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Progressive dolomitization of Florida limestone recorded by alkaline earth element concentrations in saline, geothermal, submarine springs

Johan Schijf^{1,2} and Robert H. Byrne¹

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[1] Studies in the late 1970s revealed that the effluents of saline, geothermal, submarine springs on the West Florida Shelf have compositions nearly identical to seawater, except for distinct Ca enrichments and Mg depletions, probably resulting from dolomitization. During annual visits between 1996 and 2003 we collected high-purity effluents from four submarine springs and from Warm Mineral Springs (WMS), which is located on land. Filtered effluents were analyzed for major ions and for Sr and Ba. These analyses confirm the seawater-like composition of the effluents as well as the Ca enrichment and Mg depletion. The alkaline earth elements Sr and Ba, like Ca and Ra, are significantly enriched in the effluents compared to ambient seawater, by average factors of 1.6 and 3.8, respectively (about 9 and 12 for WMS). The Mg depletion, and the Sr and Ba enrichments, while invariant over the 7-year sampling period, increase gradually from south to north, consistent with progressive dolomitization of limestone along the purported convective flow path of the warm seawater. The Ca enrichment shows no obvious trend because, besides dolomitization, gypsum dissolution is an independent source of Ca. A simple mass balance indicates that the Ca excess is fully accounted for by these two processes in all four submarine springs. This is not the case for WMS, where a residual Ca excess points to a third source of Ca, presumably limestone dissolution that occurs upon mixing of the modified seawater with fresh groundwater from the Floridan Aquifer System.

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1. Introduction

[2] Dolomitization is a process of recrystallization whereby ideally half of the Ca in CaCO_3 (calcium carbonate) is stoichiometrically replaced with Mg to form $\text{CaMg}(\text{CO}_3)_2$ (dolomite). Full understanding of this process has been hampered by persistently unsuccessful attempts to obtain a pure, crystalline precipitate in the laboratory under relevant conditions [Hsu, 1963; Land, 1998], leading to controversy about the solubility and other thermodynamic properties of dolomite. Nonetheless, it has often been confidently stated that seawater, although undersaturated with respect to different forms of calcium carbonate at great depths [Plath *et al.*, 1980; Mucci, 1983], is strongly supersaturated with respect to dolomite throughout the oceans. The fact that dolomite, while abundant in the geological record of ancient carbonate rocks, is a rare mineral in modern marine sediments, therefore seems particularly puzzling. This ‘dolomite problem’ has defied a satisfactory explanation for decades [Morse and Mackenzie, 1990; Purser *et al.*, 1994].

[3] Perfect dolomite (having an equal number of Ca and Mg ions and sometimes ambiguously referred to as ‘stoichiometric’ dolomite) is a highly ordered mineral consisting of sheets of carbonate ions, interlayered with sheets alternately made up entirely of Ca or Mg ions. Such a structure does not readily assemble. Hence the formation of dolomite is, in general, kinetically hindered under circumstances that are otherwise very conducive to its stability. The discovery and detailed study of unusual locations where substantial dolomitization appears to be ongoing has prompted the realization that certain special conditions are capable of lowering the kinetic barrier to nucleation. A number of contesting dolomitization models have been proposed that invoke these special conditions, including among others:

[4] 1. Sulfate depletion due to bacterial sulfate reduction [Vasconcelos *et al.*, 1995; van Lith *et al.*, 2002]. The exact mechanism is not altogether understood, but is thought to involve an intricate interplay of sulfate removal, alkalinity production, and ammonium production (promoting release of Mg adsorbed on silica) in the absence of silica diagenesis [Baker and Kastner, 1981].

[5] 2. High Mg/Ca molar ratios. Values of 5 or more may be necessary to make dolomite precipitate from waters with $S \geq 35$ [Folk and Land, 1975]. In hypersaline, intertidal basins called sabkhas, Ca removal by evaporative gypsum precipitation can raise Mg/Ca ratios to extreme levels.

[6] 3. Mixing of seawater and freshwater, especially in aquifers. Even when both end members are saturated with

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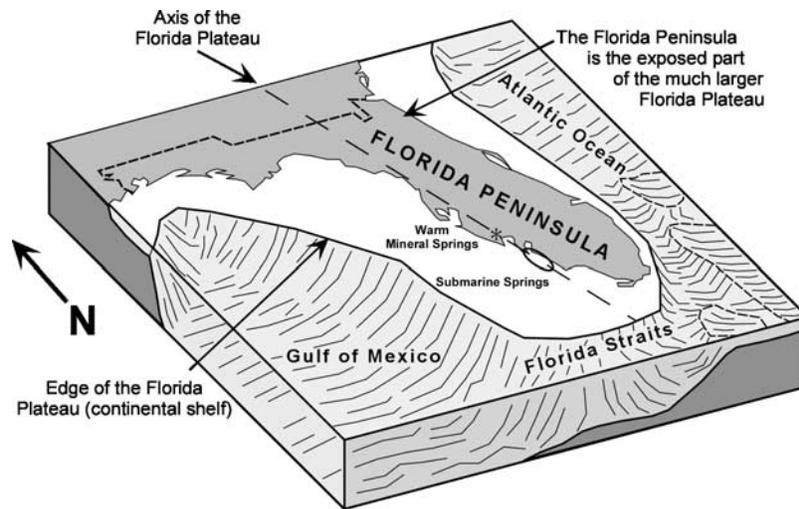


Figure 1. Schematic topographical map of the Florida Plateau. Exposed parts (gray) form the Florida Peninsula while submerged parts (white) form the continental shelf. Light gray, hatched areas are the abyssal plains of the Gulf of Mexico and Atlantic Ocean, connected by the Florida Straits. Saline, geothermal springs are found along the axis of the Florida Plateau, approximately indicated by the long-dashed line. Warm Mineral Springs (asterisk) is located on land, north of where the axis intersects the Florida coast. The area of submarine springs (enlarged in Figure 2) is circled with an ellipse. The short-dashed line is the state of Florida border.

respect to calcite, the resulting mixture may be undersaturated with respect to calcite and simultaneously supersaturated with respect to dolomite [Badiozamani, 1973].

[7] 4. Elevated temperatures, as found in hydrothermal systems [Rosenberg and Holland, 1964].

[8] 5. pH fluctuations, as may be induced by diel photosynthesis/respiration cycles [Deelman, 1999].

[9] Despite the initial promise of these models, several of which have been challenged on various grounds, most have failed to adequately explain the near-perfect stoichiometry, high crystallinity, and vast extent of ancient dolomite deposits. As a rule, when the kinetic barrier to nucleation is lowered and dolomite precipitation is accelerated, the typical product is a Ca-rich, poorly ordered ‘protodolomite’ [Folk and Land, 1975]. Furthermore, the models do not consider the necessary supply of Mg in a truly quantitative sense and can only account for dolomitization on a local scale. Hanshaw *et al.* [1971] showed with a simple calculation that under static conditions (e.g., in marine sediments) even large volumes of interstitial fluid become rapidly devoid of Mg and dolomitization does not proceed beyond a surficial layer, a phenomenon termed the “armoring effect”. Thus, at the vanishingly slow precipitation rates observed in the laboratory, regionally extensive dolomites form only if a perpetual circulation of Mg-rich fluids is sustained for geologic periods of time. The most plausible scenario is held to be the continuous movement of saline groundwater through a limestone aquifer.

[10] Hanshaw *et al.* [1971] contemplated freshwater recharge in the Floridan Aquifer System as a driver of groundwater circulation, but determined that dissolution of low-Mg calcite is an insufficient source of Mg and that an admixture of seawater or brine is almost certainly required. While the mixing model of Badiozamani [1973] was convincingly refuted as a mechanism for regionally exten-

sive dolomitization [Melim *et al.*, 2004], it has been argued that mixing zones between freshwater and seawater can indirectly cause dolomitization by generating a density-driven circulation of seawater, possibly in combination with transgressive or regressive displacement of the mixing zone due to sea level change [Randazzo and Hickey, 1978; Randazzo and Cook, 1987; Muchez and Viaene, 1994; Vahrenkamp and Swart, 1994]. In some cases, freshwater does not seem to be a factor in the dolomitization process and an alternative means of circulating large volumes of seawater has to be conceived. From a systematic study of blue holes, Whitaker *et al.* [1994] concluded that a dolomitizing fluid of near-seawater composition is traversing the Great Bahama Bank from west to east at a depth of a few hundred meters, either propelled by geothermal convection, or by a difference in sea level across the platform produced by the Florida Current. In view of the low temperature of the fluid ($\sim 21^{\circ}\text{C}$) when it emerges on the east side of Andros Island, Whitaker *et al.* [1994] deemed the second possibility more likely. At Enewetak Atoll, in the western Pacific Ocean, dolomite is found at 1250–1400 m below sea level. From $\delta^{18}\text{O}$ analysis of drill core samples, Saller [1984] identified the dolomitizing fluid as either warm brine (28°C) or cool seawater ($\sim 16^{\circ}\text{C}$), and suggested that it may have circulated by geothermal convection. He favored cool seawater, since nearly identical temperature profiles in deep wells and in the adjacent ocean down to ~ 1200 m indicate that the limestone strata are presently in open communication with the ocean and probably were so in the past.

[11] Beneath the southern half of the Florida Peninsula, which is the exposed part of one of the largest carbonate platforms in the world (Figure 1), groundwater is principally composed of saline to hypersaline solutions [Manheim and Horn, 1967; Henry and Kohout, 1972] and freshwater

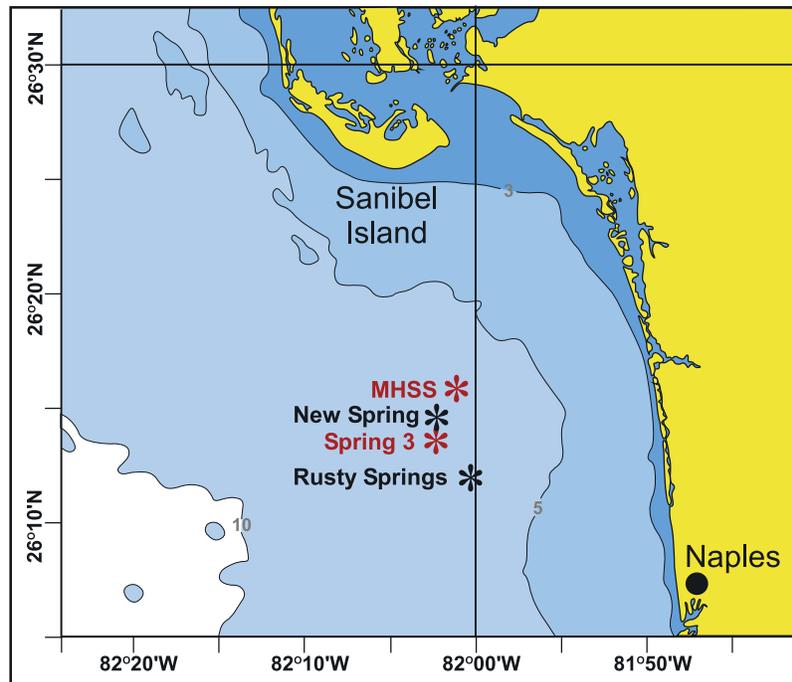


Figure 2. Nautical chart showing the four saline, geothermal, submarine springs. Depth contours in fathoms (1 fathom = 1.83 m). The springs are located in an area south of Sanibel Island and northwest of the town of Naples, approximately 15 km offshore. Coordinates were recorded by shipboard GPS as follows: Mud Hole Submarine Springs (MHSS) 26°15.84'N 82°01.05'W; New Spring 26°14.27'N 82°02.53'W; Spring 3 26°13.79'N 82°02.42'W; Rusty Springs 26°12.06'N 82°00.30'W.

recharge is of minor importance. As early as the mid-1960s, seawater was proposed to flow northward by geothermal convection, at depths of 800–1000 m, through the cavernous and highly permeable “Boulder Zone”, consisting of limestone and dolomitic limestone of Eocene age, confined from above by Oligocene and Miocene limestone and sands of low permeability, and from below by an impermeable layer of anhydrite at the top of the Paleocene Cedar Keys Limestone [Kohout, 1965, 1967; Henry and Kohout, 1972]. This seawater is believed to originate in the depths of the Florida Straits and to move toward the central axis of the Florida Plateau, where borehole temperatures reach maximum values of around 42°C.

[12] A unique feature of this convection system is that the fluids emerge on the shallow West Florida Shelf, where the axis of the Florida Plateau runs close to the Gulf coast. Submarine springs have long been known to occur in this area [Brooks, 1961; Kohout, 1966]. Thermal anomalies found on infrared imagery in the late 1960s and preliminary chemical analyses by the USGS in the early 1970s (neither published until much later [Kohout *et al.*, 1981]) had shown that these were not the usual cold, freshwater springs. Detailed geochemical analyses of water samples collected by SCUBA divers [Breland, 1980; Fanning *et al.*, 1981] supplied the first solid evidence that the spring effluents are warm (~35°C), anoxic ($\text{H}_2\text{S} \sim 4 \mu\text{mol/kg}$), have a composition similar to seawater with a salinity of about 35, and are highly enriched in silicate, sulfate, and especially Ra isotopes [Fanning *et al.*, 1981, 1982]. A distinct enrichment of Ca combined with a comparable depletion of Mg also revealed that the limestone substrate undergoes active dolomitization as a result of its interaction with the geo-

thermal fluids. Whereas the geochemical significance of submarine groundwater discharge [Simmons, 1992; Moore and Shaw, 1998; Moore, 1999] and especially submarine springs [Kohout, 1966; Glazovskiy *et al.*, 1973] has been emphasized many times, most geothermal springs emerge from igneous rocks [Degens and Ross, 1969; Vidal *et al.*, 1978; Corliss *et al.*, 1979]. To our knowledge, the only other report on the geochemistry of submarine warm springs emerging from carbonate rocks is Stüben *et al.* [1996], who described a limestone aquifer in the Capo Palinuro region of southern Italy that somewhat resembles the convection system discussed here. We present major ion, Sr, and Ba analyses of a large quantity of effluent samples, collected from four saline, geothermal, submarine springs during annual visits between 1996 and 2003. Their measured compositions are compared with those of Warm Mineral Springs (WMS), a brackish spring ($S \sim 17$) that is located on land, and Crescent Beach Spring (CBS), a large freshwater submarine spring on the East Florida Shelf that was sampled by the USGS in 1999 [Swarzenski *et al.*, 2001].

2. Study Area

[13] The southern part of the central axis of the Florida Plateau runs approximately parallel to the west coast of Florida (Figure 1). In accordance with the model of Kohout [1965, 1967], the four saline, geothermal, submarine springs (hereafter simply referred to as “the submarine springs”, explicitly excluding CBS) are found roughly along this axis, about 15 km offshore, directly south of Sanibel Island and northwest of the town of Naples (Figure 2). To the north of this area the axis intersects the coast and runs near the town

of North Port, where a single saline geothermal spring is located on land (Figure 1). Warm Mineral Springs (WMS), emerging at the bottom of a large sinkhole, feeds a 5700-m² lake that drains to the southwest via a small stream. This spring is privately owned and exploited as a health spa and tourist attraction.

[14] The West Florida Shelf in the submarine springs area, at a mean depth of 12–14 m, consists of flat to gently sloping sandy sediments with little vertical relief, few rocky outcrops, and sparse benthic communities. In contrast, some of the springs attract an abundance of marine life, including large, ecologically valuable species like loggerhead turtle (*Caretta caretta*), nurse shark (*Ginglymostoma cirratum*), and goliath grouper (*Epinephelus itajara*). Occasionally, our volunteer divers reported being enclosed by an almost solid vertical wall of pinfish (*Lagodon rhomboides*) that seemed to hover on the boundary between the warm spring effluent and the surrounding colder seawater. The submarine springs are consequently quite popular with commercial and recreational fishermen, who over the years have littered the seafloor with abandoned crab traps and refuse such as rope, plastic crates, PVC pipe, and glass bottles.

[15] *Fanning et al.* [1981] presented the locations of six submarine springs, which they designated Spring I–VI (Spring I is Mud Hole Submarine Springs – MHSS). All except Spring II (Steward Spring), which is located some distance to the west of the others, were revisited between 1996 and 2003. We retained the name Spring 3, but renamed Spring V to Rusty Springs for easy reference. During some of our annual cruises, a detailed bottom survey of a semicircular area encompassing MHSS, Spring 3, and Rusty Springs, was conducted using Kongsberg Simrad EM-3000 multibeam bathymetry. On the processed maps these springs stand out as distinct features in the otherwise flat seafloor (D. F. Naar, personal communication). The survey revealed three more such features that were subsequently investigated by SCUBA divers. This led to the discovery of New Spring in 2001. The other two features, to the northeast and south of MHSS and apparently corresponding to Spring IV and VI, were initially given the names Sinister Spring and Dormant Spring. Both are bowl-shaped depressions in the seafloor, sharing some characteristics with submarine springs, but their bottom was found to be covered with a thick, semi-suspended layer of mucose sediment, and no evidence of geothermal flow was detected. These currently extinct springs were clearly active in the late 1970s, suggesting that flow in some areas may be intermittent, possibly due to periodic shifts in the system of conduits by which effluent is brought to the sediment surface. Several promising areas further along the axis, as far south as 25°44'N, were investigated, partly based on information provided by local fishermen, but no submarine springs were found.

[16] Spring 3 and New Spring are conical depressions with steep walls dropping to about 10 m below the seafloor at their deepest points. A single vent with strong flow occurs at the apex of each cone, emerging through sandy sediment and shell hash. There are no rocky outcrops and the cones were always partly filled with free-floating sponges and trash that had to be cleared out before sampling. MHSS has been known at least since 1961, when it was mentioned by *Brooks* [1961] who referred to it as the

“Mud Boil”. At that time it was not yet marked on navigational charts, as it is now. *Breland* [1980] provides a very detailed description of MHSS, including a schematic map and underwater photos of some of the vents. Rusty Springs consist of a single rocky ledge of about 50 m length, where the seafloor drops by about 3 m. A number of vents occur in an area of coarse shell hash along the bottom of this ledge. Away from the ledge, sandy sediments gradually slope back up to the mean depth of the shelf. On this slope, several round patches of about 1 m diameter were observed, whose brown color contrasts conspicuously with the surrounding sediment. Whereas no flow could be felt or ‘shimmering’ could be seen, the patches were distinctly warm to the touch when a bare hand was placed on the sediment, indicating a very low, diffuse flow of effluent. We refer to these as “seep areas” and the brown patches are probably microbial mats that derive metabolic energy from the sulfide-rich effluent. Similar mats, specifically containing sulfur-oxidizing bacteria of the genus *Beggiatoa*, have also been found at depths of more than 3 km in association with anoxic brine seeps near the base of the West Florida Escarpment [*Paull et al.*, 1992] and in the outflow stream of WMS [*Larkin et al.*, 1994]. Although some of the mat material was collected by carefully scraping it off the sediment surface into a small plastic bottle, the only organism that could be identified under the microscope was an unknown species of lenticular brown diatom. Microbial mats were not found near any of the other submarine springs and never near vents, where the fragile material would probably be disrupted by the strong flow. However, numerous small mats, but no vents, were found in an extensive area that looked promising on the multibeam survey and was investigated by SCUBA divers. This suggests that the total effluent output may be much larger than estimated by *Breland* [1980] from the flow through a single MHSS vent (25 L/s) and may affect a much larger area.

[17] Crescent Beach Spring, which is used in this work for comparison only, is located on the East Florida Shelf, about 4 km east of the town of Crescent Beach. It is a single-vent feature, like Spring 3 and New Spring, with a maximum depth of 20 m below the seafloor depth of about 18 m. Unlike the saline, geothermal, submarine springs of the West Florida Shelf, the CBS effluent has a salinity of about 6 and a temperature of about 25°C. Samples were kindly provided by P. W. Swarzenski, USGS, St. Petersburg, FL. Detailed descriptions of this spring can be found in *Brooks* [1961] and *Swarzenski et al.* [2001].

3. Methods

3.1. Spring Sampling

[18] Spring sampling was performed by SCUBA divers. Samples could only be collected from well-defined vents with a relatively large orifice (smallest dimension at least 5 cm). No effluent was ever obtained from the seep areas, where flows were too diffuse to acquire samples that met two important quality criteria: (1) to contain essentially pure effluent (i.e., minimal admixture of seawater) and (2) to contain no visible sediment (which is continuously resuspended by the spring flow). The various sampling methods discussed here reflect a brief period of trial-and-error and a gradual improvement in our spring sampling skills, eventu-

ally culminating in a protocol that allowed routine collection of uncontaminated, high-purity effluent.

[19] During our earliest visits to the springs, in 1996 and 1997, three different strategies were tested. The first was a modification of the method of *Breland* [1980]. A 30-cm length of 4"-diameter transparent acrylic core-liner, with an internal volume of ~2 L, was held in place over the vent for about 1 min until all sediment was flushed from the inside. Top and bottom were then quickly sealed with rubber stoppers and the core-liner was brought to the surface. Onboard ship, the contents were acidified (unfiltered) with 1 mL of TraceMetal grade concentrated HNO₃ (Fisher Scientific, Pittsburgh, PA) per liter of sample and transferred to acid-cleaned 1-L or 2-L Teflon bottles, which were stored in ziploc bags for transport to the laboratory. The second strategy emulated the method of *Vidal et al.* [1978]. While several good samples were obtained with these two strategies, each of them presented some problems. Both strategies were therefore abandoned for a third approach, simpler and more reliable, which was the only one used after 1998. A number of 60-mL polypropylene syringes with Luer-Lok caps (Becton Dickinson, Franklin Lakes, NJ) were carried down to the spring in a Nylon-mesh dive bag. The syringes were used as received, but were not taken out of their sterile wrappers until shortly before the dive. After removing the cap, the syringe was inserted into the vent up to the handle. The syringe was then rinsed in place by repeatedly raising and depressing the plunger. Finally, the plunger was fully extended, the syringe retracted, and the cap refitted. Several syringes were usually filled in sequence. The collection of effluent from below the sediment surface and the narrow opening of the syringe ensured a very pure sample and effective exclusion of sediment. Onboard ship, the cap was replaced with a 0.2- μ m pore size, 25-mm cellulose acetate membrane cartridge filter (Corning, Corning, NY) and the contents of the syringe were filtered into an acid-cleaned Teflon or LDPE bottle after discarding the first 5–10 mL to rinse the filter. The contents of several syringes were typically combined into a single sample of 100–200 mL. Samples in Teflon were acidified and stored as described above, whereas samples in LDPE were left unacidified. Ambient seawater was sampled at MHSS in 1997 and at Rusty Springs in 2000, in the vicinity of the springs yet outside their estimated area of influence. These samples were also collected by SCUBA divers, one with the core-liner method and two with the syringe method, at depths of less than 10 m.

[20] In 1978, *Breland* retrieved a large volume of effluent by pumping it directly to the deck of the ship through a garden hose attached to a PVC well-point that was placed over the vent [*Breland*, 1980]. Exceptionally benign conditions in 1997 enabled us to repeat this feat with some modifications. It required the ship to be positioned exactly above the spring and to be kept in place by a three-point anchoring. This allowed the divers to take one end of a 100-ft length of 1/2" Bev-A-Line tubing (Cole-Parmer, Vernon Hills, IL) down to the spring and insert it about 50 cm into the vent. The other end remained on deck, connected to a large peristaltic pump via a short length of silicone tubing. The pump was started as soon as the divers submerged. Although communication with the divers was not possible, the arrival of effluent on deck was clearly signalled by a

strong smell of hydrogen sulfide. After pumping for at least another minute, a high-capacity in-line filter (500-cm² effective area, 0.45- μ m pore size with 0.8- μ m prefilter; Gelman, Ann Arbor, MI) was connected to the other end of the silicone tubing. The filter was flushed with 1–2 L of effluent after which samples of filtered effluent were collected in several acid-cleaned 2-L Teflon bottles, acidified, and stored as described above. Each bottle was thoroughly rinsed with filtered effluent before filling.

[21] Another large sample of effluent was retrieved from Warm Mineral Springs in 1998, thanks to the kindness of its owners. This sample was collected from a metal standpipe with tap that apparently brings up effluent from deep in the spring. After allowing the standpipe to flush for at least a minute, an acid-cleaned 13-gal HDPE carboy was filled about two-thirds, directly from the tap. The carboy was packed in plastic garbage bags for transport to the laboratory, where a 2-L aliquot was filtered into an acid-cleaned Teflon bottle and acidified. The rest of the unfiltered sample was acidified inside the carboy.

[22] In total, more than 50 samples were acquired over an 8-year period. All samples from 1996 and some from 1997 were exhausted for rare earth element (REE) analysis. The remainder included 14 samples from MHSS and 13 from Rusty Springs, both of which were visited almost every year. Spring 3 was visited in 2000 and 2003, yielding a total of 5 samples, while only 2 samples were collected from New Spring in 2002, the year after its discovery. At MHSS and Rusty Springs, samples were collected from multiple vents, sometimes within a single dive. However, since poor visibility often made underwater orientation quite difficult and few fixed reference points were available, divers could not always agree on the exact location of various vents and no attempt was made to distinguish them. A total of 41 samples from the submarine springs, WMS, and CBS, both filtered and unfiltered, acidified and unacidified, was analyzed for major ions by ion chromatography and for Sr and Ba by ICP-MS (Table 1).

3.2. Ion Chromatography (IC)

[23] The 41 effluent and ambient seawater samples were analyzed for four major cations (Na⁺, K⁺, Mg²⁺, Ca²⁺) and two major anions (Cl⁻, SO₄²⁻) with a Dionex DX-500 IC, using Dionex PeakNet software. Cations were separated as a group on an IonPac CS12A column with 15 mM methanesulfonic acid (MSA; CH₃SO₂OH) as the eluent. Anions were separated as a group on an IonPac AS14 column with a mixture of 1.0 mM NaHCO₃ and 3.5 mM Na₂CO₃ as the eluent. MSA solution (70 wt.% in water) was purchased from Sigma-Aldrich (St. Louis, MO) and the carbonate solutions (each 0.5 M) from Dionex (Sunnyvale, CA). Eluents were made fresh with water from a Millipore (Bedford, MA) purification system (Milli-Q water) and purged for 20–30 min with ultra-high-purity He before each IC run. The CSRS-Ultra (cation) and ASRS-Ultra (anion) self-regenerating suppressors were also hydrated daily with 0.2 M NaOH and 0.1 M H₂SO₄, respectively, as specified by the manufacturer. These solutions were made from concentrated reagents purchased from Fisher Scientific.

[24] Each IC run started with a calibration curve, consisting of a blank and 5 standards. The latter were made once

Table 1. Overview of Effluent and Seawater Samples Taken at the Submarine Springs^a

| Year | Dates | Sample ^b | Method ^c | <i>n</i> | Total |
|-------------------|-------------|-------------------------|---------------------|----------|-------|
| 1997 | 02/24–02/26 | MHSS | corel./pump/syr. | 9 | |
| | | seawater | corel./syr. | 2 | 11 |
| 1998 ^d | 02/24 | WMS | standpipe | 2 | 2 |
| 1999 | 04/01 | Rusty Springs | syr. | 1 | |
| | 04/28–04/29 | CBS ^c | pump ^f | 1 | |
| | | seawater ^c | pump ^f | 1 | 3 |
| 2000 | 03/21–03/24 | MHSS | syr. | 2 | |
| | | Rusty Springs | syr. | 3 | |
| | | Spring 3 | syr. | 2 | |
| | | seawater | syr. | 1 | 8 |
| 2001 | 03/12–03/13 | MHSS | syr. | 2 | |
| | | Rusty Springs | syr. | 4 | 6 |
| 2002 | 04/11–04/12 | MHSS | syr. | 1 | |
| | | Rusty Springs | syr. | 5 | |
| | | New Spring ^g | syr. | 2 | 8 |
| 2003 | 04/08 | Spring 3 | syr. | 3 | 3 |
| Total | | | | | 41 |

^aEleven more samples from 1996 and 1997 had been exhausted for REE analysis (J. Schijf, unpublished results) and were no longer available. Details of the sampling methods are given in the text.

^bMHSS, Mud Hole Submarine Springs; WMS, Warm Mineral Springs; CBS, Crescent Beach Spring.

^cCorel., core-liner; syr., syringe.

^dNo submarine spring samples were collected due to poor diving conditions.

^eSample kindly provided by P. W. Swarzenski, USGS, St. Petersburg, Florida.

^fSee Swarzenski *et al.* [2001].

^gDiscovered in 2001 by multibeam survey.

from multi-element solutions (Water Pollution Standard 5 and IC Custom Standard #1; VHG Labs, Manchester, NH) and used for all IC analyses. Each standard was reanalyzed several times during an IC run. Calibrations were extremely reproducible over long periods of time. Standard analyses from 9 cation IC runs were pooled to produce a single calibration curve for each cation. A routine replacement of the anion self-regenerating suppressor caused a shift in the anion calibrations. Hence standard analyses from 8 anion IC runs before and 6 anion IC runs after the replacement were pooled separately, to produce two calibration curves for each anion. All cation calibration curves were highly linear. Anion calibration curves were found to be nonlinear [see also Schijf and Byrne, 2004] and best results were obtained with quadratic fits. While all calibration curves had small intercepts, both positive and negative, none of the intercepts were significantly different from zero at the 99% confidence level, which is consistent with the absence of procedural blanks.

[25] To verify the accuracy of the cation calibrations, a standard reference material (SRM) was analyzed repeatedly during each IC run (SLRS-4 River Water Reference Material for Trace Metals, National Research Council Canada). Because this SRM is not certified for anions, the accuracy of the anion calibrations was verified with solutions derived from a volumetric HCl standard (Sigma-Aldrich) and from a certified sulfur standard (SPEX CertiPrep, Metuchen, NJ). An additional check sample for cations was made from single-element ICP standards (SPEX CertiPrep). Analytical recoveries for each of the six ions are listed in Table 2. All exceed 93%, while measured cation concentrations are within the 95% confidence intervals of the certified SRM concentrations, except for Ca. Precision was 2–3%, based on a total of 44 replicates for cations and 70 replicates for

anions after removal of systematic outliers (see below). Likewise, cation recoveries estimated from the check sample were $(100 \pm 3)\%$ for concentrations within the calibrated range (data not shown).

[26] Since the very subtle deviations of the effluents from the ambient seawater composition [Breland, 1980] could not be distinguished within the stated uncertainties for single IC analyses, a special technique was developed to improve the accuracy and precision of ion concentration measurements. A series of 2–5 separate dilutions with Milli-Q water was made of each sample in 15-mL and 50-mL polypropylene centrifuge tubes, inside a class 100 laminar flow bench, with dilution factors ranging between 50 and 4000, depending on sample concentration. While IC should strictly be performed on unacidified samples, these dilutions increased the pH of the acidified samples sufficiently that they could be analyzed as well and compared with the unacidified samples. For each dilution within a series, the measured concentration multiplied by the dilution factor is a constant equal to the true sample concentration. Therefore, the logarithm of the measured concentrations within each series, plotted as a function of the logarithm of the dilution factors, constitutes a straight line with a theoretical slope of -1 and an intercept equal to the logarithm of the true sample concentration. Major ion concentrations were thus determined by linear regression of a series of dilutions for each sample, whereby individual dilutions were often analyzed multiple times. Linear regressions with both slope and intercept as free parameters showed that slopes were almost always within 2% of the theoretical value of -1 for all six ions. Measured concentrations were subsequently fit to lines with a slope of -1 and the intercept (sample concentration) as the only free parameter. Regression coefficients (r^2) were typically better than 0.999. This method of processing the data is statistically equivalent to calculating the average of all dilution-corrected measured concentrations within each series, yet it allowed a number of potential analytical artifacts to be recognized more easily, including a type of systematic outlier that is highly correlated for all cations or anions and characterized by excursions toward low concentrations of typically more than 2 standard deviations. The size and nonrandom nature of these outliers, as well as the fact that they also affected calibration standards, SRMs, and check

Table 2. Major Ion Concentrations of Standard Reference Materials (SRMs), Determined by Ion Chromatography^a

| Ion | SRMs | mM | <i>n</i> | Certified | Recovery, % |
|-------------------------------|----------------------|------------|----------|------------|-------------|
| Na ⁺ | NRC ^b | 96.6 ± 2.5 | 44 | 104 ± 9 | 93 ± 2 |
| K ⁺ | NRC | 17.1 ± 0.3 | 44 | 17.4 ± 0.5 | 98 ± 2 |
| Mg ²⁺ | NRC | 64.1 ± 1.4 | 44 | 65.8 ± 4.1 | 97 ± 2 |
| Ca ²⁺ | NRC | 145 ± 3 | 44 | 155 ± 5 | 94 ± 2 |
| Cl ⁻ | Aldrich ^c | 499 ± 13 | 70 | 500 | 100 ± 3 |
| SO ₄ ²⁻ | SPEX ^d | 157 ± 4 | 70 | 156 | 101 ± 2 |

^aMeasured values are the average of the indicated number of replicates (*n*) (± 1 standard deviation). Uncertainties in the certified values represent 95% confidence intervals.

^bNational Research Council Canada, SLRS-4 River Water Reference Material for Trace Metals.

^cSigma-Aldrich, hydrochloric acid volumetric standard, 1.000 M (Cat. No. 31,894-9).

^dSPEX CertiPrep, single-element sulfur standard, 1,000 ppm S as SO₄²⁻ (Lot# L5-167S).

Table 3. Spring Effluent Compositions^a

| Location | [Na ⁺] | [K ⁺] | [Mg ²⁺] | [Ca ²⁺] | [Cl ⁻] | [SO ₄ ²⁻] | [Sr ²⁺] | [Ba ²⁺] |
|------------------------|--------------------|-------------------|---------------------|---------------------|----------------------|----------------------------------|----------------------|---------------------|
| Seawater ^b | 480 | 10.4 | 54.0 | 10.5 | 559 | 28.9 | 91 ^c | 30–72 ^d |
| Rusty Springs | 499 ± 10 | 10.8 ± 0.2 | 53.7 ± 1.0 | 14.1 ± 0.2 | 565 ± 13 | 29.6 ± 0.7 | 127 ± 2 | 164 ± 5 |
| Spring 3 | 494 ± 4 | 10.6 ± 0.1 | 52.9 ± 0.6 | 14.0 ± 0.1 | 554 ± 4 | 29.3 ± 0.2 | 131 ± 0 ₃ | 200 ± 3 |
| New Spring | 489 ± 6 | 10.5 ± 0.2 | 52.1 ± 0.8 | 13.7 ± 0.1 | 557 ± 0 ₁ | 29.1 ± 0.0 ₄ | 134 ± 0 ₅ | 209 ± 1 |
| MHSS | 501 ± 9 | 10.8 ± 0.2 | 53.2 ± 0.9 | 14.5 ± 0.3 | 563 ± 11 | 29.6 ± 0.6 | 149 ± 3 | 244 ± 6 |
| WMS | 238 ± 4 | 4.8 ± 0.1 | 25.5 ± 0.4 | 12.7 ± 0.1 | 273 ± 2 | 18.0 ± 0.2 | 357 ± 3 | 320 ± 4 |
| Published ^c | 240 | 4.7 | 23.8 | 12.3 | 282 | 17.7 | 410 | - |
| CBS ^f | 79.6 (±0.6) | 1.48 (±0.02) | 9.78 (±0.09) | 6.97 (±0.09) | 92.4 (±0.3) | 7.94 (±0.04) | 97.7 ± 0.8 | 259 ± 2 |
| Published ^g | 87.00 | 1.07 | 8.72 | 6.49 | 96.75 | 7.77 | 90 | 300.7 |
| Published ^h | 88.74 | 1.64 | 10.37 | 7.39 | 102.39 | 8.50 | 100 | - |

^aStandard seawater (S = 35.00) is shown for comparison. All concentrations in mM, except Sr (μ M) and Ba (nM). Major ion concentrations determined by ion chromatography. Sr and Ba concentrations determined by ICP-MS. Values for each spring are the average of all samples collected during the period 1997–2003 (± 1 standard deviation). Errors in parentheses are based on regression statistics; see text. Springs are arranged in order of increasing latitude (south to north; Figure 2).

^bAll concentrations, except [Ba²⁺], correspond to salinity 35.00; major ions after *Millero* [1996].

^cAfter *Byrne* [2002].

^dRange of surface water concentrations across the shelf break off the South Carolina coast [*Moore and Shaw*, 1998].

^e*Scott et al.* [2004, Table 162].

^fSample kindly provided by P. W. Swarzenski, USGS, St. Petersburg, Florida.

^g*Swarzenski et al.* [2001].

^h*Toth* [1999, Table 3].

samples, ruled out simple dilution errors and indicated a more systematic problem, possibly caused by an occasional malfunction of the pneumatic injection valve. All such systematic outliers were removed. In addition, random outliers for individual ions were occasionally removed on statistical grounds. In that case, all corresponding cation or anion data for that dilution were rejected as well, even if they were not themselves anomalous.

[27] Salinities of unacidified effluent and ambient seawater samples were measured with a handheld conductivity/salinity meter (Cond 340i; WTW Measurement Systems, Ft. Myers, FL) for comparison with the major ion concentrations.

3.3. Inductively Coupled Plasma Mass Spectrometry (ICP-MS)

[28] The 41 effluent and ambient seawater samples were analyzed for Sr and Ba with an Agilent Technologies 4500 Series 200 ICP-MS. Since ICP-MS analysis of pure seawater gives rise to severe matrix effects (signal suppression), the samples were first diluted 20-fold with 1% HNO₃ in polypropylene autosampler tubes. All calibration standards and diluted samples contained 1 ppm Y and 20 ppb Cs, acting as internal standards. A typical ICP-MS run consisted of a 1% HNO₃ blank, four calibration standards, a 1% HNO₃ rinse, and a batch of about 20 samples. Each batch of samples was run twice, in arbitrary order. Most samples were analyzed at least four times (replicate analysis of two separate dilutions). Solutions were introduced into the ICP-MS with a Babington-type PEEK nebulizer and a double-pass (Scott-type) quartz spraychamber, Peltier-cooled to T = 2°C. All solutions were injected in triplicate. After each autosampler position, Milli-Q water was aspirated for 10 s followed by a 1% HNO₃ wash solution for 30 s, to rinse the outside of the autosampler probe and the sample introduction system. During instrument tuning, the formation of oxide and double-charged ions was minimized with a 10-ppb Ce solution. CeO⁺ and Ce²⁺ were typically ~1% and ~3% of the corresponding Ce⁺ peak, respectively. Sr and Ba concentrations were calculated from linear regressions of the first blank and the four calibration standards. The latter

were prepared from a custom-blended solution (SPEX CertiPrep) with a certified Ba/Sr mass ratio of 0.005, which is particularly suitable for the analysis of Sr and Ba concentrations in marine samples [*Bernstein et al.*, 1998]. Sr and Y ions were counted with the analog detector and Cs and Ba ions with the pulse counter.

[29] Ion counts were corrected for instrument drift by normalizing ⁸⁸Sr to ⁸⁹Y, and ¹³⁷Ba and ¹³⁸Ba to ¹³³Cs. No oxide or chloride polyatomic ions of major seawater constituents cause isobaric interference on any of these masses. Ba concentrations calculated from ¹³⁷Ba and ¹³⁸Ba were usually equal within 1% and were averaged. Monitoring of internal standard count rates indicated that signal suppression was typically on the order of 10–20% throughout the mass range of interest. Long-term drift, due to deposition of solids behind the orifice of the Ni cones, was negligible for the 2-hour duration of an ICP-MS run. A reanalysis of the first sample in the batch at the end of each ICP-MS run was always equal to the initial value within 1–2%, indicating that the internal standards were adequately correcting for residual matrix effects and that matrix matching of the calibration standards was not required under these conditions. Precision, as estimated either from replicate analyses of the same solution in different ICP-MS runs or from analysis of replicate dilutions of the same sample, was on the order of 2–3%. Sr blanks were below the quantitation limit of the analog detector (1 ppb). Ba blanks, probably resulting from minor carry-over between consecutive solutions, were always <1% of concentrations in the effluents but could be up to 2–3% of the lower concentrations in the ambient seawater samples. Since either level is within the analytical uncertainty and elevated blanks did not occur systematically, they were not corrected for.

4. Results

4.1. Concentrations of Sr, Ba, and the Major Ions

[30] Table 3 lists dissolved concentrations of the major ions, Sr, and Ba, for each submarine spring, in the form of averages (± 1 standard deviation) taken over all years, vents,

sampling protocols, and methods of sample preservation. It is thus remarkable that standard deviations are generally <2% and in no case >3% of the average concentrations. This suggests that the effluent compositions of both MHSS and Rusty Springs were constant throughout the period 1997–2003, within analytical uncertainties. Although there is less supporting evidence because of the smaller number of samples, the same is probably true for Spring 3 and New Spring.

[31] Major ion concentrations support the observation of *Breland* [1980] that compositions of the submarine spring effluents are very similar to that of standard seawater ($S = 35.00$), also given in Table 3. On the other hand, Sr and Ba concentrations in the submarine springs are markedly different from those in seawater. Strontium, albeit more variable in coastal waters [*De Deckker*, 2004], behaves conservatively in the ocean, with a typical concentration of about $90 \mu\text{mol/L}$ [*Byrne*, 2002]. Sr concentrations in three seawater samples ($87\text{--}91 \mu\text{mol/L}$; data not shown) collected in the vicinity of MHSS (1997), CBS (1999), and Rusty Springs (2000), are equal to or slightly below this value. Concentrations in the submarine springs ($127\text{--}149 \mu\text{mol/L}$; Table 3) are distinctly higher than in the ambient seawater. Based on USGS analyses, *Kohout et al.* [1981] reported a Sr concentration of $\sim 16 \mu\text{mol/L}$ for MHSS, a factor of six less than in seawater and almost certainly erroneous. Barium displays classic nutrient-like behavior in the open ocean, with concentrations that are low in surface waters but increase strongly with depth. *Moore and Shaw* [1998], who measured dissolved Ba concentrations in surface waters across the shelf break off the South Carolina coast, reported values of $30\text{--}70 \text{ nmol/L}$, near the lower end of the oceanic range [*Byrne*, 2002]. Ba concentrations in the ambient seawater ($44\text{--}59 \text{ nmol/L}$; data not shown) fall within those bounds and are more variable than the Sr concentrations. Ba concentrations in the submarine springs ($164\text{--}244 \text{ nmol/L}$; Table 3) exceed the highest value reported for abyssal seawater, $\sim 150 \text{ nmol/L}$ in the Pacific Ocean [*Byrne*, 2002].

[32] Also listed in Table 3 are major ion, Sr, and Ba concentrations in WMS and CBS. WMS major ion concentrations are only about half those in the submarine springs and in the ambient seawater, corresponding to a salinity of approximately 17. An exception is its Ca concentration, which is higher than in standard seawater, but slightly lower than in the submarine springs. The major ion composition of the WMS effluent is compared in Table 3 with concentrations reported by *Scott et al.* [2004], which are ‘dissolved’ ($0.45\text{-}\mu\text{m}$ filtered) values, except for Cl, SO_4 , and Sr, which are based on unfiltered samples. Agreement with these values is generally good, but our Sr concentration is substantially lower. It is, however, in excellent agreement with an earlier (1972) value of $354 \mu\text{mol/L}$, also listed by *Scott et al.* [2004]. Strontium and barium are much more enriched in WMS than in any of the submarine springs. The major ion concentrations of *Scott et al.* [2004] are significantly lower in filtered than in unfiltered samples. More incongruously, the opposite was found for Na. We could detect no difference between filtered and unfiltered samples for any of the elements analyzed in any of the springs.

[33] Our single CBS sample is compared in Table 3 with two samples tabulated by *Swarzenski et al.* [2001], both

identified only as “CBS”. One of these samples was probably collected around the same time as our sample, yet the other was apparently taken from *Toth* [1999], who reported identical data for a sample collected in 1995, albeit with a different temperature (28.7°C vs. 24.91°C). The two samples are notably dissimilar, for instance, Na concentrations differ by 2%, but K concentrations by more than 50%. It is not clear whether this reflects real, temporal variations in composition, sampling artifacts, or analytical problems as *Swarzenski et al.* [2001] provide few details about their sampling protocol and analytical techniques. Na and Cl concentrations in our CBS sample are lower than in either of the two published samples, while concentrations of the other major ions and Sr are intermediate. With respect to standard seawater, the Sr concentration is distinctly elevated, whereas the Ca concentration is lower by more than 30% and those of the other elements by factors of $\sim 5\text{--}10$ (Table 3). The Ba concentration is significantly lower than the value reported by *Swarzenski et al.* [2001], yet similar to concentrations in the submarine springs.

4.2. ‘Salinity’-Normalized Concentrations

[34] The 2–3% uncertainty in the Na and Cl concentrations may be analytical and may represent actual salinity fluctuations due to annual changes in coastal waters or a minor but variable degree of mixing between the pure submarine spring effluents and ambient seawater, caused by tidal action. Ion chromatography measures cations and anions as two separate groups, whereby errors arising from sample dilution and instrument instability are always highly correlated within each group. Consequently, either source of variability affects all major ions proportionally and can be removed by normalizing their concentrations to salinity or a suitable proxy. As chlorinities are not available for our samples (dilutions were done volumetrically and densities not determined), salinities were derived from Cl concentrations in molar units, relative to standard seawater. Such calculations yield a salinity of 35.2 ± 0.7 for MHSS, similar to values of $34.91\text{--}35.13$ reported by *Breland* [1980]. Salinities of 34.9 , 34.7 ± 0.3 , and 35.4 ± 0.8 were found for New Spring, Spring 3, and Rusty Springs, respectively. The chlorinity-normalized Na concentration of *Breland* [1980] deviates from the seawater value by just 0.3%, yet salinities calculated from the Na concentrations in Table 3 are higher than Cl-based salinities by almost one unit. This points to a slight positive bias in the concentration of Na (and possibly the other major cations), within experimental error and not evident in the analytical recoveries (Table 2). Since Na-based and Cl-based salinities for WMS (17.1) and CBS (5.8) are in progressively better agreement, the effect appears to diminish with decreasing Na concentration and is therefore probably analytical in nature. Salinities measured directly with a handheld conductivity/salinity meter on unacidified samples are generally closer to the Cl-based values, although it should be noted that compositions different from seawater may lead to excursions from the known relation between salinity and conductivity.

[35] In view of the positive Na bias, no one element could be used as a proxy for salinity to normalize all others. Hence cation concentrations (including Sr and Ba) were normalized to Na, but SO_4 was normalized to Cl. Results are presented in Table 4 for all springs and also for the ambient

Table 4. Elemental Ratios in Ambient Seawater, Submarine Springs, WMS, and CBS^a

| Location | K/Na | Mg/Na | Ca/Na | SO ₄ /Cl | Sr/Na | Ba/Na |
|-----------------------|------------------|------------------------------|------------------|---------------------|----------------|----------------|
| Seawater ^b | 0.0218 | 0.1126 | 0.0219 | 0.0517 | 0.190 | - |
| 1997 ^c | 0.0215 ± 0.0001 | 0.1128 ± 0.0001 | 0.0220 ± 0.0001 | 0.0519 ± 0.0001 | 0.175 ± 0.002 | 0.119 ± 0.005 |
| 1999 ^{d,e} | 0.0219 (±0.0002) | 0.114 (±0.001) | 0.0222 (±0.0003) | 0.0517 (±0.0003) | 0.178 (±0.002) | 0.089 (±0.002) |
| 2000 ^f | 0.0218 (±0.0002) | 0.1134 (±0.0008) | 0.0219 (±0.0002) | 0.0519 (±0.0004) | 0.173 (±0.002) | 0.106 (±0.005) |
| Rusty Springs | 0.0216 ± 0.0003 | 0.1076 ± 0.0005 | 0.0282 ± 0.0003 | 0.0524 ± 0.0004 | 0.255 ± 0.004 | 0.33 ± 0.01 |
| Spring 3 | 0.0214 ± 0.0001 | 0.1072 ± 0.0005 | 0.0283 ± 0.0002 | 0.0529 ± 0.0003 | 0.266 ± 0.003 | 0.406 ± 0.008 |
| New Spring | 0.0215 ± 0.0002 | 0.1067 ± 0.0003 | 0.0280 ± 0.0002 | 0.0523 ± 0.0001 | 0.274 ± 0.005 | 0.429 ± 0.008 |
| MHSS | 0.0215 ± 0.0002 | 0.1063 ± 0.0004 | 0.0289 ± 0.0003 | 0.0526 ± 0.0003 | 0.298 ± 0.003 | 0.488 ± 0.009 |
| MHSS ^g | 0.0217 | 0.107 | 0.0299 | 0.0525 | - | - |
| WMS | 0.0202 ± 0.0001 | 0.1071 ± 0.0000 ₄ | 0.0535 ± 0.0003 | 0.066 ± 0.001 | 1.503 ± 0.008 | 1.345 ± 0.004 |
| CBS ^e | 0.0186 (±0.0003) | 0.123 (±0.001) | 0.088 (±0.001) | 0.0860 (±0.0005) | 1.23 (±0.01) | 3.26 (±0.03) |

^aValues for each spring are the average of all samples collected during the period 1997–2003 (±1 standard deviation). Errors in parentheses were estimated from errors in the corresponding concentrations; see text. All ratios in mol/mol, except Sr/Na (10⁻³ mol/mol) and Ba/Na (10⁻⁶ mol/mol). Springs are arranged in order of increasing latitude (south to north; Figure 2).

^bAfter *Millero* [1996] and *Byrne* [2002] (see Table 3).

^cCollected in the vicinity of MHSS (depth ~7 m).

^dCollected in the vicinity of CBS (surface).

^eSample kindly provided by P. W. Swarzenski, USGS, St. Petersburg, Florida.

^fCollected in the vicinity of Rusty Springs (depth ~7 m).

^g*Breland* [1980].

seawater samples. Ion ratios were calculated for each sample separately and then averaged, same as the concentrations. Two cation ratios of one MHSS sample deviated from their average values by more than 2 σ (in opposite directions). This sample had an anomalously high salinity (37.3, based on Cl) and was excluded from the calculation of average ion ratios and concentrations. Errors in Table 4 are standard deviations of the average, except when only a single sample was taken, in which case the error was estimated from the statistics of the linear regressions that were performed to determine the concentrations (see section 3.2).

5. Discussion

5.1. Alkaline Earth Element Enrichments and Depletions: Evidence for Dolomitization

[36] All salinity-normalized major ion concentrations in the ambient seawater are in excellent agreement with their known values in standard seawater, within the corresponding uncertainties (Table 4), which are typically 0.5–1% of the average, substantially less than the 2–3% variation in the absolute concentrations. This confirms that the latter variation, whether real or analytical, is coherent among cations and anions and effectively removed by normalization. These results give ample confidence in the quality of the IC data. Sodium was measured with a different technique than Sr and Ba, so it is unknown if the slightly lower Sr/Na ratios in the ambient seawater reflect the aforementioned positive Na bias, or an actual depletion of Sr. With respect to standard seawater, the ambient seawater is depleted in Sr by about 8%. *De Deckker* [2004] recorded variations in the Sr/Cl ratio of a similar magnitude in coastal seawater off western Australia and attributed these to the presence of celestite-producing acantharia, in accordance with *Bernstein et al.* [1987]. It seems more likely that these variations are due to the nearshore contribution of freshwater from rivers, aquifers, and precipitation. Variations in the ambient seawater Ba/Na ratios are dominated by variations in the concentration of Ba, which is particularly variable in coastal waters [*Moore*, 1997, 1999; *Moore and Shaw*, 1998].

[37] In order to resolve the subtle enrichments and depletions of major ions in the submarine springs with respect to seawater – some of which are small enough that they are largely masked by the observed salinity variations – *Breland* [1980] used the sensitive method of ion difference chromatography [*Mangelsdorf and Wilson*, 1971] and presented his data as chlorinity-normalized concentrations (in molal units). Table 4 shows that salinity-normalized major ion concentrations in the MHSS effluent are very similar to the values of *Breland* [1980]. To emphasize the small deviations in composition, each ion/ion ratio in the spring effluents was divided by the corresponding value in seawater. The seawater values, which should be independent of salinity, are actually the measured averages of the three ambient seawater samples, so as to remove all remaining analytical bias. The results are shown in Figure 3, with values smaller or larger than 1 indicating depletion or enrichment of the numerator ion with respect to seawater, respectively.

[38] Figure 3 confirms a number of previous observations and also reveals several new ones. In general, the submarine springs are depleted in Mg by 5–6% and enriched in SO₄ by 1–2%. On the other hand, the 27–31% enrichment of Ca is significantly less than the value of 36% reported by *Breland* [1980]. K/Na ratios of the submarine spring effluents are identical to those of the ambient seawater, within the precision of the measurements. The very subtle K depletion of 0.9% with respect to chlorinity, found by *Breland* [1980] for the MHSS effluent, could thus not be resolved with our analytical technique. *Breland* [1980] did not analyze the spring effluents for Sr and Ba. Strontium is enriched by 45–70% with respect to seawater. Although Ba is clearly enriched with respect to seawater, its exact degree of enrichment is difficult to quantify, because Ba is not a conservative element in seawater and its concentration therefore varies relative to salinity (Table 4). With respect to the average of the three ambient seawater samples the Ba enrichment ranges between about 200% and 350%.

[39] The availability of data for effluents from multiple submarine springs over an extended period of time, as well as the addition of two elements (Sr and Ba), allow us to make two new observations (Figure 3). First, whereas Mg is

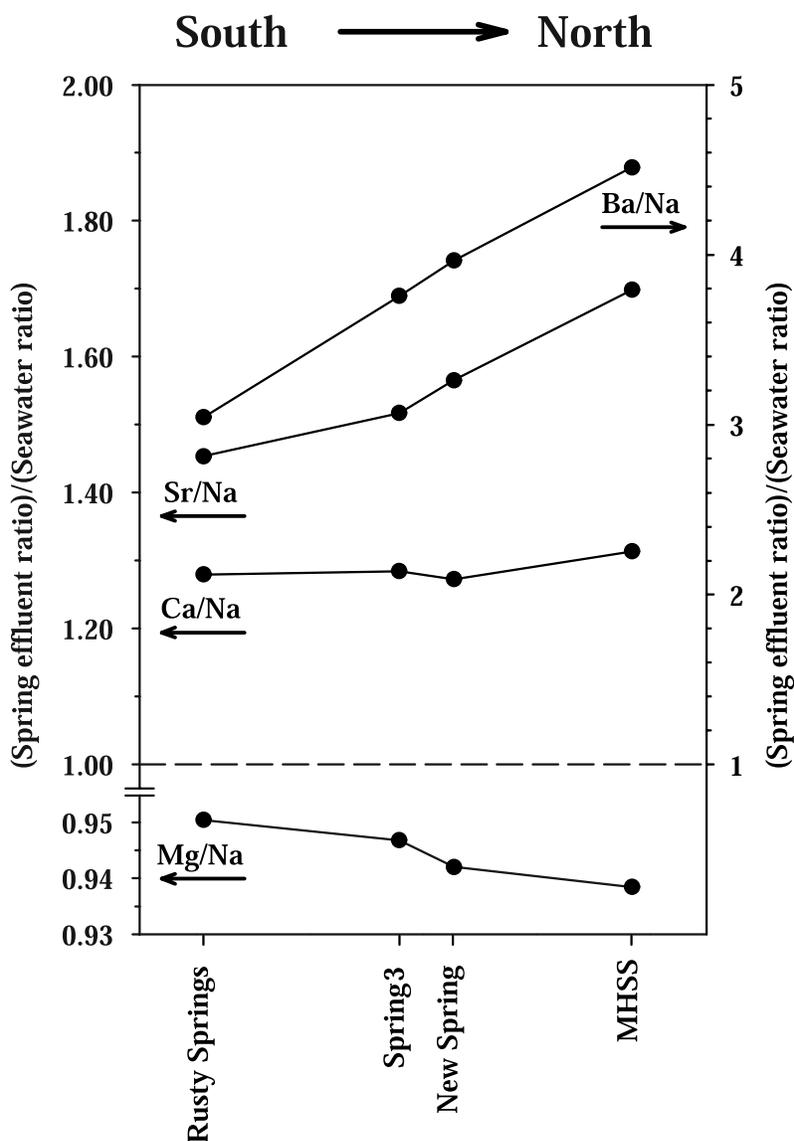


Figure 3. Spring effluent ratios of alkaline earth element to Na concentrations, where Na represents salinity, normalized to corresponding seawater ratios. Values below (above) the dashed line signify depletion (enrichment) with respect to ambient seawater. Relative latitudes of the springs (see Figure 2) are reflected by their arrangement along the abscissa. The small arrow underneath each label indicates whether the ratio should be read on the left or on the right ordinate. Note the different scales.

depleted in the spring effluents, the other alkaline earth elements are enriched to a degree that increases with their atomic number: Ca (27–31%) < Sr (45–70%) < Ba (200–350%). Radioactive Ra (not shown in Figure 3), the heaviest of the alkaline earth elements, continues this trend with enrichment factors of 10^2 – 10^3 , depending on the isotope [Fanning *et al.*, 1981, 1982]. Second, all alkaline earth elements show a more or less linear trend of increasing depletion or enrichment with increasing latitude (south to north). The only exception is Ca, which is enriched in all submarine springs, but shows no clear trend from south to north. While differences between the salinity-normalized Sr and Ba concentrations in the different springs are ostensibly significant with regard to their uncertainties, this is not the case for Mg. We therefore performed a two-tailed Student's *t*-test [Zar, 1996] to determine the statistical significance of

differences in Mg/Na ratios between all possible pairs of submarine springs. The results, in the form of P-value upper bounds, are shown in Table 5, where for example $P < 0.005$ signifies that it is more than 99.5% certain that the differ-

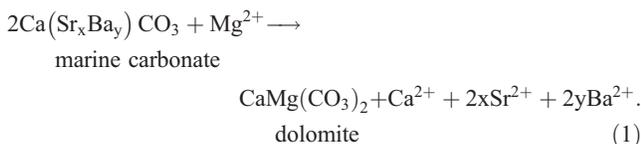
Table 5. Statistical Significance of Differences of the Mg/Na Ratios Among the Four Submarine Springs (P-values, Two-Tailed Student's *t*-Test)^a

| | New Spring | Spring 3 | Rusty Springs |
|------------|------------|------------------|------------------|
| MHSS | <0.50 | <0.005 | <0.001 |
| New Spring | | <0.20 | <0.05 |
| Spring 3 | | | <0.20 |

^aSprings are arranged top-to-bottom and left-to-right in order of decreasing latitude (north to south; Figure 2). Entries on the main diagonal are for adjacent springs. Entries in bold indicate that the Mg/Na ratios of the corresponding pair of springs are significantly different at the 95% confidence level, or better.

ence between Mg/Na ratios of the corresponding pair of springs is statistically significant. Table 5 indicates that, while differences between adjacent springs are not significant, they are significant for any pair of springs that has either one or two springs between them. It follows that, overall, the south-north trend of increasing Mg depletion may be meaningfully interpreted.

[40] All these observations strongly support the hypothesis of *Breland* [1980] and *Fanning et al.* [1981], who have both argued that, while there may be other explanations, dolomitization of Florida limestone in contact with seawater is the most plausible explanation for the composition of the submarine spring effluents, specifically the simultaneous depletion of Mg and enrichment of Ca. A similar argument was made for warm submarine springs on the west coast of Italy by *Stüben et al.* [1996]. If we artlessly represent the marine carbonates (limestone) of the Florida Plateau as a pure calcium carbonate with minor amounts of Sr and Ba ($x, y \ll 1$), the simultaneous removal of Mg and release of Ca, Sr, and Ba upon dolomitization can be captured with the following reaction:



This representation is, in several ways, an oversimplification. Florida limestone is of marine origin and therefore consists in large part of magnesian calcite with Mg contents of a few percent [*Hanshaw et al.*, 1971; *Plath et al.*, 1980]. Nevertheless, dolomite contains Mg at levels of more than ~35% to ideally 50% [*Hanshaw et al.*, 1971], so the dolomitization process clearly involves uptake of Mg. Although the exact mechanism of Sr exclusion is not well understood, it is generally known that the Sr content of dolomites is significantly lower than that of marine carbonates [*Zenger et al.*, 1980]. One line of reasoning posits that the ionic radius of Sr^{2+} (1.12 Å) is much closer to that of Ca^{2+} (0.99 Å) than that of Mg^{2+} (0.66 Å), and that Sr is thus more likely to occupy a Ca site than a Mg site. Since dolomite has only half the number of Ca sites that calcium carbonate does, Sr would tend to be excluded during dolomitization. Very little has been published about Ba in marine carbonates, but a similar argument could be made in view of the much larger ionic radius of Ba^{2+} (1.34 Å). This would be expected to cause an even stronger exclusion of Ba than of Sr, in agreement with its greater degree of enrichment in the effluents. The observed order of enrichments ($\text{Ca} < \text{Sr} < \text{Ba} < \text{Ra}$) must be interpreted with caution however, since, while they are all probably related to the dolomitization process, the mechanism may be different for each element. For instance, it would appear more probable that the source of Ba in the effluents is gypsum dissolution (see section 5.2). *Fanning et al.* [1981] pointed out that the different degrees of enrichment of ^{228}Ra and ^{226}Ra , which respectively derive from ^{232}Th and ^{238}U decay, indicate a source material with a low Th/U ratio, more likely to be limestone than clay, although the removal of both U and phosphate from the spring effluents may be due to U sequestration in apatite.

[41] If we assume, as *Breland* [1980] and *Fanning et al.* [1981] did, that Na (and Cl) are unaltered by interactions between warm seawater and the limestone of the Florida Plateau, then the Mg/Na, Sr/Na, and Ba/Na ratios in Figure 3 are consistent with chemical evolution of the geothermal fluids due to dolomitization, going from south to north. Since this matches the direction of convective motion in the model of *Kohout* [1965, 1967], the observed trends moreover suggest progressive dolomitization (always viewed here from the perspective of the solution phase) along the flow path of warm seawater beneath the Florida Plateau. A stoichiometric replacement of Mg for Ca as in reaction (1) would lead to an expected trend of the Ca/Na ratio opposite to that of the Mg/Na ratio, which is clearly not the case (Figure 3).

[42] The situation is even more complicated for the effluents of WMS and CBS, which appear to be mixtures of seawater (possibly altered by dolomitization) and fresh groundwater from the Floridan Aquifer System. The latter dominates in the CBS effluent, which has a major ion composition that is completely different from the ambient seawater and is also strongly enriched in Sr and Ba (Table 4). The WMS effluent has a salinity that is only half that of the submarine springs and the ambient seawater. However, it is neither diluted seawater, nor is its composition quite like that of the submarine springs. The WMS effluent is depleted in K by almost 7%. It is more strongly depleted in Mg than the submarine springs, more strongly enriched in SO_4 , and much more strongly enriched in Ca. Its Sr and Ba concentrations are higher than in any of the other springs, including CBS. The Ca concentration of the WMS effluent, which is higher than that of standard seawater even though its salinity is only about 17, indicates that there must be additional sources of Ca.

5.2. Calcium Mass Balance

[43] If the compositions of the submarine spring effluents truly reflect various degrees of marine limestone dolomitization with seawater as the source of Mg, then, according to reaction (1), for each mole of Mg removed a mole of Ca should be released. In other words

$$[\text{Ca}^{2+}]_{\text{exc}} = [\text{Mg}^{2+}]_{\text{def}}, \quad (2a)$$

where the excess (exc) and deficit (def) are the concentrations of Ca and Mg (in mol/L) in the effluent above and below their concentrations in seawater of the same salinity (based on the concentration of Na or Cl in the effluent). It is immediately clear from Figure 3 that equation (2a) cannot be true for all of the submarine springs, since $[\text{Mg}^{2+}]_{\text{def}}$ increases steadily from south to north, whereas $[\text{Ca}^{2+}]_{\text{exc}}$ remains more or less constant.

[44] *Breland* [1980] argued that additional Ca might be derived from the dissolution of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), a common accessory mineral in the limestone of the Florida Plateau, probably of evaporitic origin [*Randazzo and Hickey*, 1978; *Randazzo and Cook*, 1987]. Seawater is strongly undersaturated with respect to gypsum [e.g., *Krumgalz et al.*, 1999] and the temperature dependence of gypsum solubility is small at 25°C [*Martell and Smith*, 1982], suggesting that the warm, seawater-like geothermal fluids may be undersaturated as well. Gypsum dissolution,

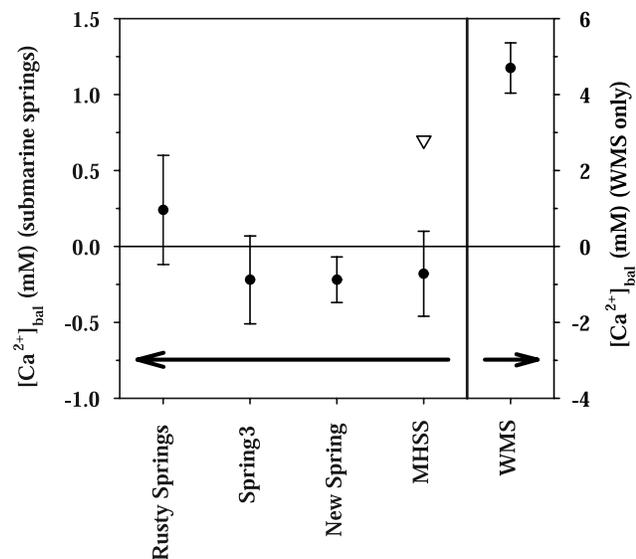


Figure 4. The calcium mass balance, expressed as $[Ca^{2+}]_{bal}$ calculated from equation (3), for the submarine springs and WMS. A value equivalent to zero indicates that Ca enrichment in the corresponding spring effluent is fully accounted for by a combination of dolomitization and gypsum dissolution. The open triangle is $[Ca^{2+}]_{bal}$ for MHSS as calculated by *Breland* [1980]; no analytical uncertainty was reported for this value, but the error bar is probably within the size of the symbol. The arrows and vertical line emphasize that the submarine springs and WMS data are shown on separate ordinates.

releasing a mole of SO_4 for every mole of Ca released, could furthermore explain the SO_4 enrichment of the spring effluents. Assuming that dolomitization and gypsum dissolution are the only two sources of the Ca enrichment, equation (2a) is modified to

$$[Ca^{2+}]_{exc} = [Mg^{2+}]_{def} + [SO_4^{2-}]_{exc}, \quad (2b)$$

where subscripts have the same meaning as in equation (2a). To test whether the assumption is valid, a Ca balance term, $[Ca^{2+}]_{bal}$, can be defined as the difference between the two sides of equation (2b):

$$[Ca^{2+}]_{bal} = [Ca^{2+}]_{exc} - [Mg^{2+}]_{def} - [SO_4^{2-}]_{exc}. \quad (3)$$

If the Ca enrichment of the submarine spring effluents is indeed completely accounted for by the independent processes of dolomitization and gypsum dissolution, the Ca mass balance should be closed and $[Ca^{2+}]_{bal} = 0$. Calculations were performed for the submarine springs and for WMS and the results are shown graphically in Figure 4. Errors were estimated from the precisions of the ion/ion ratios in Table 4. Within analytical uncertainty, it appears that $[Ca^{2+}]_{bal} = 0$ for each of the submarine springs, most likely including New Spring for which the precision is based on duplicate analyses of a single sample and thus probably underestimated. This result is in disagreement with that of *Breland* [1980], who was unable to fully account for the Ca enrichment observed at MHSS and found $[Ca^{2+}]_{bal} \sim$

0.7 mM. *Breland* [1980] did not give errors with his chlorinity-normalized concentrations, but in view of the greater sensitivity of his technique, the analytical uncertainty is probably smaller than ours, indicating that his $[Ca^{2+}]_{bal}$ is significantly different from zero. The comparison in Table 4 suggests that this discrepancy is due to the higher Ca enrichment found by *Breland* [1980]. Since our Ca/Na ratio in the ambient seawater is statistically identical to that in standard seawater, we have confidence in our results for the submarine springs. On the other hand, the sensitive technique used by *Breland* [1980] suggests that his results are reliable too. The higher Ca concentrations may be due to a sampling artifact. The difficulty of excluding resuspended limestone sediment from effluent samples was discussed in section 2, yet *Breland* [1980] does not mention whether his samples were filtered.

[45] Figure 4 shows that the WMS effluent contains nearly 5 mM excess Ca that is not accounted for by dolomitization or gypsum dissolution. The low salinity (~ 17) of the WMS effluent indicates that it is a mixture of seawater (or spring effluent) and probably fresh groundwater from the Floridan Aquifer System. *Back and Hanshaw* [1970] and *Badiozamani* [1973] have shown that such mixing can result in a solution that is undersaturated with respect to calcium carbonate, even if both end members are saturated. The residual Ca may thus be due to additional dissolution of limestone after mixing.

5.3. Mineral Solubilities and the Origin of Spring Effluent Compositions

[46] The observations discussed above provide compelling evidence that the composition of the submarine spring effluents is the result of a dolomitization process that has modified fluids of seawater composition to various extent as the fluids travel north in contact with the limestone of the Florida Plateau. Reaction (1) explains the depletion of Mg and the simultaneous enrichments of Ca, Sr, and possibly Ba. In addition, various degrees of gypsum dissolution fully account for the remainder of the Ca enrichment and the enrichments of SO_4 and possibly Ba. Neither of these processes appears to significantly affect the concentrations of Na, K, and Cl. Other observations, such as a strong enrichment of Si, and depletions of U and phosphate, suggest that dissolution of other minerals may play a role, specifically aluminosilicates (clay) or chert, and apatite, where the latter may be a source of the pronounced ^{226}Ra enrichment [*Fanning et al.*, 1981]. It should be emphasized that, whereas dolomitization and gypsum dissolution leave a discernable signature on the chemical composition of the spring effluents, the anomalies are in most cases very subtle and not plainly evident except after very careful measurement and correction for analytical variability and changes in salinity. As was also argued by *Fanning et al.* [1981], it seems highly unlikely that solutions with these compositions could be formed in any other way than via a slight modification of seawater by dolomitization. Although concentrated brines occur at depth in various strata below South Florida [*Manheim and Horn*, 1967], these often have compositions very different than seawater. Hence a simple dilution of these brines or, alternatively, partial dissolution of the evaporites from which they were formed, would almost certainly not yield effluents with the compositions found here.

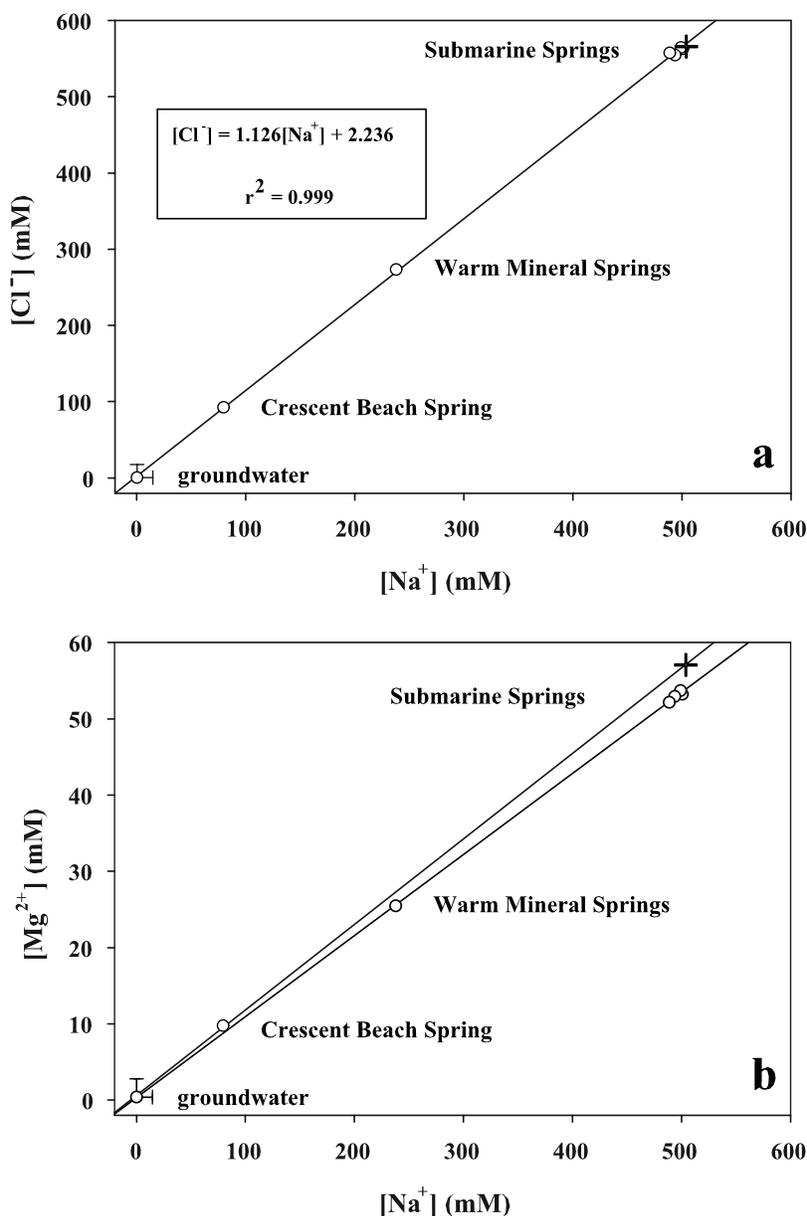


Figure 5. Mixing lines defined by the Na^+ and (a) Cl^- or (b) Mg^{2+} concentrations of fresh groundwater from the Floridan Aquifer System and of all spring effluents analyzed in this work (Table 3). The crosses represent ambient seawater. Points labeled “groundwater” are the median of 18 samples from Central Florida, analyzed by *Back and Hanshaw* [1970] and converted to millimolar units. The small error bars on these points indicate the upper bound of each concentration range. Solid lines are linear regressions.

[47] The situation is distinctly different for the other two springs, WMS, which may be connected to the submarine spring system but has only half the salinity of seawater, and CBS, whose effluent is slightly brackish but does not appear to have a seawater-like composition. Assuming that brines do not contribute to any of the spring effluents discussed here, the two main sources of water beneath the Florida Plateau are fresh groundwater from the Floridan Aquifer System and seawater. It is instructive to ascertain whether the compositions of WMS and CBS can be explained as simple mixtures of these components. In Figure 5a, Na concentrations are plotted against Cl for WMS, CBS, and the submarine springs. It is immediately clear that all springs fall on a mixing line between the two end members,

which are represented by published analyses of groundwaters from Central Florida [*Back and Hanshaw*, 1970] and by our own analyses of ambient seawater. Since neither Na nor Cl are affected by dolomitization, a further refinement can be made by plotting Na against Mg, the best indicator of dolomitization, as is shown in Figure 5b. It confirms that CBS is a simple mixture of groundwater and seawater, but WMS appears to be a mixture of groundwater and spring effluent, and may thus indeed be connected to the submarine springs system. These results make sense from a geophysical standpoint, since CBS is fed by fresh groundwater emerging into the coastal ocean, thereby turning slightly brackish from mixing with ambient seawater, whereas WMS is a geothermal, saline spring that emerges

Table 6. Concentrations of the Major Ions (mM) and Sr (μM) in Fresh Groundwater From the Floridan Aquifer System (A), in Ambient Seawater (B), and in Mud Hole Submarine Springs (C)^a

| Ion | A-Aquifer ^b | B-Seawater ^c | C-MHSS | Mixture 1 (84%A + 16%B) | Mix1/CBS, % | Mixture 2 (52%A + 48%C) | Mix2/WMS, % |
|-------------------------------|------------------------|-------------------------|--------|----------------------------|----------------|----------------------------|----------------|
| Na ⁺ | 0.32 (0.14–14.8) | 504 | 501 | 81.0 | 102 | 241 | 101 |
| K ⁺ | 0.023 (0.005–0.31) | 10.9 | 10.8 | 1.77 | 120 | 5.18 | 108 |
| Mg ²⁺ | 0.40 (0.09–2.8) | 57.1 | 53.2 | 9.48 | 97 | 25.8 | 101 |
| Ca ²⁺ | 1.4 (0.62–3.6) | 11.1 | 14.5 | 2.99 | 43 | 7.70 | 61 |
| Cl ⁻ | 0.28 (0.11–17.4) | 566 | 563 | 90.8 | 98 | 270 | 99 |
| SO ₄ ²⁻ | 0.39 (0–4.8) | 29.3 | 29.6 | 5.02 | 63 | 14.4 | 80 |
| Sr ²⁺ | 2 | 88.3 | 149 | 14.5 | 15 | 71.8 | 20 |

^aCBS and WMS compositions fall on mixing lines between A and B, and between A and C, respectively, with respect to Na and Mg (Figure 5). Two linear mixtures were determined that best reproduce the Na, Mg, and Cl concentrations of CBS and WMS. Element-by-element ratios, expressed as a percentage, correspond to the fractions of the CBS and WMS major ion and Sr concentrations (Table 3) that are explained by these mixtures. Fractions substantially below or above 100% may indicate dissolution or precipitation of minerals. Barium, which does not behave conservatively in the marine environment, was excluded from the calculations.

^bMedian and range of 18 groundwaters from Central Florida [Back and Hanshaw, 1970], except Sr, which is an upper bound value [Katz et al., 1997].

^cAverage composition of the three ambient seawater samples.

on land and probably interacts with groundwater from the Floridan Aquifer System. The other submarine springs presumably lie outside its influence [Hanshaw et al., 1971]. Based on the results for Na, Mg, and Cl, we can construct mixtures between the two pairs of end members that reproduce the concentrations of these elements in the CBS and WMS effluents (Table 6). A mixture of 84% groundwater and 16% seawater, and a mixture of 52% groundwater and 48% MHSS effluent closely match the compositions of CBS and WMS, respectively, as the concentrations of Na, Mg, and Cl are all reproduced within 1–3% for both springs. Note that the temperature of WMS, a nearly 1:1 mixture of groundwater and MHSS effluent, falls almost exactly in between those of the end members (taking the median groundwater temperature from Back and Hanshaw [1970]). Comparing the composition of these two mixtures with the actual measured compositions, it follows that CBS is enriched in Ca and SO₄ with respect to the corresponding mixture by a factor of about 2, and in Sr by a factor of about 7 (Table 6). WMS is slightly enriched in SO₄ with respect to the corresponding mixture, in Ca by about a factor of 2, and in Sr by more than a factor of 5. Barium was excluded from these calculations, because its concentration in two of the end members is either unknown or highly variable.

[48] In order to explain some of the remaining anomalies we have calculated the saturation state for CBS, WMS, and MHSS with respect to some commonly occurring minerals in the system, namely gypsum, celestite, barite (containing

Sr), aragonite, and calcite (with or without Mg). Saturation states with respect to dolomite were not determined, because of the lack of suitable solubility data as functions of ionic strength and temperature, as well as the highly variable stoichiometry and crystallinity of Florida dolomites [Hanshaw et al., 1971]. Solubility product data were taken from the literature and corrected for both salinity (ionic strength) and temperature. Temperatures for CBS, WMS, and MHSS effluents, were taken from Swarzenski et al. [2001], Scott et al. [2004], and Fanning et al. [1981], respectively. All solubility products are stoichiometric i.e., expressed in terms of total concentrations, so that they can be directly utilized without the need for rigorous speciation modeling. Saturation states are therefore determined by comparison with ion concentration products, rather than ion activity products, and the results are shown in Table 7. All three springs are undersaturated with respect to gypsum by factors of 3–5. Interestingly, while MHSS is undersaturated with respect to both celestite and Sr-barite, CBS is saturated with respect to Sr-barite, and WMS with respect to both. Shaw et al. [1998] have claimed evidence for barite supersaturation in saline groundwaters of the South Atlantic Bight by an order of magnitude or more, yet they report no sulfate concentrations and give few details of their thermodynamic calculations. It seems implausible that a poorly soluble mineral like barite could remain so supersaturated in the presence of the profusion of nucleation sites available on the surfaces of the aquifer's limestone substrate. This suggests that the higher Ba concentration for CBS reported

Table 7. Saturation State of CBS, WMS, and MHSS, With Respect to the Minerals Gypsum (CaSO₄·2H₂O), Celestite (SrSO₄), Barite (BaSO₄), and Various Forms of Calcium Carbonate (CaCO₃)^a

| Mineral | Solubility Product | | | Ion Concentration Product | | | Ω | | |
|------------|-----------------------|-----------------------|-----------------------|---------------------------|-----------------------|-----------------------|-------------|-------------|-------------|
| | CBS | WMS | MHSS | CBS | WMS | MHSS | CBS | WMS | MHSS |
| Gypsum | 3.0×10^{-4} | 7.1×10^{-4} | 1.3×10^{-3} | 5.5×10^{-5} | 2.3×10^{-3} | 4.3×10^{-4} | 0.18 | 0.32 | 0.33 |
| Celestite | 2.97×10^{-6} | 6.58×10^{-6} | 1.31×10^{-5} | 7.76×10^{-7} | 6.42×10^{-6} | 4.41×10^{-6} | 0.26 | <u>0.98</u> | 0.34 |
| Sr-barite | 1.84×10^{-9} | 5.27×10^{-9} | 1.34×10^{-8} | 2.06×10^{-9} | 5.74×10^{-9} | 7.23×10^{-9} | 1.11 | <u>1.09</u> | 0.54 |
| Calcite | 5.51×10^{-8} | 1.76×10^{-7} | 4.20×10^{-7} | 5.62×10^{-8} | 1.44×10^{-7} | 5.40×10^{-7} | <u>1.02</u> | <u>0.82</u> | <u>1.29</u> |
| Mg-calcite | 9.97×10^{-8} | 2.63×10^{-7} | 5.21×10^{-7} | 5.62×10^{-8} | 1.44×10^{-7} | 5.40×10^{-7} | <u>0.56</u> | 0.55 | <u>1.04</u> |
| Aragonite | 9.69×10^{-8} | 2.85×10^{-7} | 6.14×10^{-7} | 5.62×10^{-8} | 1.44×10^{-7} | 5.40×10^{-7} | 0.58 | 0.51 | <u>0.88</u> |

^aSr-barite and Mg-calcite contain minor amounts of Sr and Mg, respectively. Solubility product data from Krumgalz et al. [1999] (gypsum), Rushdi et al. [2000] (celestite and Sr-barite), Plath et al. [1980] (Mg-calcite), and Mucci [1983] (calcite and aragonite). All solubility products are based on total concentrations. Ion concentration product (ICP) based on total cation and anion concentrations calculated from data in Table 3 (see text for total carbonate concentrations). Saturation state Ω is the ratio of the ICP and the solubility product, where values larger and smaller than 1 represent supersaturation and undersaturation with respect to the corresponding mineral, respectively. Solutions near or above saturation are underlined for emphasis.

by *Swarzenski et al.* [2001] as well as the higher Sr concentration for WMS reported by *Scott et al.* [2004] may be in error. Whereas the applicability of the data of *Rushdi et al.* [2000] does not extend down to the salinity of CBS, additional data from *Templeton* [1960] for pure barite indicate an even greater degree of saturation.

[49] Saturation with respect to calcium carbonate was calculated for both pure aragonite and pure calcite, and also for calcite containing Mg. While MHSS and CBS are close to or above saturation for two of these forms, WMS is significantly undersaturated for all three. This is an example where the mixing of two saturated solutions yields an undersaturated solution, as was suggested in the dolomitization model of *Badiozamani* [1973]. However, this model has been partly refuted (see section 1) and we do not mean to imply that mixing of the two end members is driving dolomitization in this case. Total carbonate concentrations used to calculate the ion concentration product were derived from the following equation [*Mucci, 1983*]:

$$[\text{CO}_3^{2-}]_{\text{T}} = \frac{A_{\text{c}}}{2 + \left(\frac{10^{-\text{pH}}}{K_2}\right)}, \quad (4)$$

where A_{c} is the carbonate alkalinity and K_2' is the apparent second carbonic acid deprotonation constant in seawater. The latter was calculated as a function of salinity and temperature from the data of *Mojica Prieto and Millero* [2002]. Alkalinities for CBS, WMS, and MHSS were taken from *Toth* [1999], *Scott et al.* [2004], and *Fanning et al.* [1981], and converted to molar units. All were assumed to be total alkalinities, A_{T} . Insufficient data are available to estimate borate alkalinities (the largest noncarbonate contribution to A_{T}), but the corrections are probably small. Consequently, total alkalinity was substituted for A_{c} in equation (4). Further uncertainty is introduced because pH values, taken from the same references, were measured with different techniques and may not be expressed on the same pH scale as the constants of *Mojica Prieto and Millero* [2002]. Ion concentration products for carbonate minerals in Table 7 must thus be viewed as approximations. The uncertainty in the ion concentration products for sulfate minerals is probably no greater than 3%. Some uncertainty is also inherent in the calculation of the solubility products, estimated in the original publications as ~5% for the carbonate and ~10% for the sulfate minerals. Taken together, these uncertainties are not large enough to significantly alter our conclusions.

[50] Based on these calculations the effluent compositions of the various springs can be rationalized as follows. CBS is a submarine freshwater spring that is fed by groundwater from the Floridan Aquifer System. Its effluent is made slightly brackish by a small admixture (~16%) of seawater. Dissolution of gypsum probably accounts for the enrichments of Ca and SO_4 . Since the Ca enrichment is somewhat greater than that of SO_4 (Table 6), additional Ca may derive from limestone dissolution. While the effluent is nearly saturated with respect to calcite, it is undersaturated with respect to magnesian calcite (Table 7). Since magnesian calcite contains only a small amount of Mg, its dissolution would probably not appreciably alter the Mg concentration of the effluent. Strontium and barium are both strongly

enriched in the effluent, which is actually saturated with respect to strontian barite (but not celestite). Since the CBS effluent is not affected by dolomitization, the source of these enrichments must be gypsum or limestone dissolution.

[51] The submarine spring effluents consist of seawater that has been modified by dolomitization, causing simultaneous enrichment of Ca and depletion of Mg. Additional Ca enrichment and enrichment of SO_4 can be quantitatively accounted for by gypsum dissolution (Figure 4). Sr and Ba enrichments follow the trend of increasing dolomitization from south to north, but neither reaches saturation with respect to its sulfate salt (Table 7). These enrichments must therefore be predominantly due to the dolomitization process, although gypsum dissolution may contribute as well. This suggests that Florida limestone contains significant quantities of both Sr and Ba and may be their main source in the CBS effluent. The WMS effluent appears to be an almost 1:1 mixture of submarine spring effluent (as represented by the MHSS composition) and fresh groundwater with which it interacts on its way up through the Floridan Aquifer System. The effluent contains more Ca than such a mixture would suggest (Table 6) and this is again due to limestone dissolution, as the effluent is undersaturated with respect to all three forms of calcium carbonate (Table 7). This dissolution in turn could explain the very high enrichments of Sr and Ba. In this case the Sr enrichment actually surpasses the Ba enrichment, which is limited by supersaturation with respect to (strontian) barite, until it is itself limited by supersaturation with respect to celestite (Tables 3 and 7).

[52] It must be noted that it is implied here that chemical evolution of the geothermal fluids does not progress past the composition of MHSS. Extrapolating from the curves in Figure 3 to the more northerly location of WMS, the modified seawater end member should be much more depleted in Mg and enriched in Sr and Ba (and possibly Ca). Of course, Sr and Ba concentrations would be buffered by supersaturation long before the extrapolated values were reached. Still, one might predict the WMS effluent to be more Mg-depleted than it actually is. Such an increased depletion of Mg could however be partially offset by limestone dissolution, contributing Mg. Alternatively, chemical gradients in the submarine springs area may reflect locally strong thermal or mineralogical gradients. With multiple processes occurring independently (mixing, dolomitization, gypsum and limestone dissolution, celestite and barite precipitation) and without more detailed knowledge of the dolomitization process and the compositions of the minerals involved, the system is simply not sufficiently constrained to distinguish between various possibilities. Similar problems were encountered by *Stüben et al.* [1996], who attempted to ascertain the chemical origin of warm spring effluents on the west coast of Italy. *Stüben et al.* [1996] modeled the effluents as a warm mixture of fresh groundwater and seawater modified by dolomitization, further altered by mineral dissolution/precipitation, a system much like the one described here. Unfortunately, the fluids sampled by *Stüben et al.* [1996] were strongly diluted with ambient seawater and, unlike the present case, the composition of the pure effluent could not be exactly determined. *Stüben et al.* [1996] tried to circumvent the issue by making the somewhat questionable assumption that dolomitization depletes Mg to zero in the modified seawater end member.

With this assumption they arrived at an end member temperature of 50.5°C and an end member Si concentration of 851 μM , almost an order of magnitude higher than Si concentrations found for the submarine springs by *Fanning et al.* [1981].

6. Conclusions

[53] In this work we have presented a refinement of the dolomitization model for the composition of geothermal, saline, submarine springs by *Fanning et al.* [1981], which in turn was based on the circulation model of *Kohout* [1965, 1967]. We have shown that enrichments of the alkaline earth elements increase in the order $\text{Ca} < \text{Sr} < \text{Ba} < \text{Ra}$. These enrichments (as well as the Mg depletion), and consequently the dolomitization by which they are caused, appear to progress in the direction of flow from south to north and Warm Mineral Springs may well be physically or chemically connected to this system. This accounts for a spatial progression of spring effluent compositions, which are however remarkably stable through time on a scale of decades. We have also shown that the compositions of all these springs can be modeled as mixtures of two out of three end members: fresh groundwater, seawater, and seawater modified by dolomitization (spring effluent). The concentrations of certain elements are further modified by dissolution or precipitation of common minerals like limestone, gypsum, celestite, and barite.

[54] A major barrier to a deeper understanding of the composition of these spring effluents is the lack of a full description of all processes and minerals involved. This may be partially addressed by studies of additional potential elemental enrichments and depletions, some of which (e.g., silicate, borate, phosphate, radium, and uranium) have already been reported, while others (e.g., iron, manganese, trace metals) remain to be determined. A prime impediment is insufficient knowledge of the age, provenance, path, and flow rate of the seawater that forms the spring effluents, and of the composition of the minerals with which it interacts. This knowledge is difficult to acquire by virtue of the great depth at which these processes take place. New insight is expected from isotopic analyses, such as $^{87}\text{Sr}/^{86}\text{Sr}$, ^3H , or $\Delta^{14}\text{C}$, to determine age and provenance of the water [*Katz and Bullen*, 1996; *Katz et al.*, 1997] and $\delta^{18}\text{O}$, $\delta^{13}\text{C}$, or $\delta^{34}\text{S}$, to determine the contributions of biotic processes (organic matter oxidation, sulfate reduction, nutrient uptake) versus abiotic processes (mineral dissolution/precipitation) [*Einsiedl and Mayer*, 2005].

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