

Physical Factors on the Sandy Beach. Part II. Chemical Changes—Carbon Dioxide Concentration and Sulphides.

By

J. Ronald Bruce, M.Sc., A.I.C.,

Marine Biological Station, Port Erin.

With 3 Figures in the Text.

CONTENTS.

	PAGE
INTRODUCTORY	553
CARBON DIOXIDE CONCENTRATION AND EXCESS BASE :	
The Gaseous Exchanges of Marine Organisms	554
Regulation of pH in the Sea and on the Shore	554
SULPHIDES AND THE BLACK LAYER	555
Examination of the Natural Conditions	556
Conclusions Based on Shore Observations	559
The pH of the Black Layer	559
Determination of Sulphides in Sand	560
The Rate of Oxidation of Sulphides	561
Conclusions as to the Source and Fate of Sulphides in the Beach	562
SUMMARY	564
REFERENCES	565

INTRODUCTORY.

THE sandy beach, considered as the environment of living organisms, affords a range of physical factors of unusual type and complexity (Bruce, 1928). A vast assemblage of animal and plant forms, more or less consonant in physiology and distribution with the demands of that environment, introduces the biological factor into the physical nexus. The gases evolved in respiration and carbon-assimilation, the ultimate residues of digestive processes, and the products of bacterial degradation of dead organic matter, become, in their turn, factors in the life-processes from which they arose. Factors of this kind, biochemical and biophysical, arise rather from the products than from the direct activities of life, and are among the outstanding influences on the sandy beach. In common with the more purely physical factors, however, their exact measurement is a matter of some difficulty.

Carbon dioxide—that elusive constituent of sea-water—becomes associated with the limy matter of the sand, and hydrogen-ion concentration ceases to be an effective index of its changes. Metabolic processes may be, and often are, confined to certain narrow zones in the sand, and the measurement of their products is rendered correspondingly difficult and uncertain. Salts and ions are adsorbed on to the relatively enormous aggregate surface of the sand-grains, and their apparent bulk-concentration is thereby vitiated. Organic matter is so greatly diluted with incombustible material that its accurate determination is very difficult, and in any case no distinction is made, in analysis, between the living and dead organic materials which are so intimately associated in beach sands. Finally, the great barrier to ready diffusion presented by the sand itself leads to oxygen-deficiency and many special reactions in its depths, including the formation of hydrogen sulphide through bacterial agencies, and the appearance of the well-known black layer.

The paper is a contribution to the knowledge of some of these factors, chemical in nature, but biological in origin.

CARBON DIOXIDE CONCENTRATION AND EXCESS BASE.

The Gaseous Exchanges of Marine Organisms.

The gaseous metabolic exchanges of aquatic organisms, whether output or intake of carbon dioxide, involve an alteration in the hydrogen-ion concentration of the medium, the extent of such alteration, for a given difference of CO_2 -concentration varying with the buffer-effect of the medium. The "excess-base," the pH, and the CO_2 -concentration form a triple group of values, of which any two serve to define the third, and this fact has been made the basis of a method for estimating the carbon dioxide exchanges of marine, brackish-water, and freshwater organisms (Bruce, 1924).

Regulation of pH in the Sea and on the Shore.

In the open sea, where extended surface and continual agitation ensure the maintenance of equilibrium with the air, the concentration of carbon dioxide can never become a limiting factor in the life of plants or animals. In rock-pools, on the other hand, whatever their salinity and excess-base content, the accumulation of the gaseous products of metabolism will ultimately set a limit to their production, which cannot take place beyond certain limits of hydron and hydroxyl-ion tolerance. It follows, therefore, that dilution, quite apart from any effects of lowered salinity *per se*, must lead to a narrowing of the potential range of metabolic activity corresponding to the reduction of excess base or buffer content. A few organisms have become adapted to extremes of pH, but even in the case

of certain highly resistant algæ, a final barrier to the progress of carbon-assimilation is reached when, in the neighbourhood of pH 10, the entire bicarbonate reserve is exhausted.

The inhabitants of the sandy beach, however, are in this respect more favourably situated, since in the intimate presence of sand, with its admixture of calcareous particles, a local increase in the concentration of hydrogen ions leads to solution of calcium carbonate, and a restoration of the acid-base equilibrium.

Experiment. A sample of sea-water, pH 8.2, and excess base 23.7, was treated, at room temperature, with carbon dioxide until the pH was reduced to 6.4, and then stirred in a closed vessel, with a considerable quantity of sand, and out of contact with the air. The reaction is slow, but after 5½ hours' stirring, it was found that the pH was 7.5, and that the excess base had risen to 39.0.

In a state of nature, this greatly increased concentration of the bicarbonate ion, after diffusion to the photosynthetic zone on the surface of the beach, occupied by diatoms and holophytic dinoflagellates, would add to their potential reserves of available carbon dioxide. High concentrations of carbon dioxide, such as that employed in the above experiment, are not, of course, realised as a result of respiratory activity, but equal and even higher concentrations are found in those parts of the sandy beach where rapid decomposition of organic matter is in progress, and a sample of the interstitial sea-water from such a locality, with a salinity of 29.6‰, and a pH of 8.3, was found to contain the enormous excess base of 120.4. It is evident, therefore, that the calcareous matter in the sand functions in a manner precisely analogous to the limy reserves in the shells of certain bivalve molluscs (Collip, 1920), and by its regulatory influence upon hydrion concentration contributes an important chemical factor to the conditions of life on the beach.

SULPHIDES AND THE BLACK LAYER.

The existence of a darker zone, at a slight but variable depth below the surface of the sandy beach, is familiar to observers on almost every part of the coast. It was early recognised that the phenomenon was closely connected with the formation of black deposits in the depths of certain seas, notably the Black Sea, the Caspian Sea, and certain inlets of the Baltic. The features exhibited in common by the littoral and deep-sea deposits include (a) their dark or black colour, discharged on exposure to the air; (b) the evolution of a stench of, or resembling, hydrogen sulphide; and (c) their occurrence under similar conditions of stagnation and oxygen deficiency (Andrussow, 1897; Johnstone, 1921).

Omelianski (1906) showed that, in the case of the Black Sea deposits,

the dark colour was in reality due to ferrous sulphide, and Johnstone (1921) established the same conclusion for the sands of the Lancashire coasts. The rapid oxidation of this substance to the brown or yellowish ferric oxide underlies the colour-change on exposure to the air. It is evident, then, that the level at which the black layer occurs—and its upper surface is usually quite sharply defined—represents a position of equilibrium between the sulphide-producing reactions in the depths, and the oxidising effects of the atmosphere from above. The factors entering into such a system are obviously of a complex kind, and must involve not only the temperature and concentration of the reactants, but the varying rate of their addition to the reacting system. On the one hand, the supply of sulphur is conditioned by the local intensity of metabolism, the access of decaying organic matter, and availability of inorganic sulphates; on the other hand, the rate of diffusion of oxygen to the reaction-zone is influenced by the grade and porosity of the sand, and its solubility by the salinity of the interstitial water. When it is realised, further, that bacteria play an active part in the process, and that the ultimate reactions may be 'heterogeneous,' taking place at the interface between the sand-grains and water, it will be obvious that to measure the final products, and to define a few of the conditions, represents the only possible approach to a solution of the problem.

Examination of the Natural Conditions.

Locality. The black layer is well developed on the sandy beach at Port Erin, where the following observations were made (see Plan of Port Erin Bay, Fig. 1). At the south end of the beach, harbour-works and a solid masonry pier, 200 feet in length, afford protection from wave-action, and have led to considerable silting and accumulation of organic débris. Several streamlets discharge on to the beach after heavy rain, but only one, that debouching between stations 11 and 15 (see Plan), is at all permanent or of any considerable volume. There is no access of sewage, from any source, and every form of pollution is rigorously excluded from the beach.

Methods. Samples of the sand were collected by means of a simple borer, fashioned on the lines of a cork-borer. This consisted of a tube, 60 cm. long, and 10 cm. in diameter, made from heavy-gauge tinsplate, and soldered at the joint. The upper end was reinforced by a collar of sheet iron, 6 cm. deep, and this was pierced with holes, permitting a length of iron tubing, 1.5 cm. in diameter, to be inserted from side to side, to form a handle. In use, the sampler was forced vertically into the sand, by rotation, the depth attained rarely exceeding 40 cm., owing to the resistance offered by the sand. Not infrequently, stones or gravel obstructed the passage of the sampler at a much less depth.

Samples of the sand, and wherever possible of the water draining into the bore-hole, were taken at 27 stations on the beach. The physical characters of the samples were noted immediately, and the chemical tests were made, in every case, within an hour of sampling. The survey was carried out, for the most part, in the months of November and December, but observations have extended, in all, over four years (1923-27), and in every month of the year there is a remarkable similarity of the subsurface conditions. The following values, and their schematic representation in Fig. 1, may be taken, therefore, as generally applicable.

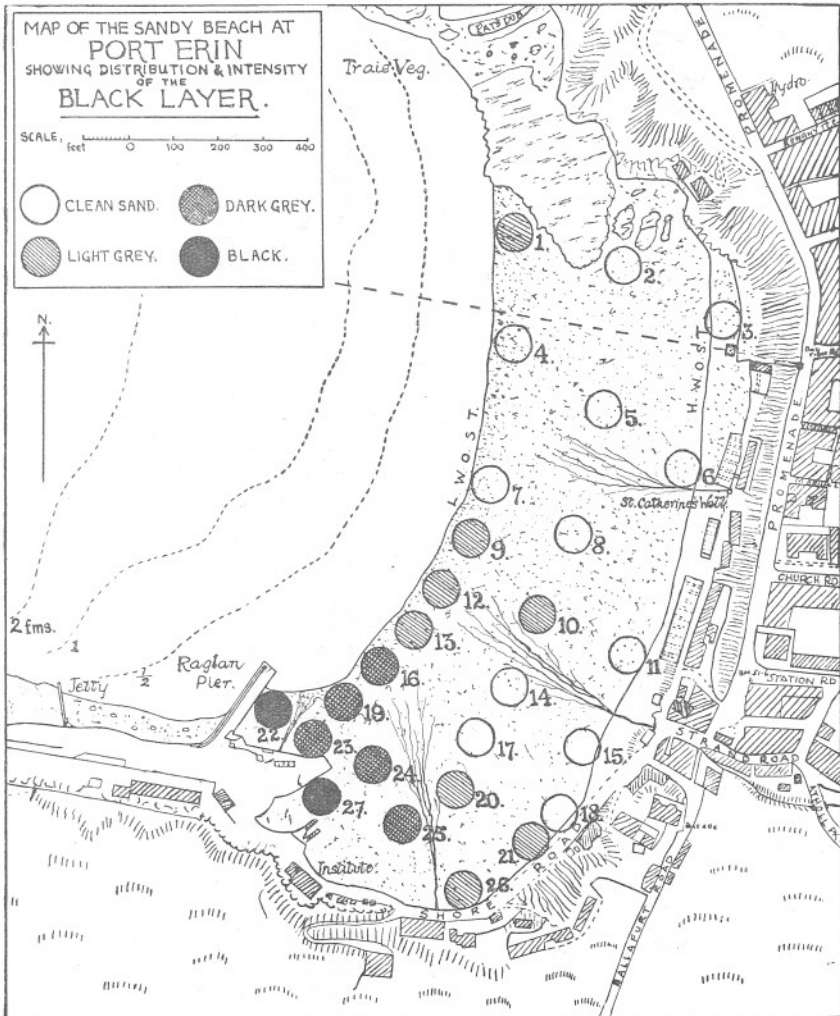


FIG. 1.—Map of Beach at Port Erin (based upon the Ordnance Survey Map with the sanction of the Controller of H.M. Stationery Office).

TABLE SHOWING THE DISTRIBUTION, IN DEPTH AND AREA, OF THE BLACK LAYER, AND OF THE SALINITY AND pH OF THE INTERSTITIAL WATER, ON PORT ERIN BEACH, ISLE OF MAN.

Station. (See Plan, Fig. 1.)	Water Sample.		Depth-Range. *cm.	Sand Sample.
	Salinity. ‰	pH (corr.).		Description.
1.	32.75	7.9	0-15	Clean sand and gravel
			15-36	Less gravelly, light grey round rocks and stones
2.	-	-	0-4	Clean sand
			4-16	Gravel
3.	-	-	16-28	Less gravelly
			0-5	Clean sand
4.	29.55	8.1	5-38	Coarse gravel and pebbles
			0-20	Sand, clean, but gravelly below
5.	-	-	0-5	Clean sand
			5-25	Pebbly gravel
6.	-	-	0-5	Coarse clean sand
			5-45	Pebbles
7.	32.36	8.05	0-27	Sand, gravelly below
8.	-	-	0-10	Clean sand, gravelly below
9.	31.48	7.9	0-24	Grey sand, gravelly below
10.	-	-	0-10	Clean sand
			10-27	Grey sand, gravelly below
11.	-	-	0-12	Clean sand and gravel
			12-40	Very coarse gravel
12.	15.68	8.2	0-10	Clean sand
			10-22	Grey sand, gravelly below
13.	32.23	8.0	0-10	Clean sand
			10-16	Sand grey, gravelly below
14.	-	-	0-13	Clean sand, coarse gravel below
15.	-	-	0-13	Sand and gravel, coarse pebbles below
			0-12	Light grey sand
16.	32.11	7.9	12-41	Dark grey sand
			0-7	Clean sand, gravelly below
17.	-	-	0-33	Clean sand, gravelly below
			0-12	Grey sand
18.	-	-	12-30	Dark grey sand
			0-10	Clean sand
19.	31.34	7.85	10-27	Light grey sand
			0-20	Clean sand, grey below
20.	-	-	0-3	Grey sand
			3-36	Black sand
21.	32.23	8.0	0-10	Clean sand
			10-40	Very dark grey sand
22.	-	-	0-7	Clean sand
			7-17	Grey sand
23.	32.5	7.8	17-29	Dark grey sand
			29-58	Sand lighter than above
24.	-	-	0-4	Clean sand
			4-19	Grey sand
25.	-	-	19-55	Dark grey sand
			0-20	Clean fine sand
26.	-	-	20-41	Light grey sand
			0-4	Clean sand
27.	29.6	8.3	4-10	Dark grey sand
			10-40	Very black sand

* The final depth (*italics*) is that reached by the sampler, and is not necessarily the termination of a particular zone.

Conclusions based on Shore Observations.

Several general conclusions emerge from these figures. In the first place, the darker zone is practically confined to the south end of the beach (Fig. 1), where, as the present field-notes and previous mechanical analyses (Bruce, 1928) indicate, the finer sand-grades are predominant. The layer assumes its most marked development in the immediate vicinity of harbour-works, where the circulation of air and water in the sand must necessarily be impeded, and where organic débris, washed from other parts of the beach, naturally accumulates. The fact that a slight darkening occurs at Station 1, at the north end of the beach, where there are underlying rocks, supports this view. In general, the darkest layers occur near low-water mark, where the period of exposure to the air, with consequent oxidation, is naturally at a minimum, and here also the layer approaches to within 3 or 4 cm. from the surface; at Stations 21 and 26, the only two points at high-water mark where a slight darkening is noted, the darker zone is at 20 cm. below the surface.

The pH of the Black Layer.

On several occasions during the course of the field work, a more detailed investigation has been made of the pH and other properties of the successive depth-zones. This has been done by separating the core of damp sand from the sampler, and slicing it into short cylinders, about 5 cm. in thickness. Each "sub-sample" was then filtered under slight suction, and tests made, without delay, upon the several filtrates. Two examples are given:—

Station. (Fig. 1.)	Depth-Range. cm.	Description.	pH of Filtrate. (corrected).
24 (June, 1923)	0- 2	Clean sand	8.0
	2- 7	Slightly grey	7.9
	7-12	Darker	7.95
	12-17	Dark grey	8.05
	17-22	Dark grey	8.1
23 (Nov., 1923)	0- 5	Clean sand	7.9
	5-10	Clean sand	7.9
	10-20	Grey sand	7.9
	20-40	Very dark and malodorous	8.1

In all cases, the filtrate from the dark layers, originally clear, became opalescent on exposure to the air, and the pH fell. In neither of the above cases did the lead acetate test reveal the presence of soluble sulphides or free hydrogen sulphide in the filtrates, although on addition of acid to the black sandy residue the gas was copiously evolved.

Determination of Sulphides in Sand.

Many previous workers have expressed the need for a method of determining the sulphide-content of sands or muds. The determination is one which presents several practical difficulties. It must be carried out on the moist sample, with the least possible delay, since oxidation proceeds with great rapidity, especially on the relatively large surface of a small sample. Evaporation leads to change of weight, while any attempt at previous drying leads to the complete disappearance of the sulphide. After many trials, an effective method was evolved, in which the *volume* of hydrogen sulphide, liberated from a known *volume* (10 c.c.) of the damp sand, is determined, the result being expressed in volumes of H_2S per cent. The use of volume, rather than weight of sand, is justified on the ground of its more immediate biological application (in connection with density of population, etc.), and in view of the fact that the weight of a sample of indefinite moisture-content has, in any case, no useful significance.*

Method. The sample is taken by thrusting into the compacted sand a $\frac{3}{4}$ " brass cork borer, fitted with a glass plunger bearing two marks, and so arranged that when pushed in from one mark to the other, a 10 c.c. cylinder of sand exudes at the other end, where it is cut off squarely, and allowed to fall into 25 c.c. N/50 Iodine solution, contained in a wide-mouthed Erlenmeyer flask, thus immediately "fixing" any free hydrogen sulphide. To the mixture of sand and iodine solution, 5 c.c. of 5N. HCl (specially pure and Chlorine-free) were added, setting free CO_2 and H_2S , the latter combining with the excess of iodine. After standing five minutes, the mixture is titrated with standard sodium thiosulphate solution, with starch as indicator. The end-point is perfectly easy to determine, in the presence of the sand and turbid solution. The N/50 iodine is, of course, periodically standardised against the thiosulphate, and its concentration is conveniently expressed in c.c. of H_2S , measured as at N.T.P., equivalent to 1 c.c. of iodine solution.

Employing the above method, numerous determinations have been made of the sulphide content of the black layer *in situ*. This is found to vary in samples taken at Port Erin from 10 or 12 volumes up to 78 volumes per cent. Only occasionally is free hydrogen sulphide present, and the total, both free and combined, has never been found to exceed 20% of the theoretical total, assuming that the whole of the available ferric oxide were converted into ferrous sulphide. It is of interest to note, however, that the actual iron-content of the black sand, determined in one case as 1.13% of Fe_2O_3 , is considerably above the normal value for shore sands,

* The mean dry weight of sand in a 10 c.c. moist sample, collected and delivered by the borer-sampler, as indicated in the method, is 14.0 g.

and may indicate that *Crenothrix*, the iron-bacterium, is as active in this region as it appears to be, under similar conditions, in the beaches of the Clyde Sea Area (Ellis, 1925).

The Rate of Oxidation of Sulphides.

The oxidation of the sulphides in beach-sand takes place, as already indicated, mainly in the surface layers, to which the atmospheric oxygen has ready access. At the same time, oxidation is by no means confined to these layers, and the sharpness of the upper boundary of the black layer

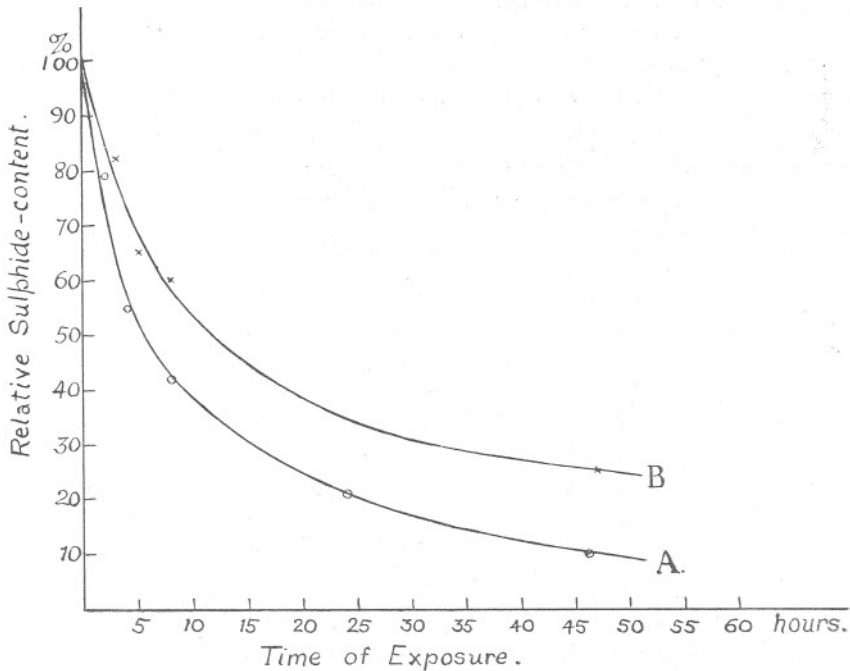


FIG. 2.—Rate of oxidation of Sulphides in sand. A. In air; B. In sea-water.

gives a fallacious impression of a sudden discontinuity of reaction. This zone of demarcation is to be regarded rather as the end-point of one stage of a serial process—a stage rendered evident by the colour change of one of the reactants, ferrous sulphide. The fact is, that free oxygen exists, in appreciable concentration, even in the blackest shore sands, and the occurrence in them of numerous organisms—annelids (especially cirratulids), small crustaceans, echinoderms, etc., none of which are known to be even facultatively anaerobic—has been recognised for many years (Lewy, 1846).

A sample of black sand from Station 23 on Port Erin beach (Fig. 1) was

found to contain 24 volumes per cent of hydrogen sulphide, while the interstitial water drained from the sample contained 1.81 c.c. of oxygen per litre, or roughly 25% of the saturation concentration. For certain precautions to be observed in the determination of oxygen by Winkler's method in the presence of sulphides reference should be made to Fox, 1905.

Experiment. The effective velocity of the oxidation reaction, under natural conditions on the beach, depends, as already indicated, upon several factors difficult to reproduce in the laboratory. The results obtained in a given experiment must, therefore, be accepted as relative only. Two series of equal samples of fine sand from the black layer were taken by means of the 10 c.c. borer-sampler, and exposed to oxidation in shallow evaporating dishes, special precautions being taken to ensure homogeneity of sampling and conditions. One series stood in the air, the other beneath a very thin film of sea-water, and both at 15° C. Samples were removed periodically for sulphide determination, with the following result :—

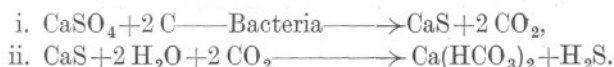
Time Interval. Hours.	Relative Sulphide Content.	
	Series A (in air).	Series B (in water).
—	100	100
2	79	—
3	—	82
4	55	—
5	—	65
8	42	60
24	21	—
46	10	—
47	—	25

As might be expected (Fig. 2), the rate of oxidation is somewhat slower when the pores between the sand-grains are filled with water, but in either case, twelve hours (the maximum period of intertidal exposure of the beach) suffices, under the conditions stated, for a 50% reduction of the sulphide-content.

Conclusions as to the Source and Fate of Sulphides in the Beach.

From the preceding observations upon the occurrence and concentration of ferrous sulphide in shore sands, and the conditions of its oxidation, it may be permissible to draw certain conclusions as to the source and fate of sulphur in the beach, and as to the agencies at work at each stage of the process. Recent hydrological work in the Black Sea (Danilčenko and Čigirin, 1926) emphasises the conclusion that the reduction of sulphates

by bacterial agency, in the presence of organic matter, is a more important source of sulphide than the direct bacterial decomposition of the organic matter itself. The reduction takes place in two stages:—



If the same reaction took place in the midst of a mass of sand, the hydrogen sulphide would at once combine with the hydrated iron oxide, itself possibly of bacterial origin, which forms a coating on the grains, giving rise to ferric and ferrous sulphides, while the calcium bicarbonate would add to the already high concentration of excess-base which has been found under such conditions (p. 555).

In the present state of knowledge, it is not possible to say whether the reduction of sulphates or the direct decomposition of organic detritus is the more important source of sulphur in the beach. The almost invariable association of putrefying algal débris with the black sand of littoral and shallow water deposits, and the known high content of ethereal sulphates in the marine algæ, suggest the hypothesis that these compounds, on hydrolysis, furnish both the sulphate ion and the organic residue demanded by the first-named process—the possibility, at any rate, is being further pursued.

On the access of air, the black iron sulphides, whatever their source, are oxidised:—



the nett result being the conversion of the hydrogen sulphide into free sulphur, and the reformation of ferric oxide, ready again to enter the reaction. It will be noted that, as a result of these processes, there should be a continuous increase in the amount of free sulphur in the sands. Buchanan (1891) was only able to find 0.003% of free sulphur in certain oceanic deposits, and while an analysis of the black sand at Port Erin has yielded over twenty times this amount (0.07%) the proportion is still very low. Since sulphur is practically insoluble in sea-water, its removal from the beach is probably effected by direct oxidation, through sulphites to sulphates, while under certain special conditions (which are apparently imitated in sealed vessels) ferrous sulphide may combine with free sulphur, giving rise to iron pyrites, FeS_2 .

No reference has been made, so far, to the possible rôle of thiobacteria, since the investigations of Ellis (1924), still in progress, point to the conclusion that *Beggiatoa*, at any rate, does not flourish except in the higher concentration of organic matter afforded by actual sewage pollution. At the same time, it is not improbable that other members of the group

may flourish under less polluted conditions, and by the oxidation of hydrogen sulphide and secretion of sulphur, add to the chemical and biological significance of this element on the sandy beach.

The views as to the source, reactions and destination of sulphur, which

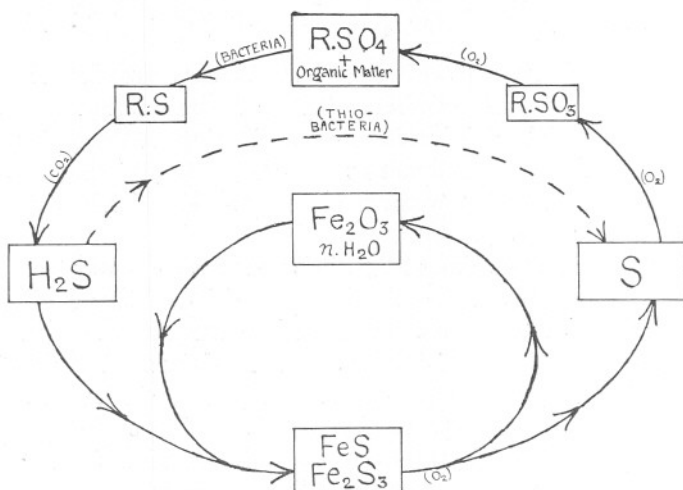


FIG. 3.—Scheme of circulation of Sulphur in the Sandy Beach.

the foregoing observations and experiments have suggested, are embodied in a diagram (Fig. 3), in which the reactions and compounds on the right side are oxidative, those on the left, reducing or anaerobic. It may be claimed that, while points of detail remain to be investigated, the general lines of the sulphur-cycle in the sea-bed and in the sandy beach are provisionally established.

SUMMARY.

1. The presence of living organisms and their metabolic products introduce a further series of biochemical factors into the physical conditions of life on the sandy beach.

2. The gaseous exchanges of animals and plants lead to changes in the pH of the interstitial waters of the beach, but the calcareous matter associated with the sand acts as an alkali-reserve, preventing undue rise of acidity, and incidentally widening the potential range of carbon-assimilation of the surface flora.

3. The conditions leading to the formation of the "black layer" are surveyed and discussed, with special reference to Port Erin beach. An iodimetric method for the determination of sulphides in sand is described,

and is used to demonstrate the rate of oxidation when the black sand is exposed to the air.

4. It is concluded that the formation of ferrous sulphide in the beach is associated with diminished circulation of air and water in the mass of the sand, due either to gross obstruction or to fineness of grade, or both. The presence of organic detritus, usually of an algal nature, appears to be essential to the reaction, and bacteria play an important rôle in the sequence of changes. Sulphur, in common with other elements, passes through a cycle of reactions on the sea-bottom and in the sandy beach.

REFERENCES.

- ANDRUSSOW, N. (1897). *La Mer Noire*. 7^{me} Cong. Géol. Internat., Guide des Exc.
- BRUCE, J. R. (1924). A pH Method for Determining the Carbon Dioxide Exchanges of Marine, Brackish Water, and Freshwater Organisms. *Brit. Journ. Exp. Biol.*, **2**, 57-64.
- BRUCE, J. R. (1928). Physical Factors on the Sandy Beach, Part I, *Journ. Mar. Biol. Assoc., N.S.*, **15**, 535-552.
- BUCHANAN, J. Y. (1891). On the Occurrence of Sulphur in Marine Muds, etc. *Proc. Roy. Soc., Edin.*, **18**, 17-39.
- COLLIP, J. B. (1920). Studies on Molluscan Celomic Fluid. *Journ. Biol. Chem.*, **45**, 23-49.
- DANILČENKO, P., AND ČIGIRIN, N. (1926). Sur l'Origine de l'Hydrosulfure dans la Mer Noire. *Trav. du lab. et de la Stat. Biol. de Sebastopol*, Ser. ii, No. 10, 141-191.
- ELLIS, D. (1924). An Investigation into the Structure and Life-History of the Sulphur Bacteria (I). *Proc. Roy. Soc., Edin.*, **44**, ii, 153-167.
- ELLIS, D. (1925). An Investigation into the Cause of the Blackening of the Sand in Parts of the Clyde Estuary. *Journ. Roy. Tech. Coll., Glasgow* (1925), 144-156.
- FOX, C. J. J. (1905). On the Determination of the Atmospheric Gases Dissolved in Sea-Water. *Cons. Intern. Explor. Mer, Publ. de Circ.* **21**.
- JOHNSTONE, J. (1921). On Black Littoral Sands in Lancashire. 29th Ann. Rept. (for 1920), *Lancs., Sea-Fish. Lab.*, 106-109.
- LEWY, B. (1846). Recherches sur la Composition des Gaz que l'Eau de Mer tient en Dissolution dans les différents moments de la journée. *Ann. Chim. et Phys.*, iii, **17**, 5-23.
- OMELIANSKI, W. (1904-1906). Der Kreislauf des Schwefels, in F. Lafar's "Technische Mykologie," Bd. 3.

