ELSEVIER

Chemical Geology 179 (2001) 187–202

CHEMICAL GEOLOGY
INCLUDING
ISOTOPE GEOSCIENCE

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Using multiple geochemical tracers to characterize the hydrogeology of the submarine spring off Crescent Beach, Florida

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Abstract

A spectacular submarine spring is located about 4 km east of Crescent Beach, FL, in the Atlantic Ocean. The single vent feature of Crescent Beach Spring provides a unique opportunity to examine onshore–offshore hydrogeologic processes, as well as point source submarine ground water discharge. The Floridan aquifer system in northeastern Florida consists of Tertiary interspersed limestone and dolomite strata. Impermeable beds confine the water-bearing zones under artesian pressure. Miocene and younger confining strata have been eroded away at the vent feature, enabling direct hydrologic communication of Eocene ground water with coastal bottom waters.

The spring water had a salinity of 6.02, which was immediately diluted by ambient seawater during advection/mixing. The concentration of major solutes in spring water and onshore well waters confirm a generalized easterly flow direction of artesian ground water. Nutrient concentrations were generally low in the reducing vent samples, and the majority of the total nitrogen species existed as NH_3. The submarine ground water tracers, Rn-222 (1174 dpm l^{-1}, dpm), methane (232 nM) and barium (294.5 nM) were all highly enriched in the spring water relative to ambient seawater. The concentrations of the reverse redox elements U, V and Mo were expectedly low in the submarine waters. The strontium isotope ratio of the vent water ($^{87}Sr/^{86}Sr = 0.70798$) suggests that the spring water contain an integrated signature indicative of Floridan aquifer system ground water. Additional Sr isotopic ratios from a series of surficial and Lower Floridan well samples suggest dynamic ground water mixing, and do not provide clear evidence for a single hydrogeologic water source at the spring vent. In this karst-dominated aquifer, such energetic mixing at the vent feature is expected, and would be facilitated by conduit and fractured flow. Radium isotope activities were utilized to estimate flow-path trajectories and to provide information on potential travel times between an onshore well and the spring. Using either ^{223}Ra and ^{224}Ra or ^{228}Ra, and qualifying this approach with several key assumptions, estimates of water mass travel times from an upper Floridan well in Crescent Beach to the submarine vent feature (distance = 4050 m) are in the order of $\sim 0.01–0.1$ m min^{-1}.

Keywords: Submarine ground water discharge; Radium isotopes; Carbonate aquifer; Northeastern Florida; Submarine spring

1. Introduction

Biogeochemical reactions that occur in estuaries or other river-dominated ocean mixing zones play a fundamental role in coastal ocean mass balance cal-

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0009-2541/01/$ - see front matter
PII: S0009-2541(01)00322-9

culations (Sholkovitz, 1977; Shiller and Boyle, 1991). In a recent series of conceptual papers, Moore (1996, 1999) contended that it is necessary to extend this reaction zone to include 'subterranean estuaries', a region at the land–sea margin where interstitial fluids, regardless of origin, are readily exchanged with coastal bottom water. Moore and others concluded that many of the well-known reactions and processes are quite similar for surface and subterranean estuaries, and that a vigorous subsurface flux could introduce significant concentrations of nutrients or other reactive constituents into the coastal ocean (Bokuniewicz, 1980; Johannes, 1980; Giblin and Gaines, 1990; Lapointe et al., 1990; Valiela et al., 1990; Reay et al., 1992; Simmons, 1992; Bugna et al., 1996; Cable et al., 1996a,b; Shaw et al., 1998; Corbett et al., 1999; Krest et al., 2000). By omitting such a subterranean component, one might significantly underestimate the overall delivery of constituents during their transport out to sea. Furthermore, accurate estimates of submarine ground water discharge are also critical for coastal water managers, who need to assess long-term aquifer yields and rates of saltwater intrusion in view of surging population increases along most coastlines (Cooper et al., 1964; Smith, 1988).

Submarine ground water discharge (SGD) is generally a widespread coastal feature that occurs wherever hydrogeologic gradients enable lateral and upward ground water transport (Johannes, 1980). There is an abundance of historic and recent evidence for global submarine ground water discharge (Warren, 1944; Zektzer et al., 1973), which for example, links SGD to past easily accessible potable water reserves for maritime activity, endemic biological communities (Kohout and Kolipinski, 1967) or even coastal water supply issues (Bush and Johnston, 1988). 'Leaky' land–sea margins where the flow of SGD is likely to be enhanced include:

1. Karstic coastlines, e.g. dissolution features and conduits can enhance ground water/surface water exchange (Back et al., 1979; Paull et al., 1990; Spechler, 1994; Swarzenski and Reich, 2000);
2. Modern and paleo-river channels, e.g. 'layer-cake' stratigraphy can form 'hydro-conduits' (Chapelle, 1997);
3. Geo-pressured aquifers, e.g. rapid deposition/accumulation of fine-grained sediments above a hydrologically productive unit can disperse interstitial water upward (Kohout, 1960; Lusczynski and Swarenski, 1966; Manheim, 1967; Kohout et al., 1976);
4. Geothermal aquifers, e.g. seawater intrusion may initiate conductance-driven cycling of water (Kohout, 1967);
5. Shorelines that are mountainous or have large tidal amplitudes (large hydraulic head gradients), and
6. Lagoons, e.g. heightened evaporation may hydraulically drive interstitial water upward (Simms, 1984; Martin et al., 2000).

This paper examines the point-source submarine discharge at Crescent Beach Spring, FL, where a significant flow of freshened ground water is released about 4 km from shore into the Atlantic Ocean through a well-defined dissolution/collapse feature.

2. Geologic framework

The marine carbonate Floridan is one of the world's most productive aquifer systems. Parts of South Carolina, Georgia, Alabama and all of Florida depend on this aquifer almost entirely as a reliable source for municipal, agricultural and industrial water (Parker et al., 1955). Calcite and dolomite dominate the mineralogy of the Floridan aquifer system. The Floridan aquifer system can be subdivided into two moderately high permeability aquifers, referred to as the Upper and Lower Floridan aquifers (Table 1). In northeastern Florida, water within this aquifer system can be artesian, depending on the presence and permeability of overlying strata (Stringfield, 1966; Leve, 1970; Johnston, 1983). A series of relatively impermeable Miocene and younger beds can confine the aquifer in this region. Groundwater is thus often under sufficient pressure to flow freely at land surface. A relatively large volume of water is discharged from the Floridan aquifer system in this manner through terrestrial springs, fractures and sinkholes (Stringfield, 1966; Rosenau et al., 1977), and it is expected that this upward flow is also

Table 1
Generalized hydrogeologic cross-section of northeastern Florida (adapted from Spechler, 1994)

System	Series	Stratigraphic Unit	Hydrogeologic Unit	thickness (m)	Lithology	Hydrologic properties
Quarternary	Holocene to Upper Miocene	Undifferentiated surficial deposits	Surficial aquifer system	6-36	Discontinuous sands, clays, shell, and limestone	Sands, shell, limestone and coquina deposits provide local ground water source
Tertiary	Miocene	Hawthorn Formation	Intermediate confining unit	30-150	Interbedded phosphatic sands, clays, limestone and dolomite	Limited permeability clays
	Eocene	Upper: Ocala Limestone	Floridan aquifer system: Upper Floridan aquifer	30-100	Massive fossiliferous chalky to granular marine limestone	Principal source of ground water
		Middle: Avon Park	Middle semi-confining unit	210-335	Alternating beds of granular and chalky limestone, dense dolomites	Low permeability limestone and dolomite
			Lower Floridan aquifer: Upper zone			Principal source of ground water
			Semiconfining unit			Low permeability limestone and dolomite
		Lower: Oldsmar Formation	Fernandina permeable zone	90-150		High permeability, salinity increases with depth
	Paleocene	Cedar Keys Formation	Sub-Floridan confining unit	about 150	Uppermost appearance of evaporites, dense limestones	Contains high salininy water, low permeability

maintained along the seaward side of the land/sea margin, possibly even out to the shelf break (Manheim, 1967).

A lowered potentiometric surface of the Upper Floridan aquifer currently observed in many parts of coastal northeastern Florida is thought to be due to increased coastal ground water withdrawals, as well as submarine discharge of artesian water (Stringfield, 1966; Leve, 1970; Spechler, 1994). Historic submarine discharge has been observed to occur off Beaufort, SC to Biscayne Bay, FL, as well as at many sites off the west coast of Florida (Rosenau et al., 1977; Cable et al., 1996a,b). Early reports described the occurrence of point source submarine springs offshore from St. Augustine, Eau Gallie and Cape Kennedy, FL (Stringfield, 1966). Additional submarine springs and vents are also likely to exist along the east coast of Florida.

In the Jacksonville/Fernandina Beach region, the continental shelf is about 110-km wide (Meisburger and Field, 1976), and a large volume of freshened, artesian ground water is known to exist beneath the Atlantic Ocean (Manheim, 1967; Manheim and Paull, 1981). In the mid-1960s, the on-shore freshwater head was believed to be sufficiently high to cause the outflow of artesian water at distal submarine outcrops (Manheim, 1967). Interstitial fluid analyses from a JOIDES drilling program confirmed the presence of a freshened plume of ground water beneath the shelf to a depth of ~900 m (Wait and Leve, 1967; Hathaway et al., 1979; Manheim and Paull, 1981). Ground water could thus migrate either upward or laterally through the overlying confining units to eventually discharge into Atlantic bottom water through submarine springs, sinks or fractures (Meisburger and Field, 1976). This is a favored mechanism to explain the discharge of submarine ground water at Crescent Beach Spring.

3. Crescent Beach Spring

3.1. Hydrogeology and geochemistry

Crescent Beach Spring (Lat 29°46.087N, Long 81°12.478W), located 4 km off the coast of Crescent Beach, FL (Fig. 1), produces a large, localized 'boil' that is visible on the surface of the Atlantic Ocean, in

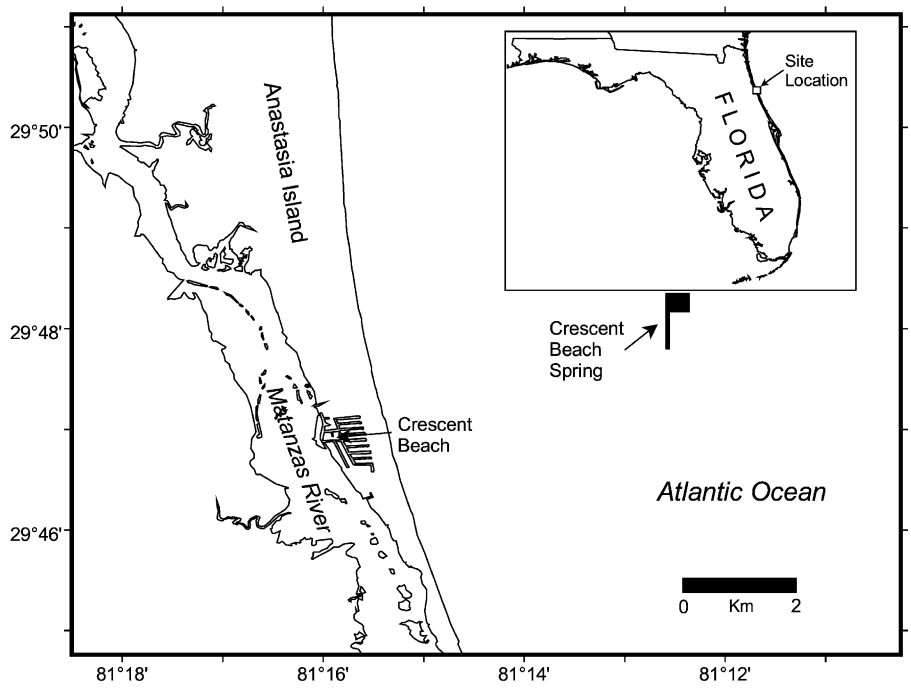

Fig. 1. Site location map of Crescent Beach Submarine Spring and surrounding area in northeastern Florida, USA.

spite of the 18-m water depth. Hydrogen sulfide can usually be detected by smell on the down-wind side of the discharge plume during calm sea conditions. Although Crescent Beach Spring must have evoked the interest of seamen and scientists for centuries, the US Coastal Survey conducted the first systematic study of the spring and the surrounding seafloor in 1875. Brooks (1961) later recreated a section of the original bathymetry surrounding Crescent Beach Spring, which was remarkably accurate compared with today's high resolution bathymetric instrumentation. The spring was revisited in 1923 by the US Coast and Geodetic Survey, and Stringfield and Cooper (1951) were the first to document the detailed hydrogeology and artesian nature of Crescent Beach Spring. Brooks (1961) presented a descriptive underwater account of the hydrogeology of the spring and surroundings; in this paper, the author also derived a first-order estimate for the spring discharge, $\sim 42.5\ m^3\ s^{-1}$, based on visual observations and variable density flow. Based on such a flow rate, Crescent Beach Spring could be considered a first-order magnitude spring ($Q > 2.8\ m^3\ s^{-1}$). The large discharge rate of this submarine spring is likely to produce an integrated ground water mass that cannot readily be isotopically or geochemically associated to only one hydrologic unit.

The likely source aquifer for Crescent Beach Spring is the Eocene Ocala Limestone or Avon Park Formation (Stringfield, 1966; Leve, 1970), which are two of the most productive formations within the Floridan aquifer system. From an idealized hydrogeological cross-section across Putnam and St. John's Counties, surficial waters recharge the Ocala Limestone through a complex network of lakes and sinkholes east of Gainesville, FL (Fig. 2). These sinkholes penetrate and interrupt the Hawthorn confining beds (Brooks, 1961), and facilitate the vertical transport of surface water to the aquifer. In northeastern Florida, the overlying clay-rich Miocene Hawthorn Group and younger formations serve as effective confining units for the artesian waters of the Ocala Limestone. The Hawthorn Group decreases in thickness along a north-to-south transect, and is $\sim$30-m thick along the coast at Crescent Beach. At the Crescent Beach Spring vent, the more soluble

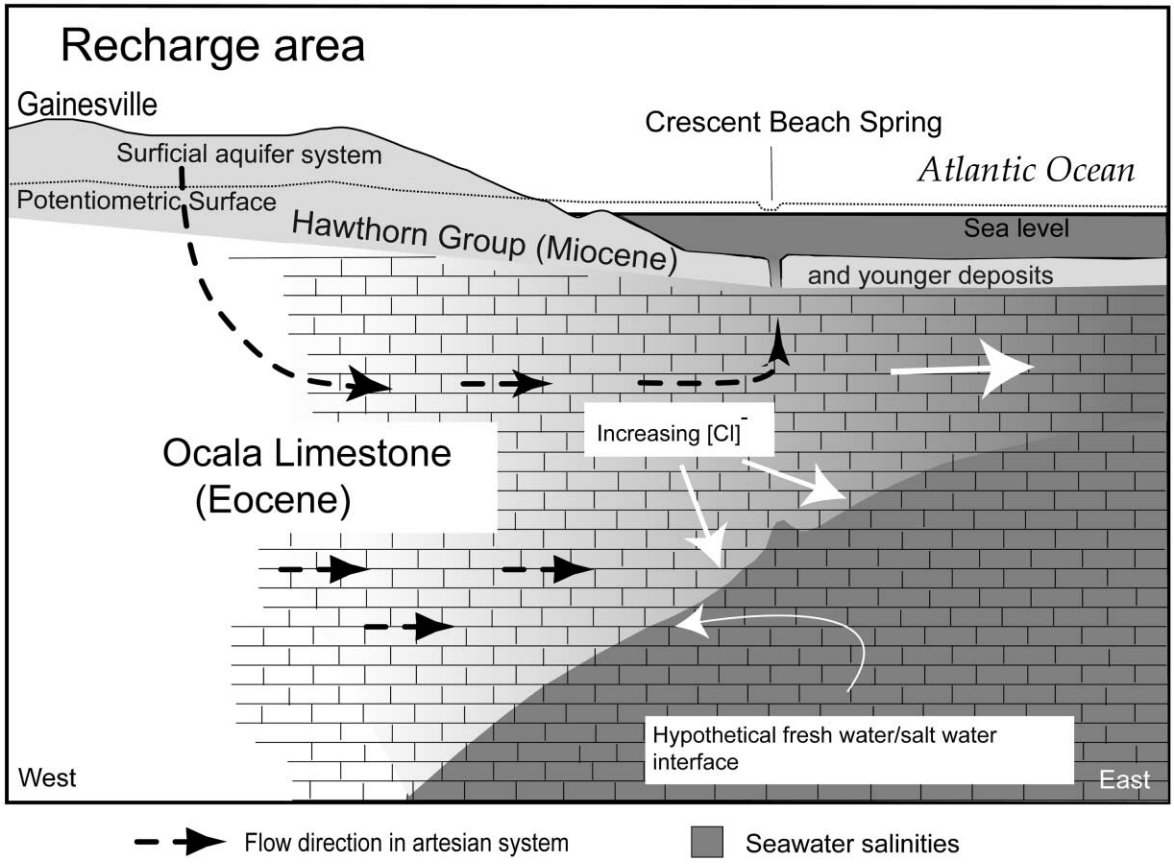

Fig. 2. West-to-east cross-section of the artesian coastal aquifer system in the vicinity of Crescent Beach, FL, USA. Idealized Ghyben–Herzberg contact between freshwater and seawater is shown; shaded area represents approximate extent of saltwater intrusion. (Modified from Stringfield and Cooper, 1951).

Hawthorn clays have been eroded away entirely, enabling the Ocala Limestone to be in direct contact with overlying seawater. As indicated by the lowered potentiometric surface along much of the coastline (Fig. 3), the submarine discharge of artesian water is probably not confined to Crescent Beach Spring. Instead, a large discharge area may occur anywhere along the inner continental slope, wherever the confining units are thin or absent.

A detailed high-resolution seismic record (Fig. 4) at Crescent Beach Spring reveals a very well-defined vent feature that appears to have been developed and maintained from sustained submarine discharge of artesian water (Kindinger et al., 1999). The upper extent of the Crescent Beach Spring vent feature lies at a water depth of approximately 18 m; the deepest point of the vent trough is at a depth of ~38 m. The areal extent of the bottom trough has a diameter of ~25 m, and one steep-walled throat opening was observed while scuba diving.

The seismic record also reveals multiple large collapse features directly adjacent to the Crescent Beach Spring vent, as indicated by the presence of a series of fractures. Although little evidence for direct faulting was reported along this region of the Atlantic inner continental shelf (Meisburger and Field, 1976), seismic data suggest small scale fracturing surrounding the spring vent.

The geochemical signature of submarine ground water may be quite distinct from coastal bottom water (Glazovskiy et al., 1973; Zektzer et al., 1973). Chemical reactions due to the mixing of these two

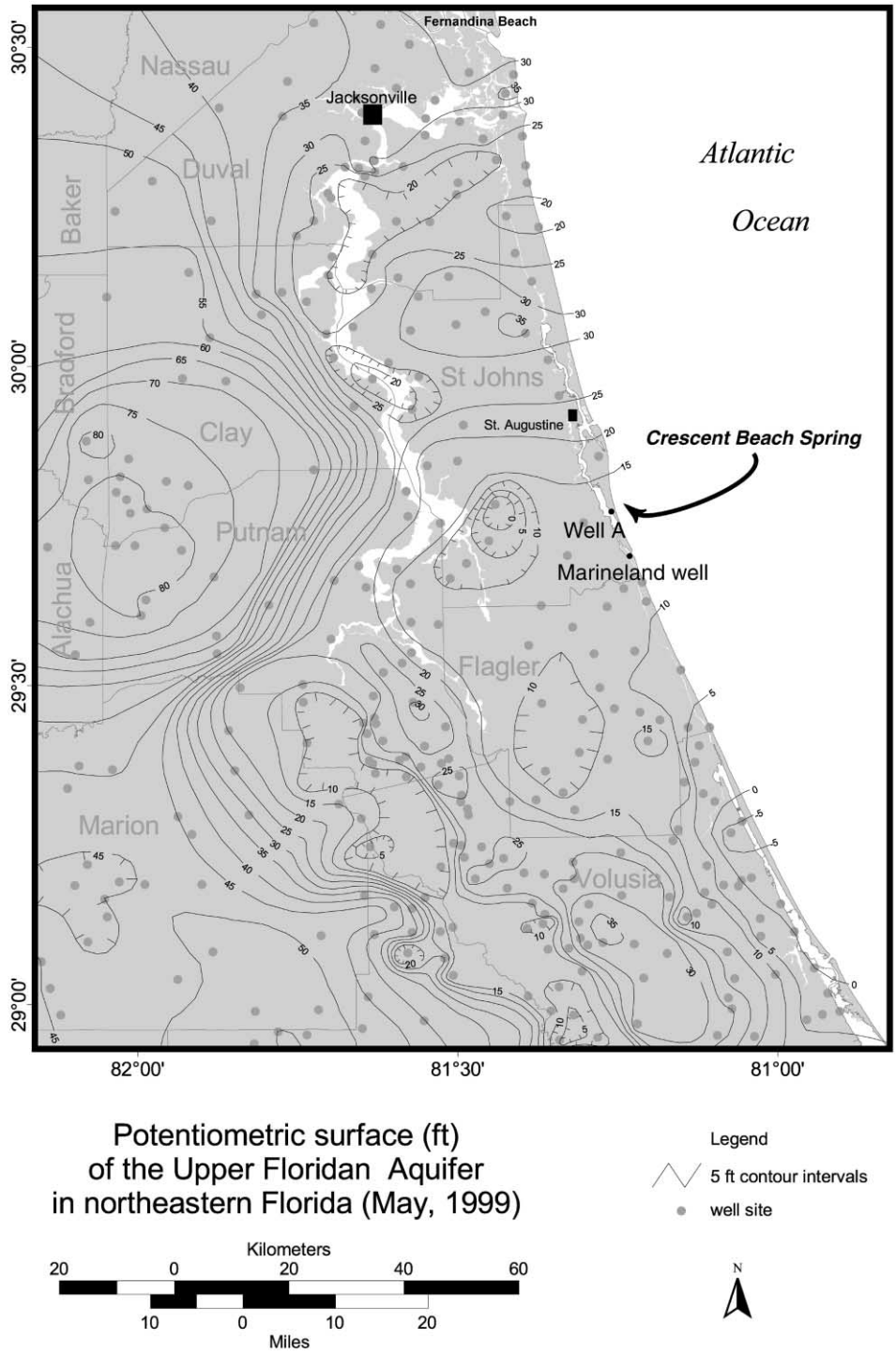

Fig. 3. Potentiometric surface map of the Upper Floridan aquifer in northeastern Florida, USA (May 1999). (Adapted from Bradner and Knowles, 1999).

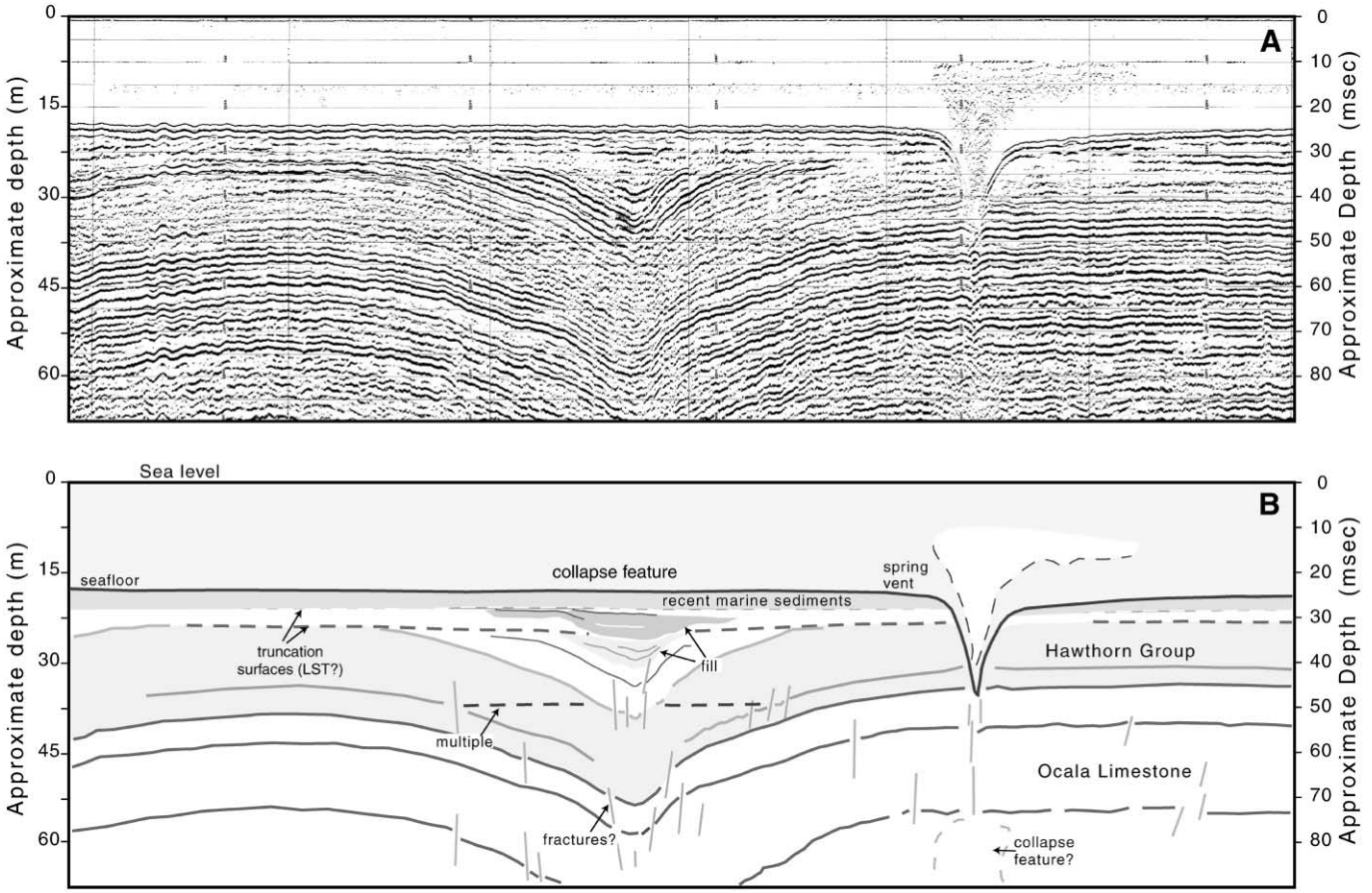

Fig. 4. High-resolution seismic profile (A) of Crescent Beach Spring and surrounding area. The spring discharge is visible in the seismic image. Interpretation (B) depicting the underlying geologic framework.

water masses and their associated particles can be very similar to those that occur in a more classic estuarine setting (Sholkovitz, 1977; Moore, 1999). Most submarine ground water discharge (SGD) occurs as diffuse upward seepage, and identifying sites or quantifying rates of SGD across the sediment–water interface can prove to be difficult, simply due to the enormous dilution effect as SGD mixes into seawater (Moore, 1996; Moore and Shaw, 1998; Shaw et al., 1998). In sharp contrast to diffuse seepage, well-defined submarine springs can occur in karstic coastal environments, and are direct point sources of ground water to coastal bottom waters.

Ocala Limestone ground water consists of relatively rich Ca–HCO_3 water that generally tends to increase in hardness from the area of recharge eastwards towards the coast (Stringfield, 1966). In this region, ground water chloride concentrations increase from north to south. At Crescent Beach and surroundings, the chloride concentrations of Upper Floridan ground water have historically ranged from about 100 to 112 mM (Warren, 1944; Leve, 1970; Spechler, 1994).

4. Field and analytical methods

The field effort at Crescent Beach Spring was conducted during 27–28 April 1999. Differential GPS-interfaced seismic profiling was first used to locate and map the deepest vent opening. At this site, a guide buoy was deployed, from which divers were able to locate the most active vent feature. A computer interfaced CTD hydrographic profiler was deployed to record the water column structure. Superimposed on the profiles of water column temperature, salinity and light transmission are discrete values taken from the spring water (Fig. 5). To obtain uncontaminated water samples from Crescent Beach Spring, divers drove a 1-m-long, 3.8-cm-diameter fine-mesh well point into shell hash and coarse sand present in the spring opening (maximum water depth = 38 m). A single nylon tube was attached to the well point and connected to a shipboard peristaltic pump. Salinity, temperature, conductivity, pH and dissolved oxygen of the spring discharge were continuously monitored during sampling to eliminate the possibility of contamination with ambient seawater. In an effort to tie submarine discharge at Crescent Beach Spring to onshore hydrologic characteristics, ground water wells close to the town of Crescent Beach (Well A and Marineland well) were also sampled.

Groundwater, spring and seawater were analyzed for a suite of constituents that included major solutes (Cl, Na, SO_4, Mg, Ca, K, Sr, F, SiO_2), nutrients [NO_2–N, PO_4–P, NO_2–N + NO_3–N, NH_3–N, soluble reactive phosphorus (SRP), total P and N], select trace elements (Mn, Mo, Ba, U, V, Fe), submarine ground water tracers (CH_4 and ^{222}Rn), a suite of four naturally occurring radium isotopes ($^{223,224,226,228}Ra$) and ^{228}Th. Major solute and nutrient analyses were conducted at the USGS/WRD Quality of Water Service Unit lab in Ocala, FL, using standard USGS sampling protocols (i.e. Spechler, 1994 and references therein). Trace element ICP-MS analyses were conducted on 0.4-μm-filtered waters (Shiller and Boyle, 1991). The analyses were performed using a sector field ICP-MS (Finnigan MAT Element 2) at the University of Southern Mississippi, as per methods of Roduskin and Ruth (1997). Samples were first diluted 10-fold with 0.1 M HNO_3 and analyzed versus aqueous standards, similarly diluted with 0.1 M HNO_3. Each of the six elements was determined in triplicate. Methane samples were collected in glass BOD bottles and stored on ice for subsequent analyses. Methane concentrations were determined using a gas chromatograph with a flame ionization detector (Corbett et al., 1999). The limit of detection for CH_4 was routinely estimated at 1.0 nM. Radon gas was extracted, transferred and quantified using methods described in Corbett et al. (1999). After initial Rn counting, the samples were sealed and stored for at least 1 week to allow ^{222}Rn in-growth from ^{226}Ra. Excess or unsupported ^{222}Rn was reported as the difference between total ^{222}Rn minus the supported (i.e. ^{226}Ra) activity, and decay corrected to the sampling date and time.

Radium and thorium isotopes were quantitatively extracted from all water samples onto MnO_2-impregnated acrylic fiber. The fibers were subsequently rinsed in distilled, de-ionized water to remove sea salts, partially air-dried and then placed into an He gas recirculating line. Scintillation signals were routed via a photo-multiplier tube base to a delayed coincidence computer program that time-discrim-

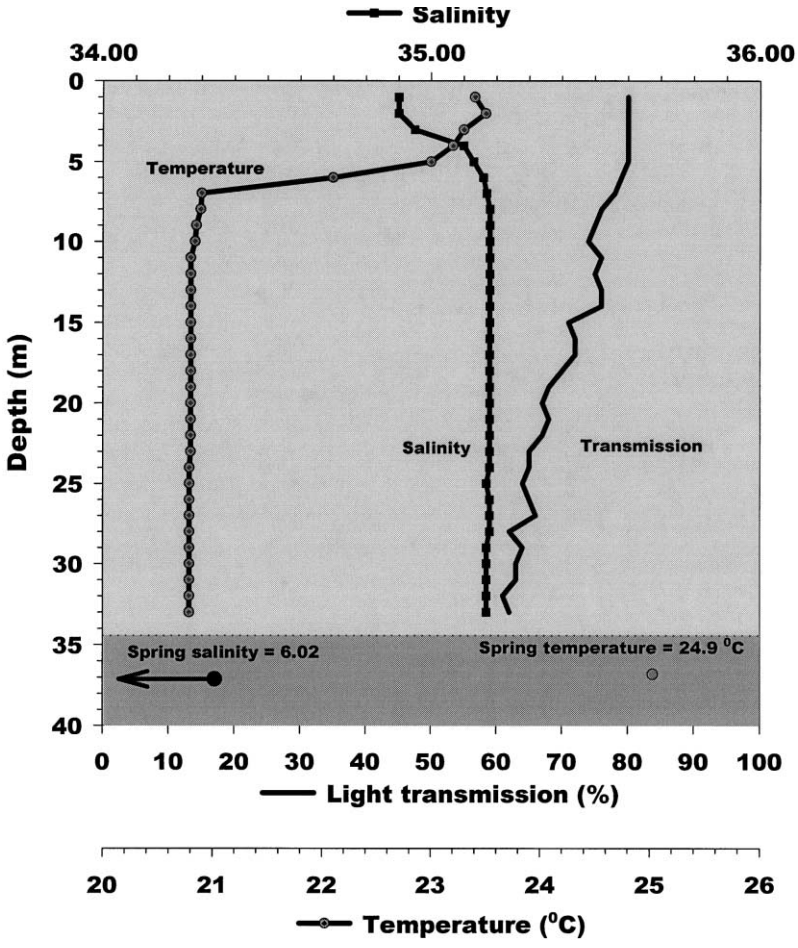

Fig. 5. Water column temperature, conductivity and light transmissivity profiles sampled from the R/V Gilbert by CTD above the spring vent (04-28-99). The thermocline occurred at a depth of approximately 6–7 m. The submarine spring water values (measured from the flow-through system) are also included for comparison-note the scale offset for the spring salinity value (6.02).

inate alpha decays of ^{219}Rn and ^{220}Rn produced by the radioactive decay of ^{223}Ra and ^{224}Ra (Moore and Arnold, 1996). The Mn fibers were subsequently re-analyzed after about 4–6 weeks to allow for the initial excess ^{224}Ra to equilibrate with ^{228}Th, which was also quantitatively adsorbed to the fiber. Background activities in each of the two delayed coincidence systems were monitored after every sample run, and were typically in the order of 0.015 and 0.150 counts per minute (cpm) for ^{223}Ra and ^{224}Ra, respectively. Isotopic standards derived from ^{227}Ac and ^{232}Th were run periodically, as well as after each batch sample analysis (approximately every 12th sample). Radium-226 activities were measured on a separate water sample either by Rn emanation or by gamma spectrometry (Moore, 1997). Uncertainties in Ra isotope activities correspond to 1σ counting errors.

5. Results and discussion

The major solute composition of spring water was compared to ground water collected from an onshore well in Crescent Beach, as well as to the composition of average seawater (Table 2). There is an obvious similarity between the major solutes in well water and spring water. In contrast, concentrations of the

Table 2
Composition of major solutes (mM) in an onshore well, two spring vent samples and 'average' seawater

Major solutes	Well A[a] (mM)	CBS[b] (mM)	CBS[c] (mM)	Seawater[d] (mM)
Chloride	101.54	96.75	102.39	545.79
Sodium	87.00	87.00	88.74	468.03
Sulfate	8.54	7.77	8.50	28.21
Magnesium	10.29	8.72	10.37	53.08
Calcium	7.49	6.49	7.39	10.25
Potassium	1.53	1.07	1.64	10.21
Strontium	0.11	0.09	0.10	0.09
Fluoride	0.05	n/a	0.04	0.07
Silica	0.71	n/a	0.32	0.18
Temperature (°C)	22.00	24.90	24.91	n/a
pH (at 25 °C)	7.39	7.45	7.13	n/a

[a]Well A at Crescent Beach. This Upper Floridan well is located in Crescent Beach, FL. (see Fig 3 for location).
[b]Crescent Beach Spring vent water.
[c]Crescent Beach Spring vent water.
[d]'Average' surface seawater composition (Drever, 1988).

four most abundant ionic species in seawater (chloride, sodium, magnesium and sulfate) are enriched by at least a factor of three to four over spring water values (Drever, 1988). These results provide convincing evidence that the discharged water at Crescent Beach Spring is not newly recycled seawater, but is geochemically similar to artesian ground water ubiquitously present along the coast at Crescent Beach. Therefore, the artesian flow regime observed along coastal northeastern Florida does appear to extend onto the continental shelf (Fig. 2), as envisioned much earlier by Stringfield (1966) and Manheim (1967). The source aquifer for the spring water is not likely to be confined to a single hydrogeologic formation, but is rather the result of a complicated, karst-influenced mixing regime that includes both younger and older ground water.

Select trace constituents (Table 3) from spring water and ambient seawater suggest some interesting deviations from 'average' seawater values (Drever, 1988). It is recognized that certain trace element concentrations reported in Drever (1988) have been revised (e.g. Donat and Bruland, 1995), however, general trends in elemental seawater concentrations remain similar. Manganese concentrations were in an order of magnitude greater in ambient seawater at Crescent Beach Spring (31.0 nM) than in 'average' seawater (3.6 nM). These concentrations coincide with elevated Mn levels (90.9 nM) observed in the vent spring water. Similarly, the concentration of Fe in the vent water was also enriched relative to ambient seawater. The behavior of these two redox couples conforms to a predictable oxidation state transformation in the reducing ground waters from the more particle reactive +III(Fe) and +IV(Mn) to the reduced, more soluble +II states. Barium was highly enriched in the vent water (300.7 nM) relative to ambient (55.3 nM) and 'average' (72.8 nM) seawater. The depletion of Ba in surface seawater is likely to occur as a result of the biologically mediated precipitation of barite ($BaSO_4$). Very little dissolved U (0.1 nM) was present in the reducing vent waters compared to ambient seawater (18.4 nM). It is interesting to note that in ambient seawater above Crescent Beach Spring, uranium appears to be somewhat enriched over the stable seawater value (13.9 nM). This enrichment might be caused by sorption onto a carrier phase (i.e. MnO_2/FeOOH) or other redox-initiated mechanisms that can transfer tetravalent U bound to particles into the dissolved phase. Each of the measured redox-sensitive elements (U, Va and Mo) was significantly depleted in the reducing vent samples.

Table 4 shows a comparison of nutrient data from Crescent Beach Spring, ground water and ambient seawater. At all three sites, oxidized, dissolved species of nitrogen were either undetectable or present only at very low concentrations. Most (66–95%)

Table 3
A comparison of select trace constituents (nM) in 'average' seawater, ambient seawater and submarine spring water, as measured by sector field ICP-MS

Trace element	CBS[a]	CBS seawater[b]	Seawater[c]
Mn	90.9	31.0	3.6
Mo	9.5	218.7	104.2
Ba	300.7	55.3	72.8
U	0.1	18.4	13.9
V	21.9	47.6	39.3
Fe	64.9	3.1	35.8

These values represent an average of triplicate analyses.
[a]Crescent Beach Spring vent water.
[b]Surface ambient seawater at Crescent Beach Spring.
[c]Composition of select trace constituents in 'average' seawater (Drever, 1988).

Table 4
Nutrient concentrations (μM) in spring vent water, well water and ambient seawater

Sample	NO_2–N	NO_2–N + NO_3–N	NH_3–N	Total N	SRP[a]	Total P
Marineland well[b]	< 0.71	< 1.42	21.42	24.98	0.32	0.97
CBS[c]	< 0.71	< 1.42	21.42	22.85	1.29	1.29
CBS seawater[d]	0.71	< 1.42	2.14	< 14.28	2.58	1.94

[a] SRP = Soluble rective phosphorus.
[b] Marineland well (see Fig. 3 for location).
[c] Crescent Beach Spring water.
[d] Surface ambient seawater at Crescent Beach Spring.

of the total nitrogen existed as NH_3–N. Seawater NH_3 concentrations were in an order of magnitude lower than well and spring water concentrations, indicating possible ground water NH_3 uptake by bacteria and/or algae. Although soluble reactive phosphorus accounted for varying percentages of total P, the variability may simply be due to detection limit artifacts.

Table 5 presents parent-corrected ^{222}Rn and methane data from an onshore well at Marineland, from the actual spring vent, and from ambient surface seawater within the discharge plume. Both radon-222 and methane have been used successfully in Florida as tracers for submarine ground water discharge (Fanning et al., 1981; Corbett et al., 1999; Cable et al., 1996a,b). At Crescent Beach Spring, both tracers are enriched several fold in spring water over ground water. However, the concentrations of CH_4 in spring water and ground water are considerably lower than what has been observed from a series of Upper Floridan wells (average value of 86,000 nM) and springs (1600 nM) in northern Florida (Bugna et al., 1996). Although great care was taken to avoid loss of CH_4, it is not impossible that a small fraction of methane could have escaped during sample collection/processing. Increased methane production at Crescent Beach Spring relative to onshore ground water values may be due to an increased abundance of marine microorganisms present at the brackish water–saltwater interface of the vent opening.

Table 5
Parent (^{226}Ra) corrected ^{222}Rn activities (dpm l^{-1}) (disintegrations per minute) and methane concentrations (nM) in spring vent water, well water and ambient seawater

Sample	Excess Rn[a] (dpm l^{-1})	^{226}Ra[b] (dpm l^{-1})	Methane[c] (nM)
Marineland well	463.0	14.8	45
CBS[d]	1174.9	2.6	232
CBS seawater[e]	1.7	0.2	14

[a] Analyzed by alpha scintillation (R. Corbett, FSU).
[b] Analyzed by gamma spectroscopy (W.S. Moore); see Table 6 for additional information.
[c] Analyzed by FID gas chromatograph (R. Corbett, FSU).
[d] Crescent Beach Spring vent water.
[e] Surface ambient seawater at Crescent Beach Spring.

Analogous to CH_4, ^{222}Rn ($t_{1/2} = 3.8$ days) holds potential as a tracer of submarine ground water discharge (Cable et al., 1996a,b; Corbett et al., 1999). The observed activity of ^{222}Rn (463 dpm l^{-1}) at Marineland well is lower than an average of ~60 ground water samples from northern Florida (2100 dpm l^{-1}; Bugna et al., 1996), and similar to ^{222}Rn activities reported from a series of 73 shallow (12–22 m) wells surrounding Florida Bay (mean ~400 dpm l^{-1}; Corbett et al., 1999). In contrast, the activity of ^{222}Rn from the spring vent water was approximately 1175 dpm l^{-1}, and indicates potential regeneration of radon from the decay of ^{226}Ra during transport. This pulse of submarine ^{222}Rn is rapidly diluted into ambient seawater yielding an activity in the order of only 1–2 dpm l^{-1}, well above the supported activity due to ^{226}Ra in the water. This thousand-fold concentration difference makes radon a powerful tracer of submarine fluid advection.

Four naturally occurring radium isotopes may also provide useful information on exchange processes across the marine sediment–water interface (cf. Moore, 1996). The activities of ^{223,224,226,228}Ra in spring, well water and ambient seawater are listed in Table 6. The two shallow Upper Floridan well sam-

Table 6
Radium and ^{228}Th activities (dpm 100 l^{-1}) in well waters, vent water and ambient seawater

	Depth (m)	Salinity	^{223}Ra	^{224}Ra	^{226}Ra	^{228}Ra	^{228}Th
Well A	n/a	4.10	628.2	908.4	285.3	80.6	12.2
Marineland well	n/a	3.89	374.5	134.2	1480.1	154.3	11.0
Water column[a] (04–99); average $n = 3$	Surface	35.08	7.9	3.8	23.1	36.7	1.9
CTD cast	5	35.13	5.6	2.3	18.7	37.5	2.3
CTD cast	18	35.17	7.3	1.8	19.9	36.6	2.0
CBS seawater[b]	Surface	34.90	8.1	3.7	22.8	37.6	1.7
CBS[c]	n/a	6.02	69.1	8.8	264.4	31.4	2.3

n/a = Not applicable.
[a] Collected and analyzed by W.S. Moore (USC).
[b] Surface ambient seawater at Crescent Beach Spring.
[c] Crescent Beach Spring vent water.

ples illustrate the geologically controlled variability in ground water radium activities. The activities of the pair of short-lived Ra isotopes (^{223}Ra, $t_{1/2} = 11.3$ days and ^{224}Ra, $t_{1/2} = 3.8$ days) were depleted significantly in the Marineland well sample relative to Well A activities, yet the long-lived Ra pair (^{228}Ra, $t_{1/2} = 5.7$ years and ^{226}Ra, $t_{1/2} = 1600$ years) were enriched at least by a factor of ~ 2 in the same sample set. Such disequilibria may reflect localized variability in the subsurface geologic framework, but simple seasonal variations cannot be excluded. Crescent Beach Spring vent water has approximately the same activity of ^{226}Ra as Well A. These activities suggest that the onshore ground water in the most direct flow path of Crescent Beach Spring water may not have had enough time during transport to allow this long-lived radium isotope to decay (Fig. 6). Some additional evidence may further support this scenario. The shortest-lived radium isotope (^{224}Ra) was relatively low (8 dpm 100 l^{-1}) in the vent water, yet was present at over 900 dpm 100 l^{-1} in Well A. In this scenario of artesian easterly flow, it is possible that this isotope may have decayed away entirely during transport out to the spring, if one can exclude additional sources for ^{224}Ra. This would imply that the transport time is at least about five times the half-life (i.e. 20 days) from Well A to the spring vent.

Of course, several key assumptions are necessary to validate this estimate. The primary source of

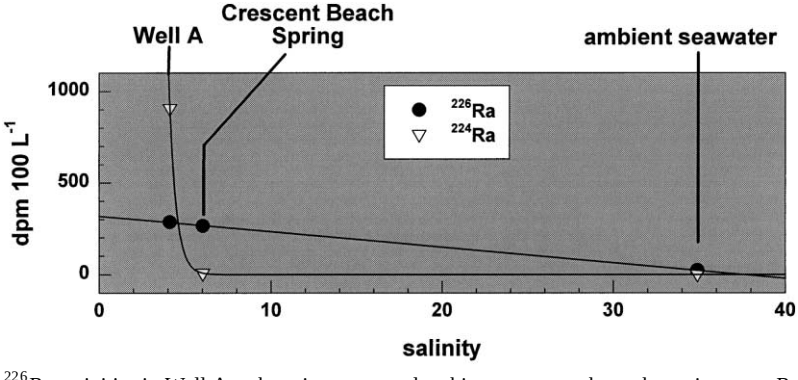

Fig. 6. Radium-224 and ^{226}Ra activities in Well A, submarine water and ambient seawater above the spring vent. Radium-224 is depleted in spring water relative to activities in Well A. The activity of ^{226}Ra was similar in both Well A samples and spring water.

^{224}Ra must be restricted to onshore ground water representative of Well A water. This may hold true as the well water is ~112 times enriched in ^{224}Ra relative to spring water. Any additional input of ^{224}Ra that may have occurred during transport must be negligible. Again, this may hold true as the activity of spring water is so depleted in ^{224}Ra. Cation exchange reactions are also less likely to be a source for newly produced Ra as the ground water and vent samples have similar salinities. Crescent Beach Spring water must also consist of only one distinct water mass, rather than a mixture of various subsurface waters. This last assumption is difficult to accept without additional tracer data (e.g. CFCs, $^{3}H/^{3}He$, SF_6), and even counter-intuitive in such a karst-dominated ground water flow regime. It is, however, unlikely that short-lived radium isotopes would be able to uniquely distinguish older from younger ground water. Lastly, the surrounding seawater at Crescent Beach Spring cannot be an additional source of ^{224}Ra because ambient seawater above the spring vent contains only about 3 dpm 100 l^{-1}.

By incorporating these assumptions and utilizing either the two short-lived ^{223}Ra and ^{224}Ra isotopes or ^{228}Ra, one can approximate a water mass travel time from an Upper Floridan well in Crescent Beach to the submarine vent feature (distance = 4050 m) to be in the order of 0.01–0.1 m min^{-1}. Such flow rates are greatest at the discharge site and decrease rapidly with distance away from the vent opening. It can be expected, however, that the assumptions of a single Ra source and a single-aged ground water mass are somewhat tenuous in this carbonate aquifer system, and that the travel time estimates, therefore, are still only a rough approximation. Despite the complex hydrogeologic regime of Crescent Beach Spring, development of radium isotope systematics to study submarine ground water discharge hold promise as an independent approach.

The naturally occurring isotopes of strontium may provide additional information on potential flow paths or mixing regimes of various ground water masses. The unique strength of strontium isotopes as a ground water tracer stems from the characteristic that removal of Sr from ground water as a result of mineral precipitation or cation exchange does not change the isotopic signature of dissolved Sr. Although ^{87}Sr is produced by the decay of ^{87}Rb, the decay process is so slow ($t_{1/2} \sim 4.8 \times 10^{10}$ year) that the $^{87}Sr/^{86}Sr$ ratio of Sr sources can be considered essentially stable (McNutt, 2000). Whereas stable water isotopes, such as hydrogen and oxygen, can be affected by in situ mineral precipitation, and can obscure the accurate determination of flow paths or mixing regimes, Sr isotopes are not affected by loss from solution.

The isotopic composition of $^{87}Sr/^{86}Sr$ is 0.70906 $\pm$ 0.00003 in the oceans, and ranges from 0.70775 to 0.70790 in Upper Floridan aquifer host rock (McNutt, 2000). Strontium isotope data from Crescent Beach Spring water ($^{87}Sr/^{86}Sr = 0.70798$) are similar to both Upper Floridan aquifer ($^{87}Sr/^{86}Sr =$ 0.708909–0.709027; Martin et al., 2000) as well as Lower Oldsmar/Cedar Keys ground water (0.70798–0.70830; G. Phelps, USGS, written communication, 2000). Such Sr isotopic ratios suggest dynamic water exchange between the various hydrogeologic units of Floridan aquifer system. It should be noted that both large production wells, as well as rapidly discharging springs have a tendency to integrate ground water from various hydrologic units into one heterogeneous water mass.

The mechanism for submarine discharge at Crescent Beach Spring is quite different from the geothermally regulated, saline Mud Holes Springs located on Florida's west coast, about 45 km south–southwest from Ft. Myers (Fanning et al., 1981, 1982). At these springs, Kohout (1965) proposed a geothermally driven saltwater flow model to explain submarine discharge of the brine waters. Fanning et al. (1981) measured a suite of radium isotope activities from several vents at Mud Hole Springs. This submarine springs system occurs close to the axial center of the Florida Platform, is geothermally influenced and contained very high ^{226}Ra (up to 11,000 dpm 100 l^{-1}) and ^{222}Rn activities (up to 96,000 dpm 100 l^{-1}). These authors calculated that the regional submarine flux of radium at Mud Hole Springs might be large enough to be a significant source to the Gulf of Mexico, even when compared to the fluvial delivery of radium from the Mississippi River. The discharge of heated seawater at Mud Hole Springs not only released high levels of Ra and Rn into the Gulf of Mexico, but also affected the delivery and composition of many reactive constituents

during diagenesis within the strata of the Florida Platform. In contrast to the regionally scaled submarine features at Mud Hole Springs, Crescent Beach Spring appears to be restricted to one dominant vent structure. The obvious geologic control on the discharge and geochemistry of these two contrasting submarine spring systems thus yield very different chemical signatures in the vent waters.

6. Summary

Our examinations of Crescent Beach Spring have shown that the flow of submarine water is confined principally to one large solution or collapse feature. Seismic reflection data illustrate the presence of additional large collapse features and fractures adjacent to Crescent Beach Spring. At the discharge vent, the Miocene and younger confining unit has been entirely eroded away, enabling direct hydrologic communication of Eocene-aged ground water with Atlantic Ocean bottom water.

The salinity of the vent water (6.02) was consistently about 17% of open ocean values. Strontium isotope ratios confirm that the source of vent water originates from the Floridan aquifer system; however, it is not possible to identify one single hydrologic unit. While there appears to be extensive mixing of Eocene-aged waters, it is unlikely that there is much mixing of Upper Floridan water with the surficial aquifer system. Geochemically, the reducing submarine spring water appears to be analogous to onshore ground water that is in the most direct path of the generalized west to east flow regime. All water samples had very low concentrations of oxidized dissolved nitrogen species and most of the total nitrogen existed as ammonia–N. The redox-sensitive elements U, Va and Mo were present at low concentrations in the reducing vent waters. Radon-222 was enriched three orders of magnitude in the vent water relative to ambient seawater above the spring. Similarly, CH_4 was also enriched $\sim$16-fold in the vent waters over ambient seawater. Radium activities were highest in the well water samples, and were utilized to provide information on a first-order estimate of travel times from an onshore well out to the spring vent (0.01–0.1 m min^{-1}).

Collectively, these tracers of submarine ground water provide useful information to identify potential submarine spring water sources and to evaluate the contribution and potential effect of discharged submarine ground water into coastal bottom waters.

Acknowledgements

We thank B. Burnett, A. Shiller and R. Corbett for their analytical assistance, the captain and crew of the R/V Gilbert for help at sea, and Jim Flocks and Don Hickey for help in collecting the mysterious submarine spring samples. Use of brand names in this paper is for identification purposes only and does not constitute endorsement by the USGS. This paper benefited from careful reviews by J. Brock, T. Edgar, S. Fitzgerald and an anonymous reviewer. Partial funding for this project was provided by the Saint John's River Water Management District (SJRWMD).

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