

## A tracer study of the Floridan aquifer in southeastern Georgia: Implications for groundwater flow and paleoclimate

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**Abstract.** Distributions of stable isotopes of water, radiocarbon, noble gases, and chloride (Cl) in groundwater from the Upper Floridan aquifer in southeastern Georgia suggest that down gradient of the Gulf Trough this aquifer contains waters representative of both regional and local groundwater flow systems. In this area, locally recharged waters tend to remain near the top of the aquifer and do not mix substantially with the regional groundwater flow system. Noble gas temperatures suggest that this region of Georgia was  $4.0 \pm 0.6^\circ\text{C}$  cooler during the last glacial period (LGP). Similar temperature changes have been reported for southern Texas and northern New Mexico, suggesting that the southern United States cooled uniformly during the LGP. Stable isotopes of water became enriched down gradient from the recharge area. These enrichments which have been observed before appear to result from local influx of shallow groundwater into the regional aquifer system rather than representing a climate change signal. An inland gradient of the stable isotope composition ( $0.60 \pm 0.14\text{‰}/100\text{ km}$  in  $\delta^{18}\text{O}$ ) was found in young (Holocene) water. After correcting for the change in the stable isotope composition of the ocean during the LGP, water that was recharged during the LGP was found to be slightly depleted in stable isotopes relative to modern recharge ( $\Delta\delta^{18}\text{O} = 0.6 \pm 0.4\text{‰}$ ). Assuming the modern inland gradient, the change in  $\delta^{18}\text{O}$  is consistent with a shift in the coastline, which was caused by the lower sea level during the LGP.

### Introduction

The Floridan aquifer system in southeastern Georgia is the most important source of freshwater in the area [Krause and Randolph, 1989]. An understanding of the groundwater flow dynamics is vital for properly managing this resource. A quantitative description of flow within this system is difficult to obtain because hydraulic characteristics vary considerably due to lateral variations in confinement and in the formation of secondary porosity and permeability [Krause and Randolph, 1989].

Natural and anthropogenic trace substances can provide insights into the dynamics of groundwater flow that complement hydraulic information. They have been used in many hydrologic studies to estimate groundwater residence times, recharge rates, sources of recharge water, and interaquifer mixing [e.g., Mazor, 1991; Phillips, 1995]. Tracers that are commonly measured in groundwater include stable isotopes of water (D,  $^{18}\text{O}$ ), tritium, and radiocarbon ( $^{14}\text{C}$ ). An additional set of tracers, the noble gases (He, Ne, Ar, Kr, and Xe), have received less attention despite their potential as hydrologic tracers [Marine, 1979; Heaton, 1984; Andrews et al., 1985; Torg-

ersen and Clarke, 1985; Stute et al., 1992b; Suckow and Sonntag, 1993; Blavoux et al., 1993].

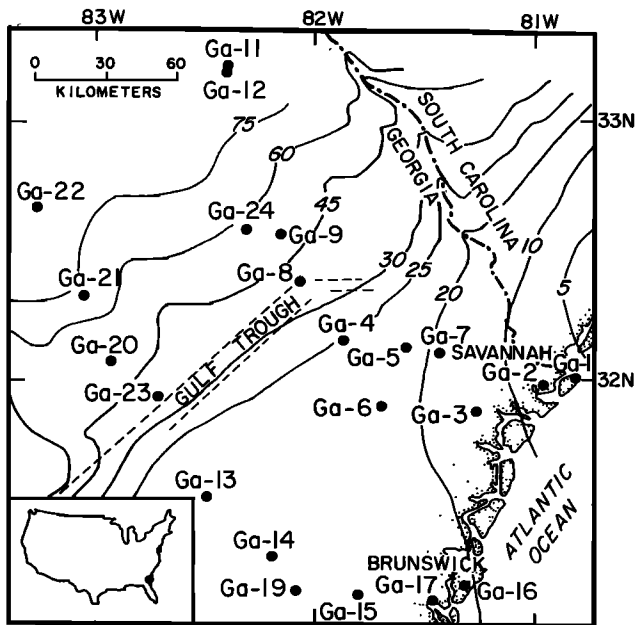
Noble gases have been used mostly in conjunction with  $^{14}\text{C}$  to develop continental paleotemperature records [Andrews and Lee, 1979; Rudolph et al., 1984; Stute and Deák, 1989; Stute et al., 1992a, 1995a, b]. These records, which typically have been obtained for confined sandstone aquifers, have shown that groundwater flow systems can be used as archives of continental paleoclimate for the last 30,000 years [Stute and Schlosser, 1993; Fontes et al., 1993]. They have also demonstrated that multitracer studies (noble gases,  $^{14}\text{C}$ ,  $^{13}\text{C}$ , D, and  $^{18}\text{O}$ ) have the potential to provide information on flow patterns and mean residence times in complicated groundwater flow systems [e.g., Stute and Deák, 1989; Blavoux et al., 1993].

Model calculations have demonstrated that in typical confined sandstone aquifers, dispersion removes high-frequency climate fluctuations, leaving only mean climate conditions of the Holocene (<10 kyr), last glacial maximum (10–20 kyr), and preceding interstadial (>20 kyr) [Stute and Schlosser, 1993]. Field studies have largely confirmed the model results. Groundwater with corrected  $^{14}\text{C}$  ages of less than 10 kyr has noble gas temperatures that are close to today's mean annual soil temperature [Stute and Schlosser, 1993; Stute et al., 1995b]. Older,  $^{14}\text{C}$  dated, groundwater generally has lower noble gas temperatures. Minimum noble gas temperatures are typically found in water with corrected  $^{14}\text{C}$  ages between 10 and 25 kyr. These temperatures are  $5^\circ\text{--}9^\circ\text{C}$  cooler than the mean annual soil temperatures of the Holocene [Stute and Schlosser, 1993].

Previous measurements of stable isotopes and  $^{14}\text{C}$  in the Upper Floridan aquifer have been used to estimate ground-

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**Figure 1.** Location of wells sampled in southeastern Georgia. The contour lines are the predevelopment potentiometric surfaces (meters above sea level), and the dashed lines are the approximate location of the Gulf Trough graben estimated by Krause and Randolph [1989].

water residence times and describe paleorecharge conditions. Mass balance calculations indicate that dissolved inorganic carbon (DIC) interacts strongly with the aquifer rock [Plummer, 1977, 1993]. This interaction dilutes the  $^{14}\text{C}$  derived from the soil zone and makes  $^{14}\text{C}$  dating difficult, although geochemical models can be used to correct  $^{14}\text{C}$  ages. Using such a model, Plummer [1993] found that groundwater residence times increased from the recharge area (<3 kyr) down gradient to the coast (>30 kyr). Plummer [1993] also found that stable isotopes collected in southern Georgia and northern Florida show unusual enrichment patterns along flow paths. In this region of the Upper Floridan aquifer, groundwaters with corrected  $^{14}\text{C}$  ages between 15 and 30 kyr were enriched in  $\delta^{18}\text{O}$  by 0.5–2.3‰ compared to average Holocene values. Maximum values were found about 50 km from the coast.

Here, we present noble gas measurements along with stable isotope,  $^{14}\text{C}$ , and chemistry data to better understand the groundwater flow dynamics of the Upper Floridan aquifer. The noble gas data provide additional constraints to the interpretation of  $^{14}\text{C}$  ages, stable isotope enrichments, and the general flow patterns of the Upper Floridan aquifer. The data are also used to develop a paleotemperature record for southeastern Georgia.

## Study Area

The Floridan aquifer system in southeastern Georgia is a massive carbonate formation of Tertiary age. The hydrology and hydrochemistry of this aquifer system have been described in detail by Johnston and Bush [1988], Krause and Randolph [1989], and Sprinkle [1989]. Briefly, the aquifer is separated into two permeable zones, the Upper and Lower Floridan aquifers, by a semipermeable dolomite layer. The aquifer is confined by low permeability sediments of Miocene age. Hy-

draulic conductivities within the Floridan aquifer range from relatively high values ( $40\text{ m s}^{-1}$ ) in cavernous limestone to relatively low values ( $0.2\text{ m s}^{-1}$ ) in massive limestone. Recharge occurs presumably into and through a sandy aquifer which slowly grades into the carbonate aquifer in central Georgia. The aquifer system thickens down dip from about 30 m at the base of the sand to more than 700 m near the coastline [Krause and Randolph, 1989]. Half way between the coastline and the recharge area lies the Gulf Trough. It is a graben that cuts across the Floridan aquifer system and is filled with clastic and carbonate rocks of relatively low permeability.

The hydraulic gradient decreases from the recharge area southeast toward the coastline (Figure 1). Model simulations of the flow suggest that water passes horizontally through the Gulf Trough. A small amount of leakage occurs from both the Lower Floridan aquifer and upper confining units into the Upper Floridan aquifer down gradient of the trough [Krause and Randolph, 1989]. Natural discharge from the aquifer occurs through a number of springs near the coast and through diffuse upward leakage.

## Methods

Samples were collected from wells open to the Upper Floridan aquifer along two flow paths in southeastern Georgia. The northern and southern flow paths are equivalent to flow paths 1 and 2, respectively, sampled by Plummer [1993]. Both flow paths extended from the sandy recharge area for more than 200 km toward the coastline. The majority of the samples were collected from large municipal wells. Typically, these wells are drilled 50–100 m into the Upper Floridan aquifer and are cased only from the ground surface to the top of the aquifer.

Noble gas samples were collected in 40-ml copper tubes. At the outlet end of the tube a clear plastic tube and a regulator valve were attached. The water pressure was raised by reducing the flow through the valve until no bubbles were detected in the plastic tube. After thoroughly flushing at high pressure, the copper tubes were sealed at each end with stainless steel pinch-off clamps.

Samples for stable isotopes of water (D and  $^{18}\text{O}$ ) and carbon isotopes of DIC ( $^{13}\text{C}$  and  $^{14}\text{C}$ ) were collected in 60 and 500-ml glass bottles, respectively. Carbon isotope samples were preserved by adding 0.2 ml of saturated  $\text{HgCl}_2$  solution. Major ion samples were filtered (0.4- $\mu\text{m}$  pore size) and collected in high-density polyethylene bottles. The pH, temperature, conductivity, dissolved oxygen (CHEMets® test kits), and alkalinity (Gram titrations) were measured at the well head.

Noble gas concentrations were determined on an MAP 215-50 noble gas mass spectrometer using the methods outlined by Stute *et al.* [1995a]. The system was calibrated using known quantities of air. Absolute concentrations of the noble gases were determined with a precision of  $\pm 1\%$  (Ar, Kr, and Xe) to  $\pm 2\%$  (He and Ne).

For carbon isotope analysis, approximately 100 ml of  $\text{HgCl}_2$  poisoned water was transferred into an evacuated glass bulb which contained approximately 30 ml of 1 N HCl. The  $\text{CO}_2$  released by the reaction with the acid was collected in a liquid nitrogen cooled trap after water vapor had been removed using an alcohol/dry ice cold trap. The  $\text{CO}_2$  was then split and collected in two glass ampoules. Carbon 13/carbon 12 ratios were measured mass spectrometrically at the University of Waterloo and  $^{14}\text{C}/^{12}\text{C}$  ratios were determined at the accelerator mass spectrometry (AMS) facility of the Eidgenössische Technische

**Table 1.** Well Construction and Water Chemistry Data

Well ID	USGS Grid Number	Distance, <sup>a</sup> km	Screen, m bsl	Temperature, °C	Ca, meq/L	Mg, meq/L	K, meq/L	Na, meq/L	Cl, meq/L	Alk, meq/L	ΣCO <sub>2</sub> , mmol/L	SO <sub>4</sub> , meq/L	SiO <sub>2</sub> , mmol/L
<i>Northern Flowline</i>													
Ga-11	26Z001	0	-110 to -108	18.2	4.5	0.21	0.11	0.01	0.16	0.14	1.12	0.02	0.16
Ga-12	26Z003	0	-116 to -102	18.8	5.2	0.29	0.09	0.01	0.20	0.23		0.02	0.37
Ga-24	27U008	62	-17 to 5	22.4	7.6	2.25	0.14	0.02	0.14	0.09	2.47	0.02	0.37
Ga-09	28U002	68	10 to 22	21.1	7.5	2.15	0.71	0.04	0.24	0.11	2.97	0.04	0.31
Ga-08	29T011	90	24 to 90	21.5	7.8	1.50	0.27	0.06	0.42	0.10	2.08	0.07	0.69
Ga-04	30R001	121	72 to 164	23.5	7.8	1.17	0.67	0.05	0.46	0.10	2.26	0.06	0.80
Ga-05	33R021	141	43 to 103	22.8	7.9	1.39	0.50	0.04	0.37	0.10	2.16	0.10	0.83
Ga-06	31Q003	151	99 to 177	23.9	8.0	0.93	0.71	0.06	0.68	0.09	2.15	0.15	0.55
Ga-07	34R046	163	89 to 127	22.6	7.9	1.57	0.50	0.04	0.36	0.12	2.21	0.04	0.90
Ga-03	35P099	177	104 to 184	23.5	7.8	1.06	0.73	0.06	0.55	0.11	2.14	0.09	0.71
Ga-02	37P087	206	83 to 179	23.6	7.8	1.09	0.92	0.07	0.67	0.11	2.24	0.36	0.52
Ga-01	39Q001	226	56 to 172	23.5	7.8	1.26	1.48	0.06	2.17	1.15	2.35	1.50	0.63
<i>Southern Flowline</i>													
Ga-22	19V008	0	-144 to -142	19.5	5.4	0.35	0.04	0.01	0.07	0.05	0.73	0.02	0.18
Ga-21	21S003	45	-33 to -15	19.8	7.6	2.10	0.07	0.02	0.08	0.08	2.29	0.02	0.48
Ga-20	22Q003	76	-40 to 118	21.8	7.6	2.37	0.82	0.05	0.21	0.17	3.31	0.06	0.46
Ga-23		98	0 to 150 <sup>b</sup>	22.4	7.8	2.21	1.09	0.10	0.31	0.16	2.71	0.92	0.36
Ga-13	26L004	145	91 to 195	23.5	7.6	1.38	1.11	0.06	0.62	0.22	2.48	0.37	0.70
Ga-14	28J003	180	126 to 218	24.1	7.6	1.87	1.40	0.06	1.45	0.92	2.54	1.68	0.65
Ga-19	28H003	200	125 to 185	25.8	7.5	1.94	1.46	0.04	0.62	0.41	2.45	1.50	0.64
Ga-15	31H005	224	171 to 211	24.7	7.7	2.01	1.82	0.05	0.78	0.64	2.44	2.56	0.64
Ga-17	33H209	251	162 to 192	23.5	7.7	2.30	2.04	0.05	0.65	0.47	2.52	1.74	0.59
Ga-16		267	183 to 248 <sup>b</sup>	24.8	7.7	1.92	1.99	0.05	0.85	0.63	2.52	2.16	0.61

bsl, below sea level.

<sup>a</sup>Distance from recharge area along the flowlines.

<sup>b</sup>Depth of casing unknown; wells assumed to be cased to the top of the Floridan aquifer which was estimated using data from *Krause and Randolph* [1989].

Hochschule (ETH) Zürich after the CO<sub>2</sub> had been converted into graphite. The precision of the <sup>13</sup>C/<sup>12</sup>C ratios expressed in the δ notation was about 0.2‰, and the precision of the <sup>14</sup>C/<sup>12</sup>C ratios are listed in Table 2. According to the procedure applied by the Zürich AMS facility the detection limit is defined as 2 times the analytical blank of the <sup>14</sup>C/<sup>12</sup>C ratio measurements. For this study the typical detection limit was about 1.4 percent modern carbon (pmc).

Stable isotopes of water were measured using standard techniques at Lamont-Doherty Earth Observatory (HDO/H<sub>2</sub>O) and at University of Waterloo (H<sub>2</sub><sup>18</sup>O/H<sub>2</sub><sup>16</sup>O). The analytical errors expressed in the δ notation were ±1.5‰ and ±0.2‰, respectively.

Major cations (Ca, Mg, K, and Na) were measured using standard atomic adsorption spectroscopy (AAS) techniques. Cl was measured using a Ag-electrode auto-titrator, and SO<sub>4</sub> was determined using a turbidimetric technique [Tabatabai, 1974]. ΣCO<sub>2</sub> concentrations were determined volumetrically during the CO<sub>2</sub> extraction for carbon isotope analysis (±10%).

As described in detail by *Stute and Schlosser* [1993], the measured noble gas concentrations have to be corrected for excess air which typically dissolves in groundwater [Heaton and Vogel, 1981]. Because the excess air component was fractionated compared with atmospheric air in the Floridan aquifer samples, it was assumed that a portion of the excess air was lost due to gas transfer across the water table after formation. Gas exchange rates of the individual noble gases are related by their molecular diffusion constants; thus the fractional losses of individual noble gases are correlated [Stute et al., 1995b].

The fractions of the individual noble gases remaining in the water after gas exchange were approximated by a Rayleigh-type formula [Stute et al., 1995b]:

$$\frac{C_X}{C_{X(0)}} = \left( \frac{C_{Ne}}{C_{Ne(0)}} \right)^{D_X/D_{Ne}} \quad (1)$$

where (C<sub>X</sub>/C<sub>X(0)</sub>) and D<sub>X</sub> are the remaining excess air fraction and the temperature dependent diffusion coefficient [Jähne et al., 1987] for noble gas X (He, Ne, Ar, Kr, or Xe), respectively. C<sub>Ne</sub>/C<sub>Ne(0)</sub> and the amount of excess air were varied until optimum agreement between the recharge temperatures derived from Ne, Ar, Kr, and Xe was achieved using the solubility data of *Weiss* [1970, 1971] and *Clever* [1979]. Monte Carlo simulations indicate that optimized noble gas temperatures have an uncertainty (analytical plus model) of about ±0.8°C [Stute et al., 1995b]. Using this method, good agreement between the Ne, Ar, Kr, and Xe recharge temperatures was obtained for all wells except Ga-17. Noble gas temperatures for Ga-17 ranged from 17.8° to 11.0°C. The range of values is indicative of a sampling problem, and this well has been removed from the following discussion.

Dissolved oxygen concentrations measured at the outflow of the copper tubes during sampling were less than 2 μmol l<sup>-1</sup> (i.e., less than 1% of the solubility equilibrium with the soil air) at all wells except Ga-9, Ga-11, Ga-21, Ga-22, and Ga-24. These wells were located near the recharge area, and the groundwater sampled at these sites was presumably young. The dissolved oxygen data indicate that air was not introduced into the groundwater during sampling.

## Results

The chemical and isotopic tracers analyzed during this study display different patterns along the two flow paths (Tables 1 and 2; Figure 2). Patterns of conservative tracers such as stable

**Table 2.** Isotope and Noble Gas Data

Well ID	Distance, <sup>a</sup> km	<sup>14</sup> C, <sup>b</sup> pmc	$\delta^{13}\text{C}$ , ‰	$\delta^{18}\text{O}$ , ‰	$\delta\text{D}$ , ‰	$T_{\text{Ng}}$ , <sup>c</sup> °C	$T_{\text{Ne}}$ , °C	$T_{\text{Ar}}$ , °C	$T_{\text{Kr}}$ , °C	$T_{\text{Xe}}$ , °C	He Excess $10^{-8}$ cc STP g <sup>-1</sup>	Ne $10^{-7}$ cc STP g <sup>-1</sup>	Ar $10^{-4}$ cc STP g <sup>-1</sup>	Kr $10^{-8}$ cc STP g <sup>-1</sup>	Xe $10^{-8}$ cc STP g <sup>-1</sup>
<i>Northern Flowline</i>															
Ga-11	0	113 ± 0.8	-21.2	-4.80	-29.3	17.7	17.7	17.8	17.6	17.7	0.51	2.16	3.54	7.94	1.07
Ga-12	0			-4.69	-27.6										
Ga-24	62	15	-11.0	-4.32	-26.2	17.3	17.3	16.9	17.5	17.7	0.63	1.99	3.51	7.93	1.07
Ga-09	68	0.7 ± 0.1	-4.1	-4.02	-24.3	17.7	17.8	17.6	17.8	17.8	2.72	2.48	3.83	8.37	1.11
Ga-08	90	nd	-9.5	-4.18	-23.5	13.7	13.7	13.5	13.9	13.7	9.95	2.53	4.19	9.39	1.27
Ga-04	121	nd	-8.6	-3.92	-24.2	17.8	17.8	17.8	17.9	17.5	9.36	2.43	3.93	8.79	1.16
Ga-05	141	2.9 ± 0.1	-5.9	-3.70	-22.8	17.5	17.5	17.5	17.5	17.4	6.25	2.55	3.93	8.63	1.14
Ga-06	151	nd	-6.2	-4.31	-21.3	13.5	13.5	13.3	13.7	13.5	20.9	2.45	4.13	9.28	1.27
Ga-07	163	nd	-9.3	-3.64	-20.3	18.3	18.3	18.3	18.6	18.0	4.33	2.66	3.96	8.55	1.13
Ga-03	177	nd	-6.6	-4.05	-25.1	13.4	13.4	13.4	13.4	13.4	12.1	2.50	4.15	9.38	1.27
Ga-02	206	nd	-4.9	-3.93	-23.9	13.9	13.9	14.0	13.9	13.9	23.2	2.53	4.13	9.29	1.25
Ga-01	226	nd	-2.8	-3.89	-22.1	14.1	14.1	14.1	14.0	14.1	41.8	2.47	4.11	9.32	1.25
<i>Southern Flowline</i>															
Ga-22	0	75.2 ± 0.7	-17.8	-4.53	-26.5	19.5	19.5	19.4	19.6	19.4	0.51	2.21	3.47	7.61	1.01
Ga-21	45	39.5 ± 0.4	-14.1	-4.21	-23.4	18.3	18.3	18.3	18.4	18.1	1.12	2.46	3.77	8.25	1.09
Ga-20	76	nd	-3.9	-3.95	-21.8	17.1	17.1	17.2	17.0	17.2	2.49	2.56	3.91	8.58	1.13
Ga-23	98	nd	-7.2	-3.63	-21.0	14.2	14.2	14.1	14.3	14.1	9.49	2.45	4.09	9.21	1.25
Ga-13	145	nd	-7.7	-3.51	-22.6	15.6	15.6	15.2	16.1	15.7	12.3	2.36	3.97	8.80	1.19
Ga-14	180	2.9 ± 0.1	-10.3	-3.40	-21.0	16.3	16.3	16.1	16.5	16.4	24.9	2.44	3.91	8.66	1.16
Ga-19	200	1.5 ± 0.1	-11.7	-3.03	-17.4	17.7	17.7	17.6	17.8	17.7	9.74	2.44	3.85	8.47	1.12
Ga-15	224	nd	-9.2	-3.13	-18.9	17.6	17.6	17.6	17.6	17.6	13.4	2.35	3.80	8.48	1.12
Ga-17	251	nd	-6.9	-3.09	-16.7	—	17.8	11.0	11.9	12.5	6.35	1.87	3.75	8.59	1.20
Ga-16	267	0.6 ± 0.1	-3.5	-3.25	-16.5	15.0	15.0	14.9	15.0	15.0	16.5	2.41	4.00	9.00	1.21

<sup>a</sup>Distance from recharge zone along the flowlines.

<sup>b</sup>nd, not detected (<1.4 pmc); values listed have been corrected for the analytical blank.

<sup>c</sup> $T_{\text{Ng}}$ , noble gas paleotemperature.

isotopes of water and noble gas temperatures reflect changes in the properties of recharge, whereas other tracers such as Cl, <sup>13</sup>C, <sup>14</sup>C, and He reflect water-rock interaction and groundwater residence times.

### Chloride

Cl concentrations along most of the northern flow path showed little variation, while along the southern flow path, Cl concentrations generally increased toward the coast (Figures 2a and 2b). A number of sources of Cl can be postulated to explain the increased concentrations observed down gradient. These include mixing with surface or deeper groundwater which is enriched in Cl as well as seawater infiltration which may have occurred anytime during the last tens of thousands of years. Assuming a seawater source, the Upper Floridan groundwater would contain at most 0.2% seawater. Although it is difficult to interpret the observed variations without additional information, they do suggest that the groundwater movement is not simply piston flow through a confined aquifer.

### Noble Gas Temperatures

Water from 16 of the 20 sampled wells had noble gas temperatures close to either 13.7° or 17.7°C, presumably representing one of two recharge conditions corresponding to periods of different climates. The standard deviation of the mean values of each group was ±0.3°C ( $\sigma/\sqrt{n}$ ). Of the four remaining wells, three had noble gas temperatures between 13.7° and 17.7°C, and one noble gas temperature was higher than 17.7°C (Table 2).

Mean annual air temperatures observed presently in the recharge area range from 17.7° to 18.6°C. North and south of the recharge area, mean annual temperatures are about 1°C lower and about 1°C higher, respectively. In the conterminous

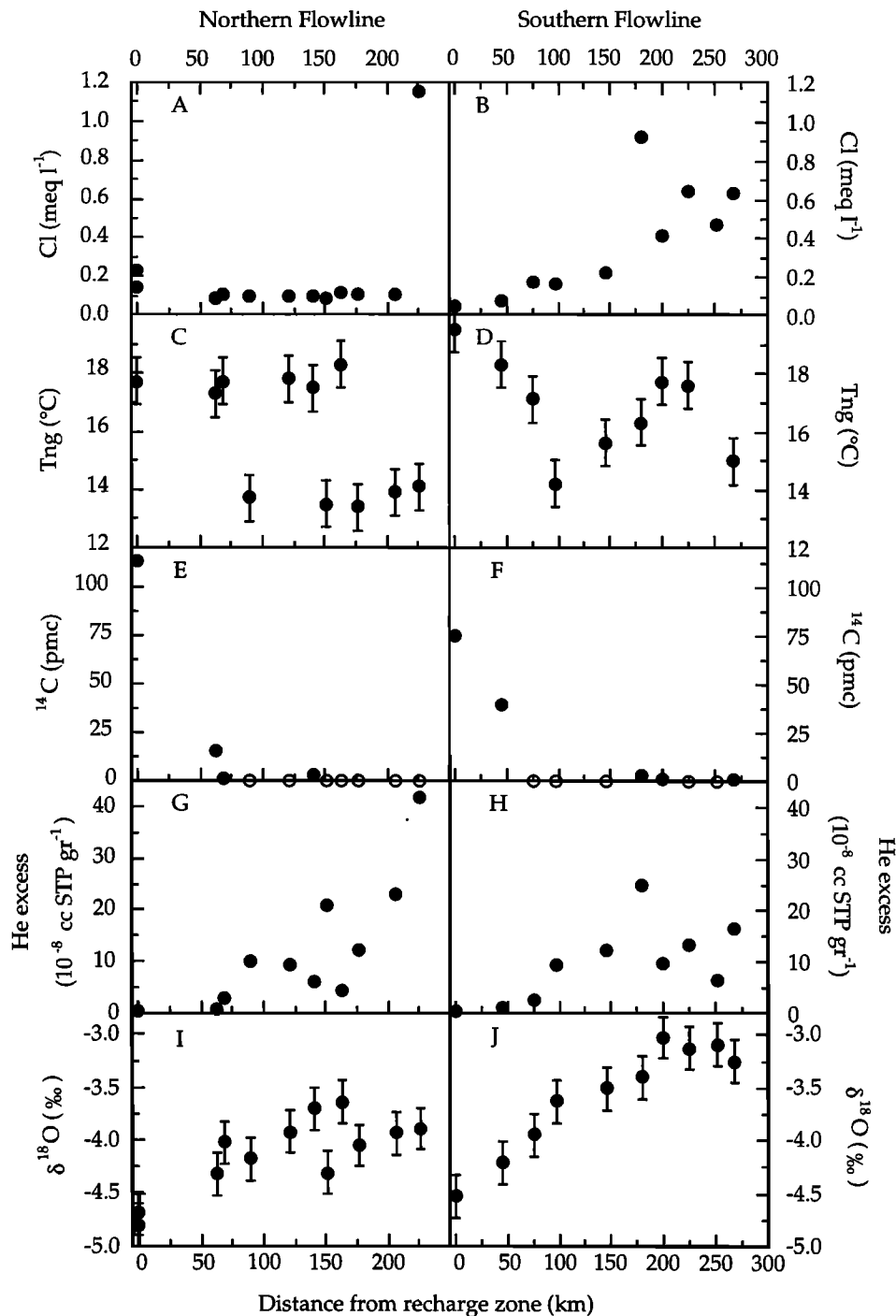
United States the mean annual ground temperature is typically 0°–2°C warmer than the mean annual air temperature [Smith et al., 1964]. The temperatures of the shallow groundwater measured at wells in the recharge area ranged from 18.2° to 19.5°C, reflecting the slightly warmer temperatures of the ground.

The noble gas temperature of the warmer group, 17.7° ± 0.3°C, is in good agreement with the expected mean annual ground temperature, 17.7°–20.6°C, suggesting that this water was recharged during a climate similar to today's. Hence these waters were most likely recharged during the Holocene. The noble gas temperature of the other wells suggests that the water was recharged during a cooler climate. A likely period of recharge for this water was during the last glacial period (LGP).

In order to verify that the water with noble gas temperatures of about 13.7°C was recharged during the LGP, groundwater ages or groundwater flow paths must be determined. Along the two flow paths, water with noble gas temperatures of about 17.7°C typically is observed near the recharge area, while water with noble gas temperatures of about 13.7°C is more likely to be found near the coastline (Figures 2c and 2d). However, between these areas, water with noble gas temperatures equal to both the warm and cold groups was observed. Whereas the locations along the two flow paths suggest that the warm group is younger than the cold group, additional age constraints are highly desirable.

### Carbon Isotopes of Dissolved Inorganic Carbon

The values of  $\delta^{13}\text{C}$  range from about -20‰ in the recharge area to -2.8‰ down gradient (Table 2). This evolution does not occur systematically along flow paths. After an initial increase during the first 70 km of flow,  $\delta^{13}\text{C}$  values fluctuate between -9.5‰ and -2.8‰. Carbon 14 values decrease

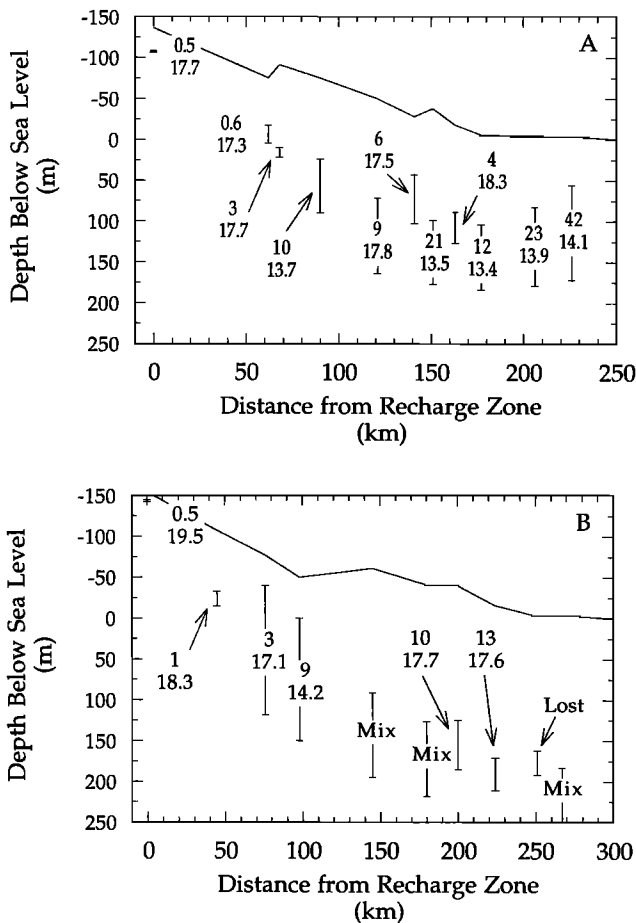


**Figure 2.** (a) and (b) Results of Cl, (c) and (d) noble gas temperature, (e) and (f)  $^{14}\text{C}$ , (g) and (h) excess He, and (i) and (j)  $\delta^{18}\text{O}$  plotted as a function of distance along flow path. In Figures 2e and 2f,  $^{14}\text{C}$  contents greater than the detection limit are plotted as solid symbols, while samples below the detection limit are plotted as open symbols.

from more than 100 pmc in the recharge zone to values below the detection limit of 1.4 pmc. The  $^{14}\text{C}$  concentrations were significantly greater than the detection limit in water from only 9 of 21 wells analyzed (Figures 2e and 2f). The values of  $\delta^{13}\text{C}$  of DIC from water which did not contain detectable  $^{14}\text{C}$  ranged from  $-9.5\text{‰}$  to  $-2.8\text{‰}$ .

Carbon 14 was not detected in 4 of the 11 wells with Holocene noble gas temperatures, indicating that the strong water-

rock interactions significantly diluted the  $^{14}\text{C}$  derived from the soil zone during the first 10–15 kyr of groundwater flow. This is supported by the observation that  $^{14}\text{C}$  was not detected in any of the wells that had noble gas temperatures of about  $13.7^\circ\text{C}$  and were recharged presumably during the LGP. The noble gas data also indicate that the four wells with detectable  $^{14}\text{C}$  which were located more than 70 km from the recharge area contain a component of young (Holocene) water. Water



**Figure 3.** Depth and screened interval of wells plotted as a function of distance along the (a) northern and (b) southern flow paths. The He excess (top number,  $10^{-8}$  cc STP  $g^{-1}$ ) and noble gas temperatures (bottom number in degrees Celsius) have been plotted for each well. The solid curve represents the surface elevation of the land. "Mix" and "lost" indicate samples that were a mixture between young and old water and samples that were lost during sampling, respectively.

from two of these wells had noble gas temperatures between  $17.7^{\circ}$  and  $13.7^{\circ}C$ , and the other two had noble gas temperatures of about  $17.7^{\circ}C$ . The intermediate noble gas temperatures probably resulted from mixing between young and old groundwater.

#### Excess He

Several sources contribute He to groundwater. Initially, He concentrations are equal to the solubility equilibrium with soil air plus a component of excess air. As groundwater flows away from the water table, it can no longer exchange with the soil air, and its He concentration increases as a result of the addition of radiogenic He and, in rare cases, mantle He. Radiogenic He originates from the  $\alpha$  decay of natural U and Th series nuclides and nucleogenic  $^3He$  production within the aquifer rock ( $^6Li(n, \alpha)^3He$ ) as well as from deeper aquitards and crustal material [e.g., Heaton, 1984; Andrews et al., 1985; Torgersen and Clarke, 1985; Stute et al., 1992b].

In many confined aquifers, terrigenous He concentrations (He excess) increase with groundwater age. This correlation has been found, for example, in the Bunter Sandstone [Andrews

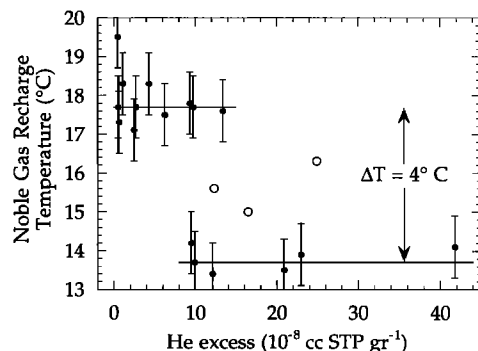
and Lee, 1979], the Uitenhage and Stampriet Aquifers [Heaton, 1984], the Molasse Basin [Andrews et al., 1985], the Great Artesian Basin [Torgersen and Clarke, 1985], the Great Hungarian Plain [Stute et al., 1992b], and several other aquifers (M. Stute et al., unpublished data, 1996). These studies have also shown that a general correlation exists between well depth and He excess. The observed accumulation rates frequently exceed the in situ production rate from U and Th series nuclides contained within the aquifer. The additional source is presumably addition of terrigenous He which was produced deeper in the crust and/or the mantle. While the accumulation rate of He varies in the different aquifers by more than an order of magnitude, these relationships imply that He excesses can be used as a relative age indicator within an aquifer system.

In the Upper Floridan aquifer from southeastern Georgia, He excesses generally increase down gradient of the recharge area (Figures 2g and 2h), although there is significant scatter between wells that were located more than 100 km from the recharge area down gradient from the Gulf Trough. Much of the scatter can be explained by the relative depth of the wells (Figure 3). Deeper wells tend to have higher He excesses than adjacent shallower wells. This suggests that groundwater ages increase down gradient from the recharge area and possibly with depth locally. Wells with noble gas temperatures of about  $17.7^{\circ}C$  tend to be up gradient and at shallower depths than wells with noble gas temperatures of about  $13.7^{\circ}C$  (Figure 3). They also tend to have lower He excess concentrations (Figure 4).

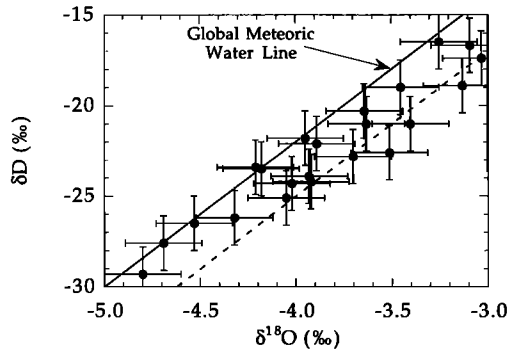
The transition between the two groups of paleotemperatures occurs at an excess He concentration of about  $10 \times 10^{-8}$  cc STP  $g^{-1}$  (Figure 4). Assuming a He accumulation rate similar to that observed in several sandstone aquifers ( $\geq 5 \times 10^{-12}$  cc STP  $g^{-1} yr^{-1}$ ; Bunter Sandstone [Andrews and Lee, 1979], the Great Artesian Basin [Torgersen and Clarke, 1985], the Great Hungarian Plain [Stute and Deák, 1989], the Carrizo Aquifer (M. Stute et al., unpublished data, 1996)), an upper limit of the transition between the noble gas temperature groups can be placed at 20 kyr ago. Despite the uncertainty of this age, it is consistent with the interpretation that the wells with noble gas temperatures of about  $17.7^{\circ}$  and about  $13.7^{\circ}C$  were recharged during the Holocene and LGP, respectively.

#### Stable Isotopes

The stable isotope composition of water from the Upper Floridan aquifer plots close to the global meteoric water line with a deuterium excess between 7 and 10‰ (Figure 5). The



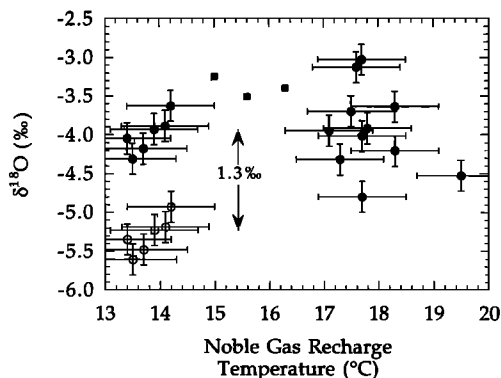
**Figure 4.** Noble gas temperatures  $T_{ng}$  plotted as a function of He excess. Wells which are mixtures between young and old waters have been indicated with open circles.



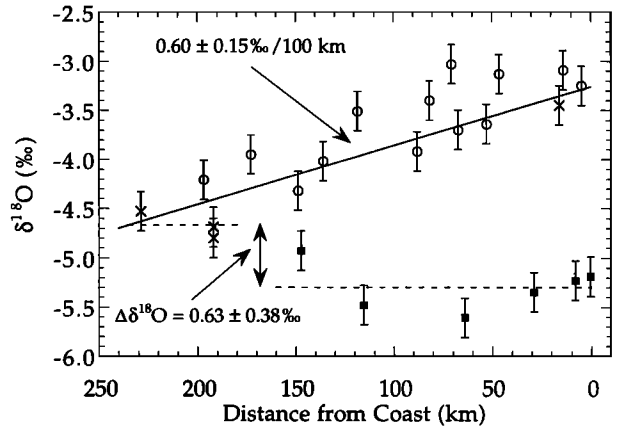
**Figure 5.** Plot of  $\delta D$  against  $\delta^{18}O$ . The global meteoric water line (solid line) and a parallel line with a deuterium excess of 7‰ (dashed line) have been plotted for reference.

isotopic composition of this water becomes heavier in  $\delta^{18}O$  by about 1.1 and 1.5‰ along the northern and southern flow path, respectively (Figures 2i and 2j). This enrichment is similar to the one reported by *Plummer* [1993]. The two water types which have been distinguished on the basis of their noble gas temperatures have similar stable isotope compositions. The entire range of  $\delta^{18}O$  values observed ( $-3.0$  to  $-4.8$ ‰) is represented in Holocene samples (Figure 6). Samples which presumably were recharged during the LGP have a smaller range of  $\delta^{18}O$  values ( $-3.6$  to  $-4.3$ ‰) which overlaps with Holocene samples. On the basis of the noble gas temperatures, the most enriched samples are of Holocene age, not of glacial age as determined by *Plummer* [1993] using  $^{14}C$  model ages.

To assess long-term variations of the stable isotope composition, a reservoir correction must be made for samples which were recharged during the LGP. During this period, isotopically light water was trapped in large glaciers, and the surface ocean was approximately 1.3‰ heavier in  $\delta^{18}O$  [*Fairbanks*, 1989]. The corresponding enrichment in deuterium would be expected to plot on a slope of less than 8 in the  $\delta D$ - $\delta^{18}O$  diagram because the enrichment of the glacial ocean is caused by evaporation [*Dansgaard*, 1964]. Our data seem to plot on such a line and therefore supports the above hypothesis (Figure 5). After correcting the observed  $\delta^{18}O$  values for this reservoir effect, the mean  $\delta^{18}O$  value of the six LGP samples is



**Figure 6.** Plot of  $\delta^{18}O$  as a function of noble gas temperature. The solid circles are the measured  $\delta^{18}O$  values, the open circles are  $\delta^{18}O$  values which have been corrected for reservoir effect, and the solid squares are  $\delta^{18}O$  values of wells which are mixtures between young and old groundwaters.



**Figure 7.** Plot of  $\delta^{18}O$  as a function of distance from the coast. The open circles and crosses are deep ( $>50$  m) and shallow ( $<50$  m) wells, respectively, with Holocene age water, and the solid squares are wells with last glacial period (LGP) age water. The  $\delta^{18}O$  composition of the LGP age water has been corrected for the isotopically heavier seawater (1.3‰) during the LGP.

$-5.30 \pm 0.24$ ‰ (Figure 6), and the difference between the mean values of Holocene samples from the recharge area and glacial samples is  $0.6 \pm 0.4$ ‰.

An inland gradient of  $\delta^{18}O$  of  $0.60 \pm 0.15$ ‰/100 km is observed for the Upper Floridan aquifer wells of Holocene age. This gradient is similar to the gradient of  $\delta^{18}O$  measured in four shallow wells ( $<50$  m deep) that presumably reflects the composition of modern precipitation. Three of the shallow wells are located in the recharge area of the Upper Floridan aquifer, and the fourth is located in the surficial aquifer near Brunswick, Georgia, about 15 km from the coast (Figure 7).

## Discussion

### Implications for Groundwater Flow

Although the tracers analyzed in this study have different patterns down gradient from the recharge area, they imply a similar groundwater flow regime. Noble gas temperatures and He excesses indicate that young (Holocene) water can be found along most of the flow path. Old water (LGP) generally is observed down gradient of the young water and at greater depths. The multitracer data do not support piston flow through a confined aquifer. Rather, the tracers suggest a more complicated regional and local flow system as suggested by the modeling work of *Krause and Randolph* [1989]. The semiconfined nature of the Floridan aquifer has been documented recently in other areas. *McConnell and Hacke* [1993] and *Landmeyer and Stone* [1995] have shown that significant amounts of young (shallow) groundwater infiltrates and mixes with the older (regional) groundwater, respectively, in the vicinity of Valdosta, Georgia, and Hilton Head, South Carolina.

Our interpretation which is mainly based on noble gas temperatures and excess He concentrations is consistent with our  $^{14}C$  data. In aquifers where the  $^{14}C$  concentration is strongly affected by water-rock interactions, it is difficult to isolate the radioactive decay signal, especially if the observed  $^{14}C$  concentration is of the order of 1 pmc. Therefore observations of low  $^{14}C$  concentrations in the Upper Floridan aquifer do not nec-

essarily imply high ages of the groundwater. Rather, they seem to indicate the strength of the water-rock interaction.

The inland stable isotope gradients observed in both the shallow wells (<50 m) and the deeper Upper Floridan aquifer wells which tap water that was recharged during the Holocene are very similar. This indicates that the Holocene water infiltrates the Upper Floridan aquifer locally. In contrast with groundwater recharged during the Holocene, stable isotope compositions of glacial water are nearly constant. This suggests that most of the glacial water was recharged in the same area and represents the regional groundwater flow regime.

The extent of mixing between the local and regional flow systems in the Floridan Aquifer can be assessed using Cl concentrations,  $^{14}\text{C}$  values, and noble gas temperatures. Along the northern flow path, mixing between the local and regional flow systems appears to be small despite the large intervals of the wells open to the aquifer. Noble gas temperatures are close to either about 17.7° or 13.7°C,  $^{14}\text{C}$  is detected only in wells with Holocene temperature, and Cl concentrations are uniform over the entire length of the flow line (with the exception of Ga-1). Along the southern flow path, there is much more evidence of mixing between young and old water, especially in the region more than 100 km from the recharge area down gradient of the Gulf Trough (Figure 1). In this region, three of the six wells (Ga-13, Ga-14, and Ga-16) have noble gas temperatures that fall between about 17.7° and 13.7°C,  $^{14}\text{C}$  is detected in waters with noble gas temperatures which are less than 17.7°C, and Cl concentrations vary considerably between wells. The observed mixing may be an artifact of well construction in which large intervals (50–100 m) were open to the aquifer. The relatively reduced influence of the regional groundwater flow system along the southern flow path may be related to the Gulf Trough. The trough appears to act as a hydrologic barrier to the regional flow causing a rapid decrease and flattening of the hydraulic gradient, thus creating a potential for downward movement of groundwater.

### Implications for Paleoclimate

Noble gas temperatures indicate that southeastern Georgia was  $4.0^\circ \pm 0.6^\circ\text{C}$  cooler during the LGP than during the Holocene. This temperature decrease is similar to the cooling observed in southern Texas ( $5.2^\circ \pm 0.7^\circ\text{C}$  [Stute et al., 1992a]) and northwestern New Mexico ( $5.4^\circ \pm 0.7^\circ\text{C}$  [Stute et al., 1995a]), suggesting that the southern United States cooled uniformly during the LGP. A change in the mean  $\delta^{18}\text{O}$  values of  $0.6 \pm 0.4\text{‰}$  is also apparent between Holocene and LGP water after correcting for the change in the surface ocean stable isotope composition during the LGP (1.3‰ [Fairbanks, 1989]).

Stable isotopes are weakly correlated with temperature in modern precipitation from the southern United States (Waco, Texas, and Hatteras, North Carolina; slopes  $<0.14\text{‰}/^\circ\text{C}$  and  $R^2 < 0.17$  [International Atomic Energy Agency (IAEA), 1992]). Hence it is unlikely that the lower  $\delta^{18}\text{O}$  values found in the glacial samples result from the cooler climate. Rather, the lower  $\delta^{18}\text{O}$  values probably reflect the lower sea level of the LGP. At that time the coastline was shifted by about 100 km to the east of its present location. Assuming the modern inland gradient of  $\delta^{18}\text{O}$  ( $0.60 \pm 0.15\text{‰}/100\text{ km}$ ), a change in the distance to the coastline of this magnitude would cause  $\delta^{18}\text{O}$  values to decrease by approximately  $0.6\text{‰}$ , about the observed difference.

An alternative hypothesis relates the observed  $\delta^{18}\text{O}$  distri-

bution in the Upper Floridan aquifer to a change in the season of recharge and more intense summer tropical storms [Plummer, 1993]. This hypothesis relies on model  $^{14}\text{C}$  ages, Ar-N<sub>2</sub> recharge temperatures, and the correlation of  $\delta^{18}\text{O}$  and temperature observed in western Europe ( $\Delta\delta^{18}\text{O}/\Delta T = 0.56$ ). The slope of the correlation between  $\delta^{18}\text{O}$  and temperature varies geographically [Rozanski et al., 1993]. It seems problematic to apply the relationship derived from western Europe to Georgia, especially in light of the IAEA data from the southern United States. Furthermore, both the model  $^{14}\text{C}$  ages and Ar-N<sub>2</sub> data are inconsistent with our noble gas data which show that much of the groundwater in the region of the Upper Floridan aquifer more than 70 km from the recharge area was recharged during the Holocene. Plummer [1993] reported model  $^{14}\text{C}$  ages between 20 and 30 kyr for all of the wells in this region indicating that the water recharged during the LGP. He supported his  $^{14}\text{C}$  interpretation with Ar-N<sub>2</sub> recharge temperatures which he found to be on average about 5°C cooler in all of these wells than near the recharge area.

### Conclusions

Although chemical and isotopic tracers have different patterns in the Upper Floridan aquifer in southeastern Georgia, they indicate a similar flow pattern. Stable isotopes, noble gas temperatures, and Cl concentrations suggest that shallow groundwater infiltrates the aquifer system locally. Only a few samples are affected by mixing between the local and regional flow systems. The observed mixing may be an artifact of well construction. Groundwater age could not be determined with  $^{14}\text{C}$  because of the strong water-rock interactions and the complicated flow paths. The relative ages of the groundwater were determined by using the He excess, which indicates that waters with noble gas temperatures of about 17.7°C are younger than waters with noble gas temperatures of about 13.7°C. The most likely periods of recharge of these waters were the Holocene and LGP, respectively. Assuming these ages, a mean annual temperature change between the modern and LGP of  $4.0^\circ \pm 0.6^\circ\text{C}$  was determined. The stable isotope enrichments found down gradient of the recharge area can be explained largely by influx of shallow groundwater, changes in the isotopic composition of the ocean during the LGP, and changes in the distance between the recharge area and coast during the LGP.

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