Origin of Mineralized Water in Precambrian Rocks of the Upper Paraíba Basin, Paraíba, Brazil

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ORIGIN OF MINERALIZED WATER IN PRECAMBRIAN ROCKS OF THE UPPER PARAÍBA BASIN, PARAÍBA, BRAZIL

By STUART L. SCHOFF

ABSTRACT

The upper Rio Paraíba basin, a region of more than 12,000 square kilometers in the central part of Paraíba (Estado da Paraíba), northeast Brazil, has ground water that is generally poor in chemical quality. Although some good water has been found, only about 3 percent of the wells yield water having less than 500 milligrams per liter of dissolved solids, and only 11 percent yield water having less than 1,000. The minimum dissolved-solids concentration, in milligrams per liter, is 334; the maximum, about 25,000; and the average, 4,300.

The foregoing figures are based on a study of 212 chemical analyses of water from 106 water-supply wells that were drilled by or for the Superintendência do Desenvolvimento do Nordeste (SUDENE). This study is part of a general investigation initiated by SUDENE into the causes of, and possible remedies for, the high mineralization of the water.

The region is one of the most arid in northeast Brazil. One precipitation station has an average annual precipitation below 300 millimeters, and another has somewhat more than 600 millimeters. A large fraction of the precipitation received in the region escapes as runoff, and evaporation takes a heavy toll the year around.

The entire region is underlain by crystalline rocks of Precambrian age consisting of various kinds of migmatite, gneiss, schist, and granite. Saprolite and alluvium have been derived from the crystalline rocks. All the rock materials in the basin, therefore, may be characterized as crystalline rock in various stages of decomposition from completely fresh to deeply weathered.

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The rocks of the basin probably have influenced the chemical character of the ground water in varying degree, but their effect is obscured by other factors. The water from wells drilled into gneiss, for example, ranged from the second lowest to the highest in concentration of dissolved solids and included both chloride and bicarbonate water types.

In several respects the ground water bears a strong resemblance to sea water. Chloride is the predominating anion in the ground water, as it is in sea water, but the rocks of the region probably contain only insignificant amounts of it. The chloride in the ground water, therefore, could more readily have been inherited from sea water than dissolved from the bedrock. Magnesium predominates over calcium in the ground water of the basin, as it does in sea water, whereas calcium generally predominates in ground water from continental sources.

It is suggested that the ground water contains some residual sea water, introduced during an Upper Cretaceous marine invasion of the land, and that this water has been diluted by meteoric water and largely flushed out of the rocks in a process that is still incomplete but is continuing. The process has operated unevenly, in accord with diverse rates of circulation of water in fracture systems having a wide variety of hydraulic characteristics. Thus, the mineralized and the dilute waters are interspersed haphazardly through the region.

Any action by man that would accelerate the dilution of the mineralized ground water with fresh water or remove it from the rocks would tend in the same direction as the natural process, but man's efforts are unlikely to accomplish large observable improvements in water quality, except perhaps locally. Planned pumping of a well over a period of years might withdraw enough mineralized water from a small system of fractures and promote the infiltration of enough fresh water to create worthwhile changes in chemical quality. A program of regional pumping and recharge having water-quality improvement as an objective, however, probably would be impractical.

INTRODUCTION

This report summarizes observations on the chemical character of the ground water in the upper part of the Rio Paraíba basin, Paraíba, Brazil. The report represents one phase of an investigation of the salinity of the ground water in northeast Brazil that the Division of Hydrogeology of the Superintendência do Desenvolvimento do Nordeste (SUDENE) is conducting. The objective of SUDENE in this investigation is to collect and study the available data on the chemical character of the water to develop ways for finding the best water to be had or for improving the quality of the available water, if possible.

Thousands of wells have been drilled in northeast Brazil during the past half century because at many locations a well offers the

best, if not the only, hope of developing a water supply. Even some of the main streams are intermittent in substantial parts of the region, and even where they are perennial, some streams contain saline water. Impounding surface water offers only a partial solution of the regional water-supply problem, as not enough good damsites are available to enable impoundment of water for the whole region. Small impoundments—farm ponds—have provided water for both humans and cattle but are subject to the vagaries of weather and sometimes go dry. Inevitably the residents of the region have had to resort to wells, although at many locations an individual well has small chance for success.

Wells thus far have provided only a partial and uncertain solution to the general water-supply problem of northeast Brazil because of limitations on both the quantity and the quality of the ground water. Wells in about half of the region can only be drilled into various kinds of crystalline rock. Like crystalline rocks generally, these rocks contain only small to moderate quantities of ground water, mostly in fractures. Unlike the crystalline rocks of some other places, notably the United States (White and others, 1963, p. 5–6, 14, 16–17, 25–26), they contain water which generally is so highly mineralized that it is acceptable only to animals. The human population, therefore, must find water elsewhere.

The investigation on which this report was based was made cooperatively by SUDENE and the U.S. Agency for International Development (USAID) under the Alliance for Progress. Geraldo de Azevedo Gusmão, chief of the Division of Hydrogeology, was in charge for SUDENE, and the author of this report was in charge for USAID.

PURPOSE AND SCOPE

This report presents facts about the chemical character of the ground water in a part of northeast Brazil that is underlain exclusively by crystalline rocks and seeks to relate that character to the existing topographic, climatic, and geologic environment and to regional geologic history. Thus, it seeks first to explain the high degree of salinity found in the water, and then, in the light of this explanation, the report explores possibilities for increasing the effectiveness of well development and ground-water utilization in the area.

The region discussed in this report is the upper part of the basin of the Rio Paraíba, Paraíba (Estado da Paraíba), northeast Brazil (fig. 1). It includes over 12,000 square kilometers between long 36°00′ W. and 37°15′ W. and between lat 6°45′ S. and 8°15′ S. It is in the south-central part of Paraíba and adjoins Pernambuco (Estado de Pernambuco), which is to the south. Its eastern boundary is a few kilometers west of Campina Grande, the second largest city in Paraíba.

PREVIOUS WORK

SUDENE, operating first through its Grupo de Trabalho de Águas Subterrâneas and later through its subsidiary, the Companhia Nordestina de Sondagens e Perfurações (CONESP), has had more than 100 wells drilled in the upper Paraíba basin. Most, if not all, of these wells were drilled into crystalline rocks of Precambrian age. Most of the wells that yield water were sampled at least once, many were sampled twice, and a few were sampled three or four times. The well-development work in this and other regions of crystalline rock led several of the participating geologists to seek explanations for the mineralization of the ground water. Their views are summarized in the following paragraphs.

Texeira and Oliveira (1962, p. 9) considered the biotite in the rocks to be responsible for much of the mineralization, but Costa (1963, p. 22; 1965, p. 21) concluded, for a different locality, that alkali feldspars were a principal source of dissolved mineral matter. Costa also found that concentration of dissolved solids is nearly twice as great in water from granite as in that from gneiss and nearly twice as great in water from fractures at low angles to regional structure as in that from fractures transverse to that structure. In addition, he stated that the longer a well is pumped, the better its water will become.

Siqueira (1963a, p. 26, 28–31; 1963b, p. 29) discussed the solution of minerals by rainwater. He proposed regular pumping of wells, to be started soon after the beginning of each annual rainy season, as a means of bringing about gradual improvement in water quality.
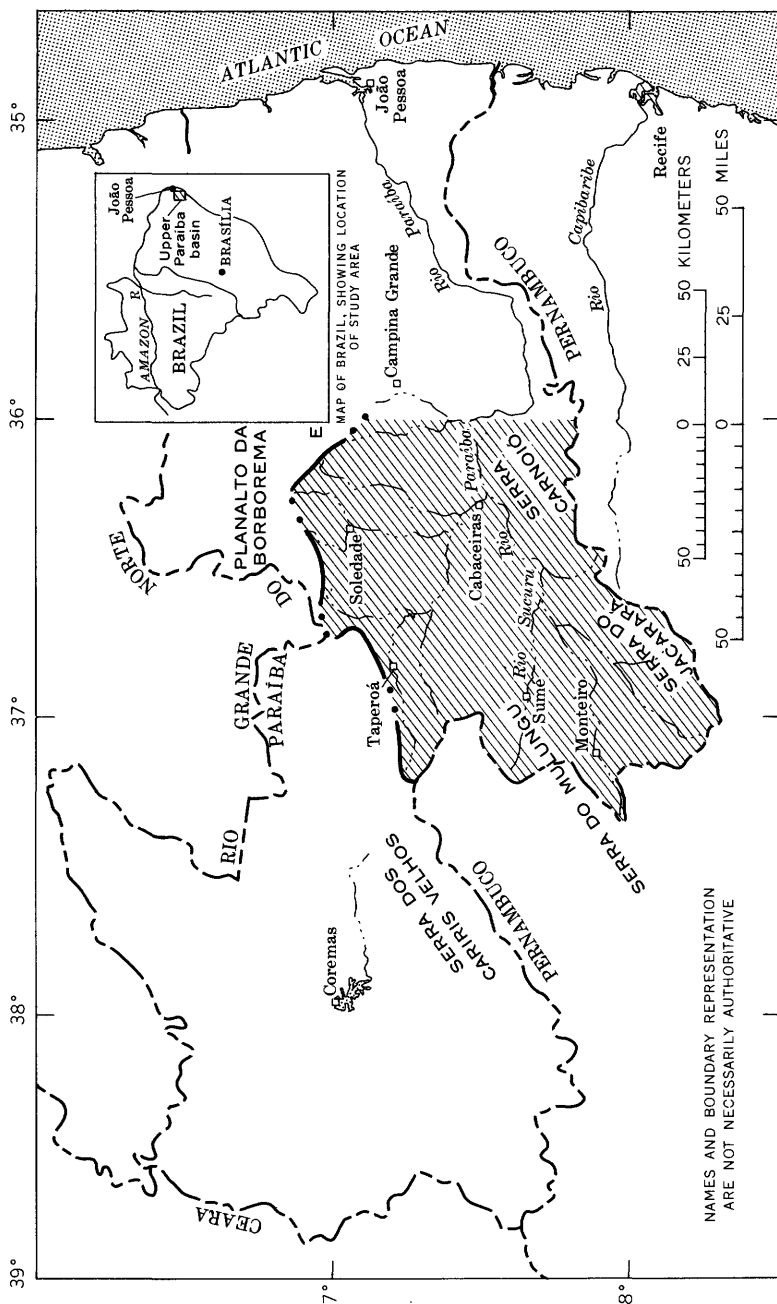
FIGURE 1.—Index map showing the location of the upper Paraíba basin (shaded).

Leal (1966, p. 17) thought the fairly arid climate was largely responsible for the high mineral content of both surface and ground water. He observed that the crystalline rocks lack significant local petrographic differences that might explain observed local differences in mineralization of the water.

Fundamental to the views expressed in the preceding paragraphs is a concept based on the fact that the water—presumably rainwater—entering the rocks is less mineralized than the water presently obtainable from the rocks. This leads to the concept that the water, then, is becoming increasingly mineralized through progressive dissolving of the rocks.

The author shared this concept when he tried to relate the principal ions ordinarily found in water to the common rock-forming minerals that contain them. He commented on the abundance of chloride in the ground water of northeast Brazil in contrast with the general scarcity of chloride in crystalline rocks (Schoff, unpub. data, 1964).[1]

Unlike the other investigators, Cruz (1966, p. 7–8), on the basis of 400 chemical analyses of water from crystalline rocks in northeast Brazil, ventured to suggest that the rocks have at most only a minor influence on the chemical quality of the water. Observing that the chloride concentration increases directly with the total dissolved-solids concentration, he further suggested that the chloride had been introduced in saline solutions from outside the region, but he did not identify the external source.

METHODS OF THIS INVESTIGATION

This investigation consisted primarily of the collection, study, and interpretation of 212 chemical analyses of water representing 106 wells together with geologic and other data relating to the upper Paraíba basin. Although a few new analyses were added from time to time while the investigation was in progress, the bulk of the field and laboratory work was completed before the investigation had begun. The author traveled through the region three times on main roads and inspected several wells in the southwest part of the region, some of them while the drilling operations were still in progress. He also had opportunity to discuss the region and its ground-water problems with the geologists who had charge of those operations.

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[1] Presented to the fifth session of the Brazilian Sociedade de Intercambio Cultural e Estudos Geológicos, in Ouro Preto.

The water samples were collected from wells drilled by SU-DENE, CONESP, and private companies under contract, mainly in the years 1963–65. Geologists of SUDENE and CONESP selected the well sites on the basis of geologic and socioeconomic conditions; they usually chose sites near towns where as many people as possible would have access to the wells or where cattle could reach them. The same geologists supervised the drilling operations and the installation of pumps, windmills, and storage and other facilities; they collected the water samples or supervised their collection by subordinates. The wells were drilled by the percussion method, were 6 or 8 inches in diameter, and were cased only from the land surface to the top of the solid rock or a short distance into the rock.

The water samples were collected in liter bottles and were analyzed chemically in the water laboratories of SUDENE and CO-NESP, in Recife, Pernambuco. Both laboratories determined the dry residue at 110°C and reported constituents in milligrams per liter. The SUDENE laboratory determined sodium and potassium separately by flame photometer, but CONESP estimated these cations by the difference method (Hem, 1969, p. 87–89) and reported them together as if entirely sodium.

The author studied the analyses by tabulating them, identifying maximum and minimum concentrations of the constituents, calculating averages and various ratios of one or more constituents to others, and plotting various characteristics and ratios on maps and diagrams. The results of this work were compared with similar data for sea water and with representative published chemical analyses of ground water identified with certain types of rock. The analyses were also correlated with the geology of the region as represented on published geologic maps or as reported by field geologists.

Averages were made where more than one sample from the same well was analyzed. Averaging may be of dubious value where analyses are as unlike as some of those from wells in the upper Paraíba basin but, lacking plausible criteria for selecting one analysis as more valid or more representative than another, the author felt compelled to resort to this approach. Where comparisons between wells or groups of wells are given, they are comparisons between averages for the wells except, of course,

where only one analysis was made. Maximum and minimum concentrations of individual ions mentioned in the text are the concentrations in individual analyses.

TOPOGRAPHY AND CLIMATE

The upper Paraíba basin is part of a peneplain undergoing dissection. Accordant, rather broad divides give the impression of a plain, from which scattered ridges and low mountains project. The drainage net is well developed, but the tributary valleys, though numerous, are fairly shallow. Local relief, in fact, is fairly low, although the total relief in the region studied is 700 m (meters) or more. The divide marking the southern boundary is locally more than 1,000 m above sea level.

Considered as a whole, the basin of the Rio Paraíba has the shape of a funnel, its small end being at the Atlantic coast. The river heads nearly 300 km (kilometers) from the coast and flows east-northeast to the ocean at João Pessoa. The widest part of the basin, 175 km wide, is in the region described in this report. Near its midpoint the basin is about 75 km wide, and it shrinks to 30 km or less near the coast.

The upper part of the basin is among the driest parts of northeast Brazil, according to Rangel (1965, p. 7) and Siqueira (1963c, p. 4). Annual precipitation averages 279 mm (millimeters) at Cabaceiras in the east-central part and 642 mm at Monteiro in the southwest, most of it coming in the period from March to May (Torres and Mortera, 1948). The northern and eastern parts of

the region seem to receive less precipitation than the southern part. Rangel explained that the topography prevents airborne moisture north, east, and west of the region from entering it regularly. By "topography" he doubtless meant the surrounding low mountains, considered necessarily in relation to the prevailing winds.

The reported average annual precipitation is hardly negligible, but its effectiveness is less than the quantities indicate. Soil and rock in the basin have only small capacity for storing water, which therefore largely runs off or is evaporated or transpired. Evapotranspiration dissipates a large part of available water the year around because there is no cold season, and the vegetation, though sparse, takes up water when it is available. To these factors must be added the fact that the precipitation is concentrated in but three of the 12 months and varies from year to year within wide limits. Judged by the vegetation that can be supported by the precipitation, on either a long- or short-term basis, the climate is fairly described as semiarid.

GEOLOGY

The bedrock of the upper Paraíba basin comprises varied crystalline rocks, all of Precambrian age. The bedrock is overlain by saprolite at many places and by alluvium in the bottoms of the valleys. The saprolite and the alluvium have been derived from the bedrock by weathering, and the alluvium has been transported greater or lesser distances down the valleys.

Most of the region considered in this report is shown on the photogeologic quadrangle maps published by the Departamento Nacional da ¡ Produção Mineral (DNPM), "São João do Cariri" and "Garanhuns" quadrangles (Moraes and others, 1963, 1964). These maps, although not rigorously checked in the field, give the general geological framework of the basin. Their lithologic descriptions probably were assembled from published and unpublished reports on scattered localities in these and adjacent quadrangles.

Half or more of the basin as shown on the photogeologic maps is underlain by rocks described as predominantly migmatite but including crystalline limestone, quartzite, mica schist, leptinite, amphibolite, and granite (fig. 2). The migmatites themselves are varied, ranging from banded to porphyritic and brecciated gneiss, and occupy two broad areas elongated east-west, one in the north
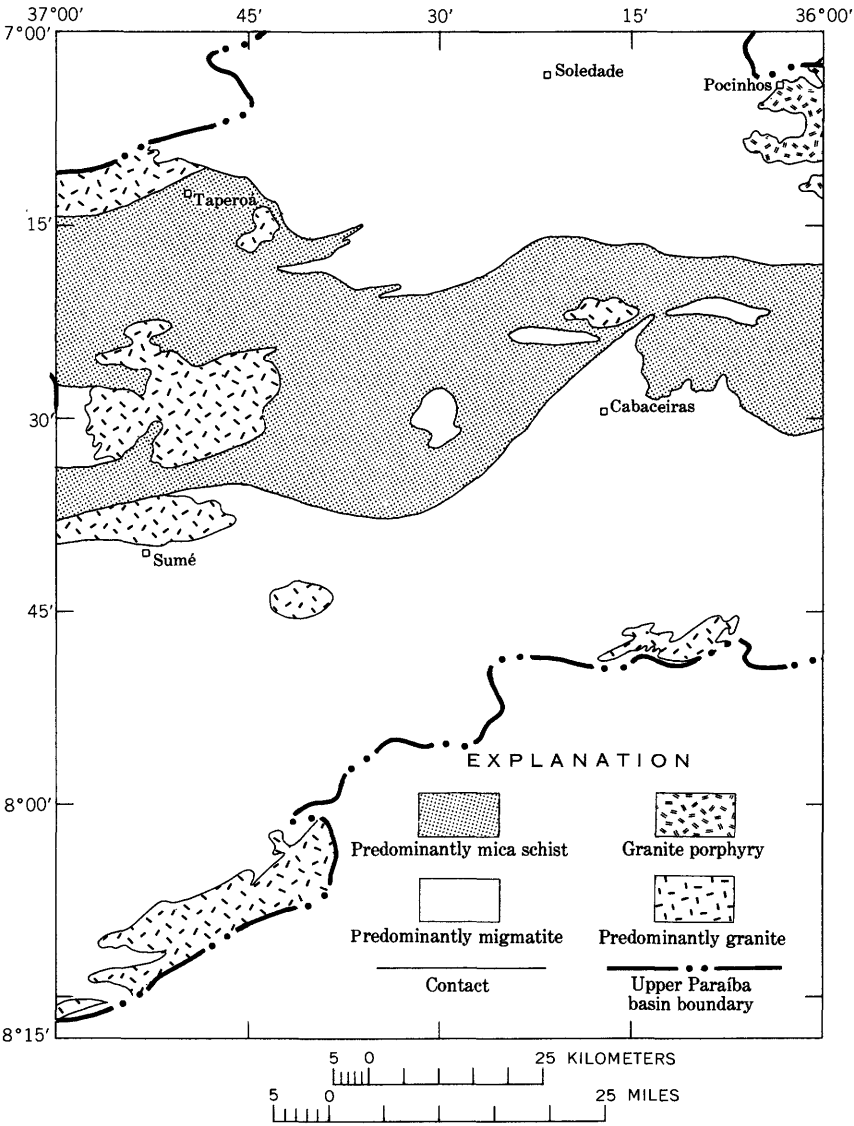
FIGURE 2.—Principal geologic units in the upper Paraíba basin between meridians 36° and 37° W. (After Moraes and others, 1963, 1964.)

and the other in the south. Within these are smaller areas mapped as predominantly granite.

Between the two areas of migmatite is a band, ranging in width from 10 to 45 km, which is underlain principally but not exclu-

sively by mica schist. The schist is described as grading at places into migmatite, and within its area are smaller areas mapped as predominantly migmatite or as granite.

Granitic rock is mapped as occurring in eight localities, mostly but not exclusively in the west half of the area shown in figure 2, and granite porphyry occurs in the northeastern part, mainly southeast of the town of Pocinhos. These rock types predominate, but within their areas are included unmappable gradational migmatite or schist.

Viewed broadly, the rocks in the basin are monotonously uniform, differing sufficiently in mineral composition and arrangement to be given different names, such as "schist" and "migmatite," but perhaps differing little in chemical composition. Viewed as aquifers, the rocks are a diverse collection of intergrading types for which petrologic descriptions are virtually nonexistent, at least in an areal sense. Thus, it is impossible to identify with any certainty the rock type that constitutes the "aquifer" simply by noting from the map the outcrop area in which a well is located.

Data on the character and thickness of the saprolite and alluvium are virtually lacking because little attention has been paid to these materials, SUDENE's objective in the well-drilling program having been the study of the water in the bedrock. The bedrock can be seen only a meter or so below the land surface in many roadcuts, and bare rock crops out in hills, ridges, and even fairly flat fields, suggesting that the saprolite is thin under large areas. Yet, considerable thicknesses of saprolite, perhaps 10 m or more, may be present where the bedrock cannot be seen.

The alluvium is confined to the valley bottoms and presumably consists of intergrading beds of clay, sand, and gravel. It may contain a relatively high proportion of silt and clay if it is similar to the alluvium in the adjacent upper Capibaribe basin, which is geologically similar to the upper Paraíba basin. In the upper Capibaribe basin several auger holes at one locality disclosed layers of fine sand in the alluvium, and the alluvium along the main stream is distributed in a chain of more or less independent deposits interrupted by bedrock outcroppings (Chada and others, 1969).

So far as they affect the chemical character of the ground water, all the rock materials in the basin may be regarded as crystalline rock in various stages of decomposition from fresh to

deeply weathered. Water moving down from the land surface, presumably starting as rainwater containing little dissolved matter, has the ability to dissolve mineral matter according to its contact with the rock materials. Certain elements present in the fresh rock are absent from the saprolite and alluvium, having been removed or rendered insoluble in the process of weathering. Thus, water which has resided only in saprolite should differ chemically from water that has resided mainly in the bedrock, but the difference cannot be appraised. All the water samples came from wells drilled into bedrock, but some of the water may have been a recent arrival from a saprolitic or alluvial environment.

HYDROLOGY

Ground water in the bedrock of the upper Paraíba basin occurs mainly in fractures. The rock itself is mostly dense and solid and lacks significant interstitial porosity. Wells drilled into solid rock between fractures are certain failures, but wells that intersect water-bearing fractures may yield up to 10,000 liters per hour. The fractures differ greatly in size and other characteristics. They are linear features, generally having great length compared with their width. They probably become both narrower and fewer with depth below the land surface, but none has really been followed downward.

The drilling of 67 wells into crystalline rocks of one locality in northeast Brazil showed that only 28 percent of the identifiable water-bearing fractures is in the zone 60–100 m below the land surface, and only 20 percent of the well discharge could be attributed to that zone. Most of the fracture systems probably consist of one, or at most a few, breaks in the rock rather than extensive shattered zones that could have hydraulic properties approaching those of a homogeneous aquifer.

Some fractures are open and yield water freely. Others are clogged with debris or are recemented with mineral matter and yield nothing. Some are so situated that they receive water from streams, but some receive little or none or are quickly drained. Some cross topographic contours and have sufficient hydraulic gradient so that water can circulate actively through them; but others, paralleling topographic contours, may have low gradients and little flow.

The ground water, controlled by the fractures, circulates in an intricate but sparse network of slowly moving sheets, either ver-

tical or variously inclined. This network has little resemblance to a body of water moving on a broad front through an infinitude of interconnected pores as in sand, for example. Although the fractures individually are vastly larger than the pores in sand, the total porosity of the aquifer is low because the fractures are generally separated by large blocks of solid rock. The route of travel of the water is likely to be indirect, first along one set of fractures and then at an angle along another set, and deviates substantially at many places from the direction of maximum hydraulic gradient. The rate of movement of water in any single fracture is controlled by the rate of passage through the most constricted place.

Ground water in the saprolite and alluvium doubtless tends to move in the broad-front manner, because these materials, however fine grained they may be, have pore space fairly evenly distributed throughout. They do not have uniform permeability, however, and the water in them seeks routes through their relatively coarse and permeable parts as dictated by the hydraulic gradient.

CHEMICAL CHARACTER OF THE GROUND WATER

As represented by the available chemical analyses, the ground water in the upper Paraíba basin is characterized by generally high concentrations of dissolved solids, by wide differences among individual wells in the concentrations of dissolved solids and the various ions, by lack of geographic trends in the distribution of high and low concentrations, and by extreme hardness.

The concentration of dissolved solids in individual analyses ranges from less than 350 to about 25,000 mg/l (milligrams per liter), and the average for the basin is about 4,300. The average concentration is about 40 percent lower in the south half of the basin than in the north half—3,100 mg/l compared with nearly 5,400 mg/l—but a progressive decrease in concentration from north to south is not apparent (pl. 1). Only 11 percent of the 105 wells represented by 212 chemical analyses had water containing less than 1,000 mg/l of dissolved solids, and only 3 percent had water containing less than 500 mg/l.

The few wells having water containing less than 1,000 mg/l of dissolved solids are distributed haphazardly about the region, some in the north and some in the south and generally rather near wells having moderately to highly mineralized water. Irreg-

ularity also characterizes the distribution of the various ions dissolved in the water. The geographic distribution of high and low concentrations differs in detail from ion to ion because the water is not all the same chemical type—the same ions do not predominate in all wells—and distribution is irregular for each ion.

The hardness of the water ranges from about 50 to more than 8,000 mg/l as $CaCO_3$, and at 46 percent of the wells it exceeds 1,000 mg/l. The water is somewhat acidic, as indicated by pH values determined both in the field and in the laboratory. The determinations of pH range from 5.2 to 8.0, but a great majority are between 6.5 and 7.5, and more are below 7.0 than are above.

Table 1 gives maximum, minimum, and average concentrations, in milligrams per liter, of total dissolved solids and of the individual ions that were determined, together with the concentrations of these materials in sea water. The maximums and the averages for the upper Paraíba basin are compared with sea water in ratios obtained by dividing the values for the basin by those for sea water. The average concentration of calcium in the upper Paraíba basin water, for example, is 0.60 as great as in sea water, and the maximum is 4.06 times as great. The following observations based on table 1 are noted:

1. Compared with sea water, the ground water of the upper Paraíba basin, on the average, is relatively low in dissolved solids. The dissolved-solids concentration is only 12 percent as great as in sea water, and even the most mineralized water

TABLE 1.—*Minimum, maximum, and average concentrations of dissolved mineral matter in ground water of the upper Paraíba basin compared with sea water*

[Sea water: From Rankama and Sahama (1950, p. 287, 291)]

	Mini-mum (mg/l)	Maxi-mum (mg/l)	Average (mg/l)			Ratio of ground water to sea water		
			North half	South half	Entire region	Sea water (mg/l)	Average concen-tration	Maxi-mum concen-tration
Calcium (Ca) _	9.6	1,624	260	221	241	400	0.60	4.06
Magnesium (Mg) _____	6.8	1,064	244	154	201	1,272	.16	.84
Sodium (Na) _	17	5,233	1,140	523	844	10,561	.08	.50
Potassium (K)_	3.8	450	70	·22	43	380	.11	1.18
Bicarbonate (HCO₃) ____	51	1,020	442	441	441	140	3.15	7.28
Sulfate (SO₄) _	4.8	1,930	194	121	159	2,649	.06	.73
Chloride (Cl) _	14	13,700	2,572	1,317	1,968	18,980	.10	.72
Total dissolved solids _____	334	[1]25,200	5,390	3,138	4,306	34,400	.12	.73

[1]Result of one analysis. The average of two samples collected on different dates is 23,500 mg/l.

in the basin has a dissolved-solids concentration only 73 percent as great.

2. The average concentration of bicarbonate in the basin is three times as great as in sea water. Bicarbonate is the only ion for which average concentration is greater in the basin than in sea water.

3. The average concentration of calcium in the basin is 60 percent as great as in sea water. The concentrations for the other ions given in table 1 are relatively low—16 percent as great as in sea water, or lower.

4. The maximum concentrations of calcium and bicarbonate are several times greater, and the maximum for potassium is somewhat greater, than the concentrations of these ions in sea water.

Table 2 compares the ground water of the upper Paraíba basin with an average of 46 published chemical analyses representing water from 10 varieties of igneous rocks from widely separated places. In a general way these rocks are similar to those in the upper Paraíba basin, but the proportions represented by the various rock types are not necessarily the same. The proportions are not well enough known for the basin so that any procedure for weighting the published analyses seems to be possible; the comparisons, therefore, are not quantitatively precise. All the published analyses except one record concentrations of dissolved solids below 1,000 mg/l, and the water samples came from localities

TABLE 2.—*Comparison of maximum and average concentrations of dissolved mineral matter in ground water from the upper Paraíba basin with an average of 46 analyses of ground water from crystalline rocks*

[Average for published analyses from Hem, 1959, table 6, Nos. 2–5, 9; table 11, No. 1; from White and others, 1963, table 1, Nos. 2–15; table 2, Nos. 1–3, 8–16; table 10, Nos. 1–13, 15. Included are analyses representing 11 basalts, eight granites, seven schists, six gneisses, six rhyolites, three gabbros, two quartz monzonites, one granodiorite, one slate, and one greenstone]

	Average for published analyses (mg/l)	Ratio of upper Paraíba basin average to published analyses	Ratio of upper Paraíba basin maximum to published analyses
Calcium (Ca) _____	32	7.5	51
Magnesium (Mg) ____	13	15.5	82
Sodium (Na) _____	36	23.4	145
Potassium (K) _____	2.7	15.9	167
Bicarbonate (HCO_3) _	165	2.7	6.2
Sulfate (SO_4) _____	35	4.5	55
Chloride (Cl) _____	25	79.0	548
Total dissolved solids _	350	12.3	72

having climates ranging from humid to arid. Presumably the samples represent ground water derived from precipitation in the vicinity of the sampling point, and their chemical character is primarily due to solution of the host rock. The following points are noted:

1. Bicarbonate is the only constituent for which the average for the published concentrations exceeds the concentration in sea water (tables 1, 2). (It does so in 18 of these analyses, and it averages about 16 percent greater. The maximum is 710 mg/l.)

2. In all respects, the water from the upper Paraíba basin contains, on the average, more dissolved matter than the average of the 46 published analyses. The difference is greatest for chloride, 79 times greater, followed by the sodium, 23 times greater; the smallest difference is for bicarbonate, only 2.7 times greater.

3. For some of the materials, the differences between the maximums for the basin and the averages of the 46 analyses are enormous—548 times greater for chloride, for example.

RELATION OF ROCKS TO CHEMICAL CHARACTER OF WATER

Correlation of rock type with the chemical character of water is rarely simple or obvious, and in the upper Paraíba basin it is complicated by an apparent diversity of lithology; the latest maps (Moraes and others, 1963, 1964) group a large variety of lithologic types together into major outcrop areas. This problem is coupled with a paucity of data specifically applicable to the water samples that were analyzed; the descriptions of the rocks at the well sites are sketchy. Two schists can be mineralogically distinct and potentially able to influence the chemical character of their contained water quite differently. A schist and a gneiss, distinguished by difference in the arrangement but not the kind of their minerals, may be chemically equivalent. Provided with only a terse "mica schist" or "gneiss" to identify the rocks penetrated, the author has found it impossible to relate the chemical character of the ground water to the rock type at specific wells, but he has tried to relate the chemical character of the water to the principal kinds of rock as mapped (pl. 1) and to the rocks as identified at some of the wells by the geologists assigned to well-drilling operations. The rock groups thus considered are migma-

tite, mica schist, and granite and pegmatite as mapped and gran-
ite and gneiss as identified by field geologists. In all rock groups
great diversity of chemical character is evident, the wide range in
dissolved-solids concentration being especially noteworthy. The
situation with respect to gneiss, as outlined in the following para-
graphs, is representative.

The SUDENE geologists identified the host rock of the water
at 40 wells as gneiss but the water quality differs greatly from
well to well. The dissolved-solids concentration in the water
ranged from 412 mg/l (second lowest in the upper Paraíba basin)
to about 23,000 mg/l (the highest). At more than half the wells,
the concentration was below 2,000 mg/l—at six of them (15 per-
cent) it was below 1,000 mg/l, and at 15 (37 percent) it was
1,000–2,000 mg/l. But at seven wells the concentration was be-
tween 4,000 and 10,000 mg/l, and at three it was over 10,000 mg/l.

The sodium concentration in the water from these wells ranged
from 68 to about 5,100 mg/l, and the chloride ranged from 47 to
about 12,700 mg/l (average of two determinations). The concen-
tration of calcium exceeded that of magnesium in the water at 10
wells, but magnesium predominated at 29 wells. At one well, cal-
cium and magnesium were equal. The bicarbonate concentration
was greater than the chloride concentration at 10 wells, but
chloride predominated at 30.

Judged by dissolved-solids concentration, the water from gneiss
seems to be better in chemical quality than water from granite
and pegmatite, as Costa (1965, p. 21) suggested. Of 40 wells in
gneiss, about half had fairly potable water (dissolved-solids con-
centration below 1,000 mg/l) or reasonably acceptable water (dis-
solved-solids concentration 1,000–2,000 mg/l). In sharp contrast,
64 percent of the wells in granite and pegmatite yielded water
having dissolved-solids concentration between 4,000 and 11,000
mg/l. This difference in chemical quality is probably due to local
structural, topographic, hydrologic, and perhaps climatic condi-
tions favoring or impeding the circulation of ground water. It is
due to the lithologic character of the rock mainly insofar as li-
thology has helped to control the fracturing of the rock and, hence,
the circulation of the ground water.

In summary, the lithologic data are sketchy and generally inad-
equate for correlating the chemical character of the ground water
with the mineralogic composition of the host rock to a precise de-
gree. Grossly considered in relation to generalized outcrop areas

and broadly generalized rock identifications, the water in the upper Paraíba basin displays such great differences in so many respects from one place to another that close lithologic control of the chemical character of water cannot be identified. The composition of the host rock, however, has no doubt contributed in some measure to the chemical character of the water, whether this contribution is identifiable or not.

SIMILARITY OF GROUND WATER TO SEA WATER

As a means of studying the chemical analyses, seven ratios were calculated from the concentrations of the ions (in equivalents per million) in the water of the upper Paraíba basin; these ratios were compared with similar ratios based on published analyses, some of which are averaged in table 2. The ratios were plotted in diagrams (pl. 1A–C) those for the upper Paraíba basin being divided into groups according to the dissolved-solids concentration and those for the published analyses being divided according to the rock types they represent. The value of the ratio for sea water is shown in each diagram as a line of reference.

Some of the ratios nearly duplicate the patterns made by others, the chief difference being in the numerical size of the resulting values. Other ratios have such a wide range of values for all the groups of water that no trends are apparent between groups. The meaningful ratios are discussed below.

MAGNESIUM : CALCIUM

The ratio magnesium:calcium (Mg:Ca) has about the same range of values in all five groups of water for the upper Paraíba basin. The ratio is relatively independent, therefore, of the concentration of dissolved solids. It ranges in all five groups from calcium dominant to magnesium dominant; but, in a majority of the water samples that were analyzed, the magnesium predominates as it does in sea water. On plate 1A the Mg:Ca ratios for the upper Paraíba basin are fairly close to the sea-water reference line. The Mg:Ca ratios for the published analyses, also shown on plate 1A, fall farther from the sea-water reference line than those for the upper Paraíba basin, and most of them show calcium predominating over magnesium.

The ratios representing water from gabbro and basalt have virtually the same range of values as those for the upper Paraíba basin. Judged solely according to this ratio, water from gabbro and basalt might by concentration become like the water from the upper Paraíba basin, but gabbro and basalt in the basin are prob-

ably less abundant than granitic and metamorphic rocks. Those rock types, as represented by the published analyses, have Mg:Ca ratios overlapping the left end of the Mg:Ca group for the upper Paraíba basin, but half or more fall beyond the upper Paraíba basin ratios—that is, farther from the sea-water reference line. Most of the Mg:Ca ratios for water from limestone and marble fall to the left of those for the upper Paraíba basin, and all show calcium predominating. Water samples from dolomite have Mg:Ca ratios resembling those for the upper Paraíba basin (expectably so because of the magnesium content of the rock), yet only one shows predominance of magnesium over calcium. Only six analyses of water from dolomite are shown, however, and these may be too few to be truly representative.

The important fact is that the Mg:Ca ratios for the water in the upper Paraíba basin are, as a group, more like the Mg:Ca ratio for sea water (magnesium dominant) than are those for the published analyses from continental sources (calcium dominant).

CALCIUM+MAGNESIUM:SODIUM+CHLORIDE

The ratio calcium+magnesium:sodium+chloride (Ca+Mg:Na+Cl) compares the sum of two cations that occur as silicates in igneous rocks and as carbonates in sedimentary and metamorphic rocks with the sum of a third cation and an anion. The third cation (Na) occurs in rock-forming minerals in igneous rocks and also in evaporites and is abundant in sea water. The anion (Cl) is scarce in igneous and metamorphic rocks, such as those in the upper Paraíba basin but is abundant in sea water and in evaporites.

This ratio in the ground water from the upper Paraíba basin varies with the concentration of dissolved solids, being closer to the sea-water reference line in the water having dissolved-solids concentration above 2,000 mg/l than in water having solids below 2,000. This relation is shown on plate 1B by the ratios in the upper part of the figure being displaced toward the right.

The ratios Ca+Mg:Na+Cl for water from representative rock types are partly in the same range as those for the upper Paraíba basin, but most of them fall well to the right (pl. 1B)—that is, farther from the sea-water reference line than those for the basin. Even the least mineralized water of the upper Paraíba basin seems to have more in common with sea water than has any of the water from the representative rock groups. It is true that this ratio for the granite-rhyolite group has almost the same

range of values as all five groups of upper Paraíba basin water together, but about two-thirds of the individual ratios in this category are to the right of the vast majority of upper Paraíba basin ratios—that is, farther from the sea-water reference line.

CALCIUM+MAGNESIUM:SODIUM AND CALCIUM+MAGNESIUM:CHLORIDE

The two ratios calcium + magnesium :sodium $(Ca + Mg:Na)$ and calcium + magnesium :chloride $(Ca + Mg:Cl)$ are variations of the ratio $Ca + Mg:Na + Cl$, inasmuch as they have the same dividend as that ratio but the two elements of that divisor are used independently. The values of the ratios are larger than values of $Ca + Mg:Na + Cl$ because the divisors are smaller, but the grouping is about the same. Both of these ratios display, for the upper Paraíba basin water, progressive displacement away from the sea-water reference line as the concentration of dissolved solids becomes less; the displacement is more pronounced for the ratio $Ca + Mg:Cl$ than for $Ca + Mg:Na$. Both ratios show the water from the representative rock types to be farther from the sea-water reference line than is most of the upper Paraíba basin water. Both show water from granite and rhyolite in virtually the same range of values as the upper Paraíba basin water, but for the ratio $Ca + Mg:Cl$ the emphasis is strongly away from the sea-water reference line, and most points for granite and rhyolite are to the right of the majority of points for upper Paraíba basin water. For the ratio $Ca + Mg:Na$, on the other hand, the individual values for granite and rhyolite are rather uniformly distributed. Judged according to this ratio alone, the water in granite and rhyolite might, by concentration, become like the water in the upper Paraíba basin.

BICARBONATE:CHLORIDE

The ratio bicarbonate :chloride $(HCO_3:Cl)$ compares two anions, one that seems to be more characteristic of continental water than of sea water and one that is prominent in sea water. Plate 1C shows that this ratio is rather like plate 1B, which shows the ratio $Ca + Mg:Na + Cl$, except that the lines of dots have been stretched. This stretching exaggerates the displacement in the five groups for the upper Paraíba basin so that, in terms of this ratio, water having less than 4,000 mg/l of dissolved solids seems to have little in common with water having more than 4,000 mg/l. The $HCO_3:Cl$ ratios for the water from representative rock types, based on the published analyses, are farther from the sea-water reference line than those for the upper Paraíba basin. As on plate

1*A* and 1*B* for the other ratios, the upper Paraíba basin water having high dissolved-solids content is the closest to the sea-water line.

The ratios suggest that the water in the upper Paraíba basin containing large amounts of dissolved solids is more like sea water than is the fresher water. The upper Paraíba basin water, on the whole, is more like sea water than representative waters of published analyses, which probably are not in any way related to sea water. Both sea water and a commingling of meteoric water with sea water or brine seem to be plausible sources for the high mineralization of the ground water in the upper Paraíba basin.

PROCESSES OF MINERALIZATION

Ground water ordinarily is regarded as fairly stable in chemical quality, but it probably does not remain indefinitely at the same level of concentration. Whether the water entering the ground is fresh rainwater containing only a little carbon dioxide or is already mineralized in some degree, it will generally dissolve additional mineral matter from its host rocks. The amount of new matter taken into solution will depend on the chemical quality of the water and the composition of the rocks, as well as such factors as temperature, pressure, and residence time in the rocks. The water can also become more mineralized through concentration as a result of evaporation or by mixing with more highly mineralized water from another source. On the other hand, mineralized water may be freshened by dilution with fresh or less mineralized water or by partial drainage of the mineralized water and substitution of fresh water. The freshening process must have operated repeatedly throughout geologic history to permit marine sandstones and limestones once saturated with sea water to become fresh-water aquifers. This is the process that seems to have operated, and to be still in progress, in the upper Paraíba basin. Before discussing it in detail, however, the process of progressive increasing mineralization as it might apply in the upper Paraíba basin is considered.

The process of increasing the mineral content of ground water assumes that water, which initially is virtually free of mineral

matter, progressively dissolves more and more mineral matter during its residence in the rock or, that it is concentrated by evaporation, or that both actions occur. Involved in this process are the climatic environment, including precipitation, temperature, and evaporation; the chemical quality of the precipitation; the nature of the hydrologic system of the region; the rate of ground-water circulation; the availability in the rocks of the more common solids dissolved in the water; and the fate of the weathered rock.

Influence of Climate on Mineralization of Water

The precipitation in the upper Paraíba basin, even though the region is classed as semiarid, is enough so that in at least some years part of the water doubtless is free to recharge the underground supply. High temperatures the year around promote high evaporation rates, which reduce the amount of water available for recharge and also increase the dissolved-solids content of the remaining water. Evaporation affects the water on the land surface in ponds, lakes, and streams, the water in the soil, and the water in the rocks at shallow depth. It can have little effect, under present conditions in the upper Paraíba basin, on water at the depth of the water table because that depth is generally too great. The static water levels in the southwestern part of the region may fairly represent the whole basin, and they are more than 3 meters below land surface at 40 of the 50 wells reported by Costa (1965, p. 21–22). Hence, the increase of concentration of dissolved solids by direct evaporation of ground water is probably restricted to a small part of the region. Concentration by evaporation, then, occurs chiefly before the water reaches the zone of saturation or as it leaves.

Influence of Chemical Quality of Precipitation on Mineralization of Water

The chemical quality of the precipitation falling in the region can only be estimated. D. W. Fisher, of the U.S. Geological Survey, (oral commun., 1968) estimated on the basis of weather charts and by comparison with other regions that the precipitation in the upper Paraíba basin might contain 0.05 mg/l of magnesium, 0.04 mg/l of sodium, and even less calcium and potassium. Chloride, he thought, might amount to as much as 1 mg/l; sulfate, 0.8 mg/l; and nitrate, perhaps 0.3 mg/l. More than the indicated amount of chloride often is found in the precipitation near seacoasts, but the upper Paraíba basin is too far inland

(200–275 km) for airborne oceanic salt to reach it. If Fisher's estimate is approximately correct, a great deal of rainwater would have to be evaporated to achieve the concentration of salts found in the ground water of the upper Paraíba basin, but the available capacity of the rainwater to dissolve mineral matter should be large.

Relation of Hydrologic System to Mineralization of Water

The hydrologic system in the bedrock of the upper Paraíba basin is a fracture system, which doubtless favors the solution of mineral matter by ground water because in general it keeps the water in contact with the rock for a fairly long time. Opportunity for contact of water with rock is inversely proportional to the rate of water circulation throughout the fractures. Circulation rates in the region probably are infinitely varied below some maximum, which in favorable circumstances could be fairly high. At the other extreme, the circulation in some fractures probably is so slow that the water is virtually stagnant. The average circulation rate probably is fairly low, and residence time of water in the rock, therefore, fairly long.

The rate of water circulation in the saprolite and alluvium partly determines the amount of mineral matter that ground water dissolves from those materials, and this could affect the mineral content of water which passes first through such materials en route to the bedrock. Saprolite and alluvium may approach uniformity in porosity and for this reason may have higher rates of water circulation than the bedrock, although neither is likely to qualify as highly permeable in the upper Paraíba basin. The amount of mineral matter removed from these rock materials by the water resident in them is not known because no water samples were collected from them for analysis. At many places in the region, the water bypasses them and enters the bedrock directly or through a thin layer of soil.

Availability of Principal Ions

The cations in the ground water of the upper Paraíba basin are available as silicates in the feldspars, pyroxenes, amphiboles, and micas that ordinarily make up igneous and metamorphic rocks like those in the region. Calcium occurs in labradorite and in the pyroxenes and amphiboles; magnesium, in the pyroxenes, amphiboles, and biotite; sodium, in anorthoclase, albite, and oligoclase; and potassium, in orthoclase, muscovite, biotite, and lepidolite. In

addition, calcium and magnesium occur as carbonates in marble and magnesite. These rocks are not especially abundant among the crystalline rocks of northeast Brazil, but they are locally important. A magnesite deposit in the Estado do Ceará, for example, is described as 400 m thick (Bodenlos, 1950, p. 131).

The anions are less easily accounted for than the cations. The bicarbonate may come from solution of the carbonate rocks, but it is abundant in the ground water in amounts that seem to be out of proportion to the volume of carbonate rock probably in the basin. The sulfate might originate from the oxidation of sulfide minerals. Such minerals are not known to be especially abundant in the rocks of the upper Paraíba basin, but sulfate is the least abundant of the three anions determined in the water analyses, and its origin therefore is not a problem in accounting for the process of increasing mineral content of the ground water. Chloride, on the other hand, is a problem because it is found in the ground water in amounts nearly as great as 14,000 mg/l, whereas its concentration in the rocks is probably negligible.

The amount of chloride in rocks is part of the question of average chemical composition of the earth's crust, for which various estimates have been made (Parker, 1967, tables 19 and 20). The estimated average amount of chloride in igneous rocks, including those which have been metamorphosed, reaches a maximum of 0.05 percent; basalt and ultramafic rocks contain a minimum of 0.005 percent, and syenite contains a maximum of 0.052 percent. A commonly quoted figure within the indicated range was given by Rankama and Sahama (1950, ·p. 226) as 314 grams per ton (0.0314 percent).

Concentrating Chloride

It is easier to suggest that the amount of chloride in the more mineralized water of the Paraíba basin is the result of concentration by progressive evaporation than to explain the process. The average chloride value of 314 mg/kg (milligrams per kilogram) in igneous rock is only about 1/65 the amount of magnesium, 1/82 the amount of potassium, 1/90 the amount of sodium, and 1/115 the amount of calcium. Yet in the water of the upper Paraíba basin, on the average, chloride is more abundant than any of these ions. The highest chloride concentration in the water from the upper Paraíba basin is nearly 13 times the magnesium concentration, and the average chloride concentration is 8½ times

the average for magnesium. A process of concentration that would raise the ratio of chloride to magnesium from 1:65 to 13:1 would have to be selective.

Chloride, potassium, and sodium remain in solution at concentrations above those at which calcium and magnesium are precipitated. Hence, the concentration of the first three can be increased if the last two are precipitated, but to raise the chloride:magnesium ratio from 1:65 to 13:1 would imply the precipitation of considerable magnesium (and calcium), presumably as carbonates. In this case, limestone, dolomite, or caliche should be present within the basin, but large deposits of these rock types are unknown.

Potassium in water may be absorbed in clays or tied up in new potassium-bearing micalike minerals, but the bulk of all the sodium dissolved during weathering accumulates in the ocean (Rankama and Sahama, 1950, p. 432–433); that is, the sodium stays in solution, as does chloride. If sodium and chloride were being dissolved from igneous rocks, where the sodium is 90 times as abundant as the chloride, and if the concentrations were being increased by evaporation, the ratio sodium:chloride should not be greatly changed from the ratio in the rocks. This is nowhere near the truth in the upper Paraíba basin.

Instead of a 90:1 ratio, the sodium is only 0.38 times the chloride in the most mineralized ground water and 0.43 times in the average ground water. In sea water, for comparison, the sodium is 0.56 times the chloride. It is clear that the relationship of sodium to chloride in the upper Paraíba basin ground water is not the same as in sea water, but it is not at all like the 90:1 ratio in crystalline rock.

Quantities of Rock and Chloride

The crystalline rocks in the upper Paraíba basin probably contain no more chloride than similar rocks elsewhere, although chemical analyses are lacking. If the figure 314 grams of chloride per ton of rock is taken as a starting point, the magnitude of the chloride problem can be appraised, at least approximately. Restated, this figure means that 1 kg of average rock would have to be broken down to release 314 mg of chloride. To release the average amount of chloride in the ground water of the upper Paraíba basin—about 2,000 mg/l—would require decomposing 6.4 kg of rock for each liter of water. To release the chloride in a liter

of the water containing the highest concentration of chloride (13,700 mg/l) would require the decomposition of nearly 44 kg of rock. How much rock would have to be decomposed to release the chloride in the ground water currently stored in the crystalline rocks of the upper Paraíba basin cannot be plausibly estimated because the quantity of water in storage is poorly known: The number, length, and depth of fractures, and their freedom from obstruction are unknown in any total sense. The amount of water that might be withdrawn by pumping may give, however, an estimate of the magnitude of the problem but not the full answer. Thus, if 100 of the SUDENE wells were each to be pumped at a modest rate of 1,000 liters per hour, 5 hours a day, for 1 year, they would discharge more than 180,000,000 liters of water which, at the basin average of about 2,000 mg/l, would contain 360,000,000 g (360,000 kg) of chloride. To produce this amount of chloride would require decomposition of 1,150,000,000 kg of average rock. Although this figure is no measure of the total amount of rock that has been decomposed, it does introduce the problem of disposal of the part of the rock not taken into solution.

Fate of Decomposed Rock

If the chloride in the ground water were derived solely from the bedrock in the upper Paraíba basin, a considerable quantity of decomposed rock (saprolite) should have resulted. The chloride amounts to only a fraction of 1 percent of the rock, leaving more than 99 percent of the rock material to be accounted for in some other way. A considerable part of this material also goes into solution, and it either remains in solution or is redeposited. This part, of course, makes its contribution to the total dissolved-solids content of the water, but there is also the insoluble residuum, the saprolite. The saprolite either accumulates as weathering proceeds or gradually moves by mechanical slumping and soil creep into the valleys, where it becomes incorporated in the alluvium and is further moved out of a given area by stream transport. The streams also carry dissolved mineral matter in solution, including chloride, and this dissolved material is lost to the region, making no contribution to the concentration of dissolved solids in the ground water remaining behind.

The problem in the upper Paraíba basin is that very little saprolite is found in the region. As noted elsewhere in this report

(p. H11) the saprolite is thin where the author has observed it, and this means either that not much has been produced or that much of it has been carried away. In the first case, not much mineral matter would have been dissolved from rocks; and in the second, the dissolved materials would largely have been carried off in the water that transported the solid part of the decomposed rock, unless perhaps the wind had carried the solid part as dust. In neither case would a large contribution have been made to the total solids content of the ground water.

Summary on Increasing Mineralization

Some factors operative in the upper Paraíba basin would seem to favor the process of increasing the mineral content of the ground water through dissolving progressively more mineral matter from the rock and reducing the volume of water by evaporation. Among these are the climatic conditions, the chemical quality of the precipitation, the prevailing hydrologic system, and the availability of some of the principal minerals in the rocks of the region. On the other hand, the abundance of chloride among the anions in the ground water as compared with its relative scarcity in the rocks, together with the absence of saprolite that should have been developed in extraction of chloride from the rocks, makes the process of doubtful validity as an explanation of the high chloride content of the water.

DECREASING MINERALIZATION

The hypothesis is presented here that the present ground water in the upper Paraíba basin contains some residual sea water or perhaps brackish lagoonal water and that this residual water has been unevenly and incompletely diluted and flushed out of the rocks, being only partly replaced by fresh water. The process is far advanced and is continuing.

This hypothesis rests primarily on the resemblance of the ground water to sea water, as described in the section "Chemical Character of the Ground Water," and secondarily on the problems inherent in the concept of increasing mineralization through rock decomposition, chiefly the difficulty of accounting for the high chloride content of the water in the face of the negligible chloride content of the rocks. It is suggested that sea water was probably introduced during the last recorded marine invasion of northeast Brazil, which occurred in Late Cretaceous time. The hydrogeologic history of northeast Brazil since that time, to be summa-

rized in a subsequent section, outlines the process of dilution and displacement of sea water by fresh water.

Flushing of the sea water would proceed relatively fast in large open fractures or fracture systems having active water circulation. In such fractures, the process is essentially complete and the water now available is of good chemical quality. The flushing would go slowly in small fractures having sluggish water circulation, and in them the process is not complete. The wide range in the "permeability" of the fractures and the random distribution throughout the basin of "permeable" and "less impermeable" fractures account for the wide range in chemical quality of the water and the random occurrence of both good- and poor-quality water. Thus, the water quality reflects the degree of flushing that has occurred, and flushing has been governed by the hydraulic characteristics of the rock.

The dilution has not been a simple proportional reduction in the concentrations of all the ions. The concentrations of some ions are relatively larger fractions than others of the corresponding amounts in sea water, and the average bicarbonate concentration in the basin is more than three times as high as in sea water (table 1). These facts suggest that modification of the chemical character of the water has occurred along with the dilution, through the local solution of constituents from the rock and deposition of constituents from solution. The details of this modification are beyond the scope of this paper, but the bicarbonate is perhaps an example. Bicarbonate seems to be a characteristic ion in continental water that somehow becomes minimized in sea water. The bicarbonate concentration in 38 percent of the published analyses of ground water from typical crystalline rocks averaged in table 2 is greater than the bicarbonate concentration in sea water, even though the total concentration of dissolved solids in most of these analyses is much below 1,000 mg/l (less than 3 percent of the concentration in sea water). Water on the continents, then, acquires bicarbonate. Sea water loses it. Since the time that sea water was introduced in the rocks of the upper Paraíba basin, that water has acquired a great deal of bicarbonate.

HYDROGEOLOGIC HISTORY OF NORTHEAST BRAZIL, LATE CRETACEOUS TO PRESENT

Whether an origin as sea water is probable, or is merely possible, as an explanation of the dissolved-solids content of the

ground water in the upper Paraíba basin depends on the events of geologic history in the region, including hydrologic responses to them. This is hydrogeologic history.

The last recorded advance of the sea over northeast Brazil was in late Cretaceous time, some 70 million years ago, when there was deposition of sediments now found in a narrow belt along the east coast and in a broad belt along the north coast (fig. 3). Once the sediments probably extended farther inland than their present outcrops, which have been reduced by erosion, but no remnants remain to prove that they, or the sea, actually covered the upper Paraíba basin. The present inland boundaries of the Cretaceous outcrops are 100–175 km from the boundaries of the basin, and in this distance the marine strata could have thinned to zero or even have graded into continental deposits.
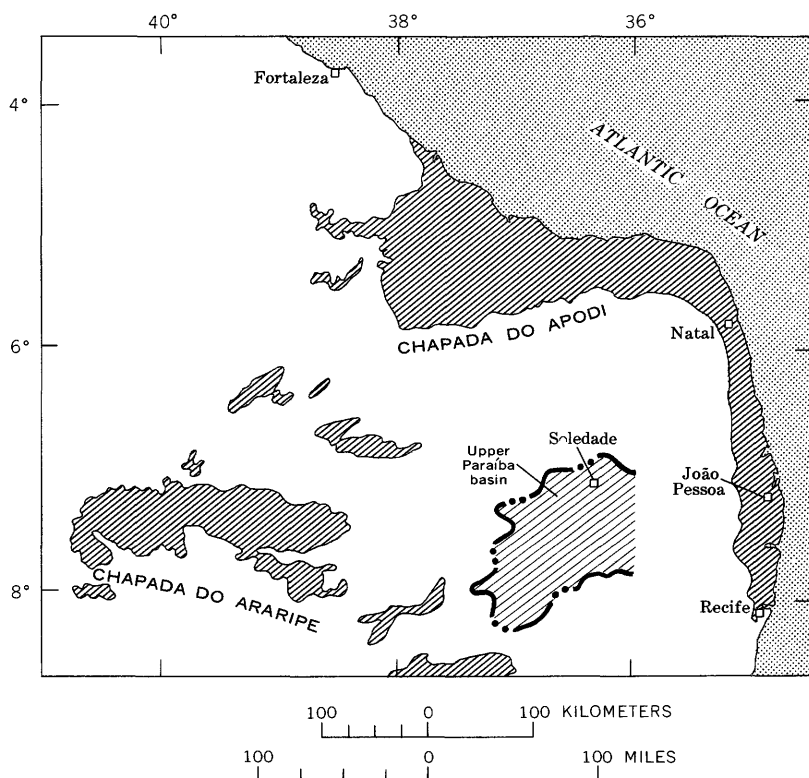

FIGURE 3.—Map showing distribution of rocks of Cretaceous age (shaded) in northeastern Brazil. Coastal areas where the Cretaceous rocks are covered by Tertiary continental deposits are shown as Cretaceous. (After Lamego, 1960.)

Some writers (Azevedo, 1962, p. 98) have described the marine Cretaceous invasion as extending southward from the north coast (Chapada do Apodi) to the Chapada do Araripe (fig. 3), but Karl Beurlen (oral commun., 1967) saw no such connection. The marine Cretaceous rocks of the north coast, he said, are younger than the Cretaceous in the Chapada do Araripe, and the water-bearing sandstones in the Chapada do Araripe, moreover, are fluviatile in origin; their connections formerly were eastward to the Cretaceous strata in the Jatobá basin and westward to the Cretaceous strata in the Maranhão basin (beyond the west boundary of fig. 3).

Yet, not all the Cretaceous strata in the Chapada do Araripe are fluviatile. Totaling about 600 m in thickness (Duarte, 1962, p. 13), they consist, from the base upward, of a thick sandstone and conglomerate, a sequence of limestone, clay, gypsite, and locally siltstone, and a second thick sandstone. In the middle unit are fossil fish, ostracodes, mollusks, and a few echinoids. Because echinoids are marine invertebrates, Beurlen (1964, p. 337) regarded the middle unit as deposited, at least in part, in a brackish or marine environment. If this were true, the underlying sandstone, fluviatile or not, once must have been saturated with brackish or salty water, yet today the water in that sandstone averages about 500 mg/l of dissolved solids, and at most has only about 1,000 mg/l (Anjos, 1963, p. 14). Here the flushing of sea water from the aquifer is essentially complete.

The rocks of Cretaceous age along the north coast, which in considerable part are marine in origin, likewise must once have contained sea water. The dilution and flushing process should have started later in them than in the Chapada do Araripe because the coastal area would be last to emerge from the sea and, in addition, the process would go more slowly due to lower hydraulic gradients (that is, the area is not so high above sea level). Indeed, the water now in these rocks seems to be more mineralized than that in the Chapada do Araripe. In nine analyses, more than half of which represented water from limestone rather than sandstone, the dissolved-solids concentration ranged from 219 to 4,800 mg/l and averaged 1,600 mg/l—60 percent more than the most mineralized water from the sandstone of the Araripe area.

If the sea had advanced inland to the Chapada do Araripe, it could also have advanced into the upper Paraíba basin. The basin

is closer to the present Atlantic coast than is the Chapada do Araripe, and part of it is no higher in altitude than the land surface around the eastern end of the Araripe area. No major mountain range separates it from the ocean. Proof, however, in the form of incontestably Cretaceous rocks within the basin, is lacking.

The history of northeast Brazil during the Cenozoic Era is the history of an emergent land undergoing erosion. Referring to the region as the Brazilian shield, Beurlen (1964, p. 395–396) wrote, "*** there were no great transgressions or orogenic movements. * * * The Cenozoic was a time of geological rejuvenation due to a fundamental uplift, which stimulated erosion and formed the present drainage system. Weathered zones, peneplains at different levels, and more or less dissection of the peneplains, were the most important phenomena ***." [2] During this period of 70 million years then, the Cretaceous sediments were largely stripped from the land. Meanwhile, rain fell, soaked into such permeable strata as the sandstones of the Chapada do Araripe or the limestone that caps the Chapada do Apodi, and flushed the original water in them toward the natural exits.

Rain fell on the Precambrian rocks, also, wherever they were exposed and whenever they were uncovered by removal of overlying sedimentary rock. Such meteoric water entered and moved through the fracture systems where it could and, building up hydraulic head, flushed any salty water contained in the fractures toward natural exits and ultimately back into the ocean. This process could not begin in the Precambrian rocks that were buried under Cretaceous strata until the Cretaceous rocks were removed; or, if it did begin in places, it went slowly at first. Moreover, the process continued at a slower rate than in the sedimentary rocks because the permeability of the Precambrian rocks is less and the total available hydraulic gradient was less at any given time or place. The Precambrian rocks, having been buried under others, lay closer to sea level.

The process of flushing the saline water doubtless was accelerated or retarded in response to climatic fluctuations, especially during the Pleistocene Epoch. Ab'Sáber (1957) has shown, on the basis of pediplains, pediments, peneplains, and terraces and the gravels deposited on them, that many climatic changes occurred in Brazil. Surely the northeast did not escape them.

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[2] Translation from the Portuguese by S. L. Schoff.

The climatic variations would have been responses to glaciation in other parts of the world and to resulting changes in sea level. Fray and Ewing (1963, p. 126) reported, on the basis of sediment cores from the Argentine shelf, that the level of the sea was lower than the present level by as much as 150 m at three different times in the last 35,000 years. A lowering of the ocean would cause the continents to emerge, to stand higher, and to seem to be larger than they are now. These changes would be accompanied by modifications in both oceanic and atmospheric circulation. In a specific locality, such as the upper Paraíba basin, they could spell the difference between a humid and an arid climate.

Exactly how the climatic fluctuations of the Pleistocene were related to the glaciers may not be so important as the fact that variations occurred. Budel (1953, p. 3) and Fairbridge (1961, p. 555) correlated cooling and glaciation with increased worldwide precipitation, whereas Bigarella and Andrade (1965, p. 449) concluded from a study of pediments, pediplains, and associated deposits that "semi-arid conditions prevailed from north to south in Brazil during the times of Pleistocene ice." Either way, the humid periods would have provided the fresh water, which would dilute the salty water in the rocks and, by raising water levels and hydraulic gradients, speed it seaward. The intervening arid periods would have retarded the process or permitted it to stop. The process may even have been reversed temporarily if the high evaporation that often accompanies aridity succeeded in increasing the mineral content of water on the land and this water entered the rocks. Viewed over the long term, the chemical character of the ground water in northeast Brazil could hardly have been static through the last 70 million years, and especially not through the Pleistocene.

IMPROVING THE QUALITY OF GROUND WATER

Little can be done, as a rule, to improve the chemical quality of ground water while it is still in the aquifer because the quantity of poor-quality water in a homogeneous aquifer is vast in comparison with the remedies that might be applied. Usually, no procedure for improvement seems to be practical because the resulting improvement would be very small with respect to the expense involved. Viewed regionally, the same observation is doubtless true in fracture-type aquifers. While it is not the author's intention to propose action designed to improve the chemical quality of the ground water in the crystalline rocks of the entire upper Pa-

raíba basin, individual fractures and fracture systems do constitute relatively small and independent aquifers, a fact which suggests that some local improvement in water quality might be achieved if appropriate procedures were followed.

If the mineralized water in the rocks is being diluted and flushed, it is undergoing natural improvement, albeit slowly. Any process that accelerates the dilution or permanently removes mineralized water from the rocks is a step in the same direction. Pumping mineralized water from a well may provide space in the rocks for fresh meteoric water, as Siqueira (1963a, p. 26, 28–31; 1963b, p. 29; 1967, p. 27) proposed; it also disposes of some small fraction of the mineralized water.

The amount of dilution of the mineralized water that might be achieved in this way is dubious and probably small because in a fracture system the actual contacts or interfaces of fresh water with mineralized water would be quite small. Even in a homogeneous aquifer, the mixing of injected fresh with native mineralized water occurs only in a narrow peripheral zone, leaving most of the fresh water unaltered (Cederstrom, 1957, p. 46; summarized 1964, p. 270–271).

The objective in a pumping program could well be the removal from the rocks of as much mineralized water as possible, due concern being given the use and disposal of the pumped water and the cost of operation. Done in the appropriate season, pumping would provide storage in the fracture-type aquifer for a new charge of fresh water. Then, when both fresh and mineralized water are in the rocks, intermittent pumping could be employed to promote their mixing, so far as possible. Into the cone of dewatering or pressure relief would move some mineralized and some fresh water that would become mixed as the cone is replenished, prior to the next period of pumping.

The pumping regimen—whether steady in dry season and intermittent in rainy season, or vice versa—would depend on how long it takes for rain water to infiltrate to the zone of saturation, and this could be different for each fracture system and perhaps for each well. Periodic sampling of the pumped water and determination of the dissolved-solids concentration conceivably could disclose trends signaling the arrival of recharge water at a well and, after pumping, its exhaustion.

Inevitably, problems such as the following may arise: (1) Some pumping of ground water will seem to have no effect on the

chemical quality of the water pumped, and (2) some pumping may have an adverse effect even though all circumstances seem to be favorable. The first situation may occur because the fracture system tapped by a discharging well has too much storage capacity in relation to the discharge or the recharge for changes in chemical quality to be detectable. The second situation may arise because the well taps a fracture or set of fractures which has considerable storage capacity but poor connections to discharge areas, and the mineralized water contained therein, long virtually stagnant, drains out into the well as fast as it can be pumped. Neither the well driller nor the geologist can tell with certainty from surface indications which of these conditions exists.

Pumping can effect the greatest apparent improvement where the dissolved-solids concentration is high because the high concentration could be due to feeble circulation combined with small storage capacity. The removal of only a little water and the creation of only small storage for addition of fresh water may result in considerable improvement in quality. For highly mineralized water, however, the practical results may be small, even if dissolved-solids concentration is reduced as much as 25 percent, for example, from 20,000 mg/l to 15,000 mg/l. On the other hand, improvement in quality would be worthwhile if 1,600 mg/l could be reduced to 1,200 mg/l. At this level of mineralization, however, the natural dilution process has already progressed to the point that further improvement would be attained with difficulty and great expense. The reason for such a relatively low level of mineralization is likely to be precisely the reason that further improvement in water quality will be difficult to attain by pumping; that is, a fracture-system reservoir of relatively large storage capacity and active circulation that would minimize the effects of pumping.

Artificial recharge of fresh water to some fracture systems would be worthwhile; the fresh water thus temporarily stored (Cederstrom, 1964, p. 272; Cederstrom and Assad, 1964, p. 24–28, 36–39) in the rainy season would otherwise be lost to runoff. By building up head, artificial recharge might locally accelerate the flushing of mineralized ground water and its movement toward places of discharge, but as already noted, it would not extensively dilute mineralized water already in the rocks.

CONCLUSIONS

Ground water in the Precambrian crystalline rocks of the upper Paraíba basin, as shown by evaluations of several chemical

ratios, has a number of characteristics that resemble those of sea water. The quality of the water lies between that of sea water and that of the fresh water which is common in similar crystalline rocks of other widely scattered localities. Chemically, therefore, the ground water of the upper Paraíba basin seems to represent a commingling of sea water with meteoric water.

On the other hand, most of the principal constituents of the ground water could have been dissolved from the rocks in the region and might have been concentrated in the water by progressive evaporation. Chloride, however, ordinarily the least abundant anion in crystalline rocks, is the most abundant anion in the mineralized water of the basin. Chloride is also the most abundant anion in sea water. Sea water, then, is a more likely source of chloride than the bedrock of the area.

Chloride is only 1/65 as abundant in crystalline rock as magnesium, on the average, but it is about 13 times more abundant in the ground water of the basin. Progressive evaporative concentration by which the ratio chloride:magnesium is changed from 1:65 to 13:1 seems to be improbable. A similar but even greater change would be required with respect to calcium and potassium. Progressive concentration by evaporation of meteoric water that entered the region as rain therefore seems inadequate to explain the mineral content of the ground water.

Sea water or brackish lagoonal water could have been introduced to the rocks of the basin during the last recorded marine invasion of northeast Brazil, which occurred in Late Cretaceous time, some 70 million years ago. No evidence remains, however, that the sea actually entered the upper Paraíba basin other than in the chemical character of the ground water itself. Scattered remnants of Cretaceous marine strata in areas near the basin suggest that the sea might have also covered the basin.

If sea water was once present, it has been greatly diluted and largely drained out of the rocks, but the process has operated unevenly. Pockets of highly mineralized water remain wherever the circulation of the ground water has been most sluggish, and this is the water most like sea water. Concurrently with dilution and doubtless owing in part to changes in concentration caused by dilution, some constituents were dissolved from the rocks and some were precipitated from solution. As a result, the relative proportions of the constituents in the ground water are different from those in the original sea water.

The history of the region since deposition of the Cretaceous rocks is a history of retreat of the sea, initiation of erosion, stripping away of much of the sediment, and (during the Pleistocene Epoch at least) wide climatic variations. The Pleistocene climates, alternating between humid and arid, could have had important effects on regional hydrology and on the process of diluting and draining the sea water from the rocks.

Under the hypothesis here proposed, the chemical quality of the ground water is imperceptibly improving and any procedure adopted by man that permanently removes mineralized water from the rocks or dilutes it is operating in the same direction as the natural process. The pumping of ground water from a certain well or group of wells, for example, may effect local improvement in water quality, chiefly where the fracture systems have small storage capacity compared with the pumping capability. Much pumping would probably be required, however, to create a significant improvement, and widespread pumping to effect water-quality improvement on a regional scale seems to be impracticable. Artificial recharge should accomplish some dilution of the mineralized ground water locally, but recharge would be of value primarily as a means of temporarily storing water that otherwise would escape to the sea as runoff.

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