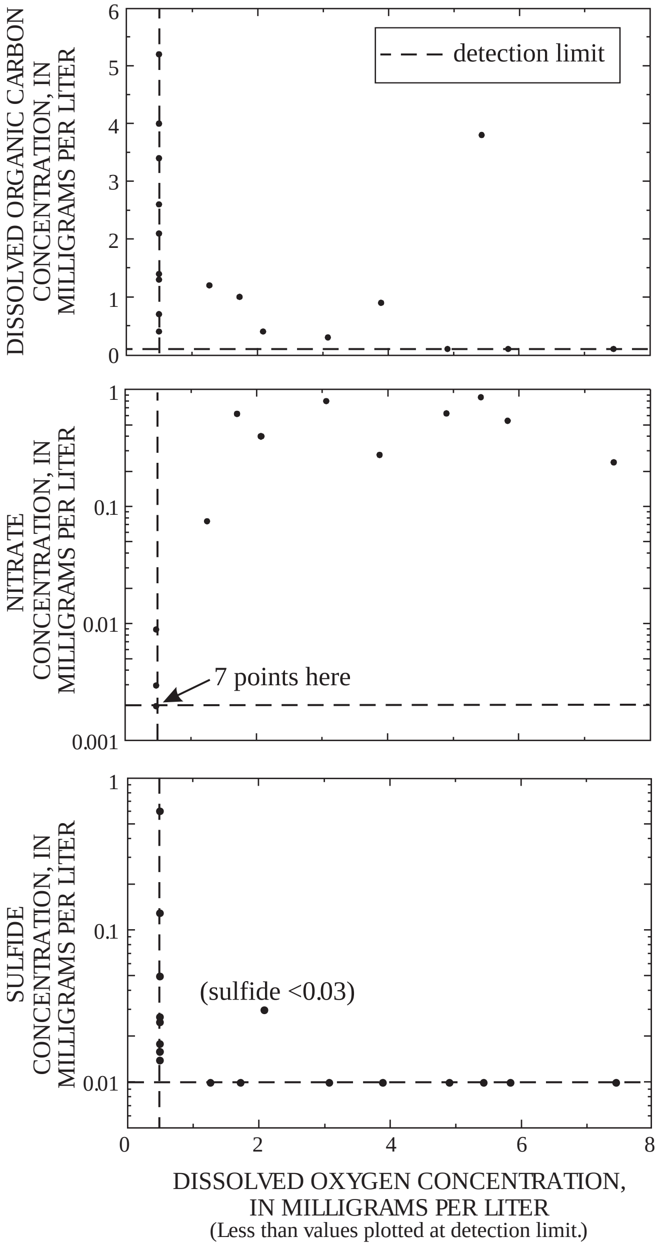


Figure 21. Relation between concentrations of dissolved oxygen and dissolved organic carbon, nitrate, and sulfide for low sulfate ground water (less than 30 milligrams per liter) from the Upper Floridan aquifer.

After dissolved O_2 is by consumed (aerobic respiration), microbial populations typically use nitrate (denitrification), ferric iron (Fe (III) reduction), and sulfate (dissimilatory sulfate reduction) as electron acceptors (anaerobic respiration) (Chapelle, 1993). The source of iron is probably iron oxyhydroxides, either from overlying surficial deposits or from trace amounts in the carbonate rocks. These reactions can be represented as:

$$4NO_3^- + 5H^+ + 5CH_2O \rightarrow 5CO_2 + 2N_2 + 7H_2O\ , \tag{8}$$

$$4Fe(OH)_3 + CH_2O + 8H^+ \rightarrow CO_2 + 4Fe^{2+} + 11H_2O\ , \tag{9}$$

$$SO_4^{2-} + 2CH_2O + H^+ \rightarrow 2CO_2 + HS^- + H_2O\ . \tag{10}$$

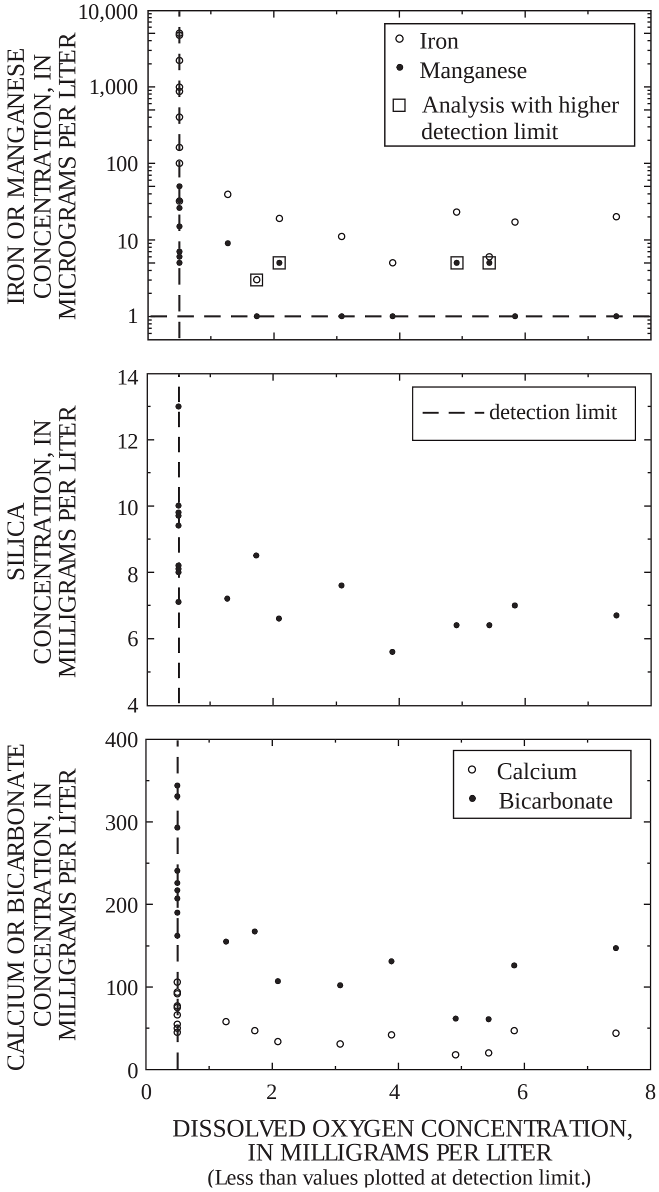


Figure 22. Relation between concentrations of dissolved oxygen and iron, manganese, silica, calcium, and bicarbonate for low sulfate ground water (less than 30 milligrams per liter) from the Upper Floridan aquifer.

Anaerobic waters usually had higher P_{CO_2} values (greater than $10^{-2.4}$) than aerobic waters (fig. 17). P_{CO_2} is, thus, an indicator of the extent of microbial reactions. Compared to aerobic ground waters, anaerobic waters had distinctly lower nitrate concentrations (less than 0.01 mg/L as nitrogen), higher iron concentrations (greater than 50 µg/L), and usually contained sulfide (figs. 21 and 22). This is consistent with microbially mediated denitrification, iron reduction, and sulfate reduction. These reactions also increase alkalinity (or acid neutralizing capacity) because hydrogen ion is consumed (Stumm and Morgan, 1981; p. 193-194).

High iron concentrations in shallow ground water in Sumter County is problematic because it is often above drinking water standards. These shallow, anaerobic waters with high iron concentrations (greater than 1,000 µg/L) had relatively low sulfide concentrations (less than 0.05 mg/L). This is consistent with iron reducing bacteria inhibiting sulfate reducing bacteria by outcompeting them for available electron donors (H_2 or acetate; Chapelle and Lovely, 1992). Deeper low sulfate waters had lower iron concentrations and often had higher sulfide concentrations. As sulfide concentrations increase in the deeper anaerobic waters, iron may be removed by precipitation of insoluble iron sulfide minerals. A good relation exists between manganese and iron concentrations (r^2 of 0.72), indicating that manganese reducers also may be active, with similar efficiencies for using electron donors as iron reducers.

Silica concentrations were higher in the anaerobic waters than in the aerobic waters (fig. 22). Several studies have shown that organic acids may enhance the dissolution of quartz and potassium feldspars (Bennett, 1991; McMahon and others, 1995). The higher DOC concentrations in anaerobic waters from this study may also increase the dissolution of silicate minerals. Potassium and silica concentrations usually increase together, suggesting that potassium feldspar may be the source of this additional silica.

The CO_2 produced by microbial oxidation of organic matter allows more calcite to dissolve (equation 2). Thus, although all of the low sulfate waters were near calcite equilibrium, higher P_{CO_2}, anaerobic waters sometimes contained more than twice as much calcium and bicarbonate as the lower P_{CO_2}, aerobic waters (fig. 22). The greater amount of calcite that the anaerobic waters dissolve, compared to the aerobic waters, may be important in the geomorphic evolution of the area. For example, the parts of Citrus and Marion Counties that were the focus of this study are topographically higher than most of the study area in Sumter County. Less calcite dissolution in these parts of Citrus and Marion Counties (where ground water is aerobic) could perpetuate the existence of topographic highs. In lower lying Sumter County (where ground water is anaerobic), CO_2 charged ground water is chemically more aggressive, resulting in more calcite dissolution and possibly additional karstification in these areas.

Deeper ground waters with low sulfate concentrations tend to be chemically similar to shallow anaerobic ground waters. These shallow waters probably have a longer residence time in the aquifer than their aerobic counterparts. Similarly, deeper waters have longer aquifer residence times, resulting in a greater extent of microbially mediated reactions.

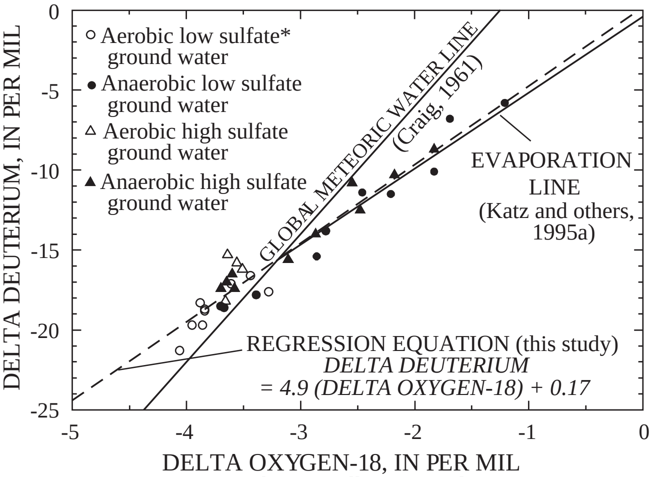
Specific microbial populations were not quantified for this study. However, the presence of sulfate reducing bacteria was determined for selected aerobic and anaerobic waters (wells 3, 5, 6, 10, 11, 12, 13, 22, and 25). Methods for preparing autoclaved vials, which contained a selective media favorable for the growth of sulfate reducing bacteria, were modified from Postgate (1979) and are described in detail by Kauffman (1994). In the field, a 3-mL sample of unfiltered ground water was injected into the vial using a sterile syringe and needle. A black precipitate appeared after several days in all samples, indicating that sulfate reducing bacteria were present in all water samples. The presence of bacteria on the media is not evidence that they are active in the subsurface. However, sulfate reducing bacteria were viable when conditions were favorable for their growth. (Sampling methods precluded the collection of water directly from the aquifer, and so the bacteria, alternatively, could have originated from the well or pump.)

Isotopic Composition of Ground Water

Isotopes can be useful in understanding sources of water and reactions affecting the chemical composition of ground water (Fritz and Fontes, 1980; Toran, 1982; Mazon, 1991). Ground-water samples were analyzed for stable isotopes of hydrogen (deuterium or ^{2}H), oxygen (oxygen-18 or ^{18}O), inorganic carbon (carbon-13 or ^{13}C), and sulfur (sulfur-34 or ^{34}S). Isotopes are presented in delta (δ) notation as the ratio of the heavy to the light isotope, normalized to a standard (equation 1). A larger δ value is, thus, considered “heavier” or enriched in the heavier isotope, compared to a smaller value, which is referred to as “lighter” or more depleted. Results and interpretation of the isotopic data are discussed in the following section.

Deuterium and Oxygen-18

Deuterium and oxygen-18 are influenced by processes affecting the water, rather than the solutes, at the low temperature and pressure of shallow aquifers. These isotopes are useful in identifying waters that underwent evaporation, recharge under different climatic conditions than the present, and mixing of waters from different sources. Modern meteoric water usually falls along a global meteoric line, defined by the relation between δD and δ^{18}O ($\delta D = 8\ \delta^{18}O + 10$; Craig, 1961). Rainwater within Florida generally plots along the global meteoric water line (Swancar and Hutchinson, 1995; Meyers and others; 1993; Katz and others, 1995a). A good relation exists between δD and δ^{18}O in ground water from this study (r^2 of 0.94; fig. 23). Isotopically light waters plot near the global meteoric water line (Craig, 1961), but isotopically heavier waters are offset to the right of the line (enriched in δ^{18}O). This same relation was found by Swancar and Hutchinson (1995) for water from the Upper Floridan aquifer in west-central Florida.



* Less than 30 milligrams per liter.

Figure 23. Relation between delta deuterium and delta oxygen-18 in water from the Upper Floridan aquifer.

The δD and $\delta^{18}O$ composition of the low sulfate waters appears to be related to ground-water age and evaporation prior to recharge. Isotopically light waters contained DO and are probably recent recharge that is part of the rapid, shallow flow system described by Faulkner (1973). Swancar and Hutchinson (1995) reported a relation between tritium and δD and $\delta^{18}O$ in waters from the shallow part of the Upper Floridan aquifer in west-central Florida, and concluded that isotopically light waters were younger than heavy waters. The isotopically heavier, low sulfate waters from this study were anaerobic and occur either at shallow depths in Sumter County, where aquifer recharge and transmissivity are lower (Ryder, 1985), or in the deeper ground water. These waters are probably older than the oxygenated waters from shallow wells in Citrus and Marion County.

Some of the isotopically enriched waters appear to have undergone evaporation prior to recharging the aquifer. The heaviest δD and $\delta^{18}O$ values were from two wells with low sulfate concentrations from eastern Sumter County (wells 1 and 2). These waters had elevated chloride concentrations (19 and 29 mg/L, respectively), which is consistent with evaporative concentration. This site is surrounded by numerous ponds and lakes. Katz and others (1995a) found that ground water downgradient from a seepage lake in north-central Florida was enriched in δD and $\delta^{18}O$ because of recharge from the lake. In that study, δD and $\delta^{18}O$ from the ground water plotted along a mixing line between the lake, which reflected evaporation, and the meteoric water line. The enriched δD and $\delta^{18}O$ values for this study plot near Katz and others' (1995a) evaporation line (fig. 23), indicating that evaporation may have caused the isotopic enrichment and offset from the global meteoric water line.

The high sulfate waters usually were more enriched in δD and $\delta^{18}O$ than low sulfate waters that contain DO (fig. 23). However, high sulfate waters were not isotopically distinct from anaerobic, low sulfate waters. The range of δD and $\delta^{18}O$ for the high sulfate waters may indicate mixing between recent recharge and older waters. However, a straightforward mixing relation is not apparent. The most isotopically enriched high sulfate water (from well 18) was analyzed for tritium during a previous sampling. It contained no tritium (A. Swancar, U.S. Geological Survey, written commun., 1992), indicating that this water is not recent recharge. Climatic differences during the time of recharge, including more evaporation, may explain the isotopic composition of the high sulfate waters, which are presumably older than the aerobic low sulfate waters.

Carbon-13

Processes affecting the stable isotope composition of inorganic carbon ($\delta^{13}C$) include carbonate mineral dissolution and precipitation, microbially mediated processes that oxidize organic carbon and generate CO_2, and mixing of waters. $\delta^{13}C$ values ranged from -12.3 to -6.6 per mil. For low sulfate waters, $\delta^{13}C$ values usually were lighter for waters with higher P_{CO_2} values (fig. 24). This is consistent with microbial oxidation of organic matter, which typically has an isotopically light $\delta^{13}C$ value around -25 per mil (Rightmire and Hanshaw, 1973; Buchardt and Fritz, 1980). As light organic carbon is oxidized to CO_2 (equations 7 through 10), the amount of dissolved CO_2 and the corresponding P_{CO_2} increase, provided that the system is closed to the atmosphere.

Several low sulfate waters were enriched in $\delta^{13}C$ (well 1 and to a lesser degree well 2) (fig. 24). These waters also had enriched δD and $\delta^{18}O$ values, indicative of water recharged from an evaporating surface-water body. Katz and others (1995b) attributed isotopically heavy inorganic carbon in ground water beneath a north-central Florida lake to methanogenesis produced by the reduction of CO_2. The anomalously heavy $\delta^{13}C$ value

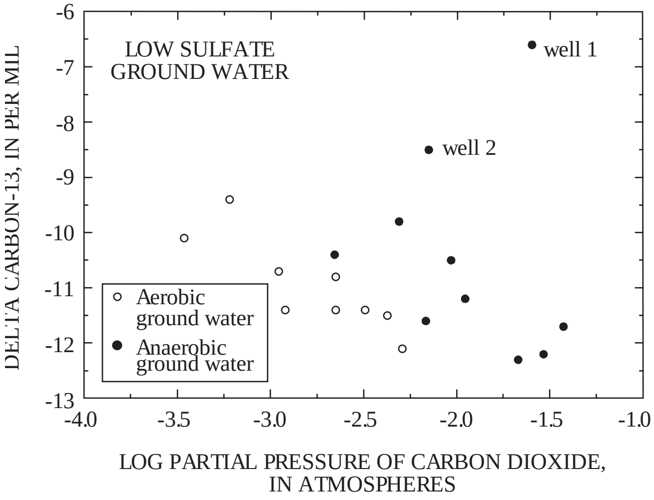


Figure 24. Relation between delta carbon-13 and partial pressure of carbon dioxide for low sulfate ground water (less than 30 milligrams per liter) from the Upper Floridan aquifer.

observed in ground water from well 1 similarly may be the result of methanogenesis, although methane was not analyzed. During CO_2 reduction, methanogenic bacteria preferentially oxidize isotopically light CO_2 to CH_4 (methane), resulting in heavy inorganic carbon in the water. Water from well 1 did not contain DO or sulfide, and had a very low sulfate concentration (less than 0.2 mg/L). Thus, activity of sulfate reducing bacteria was probably minimal. After O_2 was consumed and Fe(III) was reduced, methanogenic bacteria probably became active and caused ^{13}C enrichment of the remaining inorganic carbon in solution. The deeper ground water at this site (well 2) is probably a mixture between the shallow ground water and water more typical of that from the Upper Floridan aquifer.

High sulfate waters also had a large range in $\delta^{13}C$ but had no obvious relation with P_{CO_2}. However, as sulfate concentrations increased to more than 150 mg/L, the range of $\delta^{13}C$ narrowed to relatively heavy values between about -10 to -8 per mil. Similar reactions involving inorganic carbon probably control $\delta^{13}C$ values at high sulfate concentrations. Higher sulfate waters apparently have undergone a greater extent of dedolomitization reactions (gypsum and dolomite dissolution and calcite precipitation) than low sulfate waters. Dolomite dissolution adds isotopically heavy carbon to the water. However, calcite precipitation removes some of this heavier carbon, resulting in $\delta^{13}C$ values that still are isotopically lighter than the dolomite.

Most deep ground waters also had heavier $\delta^{13}C$ values than their shallow counterparts. This is probably related to the greater abundance of dolomite deeper in the aquifer. Dolomite dissolution in deeper ground water is also evidenced by increased magnesium concentrations and SI of dolomite in deeper water.

Sulfur-34

Sources of sulfate and sulfide in the ground water can be evaluated by examining the sulfur isotope composition of both sulfur species (sulfate and sulfide; $\delta^{34}S_{sulfate}$ and $\delta^{34}S_{sulfide}$). Sulfate sources such as atmospheric precipitation, marine sulfur (from gypsum dissolution or seawater), and pyrite oxidation all have distinctly different sulfur isotope signatures. The extent of sulfate reduction and precipitation of sulfide minerals also can be evaluated using sulfur isotopes. Microbially mediated sulfate reduction transforms sulfate to reduced sulfur (sulfide). The bacteria responsible for these reactions fractionate the sulfur by preferentially using isotopically light sulfur (sulfur-32), causing the remaining sulfate to become isotopically enriched in sulfur-34.

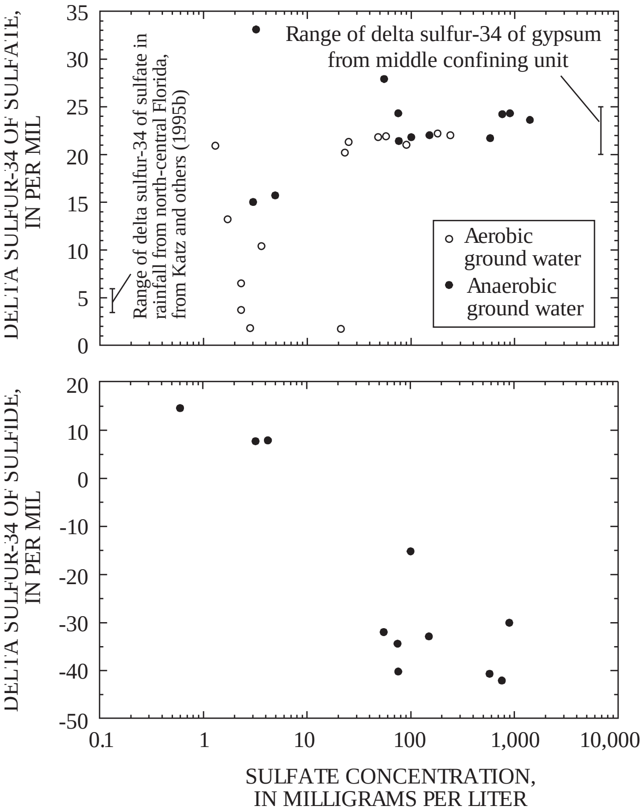


Figure 25. Relation between delta sulfur-34 of sulfate and sulfate concentration and delta sulfur-34 of sulfide and sulfate concentration in water from the Upper Floridan aquifer.

Sulfate

Values of $\delta^{34}S_{sulfate}$ in the ground water ranged from 1.7 to 33.1 per mil. The low sulfate ground water had a much greater range in $\delta^{34}S_{sulfate}$ than the high sulfate ground water (fig. 25). Most of the low sulfate waters are within the range of $\delta^{34}S_{sulfate}$ values reported by Rightmire and others (1974) for waters from the recharge area of the Upper Floridan aquifer (8.1 to 23.2 per mil). Rainwater collected during 1991 and 1992 from an inland site in western Putnam County (about 40 mi to the northeast of the study area) had three-month composite $\delta^{34}S_{sulfate}$ values ranging between 3.4 and 5.9 per mil (Katz and others, 1995b). This is similar to ranges reported by Östlund (1959) and Jensen and Nakai (1961) for $\delta^{34}S_{sulfate}$ in rainwater in unindustrialized regions (between 3.2 and 8.2 per mil).

The greater range of $\delta^{34}S_{sulfate}$ for the low sulfate waters compared to rainwater probably reflects differences in the extent of reactions influencing sulfate and spatial variability in $\delta^{34}S_{sulfate}$ in recharge waters. Biological uptake and microbial sulfate reduction fractionate sulfur isotopes, resulting in isotopically heavier sulfate. Adsorption of sulfate onto soils and clays also may fractionate some of the sulfur (Krouse, 1980). In addition, very small amounts of mixing with sulfate-rich water that dissolved gypsum can result in heavier $\delta^{34}S_{sulfate}$ values (discussed further below). Marine aerosols in coastal areas are probably another source for heavier sulfate in recharge waters. Oxidation of reduced sulfur, in the form of organic sulfur or a sulfide mineral such as pyrite, may explain $\delta^{34}S_{sulfate}$ values lighter than rainwater. Alternatively, localized anthropogenic sources (for example, industrial emissions and fertilizers) may result in isotopically light sulfate.

As sulfate concentrations increase, $\delta^{34}S_{sulfate}$ approaches a more constant value between 21 and 25 per mil (fig. 25). This is within the range of $\delta^{34}S_{gypsum}$ from the middle confining unit, and further indicates that gypsum dissolution is the primary source of sulfate for high sulfate waters. The only outlier is water from well 3, which had a heavier $\delta^{34}S_{sulfate}$ value of 27.9 per mil. This water also had one of the highest sulfide concentrations (1.2 mg/L), which supports that fractionation during sulfate reduction caused isotopic enrichment of sulfate.

Sulfide

Values of $\delta^{34}S_{sulfide}$ ranged from -42.1 to 14.6 per mil for the 11 samples that had sufficient sulfide to analyze (fig. 25). Low sulfate waters all had positive $\delta^{34}S_{sulfide}$ values, whereas high sulfate waters all had negative $\delta^{34}S_{sulfide}$ values. The positive values are indicative of a greater extent of sulfate reduction from a limited pool of sulfate, resulting in lower sulfate concentrations and heavier $\delta^{34}S_{sulfide}$ values. For the high sulfate waters, the abundant supply of sulfate with a relatively constant $\delta^{34}S_{sulfate}$ value resulted in fairly uniform $\delta^{34}S_{sulfide}$ values (usually between -30 and -45 per mil). Rye and others (1981) found positive $\delta^{34}S_{sulfide}$ values in water from the Upper Floridan aquifer near the recharge area and negative values further downgradient, where sulfate concentrations and aquifer residence time increased.

For low sulfate waters, the range of $\delta^{34}S_{sulfide}$ (7.7 to 14.6 per mil) is very similar to the range of $\delta^{34}S_{sulfate}$ in waters not containing sulfide. This suggests that most of the original sulfate was reduced to sulfide. However, sulfate concentrations for sulfide-bearing waters were higher than their corresponding sulfide concentrations (in mmol/L), which indicates a removal mechanism for sulfide. Bicarbonate concentrations were also elevated for these waters (greater than 240 mg/L) and were in excess of that expected from calcite dissolution based on calcium concentrations. This is consistent with microbially mediated sulfate reduction, which increases alkalinity. Only one low sulfate water was analyzed for sulfur isotopes of both sulfate and sulfide (well 14). This water had an unusually heavy $\delta^{34}S_{sulfate}$ value (33.1 per mil), which is further evidence of sulfate reduction. Because the sulfide concentration was relatively low for this water (0.03 mg/L), significant amounts of sulfide must have been removed from solution, probably as a sulfide mineral such as pyrite. Based on isotope mass balance calculations and assuming that the total amount of sulfur reduced (in mmol/L) equals the excess bicarbonate concentration over that expected for calcite dissolution (equation 2), between 50 and 85 percent of the original sulfur may have been removed from solution by pyrite precipitation.

The difference between the $\delta^{34}S$ values of sulfate and sulfide ($\Delta^{34}S$) ranged from 25.4 to 66.3 per mil for the nine waters with $\delta^{34}S$ analyses of both sulfate and sulfide (see appendix). Most of the $\Delta^{34}S$ values were around 60 per mil, which is near the value expected for fractionation at isotopic equilibrium between sulfate and sulfide (Rye and others, 1981). This indicates slow sulfate reduction in waters with long residence times in the aquifer. These waters were all from deeper wells, supporting that they are part of a slower regional flow system. Lesser $\Delta^{34}S$ values may indicate that sulfate reduction took place at a considerably faster rate (Rye and others, 1981). Sulfate reduction from laboratory experiments, which are run at considerably faster rates than sulfate reduction in ground water with long residence times, typically have lower $\Delta^{34}S$ values between 20 and 30 per mil (Pearson and Rightmire, 1980; Rye and others, 1981). The shallow ground water from well 14 had the lightest $\Delta^{34}S$ value of 25.4 per mil. This may indicate faster sulfate reduction, perhaps during recharge through organic-rich soils, where carbon is not limited.

Total Sulfur

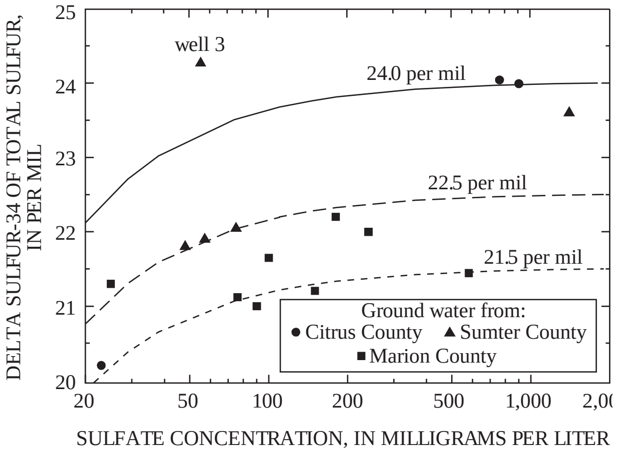
When sulfur occurs as both sulfate and sulfide, evaluating the sulfur isotope composition of total sulfur in solution ($\delta^{34}S_{total}$) can allow a more accurate assessment of sulfur sources. The computed $\delta^{34}S_{total}$ value is based on the concentration and isotopic composition of sulfate and sulfide:

$$\delta^{34}S_{total} = \frac{\delta^{34}S_{sulfate}m_{sulfate} + \delta^{34}S_{sulfide}m_{sulfide}}{m_{sulfate} + m_{sulfide}} \qquad (11)$$

where $m_{sulfate}$ and $m_{sulfide}$ are the sulfate and sulfide concentrations in mmol/L. A $\delta^{34}S_{total}$ value was not computed for waters that had insufficient sulfate or sulfide for $\delta^{34}S$ analysis; when sulfide was not present it was assumed that $\delta^{34}S_{total}$ equals $\delta^{34}S_{sulfate}$. Water from well 3 had the largest difference between $\delta^{34}S_{sulfate}$ (27.9 per mil) and $\delta^{34}S_{total}$ (24.3 per mil). This $\delta^{34}S_{total}$ value is within the range of the sulfur isotope composition of gypsum from the middle confining unit. For the remainder of ground waters, the calculated $\delta^{34}S_{total}$ value differed by less than 2 per mil from the $\delta^{34}S_{sulfate}$ value (see appendix).

Although a common source of gypsum is evident for the high sulfate waters, two separate groups are apparent based on $\delta^{34}S_{total}$ values. One group has values between 23.6 to 24.3 per mil, and the other group has $\delta^{34}S_{total}$ values between 21.0 and 22.2 per mil. Some of the waters in the isotopically heavier group had the highest sulfate concentrations or were from the deepest wells. None of these waters contained DO, and all are located in Sumter or Citrus Counties. The isotopically lighter group of waters could represents a mixture of more recent recharge with deeper ground water. Some of these lighter waters also contained DO, which supports mixing with recent recharge.

Isotope mass balance calculations were used to test the possibility that mixing is responsible for the observed range of $\delta^{34}S_{total}$ for the high sulfate waters. Mixing also was evaluated for the two waters with slightly elevated sulfate concentrations (between 20 and 25 mg/L) that had $\delta^{34}S_{sulfate}$ values in the range of marine sulfate (wells 19 and 26). The calculations considered mixing between a typical recharge water (sulfate concentration of 2 mg/L and $\delta^{34}S_{total}$ value of 5 per mil) and a deep ground water in equilibrium with gypsum (sulfate concentration of 1,800 mg/L). Initially the mixing line was calculated with a $\delta^{34}S$ value of 24.0 per mil for the water in equilibrium with gypsum (similar to measured $\delta^{34}S$ of gypsum from the study area of 24.0 and 24.5 per mil). Calculated $\delta^{34}S$ values were much heavier than observed values for the isotopically lighter group of waters, when assuming the $\delta^{34}S$ value for gypsum was 24.0 per mil (fig. 26). Thus, the mixing line was recomputed with lighter $\delta^{34}S_{gypsum}$ values. The isotopically lighter waters plot between mixing lines with $\delta^{34}S_{gypsum}$ of 21.5 and 22.5 per mil (fig. 26). These mass balance calculations illustrate how the computed $\delta^{34}S$ composition for the water is equivalent to the assumed isotopic composition of the gypsum when sulfate concentrations are greater than about 100 mg/L. Thus, gypsum of a variable isotopic composition (between 21 and 24 per mil) apparently influences sulfate in the ground water. Waters with lower sulfate concentrations plot on mixing lines between the recharge water and the isotopically lighter gypsum. This includes the two samples with low, but slightly elevated, sulfate concentrations between 20 and 25 mg/L (fig. 26).



[Lines calculated assuming mixing between a low sulfate wate (2 milligrams per liter) with a delta sulfur-34 value of 5 per mi and a sulfate-rich ground water (1,800 milligrams per liter) wi the delta sulfur-34 value specified on the line.]

Figure 26. Relation between delta sulfur-34 of total sulfur (sulfate plus sulfide) and sulfate concentration in water from the Upper Floridan aquifer, plotted with mixing relations between dilute ground water and water in equilibrium with gypsum.

The sulfur isotope composition of gypsum may vary spatially in the study area. All high sulfate waters from Marion County were isotopically lighter ($\delta^{34}S_{total}$ values between 21.2 and 22.0 per mil) than high sulfate waters from Citrus County (24.0 per mil, similar to $\delta^{34}S$ values of gypsum from Citrus County). When evaporites were deposited during the middle Eocene, evaporative basins were isolated, and gypsum and anhydrite were not formed simultaneously or uniformly over the study area. Reducing conditions were probably present in some of the basins, resulting in gypsum that was isotopically heavier than the seawater. This is consistent with the association of pyrite with gypsum from the ROMP 110 core (Southwest Florida Water Management District, written commun., 1993).

Isotopically lighter gypsum indicates that more oxidizing conditions existed when evaporites were deposited, perhaps due to better circulation with open marine water. In eastern Marion County, which is outside of the study area, continuous evaporites do not occur in the Avon Park Formation (Miller, 1986). This could indicate that there was a connection to the open sea to the east during the middle Eocene, precluding the development of evaporative basins in that area. The part of Marion County within the study area would have been closer to this area of open circulation, whereas Citrus County would have been further away, perhaps making it more prone to reducing conditions. Further evaluation of the sulfur isotope composition of gypsum in the study area may help resolve spatial variability in evaporites and allow a better understanding of the depositional environment.

Other explanations for the differences in sulfur isotope composition of high sulfate ground waters are precipitation and oxidation of sulfide minerals (such as pyrite). Isotopically lighter waters may have oxidized isotopically light pyrite. Several of these waters contained DO, and so pyrite oxidation is possible. However, about half of the high sulfate waters with $\delta^{34}S_{total}$ values between 20 and 22 per mil did not contain DO, which was probably consumed by microbial populations. Given the similar isotopic composition for the aerobic and anaerobic ground waters, pyrite oxidation is probably not a significant source of sulfate.

Conversely, the isotopically heavier waters could be influenced by removal of reduced sulfur from solution, probably by precipitation of pyrite. Water from well 3 had a $\delta^{34}S_{total}$ value that was considerably heavier than predicted from strict mixing between dilute recharge and water in equilibrium with gypsum (fig. 26). This indicates that some of the sulfide was removed from solution, presumably as a sulfide mineral. Likewise, the isotopically heavier waters from Citrus County also could be influenced by sulfate reduction and pyrite precipitation. These waters are downgradient from the isotopically lighter waters in Marion County, presumably along deep slow flow paths from Marion County (fig. 6). Therefore, these waters probably had a longer residence time in the aquifer than waters from Marion County.

GEOCHEMICAL MODELING

Geochemical mass-balance modeling was used to evaluate chemical and isotopic differences between shallow and deep ground water. The interaction between shallow and deep ground water in the study area is poorly understood. Shallow ground water is usually characterized by a rapid flow system and relatively low concentrations of dissolved solids, whereas deeper ground water is usually characterized by a slower regional flow system with higher sulfate concentrations. High sulfate concentrations, however, do occur in the shallow ground water in isolated locations (fig. 11). In these areas, the source of sulfate appears to be similar to the deeper ground water. Sulfate also does not increase with depth at all locations, which may mean that the shallow flow system penetrates deeper in these area. An evaluation of chemical changes between shallow and deep ground water may help define the relation between the flow systems. The wide range of sulfate concentrations in the high sulfate waters and concurrent increases in other solutes indicate that differences in the extent of geochemical reactions or a range of mixing control sulfate concentrations.

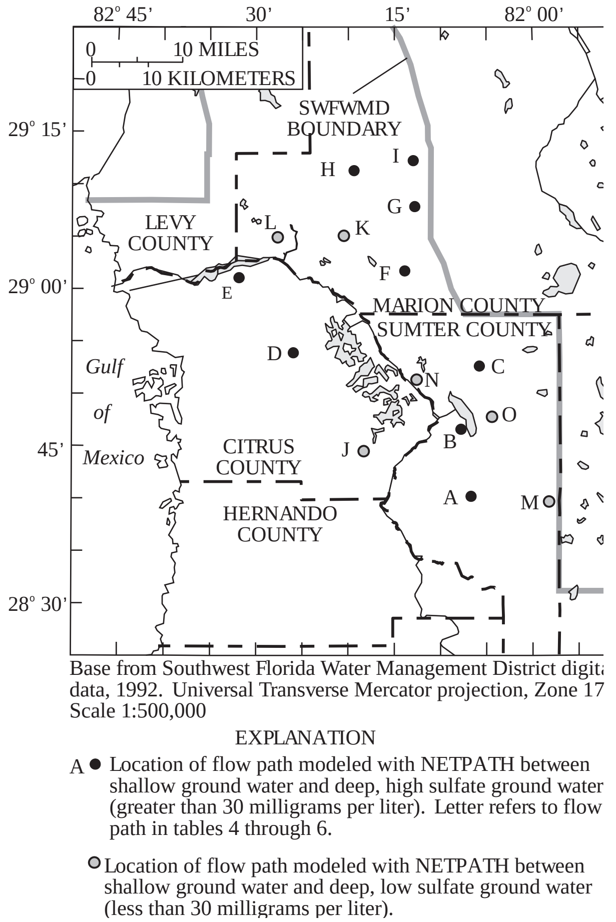
The model NETPATH (Plummer and others, 1991) computes a set of reactions (including mineral dissolution or precipitation, ion exchange, and gas exchange) based on the net mass transfer of elements between initial and final waters, given a set of constraints (elemental, isotopic, electron balance). The model also can compute an isotopic composition for the final water, given the isotopic composition of the initial water, isotopic composition of dissolving phases, and fractionation factors of precipitating phases. Although the resulting models are not unique and cannot always be validated, certain models can be rejected based on violations of thermodynamics (for example, dissolution of a mineral from a supersaturated water) or large discrepancies between observed and computed $\delta^{13}C$ and $\delta^{34}S$ values of the final water. Descriptions of the mass-balance modeling approach, including relevant equations, are presented in detail elsewhere (Plummer, 1977; Plummer and Back, 1980; Plummer and others, 1983; Plummer and others, 1990; Busby and others, 1991).

Modeling in this report focuses on vertical changes in chemical composition between shallow and deep ground water. To be consistent with modeling terminology these are referred to as “flow paths.” Because the study area is dominated by aquifer recharge, the shallow ground water is probably a good approximation of water that recharged the aquifer before moving to deeper parts of the aquifer. However, the modeling scenarios are limited by lack of head measurements in the deeper part of the aquifer, and a direct hydraulic connection between the two waters usually has not been established. Nonetheless, geochemical modeling can elucidate dominant reactions in the evolution of the deeper ground water and can give insights into how the shallow and deep flow systems are related.

Constraints considered in all models were sulfur, calcium, magnesium, carbon, iron, and electron balance. Electron balance was necessary for modeling redox reactions such as oxidation of organic matter. Reaction phases considered were gypsum, dolomite, calcite, organic matter (represented as CH_2O), CO_2 gas, pyrite, and goethite. Pyrite precipitation was included as a sink for sulfur, which also allowed for the fractionation of $\delta^{34}S$ during sulfate reduction. Goethite was included in models to balance iron, which was necessary when pyrite precipitation was calculated. When shallow waters contained dissolved oxygen and nitrate, nitrate was added as a constraint and O_2 and N_2 gas were added as phases (representing aerobic respiration and nitrate reduction; equations 7 and 8). Mixing with sulfate-rich water also was used to assess the feasibility of upwelling in explaining high sulfate waters. Nine flow paths were modeled where sulfate concentrations are high (greater than 30 mg/L) in the deep ground water, and six flow paths were modeled where sulfate remains low in the deep ground water. The locations of the flow paths are shown in figure 27; the depth of open hole intervals of wells for modeled flow paths are shown in figure 28.

Reactions Controlling the Composition of Deep, High Sulfate Ground Water

Gypsum and dolomite dissolution were calculated for all high sulfate models (table 4). These reactions are consistent with the saturation state of the waters. Calcite precipitation was computed for all models expect for flow path I, which computed calcite dissolution. Water from the shallow well for this flow path (well 33) was undersaturated with respect to calcite, making additional calcite dissolution possible. Deep ground waters were all saturated to supersaturated with calcite, making calcite precipitation a plausible reaction. Although similar reactions were modeled, the magnitude of dominant reactions between flow paths varied by over an order of magnitude. This is because of the wide range of differences between the chemical composition of shallow and deep ground waters.



Base from Southwest Florida Water Management District digit
data, 1992. Universal Transverse Mercator projection, Zone 17
Scale 1:500,000

EXPLANATION

A ● Location of flow path modeled with NETPATH between shallow ground water and deep, high sulfate ground water (greater than 30 milligrams per liter). Letter refers to flow path in tables 4 through 6.

○ Location of flow path modeled with NETPATH between shallow ground water and deep, low sulfate ground water (less than 30 milligrams per liter).

Figure 27. Locations of flow paths between shallow and deep ground water modeled using NETPATH. (Index numbers and specific information about wells shown in figure 8 and table 3.)

Several models were computed for most flow paths. These models varied by differences in minor amounts of mass transfer of pyrite, goethite, CO_2 or O_2 exchange, and CH_2O; major reactions described above were very similar for most models for a specific flow path. Differences in minor reactions influence the calculated $\delta^{13}C$ and $\delta^{34}S$ values of the final water. Models including pyrite precipitation had $\delta^{34}S$ values that were heavier than observed values, whereas models not including pyrite precipitation had computed $\delta^{34}S$ values closer to observed values. Therefore, models without pyrite precipitation or with the least amount of pyrite precipitation are included in table 4.

For flow path G, models with pyrite and goethite precipitation were virtually identical. Both shallow and deep waters contained DO. Thus, pyrite precipitation is

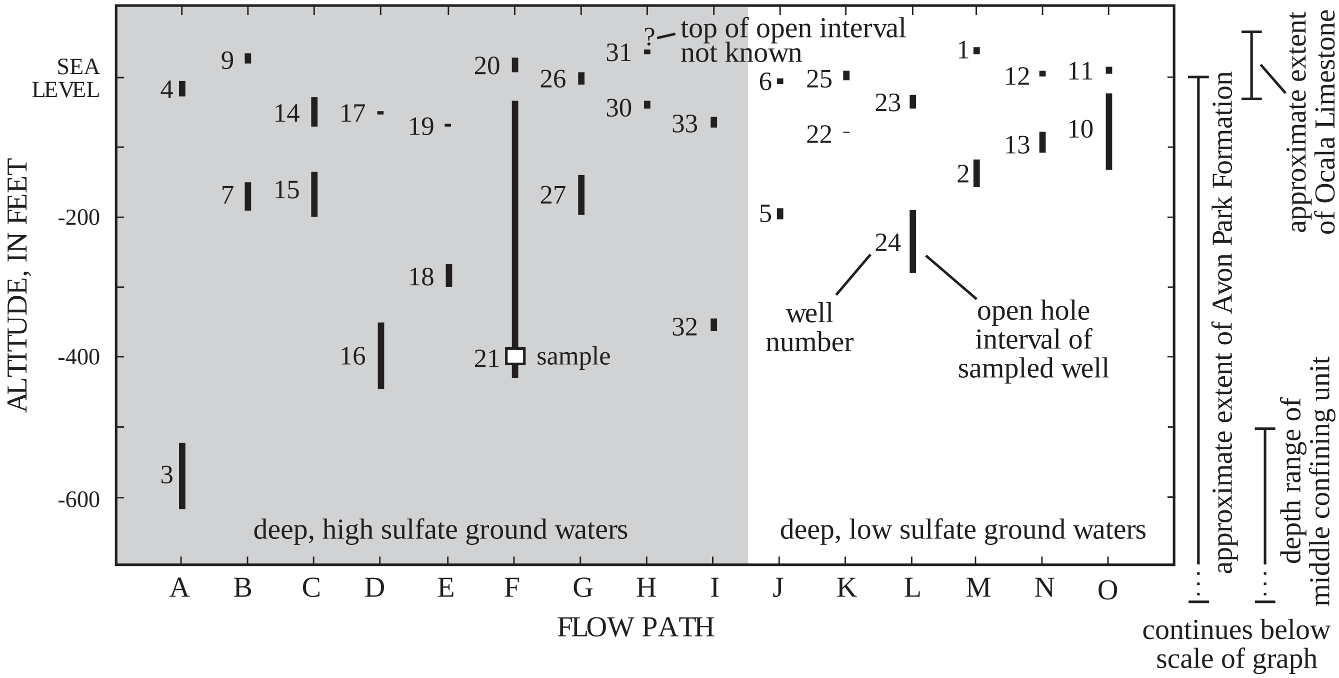


Figure 28. Depth range of open hole intervals of shallow and deep wells for flow paths modeled with NETPATH.

Table 4. NETPATH models between shallow ground water and deep, high sulfate ground water

[Units in millimoles per liter (mmol/L) unless otherwise noted; positive mass transfer indicates dissolution or ingassing; negative mass transfer indicates precipitation or outgassing; gyp, gypsum; dol, dolomite; cal, calcite; δ^{34}S, delta sulfur-34; ‰, per mil; calc, calculated; obs, observed; δ^{13}C, delta carbon-13; --, not modeled; isotope data used in models unless otherwise specified: δ^{13}C of CH_2O = -25.0 per mil; δ^{13}C of calcite = 0 per mil when dissolving; for precipitating phases, δ^{13}C or δ^{34}S computed by model based on Rayleigh calculations and fractionation factors defined at the midpoint (X=0.5) between initial and final water compositions; δ^{13}C (observed) based on DOC of -25.0 per mil; δ^{34}S (observed) based on measured δ^{34}S of sulfate and sulfide; all models also include goethite dissolution or precipitation (less than 0.06 mmol/L); all models include nitrogen outgassing (less than 0.04 mmol/L), except flow paths A, C, and G]

Flow path	Initial well	Final well	Gyp	Dol	Cal	CH_2O	O_2	CO_2	δ^{13}C (total C), ‰				δ^{13}C (total C), ‰			
									calc[1]	gyp	calc[2]	obs	calc[3]	dol	calc[4]	obs
A	4	3	0.56	0.32	-0.52	0.03	--	-0.19	21.4	24.5	23.7	24.5	-9.6	--	--	-9.6
B	9	7	14.11	4.25	-8.13	0.23	--	-1.05	22.0	23.5	23.4	23.6	-2.0	-8	-9.6	-9.5
C[5]	14	15	0.86	0.41	-1.77	--	--	-1.79	26.1	20.0	24.1	22.2	-9.4	--	--	-9.9
D	17	16	7.93	3.04	-6.74	0.98	0.77	--	22.0	24.0	24.0	24.1	-4.9	-6	-9.9	-9.6
E	19	18	9.19	2.32	-4.12	1.37	0.97	--	22.0	24.0	23.9	24.0	-7.4	-3	-9.5	-9.4
F	20	21	6.05	1.53	-3.43	0.82	0.34	--	22.0	21.5	21.5	21.5	-8.0	-2	-9.2	-9.4
G	26	27	2.24	0.64	-1.30	0.29	0.20	--	21.9	--	--	22.0	-8.3	-5	-10.3	-10.2
H	31	30	0.11	0.12	-0.21	0.10	--	-0.64	21.1	--	--	21.7	-11.1	--	--	-10.2
I	33	32	1.56	0.81	0.14	2.09	1.90	--	21.6	--	--	21.3	-13.5	--	--	-12.5

[1] Using δ^{34}S of gypsum equal to 22 per mil.

[2] Using variable δ^{34}S of gypsum shown in previous column.

[3] Using δ^{13}C of dolomite equal to 0 per mil.

[4] Using isotopically lighter δ^{13}C of dolomite shown in previous column.

[5] Model has pyrite precipitation (0.04 mmol/L).

not possible, and the model containing goethite precipitation (which is supersaturated in both waters) is included in table 4. A model with pyrite oxidation also was considered because of the aerobic ground water. This model is virtually identical to the one presented in table 4, except that 1 percent of the sulfur (0.02 mmol/L) comes from pyrite oxidation, resulting in calculated $\delta^{34}S$ being 1 per mil lighter.

The sulfur isotope composition of gypsum probably varies within the study area, as previously noted. Changing the $\delta^{34}S$ value of gypsum within the reported range for the Floridan aquifer system (20.0 to 24.5 per mil) resulted in a better agreement between modeled and observed values for most flow paths (table 4). Like many modeling endeavors, however, solutions are not unique. For example, changing pyrite fractionation factors to be more representative of kinetic fractionation seen in the shallow ground water (for example, $\Delta^{34}S$ value of 25.4 per mil for well 14) also significantly affects calculated $\delta^{34}S$ values.

Calculated and observed $\delta^{34}S$ values did not agree for two flow paths (A and C). This could indicate that too much or too little pyrite precipitation was modeled, or that the shallow water is not representative of water that reacted to form the deeper water. The latter is probably the case for flow path C, where the shallow water had already undergone a significant amount of sulfate reduction, reflected by an unusually heavy $\delta^{34}S_{sulfate}$ value (33.1 per mil). For flow path A, the observed $\delta^{34}S$ value for the deep water was heavier than the modeled value, indicating that some pyrite precipitation probably occurred that was not computed by the model. This deep water (well 3) had a heavy $\delta^{34}S_{total}$ value, indicating pyrite precipitation (fig. 26).

The difference between observed and modeled $\delta^{13}C$ values for some of the flow paths can be explained by analytical uncertainties and assumed values of $\delta^{13}C$ of organic matter (CH_2O). However, five flow paths (B, D, E, F, and G) had calculated $\delta^{13}C$ values that were considerably heavier than observed values when assuming 0 per mil for $\delta^{13}C$ of dolomite (near values measured in the study area). For these flow paths, an isotopically lighter dolomite (between -2 and -8 per mil) is needed for the calculated $\delta^{13}C$ to approximately equal the observed value (table 4). Isotopically light dolomites (-2.8 to -7.5 per mil) have been observed in the Floridan aquifer system (Hanshaw and Back, 1972). Based on mass balance modeling, Plummer (1977) concluded that isotopically light dolomite (between -1.5 and -3.9 per mil) was dissolving along a regional flow path in the Upper Floridan aquifer in southwest Florida. Isotopically light dolomites may be more soluble in ground water than heavy dolomites, perhaps due to differences in their origin, stoichiometry, or degree of crystallinity.

Most models had some oxidation of organic matter and CO_2 or O_2 exchange. In Citrus and Marion Counties, where aquifer recharge is high, shallow waters contained DO and nitrate, whereas deep waters typically were anaerobic (except for flow path G). Two different types of models were computed for flow paths in these counties. One had significant amounts of CO_2 ingassing; the other did not contain CO_2, but instead had O_2 ingassing (or reduction) and usually had more than twice as much organic matter oxidation as the corresponding CO_2 ingassing model. Isotopic data for these two types of models were identical. The O_2 reduction models simulate aerobic respiration in the shallow ground water. These models are probably more realistic because an oxygen source is readily apparent. Thus, the aerobic respiration models are included in table 4. The CO_2 ingassing models apparently are a net result of the CO_2 produced by the consumption of organic matter in aerobic respiration (equation 7). The amount of modeled O_2 reduction, however, was higher than the amount of dissolved oxygen in the shallow ground water. Additional dissolved O_2, as well as soil CO_2, could enter the shallower part of the aquifer as rapid recharge, perhaps through preferential flow through sinkholes.

Flow paths with CO_2 outgassing models typically are in Sumter County, where recharge is slow and shallow ground water is probably older. Mechanisms for outgassing of CO_2 are not apparent. Calculated outgassing may be related to charge imbalance in the analytical data. Alternatively, the shallow ground water for these flow paths may not be representative of water that evolved to the deeper water.

Evaluating Upwelling as Source of Sulfate

This modeling exercise illustrates that dedolomitization reactions are significant in controlling the composition of deep, high sulfate ground water. These reactions are driven by gypsum dissolution. However, gypsum occurs deeper in the aquifer than open intervals of most deep wells (fig. 28; table 1). Although it is possible that trace gypsum occurs in upper intervals of the Avon Park Formation, it has not been observed in core samples or well cuttings. Alternatively, the deeper ground water could have a mild upward flow component from near the base of the aquifer, where evaporites occur. Upward flow was measured within the open borehole of several wells finished in the Avon Park Formation in Marion County (fig. 9), and an upward head gradient exists in ground water from the Avon Park Formation near Lake Panasoffkee (fig. 7).

In southwest Florida, high sulfate concentrations in shallow parts of the confined Upper Floridan aquifer are attributed to upwelling of sulfate-rich water that dissolved evaporites at the base of the aquifer (Jones and others, 1993; Sacks and Bullen, 1993; Johnson, 1994; Sacks and others, 1995). This corresponds to an area where dedolomitization reactions had previously been modeled (Plummer, 1977; Plummer and others, 1983). In the present study area, dedolomitization reactions similarly could be occurring deeper in the aquifer, where gypsum is present, rather than between the sampled shallow and deep wells.

To test whether upwelling could explain the high sulfate concentrations observed in the deeper ground water, upwelling was modeled with NETPATH (fig. 29). The shallow ground water was mixed with a sulfate-rich ground water at equilibrium with respect to gypsum. Water from ROMP 110 (collected by SWFWMD during drilling) was used as the composition of the upwelling water because it had a very high sulfate concentration (1,800 mg/L) and was at equilibrium with gypsum (see appendix).

Upwelling models are presented in table 5. For five of the flow paths, gypsum dissolution was not computed, and mixing accounted for all of the sulfate in the deep ground water. Models for the other flow paths had significantly less gypsum dissolution than models without mixing. The amount of mass transfer of carbonate minerals also was usually much smaller than for models not considering upwelling (fig. 29). Therefore, in addition to gypsum dissolution, the chemical composition of the deep, upwelling water already reflects significant amounts of dolomite dissolution and calcite precipitation.

Isotopic data were not available for the high sulfate water from ROMP 110. Thus, it is difficult to evaluate the reasonableness of reactions based on calculated isotopic data. $\delta^{13}C$ and $\delta^{34}S$ values were assumed for the upwelling water to compare the calculated and observed isotope compositions (table 5). The $\delta^{34}S$ composition of the upwelling waters apparently varies within the aquifer (reflecting a variable $\delta^{34}S_{gypsum}$). Computed and observed $\delta^{34}S$ values were similar when $\delta^{34}S$ of the upwelling water was within the range of gypsum from the aquifer. However, exceptions noted in the preceding section still held (flow paths A and C).

Computed $\delta^{13}C$ values were always lighter than observed values, when an assumed $\delta^{13}C$ value for the upwelling water was similar to that of high sulfate ground water from the study area (about -8.5 per mil). Thus, $\delta^{13}C$ for the upwelling water is probably heavier

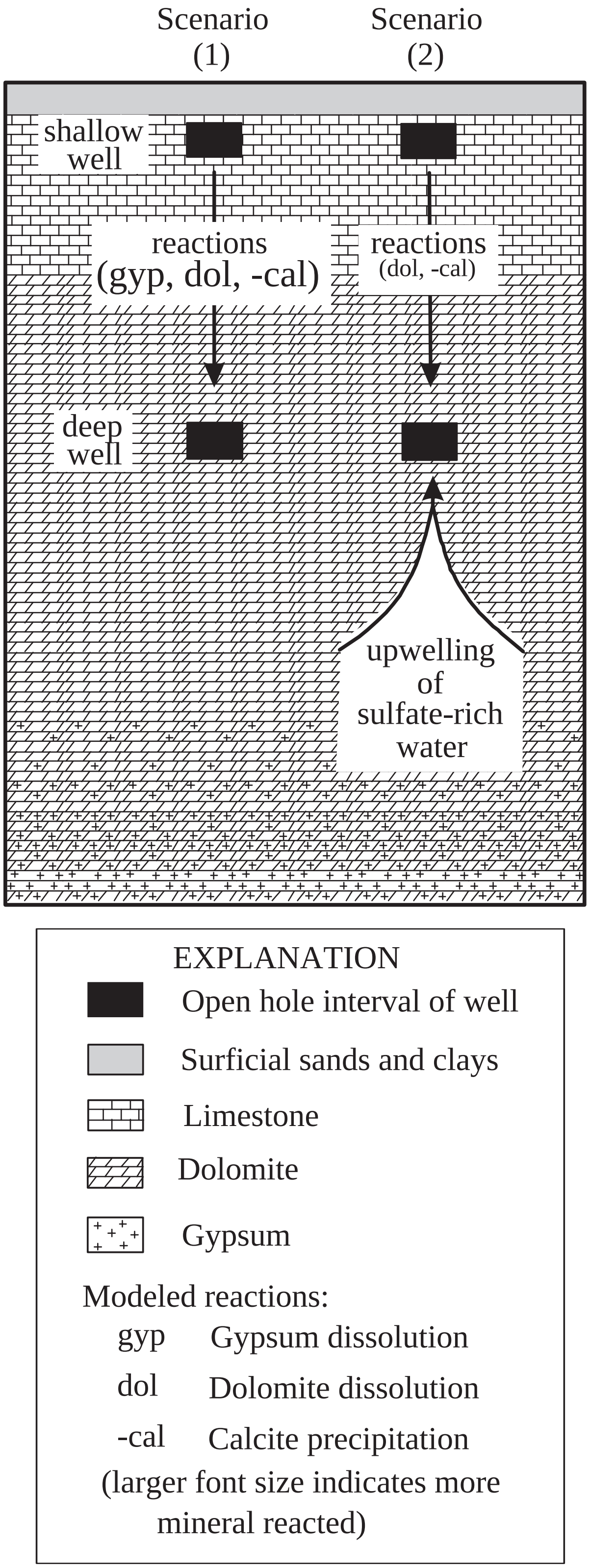


Figure 29. Scenarios of major reactions modeled with NETPATH between shallow wells and deep wells with high sulfate concentrations, considering (1) only reactions between open interval of wells or (2) reactions plus upwelling of sulfate-rich water.

Table 5. NETPATH models between shallow ground water and deep, high sulfate ground water, including upwelling of sulfate-rich water

[Units in millimoles per liter (mmol/L) unless otherwise noted; positive mass transfer indicates dissolution or ingassing; negative mass transfer indicates precipitation or outgassing; gyp, gypsum; dol, dolomite; cal, calcite; δ^{34}S, delta sulfur-34; ‰, per mil; calc, calculated; obs, observed; δ^{13}C, delta carbon-13; --, not modeled; isotope data used in models unless otherwise specified: δ^{13}C of CH_2O = -25.0 per mil; δ^{13}C of calcite (when dissolving) and dolomite = 0 per mil; δ^{34}S of gypsum = 22 per mil; for precipitating phases, δ^{13}C or δ^{34}S computed by model based on Rayleigh calculations and fractionation factors defined at the midpoint (X=0.5) between initial and final water compositions; δ^{13}C (observed) based on DOC of -25.0 per mil; δ^{34}S (observed) based on measured δ^{34}S of sulfate and sulfide; all models also include goethite dissolution or precipitation (less than 0.06 mmol/L); all models include nitrogen outgassing (less than 0.04 mmol/L), except flow paths A, C, and G]

Flow path	Initial well	Final well	Fraction upwelling[1]	Gyp	Dol	Cal	CH_2O	O_2	CO_2	δ^{34}S (total S), ‰			δ^{13}C (total C), ‰		
										Up-welling[2]	calc	obs	calc[3]	calc[4]	obs
A	4	3	0.03	--	0.14	-0.22	0.02	--	-0.13	24.5	23.7	24.5	-10.5	--	-9.6
B	9	7	0.72	0.94	--	-1.14	0.34	0.28	--	23.5	23.4	23.6	-8.6	--	-9.5
C[5]	14	15	0.05	--	0.14	-1.26	--	--	-1.62	22.0	27.8	22.2	-10.3	--	-9.9
D	17	16	0.42	--	0.47	-2.68	1.38	1.29	--	24.5	24.5	24.1	-13.6	-9.7	-9.6
E	19	18	0.39	1.96	--	-0.48	1.77	1.45	--	24.5	23.9	24.0	-15.6	-11.2	-9.4
F	20	21	0.25	1.38	--	-0.94	1.18	0.80	--	22.0	22.0	21.5	-15.3	-11.8	-9.4
G	26	27	0.10	0.30	--	-0.28	0.41	0.36	--	22.0	21.9	22.0	-12.5	-10.9	-10.2
H	31	30	0.01	--	0.09	-0.15	0.10	--	-0.61	24.5	21.4	21.7	-11.2	--	-10.2
I	33	32	0.08	--	0.30	0.91	2.17	1.98	--	22.0	21.7	21.3	-13.8	[6]-11.7	-12.5

[1] Upwelling computed as amount of mixing between shallow ground water and water from ROMP 110 at equilibrium with gypsum collected by Southwest Florida Water Management District (written commun., 1993). Analytical results from ROMP 110 (248.5 feet) in the appendix; dissolved organic carbon concentration assumed to equal 1.5 milligrams per liter; iron concentration assumed to equal 10 micrograms per liter; nitrate concentration assumed to equal 0 milligrams per liter; pH assumed to equal 7.0; temperature assumed to equal 25 degrees C.

[2] Assumed δ^{34}S value of upwelling water.

[3] Using assumed δ^{13}C value of upwelling water equal to -4 per mil and δ^{13}C of CH_2O equal to -25 per mil.

[4] Using assumed δ^{13}C value of upwelling water equal to -4 per mil and δ^{13}C of CH_2O equal to -15 per mil, except where noted.

[5] Model has pyrite precipitation (0.04 mmol/L).

[6] Same as previous column except δ^{13}C of CH_2O equal to -20 per mil.

than measured values from the study area (about -4 per mil). However, for several flow paths (D, E, F, and G), calculated δ^{13}C values were still too light when δ^{13}C of the upwelling water was as heavy as 0 per mil (similar to dolomite measured from the study area). The heavier observed δ^{13}C values may reflect isotopically heavier CH_2O; for example, using a δ^{13}C value of -15 per mil (rather than -25 per mil) usually resulted in a closer match between computed and observed values (table 5). Alternatively, isotopic exchange (or recrystallization) of calcite could result in enrichment of δ^{13}C in the final water (Plummer and others, 1991; Katz and others, 1995b). Analytical uncertainties in the chemical data for ROMP 110 also probably are reflected in the computed carbon mass transfer.

These models indicate that mixing between shallow ground water and sulfate-rich upwelling water can explain the high sulfate concentrations in the deep ground water. Differences between the shallow and deep ground water do not have to be explained solely by mineral dissolution and precipitation reactions between the open intervals of the wells (fig. 29). Mixing from a deeper source is plausible because gypsum is not found in observable quantities in intervals where wells are finished.

Reactions Controlling the Composition of Deep, Low Sulfate Ground Water

Sulfate concentrations were low in both the shallow and the deep ground water at six sites (fig. 27 and 28). Reactions occurring between the shallow and the deep ground water for these flow paths were further evaluated with NETPATH. One of these flow paths (between wells 11 and 10) had significantly higher sulfate in the shallow ground water (21 mg/L) than in the deep ground water (3.0 mg/L). Models for this flow path compute unrealistically high pyrite precipitation to explain the lower sulfate concentration in the deep well, which results in unrealistically heavy δ^{34}S values.

Water from the shallow well for this flow path had an anomalously light $\delta^{34}S$ value (1.7 per mil), which probably is from a localized surficial source and is not representative of the shallow ground water in the area. Based on its more typical $\delta^{34}S_{sulfate}$ value and low sulfate concentration, the deep ground water does not reflect this same source of sulfate. Thus, models for this flow path are considered to be unrealistic and are not presented in table 6.

Aerobic, Shallow Ground Water

Similar reactions were modeled for three flow paths (J, K, and L) that had aerobic, shallow ground water. Models with $\delta^{13}C$ values closest to observed values are presented in table 6. Major reactions were O_2 reduction, calcite and dolomite dissolution, and organic matter oxidation. Minor amounts of goethite dissolution, pyrite precipitation, and N_2 outgassing (nitrate reduction) also were usually computed. No mass transfer of gypsum was modeled. Dolomite dissolution is consistent with undersaturation in the ground water and increasing amounts of dolomite deeper in the aquifer. Calcite is within the range of saturation in the shallow ground water (-0.104 to 0.069; see appendix) and is saturated to supersaturated in the deep ground water (0.060 to 0.332; see appendix). However, microbial oxidation of organic matter produces CO_2, which should drive additional calcite dissolution.

As were the high sulfate models with aerobic, shallow ground water, models with CO_2 ingassing (rather than O_2 reduction) also were computed for these low sulfate models. The CO_2 ingassing models had about half as much CH_2O oxidation as the O_2 reduction models. The calculated CO_2 is probably the net result of aerobic respiration (equation 7), and so only O_2 ingassing models are presented in table 6. Mass transfer of minerals and computed isotope compositions are identical for CO_2 and O_2 ingassing models for a given flow path. The amount of calculated O_2 reduction is similar to that observed in the shallow water for flow path K, but is higher than measured DO in the shallow waters for the other two flow paths. Dissolved O_2 (and probably some soil-zone CO_2) may be added to the water by rapid recharge in the karstified shallow part of the aquifer.

Models for these three flow paths have considerably less mass transfer than most of the high sulfate models. For these modeling scenarios, the lesser amounts of mass transfer and minimal reactions involving sulfur indicate that the deep wells are within the shallow flow system.

Anaerobic, Shallow Ground Water

Similar reactions were modeled for the other two low sulfate flow paths (flow paths M and N, in Sumter County), both of which had anaerobic, shallow ground water. Reactions include calcite precipitation, dolomite dissolution, CO_2 outgassing, and lesser amounts of gypsum dissolution, CH_2O oxidation, and pyrite precipitation (table 6). Deep waters were supersaturated with respect to calcite, and so precipitation is possible. As dolomite dissolves between the shallow and deep ground water, the addition of calcium and inorganic carbon probably drives this calcite precipitation.

Table 6. NETPATH models between shallow ground water and deep, low sulfate ground water

[Units in millimoles per liter (mmol/L) unless otherwise noted; positive mass transfer indicates dissolution or ingassing; negative mass transfer indicates precipitation or outgassing; gyp, gypsum; dol, dolomite; cal, calcite; $\delta^{34}S$, delta sulfur-34; ‰, per mil; calc, calculated; obs, observed; $\delta^{13}C$, delta carbon-13; --, not modeled; n/d; insufficient data; <, less than; isotope data used in models unless otherwise specified: $\delta^{34}S$ of gypsum = 22 per mil; $\delta^{13}C$ of calcite (when dissolving) and dolomite = 0 per mil; for precipitating phases, $\delta^{13}C$ or $\delta^{34}S$ computed by model based on Rayleigh calculations and fractionation factors defined at the midpoint (X=0.5) between initial and final water compositions; $\delta^{13}C$ (observed) based on DOC of -25.0 per mil; $\delta^{34}S$ (observed) based on measured $\delta^{34}S$ of sulfate and sulfide; all models except flow path K include pyrite precipitation (less than 0.02 mmol/L for flow paths J and L, 0.69 mmol/L for flow path M, and 0.08 mmol/L for flow path N)]

Flow path	Initial well	Final well	Gyp	Dol	Cal	CH_2O	O_2	CO_2	$\delta^{34}S$ (total S), ‰		$\delta^{13}C$ (total C), ‰		
									calc	obs	calc[1]	calc[2]	obs
J[3]	6	5	--	0.03	0.45	0.71	0.28	--	n/d	n/d	-13.1	-12.2	-11.6
K[3]	25	22	<0.01	0.07	0.12	0.28	0.09	--	9.5	10.7	-12.0	-11.5	-11.0
L[3]	23	24	--	0.49	0.19	1.44	1.12	--	n/d	n/d	-12.8	-10.8	-10.0
M	1	2	0.15	0.51	-0.83	0.12	--	-1.67	n/d	n/d	-5.8	--	-9.2
N	12	13	0.23	0.48	-1.01	0.26	--	-0.84	n/d	n/d	-11.1	--	-12.7

[1] Using $\delta^{13}C$ of CH_2O = -25.0 per mil.

[2] Using $\delta^{13}C$ of CH_2O = -20.0 per mil.

[3] Model has nitrogen outgassing (less than 0.03 mmol/L) and goethite dissolution (less than 0.05 mmol/L).

In contrast to the aerobic ground waters for the other flow paths, these shallow ground waters already had been influenced by microbially mediated reactions that generate CO_2. This is illustrated by the lack of DO and nitrate; sulfide is also present in the shallow water for flow path N. Microbially produced CO_2 results in high P_{CO_2} values in the shallow ground water, allowing more calcite to initially dissolve compared to the aerobic shallow waters. The greater extent of microbially mediated reactions is probably related to longer aquifer residence times due to a slower, shallow flow system and less recharge compared to the aerobic ground waters.

Sulfate is very low in both shallow and deep ground waters (less than 5 mg/L). Insufficient sulfur isotope data make it difficult to evaluate the reasonableness of reactions involving sulfur. The low amount of mass transfer of gypsum indicates that these “deep” waters are mostly isolated from the deeper flow system. However, a very small amount of upwelling may influence the composition of the deep water for flow path N (well 13). For example, gypsum dissolution is not computed when the shallow water is mixed with about one percent sulfate-rich water from ROMP 110, representing upwelling. (This model still contained CO_2 outgassing.) Upwelling is plausible because the site is near the Withlacoochee River, where localized discharging conditions exist in the aquifer. Nonetheless, significant amounts of discharge do not occur from the deep flow system because the sulfate concentration is still low in the deep well.

Deep wells for the low sulfate flow paths are somewhat shallower (average depth of 234 ft) than many of the deep wells for the high sulfate flow paths (average depth of 396 ft) (fig. 28). The low sulfate, deep ground water is apparently part of the same flow system as the shallow ground water, with a longer residence time in the aquifer than the shallow water (based on the greater extent of dolomite dissolution and microbially mediated reactions). The amount of mass transfer for these flow paths is considerably less than for most of the high sulfate flow paths. This indicates either less water-rock interactions or, more likely, insignificant amounts of upwelling of sulfate-rich water. A well finished deeper in the aquifer than open intervals of these “deep wells” is expected to encounter more mineralized high sulfate water. This is supported by profiles of sulfate during drilling (fig. 2).

Uncertainty in the Nature of Interaction between Shallow and Deep Flow System

The variability in chemical and isotopic composition of deep and shallow ground water indicates that differences exist in the amount of interaction between the shallow and deep ground-water flow systems within the study area. Deeper ground water in some areas had significantly more sulfate than in other parts of the study area. Similarly, shallow ground water had elevated sulfate concentrations in some areas, but had low concentrations in most of the study area. The hydraulic connection between shallow and deep flow systems is poorly defined. Upward flow has been noted within the less permeable Avon Park Formation (figs. 7 and 9). Upwelling can be driven by aquifer discharge near the Withlacoochee River and Lake Panasoffkee. However, upwelling also occurs in recharge areas of Marion County. This upward flow may be induced by rapid shallow flow within the more permeable Ocala Limestone. Pumpage from shallow zones in the aquifer also may cause localized upward flow. In addition, upwelling could be driven by a zone of stagnation in the aquifer at the drainage divide between Rainbow Springs in western Marion County and Silver Springs in eastern Marion County (Faulkner, 1973). In this area, regional flow paths with long aquifer residence times converge from potentiometric highs to the north and south (fig. 6).

Alternatively, elevated sulfate concentrations at shallow depths in Marion County may be the result of reduced recharge where clays cap ridges (Lamonds, 1976). Jones and others (in press) concluded that recharge was slow in the Fairfield Hills area of northwest Marion County (north of the present study area, where sulfate concentrations are low). They attributed this to relict clays overlying the aquifer. In other parts of western Marion County, however, they concluded that recharge was rapid. Factors supporting relatively rapid recharge in the study area in Marion County include the presence of DO and tritium in shallow ground water (Faulkner, 19723; Swancar and Hutchinson, 1995), the lack of surface drainage, and a very flat potentiometric surface combined with high aquifer transmissivities (Ryder, 1985).

Numerous faults and fractures in the study area are associated with the structural high of the Ocala Platform (Vernon, 1951; Faulkner, 1973). Upwelling is probably accelerated by preferential vertical flow through fractures and faults that connect deeper and shallower parts of the aquifer. This study did not find an apparent relation between areas of high sulfate concentrations and mapped fault and fracture traces (Faulkner, 1973). However, a recent detailed study of ground-water quality in western Marion County found that high sulfate concentrations fell along a linear trend, similar to that of a fracture trace in the area (Jones and others, in press).

High sulfate concentrations in the deeper part of the aquifer occur at shallower intervals than zones where gypsum occurs. For example, at ROMP 110 sulfate concentrations are very high (over 1,000 mg/L) about 200 ft above the first mention of gypsum in the core (fig. 2). Besides upwelling, diffusion also probably transports some of the sulfate-rich ground water that dissolved gypsum upward within the more stagnant, deeper part of the aquifer. The occurrence of gypsum is highly variable in the deeper part of the Avon Park Formation (fig. 2). This variability undoubtedly controls how high sulfate concentrations are deep in the aquifer. It is also possible that gypsum occurs very sparsely in shallower intervals in the aquifer or that it already completely dissolved, with sulfate remaining in the aquifer because of the slow rate of flushing.

The “deep” ground waters that had low sulfate concentrations were probably too shallow to intersect the high sulfate water that occurs deeper in the aquifer. These lower sulfate concentrations indicate areas of insignificant upwelling and relatively deep circulation of the shallow flow system. Several of these wells are near Rainbow Springs and the Withlacoochee River, which are significant focuses of discharge from the shallow flow system.

Future Study Needs

Additional data are necessary to better define the complex interaction between the shallow and deep ground-water flow systems. A better network of monitoring wells finished at discrete depth intervals in the aquifer will help distinguish areas of upward flow. A potentiometric map that focuses on the deeper flow system can be used to define deep flow paths in the aquifer. Hydrologic data from this detailed network of shallow and deep wells can then be linked with measured sulfate concentrations to identify areas that are vulnerable to upwelling. Additional coring and water quality sampling throughout the Upper Floridan aquifer to gypsiferous zones of the middle confining unit are necessary to help evaluate mineralogical controls on chemical stratification in the aquifer. Vertical hydraulic conductivity measurements could help establish the connection between shallow and deep parts of the aquifer. Detailed ground-water flow modeling, coupled with new hydrologic data, also can be useful in evaluating physical processes responsible for the movement of high sulfate water and in assessing whether increased ground-water development can induce upwelling of sulfate-rich water. These additional hydrologic, geologic, and chemical data can provide a better understanding of the variable nature and occurrence of high sulfate ground water, which can help optimize ground-water resources and protect them from future degradation.

SUMMARY AND CONCLUSIONS

In inland areas of northwest central Florida, sulfate concentrations in the Upper Floridan aquifer are extremely variable and sometimes exceed drinking water standards (250 mg/L). This is unusual because the aquifer is unconfined and near the surface, allowing for active recharge. The most apparent source of sulfate is gypsum found at the base of the aquifer. However, gypsum has not been observed in shallower intervals of the aquifer. Shallow and deep flow systems occur in the Upper Floridan aquifer in the study area. Flow within the shallow system is relatively fast and discharges locally to springs and rivers; flow within the deep system is more stagnant and bypasses local discharge areas to discharge near or offshore of the coast. The sources of sulfate and geochemical processes controlling ground-water composition were evaluated in an unconfined part of the aquifer where sulfate is variable. A better understanding of sulfate sources is important because increased ground-water development could induce movement of high sulfate water to fresher parts of the aquifer. Water was sampled from thirty-three wells in parts of Marion, Sumter, and Citrus Counties, within the boundaries of the SWFWMD; these included at least a shallow and deep well at fifteen separate locations. Ground water was analyzed for major ions, selected trace constituents, DOC, and stable isotopes (δD, $\delta^{18}O$, $\delta^{13}C$ of inorganic carbon, and $\delta^{34}S$ of sulfate and sulfide).

Sulfate concentrations ranged from less than 0.2 to 1,400 mg/L, with higher concentrations usually in water from deeper wells. The waters were separated into a low sulfate group (less than 30 mg/L) and a high sulfate group (greater than 30 mg/L). Different processes control the chemical composition of these waters. High sulfate waters had concurrent increases between sulfate and other ions (for example, calcium, magnesium, strontium, aluminum, fluoride, and chloride). Gypsum dissolution is the major reaction controlling the composition of high sulfate ground water. Other solutes that increase with sulfate apparently originate from the gypsum itself, from other mineral assemblages which occur deeper in the aquifer in association with gypsum, and from residual seawater from less-flushed, deeper parts of the aquifer. These ions are subsequently transported with sulfate to shallower parts of the aquifer where gypsum is not present. The large range in sulfate concentrations indicates a range in the extent of gypsum dissolution or mixing between high and low sulfate waters.

The chemical composition of low sulfate waters is controlled by differences in the extent of microbially mediated reactions, which produce CO_2. This CO_2, in turn, influences the extent of calcite dissolution. Ground waters which underwent limited microbial reactions still contained DO and were usually in ridge areas where recharge is rapid. Anaerobic waters were in lower lying areas of Sumter County, where soils are poorly drained and aquifer recharge is slow, or were from deep wells. Anaerobic waters usually had higher concentrations of calcium, bicarbonate, sulfide, DOC, iron, manganese, and silica, and lower concentrations of nitrate compared to aerobic waters.

The δD and $\delta^{18}O$ composition of the ground water appears to be related to ground-water age and extent of evaporation prior to recharge. Aerobic, low sulfate waters had isotopically light δD and $\delta^{18}O$ values, whereas anaerobic, low sulfate waters usually were isotopically heavier. Some of the isotopically enriched waters apparently underwent evaporation prior to recharging the aquifer. High sulfate waters were usually more enriched in δD and $\delta^{18}O$ than low sulfate waters that contained DO. Mixing between recent recharge and older waters probably controls this range of δD and $\delta^{18}O$.

For most of the low sulfate waters, $\delta^{13}C$ of inorganic carbon reflects the extent of microbially mediated reactions. Waters with higher P_{CO_2} values usually had isotopically lighter $\delta^{13}C$ values, which is consistent with oxidation of isotopically light organic matter. For high sulfate waters no obvious relation was apparent with P_{CO_2}. At the highest sulfate concentrations, however, the range of $\delta^{13}C$ narrows, indicating that similar processes control inorganic carbon sources and sinks at high sulfate concentrations. This is probably related to dolomite dissolution adding isotopically heavy carbon and calcite precipitation removing isotopically heavy carbon from the water.

The range of $\delta^{34}S_{sulfate}$ in the ground water was between 1.7 and 33.1 per mil. Low sulfate waters had a much greater range in $\delta^{34}S_{sulfate}$ than high sulfate waters. This greater range of $\delta^{34}S_{sulfate}$ is probably controlled by processes influencing sulfate during recharge, including sulfate reduction and oxidation of reduced sulfur. As sulfate concentrations increase, the $\delta^{34}S_{sulfate}$ values approach a more constant value, generally between 21 and 24 per mil. This is consistent with gypsum dissolution. Several waters with isotopically heavy $\delta^{34}S_{sulfate}$ values appear to have lost sulfide from solution, probably by precipitation of a sulfide mineral such as pyrite. Values of $\delta^{34}S_{sulfide}$ ranged from -42.1 to 14.6 per mil. Low sulfate waters had positive $\delta^{34}S_{sulfide}$ values, whereas high sulfate waters had negative $\delta^{34}S_{sulfide}$ values. Sulfate reduction is slow in the deeper part of the aquifer, which is part of a sluggish, regional flow system. Isotope mass balance calculations indicate that mixing is responsible for most of the observed range of $\delta^{34}S_{total}$ for the high sulfate ground water. However, the $\delta^{34}S$ of gypsum apparently is variable and often isotopically lighter than gypsum analyzed from the study area.

Geochemical mass-balance modeling was used to evaluate reactions occurring between shallow and deep ground water at the same location. When sulfate is high in the deep ground water, dedolomitization reactions (gypsum and dolomite dissolution and calcite precipitation) control the composition of the deep water. These reactions are driven by gypsum, which occurs deeper in the aquifer than open intervals of sampled wells. Computed and measured $\delta^{34}S$ values generally matched when the $\delta^{34}S$ of gypsum ranged between 21.5 and 24.5 per mil, which is in the range of measured values for gypsum in the middle confining unit. Upward flow has been documented in deeper parts of the aquifer in the study area. To test whether upwelling could explain the high sulfate concentrations observed in the deeper ground water in the study area, upwelling was modeled with NETPATH. These models indicate that mixing between shallow ground water and sulfate-rich upwelling water can explain most of the high sulfate concentrations in the deep ground water. Therefore, differences between the shallow and deep ground water do not have to be explained solely by reactions occurring between open intervals of the wells.

When sulfate is low in the deep ground water, modeled reactions depend upon whether the shallow ground water contained DO. For aerobic, shallow ground water, major reactions were calcite and dolomite dissolution, organic matter oxidation, and O_2 reduction. For anaerobic, shallow ground water, major reactions included calcite precipitation, dolomite dissolution, and CO_2 outgassing. Differences between these models are related to the extent of microbially mediated reactions occurring shallow in the aquifer, which, in turn, is probably related to aquifer residence time and recharge rate. The amount of mass transfer for low sulfate flow paths is considerably less than for most of the high sulfate flow paths. This indicates either less water-rock interactions or insignificant amounts of upwelling of sulfate-rich ground water. The shallow flow system is apparently deeper in areas where low sulfate concentrations are found in the deep ground water.

The range of sulfate concentrations observed in the study area and differences in sulfate concentrations with depth indicate a complex interaction between the shallow and deep ground-water flow systems. The hydraulic connection between shallow and deep flow systems is poorly defined. Upwelling is probably responsible for high sulfate concentrations in intervals of the aquifer where gypsum is not found. This upwelling can be driven by localized aquifer discharge areas and perhaps by rapid flow within the shallow, more permeable, part of the aquifer. In addition, diffusion probably transports sulfate-rich water that dissolved gypsum upward within the more stagnant deeper part of the aquifer. The occurrence of gypsum is highly variable in deeper parts of the aquifer. It is also possible that gypsum occurs very sparsely in shallower intervals of the aquifer, or that it already completely dissolved, with sulfate remaining because of slow rates of flushing. Additional hydrologic, geologic, and chemical data, particularly from the deeper part of the aquifer, are necessary to better define the interaction between shallow and deep flow systems. These data can provide a better understanding of the variable nature and occurrence of high sulfate ground water, which can help optimize ground-water resources in the study area.

REFERENCES

Anderson, Warren, and Laughlin, C.P., 1982, Geohydrology of the Floridan aquifer in the Withlacoochee River Basin of the Southwest Florida Water Management District: U.S. Geological Survey Water-Resources Investigations Report 82-331, 4 sheets.

Applin, P.L., and Applin, E.R., 1965, The Comanche Series and associated rocks in the subsurface in central and south Florida: U.S. Geological Survey Professional Paper 447, 84 p.

Aucott, W.R., 1988, Areal variation in recharge to and discharge from the Floridan aquifer system in Florida: U.S. Geological Survey Water-Resources Investigations Report 88-4057, 1 sheet.

Ball, J.W., and Nordstrom, D.K., 1991, User's manual for WATEQ4F, with revised thermodynamic data base and test cases for calculating speciation of major, trace, and redox elements in natural water: U.S. Geological Survey Open-File Report 91-183, 189 p.

Bennett, P., 1991, Quartz dissolution in organic-rich aqueous solutions: Geochimica Cosmochimica Acta, v. 5, p. 1781-1797.

Brooks, H.K., 1981, Physiographic divisions of Florida: Gainesville, Center for Environmental and Natural Resources, University of Florida.

Buchardt, B., and Fritz, P., 1980, Environmental isotopes as environmental and climatological indicators, *in* Fritz, P., and Fontes, J.C., eds., Handbook of environmental isotope geochemistry: Amsterdam, Elsevier Scientific Publishing Company, p. 473-504.

Busby, J.F., Plummer, L.N., Lee, R.W., and Hanshaw, B.B., 1991, Geochemical evolution of water in the Madison aquifer in parts of Montana, South Dakota, and Wyoming: U.S. Geological Survey Professional Paper 1273-F, 89 p.

Bush, P.W., and Johnston, R.H., 1988, Ground-water hydraulics, regional flow, and ground-water development of the Floridan aquifer system in Florida and in parts of Georgia, South Carolina, and Alabama: U.S. Geological Survey Professional Paper 1403-C, 80 p.

Campbell, K.M., 1989, Geology of Sumter County, Florida: Florida Geological Survey Report of Investigation 89-98. 28 p.

Cander, H.S., 1991, Dolomitization and water-rock interaction in the middle Eocene Avon Park Formation, Floridan aquifer: Ph.D. Dissertation, The University of Texas at Austin, 172 p.

Carmody, R.W., Plummer, L.N., Busenberg, Eurybiades, and Coplen, T.B., in press, Methods for collection of dissolved sulfate and sulfide and analysis of their sulfur isotope composition: U.S. Geological Survey Water-Resources Investigations Report.

Causey, L.V., and Levy, G.W., 1976, Thickness of the potable-water zone in the Floridan aquifer: Florida Bureau of Geology Map Series 74.

Chapelle, F.H., 1993, Ground-water microbiology and geochemistry: New York, John Wiley, 424 p.

Chapelle, F.H., and Lovely, D.R., 1992, Competitive exclusion of sulfate reduction by Fe(III)-reducing bacteria: A mechanism for producing discrete zones of high-iron ground water: Ground Water, v. 20, no. 1, p. 29-36.

Chapelle, F.H., and McMahon, P.B., 1991, Geochemistry of dissolved inorganic carbon in a coastal plain aquifer, 1. Sulfate from confining beds as an oxidant in microbial CO_2 production: Journal of Hydrology, v. 127, p. 85-108.

Claypool, G.E., Holser, W.T., Kaplan, I.R., Sakai, H., and Zak, I., 1980, The age curves of sulfur and oxygen isotopes in marine sulfate and their mutual interpretation: Chemical Geology, v. 27, p. 199-260.

Cook, D.J., Randazzo, A.F., and Sprinkle, C.L., 1985, Authigenic fluorite in dolomitic rocks of the Floridan aquifer: Geology, v. 13, p. 390-391.

Craig, Harmon, 1961, Standard for reporting concentrations of deuterium and oxygen-18 in natural water: Science, v. 133, p. 1833-1834.

Crowder, R.E., Paillet, F.L., and Hess, A.E., 1994, High resolution flowmeter logging—a unique combination of borehole geophysics and hydraulics; Part I. Flowmeter techniques and equipment development: Proceedings of the Symposium on the Application of Geophysics to Environmental and Engineering Problems, March 26-30, 1994, Boston, Mass., Environmental and Engineering Geophysical Society, p. 361-380.

Faulkner, G.L., 1973, Geohydrology of the Cross-Florida Barge Canal with special reference to the Ocala vicinity: U.S. Geological Survey Water-Resources Investigations 1-73, 117 p.

Fischer, A.G., 1953, Petrology of Eocene limestones in and around the Citrus-Levy County area, Florida: *in* Miscellaneous Studies, Florida Geological Survey Report of Investigations no. 9.

Fishman, M.J., and Friedman, L.C., eds., 1989, Methods for determination of inorganic substances in water and fluvial sediments: U.S. Geological Survey Techniques of Water-Resources Investigations, book 5, ch. A1, 545 p.

Florida Department of State, 1993, Rules of the Department of Environmental Regulation, Drinking water standards, monitoring, and reporting: *in* Florida Administrative Code, chap. 17-550, p. 13-22, Tallahassee.

Fritz, P., and Fontes, J.C., eds., 1980, Handbook of environmental isotope geochemistry: Amsterdam, Elsevier Scientific Publishing Company, 545 p.

Hach Company, 1989, Water analysis handbook: Loveland, Colo., 689 p.

Halford, K.J., Murray, L.C., Spechler, R.M., Phelps, G.G., and Bradner, L.A., 1993, Potentiometric surface of the Upper Floridan aquifer in the St. Johns River Water Management District and vicinity, May 1993: U.S. Geological Survey Open-File Report 93-451, 1 sheet.

Hanshaw, B.B., and Back, William, 1972, On the origin of dolomites in the Tertiary aquifer of Florida, *in* H.S. Puri, ed., Proceeding of the seventh forum on geology of industrial minerals, Florida Bureau of Geology Special Publication no. 17, p. 139-153.

Hanshaw, B.B., Back, William, and Deike, R.G., 1971, A geochemical hypothesis for dolomitization by ground water: Economic Geology, v. 66, p. 710-724.

Hess, A.E., 1990, Thermal pulse flowmeter for measuring slow water velocities in boreholes: U.S. Geological Survey Open-File Report 87-121, 70 p.

Hess, A.E., and Paillet, F.L., 1990, Application of the thermal-pulse flowmeter in the hydraulic characterization of fractured rocks: Geophysical Applications for Geotechnical Investigations, American Society for Testing and Materials, Standard Technical Publication 1101, p. 99-112.

Hickey, J.J., 1990, An assessment of flow of the variable-salinity ground water in the middle confining unit of the Floridan aquifer system, west-central Florida: U.S. Geological Survey Water-Resources Investigations Report 89-4142, 13 p.

Hsu, K.J., 1963, Solubility of dolomite and composition of Florida ground waters, Journal of Hydrology, v. 1, p. 288-310.

Ichikuni, M., and Musha, Setsuko, 1978, Partition of strontium between gypsum and solution: Chemical Geology, p. 359-363.

Jensen, M.L., and Nakai, N., 1961, Sources and isotopic composition of atmospheric sulfur: Science, v. 134, p. 2102-2104.

Johnson, B.C., 1994, Chemical stratification, mixing, and water-rock interaction in the Upper Floridan aquifer: M.S. Thesis, Boulder, University of Colorado, 219 p.

Jones, G.W., and Upchurch, S.B., 1994, Origin of nutrients in ground water discharging from the King’s Bay springs: Ambient Ground-Water Quality Monitoring Program, Brooksville, Southwest Florida Water Management District, 133 p.

Jones, G.W., Upchurch, S.B., and Champion, K.M., in press, Origin of nitrate in ground water discharging from Rainbow Springs, Marion County, Florida: Ambient Ground-Water Quality Monitoring Program, Brooksville, Southwest Florida Water Management District, 140 p.

Jones, I.C., Vacher, H.L, and Budd, D.A., 1993, Transport of calcium, magnesium, and SO_4 in the Floridan aquifer, west-central Florida: Implications to cementation rates: Journal of Hydrology, v. 143, p. 455-480.

Katz, B.G., 1992, Hydrochemistry of the Upper Floridan aquifer, Florida: U.S. Geological Survey Water-Resources Investigations Report 91-4196, 37 p.

Katz, B.G., Lee, T.M., Plummer, L.N., and Busenberg, Eurybiades, 1995a, Chemical evolution of groundwater near a sinkhole lake, northern Florida, 1. Flow patterns, age of groundwater and influence of lakewater leakage: Water Resources Research, v. 31, p. 1549-1564.

Katz, B.G., Plummer, L.N., and Busenberg, Eurybiades, Revesz, K.M., Jones, B.F., and Lee, T.M., 1995b, Chemical evolution of groundwater near a sinkhole lake, northern Florida, 2. Chemical patterns, mass-transfer modeling, and rates of chemical reactions: Water Resources Research, v., 31, p. 1565-1584.

Kauffman, S.J., 1994, The geochemical effects of confining units on the groundwater evolution of a lithologically heterogeneous carbonate aquifer system: M.S. Thesis, Charlottesville, University of Virginia, 113 p.

Krouse, H.R., 1980, Sulphur isotopes in our environment, *in* Fritz, P., and Fontes, J.Ch., eds., Handbook of environmental isotope geochemistry, New York, Elsevier Scientific Publishing Co., p. 227-258.

Kushnir, Jacob, 1980, The coprecipitation of strontium, magnesium, sodium, potassium, and chloride ions with gypsum, an experimental study: Geochimica et Cosmochimica Acta, v. 44, p. 1471-1482.

Lamonds, A.G., 1976, Proposed Cross-Florida Barge Canal: Water-quality aspects with a section on waste-assimilation capacity: U.S. Geological Survey Water Resources-Investigations Report 76-23, 189 p.

Lawrence, F.W., and Upchurch, S.B., 1982, Identification of recharge areas using factor analysis: Groundwater, v. 20, no. 6, p. 680-687.

Mazon, Emanuel, 1991, Applied chemical and isotopic groundwater hydrology, New York, John Wiley, 270 p.

McCartan, Lucy, Plummer, L.N., Hosterman, J.W., Busenburg, E., Dwornik, E.J., Duerr, A.D., Miller, R.L., and Kiesler, J.L, 1992, Celestine ($SrSO_4$) in Hardee and De Soto Counties, Florida, *in* Gohn, G.S., ed., Proceedings of the 1988 U.S. Geological Survey workshop on the geology and geohydrology of the Atlantic Coastal Plain: U.S. Geological Survey Circular 1059, p. 129-138.

McMahon, P.B., Vroblesky, D.A., Bradley, P.M., Chapelle, F.H., and Gulley, C.D., 1995, Evidence for enhanced mineral dissolution in organic acid-rich shallow ground water: Ground Water, v. 22, no. 2, p. 207-216.

Meyers, J.B., Swart, P.K., Meyers, J.L., 1993, Geochemical evidence for groundwater behavior in an unconfined aquifer, south Florida: Journal of Hydrology, v. 148, p. 249-272.

Miller, J.A., 1986, Hydrogeologic framework of the Floridan aquifer system in Florida and parts of Georgia, South Carolina, and Alabama, U.S. Geological Survey Professional Paper 1403-B, 91 p.

Miller, R.A., Anderson, Warren, Navoy, A.S., Smoot, J.L, and Belles, R.G., 1981, Water-resources information for the Withlacoochee River region, west-central Florida: U.S. Geological Survey Water-Resources Investigations Report 81-11, 130 p.

Mularoni, R.A., 1994, Potentiometric surface of the Upper Floridan aquifer, west-central Florida, May 1993: U.S. Geological Survey Open-File Report 94-32, 1 sheet.

Nordstrom, D.K., Plummer, L.N., Langmuir, D., Busenberg, Eurybiades., May, H.M., Jones, B.F., and Parkhurst, D.L., 1990, Revised chemical equilibrium data for major water-mineral reactions and their limitation, *in* Melchior, D.C., and Basset, R.L., eds., Chemical modeling of aqueous systems II, American Chemical Society Symposium Series 416, p. 398-413.

Olson, N.K., 1972, Hard rock phosphate in Florida, *in* Puri, H.S., ed., Proceedings of the Seventh Forum on Geology of Industrial Minerals: Florida Bureau of Geology Special Publication no. 17., p. 195-210.

Östlund, G., 1959, Isotopic composition of sulfur in precipitation and sea-water: Tellus, v. 11, p. 478-480.

Pearson, F.J., and Rightmire, C.T., 1980, Sulphur and oxygen isotopes in aqueous sulphur compounds, *in* Fritz, P., and Fontes, J.C., eds., Handbook of environmental isotope geochemistry: Amsterdam, Elsevier Scientific Publishing Company, p. 227-258.

Phelps, G.G., 1994, Hydrogeology, water quality, and potential for contamination of the Upper Florida aquifer in the Silver Springs ground-water basin, central Marion County, Florida, U.S. Geological Survey Water-Resources Investigations Report 92-4159, 69 p.

Plummer, L.N., 1977, Defining reactions and mass transfer in part of the Floridan aquifer: Water Resources Research, v. 13, no. 5, p. 801-812.

Plummer, L.N., and Back, William, 1980, The mass balance approach: application to interpreting the chemical evolution of hydrologic systems: American Journal of Science, v. 280, p. 130-142.

Plummer, L.N., Busby, J.F., Lee, R.W., and Hanshaw, B.B., 1990, Geochemical modeling of the Madison aquifer in parts of Montana, Wyoming, and South Dakota: Water Resources Research, v. 26, no. 9., p. 1981-2014.

Plummer, L.N., Parkhurst, D.L., and Thorstenson, D.C., 1983, Development of reaction models for groundwater systems: Geochimica et Cosmochimica Acta, v. 47, p. 665-686.

Plummer, L.N., Prestemon, E.C., and Parkhurst, D.L., 1991, An interactive code (NETPATH) for modeling net geochemical reactions along a flow path, U.S. Geological Survey Water-Resources Investigations Report 91-4078, 227 p.

Postgate, W.R., 1979, The sulphate reducing bacteria: Cambridge, England, Cambridge University Press, p. 25-28.

Randazzo, A.F., and Bloom, J.I., 1985, Mineralogical changes along the freshwater/saltwater interface of a modern aquifer: Sedimentary Geology, v. 43, p. 219-239.

Randazzo, A.F., and Hickey, E.W., 1978, Dolomitization in the Floridan aquifer, American Journal of Science, v. 278, p. 1177-1184.

Randazzo, A.F., Koster, Mieke, Jones, D.S., and Portell, R.W., 1990, Paleoecology of shallow-marine carbonate environments, middle Eocene of peninsular Florida: Sedimentary Geology, v. 66, p. 1-11.

Rees, C.E., Jenkins, W.J., and Monster, J., 1978, The sulphur isotope geochemistry of ocean water sulphate: Geochemica Cosmochimica Acta, v. 42, p. 377-382.

Rightmire, C.T., and Hanshaw, B.B., 1973, Relationship between carbon isotope composition of soil CO_2 and dissolved carbonate species in groundwater: Water Resources Research, v. 9, no. 4, p. 958-967.

Rightmire, C.T., Pearson, F.J. Jr., Back, William, Rye, R.O., and Hanshaw, B.B., 1974, Distribution of sulfur isotopes in ground waters from the principal artesian aquifer of Florida and the Edwards aquifer of Texas, United States of America: Isotope techniques in groundwater hydrology, v. 2, Vienna, International Atomic Energy Agency, p. 191-207.

Rosenau, J.C., Faulkner, G.L., Hendry, C.W. Jr., and Hull, R.W., 1977, Springs of Florida: Florida Bureau of Geology Bulletin 31, 461p.

Ryder, P.D., 1985, Hydrology of the Floridan aquifer system in west-central Florida: U.S. Geological Survey Professional Paper 1403-F, 63 p.

Rye, R.O., Back, William, Hanshaw, B.B., Rightmire, C.T., and Pearson, F.J. Jr., 1981, The origin and isotopic composition of dissolved sulfide in groundwater from carbonate aquifers in Florida and Texas: Geochimica et Cosmochimica Acta, v. 45, p. 1941-1950.

Sacks, L.A., and Bullen, T.D., 1993, Use of $^{87}Sr/^{86}Sr$ to delineate the source of high-sulfate groundwater near the Florida coast: Abstract for fall 1993 meeting of the American Geophysical Union, EOS, 74, supplement, p. 269.

Sacks, L.A., Herman, J.S., and Kauffman, S.J, 1995, Controls on high sulfate concentrations in the Upper Floridan aquifer in southwest Florida: Water Resources Research, v. 31, p. 2541-2551.

Schmidt, Walter, and Scott, T.M., 1984, Florida karst—its relationship to geologic structure and stratigraphy, *in* Beck, B.F., ed., Proceedings of the first multidisciplinary conference on sinkholes, Orlando, Florida Sinkhole Research Institute, p. 11-16.

Scott, T.M., 1988, The lithostratigraphy of the Hawthorn Group (Miocene) of Florida: Florida Geological Survey Bulletin no. 59, 148 p.

Smith, D.L., 1982, Review of the tectonic history of the Florida basement: Tectonophysics, v. 88. p. 1-22.

Soil Conservation Service, 1979, Soil Survey of Marion County, Florida: U.S. Department of Agriculture, 148 p.

——— 1988a, Soil Survey of Citrus County, Florida: U.S. Department of Agriculture, 192 p.

——— 1988b, Soil Survey of Sumter County, Florida: U.S. Department of Agriculture, 204 p.

Southwest Florida Water Management District, 1991, Ground-water quality of the Southwest Florida Water Management District, northern region, section 2: Ambient Ground-Water Quality Monitoring Program, Brooksville, Southwest Florida Water Management District, 275 p.

Sprinkle, C.R., 1989, Geochemistry of the Floridan aquifer system in Florida and in parts of Georgia, South Carolina, and Alabama: U.S. Geological Survey Professional paper 1403-I, 105 p.

Stumm, Werner, and Morgan, J.J., 1981, Aquatic chemistry (2d ed.): New York, John Wiley, 780 p.

Swancar, Amy, and Hutchinson, C.B., 1995, Chemical and isotopic composition and potential for contamination of water in the Upper Floridan aquifer, west-central Florida, 1986-89: U.S. Geological Survey Water-Supply Paper 2409, 70 p.

Toran, Laura, 1982, Isotopes in ground-water investigations: Ground Water, v. 20, no. 6, p. 740-745.

Vernon, R.O., 1951, Geology of Citrus and Levy Counties, Florida: Florida Geological Survey Bulletin 33, 256 p.

White, W.A., 1958, Some geomorphic features of central peninsular Florida: Florida Geological Survey Bulletin 41, 92 p.

——— 1970, The geomorphology of the Florida peninsula: Florida Geological Survey Bulletin 51, 164 p.

Winston, G.O., 1976, Florida's Ocala 'Uplift' is not an Uplift: AAPG Bulletin 60, no. 6, p. 992-994.

Wood, W.W., 1976, Guidelines for collection and field analysis of ground-water samples for selected unstable constituents: U.S. Geological Survey Techniques of Water-Resources Investigations, book 1, chap. D2, 24 p.

APPENDIX

Appendix—Chemical and isotopic data from ground-water samples and calculated saturation indexes and partial pressure of carbon dioxide

[deg C, degrees Celsius; µS/cm, microsiemens per centimeter; mg/L, milligrams per liter; µg/L, micrograms per liter; atm, atmospheres; -, no data; <, less than; δ^{13}C, delta carbon-13; δD, delta deuterium; δ^{18}O, delta oxygen-18; δ^{34}S, delta sulfur-34; Δ^{34}S, difference between the δ^{34}S of sulfate and sulfide; sampling pump type: S = submersible; P = peristaltic; C = centrifugal; A = airlifted from corehole during drilling]

Well No.[1]	Well name	Sampling date (Year/ Month/ Day)	Tem- pera- ture water (deg C)	Specific conduct- ance, field (µS/cm)	Oxygen, dissolved (mg/L)	Field pH (standard units)	Nitrogen, NO_2+NO_3 dissolved (mg/L as N)	Organic carbon, dissolved (mg/L as C)
1	Kellogg shallow well	19921215	21.7	495	<0.5	7.05	0.006	3.5
2	Kellogg deep well	19921215	22.5	460	<.5	7.50	<.002	2.1
3	City of Bushnell #2 well	19930204	24.6	416	<.5	7.71	.007	<.1
4	St. Lawrence Church rectory well	19930616	23.8	322	<.5	7.43	<.002	.4
5	White well	19930224	23.8	368	<.5	7.35	<.002	4.0
6	Owens well	19930224	23.4	267	1.73	7.50	.630	1.0
7	ROMP LP-4 Avon Park (240)	19921208	24.8	2,260	<.8	7.37	<.002	1.5
8	ROMP LP-4 Avon Park (120)	19921209	24.2	333	1.4	7.71	1.800	.1
9	ROMP LP-4 Ocala	19921208	24.5	383	3.08	7.49	1.500	1.6
10	City of Coleman well	19930324	27.4	457	<.5	7.31	.009	1.4
11	Rolling well	19930324	22.8	366	1.27	7.54	.076	1.2
12	Hawkins well	19930203	22.0	529	-	6.91	<.002	5.2
12-d	Hawkins well duplicate	19930203	-	-	-	-	.002	4.9
13	Campers' World well	19930203	22.5	531	<.5	7.17	.002	2.6
14	Pilot Oil well	19921117	24.8	500	<.5	6.98	.003	3.4
15	Union Oil well	19921117	25.1	461	<.5	7.39	.003	1.2
16	Lorenz well	19930113	24.6	1,451	<.5	7.66	.003	.3
17	Wooten well	19930113	23.6	179	3.08	7.92	.808	.3
18	Budd well	19930106	24.6	1,625	<.5	7.31	<.002	2.7
19	Iacino well	19930106	22.7	228	2.09	7.96	.406	.4
20	USGS observation well CE-78	19930112	22.7	226	7.45	7.64	.242	<.1
21	ROMP 119	19930301	24.0	1,238	<.5	7.37	<.002	2.1
22	Quaglio well	19930325	24.1	275	<.5	7.85	<.002	1.3
23	Silver well	19930107	22.9	123	4.91	8.24	.633	<.1
24	Brookshier well	19930107	24.1	311	<.5	7.61	<.002	.7
25	Barton well	19930325	23.2	228	3.89	7.75	.280	.9
26	Bonnie Builders well	19930112	24.9	259	5.84	7.74	.549	<.1
27	Saddle Oak deep well	19921216	25.7	689	3.25	7.46	1.000	.1
28	Saddle Oak shallow well	19921216	25.1	607	3.65	7.55	1.300	.1
29	ROMP 120	19930302	24.6	602	<.5	7.31	<.002	1.4
30	Rowland deep well	19921119	26.7	645	<.5	7.04	.003	.5
30-d	Rowland deep well duplicate	19921119	-	-	-	-	.003	-
31	Rowland shallow well	19930615	25.1	653	2.17	7.03	.081	.3
32	Jones well	19921118	25.0	739	<.5	7.20	.006	2.6
33	Brosky well	19921118	24.0	133	5.43	8.00	.870	3.8
R110[2]	ROMP 110, 248.5 ft	19890912	22.5	2,600	-	-	-	-

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[1] Number refers to well locations shown in figure 8.

[2] Sample collected by Southwest Florida Water Management District (written commun., 1993), from 248.5 ft depth in corehole during drilling. Analysis used in NETPATH modeling of upwelling water.

[3] Duplicate analysis was -32.5 per mil.

[4] Duplicate analysis was 27.7 per mil.

Appendix—Continued

Well No.[1]	Calcium, dissolved (mg/L as Ca)	Magnesium, dissolved (mg/L as Mg)	Sodium, dissolved (mg/L as Na)	Potassium, dissolved (mg/L as K)	Chloride, dissolved (mg/L as Cl)	Sulfate, dissolved (mg/L as SO_4)	Fluoride, dissolved (mg/L as F)	Silica, dissolved (mg/L as SiO_2)	Barium, dissolved (µg/L as Ba)
1	94	1.8	12	0.68	19	<0.2	<0.1	11	<5
2	75	6.9	9.1	1.3	29	.6	.2	13	8
3	69	10	5.8	.95	8.7	55	.4	14	46
4	55	2.3	4.1	.15	7.4	4.9	.1	8.2	11
5	66	2.9	5.3	.23	11	<.2	<.1	7.1	8
6	47	2.2	7.0	.17	8.6	3.6	<.1	8.5	6
7	470	110	10	2.5	13	1,400	1.0	12	32
8	53	3.5	3.5	.85	6.3	57	<.1	5.0	8
9	61	6.9	3.1	4.6	5.2	48	.2	4.4	12
10	77	1.9	14	.45	28	3.0	.1	8.1	24
11	58	1.9	13	3.2	21	21	<.1	7.2	9
12	106	1.3	5.2	<.10	7.8	<.2	<.1	9.7	13
12-d	106	1.5	5.2	.10	7.8	.2	<.1	9.9	10
13	94	13	4.6	.60	7.3	4.2	.2	10	14
14	92	3.0	9.2	.80	17	3.2	<.1	9.8	9
15	72	13	6.0	1.3	9.6	75	.5	13	16
16	200	76	22	2.7	18	760	.9	14	4
17	31	2.2	3.0	.11	4.9	1.3	<.1	7.6	2
18	330	62	7.3	1.5	11	900	1.0	14	34
19	34	5.6	3.4	.16	5.0	23.0	<.1	6.6	<5
20	44	0.8	1.8	.15	2.8	1.7	<.1	6.7	3
21	210	38	11	2.2	15	580	1.0	15	29
22	50	3.3	2.7	.12	4.5	2.8	.1	8.0	8
23	18	2.2	2.6	.13	4.3	2.3	<.1	6.4	<5
24	45	14	3.3	.32	4.8	<.2	.1	9.4	<5
25	42	1.6	2.5	<.10	4.3	2.3	<.1	5.6	7
26	47	2.5	3.3	.17	5.7	25.0	<.1	7.0	5
27	110	18	8.4	1.1	14	240	.2	9.7	8
28	95	14	8.0	.97	14	180	.2	9.7	<5
29	93	17	8.4	1.3	12	76	.7	18	7
30	100	19	10	1.5	15	100	.6	16	9
30-d	100	19	10	1.5	14	99	.6	17	14
31	99	16	9.1	1.3	13	90	.6	17	11
32	120	21	12	1.5	20	150	.5	17	12
33	20	1.4	3.3	.40	5.4	2.8	<.1	6.4	5
R110[2]	635	148	18	3.0	19	1,800	.9	-	-

Appendix—Continued

Well No.[1]	Boron, dissolved (µg/L as B)	Iron, dissolved (µg/L as Fe)	Manganese, dissolved (µg/L as Mn)	Strontium, dissolved (µg/L as Sr)	Aluminum, dissolved (µg/L as Al)	Lithium, dissolved (µg/L as Li)	Bromide, dissolved (mg/L as Br)	Bicarbonate, field (mg/L as HCO_3)	Sulfide, field total (mg/L as S)	Dissolved solids, calculated (mg/L)
1	29	4,000	17	72	32	<5	0.07	310	<0.01	-
2	<20	160	<5	97	33	<5	.09	241	.13	254
3	<20	12	3	810	20	4	.03	199	1.2	263
4	<20	2,200	26	49	20	5	.03	190	.02	178
5	<20	990	33	130	20	6	.01	217	.05	-
6	20	<3	<1	67	20	7	.03	167	<.01	162
7	32	1,000	15	8,200	140	5	.04	131	.02	2,092
8	<20	<5	<5	300	<20	<5	<.01	108	<.01	191
9	24	<5	<5	200	26	<5	.02	157	<.03	218
10	<20	870	15	140	40	<4	.02	226	.02	245
11	<20	39	9	55	20	<4	.03	155	<.01	202
12	<20	4,700	33	94	40	8	<.01	331	.03	-
12-d	<20	4,400	38	92	30	4	<.01	330	.02	-
13	<20	32	7	940	20	<4	<.01	344	.61	304
14	22	5,000	50	130	31	<5	.09	293	.03	284
15	<20	25	<5	1,300	26	<5	.03	186	1.0	283
16	100	280	8	5,000	50	12	.05	121	.61	1,159
17	<20	11	<1	62	<20	4	.02	102	<.01	104
18	33	950	17	2,400	100	12	.05	198	1.7	1,428
19	20	19	<5	67	40	5	.03	107	<.03	132
20	<20	20	1	33	<20	<4	.02	147	<.01	131
21	22	52	2	7,100	60	13	.03	158	.80	957
22	<20	100	6	33	20	<4	<.01	162	.02	151
23	<20	23	<5	31	30	<5	.01	62	<.01	69
24	24	400	7	21	40	5	.02	207	.01	-
25	<20	5	<1	24	<20	<4	.01	131	<.01	-
26	<20	17	1	320	<20	4	.02	126	<.01	155
27	<20	10	<5	2,200	43	<5	.07	137	<.01	476
28	<20	<5	<5	1,700	38	<5	.05	127	<.01	392
29	<20	23	3	2,000	30	6	.04	286	.12	369
30	23	520	<5	3,000	37	5	.05	280	.14	403
30-d	24	400	5	2,800	24	<5	.05	280	.10	402
31	25	<3	2	2,000	30	<4	.05	306	<.01	399
32	21	720	5	2,600	44	<5	.07	271	.74	479
33	<20	6	<5	54	<20	<5	.02	61	<.01	74
R110[2]	-	-	-	-	-	-	-	168	odor	2,773

Appendix—Continued

Well No.[1]	Stable isotope ratio, in per mil						$\Delta^{34}S$ (per mil)	Log partial pressure of CO_2 (atm)	Saturation Index					Pump type
	$\delta^{13}C$	δD	$\delta^{18}O$	$\delta^{34}S$ of sulfide	$\delta^{34}S$ of sulfate	$\delta^{34}S$ of total sulfur			Calcite	Dolomite (disordered)	Dolomite (crystalline)	Gypsum	Celestite	
1	-6.6	-5.8	-1.21	-	-	-	-	-1.60	0.008	-1.957	-1.394	-	-	S
2	-8.5	-6.8	-1.69	14.6	-	-	-	-2.15	.271	-0.735	-0.175	-3.745	-4.927	S
3	-9.6	-10.3	-2.18	[3]-32.0	[4]27.9	24.3	59.9	-2.44	.368	-0.312	0.239	-1.837	-2.056	S
4	-11.6	-17.8	-3.39	-	15.7	15.5	-	-2.17	.013	-1.573	-1.018	-2.906	-4.248	S
5	-10.5	-11.5	-2.21	-	-	-	-	-2.03	.060	-1.455	-0.900	-	-	S
6	-12.1	-17.6	-3.28	-	10.4	10.3	-	-2.29	-0.035	-1.627	-1.070	-3.085	-4.224	S
7	-8.6	-14.0	-2.87	-	23.6	23.6	-	-2.33	.334	-0.184	0.367	-0.161	-0.204	P
8	-10.7	-17.4	-3.70	-	21.9	21.9	-	-2.69	.019	-1.358	-0.805	-1.873	-2.410	S
9	-6.6	-15.3	-3.64	-	21.8	21.8	-	-2.31	.014	-1.130	-0.578	-1.915	-2.689	S
10	-11.2	-18.5	-3.70	-	15.0	14.7	-	-1.95	.138	-1.494	-0.954	-3.029	-4.054	S
11	-11.5	-21.3	-4.06	-	1.7	1.7	-	-2.37	.032	-1.657	-1.098	-2.264	-3.581	C
12	-11.7	-13.8	-2.78	-	-	-	-	-1.43	-0.053	-2.267	-1.705	-	-	S
12-d	-12.1	-13.5	-2.79	-32.5	-	-	-	-1.43	-0.054	-2.205	-1.643	-	-	S
13	-12.3	-10.1	-1.83	7.9	-	-	-	-1.67	.169	-0.762	-0.202	-2.856	-3.152	S
14	-12.2	-15.4	-2.86	7.7	33.1	32.5	25.4	-1.53	-0.055	-1.799	-1.248	-2.957	-4.099	S
15	-9.4	-12.5	-2.48	-34.4	24.3	22.0	58.7	-2.14	.036	-0.874	-0.324	-1.703	-1.735	S
16	-9.4	-16.5	-3.60	-42.1	24.2	24.0	66.3	-2.64	.320	-0.004	0.548	-0.608	-0.496	S
17	-11.4	-16.6	-3.44	-	20.9	20.4	-	-2.92	.021	-1.330	-0.774	-3.650	-4.640	S
18	-8.4	-8.7	-1.83	-30.1	24.3	24.0	54.4	-2.08	.370	-0.208	0.343	-0.382	-0.807	S
19	-10.7	-19.7	-3.86	-	20.2	20.1	-	-2.95	.076	-0.870	-0.310	-2.403	-3.400	S
20	-11.4	-18.3	-3.88	-	13.2	13.0	-	-2.49	.021	-1.937	-1.378	-3.416	-4.834	S
21	-8.4	-10.8	-2.55	-40.7	21.7	21.4	62.4	-2.22	.205	-0.563	-0.009	-0.644	-0.403	S
22	-10.4	-18.6	-3.67	-	11.4	11.2	-	-2.66	.332	-0.731	-0.177	-3.175	-4.645	S
23	-10.1	-19.7	-3.95	-	3.7	3.7	-	-3.46	-0.104	-1.355	-0.797	-3.588	-4.643	S
24	-9.8	-11.4	-2.46	-	-	-	-	-2.31	.141	-0.440	0.114	-	-	S
25	-11.4	-17.1	-3.61	-	6.5	6.4	-	-2.65	.069	-1.511	-0.954	-3.301	-4.837	S
26	-10.8	-18.8	-3.84	-	21.3	21.3	-	-2.65	.093	-1.291	-0.741	-2.250	-2.706	S
27	-10.1	-15.8	-3.56	-	22.0	22.0	-	-2.35	.090	-0.806	-0.259	-1.128	-1.113	S
28	-9.5	-16.2	-3.51	-	22.2	22.2	-	-2.47	.104	-0.831	-0.281	-1.271	-1.306	S
29	-7.7	-17.0	-3.65	-40.2	21.4	21.1	61.6	-1.88	.224	-0.498	0.053	-1.638	-1.596	S
30	-10.1	-17.4	-3.58	-15.2	21.8	21.7	37.0	-1.61	-0.005	-0.909	-0.366	-1.513	-1.322	S
30-d	-9.7	-16.3	-3.64	-15.0	21.8	21.7	36.8	-1.61	-0.004	-0.908	-0.365	-1.516	-1.356	S
31	-11.9	-18.2	-3.66	-	21.0	21.0	-	-1.57	.000	-0.994	-0.444	-1.551	-1.536	S
32	-12.0	-15.6	-3.11	-32.9	22.0	21.2	54.9	-1.80	.168	-0.626	-0.076	-1.296	-1.249	S
33	-9.4	-18.7	-3.84	-	1.8	1.8	-	-3.22	-0.286	-1.944	-1.39	-3.459	-4.318	S
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