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Author(s): L. G. M. Baas Becking, I. R. Kaplan and D. Moore
Source: *The Journal of Geology*, Vol. 68, No. 3 (May, 1960), pp. 243-284
Published by: The University of Chicago Press
Stable URL: http://www.jstor.org/stable/30059218
Accessed: 11-06-2018 14:07 UTC

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VOLUME 68 NUMBER 3

THE JOURNAL OF GEOLOGY

May 1960

# LIMITS OF THE NATURAL ENVIRONMENT IN TERMS OF pH AND OXIDATION-REDUCTION POTENTIALS[1]

L. G. M. BAAS BECKING,[2] I. R. KAPLAN,[3] AND D. MOORE[2]

## ABSTRACT

1. The electron and the proton content (measured as electrode potential [Eh] and pH) of an environment characterize this environment in many ways. In this paper the electrode potential and the pH are used as empirical parameters rather than as electrochemical data capable of thermodynamic interpretation. From published and unpublished work by the authors and from the literature, more than 6,200 pairs of characteristics were gathered, covering most types of the aqueous environment as well as the potential milieu of the chief actors in these environments: algae and bacteria.

2. It appears that the Eh-pH limits of biological systems and of the naturally occurring aqueous environment almost coincide. This would indicate that there are few, if any, sterile terrestrial environments caused by limiting Eh-pH characteristics.

3. As it seems unlikely that environments will be found outside the limits outlined in this paper, physicochemical speculations on the sedimentary environment should be limited by this outline. Substances which do not occur (sulfuric acid, sulfide ion) should not be used in the electrochemical characterization of the environment.

4. The biogenic master reaction in the environment, changing one or both characteristics (Eh-pH), is reductive photosynthesis by algae and by colored bacteria. A photosynthetic mass may raise the pH of a water to 9.4; and in the absence of bivalent cations, to 12.6.

5. The intensity of sulfate reduction depends upon the sulfate content of the water and on the available hydrogen, in both organic and inorganic form. The iron concentration is also important, as iron is the principal acceptor of the $H_2S$ formed. The highly reactive, black iron sulfides may be partly oxidized with the formation of the more stable pyrite and marcasite. The reduction of iron from ferric to ferrous state takes place even in surface soil.

6. Denitrification, another biologically important reduction, may be of lesser geochemical influence.

7. Oxidative reactions comprise, apart from nitrification, chiefly the oxidation of $H_2S$ and $SH^-$ to sulfur, thiosulfate, sulfite, hydrosulfite, sulfate, and hydrosulfate and the oxidation of ferrous and manganous compounds. In contrast with the reductions, these oxidations are only in part biological. The oxidation of pyrite may give rise to extremely low pH values. Heterotrophic oxidation (respiration) results in the conversion of organic matter into $CO_2$ and $H_2O$.

8. Acid formation in peat bogs is caused largely by cation exchange on plant cell walls, chiefly, but not exclusively, on *Sphagnum*.

9. In sediments the reaction between iron phosphate complexes and $H_2S$ may liberate the acid $H_2PO_4^-$ ion.

10. Certain environments are restricted, others cover almost the maximal area outlined in this paper. A progressive increase in the environmental range, arranged in a series, follows: rain water, mine water, peat bogs, sea water, rivers and lakes, marine sediments, and evaporites, while the geothermal environment shows the maximal area.

11. The potential milieu of the green bacteria is highly restricted. Less restricted is the environment of the iron bacteria, followed by sulfate-reducing bacteria, purple bacteria, and denitrifying bacteria. Thiobacteria have a very wide potential milieu, and algae are found literally everywhere.

12. The Eh-pH characteristics are determined chiefly by photosynthesis, by respiration and by oxidoreductive changes in the iron and sulfur systems.

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[1] Manuscript received August 28, 1959.

[2] From the Bureau of Mineral Resources, Canberra, Australia.

[3] From the Department of Bacteriology, University of Southern California, Los Angeles 7, California.

## INTRODUCTION

The natural environment, taken as a unit, contains so many variables that it may seem impossible to ascribe limits to it. However, modern methods of measurement have made it possible to compare the two fundamental components of the natural environment in remarkably easy fashion. These two components—protons and electrons—are omnipresent in the natural environment; their concentrations, or more precisely their activities, can be measured electrometrically as electrode (oxidation-reduction or redox) potential and pH; and these activities may be plotted one against the other in an Eh-pH diagram. The total area of such a diagram contained by measurements delineates the natural environment.

Measurement of Eh and pH has been conducted in many scientific fields in a rather desultory fashion for nearly forty years. Most of those who have made the measurements came to the conclusion that, since they could not obtain reproducible Eh measurements, these were unreliable and so abandoned their investigations. Fortunately, some 2,000 measurements were published, covering a wide range of milieus. Most of these measurements have required readjustment before they could be used in the present outline; some authors still use the rH concept, even though its originator (Clarke, 1928) actively discouraged the use of it. Its consequences persist even when the rH itself is rejected; ZoBell (1946), for example, obviously aware of the pitfalls, warned readers against the use of rH, but still corrected his Eh readings to a standard pH, employing a factor of 60 mV. Many other authors have similarly corrected to a standard pH, their standards varying from 2.5 (Colmer, Temple, and Hinkle, 1950) to higher values, generally at pH 7. Most authors used a standard correction of 58, 59, or 60 millivolts per pH unit. Volk (1939) found that there was no such thing as a standard factor for Alabama soils, proceeded to determine the individual factor for each of over 3,000 soils, and then referred all his Eh values to a standard pH of 5.

In this paper no corrections of any sort have been applied to the data. When the work of others has been used, "corrections" have been removed, and the data restored to their original form; where this is not possible, the data have been discarded. In the majority of cases the data would fit within the limits of the natural environment as defined by us, but in two cases this is not so.

1. Eh −500mV (ZoBell, 1946). No pH was given with this reading, and the next lowest value given (−342mV, pH 7.9) was measured by this author in a core from the Gulf of California and falls short of it. Very low Eh values close to the hydrogen couple are ascribed by ZoBell to hydrogen overvoltage, which contradicts the findings of Emery and Hoggan (1958), who were recently unable to detect hydrogen in highly reduced marine sediments. It is possible that the isolated readings at extremely low Eh values were due to poisoning of the platinum electrode (with which Eh measurements are made) by too long a contact with a system containing $H_2S$. Platinum sulfide forms, and extremely low potentials result. Clean electrodes inserted into such a system show a potential close to that recorded originally by the poisoned electrode.
2. Eh −294mV; pH 4.8 (Starkey and Wight, 1945; site 59, 31/10/44). This point falls on the hydrogen-ionization line and was taken close to an iron gas pipe in waterlogged soil. We suspect that hydrogen was being generated by the iron, so that the value is not that of the soil.

## MEASUREMENT OF Eh AND pH

All the data used in this paper have been determined electrometrically, using various models of thermionic valve electrometers. Many of the pre-1945 measurements were made with instruments designed and built by the users, but lately commercial models have become available. Our own team has made use of British (Cambridge), American (Beckman), and Australian (Jones) instruments. Comparison of the Jones and Cambridge meters gave readings that agreed within the error of reading of the instruments.

### INTERPRETATION OF RESULTS

In the account of the natural environment which follows, there is little attempt to interpret the readings. The literature on the subject is full of examples of too much interpretation with too little factual basis, so we have been content to record the actual variation possible in any one environment and relate it to the microflora. By this we hope to show the importance and limitations of biological activities within the natural environment and to provide a background against which the thermodynamic calculations of Garrels, Huber, Krauskopf, and others can be set.

The two parameters we are concerned with ultimately reflect the concentrations of protons and electrons in the environment. Since protons neutralize electrons, and vice versa, it follows that an abundance of one will be reflected in a deficit of the other. Generally speaking, this is what our data show: at high pH low Eh's are more common than at low pH; whereas at low pH very high Eh's are obtainable. The process of neutralization occurs in chemical reactions in the natural environment; reactions are of four types:

i) Neither electrons nor protons involved, e.g.,

$$Fe_2O_3 + H_2O \rightleftarrows 2FeO{\cdot}OH\ .$$

ii) Protons only involved, e.g.,

$$H_2CO_3 \rightleftarrows H^+ + HCO_3^-\ .$$

iii) Electrons only involved, e.g.,

$$Fe^{++} \rightleftarrows Fe^{+++} + e^-\ .$$

iv) Protons and electrons involved, e.g.,

$$FeSO_4 + 2H_2O \rightleftarrows SO_4^= + FeO{\cdot}OH + 3H^+ + e^-\ .$$

Reactions of type i occur throughout the environment and cannot, by their nature, be reflected in Eh or pH. Type ii is confined largely to the dissociation of acids, of which the most important are $H_2S$, $H_2SO_4$, $H_2CO_3$, and $H_3PO_4$ (see fig. 2). The formation of free ammonia from $NH_4^+$ is also of this type. Ionization of metals or the oxidation of low-valence ions to higher valence ions of the same metal involve the release of electrons, being type iii reactions. A more complex reaction of this type (Baas Becking and Mackay, 1956) is

$$Fe(OH)(SH) + H_2PO_4^- \rightleftarrows FePO_4 + H_2O + H_2S + e^-\ .$$

Most reactions in the natural environment are of type iv, involving both electrons and protons. Naturally these depend upon both the pH and Eh of the system in which they take place; the equilibrium line of the reaction may be expressed in the form $Eh = Eo - 59(a/n)$ pH millivolts, in which $a$ is the number of protons and $n$ the number of electrons taking part in the reaction. The gradient of the equilibrium line on an Eh-pH diagram is entirely determined by $a/n$, which may vary from 0 to $\infty$. Many authors have assumed that the slope is always $-59$ mV per pH (that is, $a = n$), and pH corrections of electrode potentials are made on this assumption. The common reactions illustrated in table 1, all occurring in nature, show how fallacious the assumption is.

### DISTRIBUTION OF RESULTS

The total number of sets of measurements used in this paper is 6,200, of which our own contribution is about 3,500. The bulk of all measurements on organisms was made by us (1,700 of 2,100), and the measurements on environment are divided into 1,800 from us and 2,300 from the literature and unpublished sources. Even in all this wealth of data, some environments are characterized entirely by data from our own sources; for example, we know of no measurements of meteoric waters other than our own. Geothermal waters are also badly documented, although they are not as freely accessible as meteoric waters.

Work on organisms has been confined to those of geological importance—algae and a few groups of bacteria. These organisms and their environment are mutually dependent and the environmental limits are set by the activities of the organisms as shown in the accompanying tabulation.

| | |
|---|---|
| Low pH, high Eh | Iron bacteria |
| High pH, high Eh | Algae |
| High pH, medium Eh | Purple bacteria |
| High to medium pH, low Eh | Green bacteria, sulfate reducers, heterotrophic anaerobes |
| Low pH, medium Eh | Thiobacteria |

TABLE 1

COMMON REACTIONS OF IRON IN NATURE INVOLVING BOTH HYDROGEN ION AND ELECTRON TRANSFER BUT YIELDING DIFFERENT GRADIENTS FOR THE EQUILIBRIUM LINE ON AN Eh-pH DIAGRAM

| Reaction | $a/n$ | Equilibrium Line |
|---|---|---|
| $2Fe_3O_4+H_2O \rightleftharpoons 3Fe_2O_3+2H^++2e^-$ | 1 | Eh = + 220 − 59 pH |
| $Fe^{++}+2H_2S \rightleftharpoons FeS_2+4H^++2e^-$ | 2 | Eh = − 140 − 118 pH |
| $Fe^{++}+2H_2O \rightleftharpoons FeO{\cdot}OH+3H^++e^-$ | 3 | Eh = + 1058 − 177 pH |
| $3Fe^{++}+4H_2O \rightleftharpoons Fe_3O_4+8H^++2e^-$ | 4 | Eh = + 990 − 237 pH |

## NATURAL ENVIRONMENTS

### 1. GENERAL

In the course of gathering the data on environments, which are presented in the following pages, it soon became clear that many of the geologically distinct environments could not be differentiated by their Eh-pH characteristics. This is because the factors which affect Eh-pH are complex, and the components preserved in the rocks are often not those exerting the greatest influence. The scheme used to delineate environments in this paper takes into account the various controls, but it does not stress them. It is merely a working scheme and is not intended as a classification of natural environments; there are too many such classifications already.

In any particular environment there are several outstanding controls, all related to water. Water is the universal carrier of gases, ions, and un-ionized solutes. It carries, in suspension, organisms as well as less-soluble minerals on which numerous microbes may be adsorbed. The quantity and the quality of the above environmental controls determine the nature of the milieu. This milieu is further determined by the topography of the site and by its geographical location, although in the description of the various inorganic environments it will appear that these last factors are of minor importance only.

We will begin the study of environments with meteoric waters, which are as free of dissolved and suspended matter as any natural water will ever be. The interplay of lithosphere, atmosphere, hydrosphere, and biosphere, however, is so complex that we could start our considerations equally well with juvenile water or with sea water. The relation between the main types of the inorganic aqueous environment is given in figure 1, and the sequence used in their description does not attempt to represent a logical classification.

A word of caution is necessary at this stage. The effect on our data of man-made pollution of the atmosphere and of water cannot be properly estimated. Gorham (1955) has shown a distinct correlation between soot and sulfate content in rain collected near industrial areas. The lack of world-wide information on this subject means that we cannot assess how far industrial pollution extends, and the lack of measurements from before the Industrial Revolution leaves us without any standard of comparison. In this respect, therefore, the present may not precisely be "the key to the past."

### OCCURRENCE OF DISSOLVED IONS IN NATURAL ENVIRONMENT

Several inorganic compounds important in the natural environment may occur in more than one form. This is true especially of mineral acids, several of which are bivalent; there is even one trivalent example: $H_3PO_4$. Many geologists, however, seem to be unaware of this fact, and their essays into geological chemistry are full of equations containing incompatible ions at the pH involved. Perhaps the worst example is that of the sulfide ion. Some geologists apparently consider that $H_2S$ dissociates directly into $S^=$, whereas it can be shown quite clearly that the first dissociation is to $HS^-$ and that this then dissociates into $S^=$ and $H^+$. Moreover, the pH at which each dissociation occurs can be calculated, and it is found that the reaction $HS^- \rightleftharpoons S^= + H^+$ has an equilibrium pH of 14, well outside the limits of the natural environment (see also Garrels and Naeser, 1958). In the hope that it may prevent further misstatements, figure 2 shows the stability fields of various important ions in the natural environment, framed within the Eh-pH limits postulated from actual measurements.

Variation in the molecular oxygen content of water appears to have no direct influence on the electrode potential, except at very low oxygen tensions. The presence of small amounts of oxidizable matter, both organic and inorganic will, however, be reacted on by the molecular oxygen, thus generally poising the system at a lower Eh. Experiments were carried out with sea water from Cronulla, New South Wales (an estuary). The pH of the water was varied by bubbling either nitrogen or carbon dioxide through it. In some cases oxygen was bubbled in for varying lengths of time. After allowing some minutes for the system to reach equilibrium, an aliquot of water was removed for an oxygen determination by the Winkler method, and the pH and Eh immediately measured. Figure 3 illustrates that no correlation appears to exist between the Eh and the oxygen tension in the water.

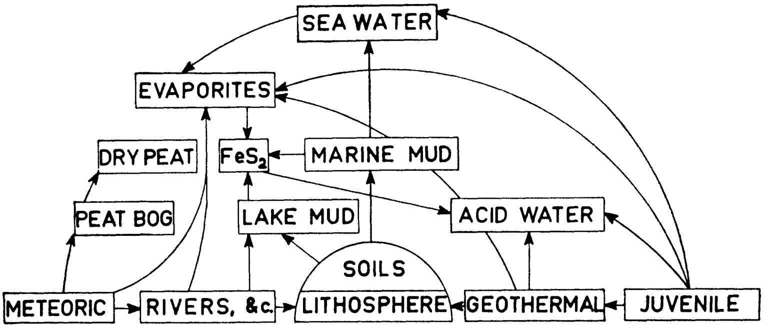

FIG. 1.—Interrelations of the natural aqueous environments considered in the present study

It is difficult to attribute any one reaction for the Eh of an oxygenated body of water. An important reaction may be the $H_2O_2$–$O_2$ couple

$$H_2O_2 \rightleftharpoons O_2 + 2H^+ + 2e^- \quad Eh = 0.68 - 0.059\,pH + 0.03 \log P_{O_2}/[H_2O_2] ,$$

which can fall within the range if the $P_{O_2}/[H_2O_2]$ ratio is correct. This reaction, however, assumes the presence of peroxides in reversible equilibrium with oxygen. These peroxides could arise from biological processes in nature and perhaps photochemical action by sunlight. The $H_2O$–$H_2O_2$ couple takes place only at a high Eh:

$$2H_2O \rightleftarrows H_2O_2 + 2H^+ + 2e^- \quad Eh = 1.77 - 0.059\ pH + 0.03 \log [H_2O_2]\,.$$

Another reaction in which hydrogen peroxide breaks down can be written for the neutral and alkaline pH:

$$1\tfrac{1}{2}H_2O_2 + OH^- \rightleftarrows O_2 + 2H_2O + e^- \quad Eh = -1.24 + 0.059\ pOH^- - 0.089 \log [H_2O_2] + 0.059 \log P_{O_2}\,.$$

This should suffice to illustrate that the $H_2O_2$–$O_2$ and $H_2O_2$–$H_2O$ systems are not simple. There may be no key reaction regulating the redox potential of an oxygenated body of water but rather a complex of several reversible and perhaps some irreversible systems. We wish to point out that we were unable effectively to change the Eh by changing the oxygen tension in experiments with sea water.

### 2. METEORIC WATERS

Eh-pH data on meteoric waters are restricted to what we have been able to measure ourselves during 1958–59. The measurements were made almost entirely in Canberra, where industrial pollution is very low, and they probably represent unpolluted rains. A few readings (10) were also made in Los Angeles early in 1959. The measurements were made at short intervals of time throughout a number of rains, the actual interval depending upon the rate of precipitation and the efficiency of the operator. In very heavy downpours a minimum time interval of two minutes was achieved.

There was considerable variation of Eh-pH characteristics in the rains studied. The variation was on two levels, within rains and between rains. Electrical storms were found to show rapid fluctuations of both Eh and pH, often as much as 2 pH units within ten minutes. Steady rain, on the other hand, was much more uniform. The rapid fluctuation during electrical storms seems to be very localized; we were able to follow two rains through the transition phase from steady rain and found in each case that the effect was limited to the actual storm center. Even one mile from the storm center the electrical discharge had no effect on the characteristics.

One further feature of the Eh-pH characteristics of rain deserves mention. Our data show a progressive increase in Eh and a concomitant decrease in pH between October, 1958, and early February, 1959, reaching a climax on February 11. Thereafter a rapid decrease in Eh was followed by an increase in pH, returning finally to the values recorded for rains during the previous October. We are investigating this problem furthering.

The available data are shown on figure 4. The pH range is in agreement with the work of Gorham (1955) in England, and that of Tamm (1953, quoted in Gorham) in Sweden. One of us (Baas Becking) measured a pH of 3.6 during an electrical storm in California in 1921, and Alexander (1958) has reported rains in Nigeria with a pH range of 5.8 to 6.8. Our own data has a pH range from 3.00 to 7.17 in a total of 769 readings.

Despite the great purity of rain, soluble constituents often exceed one milliequivalent per liter. The important anions are $SO_4^=$, $Cl^-$, $HCO_3^-$, and $NO_3^-$; $Na^+$, $Ca^{++}$, and $NH_4^+$ are the major cations. The proportions of each vary considerably; Gorham (1955) reports less than 0.09 p.p.m. nitrate in his samples, whereas Woering (1957) found from 11.8 to 37.7 p.p.m. Apart from the variation between rains, there is also variation within a particular rainstorm. The pH changes noted above in relation to lightning discharge suggest the manufacture of acid, most probably nitric. This problem has not been investigated by us, however.

### 3. PEAT BOGS

Peat bogs are of two types—low moors and high moors; the names have nothing to do with geographical situation, they refer to the bog topography. High moors build themselves up into low mounds composed

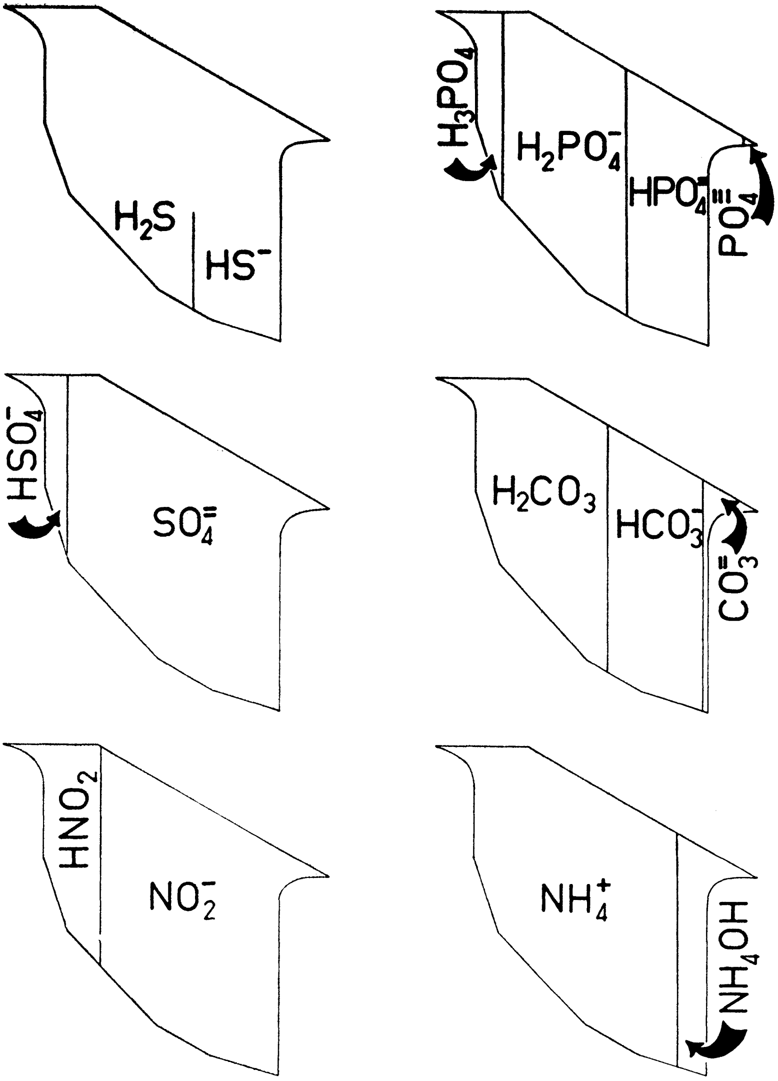

FIG. 2.—Stability fields of some important naturally occurring non-metallic compounds in terms of oxidation-reduction potentials and pH framed within the limits suggested by this work. Distribution of these compounds in un-ionized and ionized states is governed by their dissociation constants. The equilibrium pH for each dissociation is as follows:

$H_2S \rightleftharpoons HS^-$
pH 7.0

$H_3PO_4 \rightleftharpoons H_2PO_4^- \rightleftharpoons HPO_4^= \rightleftharpoons PO_4^{\equiv}$
pH 2.1 pH 7.2 pH 12.0

$HSO_4^- \rightleftharpoons SO_4^=$
pH 1.9

$H_2CO_3 \rightleftharpoons HCO_3^- \rightleftharpoons CO_3^=$
pH 6.4 pH 10.3

$HNO_2 \rightleftharpoons NO_2^-$
pH 3.3

$NH_4^+ \rightleftharpoons NH_4OH$
pH 9.4

Refer to fig. 4 for co-ordinate scale.

entirely of plant material; low moors are depressions. The two types of bog reflect differences in the source of their water. High moors derive their water almost entirely from rain (ombrogenic) and are characterized by very low salt concentrations. In these conditions decay is very slow, and a thick peat deposit can accumulate. Low moors, on the other hand, are fed by waters which have been in contact with soil and rock and hence contain much greater amounts of soluble salts. Decay is enhanced in these conditions, and many low-moor bogs deposit very little peat. One example has been described recently from North America (Swain and Prokopovich, 1954) in which peat was present in the upper layers of sediment but entirely missing from the lower layers, which were composed of marl. The differences in the two types of bog are reflected in pH as well as mineralogy. Low-moor peats have pH's from 7 to 8, apparently the upper limit of peat formation. High moors, on the other hand, have pH values generally below 6, and, in extreme cases, as low as 2.8 (Pearsall, 1938). *Sphagnum*, the major contributor to many modern peat bogs, can actively lower the pH by cation exchange on its cell walls (Baas

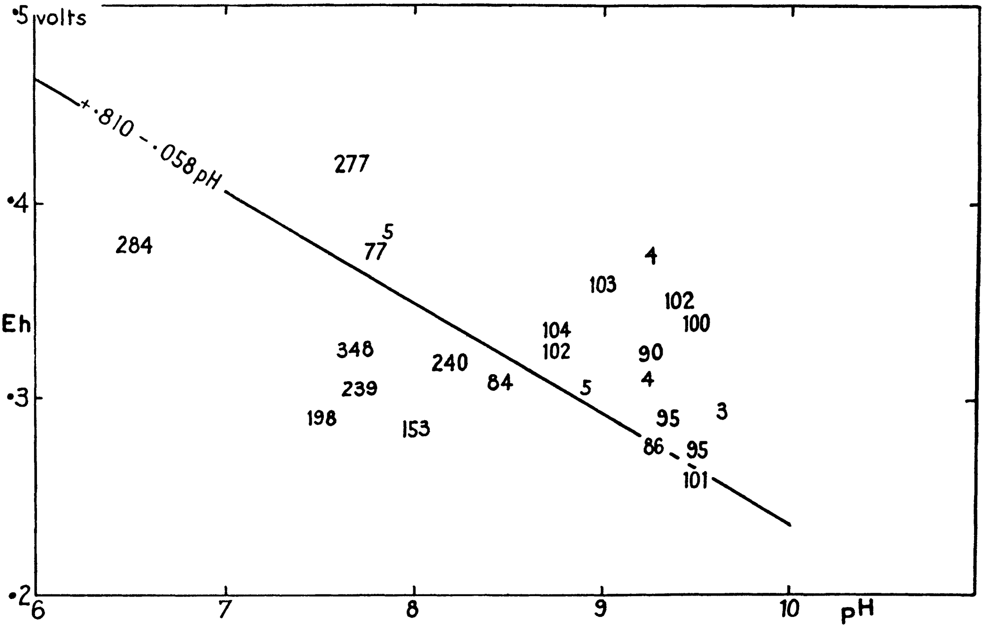

FIG. 3.—Influence of oxygen-saturation on Eh of sea water at different pH values. An approximate best-fit line drawn through the data yields an Eh = 0.810—0.058 pH volts. (Numbers indicate per cent oxygen saturation.)

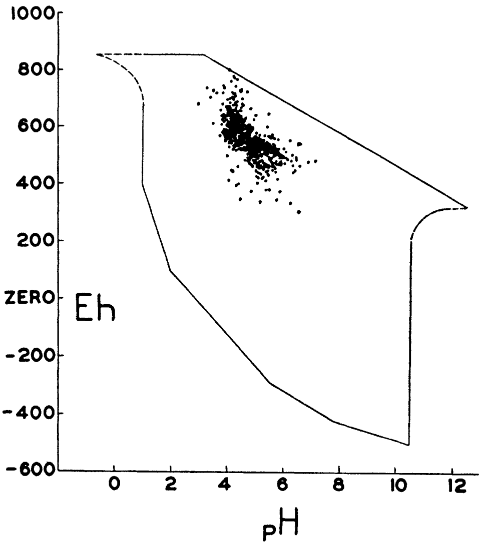

FIG. 4.—Eh-pH characteristics of meteoric waters.

Becking and Nicolai, 1934). The plant takes in metal ions and releases hydrions in their places. The Eh range in continuously waterlogged peats is apparently the same for both low moors and high moors, mostly below +400 mV and certainly below +500 mV. The lower limit of Eh is uncertain. Sulfate reduction has been reported from a high moor in Holland (Baas Becking and Nicolai, 1934), and the common occurrence of marcasite in brown coals and higher rank fuels suggests that sulfate reduction is more common than has been realized in modern deposits. It is likely, because of this, that the lower limit of Eh is in the region of negative potentials. The extreme upper limit of Eh, nearly +700 mV, is reached only when a peat bog is drained. High moors are particularly susceptible to bog bursts and subsequent drying-out, conditions in which these high potentials and low pH's develop, perhaps by concentration of their electrolyte content.

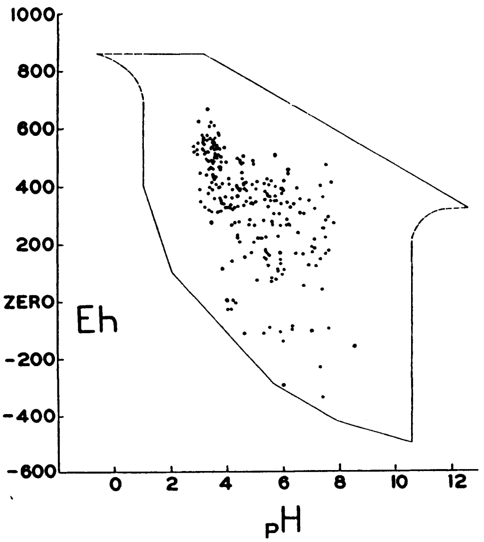

FIG. 5.—Eh-pH characteristics of peat bogs

Geological counterparts of peat bogs are almost entirely the remains of high moors. The products of low moors, full of mineral detritus and often calcareous, are represented by cannel coals and torbernites. Of the common constituents of coal, vitrain, clarain, and durain probably form under normal waterlogged conditions. (A suspension of coal in distilled water gave the following characteristics: pH 4.9; Eh +370 mV.) Fusain, on the other hand, forms as a result of partial dessication of a peat swamp (White, 1932). These conditions are precisely those which give rise to high potential and low pH in modern peats, and one may deduce with confidence that fusain formed at Eh above +400 mV, pH less than 4.0.

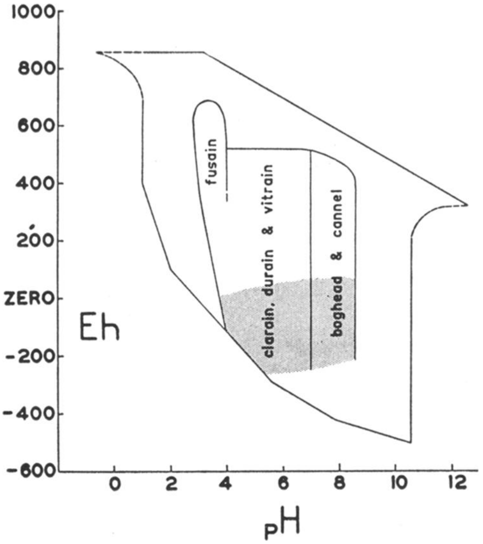

FIG. 6.—Suggested fields of formation of coal components, pyrite-marcasite field shaded.

The available data on peat bogs are shown in figure 5. Figure 6 illustrates our ideas on the correlation of the characteristics with geological equivalents. The data are world wide in distribution, as shown below:

| | |
|---|---|
| Australia | 37 |
| Antarctic | 2 |
| Canada | 4 |
| England | 140 |
| United States | 60 |
| Holland | 1 |
| | 244 |

We have no information on tundra, but we see no reason why it should differ from the the data for peat bogs.

### 4. SOILS

Rain water which strikes the ground most frequently falls upon soil of one type or another. Surprisingly little reaches stream channels by direct runoff. It is fitting, therefore, that soils should be the next environment to study. Owing to the great economic importance of soils, they have been the subject of a great deal of research; in fact, Gillespie's (1920) work on potentials in waterlogged soils is the earliest geochemical application of Eh known to the writers. It is perhaps because of the amount of work done on soil potentials and pH that they have suffered most from unusual methods of determination. Nowhere else have samples been dissolved in 0.1N $H_2SO_4$ before measurements were made.

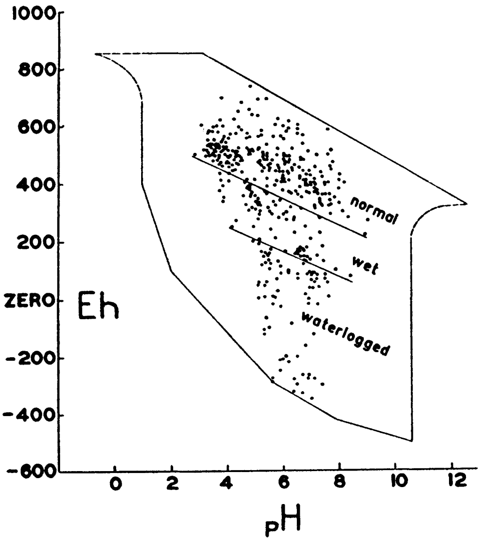

FIG. 7.—Eh-pH characteristics of soils

Many methods of sampling have been used in soil studies, although of all the methods familiar to us, only those of Starkey and Wight (1945), Pierce (1953), Quispel (1947), and Pearsall (1938) can be considered completely reliable. All four teams used direct measurements, inserting their electrodes directly into the soil. Other workers have taken samples to the laboratory and there subjected them to various treatments. Owing to the total lack of readings *in situ* on soils with high pH, we have had to accept determinations on soil solutions in this region, so that our assessment of soil conditions could be reasonably comprehensive. We acknowledge that values from alkaline soils may be inaccurate, but, as these soils are normally far too dry for direct measurements, we do not see how else the data could be obtained.

Mineral soils range in pH from 2.8 to over 10, and in Eh from +750 mV to −350 mV. Our data are probably quite adequate in terms of Eh range, and in the acid limit of pH, but our most alkaline pH reading for which we have an Eh value as well is 9.0, at least one pH unit too low. Unfortunately, soils of such high pH are not found in Australia, so that we are unable to remedy the deficit.

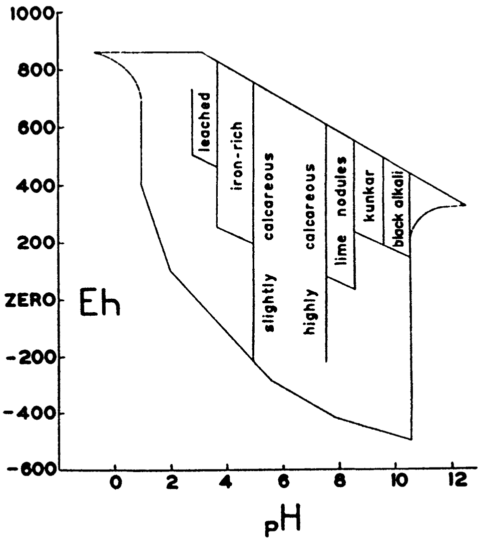

FIG. 8.—Suggested stability fields of various soil types.

We do not propose to put forward a classification of soils based upon Eh-pH measurements. Some subdivision, of use to geologists, is possible. From observations in the literature, soils may be divided into three categories: normal, wet, and waterlogged. Wet soils are those subject to seasonal waterlogging but which may be quite dry at other times of the year. These types can be divided from each other, as in figure 7. The other categories of soil are clearly marked by their pH range on the acid side, where our information is concentrated, and there is a suggestion of a similar division on the poorly documented alkaline side. One may state the differences as follows: Normal soils range in pH from 2.8 to 10+; wet soils range from 3.7 to 8.5(?); and waterlogged soils range from 5.0 to 8.0. The acid limits of each category correspond to mineral differences (compare fig. 8 with Pearsall, 1950, his fig. 16, p. 77). In waterlogged soils lime persists indefinitely, thus limiting the pH at 5; in wet soils the occasional draining is sufficient to remove lime but not enough to remove iron and alumina. A second limit at pH 3.7 seems to operate. Where conditions are well drained so that complete leaching can take place, even the iron and alumina are removed, and the pH can fall to 2.8. Completely leached soils of this nature are called "podsols" and are often associated with peat development. Mineral acids from the peat waters may be responsible for the very low pH's.

| | |
|---|---|
| Australia | 43 |
| Britain | 201 |
| Central Europe | 5 |
| Russia | 45 |
| Tropics | 9 |
| United States | 109 |
| Cuba | 2 |
| | 414 |

Alkaline soils occur predominantly in arid regions. They differ from acid soils in the direction of ground-water movement, downward in acid soils, upward in alkaline soils. The upward movement is accompanied by precipitation of calcium and sodium salts in the soil profile. These salts are responsible for the high pH. The correlation of high pH and arid conditions of formation suggests that soils of high pH would not form under water logged conditions, and the scanty evidence at our disposal agrees with this postulate.

A subdivision of soils is given in figure 8. The data used in the compilation of the figures are obtained from various countries, as shown in adjoining column.

### 5. GROUND WATER

Our information on ground water is very scant and is included for only two reasons—to show that it neither conflicts with much more abundant data on surface waters nor transgresses the limits we have set for the natural environment. We have restricted ground water to water of meteoric origin occurring in rocks, but which was not there from the time when the rocks were deposited. Connate waters, on which we have even less information, are recorded separately. We have also excluded from this category mine waters, largely because the artificial conditions induced by mining encourage a distinct bacterial flora.

Ground waters vary considerably in their salinity. In mountain country the salinity is low, but in flatter regions much higher concentrations are found. The highest salinities occur in the more arid areas. Such information as we have from inland Australia, where the rainfall is less than 10 inches per year and the salinity commonly exceeds 10,000 p.p.m., does not show any difference in Eh-pH characteristics from waters of eastern Australia, where the salinity is below 200 p.p.m.

Many ground waters which break forth naturally at the surface as springs are very selective in their dissolved constituents. Quoting local examples again, ironstone springs occur commonly in parts of New South Wales, and there are a few examples of waters supersaturated in $CO_2$. Only the latter seem to have distinct characteristics, showing a narrow range of both Eh (around +330 mV) and pH (around 6.1).

The Eh range of ground waters is not well known, but both it and the pH range may well be equal to those of waterlogged soils (see fig. 7). Secondary effects are often induced in these waters when they appear at the surface—algae may increase the pH to 9.4 by photosynthesis, and an increase in temperature or release of pressure may alter the $CO_2$ tension.

The data on ground waters are distributed as follows:

| | |
|---|---|
| Bikini Atoll | 3 |
| Australia | 69 |
| New Guinea | 1 |
| United States | 3 |
| | 76 |

They are shown on figure 9.

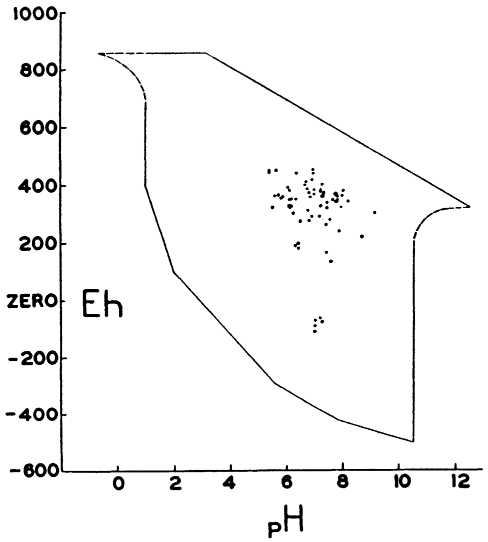

FIG. 9.—Eh-pH characteristics of shallow ground water.

### 6. MINE WATER

We have found only two published readings on mine waters, despite an intensive search of the literature. Fortunately, unpublished information increases the total number of readings to fifty-six, which enables us to gain some idea of the possible variation. The most striking feature is the low pH attained by these mine waters in oxidized zones of the mines. This peculiarity is directly attributable to the presence of pyrite, since it can occur in coal mines as well as in metalliferous mines and is not found in water from a manganese mine in South Australia, from which pyrite is absent (pH 8.55; Eh +277 mV). Such data as we have been able to accumulate show remarkably close comparison with the development of iron bacteria in laboratory cultures, although the latter have their starting point about halfway along the line of points from mine waters.

These findings are in accord with the acid line of paragenesis of vanadium minerals described by Evans and Garrels (1958), a paragenesis occurring only in the presence of pyrite. Evidence for Evans and Garrels' other line of descent is lacking, so far, as our available data are almost entirely confined to pyritiferous mineral lodes. The reading from the South Australian manganese mine may be on this line of descent.

Oxidation of pyrite is a chemical system which has been neglected by geochemists. Recent investigations by us have shown quite conclusively that the first stages of oxidation are entirely inorganic—pyrite exhausted of contaminants by thorough washing in oxalic acid and subsequent long boiling in distilled water gave an initial pH of 6.2, but it oxidized in under 24 hours to pH 3.1, the Eh rising concomitantly to +650 mV. Repetition of this process several times invariably gave an end point around +650 mV. Higher Eh's are only to be obtained in the presence of organisms—iron bacteria which can give rise to Eh +860 mV and pH lower than 2.0. The results will be published separately.

The data on mine waters were obtained from pyritic ore bodies in New South Wales and Western Australia and from the states of Utah and Arizona in the United States. The American data were supplied in personal communication by Dr. M. Sato (1959), whose work has now been published. Two readings from coal mines in Pennsylvania were taken from Colmer, Temple, and Hinkle (1950). Figure 10 shows how the points are distributed. The boundary between oxidized and primary ore is based partly on Sato's (1959) data and partly on our own analyses of waters and experiments with the oxidation of pyrite.

### 7. FRESH-WATER RIVERS AND LAKES

Surface streams vary considerably in their content of dissolved matter. Two main types are recognized by ecologists: *oligotrophic*, with low concentrations, and *eutrophic*, with high concentrations, of inorganic ions. The inadequacy of this twofold division has led to the creation of numerous other types—mesotropic, alkalitrophhic, apatotrophic, dystrophic—but there is little advantage to be gained in continuing the practice.

In general, oligotrophic waters are found in areas of high relief and high rainfall, especially where the calcium carbonate content of rocks and soil is low. They are generally associated with leached soils. Eutrophic waters occur in areas rich in lime and in lowland regions. It is usual for oligotrophic waters in the uplands to change into eutrophic waters downstream. The reverse change is unlikely to take place.

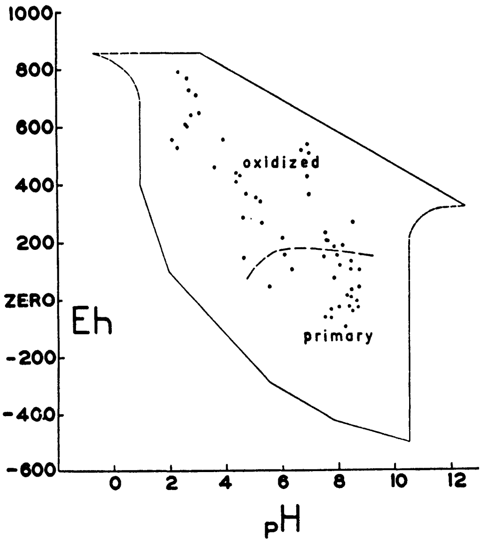

FIG. 10.—Eh-pH characteristics of mine waters. An attempt is made to distinguish between the water coming from the primary ore and that draining from the oxidized ore.

Owing to the great diversity of surface fresh waters and the ill-defined boundary at which an oligotrophic water becomes eutrophic, it has not been found possible to differentiate the two by their Eh-pH characteristics. As a generalization one may say that oligotrophic waters have pH's on the acid side of the range, and eutrophic waters tend to be more alkaline. In the majority of cases, where the pH falls in the vicinity of 7, oligotrophic cannot be distinguished from eutrophic.

The distribution of Eh and pH in fresh waters is shown in figure 11. In the T-shaped catena, river waters are confined to the crossbar of the T, lower potentials occurring only where the water is stationary in lakes. Of the data shown, pH values below 6 are invariably oligotrophic waters, whereas those above 8 are eutrophic. The data have a more restricted geographical distribution than some environments, even though a total of 347 sets of data are available. They are distributed as follows:

| | |
|---|---|
| Australia | 143 |
| Britain | 47 |
| Russia | 12 |
| United States | 145 |
| | 347 |

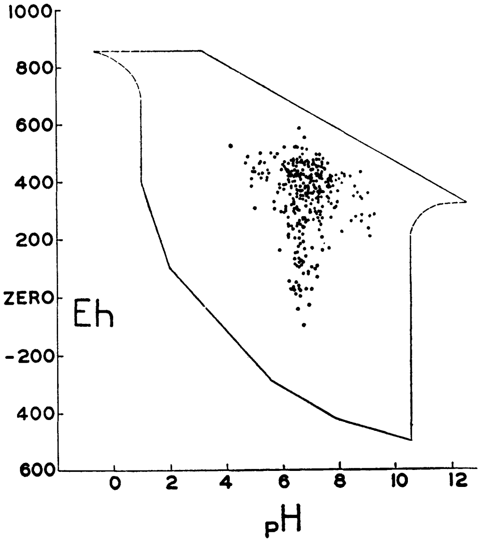

FIG. 11.—Eh-pH characteristics of fresh waters

### 8. FRESH-WATER SEDIMENTS

As may be expected, fresh-water sediments show close comparison in their Eh-pH distribution with the waters in which they are deposited. There is a much more obvious pH control in the sediments, at least in the data available to us, and, although a **T**-shaped catena occurs, the vertical stroke is much stronger than the crossbar. This is a consequence of the type of sediment prevalent in fresh water. The soluble mineral matter content of most fresh waters is dominated by calcium carbonate, which is generally sufficiently concentrated as a nutrient for plants. A controlling factor in the precipitation of limestone (or marl) is, according to Kindle (1929), the depth of the thermocline beneath the water surface.

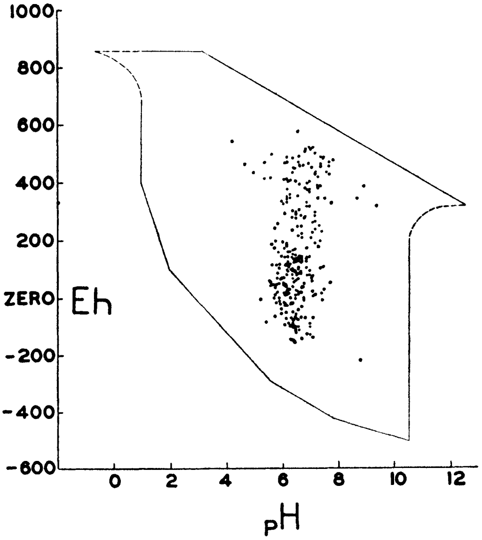

FIG. 12.—Eh-pH chracteristics of fresh-water sediments.

The Eh of fresh-water sediments shows considerably more variation than the pH. In the intermittent Lake George, New South Wales, a 10-foot auger hole put down at the northern end of the lake showed consistently high Eh's, varying from a maximum of +586 mV at a depth of one foot to a minimum of +460 mV at a depth of eight feet. Eh readings above +500 mV are exceptional in other lakes, where permanent water bodies have encouraged the development of stagnation in the depths and the consequent onset of reducing conditions. The lowest Eh's recorded are −150 mV, but it is quite likely that much lower values exist in eutrophic lakes well below the mud surface. The majority of cores from lake sediments do not penetrate the mud for more than three feet.

To a large extent, reducing conditions are much more likely in the sediments of eutrophic lakes than in those of oligotrophic waters. This is a direct consequence of the greater concentration of dissolved substances in the former. If sulfate-reducing bacteria are to function, there must be an adequate supply of sulfate for them to reduce; in oligotrophic waters the supply is often inadequate.

Highly oxidized sediments are usually restricted to the shallows of such lakes as have been studied. Even in the shallows reducing conditions can set in if stagnation develops. This is encouraged by a high proportion of clay-sized sediment in the bottom deposits, whereas sandy-bottom sediments are most often oxidized.

Siderite is more common as the reduced form of iron in fresh-water sediments than is hydrotroilite. Unfortunately, although many authors have recorded siderite, few have measured Eh and pH. One reading is known to us, pH 7.15; Eh−125 mV (Swain, 1956). It is of interest that this value falls precisely in the stability field for siderite calculated by Krumbein and Garrels (1952).

Organic sediments in fresh-water environments are predominantly those of plants. Diatomite is abundant, as are both low-moor and high-moor peats. The latter have already been considered, and diatomites are not known to have special Eh-pH characteristics.

The data shown in figure 12 are taken from many places and from both rivers and lakes, the latter predominating. The distribution of data is as follows:

| | |
|---|---|
| Australian rivers | 28 |
| Australian lakes | 15 |
| British rivers | 6 |
| British lakes | 38 |
| Russian lakes | 88 |
| American rivers | 27 |
| American lakes | 73 |
| East African lakes | 30 |
| | 305 |

### 9. MARGINAL MARINE SEDIMENTS

The sediments described under this heading come from a variety of closely allied environments which have in common their location on the margin of sea and land. Deltas, estuaries, lagoons, and bays are all included together, as they are similar in their sediments, differing mainly in facies relationships. The data are unevenly distributed in this large and complex group. Deltas, for instance, are represented by only twenty-six measurements. To complicate matters, many of the Australian estuaries from which data have been collected are more or less restricted by sand bars across their mouths; they resemble lagoons in this respect.

The exact nature of sediments within these marginal marine milieus is controlled by many factors. Deltas alone are fairly constant in their features, perhaps because the conditions under which deltas may form are strictly limited. Estuaries, on the other hand, vary widely. Estuaries in high latitudes, and in low latitudes where there is a permanent river entering them, are characterized by an abundance of terrigenous sediment and the presence of peats near to the point of debouchure of the stream. Reduced conditions are commonplace, particularly in recently glaciated areas (Strøm, 1939), and evaporite deposits are unknown. Estuaries in low latitudes away from mountainous areas often lack a permanent supply of fresh water. This has a twofold effect, terrigenous sediment is brought into the estuary only rarely, and the lack of a competent scouring current often results in the mouth of the estuary being blocked by a sand bar. Partial isolation and concomitant high evaporation result in the concentration of the waters of the estuary and the subsequent deposition of evaporites. Good examples of this type of estuary are the Coorong, South Australia (Alderman and Skinner, 1957), and the Bocana de Virrila, Peru (Morris and Dickey, 1957).

Bays and lagoons tend to be similar in their features to estuaries, although without the influence of inflowing rivers. In high latitudes lagoons are often the site of prolific vegetation; the same may be true in tropical regions, where mangrove swamps replace the vegetation of the high latitudes. Where the lagoon is without a permanent source of fresh water, in the arid regions, its deposits are largely evaporite. Bays are more nearly marine than the other environments. They may fill with terrigenous sediment when large rivers flow into them, or, where there are no rivers, they may be filled with sediment high in calcareous matter. Minor rock types in many bays are present in shell banks. Data are available only on a small number of oyster reefs in Texas bays. They are insufficient to characterize the environment at all adequately.

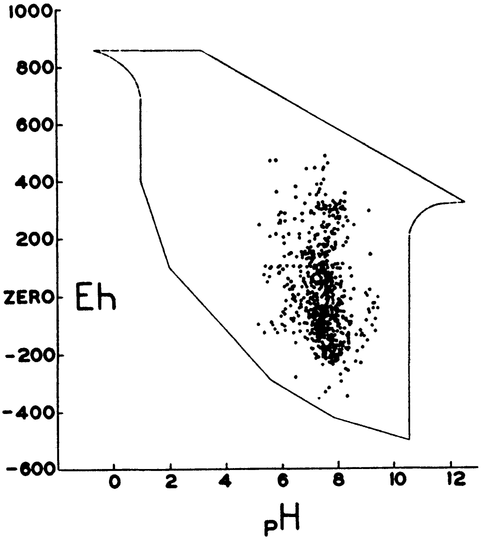

FIG. 13.—Eh-pH characteristics of marginal marine sediments.

The data shown in figure 13 are well distributed over the world, although the number of readings taken by the authors is dominated by almost 400 from Australian estuaries. In the matter of sediment types the coverage is much less comprehensive. Apart from a few points from New Caledonia, and a beach on Bikini Atoll (Emery *et al.*, 1954), we are uninformed about the Eh-pH range of calcareous sediments. Information on other types of sediment is also very poor; our data on mangrove swamps are limited to two readings from Woy Woy Creek, New South Wales, pH 5.6 and 5.8, both at Eh +475 mV. Evaporite estuaries, although they properly belong to a later section, should be mentioned here; we have, as yet, no data on them.

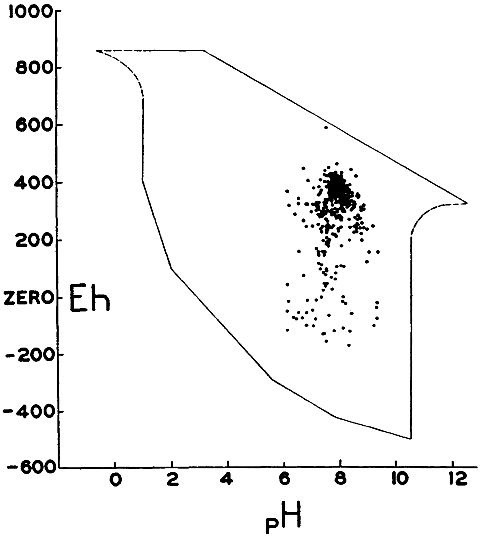

FIG. 14.—Eh-pH characteristics of sea water

Most of these marginal environments support a prolific fauna and flora, as they are collecting grounds for nutrients both from the sea and from the land. Immense beds of kelps, *Enteromorpha*, and other types of marine algae are common and may influence the pH during photosynthesis to such an extent that calcium carbonate is precipitated. Alderman and Skinner (1957) have described the deposition of primary dolomite by *Ruppia* in the Coorong, South Australia.

Algae continue to influence the environment after their death. Marine sapropels have been studied intensively by Savich (1956). His data show that highly reducing conditions are characteristic. Further information in an earlier paper (Savich, 1950) is available only as average values quoted by other authors.

The distribution of data is shown in the accompanying tabulation.

| | | |
|---|---|---|
| *Deltas:* | | |
| England | 4 | |
| Texas | 9 | |
| Louisiana | 13 | |
| Russia | 9 | |
| *Estuaries:* | | |
| Lake Macquarie, N.S.W. | 127 | |
| George's River, N.S.W. | 150 | |
| Woy Woy Creek, N.S.W. | 2 | |
| Mooney Mooney Creek, N.S.W. | 17 | |
| Port Hacking River, N.S.W. | 2 | |
| Other New South Wales estuaries | 96 | |
| Cawley Bay, Swan River, W.A. | 1 | |
| Milford Sound, N.Z. | 19 | |
| Hamana-ko, Japan | 15 | |
| Akhtanizovskii Estuary, Russia | 5 | (av.) |
| Other Russian estuaries | 8 | (av.) |
| *Lagoons:* | | |
| Aransas Bay, Tex. | 6 | |
| San Antonio Bay, Tex. | 21 | |
| *Bays:* | | |
| Caspian and Black Seas, Russia | 98 | |
| Taman Bay, Russia | 4 | (av.) |
| New Caledonia, various | 11 | |
| San Pedro Harbor, Calif. | 14 | |
| Bikini atoll | 4 | |
| | 638 | |

### 10. SEA WATER

It has not been found possible to distinguish the Eh-pH characteristics of water from marginal marine environments from surface waters away from the land. Accordingly, all values for sea water have been plotted together. The range of both pH and Eh is great, far greater than most works on oceanography would suggest. The discrepancy arises because a large number of our data were taken in or near to masses of marine algae, whose effects on sea water are pronounced (see, for example, Baas Becking and Mackay, 1956). In areas where the effects of photosynthesis are less pronounced, the Eh-pH variation of sea water is much less. The great cluster of points around 8.0; +400 mV on figure 14 represents average surface sea water. Our knowledge of variation of Eh and pH with depth is restricted to a few readings from the basins off southern California (Emery and Rittenberg, 1952), and the series of data presented by Cooper (1938). Emery and Rittenberg's data suggest a decrease in Eh and a more rigid control of pH with increase in depth. This is not borne out by Cooper's figures, but these are calculated, not measured, and it may well be that the basis for the calculations was unsound.

In surface sea water away from the land, where it is relatively little influenced by excessive amounts of marine vegetation or strong evaporation, the Eh-pH range is restricted, being represented by the thick cluster of points around pH 8.0; Eh +400 mV. The Eh control in these waters is unknown, but the pH control seems to be the delicate balance between dissolved carbon dioxide and calcium carbonate, which is usually almost at saturation in sea water (Emery, 1946; Sverdrup, Johnson, and Fleming, 1942).

The range of values given in figure 14 does not entirely cover the known range in sea water. Although in normal circumstances a buffering effect is felt at pH 9.4, when calcium carbonate is precipitated, isolated cases of higher pH's have been recorded in low latitudes in restricted bays and estuaries. A pH of 10.1 is mentioned by Stewart (1958) for a bay on the Mexican coast. No Eh is given.

Our data for sea water were obtained from the Atlantic and Pacific oceans, though the majority of the readings were made near Australia. The distribution is as follows:

| | |
|---|---|
| Antarctica | 182 |
| East coast of Australia | 282 |
| Tasman Sea | 7 |
| Florida Strait | 1 |
| South Atlantic | 10 |
| Southern California | 12 |
| Japan | 2 |
| New Zealand | 1 |
| | 497 |

### 11. OPEN-SEA SEDIMENTS

Marine sediments away from land are not well documented in their Eh-pH characteristics. Although we report nearly 600 measurements, they represent, in effect, two major environmental units only. The first is the continental shelf and landlocked basin—neritic and bathyal environments. These show a wide Eh range, varying from oxidizing coarse-grained (and often shelly) sediments with Eh values of +350 mV to the highly reducing black and green clays with Eh lower than −400 mV. In the southern California coastal sediments the surface oxidized layers have the same oxidation reduction potential as the overlying water. The lowest potentials are found in the deep basins, where organic matter accumulates due to the restricted circulation of the water which prevents aerobic decomposition. Fine-grained sediments with organic contents as high as 10 per cent (on a dry weight basis) supply the requirements for proteolytic, sulfate-reducing and methane-producing bacteria. Such environments can lead to the discharge of $H_2S$ in the overlying waters, as in the Black Sea (but not in the southern California basins). These environments are generally found only in close proximity to land which supplies the nutrients for plankton growth at relatively shallow depths to minimize the decomposition of the settling organic matter.

The mid-Pacific measurements (abyssal environment) were made by Dr. S. C. Rittenberg (unpublished data) during the Scripps Institution MIDPAC expedition of 1950. They represent data from 12 cores taken at different positions between 130 W.–170 W. longitude and 10 N.–20 N. latitude. All the readings (except three measurements on one core giving Eh +100 to +138 mV) showed potentials higher than +390 mV, the highest being Eh +581 mV at pH 8.13. These highly oxidized sediments often differed in color—from gray to green, to brown and red. Those giving the highest potentials were the so-called red clays. The bottom sea waters generally had Eh values between +330 and +400 mV. The surface sediment values were always higher than the overlying water (except in the one core mentioned above). Generally, the Eh increased with depth of the core.

Figure 15 shows the distribution of the data. The abyssal deep-sea sediments and the neritic sediments can be readily distinguished by a line passing through +375 mV. It is difficult to account for the surprisingly high potentials in the red clays at that pH. It may be possible that reactions of water with hydrated oxides of manganese ($MnO_2 \cdot H_2O$) and iron ($Fe_2O_3 \cdot H_2O$) in the presence of other trace metals may cause the formation of soluble complex ions. Such highly oxidizing ions as manganate ($MnO_4^{=}$) and ferrate ($FeO_4^{=}$) could be stable under these conditions. Another possible speculation is that oxidizing organic compounds are preferentially adsorbed on the clay particles. These may perhaps act as chelating agents of ferric and manganic ions. If the presence of soluble iron and manganese ions could be demonstrated, their possible importance as factors in the formation of manganese nodules may be worthy of further consideration.

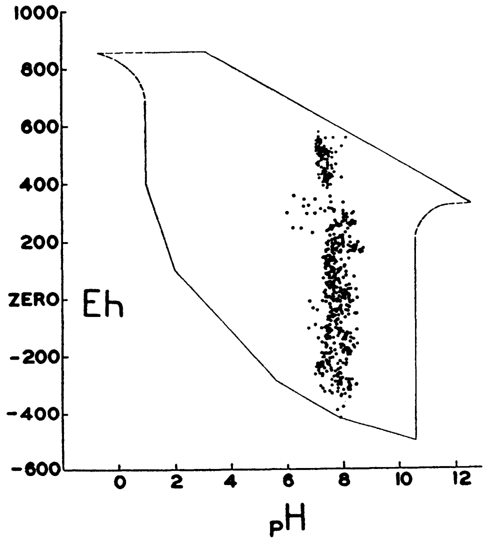

Fig. 15.—Eh-pH characteristics of open-sea sediments.

The pH of the large majority of sediments described in this section lies between 7.0 and 8.5. In general, there is a decrease in the pH of the surface sediments relative to that in the overlying water. This may amount to only 0.1 or 0.2 of a pH unit in the offshore sediments, but it can be as high as 1.0 pH unit in the red clays. There is usually an increase in pH with increase in depth of the core.

The efficient buffering of the $HCO_3^{-}$–$CO_3^{=}$ system is probably largely responsible for the control of the pH. In the neritic and bathyal environment the sediments with higher carbonate contents generally yield pH values that are a little higher than those with lower contents. A process that may be responsible for the slight lowering of pH in the surface sediments in these environments is the liberation of vast amounts of carbon dioxide through bacterial decomposition of the organic matter. In the deep-sea sediments, the high clay content (especially montmorillonite) may indicate that an important mechanism for the lowering of pH could be cation exchange at the clay-water interface. Evidence for such exchange mechanisms was recently given by Carroll (1958).

The data in figure 15 were collected from the following places:

| | |
|---|---|
| Arctic Russia | 50 |
| Black Sea | 15 |
| Gulf of Mexico | 6 |
| Southern California | 376 |
| Mid-Pacific | 150 |
| | 597 |

### 12. EVAPORITES

Evaporites may arise by solar concentration from most of the foregoing environments, with the exceptions of rain water and peat bogs. They often, at the present time, receive contributions from geothermal waters. In view of their complex origin, it is scarcely surprising that they cover a wide range of both pH and Eh.

The pH range, and to some extent the Eh range, is governed by the ions present in solution in the evaporite water. Both cations and anions may be strong or weak; a combination of two strong ions generally gives a pH near 7 (the Dead Sea and Lake Eyre are examples of this type); a strong base ($Na^+$) with a weak acid ($CO_3^=$) yields an alkaline pH (as in the unrecorded trona lakes); and a strong acid with a weak base, $Fe^{++}$ ($Al^{+++}$) and $SO_4^=$, leads to a low pH, such as we have found in Lake Cowan, Western Australia.

The Eh range responds to the state of the iron in the evaporite body. Reducing conditions in the form of fetid black muds are reported from many evaporite lakes (Strøm, 1939); in Searles Lake, California, we have found potentials as low as −500 mV at pH 10.48. At the other extreme lie the coquimbite evaporites of Peru and Australia (the latter not yet reported in the literature). Measurements made on Australian coquimbite by one of us (Baas Becking) in 1936 gave a pH 2.6, and measurements made on saturated ferric sulfate solutions in equilibrium with the air gave Eh's of +860 mV.

It seems likely that evaporites may fill almost the whole area of the natural environment, as we have outlined it. The data so far recorded do no more than suggest the wideness of the range. It can readily be seen that this environment, originally suggested by Krumbein and Garrels (1952) as being oxidative, can also be highly reducing. It is often true that, while the surface waters may give high positive Eh-values, the bottom mud is black and highly reducing (Dead Sea and marine solar evaporites). As is so often the case, the data come mainly from Australia and the United States, with the welcome addition of 10 readings from the Dead Sea, Israel. The full details of the distribution are shown in the accompanying tabulation.

Figure 16 shows the distribution of the data, and figure 17 shows our interpretation of the complete field of the evaporite environment and the distribution of key minerals within the field. This interpretation is no more than tentative; probably it will need revision when more data are available.

| | |
|---|---|
| *Australia:* | |
| Dry Creek solar salt works, South Australia (marine) | 20 |
| Lake Eyre, South Australia (non-marine) | 28 |
| Lake Cowan, Western Australia (non-marine) | 1 |
| *United States:* | |
| Pyramid Lake, Calif. (non-marine) | 23 |
| Searles Lake, Calif. (non-marine) | 29 |
| Bristol Lake, Calif. (non-marine) | 27 |
| Salton Sea, Calif. (non-Marine) | 5 |
| Various playa lakes, Calif. (non-marine) | 23 |
| *Israel:* | |
| Dead Sea (non-marine) | 10 |
| | 166 |

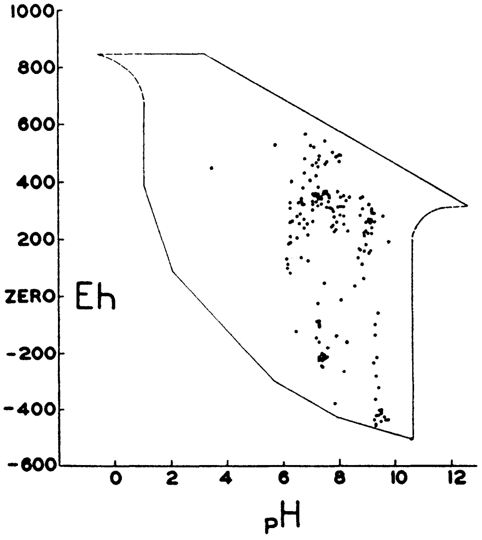

FIG. 16.—Eh-pH characteristics of evaporites

### 13. GEOTHERMAL WATERS[4]

Of all the environments studied, the geothermal is the most poorly known. All the available readings were taken by the authors and are restricted to three areas—New Zealand, Fergusson Island off western

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[4] While this paper was in the hands of the editor, 150 additional measurements were made on this environment in New Britain by Baas Becking and G. A. Taylor. The results show a low pH of 0.85 at Eh + 450 mV and +585 mV for two samples. The results generally have a similar trend to those previously measured but extend the limits to Eh +580 mV in the neutral zone at pH 6.5.

New Guinea, and the Fink hot springs near the Salton Sea, California. It is a matter of great regret to us that the recent revival of interest in geothermal problems brought no crops of Eh-pH readings in its train.

The geothermal environment shows a wide range of conditions from highly acid to highly alkaline. We have measured pH's of 1.2 in New Zealand (Kaplan, 1956), and White (1957) records pH's of 9.5 at the other end of the scale. The recorded Eh range is from +700 mV in an acid water to −185 mV in a neutral solution. We do not know how closely this approaches the actual limits of the environment, and there is no profit in speculation based on so little data.

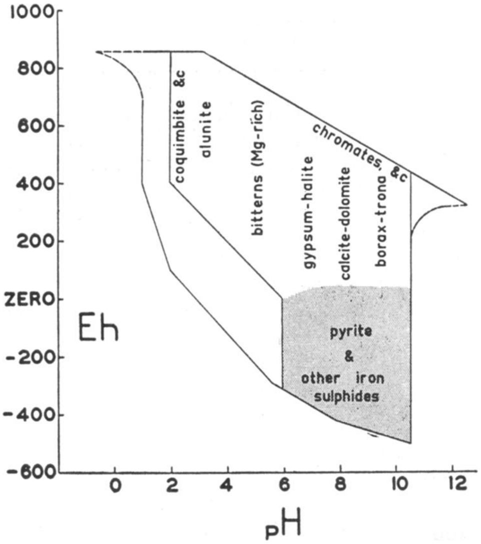

FIG. 17.—Suggested fields of formation of various evaporites.

The distribution of values (fig. 18) for this environment is as follows:

| | |
|---|---|
| Japan | 1 |
| New Zealand (Rotorua, White Island) | 30 |
| Fergusson Island, New Guinea | 5 |
| California | 6 |
| | 42 |

### 14. CONNATE WATERS

Connate waters are a special type of ground water, but their lack of contact with the open air from the time the containing rock was laid down renders them unique in many respects. They are of great importance geologically as transporters of soluble constituents during diagenesis and later. We have little information on their characteristics. Only one published study is known to us—that of Zyka (1958), which

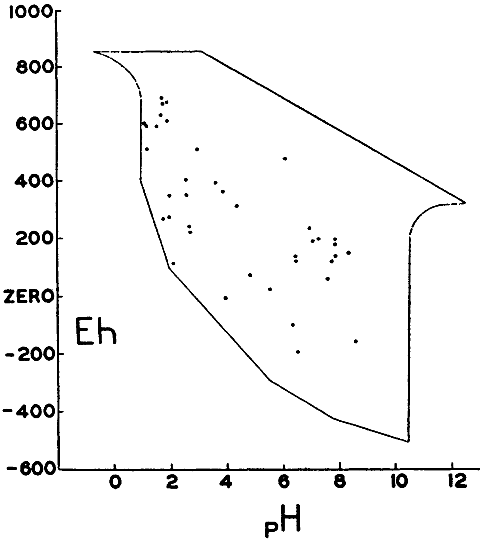

FIG. 18.—Eh-pH characteristics of geothermal waters.

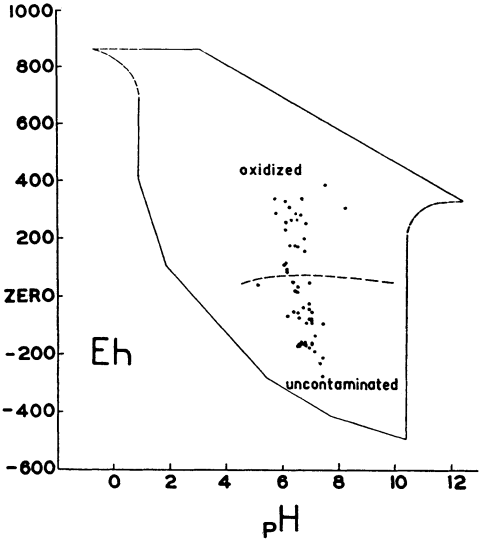

FIG. 19.—Eh-pH characteristics of connate waters.

appears to contain reliable information on Eh as well as pH. This we have supplemented with a few readings from formation waters encountered during exploratory drilling for oil in Australia and New Guinea. Our own samples show much higher potentials than the data of Zyka, and we suspect that the Australian samples were inadvertently aerated during collection at the well-head. They are of interest, therefore, only in delineating the potentialities of the connate waters. Much more work is needed on these waters. Figure 19 shows the present extent of our knowledge; all the Australian samples, with one exception, have Eh's in excess of +100 mV. Only one of the data from Czechoslovakia lies above this line. We have therefore drawn an arbitrary boundary in figure 19 between such waters that have undergone atmospheric oxidation and relatively "unacontaminated" waters.

One reading from a cold-water spring in northern California is of paramount importance to our study. This has a salinity around 33,000 p.p.m. and contains considerable sulfide, boron, and ammonia. It has a pH of 11.6 (field measurement) and an Eh, measured one month after collection, of −220 mV. We suspect that the true Eh may well be below −500 mV. The similarity of this water to the deeper brines of Searles Lake, southern California, suggests that it is also a connate water. If this is so, the reasons for the high pH are likely to be the long-sustained isolation and lack of replenishment under connate conditions. We are indebted to J. H. Feth, of the United States Geological Survey, for data on this water. The interpretation of its nature is our own.

## ORGANISMS AND ENVIRONMENT

### 1. GENERAL

The concept of a sterile earth has long dominated geology, and it is not so long ago that microbiological processes were referred to as caused by the action of "carbonaceous matter." With the advent of general microbiology the picture has changed, and now we find in many cases a tendency to ascribe too much to the action of microbes. Ivanov (1957) believes the oxidation of black iron sulfide to sulfur to be a microbiological process, whereas Verhoop already in 1940 has convincingly shown that this process is abiological; other instances could be cited. It is the task of the geochemist, in close cooperation with the microbiologist, to find a happy mean and to investigate both chemical and biological factors in a given process. However, certain biological processes are active in the environment, and often they appear as veritable master reactions. The most impressive reactions are those that thus far have no in vitro analogues, like photosynthesis, or that which can only be performed under artificial conditions in the laboratory, like the reduction of sulfate to sulfide. If we add to the reduction of the carbon dioxide by the green plant and the reduction of the sulfate to sulfide (by bacteria), the bacterial reduction of nitrate and of nitrogen and that of ferric to ferrous iron, we have enumerated the chief reductive processes in the environment which lead to the accumulation of vast amounts of organic matter. This organic matter may be utilized by organisms, the heterotrophs. The role of these heterotrophic microbes in the environment is complex. In natural waters we are inclined to believe that they are of secondary importance if they are not, at the same time, active as reducers of sulfate, nitrate, or nitrogen. They act chiefly as scavengers in muds and in soils. In waters they live on a lenten fare. However, they may generate highly reduced products and even hydrogen (Lake Eyre, Baas Becking and Kaplan, 1956) and thus influence the characteristics of their environment. As we have not studied the heterotrophs in relation to environment, this may be considered as a serious omission. Mass cultures of decomposing matter (sponges, kelps, etc.) have shown that their environmental limits lie well within the limits of microbes studied by us. Nitrogen fixation is carried out by the sulfate-reducing bacteria, the photosynthetic purple bacteria, and the blue-green algae. The importance of this function in nature is not fully understood, although in certain restricted areas, such as the geothermal environment, where these organisms exist in abundance, it may play an important role (see van Niel, 1955). The data on denitrification were taken from the literature.

Another serious omission lies in the absence of studies on flowering plants. *Zostera*, *Ruppia*, and *Potamogeton*, especially, may exert a great influence on the environment.

TABLE 2

MILIEU LIMITS AND RANGES FOR VARIOUS ORGANISMS

| ORGANISMS | pH LIMITS | pH RANGE | EH LIMITS (mV) | | EH RANGE (mV) |
|---|---|---|---|---|---|
| Algae............. | 1.20–11.72<br>(12.60) | 10.52<br>(11.40) | +630 | −220 | 850 |
| Sulfate reducers... | 4.15– 9.92 | 5.77 | +115 | −450 | 565 |
| Purple bacteria.... | 4.92– 9.75 | 4.83 | +328 | −230 | 558 |
| Thiobacteria...... | 1.00– 9.20 | 8.20 | +855 | −190 | 1045 |
| Green bacteria..... | 6.15– 9.78 | 3.63 | + 7 | −293 | 300 |
| Iron bacteria...... | 2.00– 8.90 | 6.90 | +850 | + 60 | 790 |
| Denitrifiers........ | 6.20–10.20 | 4.00 | +665 | −205 | 870 |

TABLE 3

FRACTION OF POTENTIAL MILIEU OCCUPIED BY MICROBIAL GROUPS

| Per Cent of Maximal Area | Organism |
|---|---|
| 0–10........ | Green bacteria |
| 10–20........ | Iron bacteria |
| 20–30........ | Sulfate-reducing bacteria, purple bacteria, denitrifying bacteria |
| 50–60......... | Thiobacteria |
| 70–80........ | Algae |

Animals are secondary to the prime movers of matter and energy, bacteria and algae, and do not enter into consideration.

Apart from the action of photosynthetic —or of atmospheric—oxygen on oxidizable matter many microbial oxidations may proceed independent of this oxygen, e.g., the oxidation of ferrous to ferric iron, chiefly abiological but utilized by the iron bacteria (Baas Becking, Wood, and Kaplan, 1956). The oxidation of pyrite involves both the oxidations of sulfide to sulfate and of ferrous to ferric iron. This process is also at least partly abiological. Among other oxidations we mention nitrification:

$$NH_4^+ \rightarrow NO_2^- \rightarrow NO_3^- .$$

We have very few data on this process, too uncertain to report upon. Leaving the heterotrophs as a possible major factor in the environment, we may say that the chief actors in the natural milieu appear to be algae, sulfate-reducing bacteria, thiobacteria, and iron bacteria. Minor roles are filled by photosynthetic purple bacteria, denitrifiers, nitrifiers, and photosynthetic green bacteria. More details about these organisms will be given later in this paper under separate headings. Their milieu limits and ranges are given in table 2.

Table 3 shows the extent of the potential milieu expressed as the percentage of the maximal area.

From the milieu limits of the organisms studied and from the environmental limits found in nature, we have constructed a tentative outline for the aqueous sedimentary environment which is used in all the diagrams in this paper. In a later section the nature of these limits will be further discussed.

Permanent conditions are hardly ever realized in the natural environment. Changes may be induced by chance and give rise to evanescent changes in the milieu, but most changes are periodical. In the photosynthetic zone there is a diurnal increase and a nocturnal decrease in the characteristics. There is an annual cycle in a great many environments, while in the deeper fresh water there may be a spring and an autumn turnover with concomitant changes in the characteristics. In estuaries there may be an annual isolation of the salty deeper water after the influx of river water. There may be a release of photosphate, together with a lowering of the pH and a formation of fetid black mud, at very low potentials. In some tidal lagoons this phenomenon is rare, as only occasionally is there enough fresh-water influx to isolate the deeper sea water efficiently. Fetid black mud may also be formed as an aftereffect of a plankton bloom (*Dinoflagellates*). The mass death of fish in certain regions (Walvis Bay, South Africa) has been ascribed to this metabiosis (Brongersma, 1944). A desert lake in Victoria, Australia, shows the formation of a stratified salt crust; black layers, showing sulfate reduction alternating with clear salt, formed in the dry period. An important periodic change in the characteristics must have taken place. Apart from these changes with comparatively short periods, there must be many environments that have remained stationary for a prolonged period. These stationary states are comparable to the "climax," a term used by plant ecologists (Clements and Weaver, 1924). They might be called "millennial." Sea water, and perhaps marine sediments are examples of this state. The accumulations of oil or of uranium-enriched phosphate in those sediments are witnesses of the persistence of a stationary state over a prolonged period. But even the millennial state is, like the climax, subject to oscillations of a low frequency. Basins with an active black mud may become shallower by sedimentation, and the sediment will, as it were, enter the photosynthetic zone. Uplifting and subsidence may make themselves felt. The lower the time frequency of the periodic happening, the less certain and the more speculative its interpretation.

### 2. THE INFLUENCE OF ORGANISMS UPON THE NATURAL ENVIRONMENT

i) Organisms that can persist and develop on an inorganic environment are called *autotrophs*. In their metabolism, carbon dioxide is reduced by an activated hydrogen (or, more strictly, electron donor systems which are highly reducing) and converted to cell material. This hydrogen may be generated in different ways.

*a*) Visible light may be absorbed by pigmented cells containing chlorophylls. This absorbed radiation will generate an active hydrogen which is immediately utilized. Organisms performing this photochemical reaction are called *photoautotrophs*. Higher plants and algae derive their hydrogen from the photolysis of water, while purple and green sulfur bacteria can obtain additional activated hydrogen by the oxidation of hydrogen sulfide or other reduced sulfur compounds. By means of this photosynthesis large quantities of organic carbon are produced from the reduction of atmospheric, or dissolved, $CO_2$. The carbon fixed in this way amounts to 30 mg/cm$^2$/annum over the earth's surface (Mason, 1958, p. 216–217).

*b*) Hydrogen, both molecular and activated, may also be generated by inorganic oxidations (Baas Becking, 1957). Organisms utilizing this hydrogen in the reduction of carbon dioxide are called *chemoautotrophs*. In the main, the cycles of iron, sulfur, and nitrogen are involved. In this paper we will not deal with the chemoautotrophs in the carbon cycle. Iron bacteria make use of the activated hydrogen (or electrons) generated in the oxidation of ferrous to ferric compounds. They find their counterpart in the manganese bacteria, where manganese changes from the +2 to the +4 state. The sulfur bacteria in this group (thiobacteria) make use of the oxidation of sulfides, sulfur, thiocyanate, and thiosulfate. A combination of the iron and sulfide oxidation is met with in the iron sulfides. Hydrated FeS oxidizes to $FeO \cdot OH$ and sulfur, while pyrite and marcasite oxidize via ferrous sulfate to the acid ferric sulfate. Chemosynthesis in the nitrogen cycle is performed by bacteria oxidizing ammonia to nitrite, while others oxidize the nitrite to nitrate.

ii) Organisms unable to persist in an inorganic milieu are called *heterotrophs*. Animals, parasitic and saprophytic higher plants, as well as a large group of microbes, are dependent upon organic matter synthesized by the plants. Many microbes can actually extract the available hydrogen from simple reduced organic molecules (fatty acids and alcohols) to carry out the reduction of $CO_2$ into cell material. However, some of these microbes may lead an autotrophic existence, if molecular hydrogen is made available to them, but they almost invariably need traces of vitamins. They are *facultative heterotrophs*. The organism which reduces sulfates has strains capable of persisting on molecular hydrogen, while the bacterial process of denitrification, where nitrate is changed into gaseous nitrogen and/or nitrous oxide, although usually heterotrophic, may take place in the presence of sulfur, which acts as an electron donor (and an active hydrogen generator).

Denitrification is an important geochemical process. The traces of nitrous oxide found in the atmosphere by Adel (1941) may be ascribed to it. Sulfate reduction is more important geochemically and generates highly reduced substances. The most important reduction, however, is the photosynthetic reduction of carbon dioxide by the green plant. It may be said that all oxidations in the natural environment presuppose the presence of reduced substances. Outside the plutonic or the magmatic milieu, these reduced substances are generated, directly or indirectly, by the green plant. *Philosophically, the green plant is to be considered as the only autotroph.*

The reduction of iron, for example, may take place even in top soil in the presence of organic matter. To a lesser extent, the same pertains to manganese compounds. The substances formed and utilized in microbial reactions determine both the hydrogen-ion concentration and the electrode potential of their environment.

An important concept was introduced by Derx (1946). As in a play, there is a sequence and a constant regrouping of the actors. This process is called "metabiosis," it may be called a form of symbiosis. If pectin is permitted to be decomposed microbially at the bottom of a tall glass jar to which sea water, mud, and lime have been added, with the exclusion of air, the products of the fermentation cause a lowering of the oxidation potential to such an extent that the region fit for the development of sulfate reducers is entered. A sulfate reduction will set in, and black iron sulfides will form. If the $H_2S$ tension is high enough, free $H_2S$ (or $SH^-$) will enable the green and purple bacteria to make their appearance at the illuminated side of the bottle. At the surface of the liquid the sulfide oxidizes to free sulfur, an oxidation performed by certain thiobacteria, such as *Beggiatoa* and *Thiothrix*. And when, at this surface, the electrode potential reaches positive values, iron bacteria may make their appearance. At the illuminated side of the bottle the algae slowly gain ascendance, and, finally, at positive potentials higher than +300 mV, they replace the purple bacteria entirely. The green bacteria require an even lower potential and disappear first. If the black sediment remains unoxidized for a few months, pyrite, which is much more stable than the other iron sulfides, may form. Due to the photosynthesis of the algae, the pH will rhythmically rise and fall in day and night. At the end of a sunny day it may reach 9.4. However, when the pyrite is brought into contact with the air, it will, by its oxidation, cause a remarkable increase in acidity (even negative pH's have been reported in the literature). These processes seem, at first glance, only biological. But, apart from the actors, there are also abiological elements in the play. The metabiosis is of a mixed nature. The simple experiment described above is a true microcosm, and the geochemical reactions dealt with in this paper can all be represented in the culture bottle.

### 3. ALGAE (FIGURES 20–23)

One of us recently published a study on the influence of algae on their environment (Baas Becking, 1958). From this work we take the following: "respiration and photosynthesis are primarily active upon the carbon dioxide equilibrium." Photosynthesis will remove carbon dioxide, whether as $H_2CO_3$ or as $HCO_3^-$ from the solution, thus

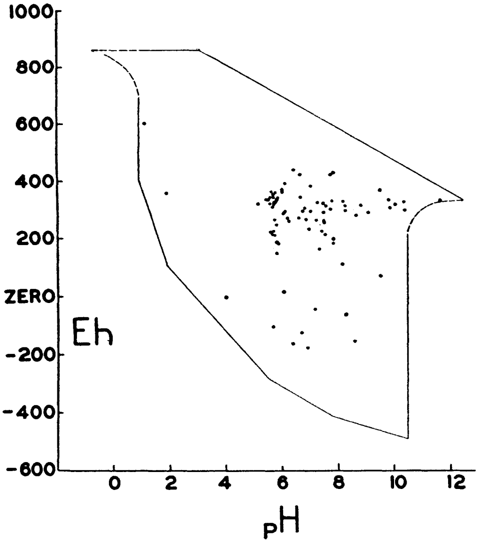

FIG. 20.—Eh-pH characteristics of some green algae and diatoms.

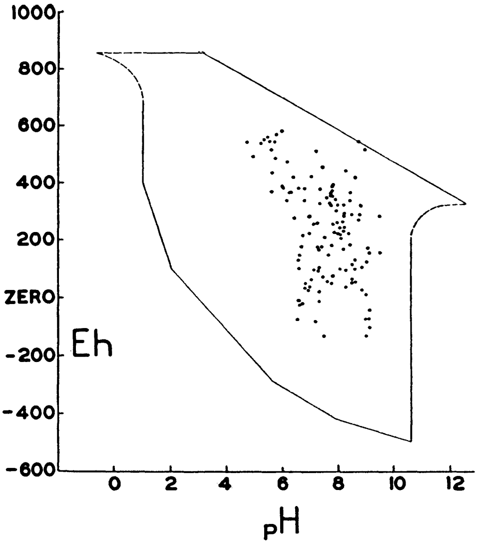

FIG. 22.—Eh-pH characteristics of *Enteromorpha*

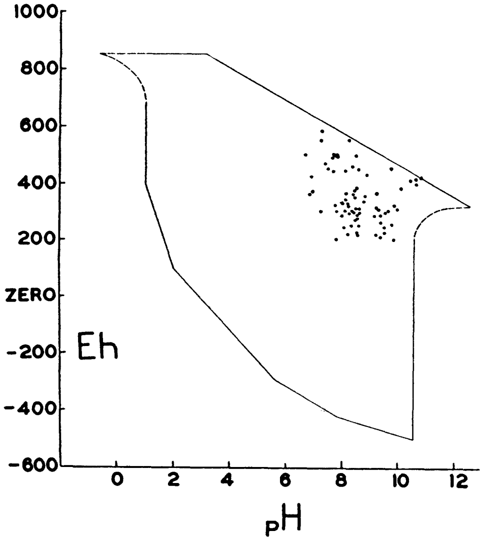

FIG. 21.—Eh-pH characteristics of *Dunaliella*, the brine flagellate.

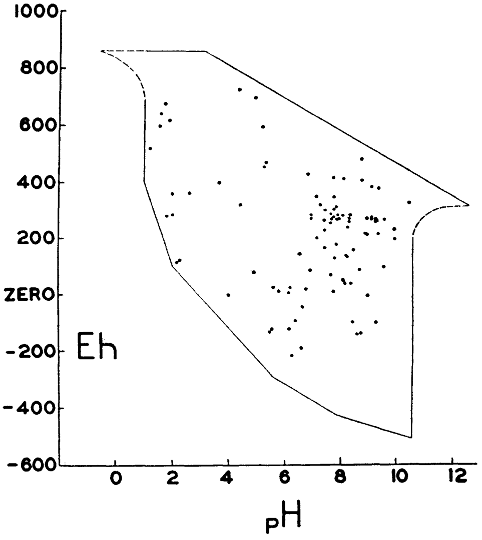

FIG. 23.—Eh-pH characteristics of blue-green algae.

increasing the pH. In sea water, and in fresh water containing much calcium, photosynthesis will, by shift of the bicarbonate-carbonate equilibrium, often cause the precipitation of calcite (Baas Becking, 1934) or of dolomite (Alderman and Skinner, 1957). The pH will rise to 9.2–9.4, after which the solution is buffered, and, inasmuch as the effect of photosynthesis is diurnal, it never lasts long enough to precipitate all the calcite or dolomite. However, if the alkaline earths are present in small quantities, as in certain fresh waters and alkaline evaporites, almost all the calcium and magnesium will disappear from the water, and at the end of the day we may get "flashes" of high pH values. In a culture of *Hormidium* (green algae) we observed a pH of 11.7. Schütte and Ellsworth (1954) observed a pH of 12.6 in a mass of *Potamogeton* (flowering plant) at the end of a sunny day in the salt vleis in Cape Province, South Africa. We cannot believe that these values mean a real geochemical extension of the environment. The lowering of the pH in algal cultures in the dark should be mainly ascribed to respiratory increase of the carbon dioxide tension.

The marine and estuarine alga *Enteromorpha* will lower both pH and Eh of its environment in the dark from +330 mV, pH 8.2 down to Eh −80 mV at pH 6.5. The effect is reversed in the light (Baas Becking and Mackay, 1955). Byewood and Challenger (1953) have shown that *Enteromorpha* liberates dimethylsulfide, probably a product of a sulfonium salt which can act as a powerful reducing agent. Another important influence upon the environment, apparently caused by green plants, is in the upper Eh limit in our general diagram, between pH 3.2 and 10.55 (12.6?). As to the cause of this phenomenon, we are still entirely in the dark. Electrochemically, the reaction $H_2O_2 + 2H_2O \rightleftharpoons 2O_2 + 6H^+ + 6e^-$ shows identical equilibrium characteristics with the empirical limit. This equation is hypothetical and actually represents the average between the reversible reaction $H_2O_2 \rightleftharpoons O_2 + 2H^+ + 2e^-$ and the irreversible one $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$, or, more correctly, the average between the two reversible reactions:

$$2H_2O \rightleftharpoons H_2O_2 + 2H^+ + 2e^-$$

and

$$2H_2O_2 \rightleftharpoons 2O_2 + 4H^+ + 4e^- .$$

In active algal cultures, however, no $H_2O_2$ could be detected by means of the lead sulfide test of Feigl (1943), which shows that the culture contained less than 0.8 mg/l of peroxide. Either this spot test was not sensitive enough, or peroxide is absent from the environment. This may indicate a rapid conversion of the peroxide to oxygen during active photosynthesis by the plant. The presence of the enzymes peroxidase and catalase not only in the green plant but also in the photosynthetic purple bacteria attest to the fact that peroxides can be efficiently degraded to oxygen and water by photosynthetic organisms. To this date, the true role of peroxide formation in plants has not been demonstrated. Another possibility lies in the excretion, by the algae, of organic compounds. We tried a large number of flavones, quinones, and anthraquinones without success.

It is difficult to say where the active role of the algae begins and the passive role ends. Blue-green algae occur at very low potentials (−200 mV) in the presence of $H_2S$. We do not know as yet whether they utilize this $H_2S$ or whether they, like *Enteromorpha*, produce sulfonium salts. All we can do is to describe briefly the environmental limits of some groups studied more intensively. *Dunaliella parva* Lerche, a brine flagellate, shows a restricted environment. It is present chiefly in evaporites in the alkaline range. It occurs only at high Eh down to +200 mV. It may be that traces of $H_2S$ are toxic. The environment of *Enteromorpha* is less restricted, as mentioned above. Since the work of Pop (1936), we know that green algae and flagellates are often resistant to $H_2S$. This also pertains to blue-greens. The environments of these groups are very wide indeed, the more so because they persist in highly acid solutions. A diatom, *Navicula grevillei*, was found in a solution of pH 1.2 (Rotorua), and the same holds for blue-greens. However, we believe that most of these environments were prepared by other organisms and that the algae, by their great adaptability, persist in these environments. Gathering all the data (Baas Becking and Wood, 1955; Baas Becking and Mackay, 1956; Kaplan, 1956; Baas Becking and Moore [lab. notes]), we find that the algal environment has been characterized by about 400 measurements, as shown in the tabulation below.

| | |
|---|---|
| Blue-greens | 123 |
| *Dunaliella* | 61 |
| Other flagellates | 50 |
| *Enteromorpha* | 121 |
| Diatoms | 6 |
| *Ecklonia* (brown alga) | 3 |
| Protococcales and other green algae | 34 |
| Total | 398 |

### 4. PHOTOSYNTHETIC PURPLE BACTERIA (FIGURE 24)

Some of these forms are autotrophic in the light. The bacteriochlorophyll contained in their cells shows a strong absorption in the near infrared, and in this region of the spectrum their photosynthesis is most pronounced. Water, however, absorbs this region of the infrared, therefore, confining the organisms to the surface of water or mud, although they may occur under salt crusts which are transparent to the infrared. As surface organisms they need a continuous supply of $H_2S$, which is changed into sulfur. This sulfur may be further oxidized to sulfate. It is also possible to grow purple bacteria on thiosulfate and on organic media. Their milieu is rather restricted. For autotrophic cultures the limits are pH 4.92 to 9.58, Eh +320 to −230 mV. For cultures on salts of organic acids the limits are pH 7.20 to 9.75, Eh +328 to −90 mV. Although sulfur is formed over almost the whole region, we do not believe that the natural formation of sulfur is chiefly due to these bacteria (Butlin and Postgate, 1954) but rather to the abiological oxidation of iron sulfides (Verhoop, 1940). Due to their conflicting requirements (light under reducing conditions), the occurrence of purple bacteria, while truly cosmopolitan, will never exert the geochemical influence of other groups, like the sulfate reducers or the iron bacteria.

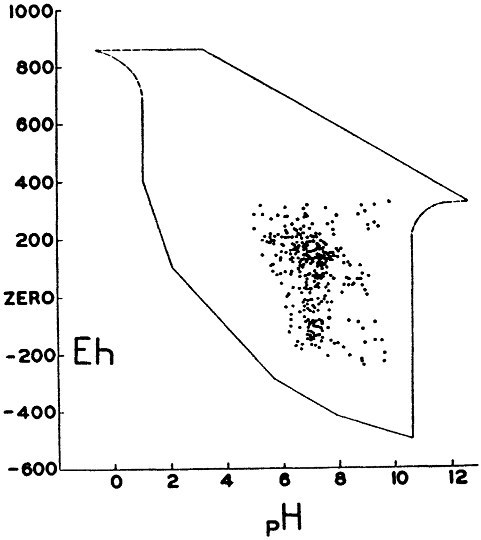

FIG. 24.—Eh-ph characteristics of the photosynthetic purple bacteria.

The data were obtained from the sources shown below.

### 5. PHOTOSYNTHETIC GREEN BACTERIA (FIGURE 25)

On these remarkable photosynthetic bacteria we only have scant data. It appears

| | | |
|---|---|---|
| Baas Becking and Wood (1955) | Natural occurrence | 12 |
| | Cultures on $Na_2S$ | 172 |
| | $Na_2S$ plus thiosulfate | 216 |
| | Organic acids | 20 |
| Kaplan, 1956 | (Rotorua, N.Z.) | 2 |
| Baas Becking and Moore | Lab. notes | 15 |
| Total | | 437 |

however, that the milieu is very restricted and confined to rather high pH's and low electrode potentials. The region in which these bacteria occur lies close to the equilibrium line for $SH^- \rightleftharpoons S + H^+ + 2e^-$.

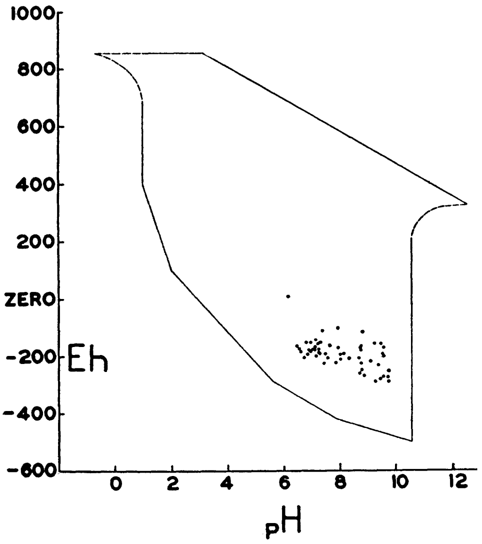

FIG. 25.—Eh-pH characteristics of the photosynthetic green bacteria.

It may well be that $H_2S$ is toxic to these organisms ($pH < 7.0$), while their upper limit may be caused by the presence of undissociated ammonia ($pH > 9.4$). The bacteria are of little geochemical importance, they oxidize $SH^-$ to sulfur, sulfur (and sometimes thiosulfate) to sulfate. In these functions they are numerically outclassed by the purple bacteria, as it is difficult to combine high light intensity and very low electrode potential, both of which are requirements for their growth in the natural environment:

| | |
|---|---|
| Baas Becking and Wood (1955).... | 46 |
| Kaplan (lab. notes).............. | 2 |
| Baas Becking and Moore (lab. notes) | 6 |
| Total....................... | 54 |

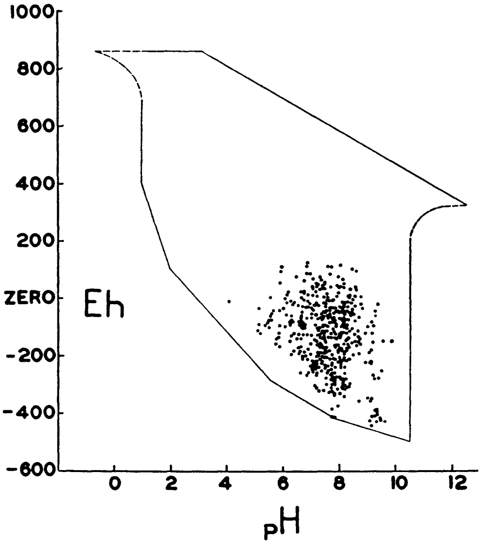

FIG. 26.—Eh-pH characteristics of sulfate-reducing bacteria.

### 6. SULFATE REDUCTION (FIGURE 26)

The region in which sulfate reduction occurs, or rather where the once-formed iron sulfides are stable, is shown in figure 26. The data were obtained from the following sources:

| | | |
|---|---|---|
| Emery, Rittenberg, and Orr......... | Marine sediments | 131 |
| Kaplan.......................... | Searles Lake, Calif. | 22 |
| ZoBell (1946)..................... | Marine sediments | 33 |
| Carroll (1958).................... | Mass cultures | 26 |
| Baas Becking and Wood (1956)...... | Sediments | 26 |
| | Iron cultures | 69 |
| | Acetate cultures | 42 |
| | Lactate cultures | 47 |
| | Carbohydrate cultures | 9 |
| Baas Becking...................... | Field notes, Lake Macquarie, N.S.W. | 18 |
| Baas Becking...................... | Lab. notes | 45 |
| Baas Becking and Moore............ | Lab. notes | 9 |
| Total.................................................... | | 477 |

The black, probably hydrated, iron sulfide becomes soluble at pH's 5.8–6.0, but the sulfate reduction continues at least to pH 4.2, as observed in a peat bog by Baas Becking and Nicolai (1934). The upper pH limit, observed by one of us in the alkaline Searles Lake, California, of sulfate reduction in the mud is 9.9. The reason for this limit is unknown; there is a possibility that the formation of undissociated ammonia (see fig. 2) at this pH is toxic to the bacteria. The lower Eh limit between pH 10 and 5 may be caused by the disulfhydryl iron, $Fe(SH)_2$ (Baas Becking, 1956), as $H_2S$ (or $SH^-$) is not sufficiently soluble to cause this low potential. The lower outline of the environment may be reproduced by titrating sodium sulfide (0.01*n*) with $FeSO_4$ (0.01*n*).

The upper Eh limit is represented by environments (natural or in cultures) which smell only faintly of $H_2S$. This would correspond to $10^{-6}$ *n*-$H_2S$. The formation of $H_2S$ from sulfate may have an important ecological consequence; it was shown by one of us (Baas Becking, 1956) that insoluble phosphates may be solublized by sulfuretted hydrogen. Reduction of sulfates does not take place in the presence of sufficient selenates (Postgate, 1949). Selenates are present in certain volcanic environments (Kaplan, 1956). In the high moors of Tasmania sulfate reduction could not be detected due to the almost total absence of sulfate in the water. Reduction occurred after the addition of sulfate to the medium. Ionic antagonisms, such as very high concentrations of divalent anions (Littlewood and Postgate, 1957), or high magnesium/calcium ratio, as found in the end brines of solar salt works, may inhibit development. The causative organisms are truly cosmopolitan, and rank amongst the most important geochemical agents in the biosphere and hydrosphere.

### 7. THIOBACTERIA (FIGURE 27)

The long filamentous forms like *Beggiatoa* and *Thiothrix*, as well as the small rodlike *Thiobacillus*, belong to this group. *Beggiatoa* and *Thiothrix* oxidize $H_2S$ ($SH^-$) to sulfur, and sulfur to sulfate, while the *Thiobacillus* also oxidize sulfur compounds of intermediate oxidation states such as thiosulfate and polythionates. The presence of iron in the medium, when sulfate is formed, will contribute to the low pH often observed in cultures of these bacteria by the hydrolysis of ferric salts, particularly if the electrode potential of these cultures is very high. Still, there is no doubt that forms like *Thiobacillus concretovorus* Parker will generate pH's close to 1.0 without the formation of appreciable amounts of ferric sulfate, as witnessed by the Eh which is lower than +600 mV. Species like *Th. thioparus* and *Th. novellus* may cause an increase instead of a decrease in pH, which possibly indicates some difference in their metabolism. Similar forms, which are abundant in the estuarine environment, cause an increase in electrode potential, often without changing the pH materially. From the above discussion it would appear that the thiobacteria can be represented by two more or less distinct areas on an Eh-pH plot. These areas are roughly separated by a vertical band

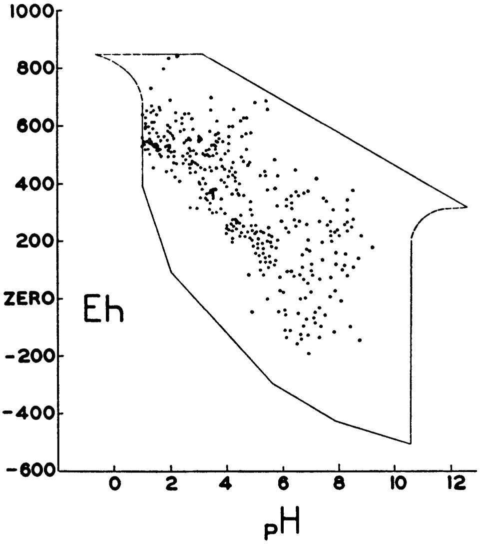

FIG. 27.—Eh-pH characteristics of thiobacteria

passing through pH 5–6 in figure 27. The two areas, taken together, cover a large part of the total environmental region: only algae show a wider milieu. In view of what has been said before and also because of the existence of a *Thiobacillus* which seems capable of the oxidation of ferrous iron, it seems difficult to disentangle the areas in which the iron and the thiobacteria occur together. The high potentials observed suggest interference of the iron system. The data listed below were chiefly gathered by Baas Becking and Wood (1955) and by Kaplan (1956).

| | | |
|---|---|---|
| Thiooxidans type on $S^0$.......... | Aerobic, sea water | 67 |
| | Anaerobic, sea water | 67 |
| | Aerobic, fresh water | 28 |
| Thiooxidans type on $S_2O_3^{=}$....... | Aerobic, sea water | 44 |
| | Anaerobic, sea water | 18 |
| | Aerobic, fresh water | 17 |
| Thioparus type on $S_2O_3^{=}$......... | Aerobic, fresh water | 17 |
| | Anaerobic, fresh water | 14 |
| | Aerobic, sea water | 10 |
| | Water from Antarctica | 1 |
| | Water from White Island (Volcanic crater), N.Z. | ... 2 |
| *Thiothrix* ...................... | Water from Bondi Sewer (Sydney) | 7 |
| Various cultures of sulfur oxidizing bacteria from Rotorua, N.Z. (Kaplan, 1956)........ | | 70 |
| Total........ | | 362 |

8. IRON BACTERIA (FIGURE 28)

According to Pringsheim (1949), the only valid genera of the common iron bacteria are *Sphaerotilus* and *Gallionella*. These groups, however, include a large number of sheathed and filamentous bacteria which have proved difficult to grow in pure culture. Two forms, occurring in acid mine water, *Thiobacillus ferrooxydans* Temple and Colmer and *Ferrobacillus ferrooxydans* Leathen, may be grown on solid media, containing ferrous sulfate. If the ferrous carbonate (or bicarbonate) is used, *Sphaerotilus* and *Gallionella* require a constant supply of reduced iron (Baas Becking, Wood, and Kaplan, 1957). By a suitable technique the development of these forms in fresh water and sea water was observed However, acid mine waters in New South Wales also contained these genera, and it could be shown that *Sphaerotilus* will thrive on a solid medium containing ferrous sulfate or pyrite (unpublished results). Moreover, bacillary forms were grown on a slide provided with a continuous supply of ferrous carbonates at high pH. It seems, therefore, that the milieu of the iron bacteria extends from pH 2.0 to 8.9, Eh from +850 to +60 mV. The affinity between iron bacteria and thiobacteria appears from the double function of Colmer's *Thiobacillus*, oxidizing both sulfur and iron compounds. It could be observed that *Sphaerotilus* materially increases the oxida-

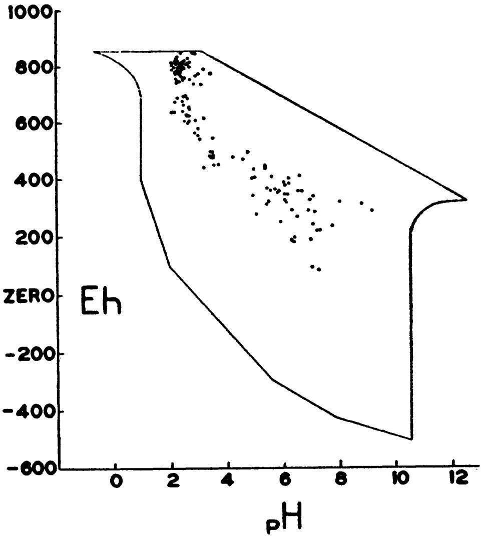

FIG. 28.—Eh-pH characteristics of iron bacteria

tion rate of ferrous sulfate. While the oxidation of sterile pyrite and of sterile $FeSO_4$ proceeds to pH 2.6 at +650 mV, infected solutions are able to form ferric compounds, both the sulfate and hydroxysulfate, increasing the electrode potential to +850 mV (unpublished).

Figure 28 is based on the following measurements:

| | |
|---|---|
| *Baas Becking, Wood, and Kaplan (1957)*: | |
| Sea water, fresh water, mass cultures... | 8 |
| Matraville, N.S.W. | 8 |
| Hawkesbury region, N.S.W. | 12 |
| Lake Macquarie, N.S.W. | 1 |
| *Colmer, Temple, and Hinkle (1950)*: | |
| Mass cultures, pure cultures | 19 |
| *Baas Becking and Moore* (lab. notes): | |
| Mine waters, mass cultures, and purified cultures | 61 |
| Mass cultures oxidizing carbonate | 2 |
| Mittagong, N.S.W. | 9 |
| Yass region, N.S.W. | 8 |
| Total | 128 |

### 9. HETEROTROPHS

We did not carry out any measurements on heterotrophs, apart from cultures of purple bacteria and of sulfate reducers on organic media. This omission constitutes a great gap in our work, partly filled by Savich's (1956) data on decomposing algae (mentioned before in the text) and by four observations on rotting sponges (*Tetilla dachyloidea*), yielding:

| pH | Eh(mV) |
|---|---|
| 8.70 | −005 |
| 7.20 | −147 |
| 6.65 | −175 |
| 6.82 | −075 |

Data on pure cultures of various heterotrophs are available in the literature. They suffer from the disadvantage that usually inordinate amounts of sometimes ill-defined organic matter are introduced, which might create conditions not representative of a natural environment. Work with such systems has been fully discussed by Hewitt (1950).

*a*) *Denitrifying bacteria.*—Elema, Kluyver, and van Delden (1936) gave 16 pairs of observations on *Micrococcus denitrificans*, while from the work of Korochkina (1936) 116 characteristics were obtained. The results are represented in figure 29. It appears that the potential range is quite high; from the upper environmental limit (preponderance of nitrate) to −200 mV. It is unknown which reducing substances are responsible for this. The pH range is from neutral to alkaline.

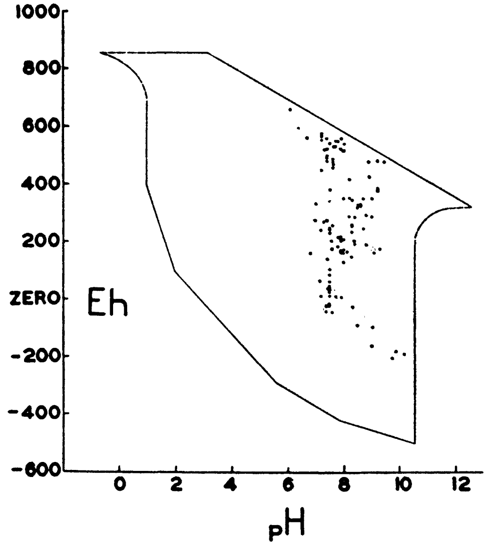

FIG. 29.—Eh-pH characteristics of denitrifying bacteria.

*b*) *Facultative and obligatory anaerobes.*—Figure 30 represents the data for oral lactobacteria (Gillespie and Rettger, 1938). Eh and pH are fairly low. The distribution of the points is quite interesting, but the data are too few to allow interpretation.

*Clostridium botulinus*, an extreme anaerobe (Gillespie and Rettger, 1938), yields, as expected, very low potentials which are included in figure 30. The group is known to be able to generate hydrogen. Some members of the genus *Clostridium* may play an important role in nature through their ability to fix molecular nitrogen and also reduce sulfate.

Figure 30 also shows the distribution of the characteristics of *Escherichia coli* (Clifton *et al.*, 1934), one of them reaching the lower Eh limit of the environment.

Methane-producing bacteria are important organisms in the breakdown and solubilization of organic matter. They are most common in anaerobic environments where plant materials have accumulated and are responsible for the formation of carbon dioxide and methane in large quantities. Their importance has been recognized, although their entire role in nature is as yet poorly understood. In figure 30 are represented 39 measurements made in the supernatant liquid and the sludge in sewage digestion tanks at the Hyperion Sewage Plant, Los Angeles. Although this is an artificial environment, it may be similar to many anaerobic sedimentary environments in nature where large quantities of organic material accumulate.

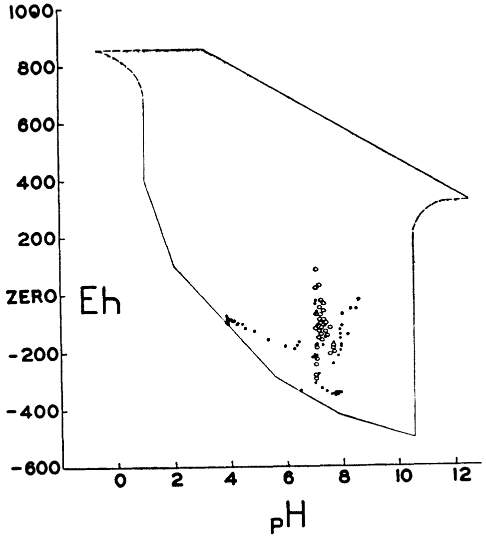

FIG. 30.—Eh-pH characteristics of the heterotrophic bacteria *Escherichia coli*, *Clostridium botulinum*, and *Lactobacillus* (shown as ●) and methane-producing bacteria (shown as ○).

Combining these results, we see that low potentials may be reached by heterotrophs, but that sulfate reducers and green bacteria still hold the monopoly of low potentials in the high pH range. In no case did the heterotrophs transgress the lower Eh limits arrived at in this paper. Further measurements on methane and hydrogen-producing bacteria may cause these limits to approach the theoretical hydrogen line.

## THE LIMITS OF THE ENVIRONMENT

While it seems tempting to apply thermodynamics to derive likely equilibrium lines to describe the limits, we have refrained from doing so at this stage. However, certain oxidoreductions as well as pH changes suggest themselves as master reactions. The potential of an aqueous environment (by which we mean the potential amplitude of its proton and electron state) is chiefly determined by oxidoreductions in the iron and in the sulfur systems, by the changes in the carbonic acid-bicarbonate-carbonate equilibrium, and by the hydrolysis of iron sulfates, and, in special cases, cation exchange. In oxygenated waters the $H_2O_2$–$O_2$ and $H_2O$–$H_2O_2$ systems may also play a role. For a large part these changes are biogenic, but a considerable role is played by purely geochemical reactions, such as the first stage in pyrite oxidation and the oxidation of the hydrated iron sulfide to sulfur. Apart from the above-mentioned reactions, there may be secretions or excretions by algae and microbes as contributary factors to the characteristics of the environment. From the data at hand it appears that the natural aqueous milieu is delimited by the following regions:

1. pH −0.6 to 3.2, Eh +860 mV. These limits are brought about by the end product of the oxidation of pyrite and marcasite, region of thio and iron bacteria. Using various concentrations of ferric sulfate, we obtained pH 1.2 to 3.0, Eh +860 mV. Near this region the iron is chiefly in a soluble, ferric state.

2. pH 3.2 to 12.6, Eh +860 to +320 mV. We have not been able to reproduce this line experimentally. Various reactions suggest themselves, but none of the likely inorganic reactions yielded characteristics remotely resembling Eh = 1040 − 59 pH

mV. As limit 2 is chiefly characterized by algae, we have tried a great number of organic substances, in the flavone and anthraquinone group, without result. Still it does not seem unlikely that organic compounds may be a cause of this limit.

3. pH 10.55, Eh +250 to −500 mV. Sodium carbonate solution in equilibrium with air yields pH values close to $pK_2$ of the carbon dioxide system, 10.33 at 25° C. The pH of artificial trona solutions is slightly lower. Higher pH values may be caused by the evanescent effect of photosynthesis and also by the excretion of ammonia or amines.

4. pH 5.6 to 10.55, Eh −290 to −500 mV. The solubility of $H_2S$ ($SH^-$) in natural waters is too low to allow for the electrode potentials observed. However, by titrating 0.01*n* $Na_2S$ with 0.01*n* $FeSO_4$, characteristics were obtained which showed a close similarity to the limits observed. This shows that iron sulfides are a contributory factor to these low electrode potentials. Free hydrogen would lower the potential still more. Although hydrogen-generating bacteria were observed by us in natural muds, the high organic content of the culture media is hardly ever realized in nature. The same pertains to low potentials observed in cultures of *Clostridium.* Metallic iron will generate hydrogen, and the very low potentials observed by Starkey and Wight (1945) near iron pipes may be caused by this reaction.

5. pH 2.0 to 5.6, Eh +100 to −290 mV. This is the region where $H_2S$ occurs in undissociated form and where the reduced iron may occur, partly or wholly, as ferrous ion. There is evidence to assume that the simultaneous oxidation of these ferrous compounds to goethite (or lepidocrocite) and sulfur may yield characteristics similar to those observed.

6. pH 1.0 to 2.0, Eh +400 to +100 mV. This limit is difficult to explain, and because of the small number of points outlining it, it should perhaps be drawn toward a higher pH. A theoretical thermodynamic equation in which ferrous ion is oxidized to magnetite gives a slope corresponding to this limit. Magnetite, however, appears to be unstable at such low pH values. From Huber's (1958) calculations it appears that this is the limit where siderite may first begin to form.

7. pH 1.0 to 0, Eh +700 to +400 mV. This is still a region in which the free ferrous ion is preponderant. The limit may be caused by the transition of this free ferrous ion to an insoluble ferrous compound or ferric compound.

Examination of figures 31 and 32, where all the observations have been gathered, shows an internal limit, described by Eh = 1060 − 177 pH mV. This line almost coincides with the equilibrium

$$Fe^{++} + 2H_2O \rightleftarrows FeO{\cdot}OH + 3H^+ + e^- .$$

Data are massed on the oxidized side, but they are sparse on the reduced side of this line.

Where surface waters only are considered and conditions persistent over moments of geological time are the only ones counted, the outline of the environment may be modified by the removal of the two "ears" on the catena—giving an acid pH limit of 1.0, which seems to be associated with the presence of thiobacteria and occurs, so far as we are aware, only in geothermal waters. On the alkaline side the limit occurs at a pH of 10.55, which is the equilibrium of $Na_2CO_3$ in contact with atmospheric carbon dioxide.

Evanescent conditions may be caused in circumstances of isolation. The photosynthesis "ear" of the environment develops when small pounds are filled with masses of growing plants. The outstanding example is the mass of *Potamogeton capense* studied by Schütte and Elsworth (1954), in which a diurnal rhythm changed the pH from 9.5 just before dawn to 12.6 in the late afternoon. The acid "ear" is drawn from analytical data presented by van der Spek (1934) on rapidly exposed pyritic marine clays from the bed of the Zuyder Zee, Holland. Development of the more than normal acid was probably due to an evaporation-concentration effect in a largely impervious sediment. We do not know how deep the acid conditions penetrated.

The third manner of exceeding the normal surface limits is by burial of sea water in strongly reducing sediments. If the water becomes truly isolated to connate, removal of all its sulfate by reduction and all its calcium, magnesium, and carbonate or bicarbonate by precipitation can yield a water rich in sulfide with an extremely high pH. In Searles Lake, California, the bottom salt brines reach pH 10.48, where the surface waters are around 8.5—9.0. The process goes even further in the case of the water from northern California, mentioned on page 264, with a pH of 11.6. We do not know what the ultimate limits of this process will be. Clearly, they may be of great importance in the diagenetic transportation of silica, which has been shown by Krauskopf (1956) to increase its solubility tremendously above pH 9. The California water, by way of example, contains 4,000 p.p.m. silica, as opposed to the general fresh-water concentration of under 20 p.p.m.

To summarize the findings, the approximate outlines of the various limits for environments and organisms are represented in figures 33*a*, 33*b*, 34*a*, and 34*b*. It is within these boundaries that the results of our

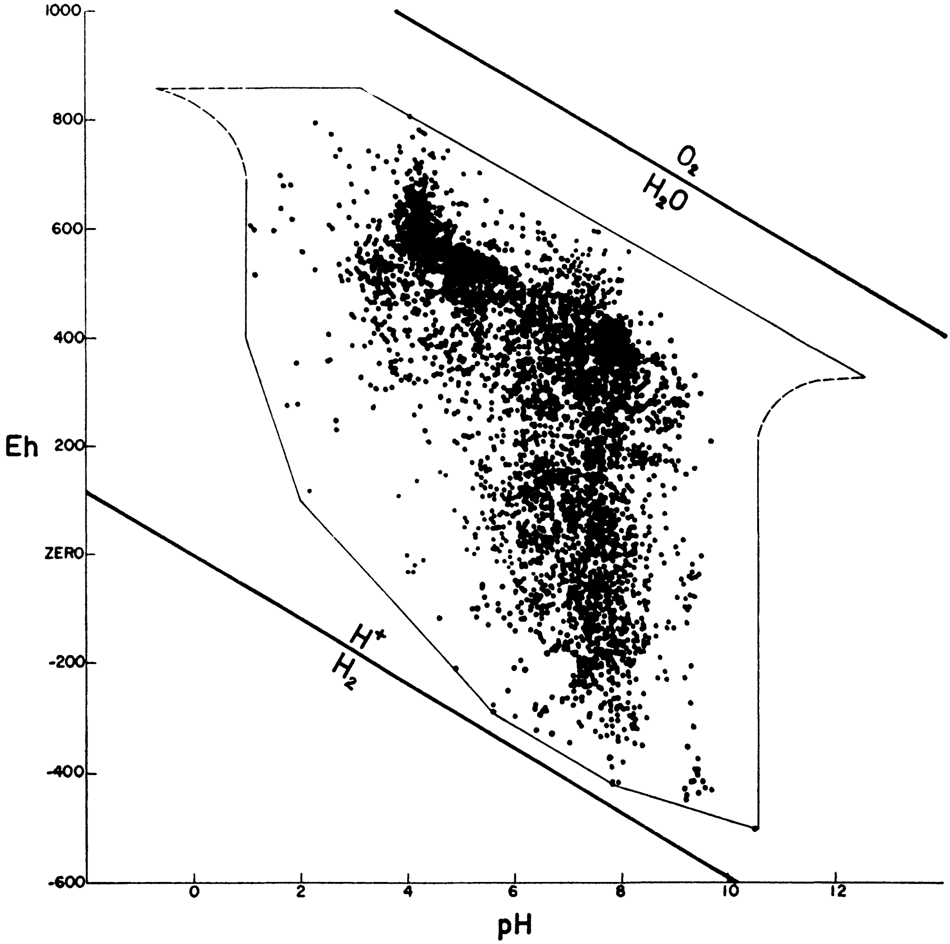

FIG. 31.—Distribution of Eh-pH measurements of the natural aqueous environments studied in the present work.

measurements lie. Although it is quite possible that future work may expand these limits, especially for the environments and organisms on which few readings have been made, they will serve to illustrate at a quick glance the potential range covered by the more typical of examples studied. It is further possible, by comparing figures 33*a* and 33*b* with figures 34*a* and 34*b*, to estimate what organisms one would expect to find in the environment with corresponding Eh-pH characteristics. It should be noted that the limits are drawn at a maximum pH range of 10.55. This does not include the result for the cold-water spring (Aqua de Ney) measured by J. H. Feth in northern California and discussed under the section on connate water. It is possible in this particular case that oxidation may have occurred from the time of sampling to the time of measurement. More reliable readings in the future therefore cause this alkaline limit to be changed somewhat.

## SUMMARY

The data presented here are given as an extension to the excellent work published earlier by Krumbein and Garrels (1952). The previous authors, however, had based their interpretations more on inductive reasoning (using other known properties of water as a basis) than on actual pH and

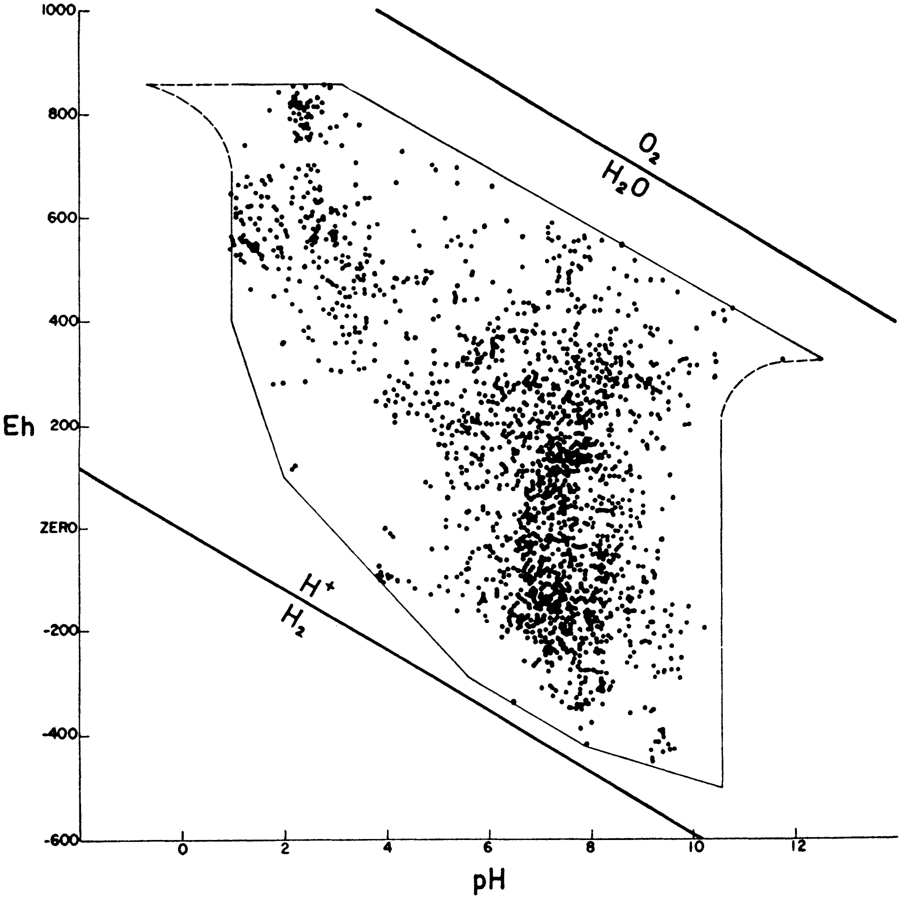

FIG. 32.—Distribution of Eh-pH measurements of geologically important organisms studied in the present work.

oxidation-reduction potential measurements. It is therefore hoped that the data presented will be of further help to the geologist in describing sedimentary environments. Our results are at present of qualitative value only. In this work we have concentrated more on establishing the limits or framework of many environments than on attempting to find definite relationships within one or two environments.

We consider that the next logical step will be to compare Eh-pH values with a careful chemical analysis of the particular sample measured. In this way it may be possible to apply the numerous theoretical physicochemical calculations present in the literature to explain the presence of various mineral species in any one environment. It is hoped that the accumulation of measurements will make it possible to equate a particular mineral species with a particular sedimentary environment in the aqueous phase and also to indicate the origin of connate waters. It should be stressed once more that, since living systems play a major role in controlling the aqueous milieu,

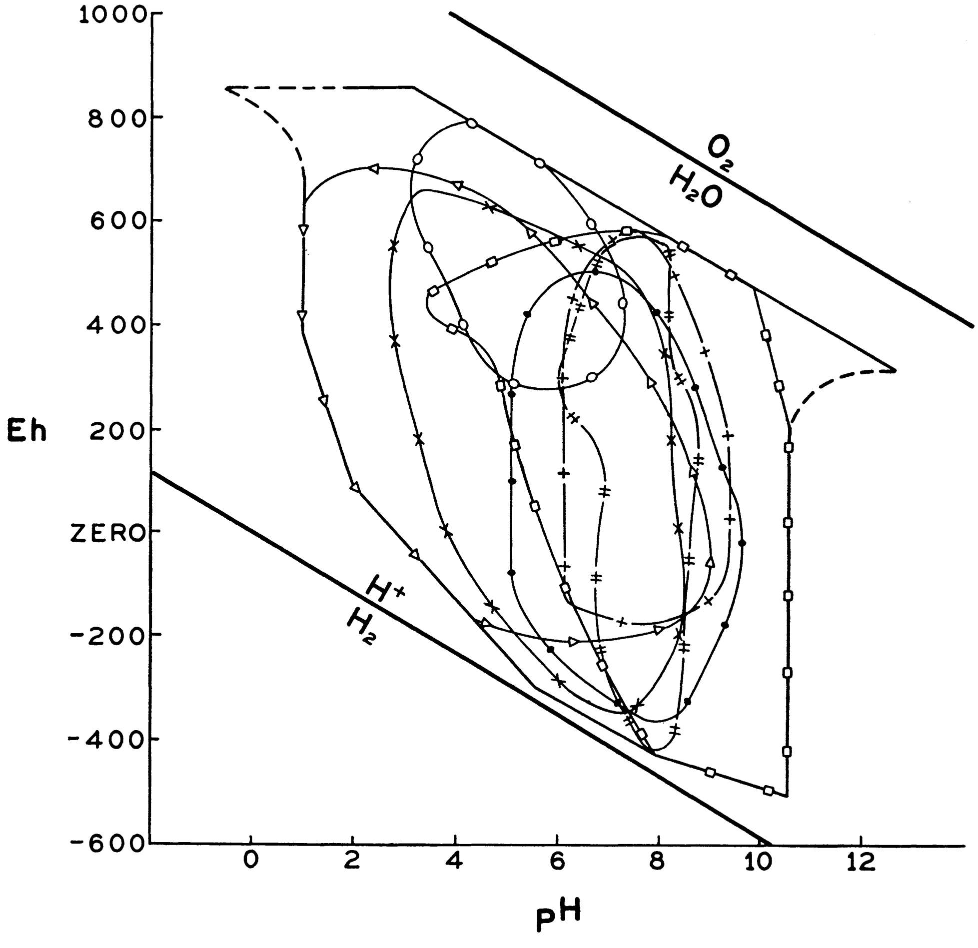

FIG. 33*a*.—Approximate "areas" of Eh and pH for some natural environments studied in this work. The "area" for each environment is bounded by a different symbol: ○○○ = meteoric water; ×××= peat bogs; ●●● = marginal marine sediments; +++ = sea water; ‡‡‡ = open-sea sediments; □□□ = evaporites; △△△ = geothermal environment.

measurements of Eh-pH may often indicate the ecology of an environment.

ACKNOWLEDGMENTS.—During the writing of this paper we have received help and encouragement from other workers in the field. Apart from the mass of published data which we have used, we have been given unpublished information by the following people: K. O. Emery, S. C. Rittenberg, and W. L. Orr—marine sediments off southern California; J. S. Burt—seawater from Antarctica; M. Sato—mine waters from Utah and Arizona; R. O. Stone—playa lakes from southern California; J. H. Feth—cold-water spring from northern California; D. Rabinowitz—evaporites from the Dead Sea, Israel.

Our colleagues in the Bureau of Mineral Resources and the University of Southern California have encouraged us throughout. We wish especially to mention: Miss E. M. Smith, who translated the whole of Savich (1956); W. J. Thomas, who assisted in the long, drawn-out and often hectic task of measuring the Eh-pH characteristics of meteoric waters; and Drs. Emery and Rittenberg, who offered many useful suggestions throughout.

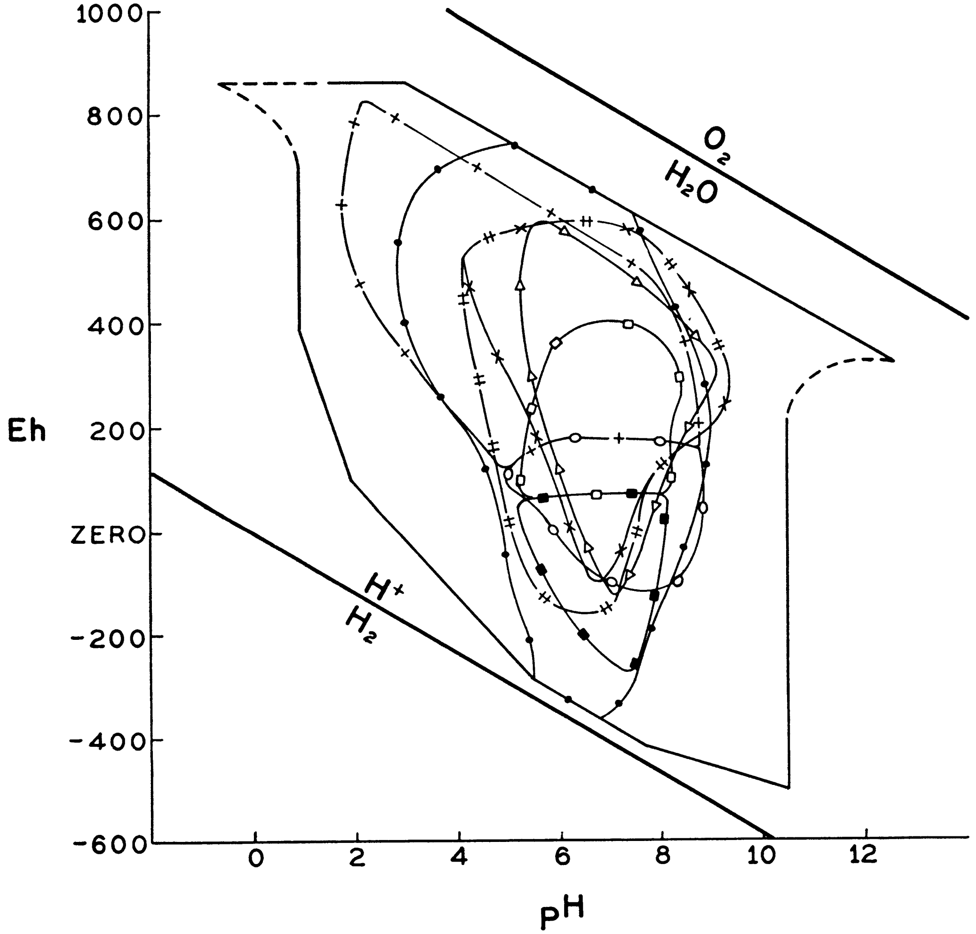

FIG. 33*b*.—Approximate "areas" of Eh and pH for some natural environments studied in this work. The "area" for each environment is bounded by a different symbol: ●●● = soils; △△△ = shallow ground water; +++ = oxidized mine water; ○○○ = primary mine water; ××× = fresh water; ‡‡‡ = fresh-water sediments; □□□ = oxidized connate water; ■■■ = uncontaminated connate water.

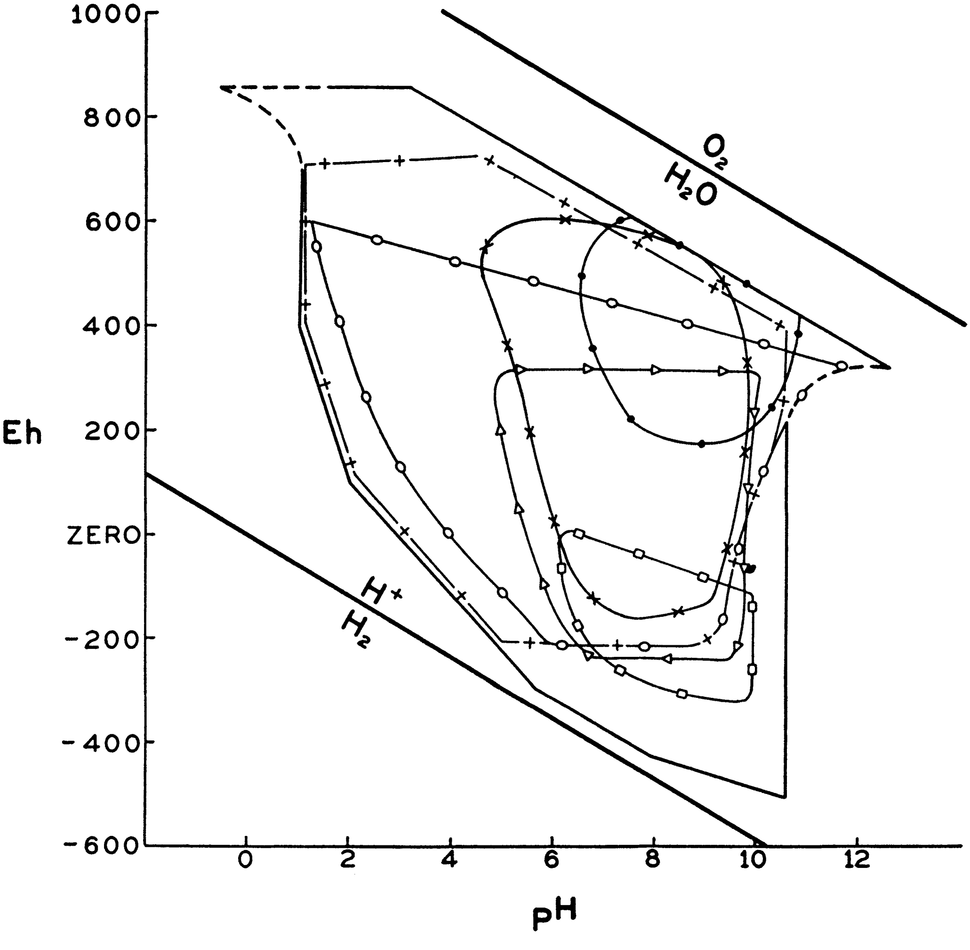

FIG. 34*a*.—Approximate "areas" of Eh and pH for the photosynthetic organisms studied in this work. The "area" for each environment is bounded by a different symbol: ○○○ = green algae and diatoms; ●●● = *Dunaliella;* ××× = *Enteromorpha;* +++ = blue-green algae; △△△ = purple bacteria; □□□ = green bacteria.

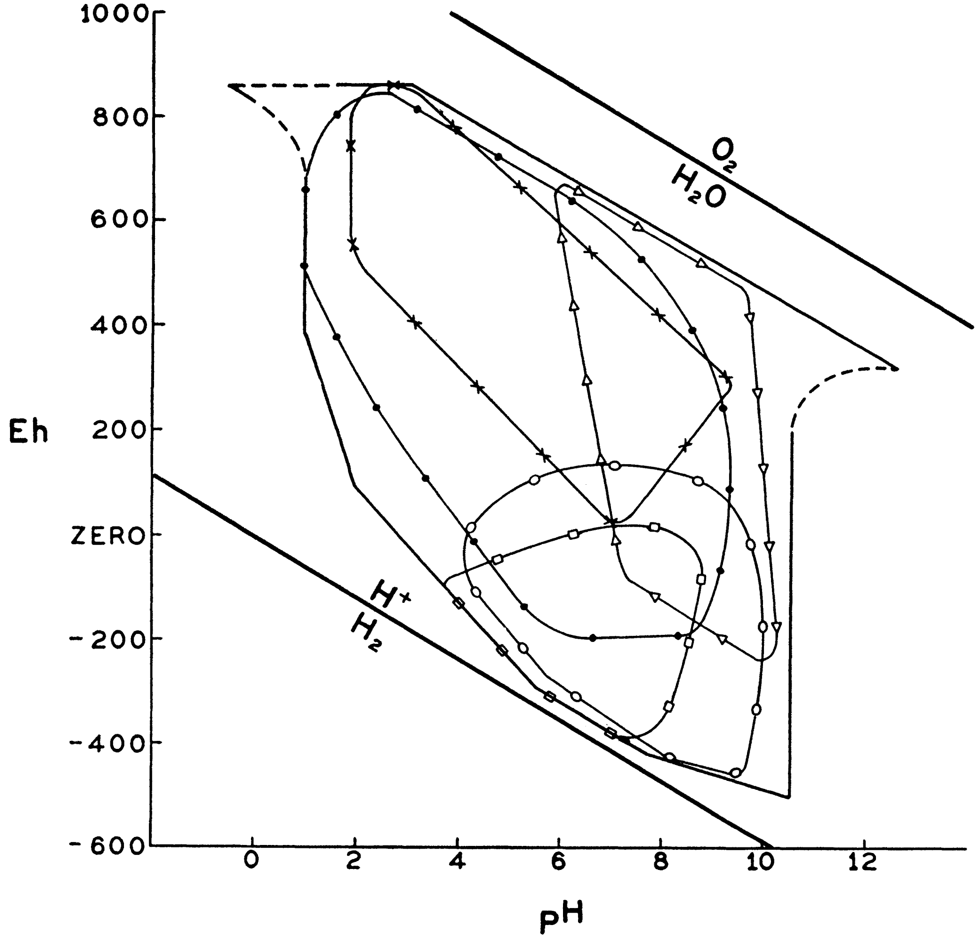

FIG. 34*b*.—Approximate "areas" of Eh and pH for some geologically important bacteria studied in this work. The "area" for each environment is bounded by a different symbol: ○○○ = sulfate-reducing bacteria; ●●● = thiobacteria; ××× = iron bacteria; △△△ = denitrifying bacteria; □□□ = heterotrophic anaerobic bacteria.

We are also indebted to Drs. R. M. Garrels and M. Sato, who read the whole manuscript and gave critical comments on a number of points.

To all these people we offer our most grateful thanks and our absolution from any interpretations we have made. The facts are theirs; the interpretation, for which we accept sole responsibility, ours.

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