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## The origin of high sodium bicarbonate waters in the Atlantic and Gulf Coastal Plains\*

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### ABSTRACT

Some sodium bicarbonate waters at depth in the Atlantic and Gulf Coastal Plains have the same bicarbonate content as the shallower calcium bicarbonate waters in the same formation and appear to be the result of replacement of calcium by sodium through the action of base-exchange minerals. Others, however, contain several hundred parts per million more of bicarbonate than any of the calcium bicarbonate waters and much more bicarbonate than can be attributed to solution of calcium carbonate through the action of carbon dioxide derived from the air and soil.

As the waters in the Potomac group (Cretaceous) are all low in sulphate and as the environmental conditions under which the sediments of the Potomac group were deposited do not indicate that large amounts of sulphate are available for solution, it does not seem probable that carbon dioxide generated by chemical or biochemical breakdown of sulphate is responsible for the high sodium bicarbonate waters in this area.

Sulphate as a source of oxygen is not necessary for the generation of carbon dioxide by carbonaceous material. Oxygen is an important constituent of carbonaceous material and carbon dioxide is a characteristic decomposition product of such material—as, for example, peat and lignite.

Experimental work showed that distilled water, calcium bicarbonate water, and sodium bicarbonate water, after contact with lignite, calcium carbonate, and permutite (a base-exchange material), had all increased greatly in sodium bicarbonate content and had become similar in chemical character and in mineral content to high sodium bicarbonate waters found in the Coastal Plain. The tests indicated that carbonaceous material can act as a source of carbon dioxide, which, when dissolved in water, enables it to take into solution more calcium carbonate. If base-exchange materials are also present to replace calcium with sodium, a still greater amount of bicarbonate can be held in solution. The presence of carbonaceous material, together with calcium carbonate and base-exchange minerals in a formation is, therefore, sufficient to account for the occurrence in it of high sodium bicarbonate waters.

### INTRODUCTION

In shallow waters in the water-bearing sands of the Atlantic and Gulf Coastal Plains the dissolved mineral matter is usually made up predominantly of calcium and bicarbonate, but in many of the deeper waters in the same formations the dissolved mineral matter is predominantly sodium and bicarbonate [8], [9]. Such a difference in character between the shallower and deeper waters has been attributed to exchange of calcium in solution in the waters for sodium of base-exchange minerals in the rock materials [14], [15]. This base-exchange reaction involves no change in the content of bicarbonate or other acidic constituents—sulphate, chloride or nitrate—present in solution, and many of the sodium bicarbonate waters are similar in content of bicarbonate—and other acidic constituents—to the shallower calcium bicarbonate waters in the same formation. Others, however, contain several hundred parts per million more of bicarbonate than the shallower calcium bicarbonate waters from which they are presumably derived. The origin of the excessive bicarbonate content of such waters is the subject of the present study.

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## GROUND WATER CONDITIONS IN THE ATLANTIC AND GULF COASTAL PLAINS

The Atlantic and Gulf Coastal Plains are underlain by sedimentary deposits of gravel, sand, clay, shale, limestone, chalk, and marl, ranging in age from Lower Cretaceous to Quaternary. The boundary between the Coastal Plain sediments and the hard crystalline rocks of the Piedmont province is called the "Fall Line." This is in reality a broad zone, marked by falls and rapids, within which there is an abrupt change in the gradient of streams as they flow from the area underlain by crystalline rocks to that underlain by unconsolidated sediments. Along the Fall Line the crystalline rocks are at or near the surface but coastward they lie at progressively greater depths and the Coastal Plain sediments progressively thicken. In general the sedimentary strata dip gently seaward, successively older formations cropping out farther and farther inland thence dipping beneath younger beds and passing to greater and greater depths in the direction of the coast. Meteoric water enters the formations along their landward margins, where they are at or near the surface, and moves down the dip of the permeable beds toward the coast. Stratigraphically and structurally conditions are favourable for the accumulation of artesian pressure. The artesian aquifers are the water-bearing gravels, sands, and limestones and the confining members are the clays, shales, and other strata of low permeability.

## CARBON DIOXIDE—BICARBONATE RELATIONS IN THE GROUND WATERS

The principal soluble material in the sediments of the Atlantic and Gulf Coastal Plains is calcium carbonate. The clastic constituents of the deposits, being the weathered residues of older rocks, have already been more or less altered and leached of their soluble constituents. Solution of calcium carbonate is, therefore, the primary action when meteoric waters containing in solution carbon dioxide from the air and soil move down through the permeable beds.

Calcium carbonate is relatively insoluble in pure water: 1 litre of distilled water dissolves only 14 mg at 25° C [10]. In the presence of carbon dioxide, however, its solubility is increased to a marked degree owing to the formation of the more soluble bicarbonate. The amount of calcium bicarbonate that can be held in solution depends on the carbon dioxide content of the water, and this in turn depends on the partial pressure of carbon dioxide in the atmosphere over the water. The most complete summary and theoretical analysis of the solubility of calcium carbonate in water is found in the papers of JOHNSTON [11], [12]. JOHNSTON presents the complete solubility curve of calcium carbonate, showing the concentration of calcium in solution at equilibrium in the system  $\text{CaO}-\text{H}_2\text{O}-\text{CO}_2$ . As JOHNSTON's graph is the logarithm of the concentration of the calcium ion plotted against the logarithm of the partial pressure of carbon dioxide, and as only a small section of his curve applies to the solubility of calcium carbonate in natural waters, ADAMS and SWIMMERTON [1] redrew his graph, showing only the relationship of calcium carbonate dissolved to partial pressure of carbon dioxide. This curve is reproduced in Figure 1. From the shape of the graph it is indicated that at low pressures a small increase in the partial pressure of  $\text{CO}_2$  corresponds to a relatively large increase in the solubility of calcium carbonate.

In their paper ADAMS and SWIMMERTON discuss the source of the carbon dioxide which enables ground waters to take into solution the amounts of calcium bicarbonate found in them. Under normal conditions the partial pressure of carbon dioxide in the air is 0.0003 atm. At this partial pressure only 63 parts per million of calcium

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carbonate (equivalent to 76.8 parts per million of bicarbonate) can be dissolved at 16° C. It is apparent, therefore, that meteoric ground waters must obtain carbon dioxide from some other source to enable them to dissolve the concentrations of calcium bicarbonate found in them. The most obvious source of this increased concentration of carbon dioxide is the soil-air, which is characterized by a much higher partial pressure of carbon dioxide than atmospheric air. The biochemical oxidative decomposition of organic matter and the respiration of plant roots result in the liberation in the soil of large amounts of carbon dioxide. ROBINSON [16] states that the air of grassland soils may contain as much as 1.5% (0.015 atm) of carbon dioxide and arable soils up to 0.5% (0.005 atm). BOUSSINGAULT and LEWY [2] found that air from a soil poor in humus and not manured for a long time contained at least 25 times as much carbon dioxide as atmospheric air; air from humus rich soil contained 90 times and that from recently manured soil 250 times that of the atmosphere. Although the composition of soil-air varies from time to time and from place to place with difference in the energy of microbiological

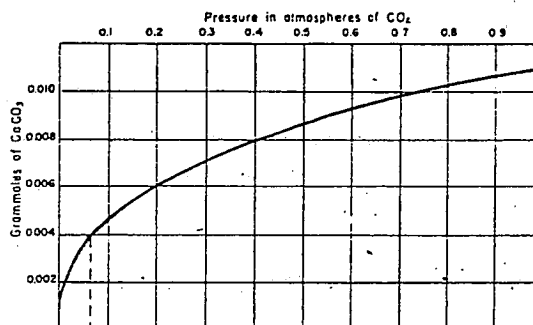


Fig. 1.—Solubility of  $\text{CaCO}_3$  at various pressures of  $\text{CO}_2$ , temperature = 16° C. Reproduced from ADAMS and SWIMMERTON.

Table 1—Analyses of waters from limestone and marl in Florida [4]

Constituent	Parts per million							
	1	2	3	4	5	6	7	8
Silica ( $\text{SiO}_2$ )	17	13	33	12	25	—	28	35
Iron (Fe)	1.5	.12	.16	.38	.12	.60	.09	Tr
Calcium (Ca)	66	54	83	137	48	52	60	98
Magnesium (Mg)	11	27	14	3.0	20	29	11	20
Sodium (Na)	14	5.5	11	28	11	20	16	47
Potassium (K)	1.8							
Bicarbonate ( $\text{HCO}_3$ )	233	288	325	423	223	295	253	337
Sulphate ( $\text{SO}_4$ )	6.0	6.5	3.0	2.0	16	4	1.7	7.6
Chloride (Cl)	26	9.0	10	42	9.0	34	14	94
Nitrate ( $\text{NO}_3$ )	Tr	Tr	Tr	Tr	Tr	—	Tr	Tr
Dissolved Solids (T.S.)	264	265	319	472	248	360	258	494
Total Hardness as $\text{CaCO}_3$ (T.H.)	210	246	265	355	202	249	195	327
Depth of well (in ft)	710	250	200	85	400	250	630	181

1. Panama City, Bay County. Municipal Supply.
2. River Junction, Gadsden County. Well of W. L. Shepard.
3. Whitehouse, Duval County. Well of Chas. F. Cox.
4. St. Augustine, St. Johns County. Municipal Well.
5. Lake City, Columbia County. Municipal Supply.
6. Arcadia, De Soto County. Courthouse Well.
7. Plant City, Hillsborough County. Municipal Well.
8. Seabreeze, Volusia County. Municipal Well.

decomposition, temperature, and other factors, it is evident that the carbon dioxide content of soil-air is much greater than that of atmospheric air. Meteoric waters moving through this carbon dioxide rich zone dissolve carbon dioxide and, thus enriched, are able to dissolve greater amounts of calcium carbonate than if they had been in contact only with normal atmospheric air.

The bicarbonate content (as calcium bicarbonate) of waters from calcareous rocks like limestone and marl, in which there is an abundance of calcium carbonate available for solution, indicates that the carbon dioxide in waters derived from the

air and soil is seldom high enough to permit the waters to take into solution more than 450 parts per million of bicarbonate as calcium bicarbonate. This amount of bicarbonate in solution corresponds to a partial pressure of carbon dioxide of about 0.05 atm, 170 times the partial pressure of carbon dioxide in the atmosphere. Most waters from limestones and marls, however, contain less than 300 parts per million of bicarbonate, which corresponds to a carbon dioxide partial pressure of less than 0.03 atm. Analyses of typical limestone and marl waters from the Coastal Plain in Florida [4] are given in Table 1.

The (calcium) bicarbonate content of waters in the sand and gravel beds of the Coastal Plain, like that of waters from limestones, does not ordinarily exceed 450 parts per million. In deposits that are relatively calcareous, the capacity of the waters to take calcium (and magnesium) carbonate into solution through the action of carbon dioxide is exhausted at shallow depths, but in formations that contain relatively little calcareous material the waters may have to travel to some depths before the carbon dioxide in them is fully utilized in solution of calcium carbonate. However, regardless of the calcium carbonate content of

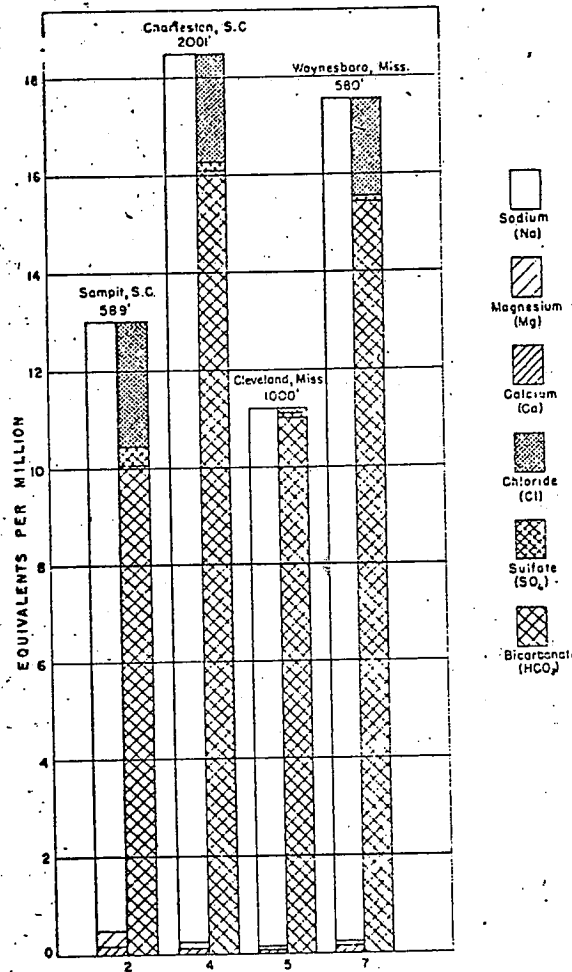


Fig. 2—High sodium bicarbonate waters in the Coastal Plain.

the materials through which they pass, the carbon dioxide in the waters derived from the air and soil is seldom high enough to permit the waters to take into solution more than 450 parts per million of bicarbonate as calcium bicarbonate. In most waters the carbon dioxide concentration thus derived is sufficient to permit the waters to take into solution only up to 250 parts per million of bicarbonate.

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In some of the sodium bicarbonate waters, however, the bicarbonate content is more than 800 parts per million and a few have been analysed that contained more than 1200 parts per million. Analyses of high sodium bicarbonate waters from the Coastal Plain in South Carolina [5] and Mississippi [20] are shown in

Table 2—Analyses of high sodium bicarbonate waters in the Coastal Plain [5, 20]

Constituent	South Carolina				Mississippi				
	1	2	3	4	5	6	7	8	9
				Parts	per million				
Silica (SiO <sub>2</sub> )	—	—	—	32	18	21	25	14	25
Iron (Fe)	0.11	0.15	0.05	1.0	7.0	1.1	1.4	0.30	0.50
Calcium (Ca)	4.0	4.0	5.6	3	1.1	3.0	2.9	2.4	12
Magnesium (Mg)	4.1	3.9	4.4	0.4	0.5	1.4	0.7	3.2	12
Sodium (Na)				421	254	290	396	571	651
Potassium (K)	281	288	277	4.4	3.7	6.0	6.0	4.0	79
Carbonate (CO <sub>3</sub> )	26	36	34	54	0	0	0	38	79
Bicarbonate (HCO <sub>3</sub> )	647	540	535	872	672	782	942	1355	1552
Sulphate (SO <sub>4</sub> )	2.0	18	21	7.2	1.2	2.0	1.6	9.0	29
Chloride (Cl)	43	91	82	92	5.0	4.7	72	54	12
Nitrate (NO <sub>3</sub> )	25	35	1.2	—	—	—	—	30	50
Dissolved Solids (T.S.)	727	743	797	1051	626	714	970	1368	1591
Total Hardness as CaCO <sub>3</sub> (T.H.)	27	26	32	9	5	13	10	19	79
Depth of well (ft)	365	589½	800	2001	1000	422	580	1375	480?

1. Well of E. Stalvey at Stalvey, Horry County, S.C.—flowing well.
2. Well of B. D. Bourne Estate at Sampit, Georgetown County, S.C.—flowing.
3. Well of Gas & Electric Co. at Summerville, Dorchester County, S.C.
4. Well of Charleston Consolidated Railway and Lighting Co. at Charleston, Charleston County, S.C.—flowing well.
5. Well of town of Cleveland, Bolivar County, Miss.—flowing well from Claiborne group.
6. Well of Mr. Weems at Subuta, Clarke County, Miss.—flowing well from Sparta sand of Claiborne group.
7. Well of town of Waynesboro, Webster County, Miss.
8. Well of Southern Lumber Co. at Jackson, Hinds County, Miss.—flowing well from Wilcox formation.
9. Well of City of Greenville, Washington County, Miss.—from Wilcox formation.

Table 2. Four of the analyses are represented graphically in Figure 2. In some of these waters, sodium and bicarbonate make up 90% or more of the dissolved mineral matter; calcium and magnesium are generally not present in them in excess of 5 parts per million. Sulphate and chloride are usually very low also, except near the coast, where the ground waters may be high in chloride due to contamination by sea water.

#### ALTERATION IN CHARACTER OF WATERS WITH DEPTH IN FORMATION

The relations between sodium waters of high bicarbonate content and calcium and sodium waters of moderate bicarbonate content in the Potomac group (Lower and Upper Cretaceous) in Virginia were discussed in a paper by CEDERSTROM [3]. The

Potomac group, which is nonmarine in origin, consists of alternating sands, clays, and sandy clays. The sands of the group are recharged from rain water which enters these strata where they are at or near the surface along the Fall Zone. Down dip of the recharge area, the water in the sands is under artesian pressure and rises in wells which penetrate into the formation. The areal distribution of the different

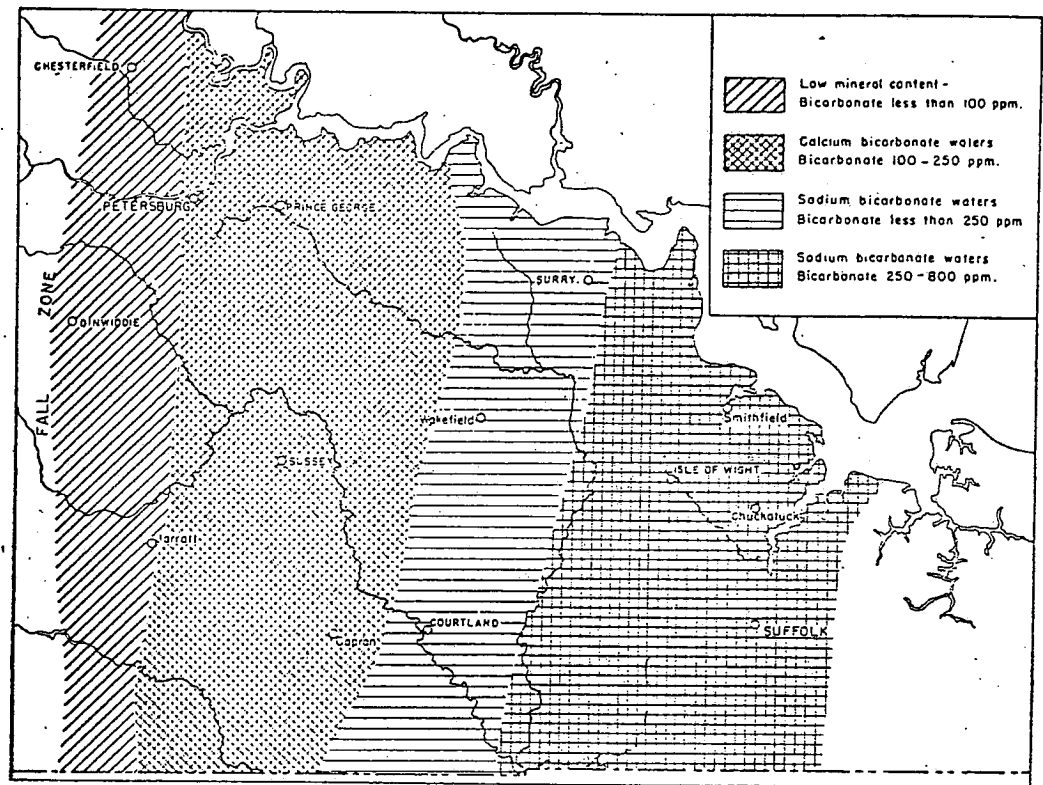


Fig. 3—Map of southeastern Virginia showing geographic distribution of the different types of water in the Potomac group.

types of water found in the sands of the Potomac group is shown in Figure 3. Along the Fall Zone, where meteoric waters enter the formation, the sands of the Potomac group yield waters that are soft and low in bicarbonate and in total mineral content. But as the waters move eastward down the dip of the permeable beds; they increase in calcium bicarbonate and in total mineral content until they contain approximately 170 to 250 parts per million of bicarbonate as calcium and magnesium bicarbonate. Then they seem to undergo a rather abrupt change in character—and become sodium bicarbonate waters. A few waters of intermediate character indicate that the change in character is due to a decrease in calcium and magnesium with an equivalent increase in sodium. During the alteration in character and for some distance to the eastward the bicarbonate content remains relatively constant. Still farther eastward from the zone of softening, however, the waters in the sands of the Potomac group again increase in bicarbonate content and in sodium content. In the vicinity of Suffolk, water from the Potomac group contains 550 to 650 parts

per million of bicarbonate; and one sample of water, from a well south of Suffolk, had 775 parts per million of bicarbonate. Graphic representations of analyses showing these changes with depth in the character of waters from the Potomac group are shown in Figure 4. To the eastward of Suffolk the waters in the Potomac group contain increasing amounts of chloride due to contamination by marine water.

Determinations of free carbon dioxide on a few samples of water from shallow wells along the Fall Zone that draw from the Potomac group indicate that the waters in this part of the area contain considerable free carbon dioxide. For example, one sample which contained 60 parts per million of bicarbonate had 45 parts per million of free carbon dioxide. Others had from 20 to 35 parts per million. On the other hand, moderately hard calcium bicarbonate waters contain very little free carbon dioxide—most of those examined for carbon dioxide had less than 2 parts per million. The amount of calcium bicarbonate in the hard waters is about that to be expected if the free carbon dioxide in the shallow waters were completely utilized in solution of calcium carbonate. For example, if the 45 parts per million of free carbon dioxide found in the Fall Zone water mentioned above were entirely utilized in solution of calcium carbonate, the bicarbonate thus formed plus the 60 parts of bicarbonate already in the water would total 171 parts per million. This amount of bicarbonate approximates that found in about 50% of the calcium bicarbonate waters from the Potomac group that have been analysed.

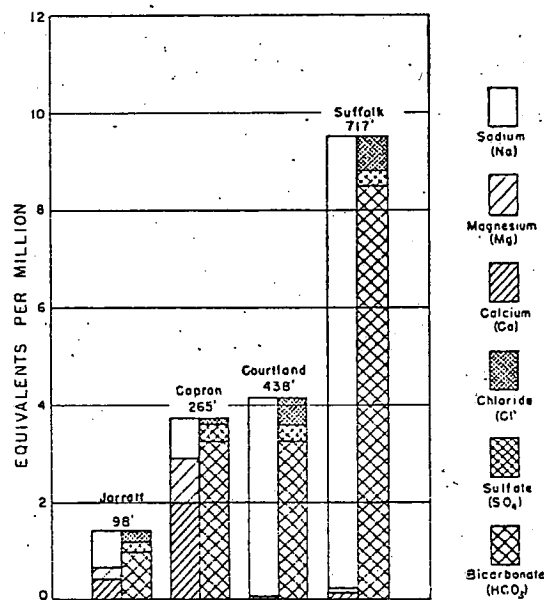


Fig. 4—Types of waters in southeastern Virginia Coastal Plain.

Although the bicarbonate content of the high sodium bicarbonate waters in the Potomac group is not as great as that of many deep sodium bicarbonate waters in other parts of the Coastal Plain, as illustrated by the analyses in Table 2, it is greatly in excess of the amount that can be attributed to the solvent action of carbon dioxide derived from the air and soil in shallow waters in the Potomac sediments along the Fall Zone. If the bicarbonate in these waters is presumed to have been taken into solution as calcium bicarbonate and the calcium subsequently exchanged for sodium, a carbon dioxide partial pressure of 0.10 to 0.20 atm would have been required, compared with a carbon dioxide partial pressure of about 0.01 atm for the bicarbonate in solution in the calcium bicarbonate waters. For concentrations of 1200 parts per million and more found in some Coastal Plain waters, carbon dioxide pressures of 0.7 atm or more would have been required for solution of calcium carbonate.

## THEORIES AS TO SOURCE OF ADDITIONAL CARBON DIOXIDE

*Reduction of sulphate by carbonaceous material as a source of carbon dioxide.*

CEDERSTROM [3] attributes the increase in bicarbonate in the Virginia waters to chemical or biochemical breakdown of sulphate by carbonaceous material, with liberation of carbon dioxide and subsequent solution of calcium carbonate and replacement of calcium by sodium. It is true that the high sodium bicarbonate waters in southeastern Virginia are low in sulphate—most of them contain less than 16 parts per million. However, analyses indicate that few waters in the formation, from the waters of low mineral content along the Fall Zone to the high sodium bicarbonate waters in the vicinity of Suffolk, contain more than 16 parts per million of sulphate. Thus the sulphate content of the high sodium bicarbonate waters is comparable to that of other waters in the formation. The continuous generation of small amounts of carbon dioxide postulated by CEDERSTROM would require continuous reduction of sulphate and this, in turn, would require continuous solution of sulphate to maintain the sulphate content of these waters on a par with that of waters to the west and up dip in the formation. To generate sufficient carbon dioxide to effect an increase in bicarbonate of 350 parts per million—the average increase in bicarbonate of the waters from the zone of softening to the vicinity of Suffolk—would require solution of 200 mg of sulphate per litre of water. As the waters in the formation are all low in sulphate and as the environmental conditions under which the sediments of the Potomac group were deposited do not indicate that large amounts of sulphate are available for solution it does not seem probable that carbon dioxide generated by chemical or biochemical breakdown of sulphate is responsible for the high sodium bicarbonate waters in this area.

*Generation of carbon dioxide by carbonaceous material without intervention of sulphate*

Sulphate as a source of oxygen is not necessary for the generation of carbon dioxide from carbonaceous material. Oxygen, as well as carbon, is an important constituent of such material and carbon dioxide is a characteristic product of vegetal alteration. Organic deposits as they are found buried in the earth's strata have practically everywhere undergone both chemical and physical changes. Loaded beneath hundreds or thousands of feet of sediments, brought downward into zones of greater temperature, and perhaps subjected to shearing stresses, the carbonaceous material undergoes changes which are referred to as dynamochemical in contradistinction to the primary biochemical action. The outstanding result of the dynamochemical process is progressive elimination of the volatile matter from organic sediments [21]. The alteration consists primarily of internal molecular readjustment which causes the detachment and elimination of simple volatile substances from the great unstable molecules that characterize vegetal debris. These emanations consist almost entirely of the simplest compounds of carbon, hydrogen, and oxygen—carbon dioxide, methane, and water, and in smaller proportions carbon monoxide and nitrogen, and sometimes traces of hydrogen sulphide and higher hydrocarbons. From peat and lignite the predominant gases evolved are the oxides, water and carbon dioxide; in later stages of alteration methane predominates [13]. Thus without the intervention of sulphate, alteration of carbonaceous material could provide carbon dioxide to underground waters filling the interstitial spaces of surrounding rock materials.



## The origin of high sodium bicarbonate waters in the Atlantic and Gulf Coastal Plains

Many sediments in the Atlantic and Gulf Coastal Plains were deposited under environmental conditions favourable for the accumulation of plant debris. For example, the character of the Potomac (Lower and Upper Cretaceous) sediments indicates that they were laid down in estuaries or along shore in comparatively shallow waters that were fresh or, at most, brackish, and the clays of the formation are more or less charged with vegetable remains, either silicified or in the condition of lignite [7]. Leaves and wood were found in Potomac sediments in a deep well in Norfolk [6] and lignite was found in a well at Claremont, Va. The sands, clays, and lignites which predominantly compose the typical beds of the Black Creek (Upper Cretaceous) formation in North Carolina were deposited in shallow sea water near shore, or perhaps in part in shallow bays and estuaries. The clays, as a rule, are dark to black in colour on account of contained carbonaceous matter; and thin seams of finely comminuted, lignitized vegetable particles are common in the formation. Pieces of lignite, ranging in size from small particles to twigs, branches, and even large trunks of trees, occur scattered irregularly through the formation [19]. A few thin seams of lignite and carbonaceous clay have been noted in the Black Creek formation in South Carolina [5].

In Texas the strata of the Wilcox (Eocene) group comprise a heterogeneous series, several hundred feet thick, of sandy lignitiferous littoral clays, cross-bedded sands, compact, noncalcareous lacustrine or lagoonal clays, lignite lentils, and stratified deltaic silts [17]. The Wilcox in Georgia [18] and Mississippi [20] also contains lignitic sand or clay and in the latter State, interbedded lignite layers.

The calcium bicarbonate waters and the sodium bicarbonate waters of comparable bicarbonate content in the Coastal Plain as a rule are colourless, but many of the high sodium bicarbonate waters are noticeably coloured. Deep waters in the Yazoo Delta region in Mississippi, which have a bicarbonate content (as sodium bicarbonate) of 800 to 1500 parts per million, have a yellow to dark brown colour, similar to the colour of swamp waters, suggesting that they may have been in contact with carbonaceous material.

It is suggested, therefore, that carbon dioxide generated by alteration of carbonaceous material in the sediments is a determining factor in the occurrence of the high sodium bicarbonate waters in certain formations in the Coastal Plain. Waters in formations containing carbonaceous material acquire additional carbon dioxide, which permits them to dissolve more calcium carbonate, the calcium thus taken into solution being then replaced by sodium through the action of base-exchange minerals—the end result of these reactions being an increase in the sodium bicarbonate content of the waters.

### EXPERIMENTAL

Lignite, as a representative of carbonaceous material, was used in the following series of tests to determine its effect, in different environments, on the mineral content of different types of waters.

1a—500 ml of distilled water on 5 gm of lignite.

1b—500 ml of distilled water on 5 gm of lignite and 1 gm of calcium carbonate.

1c—500 ml of distilled water on 5 gm of lignite, 1 gm of calcium carbonate, and 10 gm of permutite.

2a—500 ml of sodium bicarbonate water on 5 gm of lignite.

2b—500 ml of sodium bicarbonate water on 5 gm of lignite and 1 gm of calcium carbonate.

2c—500 ml of sodium bicarbonate water on 5 gm of lignite, 1 gm of calcium carbonate, and 10 gm of permutite.

3a—500 ml of calcium bicarbonate water on 5 gm of lignite.

3b—500 ml of calcium bicarbonate water on 5 gm of lignite, and 1 gm of calcium carbonate.

3c—500 ml of calcium bicarbonate water on 5 gm of lignite, 1 gm of calcium carbonate, and 10 gm of permutite.

The lignite used in these tests, which was from Hoyt, Texas, was kindly furnished by Miss TAISIA STADNICHENKO of the Geological Survey. The calcium carbonate was MALLINCKRODT'S C. P. grade.

The waters and materials, in 500 ml rubber stoppered ERLLENMEYER flasks, were mixed and shaken twice daily. After 14 days the waters were decanted through a filter paper and analysed. Analyses of the waters before and after the tests are given in Table 3 and are represented graphically in Figure 5.

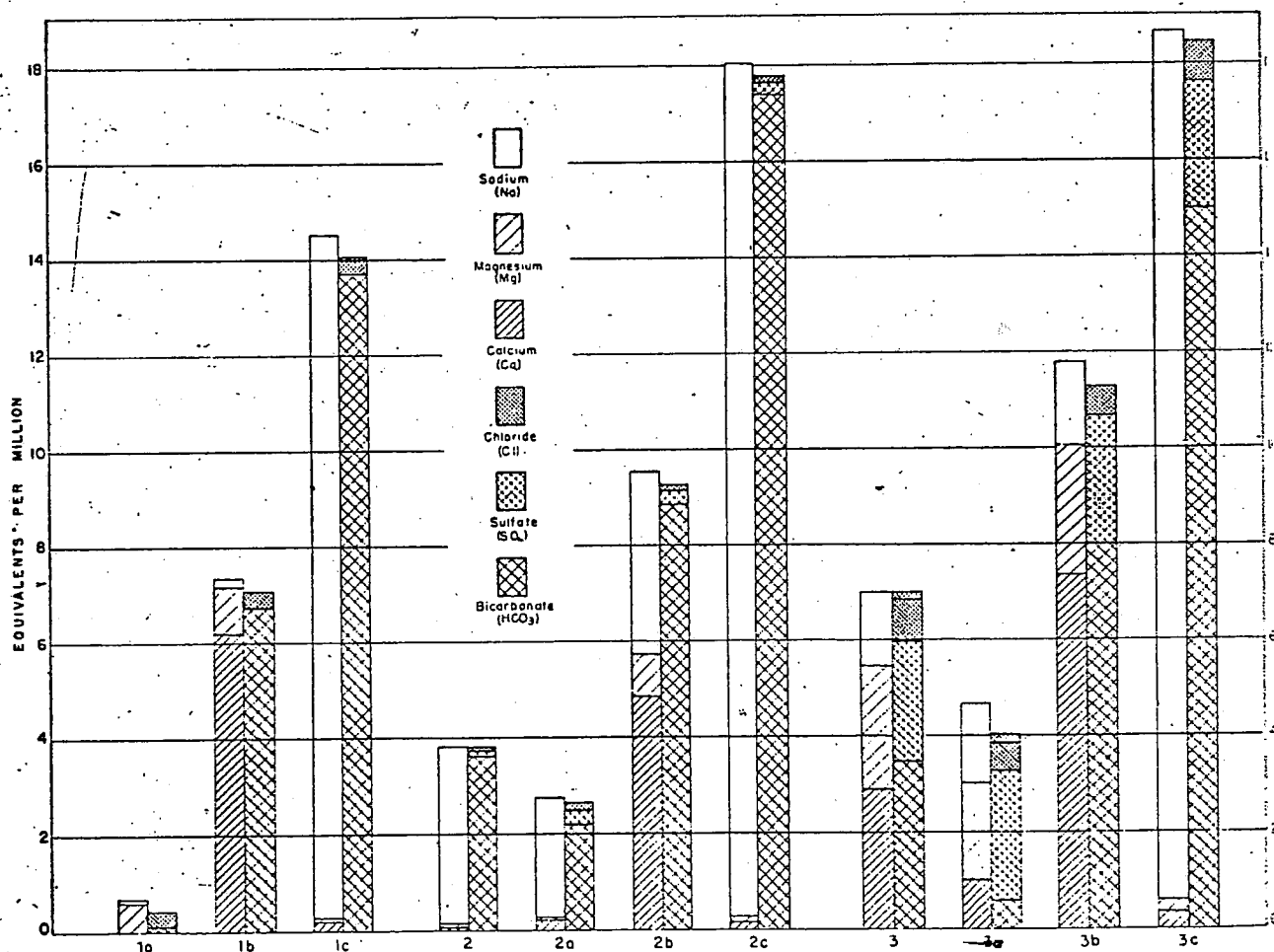


Fig. 5—Change in mineral content of (1) distilled water, (2) sodium bicarbonate water, and (3) calcium-bicarbonate water, after treatment with (a) lignite, (b) lignite and calcium carbonate and (c) lignite, calcium carbonate and permutite.

In contact with lignite alone, distilled water gained a little mineral matter, chiefly calcium and sulphate, but the sodium bicarbonate and the calcium bicarbonate waters both lost mineral matter, the sodium bicarbonate water losing 87 parts per

Table 3—Analyses showing change in mineral content of distilled water,  $\text{NaHCO}_3$  and  $\text{Ca}(\text{HCO}_3)_2$  waters on treatment with lignite, lignite and  $\text{CaCO}_3$ , and lignite,  $\text{CaCO}_3$  and permutite

	Distilled water			NaHCO <sub>3</sub> water			Ca(HCO <sub>3</sub> ) <sub>2</sub> water					
	Before	After lignite and CaCO <sub>3</sub>	After lignite CaCO <sub>3</sub> and per- mutite	Before	After lignite and CaCO <sub>3</sub>	After lignite CaCO <sub>3</sub> and per- mutite	Before	After lignite	After lignite and CaCO <sub>3</sub>	After lignite CaCO <sub>3</sub> and per- mutite		
Total Solids at 180° C	—	60	391	843	211	172	485	1007	414	322	667	1103
Loss on ignition of dried residue ...	—	34	36	40	11	22	21	30	45	63	50	43
SiO <sub>2</sub> ...	—	1.6	1.0	10	10	8.8	8.1	13	20	19	18	18
Ca ...	—	7.5	124	4.0	1.2	2.7	97	3.8	58	20	148	7.4
Mg ...	—	—	12	1.0	.6	.9	11	1.0	31	25	33	2.7
Na ...	—	1.1	3.5	319	84	58	86	403	35	36	37	408
K ...	—	1.1	1.6	9.6	1.6	1.8	3.7	10	2.4	2.4	2.7	11
CO <sub>3</sub> ...	—	—	0	24	12	0	0	18	6.9	0	0	0
HCO <sub>3</sub> ...	—	Acid*	410	786	197	134	540	1024	200	36	488	912
SO <sub>4</sub> ...	—	14	17	16	3.3	14	13	13	117	129	128	128
Cl ...	—	0	0	1	4.0	5.0	4.0	4.0	25	21	22	28
NO <sub>3</sub> ...	—	.0	0	0	.8	—	—	—	11	8.3	0	0
pH ...	6.2	4.5	7.0	8.7	8.7	6.3	7.0	8.3	8.1	5.7	6.9	8.3
Colour ...	0	25	25	45	0	45	25	45	0	25	25	40

\* 6.0 ppm  $\text{HCO}_3$  after aeration.

million of bicarbonate as sodium bicarbonate and the calcium bicarbonate water losing 178 parts per million of bicarbonate as calcium and magnesium bicarbonate. This loss in mineral content is probably the result of adsorption by the lignite. The greater loss of calcium and magnesium bicarbonate from the calcium water than of sodium bicarbonate from the sodium water is in accordance with the general rule that bivalent ions are adsorbed more strongly than univalent ions. The greater loss of calcium than of magnesium from the calcium bicarbonate water, although the two were originally present in equivalent amounts, also follows the general rule that calcium is more strongly adsorbed than magnesium.

In contact with lignite and calcium carbonate, all the waters gained calcium bicarbonate—the increase in bicarbonate being 410, 319, and 274 parts per million for the distilled water, the sodium bicarbonate water, and the calcium bicarbonate water, respectively. In control tests to determine the amount of calcium carbonate taken into solution by these waters in the absence of lignite, the distilled water and the sodium bicarbonate water gained only 48 and 40 parts per million of calcium bicarbonate, respectively. This increase may be attributed to calcium carbonate dissolved through the action of the carbon dioxide in the waters under the partial pressure of the carbon dioxide of the air above the waters. The calcium bicarbonate water lost 38 parts per million of bicarbonate—this may be attributed to loss of carbon dioxide from the water under the low partial pressure of carbon dioxide in the air above the water. Only a very small amount of the calcium carbonate taken into solution when the waters were in contact with lignite and calcium carbonate can, therefore, be attributed to the action of free carbon dioxide in solution in the waters under the normal partial pressure in the air of carbon dioxide. The great increase in calcium bicarbonate in the calcium bicarbonate water in contact with lignite and calcium carbonate as compared with the loss of calcium bicarbonate from the calcium bicarbonate water when in contact with calcium carbonate alone indicates greatly increased partial pressure of carbon dioxide in the atmosphere above the water when lignite was present.

There was not the loss in sodium content from the sodium bicarbonate water after contact with lignite and calcium carbonate that there was after contact with lignite alone. Presumably, as calcium is more strongly adsorbed than sodium, some of the calcium taken into solution when calcium carbonate is present with lignite is preferentially adsorbed and the sodium content remains unchanged.

In contact with lignite, calcium carbonate, and permutite all the waters increased greatly in sodium bicarbonate content—the increase in terms of bicarbonate being 786 parts, 803 parts, and 698 parts per million for the distilled water, the sodium bicarbonate water, and the calcium bicarbonate water, respectively. The resulting waters are similar in chemical composition and mineral content to many high sodium bicarbonate waters from deep wells in the Coastal Plain.

During the tests the waters, which were colourless at the start, acquired a yellowish colour, presumably from the lignite. This colour and the fact that the sum of the equivalent values of the basic constituents, calcium, magnesium, sodium, and potassium, in the waters after the tests was in excess of the sum of the equivalent values of the acidic constituents, bicarbonate, sulphate, chloride, and nitrate, suggest that the excess basic constituents are paired with some undetermined organic acid radical.

In a second series of tests 20 gm of powdered lignite was added to 4 litres of a sodium bicarbonate water and the bicarbonate content and hardness of the water were determined at 24-hr inter-

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vals. When successive determinations showed no change, 500 ml of the water was withdrawn for analysis. Two grams of calcium carbonate was then added to the main portion of water and the bicarbonate and hardness were determined at 24-hr intervals until they were again constant. After withdrawal of a second portion of the water for analysis, 10 gm of permutite was added to the main portion. During the first 6 hrs after addition of the permutite, the bicarbonate and hardness were determined at 72-min intervals. Thereafter the determinations were made at 24-hr intervals until successive determinations showed no change in the bicarbonate content

Table 4—Change in bicarbonate ( $\text{HCO}_3$ ) content and total hardness (TH) of a sodium bicarbonate water after addition of lignite, calcium carbonate, and permutite

Day	NaHCO <sub>3</sub> water		After addition of lignite		After addition of calcium carbonate		After addition of permutite	
	HCO <sub>3</sub>	TH as CaCO <sub>3</sub>	HCO <sub>3</sub>	TH as CaCO <sub>3</sub>	HCO <sub>3</sub>	TH as CaCO <sub>3</sub>	HCO <sub>3</sub>	TH as CaCO <sub>3</sub>
Start	310	30		Parts per million				
1			240	21	376	102	544	57
2			214	12	416	126	676	30
3			200	6	438	144	—	—
4			—	—	—	—	806	21
5			200	0	453	156	856	21
6					464	162	892	21
7					468	165	916	18
8							932	15
9							948	15
10							—	—
11							966	15
12							978	15
13							984	15
14							993	15
15							1001	15
21							1010	15

or hardness. The water was then filtered and analysed. Throughout the period of the test the flask was shaken at half-hour intervals during the working day.

The values obtained for bicarbonate and hardness during the test are shown in Table 4 and are plotted against time (in days) in Figure 6. Analyses of the water at the end of each step in the test are given in Table 5 and are represented graphically in Figure 6 at the point on the curve where the respective samples were taken for analysis.

Although in this test the materials, lignite, calcium carbonate, and permutite, were added successively after reaction with the materials already added had ceased, the mineral content of the water at the end of each step was similar to that of the waters obtained in the first series of tests (2a, 2b, and 2c) when a sodium bicarbonate water was in contact with the respective combinations of materials from the start.

In both sets of tests the bicarbonate in solution when base-exchange minerals (permutite) were present was considerably greater than when they were not present. The amount of calcium bicarbonate that could be held in solution reached a saturation point and no more calcium carbonate could be dissolved. This is clearly shown

in the second step of the second test. When, however, calcium is replaced by sodium from base-exchange minerals, much more bicarbonate can be held in solution—as shown in the third step of the second test.

*Table 5—Analyses showing changes in mineral content of sodium bicarbonate water after contact first with lignite, then with lignite and calcium carbonate, and finally with lignite, calcium carbonate, and permutite*

Constituent	At start	After lignite	After lignite and CaCO <sub>3</sub>	After lignite, CaCO <sub>3</sub> , and permutite
		<i>Parts per million</i>		
Total Solids ...	239	233	447	972
Loss on ignition	5.2	11	29	29
SiO <sub>2</sub> ... ..	2.6	2.4	3.0	14
Ca ... ..	7.6	—	51	4.1
Mg ... ..	2.7	—	9.7	1.2
Na ... ..	107	88	111	374
K ... ..	4.0	2.4	2.1	16
CO <sub>3</sub> ... ..	6.9	.0	0	0
HCO <sub>3</sub> ... ..	282	200	470	1014
SO <sub>4</sub> ... ..	13	18	19	22
Cl ... ..	4.0	4.0	4.0	4.0
NO <sub>3</sub> ... ..	1.2	—	—	—
TH ... ..	30	0	165	15
pH ... ..	8.7	7.9	7.5	8.8
Colour ... ..	0	35	35	70

#### CONCLUSIONS

The tests support the hypothesis that carbonaceous material may act as a source of carbon dioxide which, when adsorbed by water, enables the water to dissolve more calcium carbonate. If base-exchange materials are also present to replace calcium with sodium, a still greater amount of bicarbonate can be held in solution and high sodium bicarbonate waters like those in the Coastal Plain result.

If a water-bearing formation lacks any one of the three materials—calcium carbonate, base-exchange minerals, or carbonaceous matter—it is not likely that waters of high sodium bicarbonate content will be found in it. If the formation lacks calcium carbonate, even the carbon dioxide derived from the soil and air cannot be utilized and the water remains low in dissolved mineral matter, as the sand and gravel beds contain very little soluble material except calcium carbonate. Any base-exchange minerals and carbonaceous material in such a formation have no opportunity to act. If the formation lacks base-exchange minerals but contains calcium carbonate and carbonaceous materials, the waters of the formation may be expected to be hard, calcium bicarbonate waters, the amount of calcium bicarbonate in solution depending not only on carbon dioxide derived from the air and soil but also on carbon dioxide evolved by carbonaceous material in the formation. In such a formation, therefore, a calcium bicarbonate water may contain calcium bicarbonate in excess of that equivalent to the amount of calcium carbonate that can be dissolved through the action of carbon dioxide derived from the air and soil.

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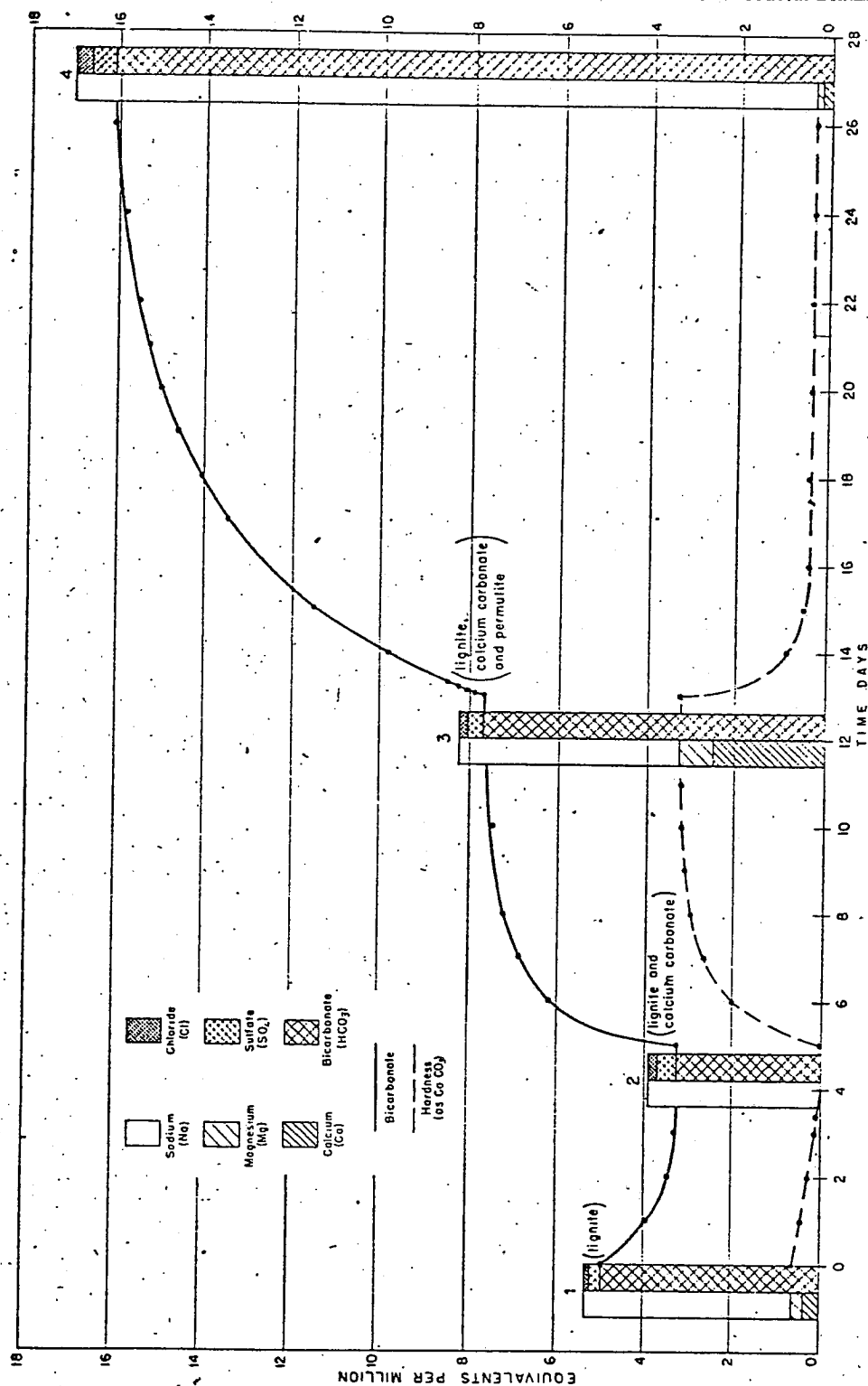


Fig. 8—Change in bicarbonate content and total hardness of a sodium bicarbonate water after addition of (2) lignite, (3) calcium carbonate and (4) permittite.

If a formation contains calcium carbonate and base-exchange minerals but no carbonaceous material, it is to be expected that the shallower waters will be calcium bicarbonate waters, altering with depth to sodium bicarbonate waters and both types of waters having an amount of bicarbonate in solution equivalent to the carbon dioxide content of the waters entering the formation. The depth at which the alteration in character begins to take place differs in different formations but alteration does not usually occur at depths less than 100 ft and in many formations does not occur at depths less than several hundred feet. It is not to be presumed from this fact that base-exchange minerals are necessarily lacking in the shallower materials, but more probably that any base-exchange minerals in them have been exhausted of their capacity to exchange sodium for calcium.

Only in a formation containing all three materials—calcium carbonate, base-exchange minerals, and carbonaceous materials—may waters of high sodium bicarbonate content be expected and these, usually, only at some depth in the formation. Conversely, the occurrence of such waters in a formation may be taken as indicative of the presence of these three materials.

It seems probable that carbon dioxide evolved by carbonaceous material would permeate water in the interstices of the rock materials in its environment and that in order to obtain carbon dioxide it would not be necessary for the waters to come in direct contact with the carbonaceous material. Nor would it be necessary that the carbonaceous material be present in definite, recognizable deposits. Disseminated organic debris in quantities not readily detected without chemical or microscopic aid could also contribute carbon dioxide to water.

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