Geochemistry of Fluoride in the Black Creek Aquifer System of Horry and Georgetown Counties, South Carolina—and its Physiological Implications

By ALLEN L. ZACK

UNITED STATES DEPARTMENT OF THE INTERIOR

CECIL D. ANDRUS, *Secretary*

GEOLOGICAL SURVEY

H. William Menard, *Director*

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By ALLEN L. ZACK

ABSTRACT

High concentrations of fluoride in ground-water supplies in certain areas of Horry and Georgetown Counties, S.C., have been the cause of dental fluorosis (tooth mottling) among persons who have lived in these areas and have ingested the water as children.

Geochemical evidence and laboratory experiments demonstrate that fluorapatite in the form of fossil shark teeth is the source of fluoride, and that the fluoride ions are liberated to the ground-water system through anion exchange, rather than by dissolution.

Calcite-cemented quartz sand in the upper third of the Black Creek Formation of Late Cretaceous age contains the fossil shark teeth. As ground water progresses downdip, the calcite matrix dissolves and hydrolyzes, releasing bicarbonate, hydroxyl, and calcium ions. The calcium ions are immediately exchanged for sodium ions adsorbed on sodium-rich clays, and the bicarbonate ions accumulate. As the shark teeth are exposed, the hydroxyl ions in solution exchange with fluoride ions on fluorapatite surfaces.

Experiments using fossil shark teeth show that sodium chloride in solution inhibits the rate of exchange of fluoride ions from tooth surfaces for hydroxyl ions in solution. The amount of fluoride removed from water and exchanged for hydroxyl ions in the presence of pure hydroxylapatite (hog teeth) was greater in saline water than in freshwater.

INTRODUCTION

The source of fluoride in water withdrawn from the Black Creek aquifer system of Horry and Georgetown Counties, S.C. (fig. 1), has long been the subject of conjecture among geohydrologists. Because the concentration of fluoride in ground water is generally high throughout the two-county area, but differs from place to place, researchers have speculated that there is a relationship between the mineralogic composition of aquifer sediments and the amount of fluoride present in water withdrawn from those

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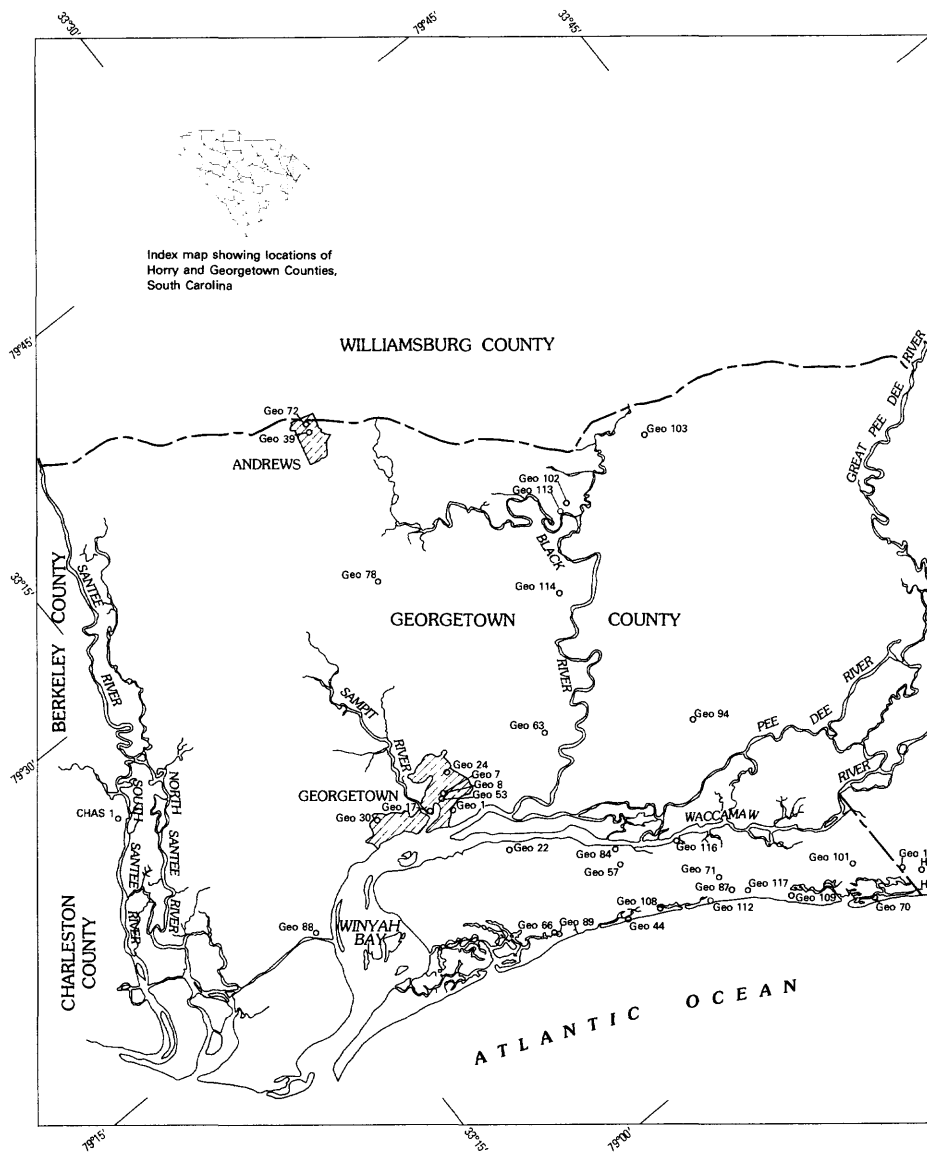
FIGURE 1.—Horry and Georgetown Counties, S.C., and vicinity, showing
prefixes indicate county location in South Carolina. North
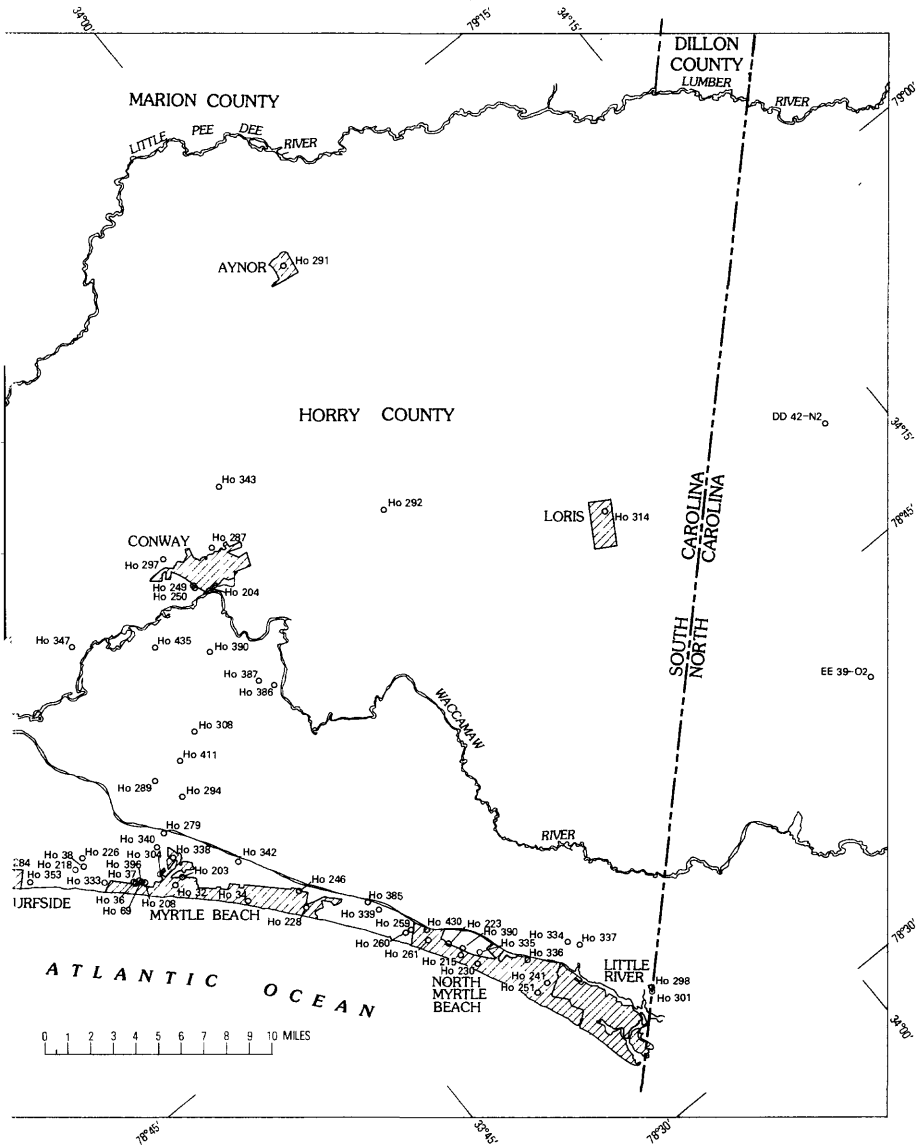
·incipal geographic features and well locations. Well number
·rolina wells numbered according to State system.

sediments. It was believed that fluoride-bearing minerals slowly dissolved, releasing fluoride to percolating ground water.

Geochemical evidence presented in this report demonstrates that fluorapatite is the mineral responsible for the occurrence of fluoride in the Black Creek aquifer system, but suggests that anion exchange, rather than solution, is the mechanism by which fluoride ions are released to the ground water.

This investigation is part of a continuing cooperative program between the South Carolina Water Resources Commission and the U.S. Geological Survey to study the ground-water resources of South Carolina.

ACKNOWLEDGMENTS

PHYSIOLOGICAL EFFECTS OF HIGH FLUORIDE CONCENTRATIONS IN THE WATER SUPPLY

High concentrations of fluoride in ground-water supplies in certain areas of Horry and Georgetown Counties, S.C., have been the cause of dental fluorosis (tooth mottling) among persons who have lived in these areas and have ingested the water as children. The mottling appears in the tooth enamel as horizontal brown discolorations, roughly indicating growth stages of the teeth. Occasional cases of dental fluorosis of the incisal edges of deciduous teeth indicate that during early tooth formation in the womb,

fluoride ions may cross the placental barrier (Jack Markusen, D.D.S., oral commun., April 30, 1978).

The U.S. Environmental Protection Agency (EPA) and the South Carolina Department of Health and Environmental Control (SCDHEC) state that the amount of water (and consequently the amount of fluoride) ingested by children is primarily influenced by air temperature, and that the higher the concentration of fluoride in the water, the greater the propensity for tooth mottling. "Based on present Environmental Protection Agency guidance, the Water Supply Division of the South Carolina Department of Health and Environmental Control anticipated the MCL (Maximum Concentration Limit) for fluoride concentration in public water supplies to be 1.6 ppm [parts per million] for the Coastal Areas of South Carolina" (Lewis Shaw, SCDHEC, written commun., June 1976). This limit is determined from MCL fluoride data contained in the National Interim Primary Drinking Water Regulations published in the "Federal Register" on December 24, 1975, and is based on an average maximum daily air temperature of 73° to 75°F (22.8° to 23.9°C). Concentrations greater than 1.6 mg/L (milligrams per liter) presumably cause dental fluorosis (tooth mottling) in young children. The 1.6 mg/L MCL has been in effect since June 1977. However, the limit is presently under review (1978) because of considerable evidence that higher fluoride concentrations are not epidemiologically damaging. Until the debate is resolved, the SCDHEC is issuing exemptions until January 1, 1981, for fluoride concentrations as great as 7.0 mg/L. It is possible that either the fluoride MCL will be raised to a new primary standard or that the MCL will be kept at 1.6 mg/L, but will be designated a secondary standard (Lewis Shaw, oral commun., August 1978).

Epidemiological studies where water is naturally high in fluoride (10.0 mg/L or less) indicate that dental fluorosis is solely a cosmetic problem. "According to the National Academy of Sciences, the daily intake required to produce symptoms of chronic toxicity after years of consumption is 20 to 80 milligrams or more —far in excess of the average intake in the U.S. Such heavy doses are associated with water supplies that contain at least 10 ppm. of natural fluoride * * *" (Consumer Reports, August 1978, p. 480).

Dentists practicing in Horry County have observed that individual tolerances to mottling vary; in fact, cases are known of identical twins experiencing different levels of dental fluorosis (S. N. Saleeby, D.D.S., oral commun., 1978). In the study area,

it has been observed that high-fluoride water (as great as 5.0 mg/L) often has no mottling effect on children; yet,in other cases, mottling has occurred where fluoride concentration is as low as 1.5 mg/L.

Fluoride concentrations of 1.0 to 1.5 mg/L in the water supply have been shown to be beneficial in helping to prevent tooth decay. "It has been shown epidemiologically that school children using domestic waters containing as little as about one part per million of fluorine [sic] experience only half to a third as much dental decay as comparable groups using fluorine-free [sic] waters * * *" (H. T. Dean quoted in Carlston, 1942, p. 9). There are numerous other studies that prove the desirability of fluoride in water supplies as an aid in preventing tooth decay (Consumer Reports, July 1978, p. 392–396, and August 1978, p. 480–482 and American Academy of Pedodontics, 1976, p. 6–29).

GEOLOGIC FRAMEWORK

The highest concentration of fluoride is encountered in water samples withdrawn from sands of the Black Creek aquifer system, the preferred source of drinking water in Horry and Georgetown Counties. In most areas, the water contains more than 1.6 mg/L of fluoride, the present (1978) maximum-concentration limit allowable for public water supplies in coastal South Carolina.

Geologic samples and borehole cores have shown that the Black Creek Formation of Late Cretaceous age contains thin continuous layers of hard calcite-cemented quartz sand in addition to alternating thin beds of unconsolidated quartz sand and sodium-rich clay. The depositional environment was marine and marginal marine; carbonaceous material and lignite occur throughout the formation.

Drillers' logs and geophysical logs indicate that the calcite-cemented quartz sand is widespread throughout Horry and Georgetown Counties and is particularly abundant in the upper third of the Black Creek Formation. Fossil shark teeth, which contain cryptocrystalline fluorapatite, $Ca_5(PO_4)_3F$, are common within the cemented sand. Under certain environmental conditions, the fossil shark teeth release fluoride ions to the associated ground water.

Shark teeth are not very common within unconsolidated sand or clay. However, the unconsolidated sand contains small amounts of fluorapatite, apparently as fossil remains. Experiments performed by immersing these sands in deionized (but pH-adjusted)

water have demonstrated that only small amounts of fluoride, less than 1.6 mg/L, can be released to the surrounding ground water from these sand units.

Phosphate nodules in the Black Creek sands are another source of fluoride ions. Apparently phosphate nodules do not release fluoride ions easily. Water withdrawn from mined phosphate deposits in eastern North Carolina usually contain less than 0.4 mg/L fluoride (H. B. Wilder, U.S. Geological Survey, oral commun., November 1978). The geochemical makeup of the water associated with these phosphate deposits is admittedly different from that of the Black Creek aquifer system. However, phosphate minerals do not appear to be a significant source of fluoride, wherever they occur.

Sharks and other marine animals were abundant in the shallow, continental-shelf areas of Cretaceous seas as is evidenced by the occurrence of numerous shark teeth and other fossils within the cemented sands. Possibly the teeth accumulated in the unconsolidated sands also, but subsequently, have been removed by leaching.

Goldschmidt (1954, p. 577) states that fluoride is present in much larger quantities in marine mammals, fishes, and birds, than in their terrestrial or freshwater equivalents, and that the inhabitants of brackish water have intermediate fluoride content in their bones. Of all the 57 items investigated by Klement (in Goldschmidt, 1954, p. 577), the greatest amount of fluoride was found in shark teeth. Apparently, fluoride in seawater accounts for the high amount of fluoride in the bones and teeth of marine animals. Also, bones and teeth of marine animals after death will, because of exposure to high-fluoride ocean water, incorporate additional fluoride ions into their apatite structure, producing almost pure fluorapatite (Goldschmidt, 1954, p. 578). Fossil shark teeth are black, presumably because they have been extensively "mottled" by high-fluoride water.

INTERPRETATIONS OF WATER-QUALITY DATA

Numerous water-quality samples (table 1) have been collected throughout the two-county area (fig. 1) from wells screened at various depths and stratigraphic positions (table 2) within the Black Creek aquifer system.

The water withdrawn can be classified as a sodium bicarbonate ($NaHCO_3$) type water and is generally the best of any available in the two-county area. However, relatively high concentrations

TABLE 1.—Chemical analyses of water samples withdrawn from sands of the Black Creek aquifer system

[Results in milligrams per liter, except as indicated.]

Well Number	Fluoride (F)	pH (Units)	Alkalinity	Bicarbonate (HCO3)	Carbon Dioxide (CO2)	Total Hardness	Calcium (Ca)	Magnesium (Mg)	Dissolved Solids	Specific Conductance (Micromhos at 25° C)	Temperature (Degrees Celsius)	Chloride (Cl)	Sulfate (SO4)	Silica (SO2)	Sodium (Na)	Potassium (K)	Total Iron (Fe)	Dissolved Iron (Fe)	Manganese (Mn)	Strontium (Sr)	Bromide (Br)	Total Aluminum (Al)	Dissolved Aluminum (Al)	Phosphorus (PO4)
HO-32	4.3	8.1	528	644	—	11	3.4	0.6	786	1320	—	124	0.2	15	314	6.1	0.24	0.04	—	—	—	—	—	—
HO-34	4.6	8.0	560	683	—	14	2.9	1.4	769	1300	—	90	0.2	17	312	3.8	0.05	—	—	—	—	—	—	—
HO-36	3.0	8.3	458	559	—	9	2.1	0.9	—	—	—	36	0.5	15	—	—	—	0.08	—	—	—	—	—	—
HO-37	4.6	7.9	531	648	—	12	2.9	0.9	670	1110	—	53	0.2	16	270	2.5	0.02	—	—	—	—	—	—	—
HO-38	3.3	8.4	439	535	—	9	2.2	1.8	—	—	—	38	0.7	13	—	—	—	0.10	—	—	—	—	—	—
HO-69	4.5	8.1	517	630	—	18	4.4	1.3	—	1140	—	61	1.9	19	—	—	0.41	0.04	—	—	—	—	—	—
HO-203	5.1	8.3	543	662	—	12	2.8	1.0	762	1280	—	94	0.4	16	308	7.5	—	0.09	—	—	—	—	—	—
HO-204	1.9	8.2	427	520	—	10	2.4	0.9	628	1060	—	95	3.8	13	250	3.0	—	0.01	—	—	—	—	—	—
HO-206	4.5	7.9	538	656	—	14	3.6	1.0	852	1440	—	155	0.4	16	342	6.3	0.09	—	—	—	—	—	—	—
HO-215	4.5	7.8	595	725	—	16	4.8	1.4	1110	1880	—	270	1.9	17	440	9.5	0.10	0.04	—	—	—	—	—	—
HO-223	5.5	8.0	595	726	—	18	4.6	1.8	1030	1800	—	225	0.4	18	408	9.5	0.81	—	—	—	—	—	—	—
HO-224	4.4	8.6	479	584	—	16	3.2	0.5	663	1190	—	72	0.2	10	280	3.4	0.21	—	—	—	—	—	—	—
HO-226	2.8	8.6	551	563	21	12	5.0	1.1	531	1071	—	79	1.3	14	280	3.7	0.41	—	—	—	—	—	—	—
HO-228	4.4	8.3	523	638	—	13	3.0	2.7	827	1400	—	150	1.1	15	332	5.0	0.10	0.09	—	—	—	—	—	—
HO-230	5.5	8.0	586	714	—	24	5.0	2.6	1010	1640	—	216	0.1	19	398	14.0	—	0.10	—	—	—	—	—	—
HO-241	4.0	7.6	591	720	—	26	5.6	1.0	1170	2080	—	304	24.0	16	450	12.0	1.20	—	—	—	—	0.20	—	—
HO-246	5.0	7.5	555	677	0	10	2.5	1.0	822	1340	—	128	0.4	15	328	6.8	1.70	—	—	—	—	0.20	—	—
HO-249	2.0	8.1	429	523	0	12	2.9	1.0	603	1050	—	80	4.0	12	240	2.8	0.24	—	—	—	—	0.10	—	—
HO-250	2.1	8.3	431	513	6	10	2.9	0.6	594	1050	—	81	3.2	12	230	2.8	0.46	—	—	—	—	0.10	—	—

TABLE 1.—Chemical analyses of water samples withdrawn from sands of the Black Creek aquifer system—Continued

Well Number	Fluoride (F)	pH (Units)	Alkalinity	Bicarbonate (HCO₃)	Carbon Dioxide (CO₂)	Total Hardness	Calcium (Ca)	Magnesium (Mg)	Dissolved Solids	Specific Conductance (Micromhos at 25°C)	Temperature (Degrees Celsius)	Chloride (Cl)	Sulfate (SO₄)	Silica (SiO₂)	Sodium (Na)	Potassium (K)	Total Iron (Fe)	Dissolved Iron (Fe)	Manganese (Mn)	Strontium (Sr)	Bromide (Br)	Total Aluminum (Al)	Dissolved Aluminum (Al)	Phosphorus (PO₄)
HO-251	4.8	7.9	614	748	0	24	5.3	2.2	1200	2020	—	328	1.2	6.1	470	14.0	0.59	—	—	—	—	0.30	—	—
HO-252	2.5	7.9	432	527	0	9	1.9	0.9	642	1100	—	97	6.4	12	259	2.3	0.14	—	—	—	—	0.20	—	—
HO-259	5.4	7.6	571	696	0	16	3.0	2.1	844	1420	—	132	1.0	14	330	14.0	0.37	—	—	—	—	0.10	—	—
HO-260	5.0	7.9	576	702	15	15	3.4	1.6	1050	1710	—	254	0.8	15	420	8.0	0.51	—	—	—	—	0	—	—
HO-261	5.0	8.4	589	688	—	18	5.5	1.9	1120	1890	27	290	2.6	4.9	444	9.9	2.30	—	—	—	—	0.10	—	—
HO-279	4.1	8.1	520	630	0	11	2.5	1.1	646	950	23	41	2.6	16	260	8.0	0.05	0.04	0	—	—	0.16	0.16	—
HO-287	2.0	8.5	390	480	0	11	1.9	0.5	596	1100	—	88	11.0	13	240	2.4	0.12	0.03	—	—	—	0.08	0.04	.34
HO-289	4.4	—	492	600	—	13	2.8	0.9	670	1100	19	60	6.0	16	280	5.0	—	—	—	0.13	0.10	—	—	—
HO-291	4.3	8.8	480	590	—	26	3.1	1.3	629	1200	20	39	1.5	17	260	12.0	0.28	0.02	—	0.08	0.30	0.12	0.03	.06
HO-292	3.0	8.7	430	530	0	27	6.4	2.5	718	1200	18	140	10.0	15	270	9.2	0.14	0.02	—	—	—	—	—	.06
HO-293	3.4	9.6	457	557	—	14	7.0	2.3	561	1000	15	18	2.5	14	230	3.9	0.08	0.01	0.01	—	—	0.06	0.03	—
HO-294	4.4	8.0	520	630	—	11	2.8	1.6	703	1300	22	72	3.8	15	290	5.8	0.14	0.07	0	—	—	0.07	0.07	—
HO-297	3.6	8.0	546	666	0	50	2.7	1.0	591	1000	16	32	2.5	13	240	52.0	0.07	0.06	0.01	—	—	—	—	—
HO-298	2.8	8.0	423	516	—	56	9.6	6.3	1570	2680	21	550	5.2	16	600	26.0	—	0.10	0.29	—	1.5	—	—	—
HO-301	1.6	8.2	530	640	—	11	10.0	7.5	1700	3100	24	720	30.0	13	690	5.2	0.08	0.01	0.01	—	—	—	—	—
HO-304	5.1	8.6	580	710	0	7	2.8	0.9	744	1200	24	89	1.9	14	310	3.9	0.13	0.03	0.01	—	0.6	—	—	—
HO-305	4.2	8.2	520	600	—	9	2.0	0.6	803	1300	21	67	3.1	37	300	3.9	5.00	0.05	0	0	—	0.07	0.07	.15
HO-308	3.1	8.2	535	620	14	7	3.2	0.3	679	1050	16	66	5.0	18	270	12.0	0.13	0.02	—	—	—	—	—	—
HO-322	3.8	—	—	—	16	—	1.8	0.7	640	1150	—	440	4.6	14	560	—	—	—	0.02	—	—	—	0.02	—

TABLE 1.—Chemical analyses of water samples withdrawn from sands of the Black Creek aquifer system—Continued

Well Number	Fluoride (F)	pH (Units)	Alkalinity	Bicarbonate (HCO₃)	Carbon Dioxide (CO₂)	Total Hardness	Calcium (Ca)	Magnesium (Mg)	Dissolved Solids	Specific Conductance (Micromhos at 25° C)	Temperature (Degrees Celsius)	Chloride (Cl)	Sulfate (SO₄)	Silica (SO₂)	Sodium (Na)	Potassium (K)	Total Iron (Fe)	Dissolved Iron (Fe)	Manganese (Mn)	Strontium (Sr)	Bromide (Br)	Total Aluminum (Al)	Dissolved Aluminum (Al)	Phosphorus (PO₄)
HO-334	4.8	8.1	620	750	0	21	4.8	2.3	1160	2075	13	28	4.2	16	260	4.0	0.15	0.15	--	--	--	0.08	0.04	--
HO-337	3.2	8.3	474	578	0	27	5.3	3.4	1210	2080	2	370	3.4	12	460	35.0	--	0.02	0	--	--	--	--	--
HO-338	3.4	8.0	530	650	--	12	3.0	1.0	732	1500	18	220	3.4	15	360	4.3	0.54	0.34	--	--	--	0.07	0.07	--
HO-343	4.5	8.3	480	590	0	25	3.9	3.6	620	950	19	44	3.5	14	240	16.0	0.35	0.02	0.01	--	--	0.26	0.05	.06
HO-347	3.0	--	509	580	20	6	1.5	0.5	594	1000	19	21	3.4	15	240	3.7	0.06	0.03	--	--	--	0.08	0.02	--
HO-380	5.4	--	575	701	0	29	6.8	2.8	924	1800	18	170	3.9	14	360	15.0	0.07	0.03	0	--	--	0	0	--
HO-383	4.8	8.1	533	650	0	13	2.9	1.5	789	1400	22	120	3.0	16	310	10.0	0.15	0.05	0	--	--	0.06	0.06	--
HO-386	3.8	8.5	530	650	0	40	9.1	4.2	740	1300	17	85	3.1	18	280	16.0	0.76	0.56	0	--	--	--	--	--
HO-387	3.5	--	591	720	0	26	5.3	3.2	907	1600	15	140	3.3	19	360	18.0	0.54	0.11	0	--	--	--	--	--
HO-390	3.8	8.9	480	590	0	8	2.4	0.6	671	1200	15	71	4.3	14	280	3.6	0.30	0.02	0	--	--	0.10	0.03	.18
HO-396	4.3	--	480	590	14	10	2.3	1.0	687	1200	20	44	3.8	16	280	6.4	0.05	0.02	--	--	--	0.08	0.03	--
HO-411	3.7	8.2	480	590	0	9	2.1	0.8	616	1200	18	42	3.4	16	250	6.5	0.09	0.04	0	--	--	0.06	0.09	.03
HO-427	3.9	8.2	510	620	--	11	2.2	1.3	627	1100	22	36	2.0	17	250	8.9	0.08	0.03	--	--	--	0.06	0.06	--
HO-430	2.5	8.7	580	710	0	17	3.6	1.9	927	1700	25	180	1.8	15	360	12.0	0.14	0.05	0.01	--	1.2	--	--	.15
HO-435	3.5	7.6	510	620	--	36	6.4	4.9	641	1000	18	41	2.8	22	240	15.0	0.10	0.10	--	--	--	0.05	0.05	--
HO-436	4.5	8.1	580	710	0	12	2.4	1.4	744	1250	22.2	54	3.5	17	300	11.0	0.14	0.04	0	--	--	0.05	0.05	.06

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Well Number	Fluoride (F)	pH (Units)	Alkalinity	Bicarbonate (HCO3)	Carbon Dioxide (CO2)	Total Hardness	Calcium (Ca)	Magnesium (Mg)	Dissolved Solids	Specific Conductance (Micromhos at 25° C)	Temperature (Degrees Celsius)	Chloride (Cl)	Sulfate (SO4)	Silica (SiO2)	Sodium (Na)	Potassium (K)	Total Iron (Fe)	Dissolved Iron (Fe)	Manganese (Mn)	Strontium (Sr)	Bromide (Br)	Total Aluminum (Al)	Dissolved Aluminum (Al)	Phosphorus (PO4)
Geo-1	1.1	8.3	380	463	—	9	2.0	0.9	513	878	24.5	46	3.0	12	219	—	—	0.17	—	—	—	—	—	—
Geo-7	0.9	8.6	367	447	—	7	1.6	0.7	476	—	—	28	1.5	12	210	—	—	0.92	—	—	—	—	—	—
Geo-8	1.1	7.9	438	534	0	6	1.5	0.5	544	887	—	38	5.0	13	216	5.2	0.10	—	—	—	—	0	—	—
Geo-13	4.5	8.2	512	624	—	12	2.4	1.4	643	—	—	38	1.4	1.5	286	—	—	0.09	—	—	—	—	—	—
Geo-17	1.1	—	402	490	21	15	2.4	0.7	599	—	25	74	3.0	13	246	—	0.04	—	—	—	—	—	—	—
Geo-22	0.9	8.4	428	479	—	7	2.1	0.4	537	856	—	27	1.8	18	220	4.7	—	0.10	0.01	—	0	—	0.02	—
Geo-24	3.8	7.7	1030	1260	—	28	6.4	3.0	2150	3670	—	625	0.8	17	874	—	—	0.66	—	—	—	—	—	—
Geo-30	1.1	8.7	386	471	—	4	1.0	0.4	490	849	—	32	0.4	14	204	3.9	0.13	0.04	—	—	—	—	—	—
Geo-39	1.5	8.3	288	351	—	10	3.4	0.3	354	590	—	5	5.9	14	139	3.6	0.17	0.02	—	—	—	—	—	—
Geo-57	1.2	—	610	740	—	19	3.8	2.4	964	1800	20	180	8.5	13	380	13.0	0.41	—	—	—	0.16	0.04	0.15	—
Geo-63	0.6	8.4	410	480	0	7	2.0	0.5	512	850	22	27	5.5	12	210	4.5	0.04	0.04	0	—	0.2	0.03	0.01	0.09
Geo-66	1.1	8.2	510	620	40	9	2.1	0.9	666	1200	23	50	3.7	14	280	6.2	0.05	0.10	0	—	0.3	0.02	0.02	0.09
Geo-70	4.0	8.4	593	642	0	8	2.4	0.6	772	1260	24	59	15.0	19	320	4.5	—	—	0.02	.16	0.6	—	0.10	—
Geo-71	3.8	8.0	590	719	12	20	4.8	1.8	885	1400	—	120	9.4	16	348	16.0	0.39	0.02	—	—	—	0.16	—	—
Geo-78	1.6	8.6	348	400	9	9	2.7	0.5	428	715	22	14	16.0	16	170	5.2	0.11	0.01	0.01	—	—	—	0.02	—
Geo-84	3.8	8.5	384	450	—	7	2.1	0.5	512	950	23	33	1.8	14	210	4.8	0.05	0.03	0.01	—	—	0.05	—	0.12
Geo-88	4.5	8.6	530	650	0	9	2.1	0.8	679	1170	24	41	6.0	12	280	17.0	0.32	—	—	—	4.1	—	—	—
Geo-94	3.7	8.5	1010	1230	5	30	6.4	3.4	2460	5800	27	830	6.3	15	980	10.0	0.17	0.28	0	—	—	—	—	0.09
Geo-95	1.2	8.7	520	620	6	13	3.5	1.1	630	1000	23	30	9.9	15	260	7.6	1.20	0.09	0	—	—	—	—	0.06

TABLE 1.—*Chemical analyses of water samples withdrawn from sands of the Black Creek aquifer system—Continued*

Well Number	Fluoride (F)	pH (Units)	Alkalinity	Bicarbonate (HCO3)	Carbon Dioxide (CO2)	Total Hardness	Calcium (Ca)	Magnesium (Mg)	Dissolved Solids	Specific Conductance (Micromhos at 25°C)	Temperature (Degrees Celsius)	Chloride (Cl)	Sulfate (SO4)	Silica (SiO2)	Sodium (Na)	Potassium (K)	Total Iron (Fe)	Dissolved Iron (Fe)	Manganese (Mn)	Strontium (Sr)	Bromide (Br)	Total Aluminum (Al)	Dissolved Aluminum (Al)	Phosphorus (PO4)
Geo-101	4.0	8.7	650	780	8	8	2.3	0.6	809	1400	25	55	2.3	18	330	4.0	0.59	0.06	0	—	0.3	—	—	0.15
Geo-102	2.1	8.6	430	510	8	4	1.4	0.2	487	900	24	6.1	1.9	14	200	2.1	0.15	0.26	0	—	—	—	—	0.18
Geo-103	2.4	8.8	450	540	6	10	3.2	0.4	532	940	24	14	1.9	15	220	2.6	0.35	0.06	—	—	1.2	—	—	0.28
Geo-107	4.3	8.2	576	690	6	7	1.7	0.6	697	1200	17	29	4.1	18	290	3.9	0.15	0.11	—	—	—	0.10	0.03	0.15
Geo-108	3.5	8.3	570	700	—	9	2.2	0.8	678	1225	22	35	2.8	13	270	6.1	0.09	0.05	—	—	—	0.06	0.06	0.6
Geo-109	3.9	8.0	590	720	—	8	2.3	0.6	711	1200	23	30	2.5	23	290	4.5	—	0.05	—	—	—	0.04	0.04	0.18
Geo-112	3.7	8.3	572	697	—	8	2.1	0.4	708	1160	24	43	3.7	14	290	6.4	—	0.08	—	—	0.2	—	0.05	0.06
Geo-113	0.5	8.5	333	390	8	13	2.0	1.8	454	900	17	51	9.2	13	170	7.0	0.31	0.02	—	—	—	—	—	—
Geo-114	0.6	8.5	378	430	15	23	5.5	2.2	421	790	22	8	0.9	13	160	3.5	0.07	0.01	0.01	—	—	—	—	—
Geo-116	4.1	8.5	490	597	34	13	3.1	1.3	694	1130	—	48	3.8	16	280	9.0	—	0.09	0.02	—	0.2	—	0.07	0.06
Geo-117	4.6	8.5	555	626	25	14	3.4	1.4	771	1280	—	83	4.2	19	320	0.9	—	0.30	0.01	—	0	—	0	0.15

TABLE 2.—*Description of wells in Horry and Georgetown Counties, S.C., and vicinity*

Well Number	Name	SCWRC* Well Number	Lati-tude	Long-itude	Depth (feet)	Screened Interval (depth in feet)
HO-32	City of Myrtle Beach, Depot St.	5S-q1	334143	785307	548	
HO-34	City of Myrtle Beach, Ocean Forest	5S-j2	334337	785034	550	--
HO-36	Myrtle Beach Air Force Base (Bombing)	5S-y5	334030	785421	572	506-560
HO-37	Myrtle Beach Air Force Base (Bombing)	5S-y8	334025	785435	214	108-214
HO-69	City of Myrtle Beach	5S-y4	334051	785429	575	--
HO-203	City of Myrtle Beach No. 6 (Shop)	5S-n1	334201	785312	780	--
HO-204	City of Conway No. 1	7R-c1	334958	790245	715	643-683 695-705
HO-206	City of Myrtle Beach No. 7 (old school house)	5S-q3	334130	785353	767	280-300 320-340 360-380 402-422 440-461 480-500 520-540 560-580 601-625 646-655 683-703 726-750
HO-215	City of North Myrtle Beach No. 1	3R-h1	334853	784218	613	264-287 355-380 402-425 467-487 548-564 590-612
HO-218	Myrtle Beach Air Force Base No. 4	6T-b2	333925	785613	787	553-558 563-578 642-646 697-702 744-774 782-787
HO-223	City of North Myrtle Beach No. 3	3R-g1	334819	784320	706	380-388 396-400 410-414 420-428 432-436 440-448 530-542 550-558 562-566 570-578 618-622 626-630 636-640 657-658 664-672 698-704
HO-224	Lakewood Water Co. Myrtle Beach	6T-m2	333755	785750	769	--
HO-226	Myrtle Beach Air Force Base No. 3	6T-b1	333938	785653	760	512-517 540-550 568-573 632-647 650-660 672-677 712-717 736-756
HO-228	City of Myrtle Beach No. 9	4R-x1	334507	784829	740	317-322 340-345 363-368 471-476 581-586 648-653
HO-230	City of North Myrtle Beach No. 4	3R-i1	334857	784108	695	304-309 322-327 336-341 372-377 395-400 522-532 545-556
HO-241	City of North Myrtle Beach No. 5	2Q-x3	335024	783843	520	446-450 454-458 462-466 482-486 490-494 500-504 512-516
HO-246	City of Myrtle Beach No. 14	4R-y1	334518	784924	780	378-382 400-404 454-458 482-486 500-504 392-396 446-466 462-466 490-494 512-516
HO-249	Conway Power Santee Cooper No. 1	7R-d1	334953	790258	719	694-709

TABLE 2.—Description of wells in Horry and Georgetown Counties, S.C., and vicinity—Continued

Well Number	Name	SCWRC* Well Number	Latitude	Longitude	Depth (feet)	Screened Interval (depth in feet)
HO-250	Conway Power Santee Cooper No. 2	7R-d2	334932	790300	725	701-716
HO-251	City of North Myrtle Beach (Cherry Grove)	2R-d2	334958	783822	576	--
HO-252	City of Conway (Temple St.)	7R-e1	334940	790425	780	594-604 635-725
HO-259	Sherwood Forest Campground No. 2	3R-o2	334737	784428	700	460-465 505-510 551-556 631-636 675-680
HO-260	Sherwood Forest Campground No. 1	3R-o1	334718	784436	700	460-465 505-510 551-556 631-636 675-680
HO-261	City of North Myrtle Beach No. 4	3R-n1	334758	784333	700	363-369 384-392 405-409 456-460 508-512 558-563 581-585 620-624 376-380 396-400 414-418 496-500 518-522 572-576 606-618
HO-279	Grand Strand Ice Company	6S-k1	334245	785517	416	--
HO-284	Town of Surfside	6T-q2	333643	785851	616	419-469 596-616
HO-287	City of Conway No. 4 (WLAT)	7Q-p1	335111	790418	1150	611-622 667-672
HO-289	Forestbrook	6S-h1	334347	785710	682	365-380 390-410 628-638 660-673
HO-291	City of Aynor No. 2	90-w1	340003	791238	359	300-350
HO-292	United Merchants	7P-t1	335654	790046	521	421-471
HO-293	St. James School	7T-L1	333725	790202	420	344-354 380-400
HO-294	Tidewater Block	6S-a1	334349	785543	400	--
HO-297	Earl Lewis	8R-a2	334918	790502	381	--
HO-298	Calabash J4	2Q-j1	335535	783502	516	496-506
HO-301	Calabash J5	2Q-j2	335535	783502	558	338-348
HO-304	City of Myrtle Beach (3rd Ave. S.)	5S-q2	334136	785352	800	342-354 364-383 391-407 416-426 519-534 612-620
HO-305	Pirate Cove Trailer Park	7T-u1	333510	790035	728	588-597 604-614 632-654 666-716
HO-308	Perry Road East	6R-q1	334605	785803	482	360-375 472-482
HO-322	Bucksport No. 1	8S-r3	334128	790607	840	--
HO-333	City of Myrtle Beach	6T-i1	335819	785643	658	308-324 354-358 400-405 450-460 556-566 608-612 654-658 330-338 385-390 425-430 476-484 572-578 630-638
HO-334	Bay Tree Golf Course	2Q-p4	335209	783928	539	460-500
HO-335	City of North Myrtle Beach	3R-b2	334900	784154	700	308-328 376-386 453-463 488-498 568-588 675-685 338-368 402-412 467-482 518-548 604-624 690-700
HO-336	City of North Myrtle Beach	3Q-u1	335022	784005	600	300-315 360-375 472-482 516-526 570-580 324-329 435-455 497-512 530-560

TABLE 2.—*Description of wells in Horry and Georgetown Counties, S.C., and vicinity—Continued*

Well Number	Name	SCWRC* Well Number	Latitude	Longitude	Depth (feet)	Screened Interval (depth in feet)
HO-337	State of South Carolina (Eagle Nest)	2Q-o1	335237	783849	354	344-354
HO-338	City of Myrtle Beach (10th Ave. N.)	5S-c1	334229	785405	840	431-441 449-454 456-471 633-663 754-764 772-797 802-807
HO-339	City of Myrtle Beach	4R-L1	334705	784605	700	588-598 610-625 640-690 735-750
HO-342	City of Myrtle Beach	5S-h1	334333	785239	780	280-300 308-318 352-362 393-403 412-427 430-450 524-529 590-620
HO-343	Aynor-Conway Career Center	8Q-k1	335237	790559	230	210-230
HO-347	Bucksport No. 2	7S-e1	334426	790447	598	300-320 330-340 392-402 408-443 448-453 463-473 492-502
HO-353	Ocean Lake Campground	6T-m5	333715	785741	482	406-416 442-482
HO-380	Azalea Sands Golf Course	3R-h3	334849	784226	380	350-360 360-380
HO-383	Cagney's Restaurant	4R-L1	334704	784704	585	564-579 580-585
HO-386	Legrand Jordan	6R-c1	334927	785724	410	330-335 377-402
HO-387	Donald Smoak	6R-d2	334907	785839	330	315-330
HO-390	City of Conway (Rural PYA)	7R-j1	334834	790019	780	495-520 650-660 670-690 716-726 740-765 770-780
HO-396	AVX Ceramics	5S-y4	334031	785429	584	398-408 440-470 554-584
HO-411	Grand Strand Baptist Church	6S-c1	334455	785726	420	--
HO-427	Carolina Utilities (Dr. Hunsburger)	6T-y1	333508	785908	380	295-300 310-320 330-335 342-358 365-372
HO-430	City of North Myrtle Beach (White Point)	3R-f1	334808	784417	560	325-370 380-385 395-420 482-502 530-560
HO-435	Michael Causey	7R-L1	334742	790147	178	168-178
HO-436	Green Lakes Mobile Home Park	7U-a2	333452	790100	740	--

TABLE 2.—Description of wells in Horry and Georgetown Counties, S.C., and vicinity—Continued

Well Number	Name	SCWRC* Well Number	Lati-tude	Long-itude	Depth (feet)	Screened Interval (depth in feet)
GEO-1	City of Georgetown [Plant No. 1]	10W-m7	332208	791638	350	---
GEO-7	City of Georgetown [Plant No. 2]	10W-m1	332218	791724	690	---
GEO-8	City of Georgetown	10W-m2	382217	791723	777	---
GEO-13	Pawleys Island	8V-r3	332607	790650	660	---
GEO-17	City of Georgetown (Black River Rd)	10W-m3	332237	791755	990	703-713 874-884
GEO-22	Arcadia Plantation	9W-n1	332258	791324	532	---
GEO-24	City of Georgetown (test)	10W-m4	332217	791721	1344	---
GEO-30	City of Georgetown (Maryville No. 1)	10X-d1	331958	791810	840	618-633 713-743
GEO-39	Town of Andrews	13V-o1	332643	793338	800	710-790
GEO-44	Pawleys Island (Pelican Inn)	8V-w2	332511	790741	529	---
GEO-53	Georgetown (test)	10w-m5	332216	791723	1848	---
GEO-57	Hagley Estates	9V-u1	332555	791002	535	---
GEO-63	Georgetown Rural Water Dist. (Fire Tower)	10V-L1	332704	791648	820	504-514 526-536 546-551 560-590 648-668
GEO-66	De Bordieu Colony	8W-o1	332150	791022	648	544-554 564-584 590-600 610-640
GEO-70	Carolina Utilities Garden City (Pt. No. 1)	7U-L1	333304	790112	715	422-442 555-565 675-685 695-715
GEO-71	North Litchfield Golf Club	8V-i1	332850	790625	571	352-362 374-384 393-413 431-451 461-471
GEO-72	City of Andrews No. 6	13V-g1	332809	793352	795	521-541 557-567 598-613 696-741 785-792
GEO-78	International Paper Co. (Saw Mill)	12V-v1	332526	792657	800	360-380 520-530 550-580
GEO-84	John Strait	9V-t1	332609	791035	---	---
GEO-87	Georgetown Rural Water Dist. (Litchfield No. 3)	8V-j1	332846	790557	555	439-454 486-526 545-555
GEO-88	Esterville Plantation	10X-v1	331506	791615	1837	1270-1295
GEO-94	Georgetown Rural Water Dist. (Plantersville)	9U-r1	333144	791256	580	486-496 540-580
GEO-95	Georgetown Rural Water Dist. (Penny Royal)	11W-v1	332022	792145	680	620-680
GEO-101	Georgetown Rural Water Dist. (Murrells Inlet)	7U-n1	333255	790330	770	450-500 720-770
GEO-102	Georgetown Rural Water Dist. (Brownsferry)	11U-f1	333555	792456	990	880-920 970-990
GEO-103	Georgetown Rural Water Dist. (Rose Hill)	11T-o1	333704	792425	918	770-794 880-890 894-918
GEO-107	Channel Marker Restaurant	7U-b1	333415	790116	760	620-650

TABLE 2.—*Description of wells in Horry and Georgetown Counties, S.C., and vicinity—Continued*

Well Number	Name	SCWRC* Well Number	Lati- tude	Long- itude	Depth (feet)	Screened Interval (depth in feet)
GEO-108	Georgetown Rural Water Dist. (Pawleys North)	8V-r1	332610	790712	---	---
GEO-109	Huntington Beach State Park	7U-x1	333017	790358	702	---
GEO-112	Georgetown Rural Water Dist. (S. Litchfield)	8V-L1	332745	790608	642	412-417 491-506 618-628
GEO-113	International Paper Co. (Brownsferry Park)	11U-o1	333246	792410	780	615-630 675-685 752-772
GEO-114	Georgetown Rural Water Dist. (Brownsferry)	11U-y1	333035	792132	710	516-526 575-596 652-662 666-696
GEO-116	Lower Waverly	8V-f1	332813	790904	785	730-740
GEO-117	Georgetown Rural Water Dist. (N. Litchfield)	8V-a1	332919	790512	557	507-557
CHN-182	State of South Carolina (Hampton Plantation)	12Y-L1	331200	792553	834	761-801
DD-42	State of North Carolina (test)*		341237	785346	880	---
EE-39	State of North Carolina (test)*		340733	783952	1020	---

*Data on North Carolina wells provided by North Carolina Department of Natural and Economic Resources, Office of Water and Air Resources.

of chloride occur in the vicinity of the Cape Fear arch (fig. 2). This important geologic feature plays the dominant role in determining the amount of saltwater [1] occurring within the Black Creek aquifer system (Zack, 1977, p. 59). Downdip and toward the flanks of the Cape Fear arch the water decreases in pH (from 9.0 inland to 8.0 on the coast) and progressively becomes more of a sodium chloride (NaCl) type as it encounters incompletely flushed saltwater. The probable source of the saltwater, which is more correctly classified as a sodium bicarbonate–sodium chloride ($NaHCO_3$-NaCl) type, near the Cape Fear arch is the diluted remains of seawater either trapped in the sediments during deposition or from a subsequent inundation.

The ratio of the concentration of sodium and chloride ions is the same as that of seawater (fig. 3). At sodium concentrations greater than about 280 mg/L, water in the Black Creek aquifer system is a $NaHCO_3$-NaCl type, indicating a mixture of meteoric and ancient seawater.

In order to determine whether the direct solution of fluoride minerals could account for the high levels of fluoride in the Black Creek aquifer system, all chemical data were analyzed with a chemical equilibrium computer program (WATEQ). This program takes, as input, individual chemical analyses, including field pH, temperature, and redox potential and computes the equilibrium distribution of preselected inorganic aqueous species. It was determined that no fluoride-bearing minerals were sufficiently soluble to account for the high levels of fluoride in the Black Creek aquifer system.

From a study of the ionic associations of fluoride and other species in the chemical analyses, it has been observed that fluoride concentration is more closely associated with bicarbonate than with any other ion or combination of ions in the samples (fig. 4). The association is not straightforward, but the following observations can be made: Fluoride (minimum 0.5 mg/L) increases with bicarbonate concentrations (minimum 390 mg/L) until limiting values of 5.5 mg/L fluoride and 750 mg/L bicarbonate are reached. There are no further increases in fluoride or bicarbonate within the Black Creek aquifer system in Horry or Georgetown Counties. These limiting values are explained in the section on calcium-carbonate solubility.

The distribution of fluoride within the Black Creek aquifer system (plate 1) is incompletely known. However, the highest

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[1] In this report, saltwater is defined as water containing 250 mg/L or more of chloride.

fluoride concentrations are encountered in the upper third of the formation, with fluoride concentration generally decreasing with
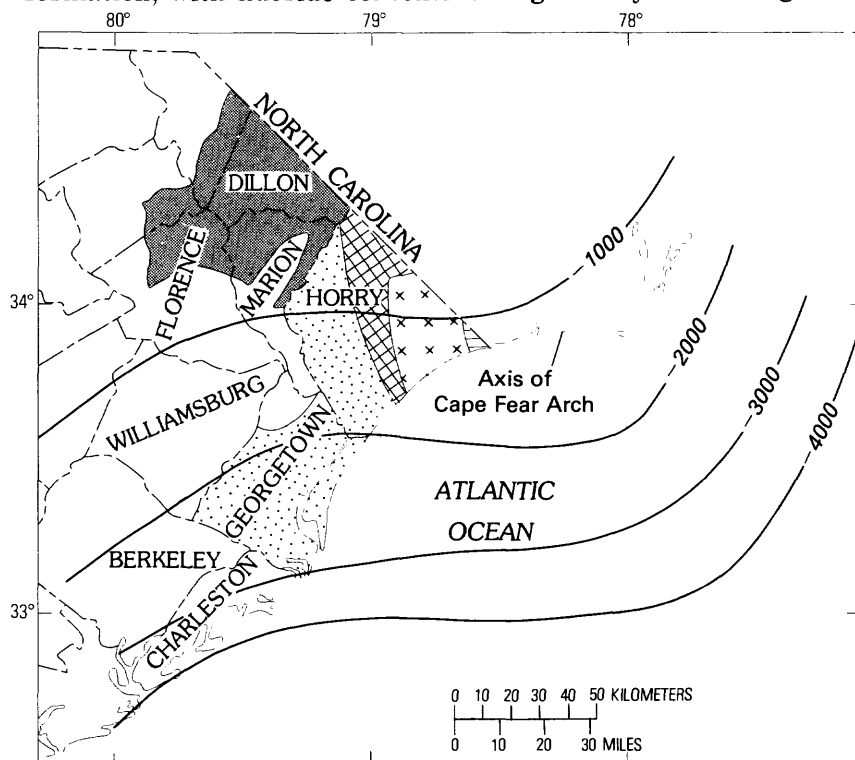

EXPLANATION

——*1000*— Structure contour on top of basement rocks. Contour interval 1000 feet, National Geodetic Vertical Datum of 1929 (modified from Maher, 1971, plate 4)

Outcrop Black Creek Formation, recharge area

All sands within Black Creek aquifer system that contain salty water (greater than 250 milligrams per liter chloride). Dissolved solids greater than 500 milligrams per liter

Upper and middle sands within Black Creek aquifer system that contain freshwater (less than 250 milligrams per liter chloride) and lower sands contain salty water (greater than 250 milligrams per liter chloride)

Upper sands within Black Creek aquifer system that contain freshwater (less than 250 milligrams per liter chloride) and lower sands contain salty water. Dissolved solids may be greater than 500 milligrams per liter

All sands within Black Creek aquifer system that usually contain freshwater. Lowermost sands may locally contain salty water

FIGURE 2.—Structure contours of the basement rocks, Cape Fear arch, location of the Black Creek Formation outcrop, and general water quality in the Black Creek aquifer system.
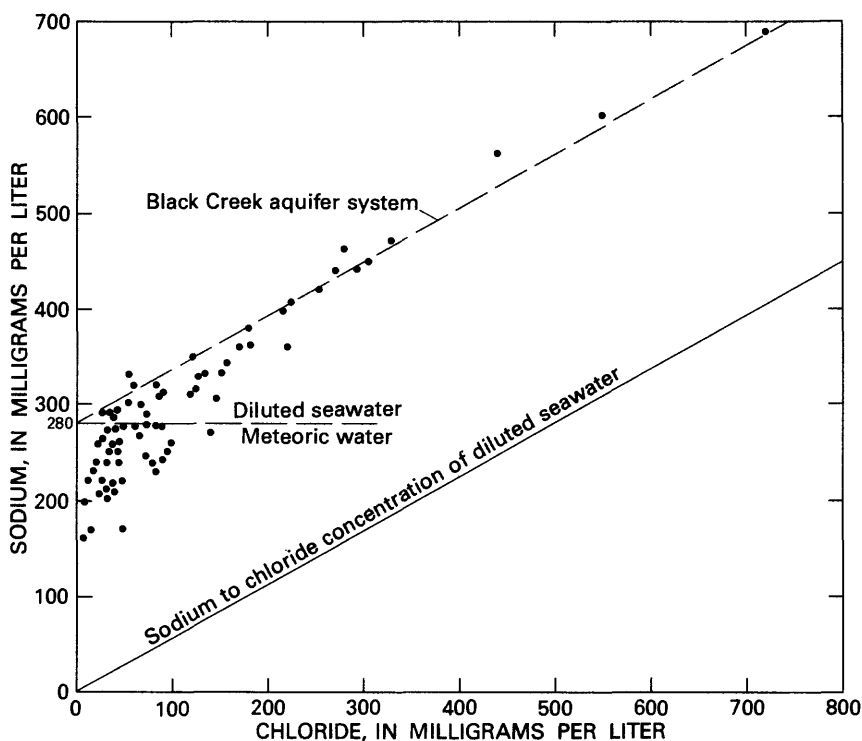
FIGURE 3.—Relation of sodium to chloride in water from the Black Creek aquifer system and in diluted seawater.

depth within the aquifer and with distance downdip. Water samples collected from wells located in the interior of Georgetown County and screened in the lower sands of the Black Creek aquifer system contain the smallest fluoride concentrations.

GEOCHEMICAL FRAMEWORK

A mechanism which can account for the close association of bicarbonate and fluoride concentrations within the Black Creek aquifer system is the dissolution of the calcium-carbonate matrix from around fossil shark teeth and the release of fluoride ions from fluorapatite through exchange with hydroxyl ions in the associated ground water. The dissolution and subsequent hydrolysis of calcium carbonate is responsible for the production of hydroxyl ions and exposes more surfaces of shark teeth where ion exchange can take place
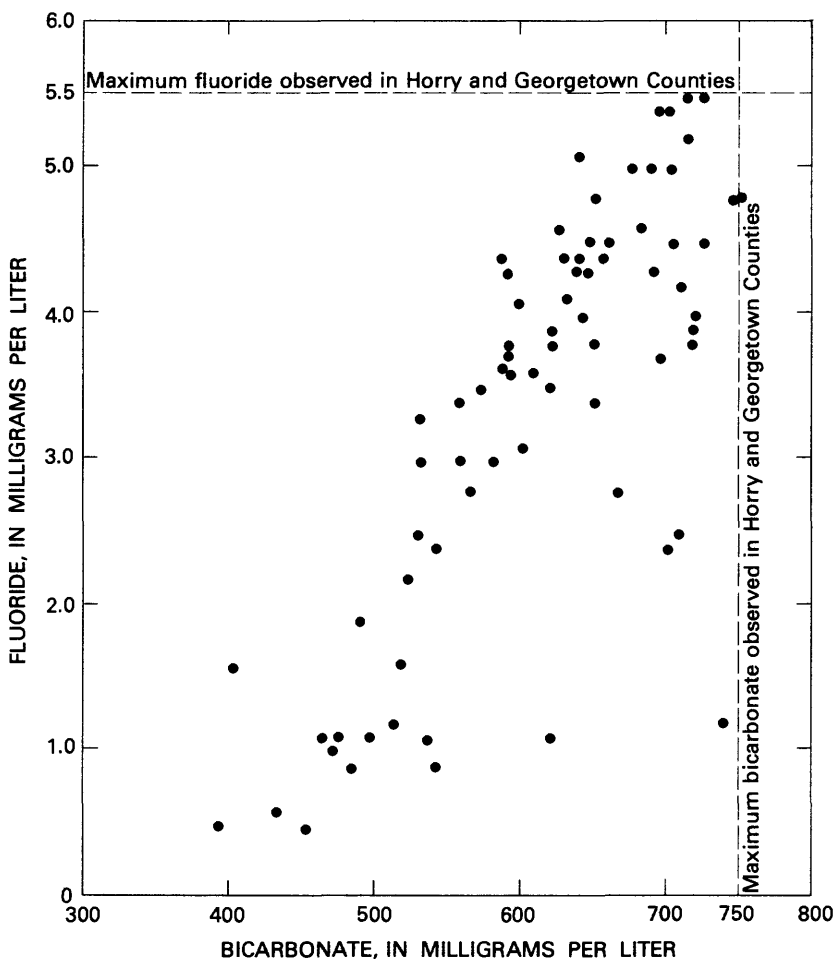
FIGURE 4.—Relation of fluoride and bicarbonate in water from the Black Creek aquifer system.

The aqueous environment affects the dissolution of calcite and the release of fluoride ions by controlling calcite solubility and, as the shark teeth are exposed, by controlling the exchange capacity of fluorapatite.

CALCIUM CARBONATE SOLUBILITY

Ground water becomes more mineralized as it progresses down-dip from the recharge areas to the coast. The degree to which ground water is mineralized with respect to certain ions depends primarily upon the length of time it has been in transit, the

mineralogy and ion-exchange capacity of the host sediments, the amount of dissolved carbon dioxide (CO_2) in the water, pH, temperature, and the solubility of the aquifer material.

Recharge from rain falling upon the exposed Black Creek Formation in Marion, Dillon, and Florence Counties (fig. 2; and Zack, 1977, p. 38) is the principal source of the freshwater within the Black Creek aquifer system. However, the movement of ground-water downdip and subsequent mineralization within the Black Creek aquifer system has been studied in detail only in Horry and Georgetown Counties.

Carbon dioxide is released to the aquifer system through the decomposition (oxidation) of carbonaceous material throughout the Black Creek Formation. Foster (1950, p. 41) attributed CO_2 production in Atlantic and Gulf Coastal Plain aquifers to this source. The downdip increase in dissolved CO_2 is indicated by a downdip increase in P_{CO_2} (partial pressure of carbon dioxide) calculated by WATEQ.

It can be demonstrated that bicarbonate ions are produced from two different sources within the Black Creek aquifer system: from the dissolution of calcium carbonate in water (whether CO_2 is available or not) and from the solution of CO_2 in water. The two reactions are independent, and the relative importance of one over the other depends upon the amount of CO_2 and oxidizable carbonaceous material available in the aquifer.

Near the inland boundaries of the two-county area, there is a small amount of CO_2 in the aquifer derived from the atmosphere and the soil zone in the recharge area. The field pH of water samples withdrawn from wells in this area screened in the Black Creek aquifer system ranges between 8.5 and 9.0. When there is only a small amount of CO_2 available to the system, most of the bicarbonate ions are produced by the dissociation of calcium carbonate in water, a hydrolysis reaction:

$$CaCO_3 + HOH = HCO_3^- + OH^- + Ca^{++}.$$

In this reaction, the pH is capable of reaching 10.0 (Garrels and Christ, 1965, p. 81). However, with CO_2 being produced by organic decomposition downdip, additional bicarbonate is produced by the following reaction in water:

$$CO_2 + HOH = H_2CO_3 \overset{<}{>} H^+ + HCO_3^-$$

The slightly acidic environment causes the further solution of calcium carbonate:

$$CaCO_3 + H^+ = HCO_3^- + Ca^{++}.$$
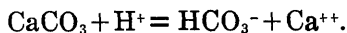
As the water percolates downdip, CO_2 addition appears to dominate and the pH drops accordingly until it reaches approximately 8.0 near the coast. Therefore the P_{CO_2} seems to determine the pH of water anywhere within the Black Creek aquifer system. The dissolution of calcite and its equilibrium relationships are discussed in further detail by Hem (1970, p. 133), Krauskopf (1967, p. 52), and Garrels and Christ (1965, p. 74–92).

The concentration of bicarbonate ions remains relatively unaffected by noncarbonate mineralogy, but calcium ions are subject to cation exchange. Sodium-rich marine clays, common throughout the Black Creek Formation, exchange sodium for calcium ions. "The capacity of a solid for chemisorption (ion exchange) is generally the result of local unsaturation of the chemical bonding within a mineral structure. In most of the important natural exchange media there is an excess of negative charge in certain areas of the crystal lattices, and positively charged ions are attracted to those areas. In general, divalent cations are more strongly adsorbed than monovalent ones, and in a solution in contact with the exchange medium the concentrations of adsorbable solutes will approximately obey the law of mass action" (Hem, 1970, p. 37).

The following reaction combines the two bicarbonate-producing reactions described above and includes the prevailing exchange reaction where sodium-rich clays are present:

$$CaCO_3 + Na_2(clay) + CO_2 + HOH = 2Na^+ + 2HCO_3^- + Ca(clay).$$

The mole ratio of sodium to bicarbonate produced by these reactions is 1:1, nearly the same as that observed from chemical analyses (fig. 5).

Cation exchange continues only where calcium carbonate is actively being dissolved. Apparently, the ion-exchange capacity of the sodium-rich clays has not yet been exhausted by the circulation of calcium-rich water through geologic time.

The leaching of calcium carbonate from the calcite-cemented quartz sand in the upper third of the Black Creek aquifer system has resulted in secondary porosity throughout these units. In effect, solution channels have been developed in and about the cemented sand, contributing to greater hydraulic conductivities. Water-well drillers prefer to screen the upper third of the Black Creek aquifer system because of the greater specific capacities (and well yields) obtainable in these units. In deeper parts of the formation, where there is no calcium carbonate to be leached from the sediments, the sands have a relatively low hydraulic
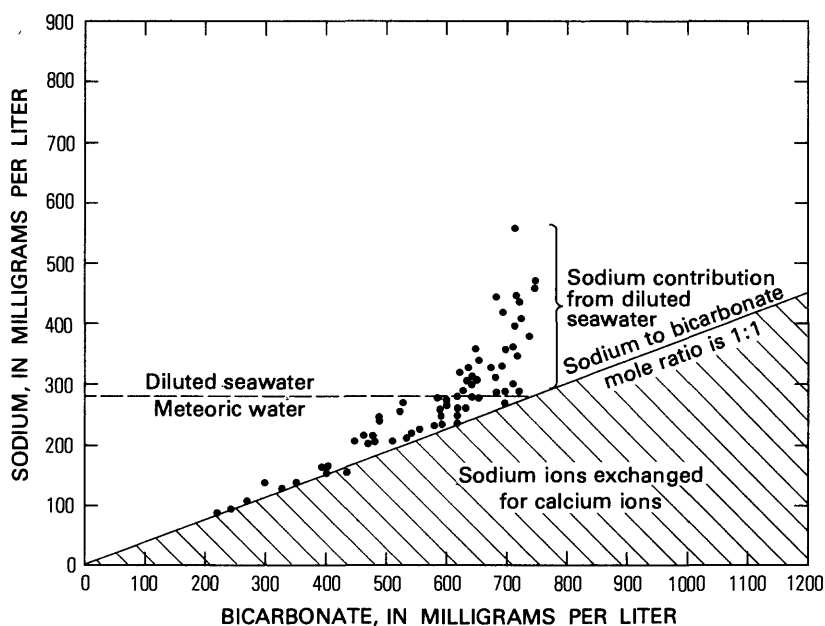
FIGURE 5.—Relation of sodium and bicarbonate in water from the Black Creek aquifer system and the mole ratio of sodium to bicarbonate produced by calcium carbonate dissolution and subsequent cation-exchange reactions.

conductivity. Wells screened in these deeper sands often produce a smaller quantity of water and, as expected, the water usually is lower in bicarbonate and subsequently lower in fluoride.

At any location within the Black Creek aquifer system, the concentration of any particular ion is affected by the amount of other ions in solution (ionic strength) and the degree to which the ground water is saturated with respect to the associated minerals. Specifically, calcite solubility depends largely on the amount of calcium ions in solution. Earlier, it was discussed that all calcium ions dissolved from calcite are exchanged for sodium ions, except those that are required to maintain calcite equilibrium.

It is reasonable to expect that the concentration of calcium would be affected by the amount of mixed seawater and meteoric water in the same way that sodium and chloride are affected. Water samples collected throughout the two-county area indicate that when sodium concentration is greater than 280 mg/L, the concentration of calcium ions is more or less determined by

seawater dilution (fig. 6). The additional calcium ions in solution where saltwater has been incompletely flushed from the aquifer system places constraints on calcium carbonate dissolution. When the water is close to saturation with respect to calcium ions, no additional calcium carbonate dissolves with an increased residence time. Therefore, as unflushed saline water is encountered downdip, the water is closer to saturation with respect to calcite; there is less tendency for calcium carbonate to dissolve and bicarbonate ions are no longer produced (fig. 7).
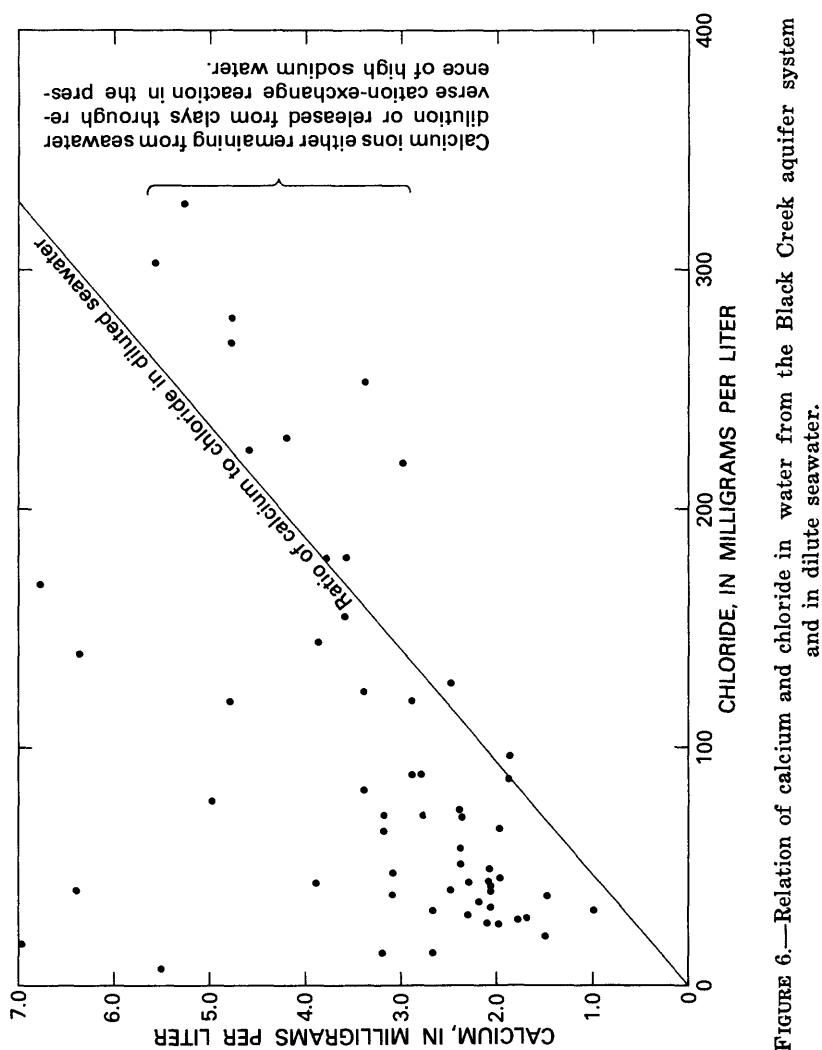
FIGURE 6.—Relation of calcium and chloride in water from the Black Creek aquifer system and in dilute seawater.

An alternative explanation for higher concentrations of cal-
cium ions in diluted seawater is that the cation exchange reaction
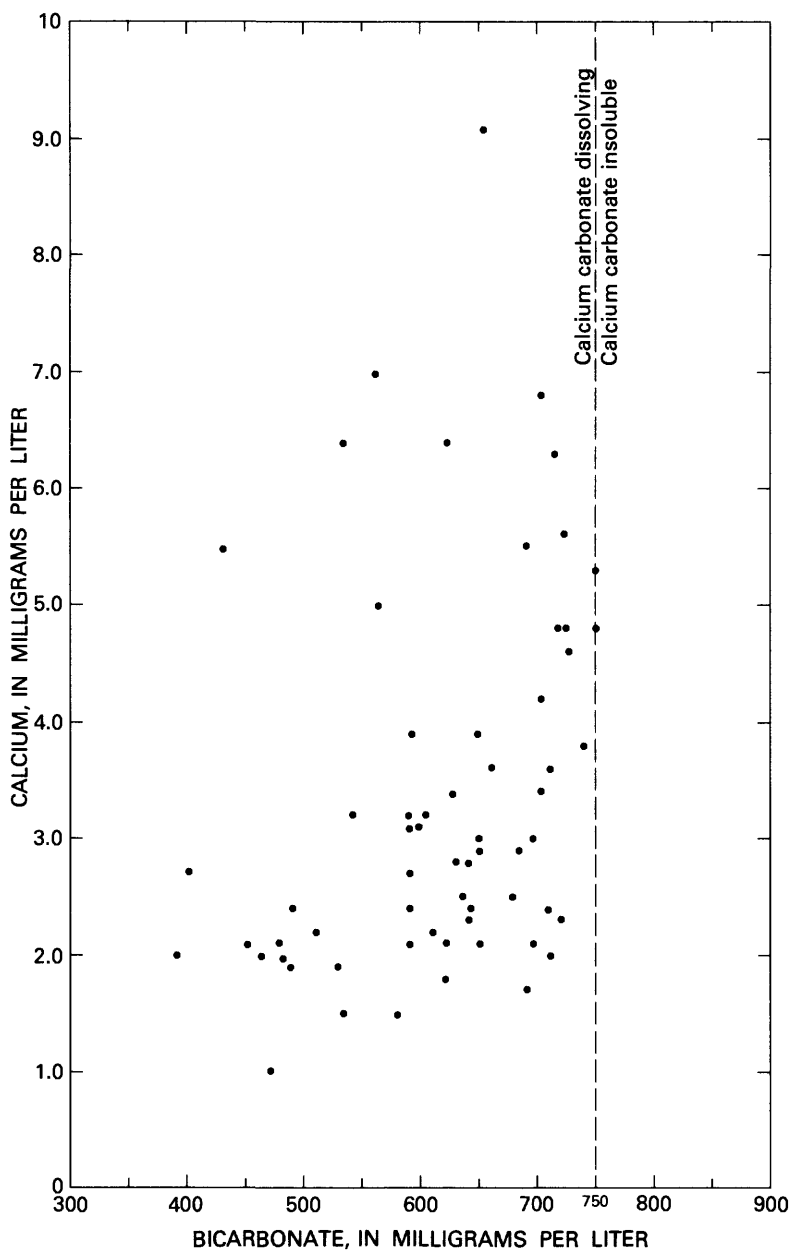
FIGURE 7.—Relation of calcium and bicarbonate in water from the
Black Creek aquifer system.

of clays exerts more control over the ionic makeup of ground water than does calcium carbonate solubility. Before seawater is encountered downdip, sodium is added to the system solely from clays. However, in the presence of saltwater, excess sodium may reverse the exchange reaction with the clays, liberating calcium ions to the saltwater. Exchange reactions proceed according to mass action, permitting the saltwater to have a higher concentration of calcium, not from seawater dilution, but from a reversal of the cation exchange reaction.

FLUORAPATITE SOLUBILITY

Fluorapatite, $Ca_5(PO_4)_3F$, and hydroxylapatite, $Ca_5(PO_4)_3OH$, are isomorphic end members in the apatite solid-solution series, $Ca_5(PO_4)_3(OH,F)$. Human and other animal teeth are composed principally of hydroxylapatite, whereas fossil shark teeth are composed principally of fluorapatite.

The solubility of apatite in water does not follow established classical principles of solubility-product equilibrium as does calcite. Levinskas and Newman in LaMer (1962, p. 973–978) state that the solubility of hydroxylapatite and the composition of the saturated solution depend strongly upon the solid content of the slurry; that is, upon the amount of surface area of solid hydroxylapatite in contact with the solute. They determined that the solubility of hydroxylapatite does not respond to additions of calcium and phosphate ions as it should after corrections for the individual ion-activity coefficients have been made. In addition, Rootare, Dietz, and Carpenter in LaMer (1962, p. 975) found that an increase in "spectator ions," such as sodium (Na^+) and chloride (Cl^-), in the solute matrix leads to a decrease in solubility. They also found that at pH values greater than 8.0, the solubility of hydroxylapatite rises sharply.

Rootare, Dietz, and Carpenter offer an explanation which appears to resolve these paradoxes. They postulate that the surface phosphate ions of hydroxylapatite undergo hydrolysis in water. LaMer (1962, p. 973–978) states that "hydoxylapatite, although a very insoluble salt, nevertheless hydrolyzes in water forming a more stable and insoluble surface complex $Ca_2HPO_4(OH)_2$ and liberating at the same time calcium (Ca^{++}) and biphosphate ($HPO_4^=$) ions in equal proportions. The release of these ions by this reaction and the simultaneous formation of a tightly bonded surface complex may account for the apparent "solubility" behavior of hydroxylapatite.

The following reactions occur:

$$Ca_5(PO_4)_3OH + 3HOH = 2[Ca_2HPO_4(OH)_2] + Ca^{++} + HPO_4^=$$

and

$$Ca_2(HPO_4)(OH)_2 = 2Ca^{++} + HPO_4^= + 2OH^-.$$
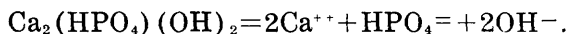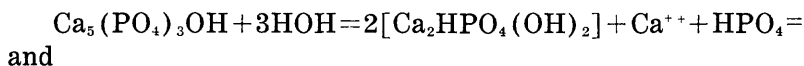
These reactions are written so as to produce $HPO_4^=$, rather than $PO_4^=$ or $H_2PO_4^-$, because $HPO_4^=$ is the major phosphate species at prevailing pH of ground water within the Black Creek aquifer system. The complex $Ca_2(HPO_4)(OH)_2$ formed by the first reaction rapidly covers the exposed surfaces of the hydroxylapatite with a strong adsorptive bond to the underlying structure. Apparently this is what ultimately contributes to the stability of hydroxylapatite.

If the surface complex of the fluorapatite end member is isomorphous with that of hydroxylapatite, its formula would be $Ca_2(HPO_4)F_2$. Accordingly, its formation would be dependent upon the amount of hydrogen ions (H^+) present in the associated water:

$$2Ca_5(PO_4)_3F + 6H^+ = Ca_2(HPO_4)F_2 + 8CA^{++} + 5HPO_4^=.$$

It seems probable, therefore, that the fluorapatite surface complex forms only where the pH of the surrounding water is less than 7.0. In such an environment, calcium, fluoride, and biphosphate ions are initially released to the water; but with the formation of $Ca_2(HPO_4)F_2$ on the surfaces of the exposed fluorapatite, the fluoride, but not all of the calcium and biphosphate ions, are removed from the solution. Therefore, with continued dissolution, the concentration of calcium and biphosphate ions increases while fluoride decreases.

Corsaro and Sutherland (1967, p. 480) have shown in laboratory tests that chloride ions further inhibit fluorapatite solubility, suggesting that the surface complex has been made even more insoluble by chloride ions.

A series of laboratory experiments was devised to observe the behavior of fluorapatite in water in the presence of sodium and chloride ions and at different values of pH.

Crushed fossil shark teeth were placed in samples of deionized water, each adjusted to the following buffered pH values: 4.0, 6.0, 8.0, and 10.0 (figs. 8 and 9). Two additional samples were prepared at pH values of 4.0 and 10.0, to which enough sodium chloride was added to increase specific conductance to 5,000 micromhos per centimeter. Measurements of calcium, fluoride, and pH were made at various time intervals for each of the six
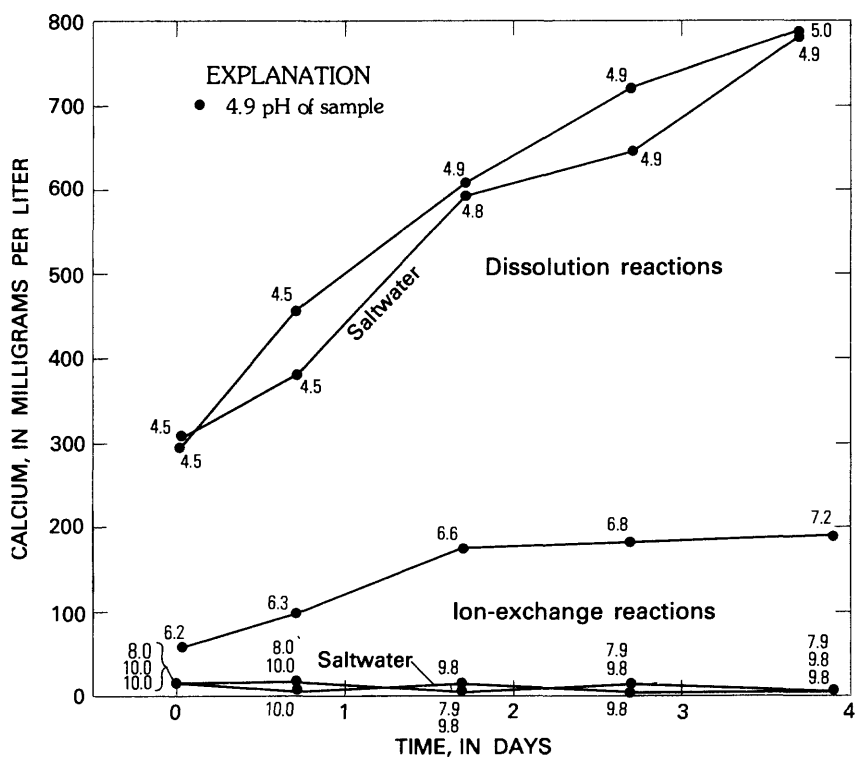
FIGURE 8.—Calcium ions released from crushed fossil shark teeth in solutions of freshwater and saltwater at various pH, with time.

samples. The solubility of fluorapatite decreased with increasing values of pH, as was evidenced by initially greater concentrations of calcium (Ca^{++}) and fluoride (F^-) at lower values of pH. With time, however, calcium ions increased and fluoride ions decreased. Apparently, the formation of the fluorapatite surface complex, $Ca_2(HPO_4)F_2$, controls its solubility.

The effect of sodium and chloride ions on fluorapatite solubility appears to be significant, particularly if the activity of fluoride and calcium are considered. The activities of fluoride and calcium are slightly less in the saltwater sample (at pH 4.0) than in the freshwater sample, indicating that the sodium and chloride ions have had an inhibiting effect on the dissolution of fluorapatite. This is in agreement with the findings of Corsaro and Sutherland (1967, p. 472). The presence of matrix anions apparently also inhibits the rate of fluoride ion exchange for hydrxyl ions in saltwater solutions.
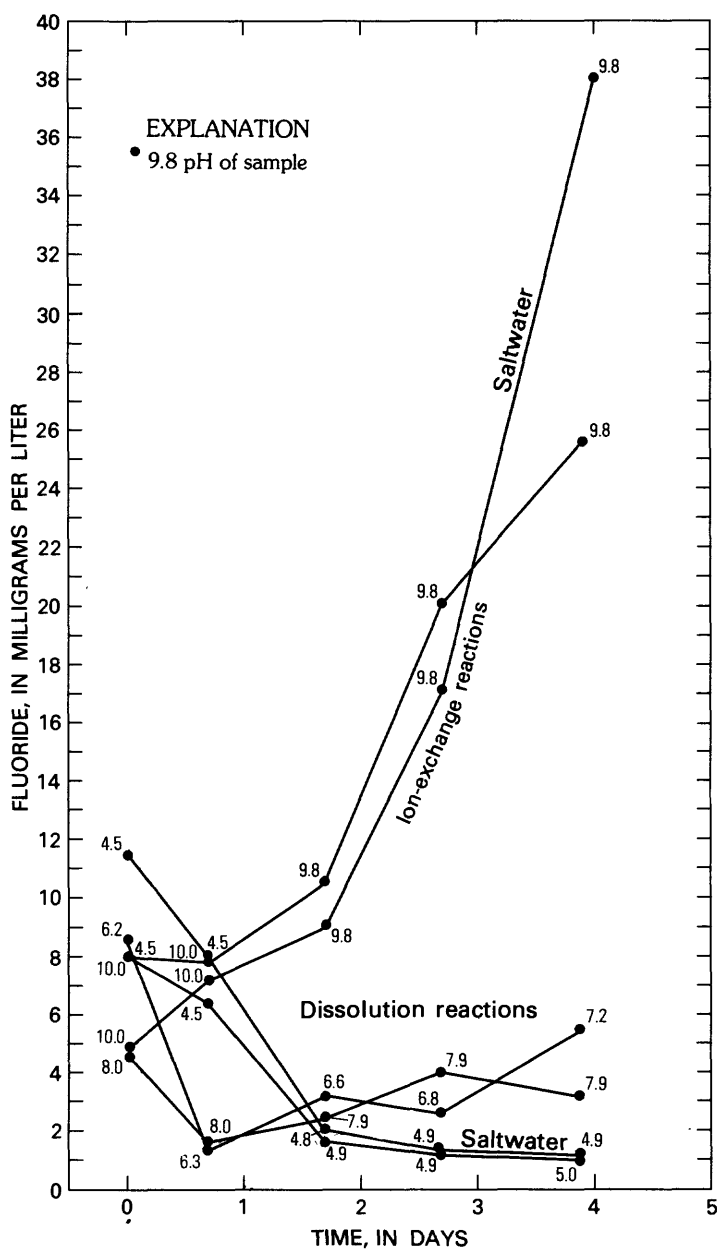
FIGURE 9.—Fluoride ions released from crushed fossil shark teeth in solutions of freshwater and saltwater at various pH, with time.

At high values of pH (above 8.0), fluorapatite solubility is at a minimum, as is evidenced by low concentrations of calcium in the experiment results (fig. 8). However, fluoride increased markedly with time, particularly at pH 10.0. This result can be explained in terms of anion exchange, in which abundant hydroxyl ions exchange with fluoride ions on fluorapatite surfaces. Calcium ions are not released to the solution because fluorapatite solubility is so small at the prevailing high pH. The continued increase of fluoride with time indicates that the concept of a surface complex probably does not apply at high values of pH.

The relationship of calcium and fluoride ion release from fluorapatite, at different values of pH and with time, can best be visualized by using fluoride to calcium ratios (fig. 10).

It is important to note that the anion-exchange capability of apatite depends upon the relative amounts of exchangeable anions incorporated both into the lattice of the mineral and present in solution. The rate of anion exchange is governed by the law of mass action. The anion exchange phenomenon would not be observed with pure hydroxylapatite in fluoride-free water and pure fluorapatite would not release fluoride ions to water having a low pH.

The exchange of hydroxyl for fluoride ions apparently accounts for most of the fluoride ions encountered in water being withdrawn from sands of the Black Creek aquifer system in Horry and Georgetown Counties. The pH has not been observed to be low enough for fluoride ions to be released through dissolution of fluorapatite, but calcium carbonate hydrolysis can provide the source of hydroxyl ions which are exchanged for fluoride ions. Calcium carbonate solubility ultimately seems to determine to what extent fluoride ions will be released to the ground water, both in terms of exposure of shark teeth and release of hydroxyl ions.

Another experiment with hydroxylapatite in water containing 10 mg/L fluoride showed that fluoride ions were exchanged for hydroxyl ions on the hydroxylapatite surfaces. Hog teeth were used for the test because they had never been subjected to high-fluoride water.[2] Therefore, the enamel was composed of relatively pure hydroxylapatite. Equal quantities of crushed teeth (in terms of surface area based on volume and weight) were placed in two solutions prepared by dissolving sodium fluoride in deionized

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[2] The composition of human teeth and hog teeth is the same: enamel (96 percent hydroxylapatite), dentin (70 percent hydroxylapatite), cementum (45 percent hydroxylapatite), pulp, and attachment tissues. The teeth of sharks, rays, and skates contain only dentin.
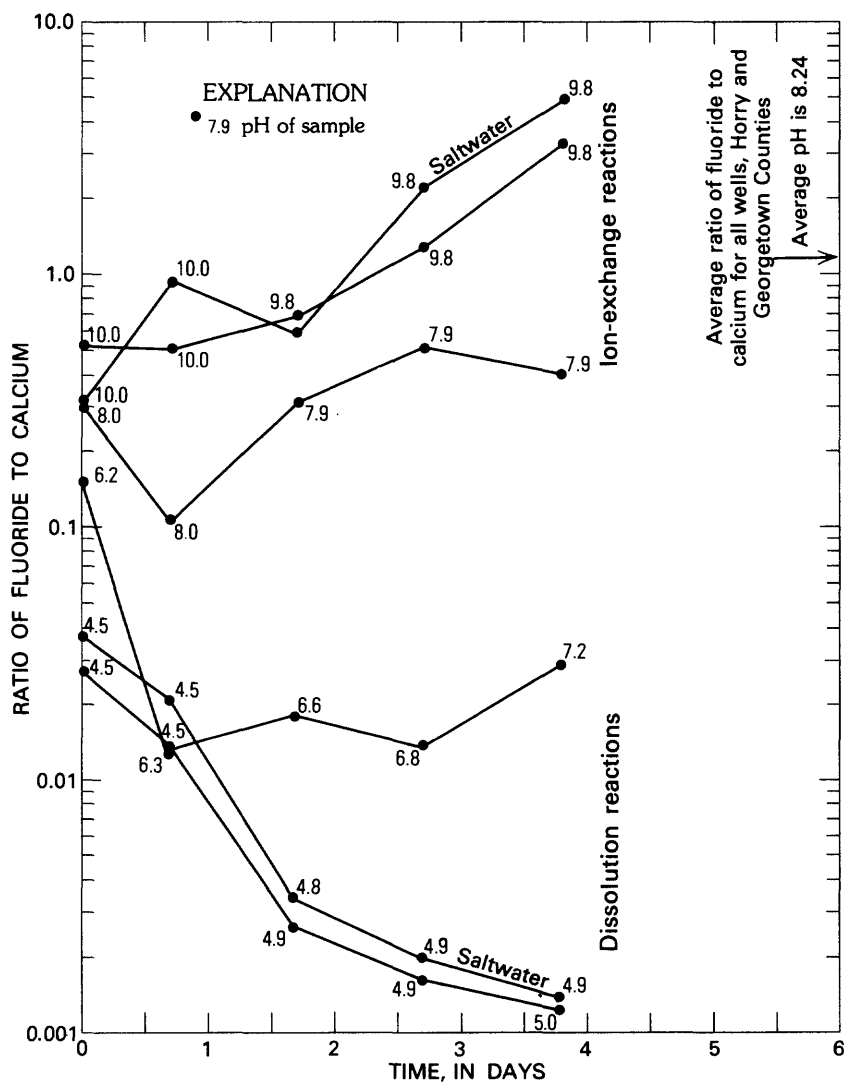
FIGURE 10.—Effect of buffered pH and salinity on ratio of fluoride to calcium produced by fluorapatite (fossil shark teeth) in water.

water. In one of the samples, enough sodium chloride was added to increase the specific conductance of the water to 5,000 micromhos per centimeter (fig. 11). There was no measureable decrease in fluoride concentration of either sample for about 15 minutes, even though the samples were shaken. With additional time, however, fluoride was removed from each solution, with more fluoride
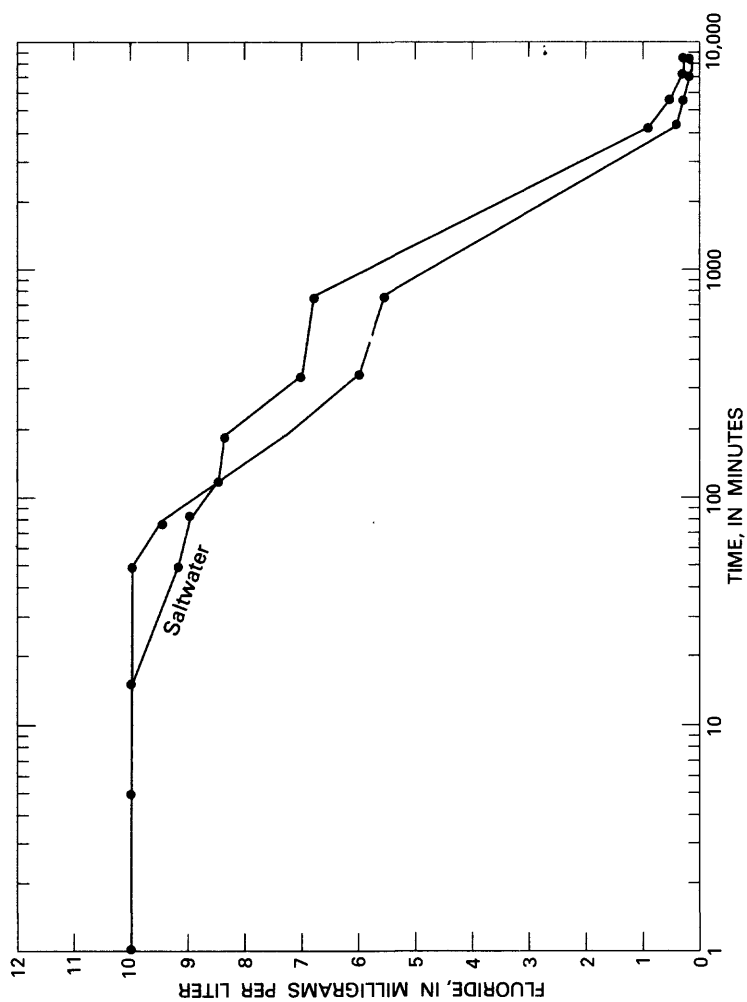
FIGURE 11.—Reduction in fluoride with time from high fluoride solutions of freshwater and saltwater containing hog teeth.

being removed from the saltwater solution than from the one containing only sodium and fluoride ions. Adjusting fluoride concentrations by the activity coefficient in each sample made these differences in concentration even greater. There was no increase in calcium at any time. These results apparently demonstrate that the addition of sodium and chloride ions in solution affects the teeth surfaces when fluoride is exchanged for hydroxyl ions in tooth enamel. The saltwater is associated with lower levels of fluoride in solution—particularly where equilibrium between the enamel minerals and the surrounding water was approached (after 7,000 minutes). This supports the shark teeth experiment where it was also demonstrated that saltwater accounted for lower fluoride levels in solution; the sodium and chloride ions had an inhibiting effect on fluoride exchange from shark teeth with hydroxyl ions in solution.

The above experiments seem to substantiate the findings of Rootare, Dietz, and Carpenter (in LaMer, 1962, p. 975) that sodium and chloride contribute to a decrease in solubility of hydroxylapatite (and presumably fluorapatite also).

SOLUTION OF CALCIUM CARBONATE AND ION EXCHANGE OF FLUORAPATITE IN THE GROUND-WATER FLOW SYSTEM

The origin and concentration levels of fluoride in the ground water of Horry and Georgetown Counties can now be explained in terms of the dissolution of calcite and the release of fluoride by fluorapatite into the flow system.

Percolating ground water in contact with calcite-cemented sand causes the calcite to dissolve releasing calcium, bicarbonate, and hydroxyl ions to the ground water. Most of the calcium ions are immediately exchanged for sodium ions, but enough calcium ions remain in solution to maintain equilibrium with calcite. As water moves downdip, carbonaceous material decomposes, producing carbon dioxide, causing additional calcium carbonate to dissolve and bicarbonate ions to become more concentrated.

Fossil shark teeth (nearly pure fluorapatite) embedded in the cemented sand are exposed by solution of the calcite cement. Fluorapatite is only slightly soluble at the prevailing pH in the Black Creek aquifer system, but fluoride is released from fluorapatite surfaces by exchange for hydroxyl ions in solution. With further calcite solution, hydroxyl production, and exposure of more fluorapatite, additional fluoride ions are released to the ground water through anion exchange.

The ionic environment of calcite and fluorapatite is altered with the mixing of freshwater with seawater in the aquifer system. Higher levels of calcium ions associated with seawater either from dilution or from reverse cation exchange (in which calcium is released from clays according to the law of mass action) hold the further dissolution of calcite in abeyance. The exchange of fluoride for hydroxyl ions is further inhibited with the increase in salinity of the water downdip. Lack of exposed fluorapatite surface and the decrease in pH of ground water downdip also work against fluoride release by exchange. The highest level of fluoride within the Black Creek aquifer system of Horry and Georgetown Counties corresponds with the highest bicarbonate concentrations; where bicarbonate is relatively low, fluoride levels are low.

DENTAL-HEALTH IMPLICATIONS OF THE ION SUBSTITUTION AND EXCHANGE MECHANISMS

Tooth enamel is composed principally of crystalline hydroxylapatite where fluoride is absent in the water supply. However, where fluoride is present in the water supply, some of the ingested fluoride ions are incorporated into the apatite crystal lattice of tooth enamel during its formation, causing the enamel to become harder and to possibly discolor. The substitution of fluoride for hydroxyl ions proceeds because fluorapatite is more stable than hydroxylapatite, under most conditions.

Fluoride substitution into tooth enamel is affected by thermodynamic activity and by the amount of fluoride complexes that form in the presence of certain other ions. The activity of fluoride decreases with increasing ionic strength of water, and fluoride complexes form more readily in heavily mineralized water than in dilute water.

Fluoride in complexed form behaves differently than if it were uncomplexed because it no longer has easy access to the apatite lattice of hydroxylapatite; the greater size and different charge prevents substitution. Also, the electrostatic effects of numerous other associated ions in solution, where the total disolved solids is high, interferes with the activity of fluoride ions. Accordingly, it seems reasonable that, given both a dilute and a heavily mineralized water having the same fluoride concentration, fluoride absorption into the body is hindered by competition from sodium and chloride ions. Subsequent incorporation of fluoride into teeth might occur at a lower or reduced rate in heavily mineralized water.

To test this hypothesis, information was gathered on the occurrence of tooth mottling among persons who used a groundwater supply from the Black Creek aquifer system as children in Horry and Georgetown Counties. Questionnaires were distributed by the South Carolina Water Resources Commission to dentists in the two-county area who subsequently polled their patients who met the above criteria. The results of the survey are inconclusive because of an inadequate number of samples and because the samples are thought to be unrepresentative in certain areas. However, several important observations can be made concerning the occurrence of dental fluorosis in areas of different levels of fluoride and total dissolved solids in the water supplies. As expected, where fluoride levels were relatively low, examples of tooth mottling were low and, where fluoride levels were high, the incidence of tooth mottling was high. However, where fluoride and total dissolved solids were both high (as in the Little River area of Horry County), examples of dental fluorosis appear to be low.

An explanation for the difference in tooth mottling of individuals within family units, as observed by dentists, may be related to the amount of salt ingested.

Fluoride ions can be exchanged for hydroxyl ions on tooth surfaces. However, for ion exchange to proceed, either fluoride ions must be abundant, or electrochemical requirements as described by Hem (1970, p. 37) on tooth surfaces would have to be different than they actually are in order to speed up the exchange reaction. Dentists apply the principle of ion exchange on tooth surfaces when they prescribe a topical fluoride treatment as a help in preventing tooth decay. In areas where fluoride is low or nonexistent in the water supply, a paste, gel, or solution containing as much as 10 percent stannous fluoride (SnF_2) is often applied to the teeth of dental patients (American Academy of Pedodontics, 1976, p. 20). If ionization is complete, the solution contains enough fluoride (75,000 mg/L) to vastly speed up the exchange rate of fluoride ions for hydroxyl ions. An effective, but temporary, barrier against dental decay is established on tooth surfaces.

There is considerable evidence that ionic substitution by systemic fluorosis (ingested and absorbed through the digestive system) rather than topical fluorosis (ion exchange on the tooth surface) is the principal process by which fluoride is incorporated into tooth enamel. Electrochemical requirements on tooth surfaces normally are not suitable for ion exchange to take place. Also, there is never an overabundance of fluoride ions in the water that

would be necessary in order to force the exchange reaction. The hog-teeth experiment gives some insight into the effectiveness of fluoride ion removal from water (and incorporation into tooth enamel) during drinking (topical fluorosis). Had fluoride been adsorbed during the first few seconds or minutes by the hog teeth, the assumption could have been made that topical fluorosis occurs by an immediate ion exchange process from water passing over the teeth. However, the teeth exchange fluoride ions slowly, suggesting that fluoride adsorption onto tooth enamel during drinking does not significantly contribute to dental fluorosis. The fact that fluoride ions are approximately the same size and have exactly the same ionic charge as hydroxyl ions suggests that ionic substitution (systemic fluorosis) is the principal mechanism by which tooth mottling occurs.

On initial observation, there seems to be difficulty reconciling the various roles that sodium and chloride ions play during the release of fluoride from fluorapatite through ion exchange and the subsequent incorporation of fluoride ions into tooth enamel by ionic substitution (systemic fluorosis) and by ion exchange (topical fluorosis).

The laboratory experiments with fossil shark teeth and with hog teeth demonstrate that exchange of hydroxyl ions in solution for fluoride ions in fluorapatite is inhibited by the presence of sodium or chloride ions or both. If topical fluorosis were an important natural process, adsorption of fluoride ions would be enhanced by sodium and chloride ions in solution. However, ionic substitution of fluoride ions into tooth enamel (systemic fluorosis) is not an exchange reaction and is probably inhibited by sodium, chloride, and other ions in solution because of electrostatic effects, the formation of fluoride complexes, and the possible competition in entering the blood stream between fluoride and sodium ions, or between fluoride and chloride ions, or both during the digestive process.

WATER TREATMENT FOR FLUORIDE REMOVAL

At present, some municipalities and water districts in Horry and Georgetown Counties are obtaining low-fluoride ground water, when wells are constructed, by screening those sands devoid of the calcite-cemented quartz sands containing shark teeth. Other water districts are experimenting with ground water from Tertiary and younger formations above the Black Creek

Formation in which fluoride levels are low. With treatment for iron and hydrogen sulfide removal, this water could either be used by itself or could be mixed with existing supplies of water from the Black Creek aquifer system.

If present water supplies are retained in Horry and Georgetown Counties and lower fluoride levels are desired or required, defluoridation would appear to be the only alternative to abandoning these supplies. Defluoridation is admittedly more difficult than the removal of other ions, such as calcium or iron, but Maier (1970, p. 437) states that there are presently three methods that have proved to be practicable under varying conditions of raw-water quality and availability of treatment chemicals. The methods involve the use of activated alumina, bone char, or magnesium compounds. Maier discusses the various methods to dispel the view that defluoridation involves excessive treatment and operating costs.

During this investigation, laboratory experiments in which high-fluoride (4.2 mg/L) ground water was passed through a column (approximately 10 mm³) of crushed hog teeth (hydroxyl-apatite) demonstrate that fluoride ions are removed from the circulating water at a rate depending on the velocity that water passes through the column and on the amount of exposed surfaces of the tooth particles. Depending on the rate of passage through the column, 10 percent to 100 percent of fluoride-ion removal was measured in the water. Upon saturation of the hydroxylapatite surfaces with fluoride, sodium hydroxide or another hydroxyl-ion source could be backwashed through the column, liberating the fluoride ions and reestablishing the fluoride exchanging capabilities of the hog teeth. It appears practicable that an inexpensive home-defluoridation column such as this, substituting, perhaps, an artificial hydroxylapatite for the hog teeth, could be devised. Where fluoride is particularly high, and the threat of tooth mottling exists, such a unit would permit the continued use of the supply, rather than resorting to the purchase of bottled water.

SUMMARY

The Black Creek aquifer system is the most important source of ground water in Horry and Georgetown Counties, S.C., and is used extensively for municipal, industrial, and domestic water supplies. Unfortunately, water from the Black Creek aquifer system often contains more than 1.6 mg/L fluoride, the present maximum-concentration limit allowable for public water supplies in coastal South Carolina.

The source of the fluoride is fossil shark teeth which contain the mineral fluorapatite. The shark teeth release fluoride ions to circulating ground water through an anion exchange mechanism with hydroxyl ions, rather than through dissolution.

The shark teeth occur within lenses of calcite-cemented quartz sand in the Black Creek Formation. As water moves downdip, the calcite hydrolyzes, producing hydroxyl ions and increases the pH. With the dissolution of the calcite and exposure of the teeth, the associated hydroxyl ions exchange with fluoride ions on the surfaces of the fossil shark teeth.
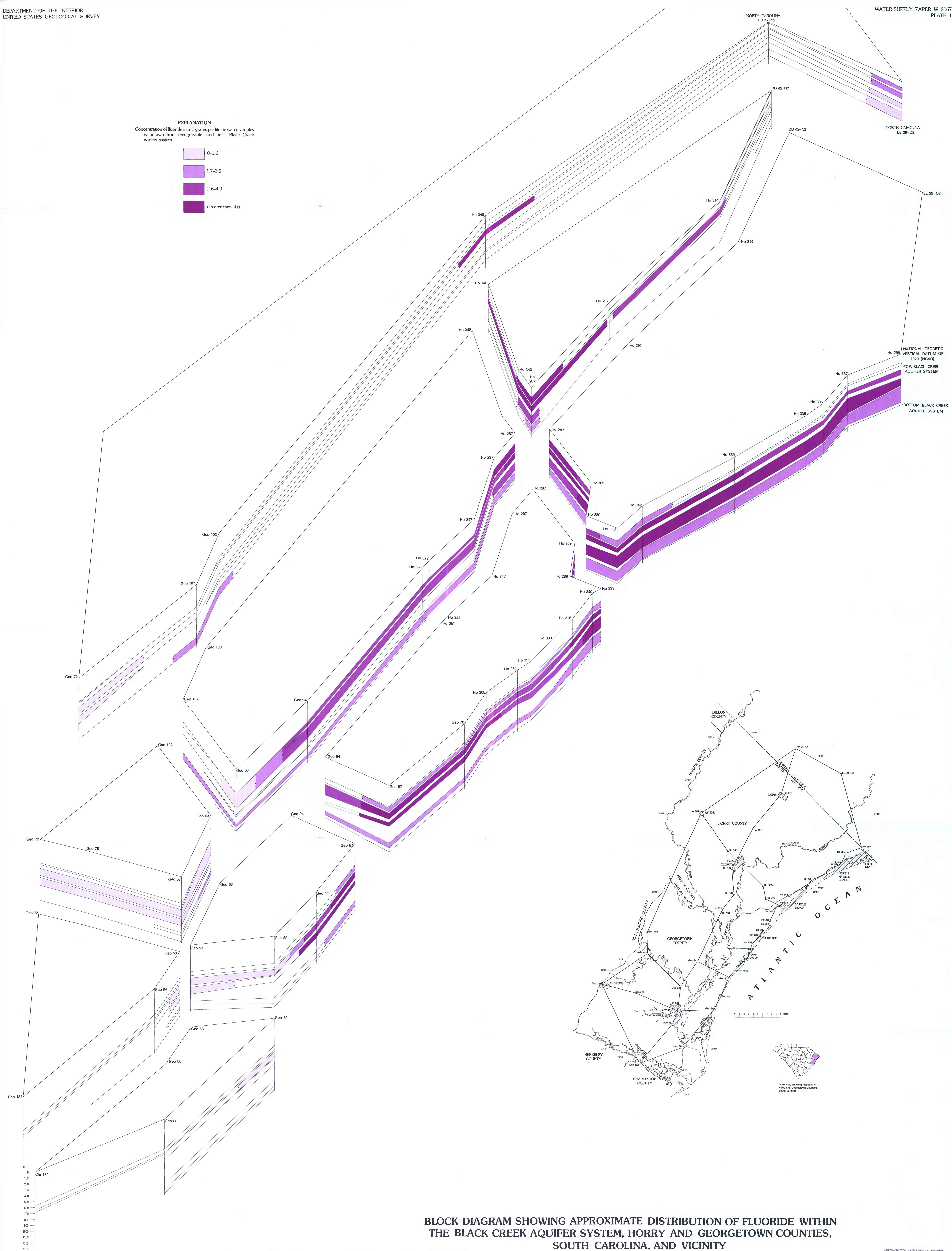
Relatively pure hydroxylapatite (hog teeth) placed in high-fluoride water incorporated fluoride ions into the crystal lattice while releasing hydroxyl ions, again through anion exchange. Reducing fluoride by using a hydroxylapatite exchange medium might have value where excessive fluoride concentrations occur in water supplies.

The exchange of hydroxyl ions in solution for fluoride ions in fluorapatite is inhibited by the presence of sodium ions or chloride ions or both. Accordingly, adsorption of fluoride ions is enhanced by sodium and chloride ions in solution. However, the presence of sodium and chloride ions in the water supply presumably provides protection against tooth mottling because of the possible formation of complex ions, electrostatic effects, and a competition from these ions as fluoride is absorbed into the body.

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EXPLANATION

Concentration of fluoride in milligrams per liter in water samples
withdrawn from recognizable sand units, Black Creek
aquifer system

- 0–1.6
- 1.7–2.5
- 2.6–4.0
- Greater than 4.0

BLOCK DIAGRAM SHOWING APPROXIMATE DISTRIBUTION OF FLUORIDE WITHIN
THE BLACK CREEK AQUIFER SYSTEM, HORRY AND GEORGETOWN COUNTIES,
SOUTH CAROLINA, AND VICINITY