

Why is the sea salt? / by William Mackie.

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Publication/Creation

Inverness : Printed at the Courier office, 1902.

Persistent URL

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WHY IS THE SEA SALT?

BY

WILLIAM MACKIE,

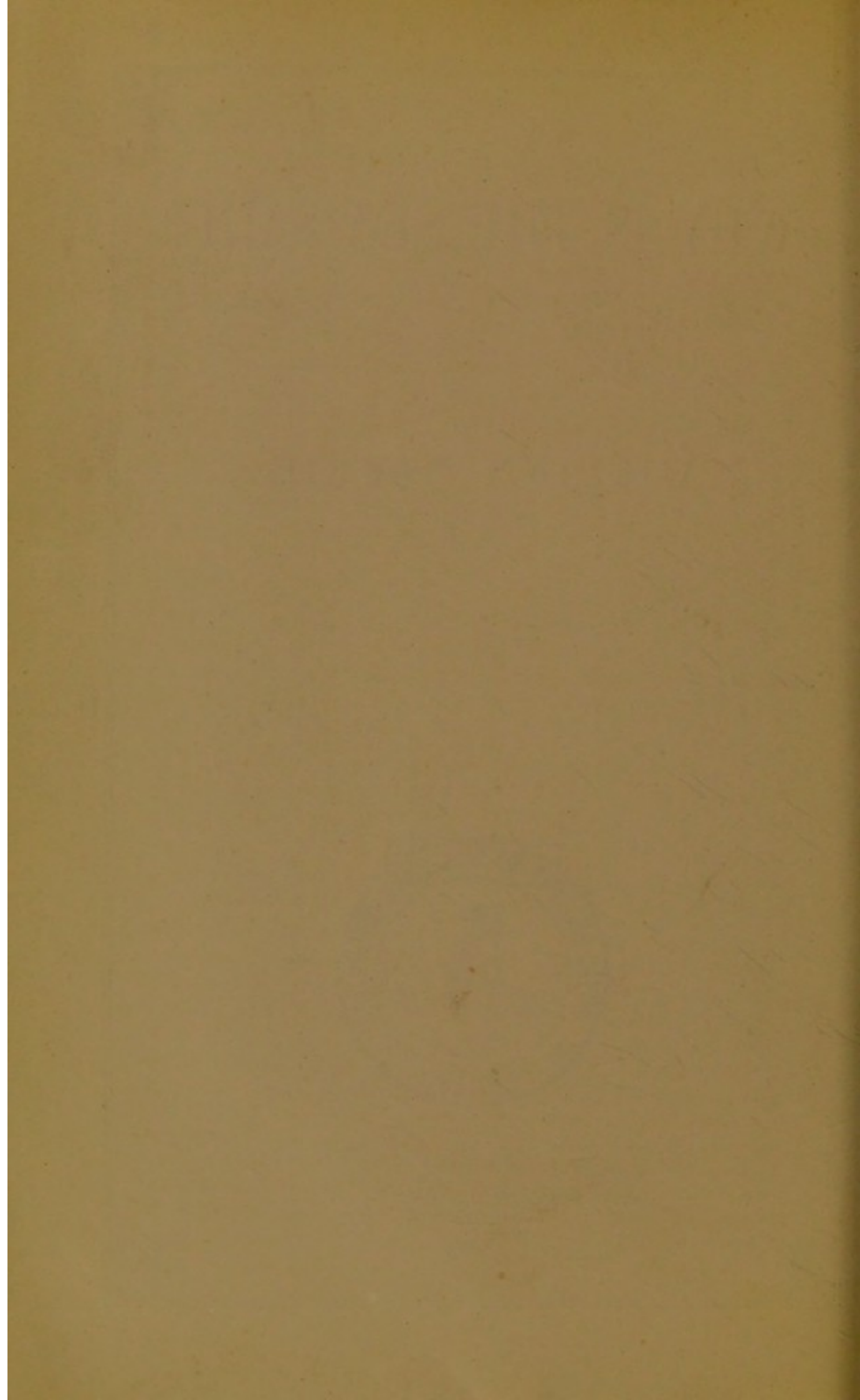
M.A., M.D.



INVERNESS :

PRINTED AT THE "COURIER" OFFICE.

1902.



WHY IS THE SEA SALT?

The following paper was read at a meeting of the Inverness Scientific Society, held in the Waverley Hotel, Inverness, on 14th March 1899 :—

In the two papers which I have had the honour on former occasions of reading before this Society, I dealt more particularly with the mechanical products resulting from the disintegration and denudation of the rock-system of the earth's crust. To-night my subject has to do with the substances liberated during the operation of the same agencies that pass into solution and are carried off in invisible form—their existence revealed only by arts known to the chemist—by every rill and river to the ocean.

To demonstrate the processes by which these compounds have been formed under existing conditions, to trace the further changes that have come to them both on the land surface and in the sea, and generally to consider in what way the waters of the ocean have attained their present degree of saltiness, will be among the objects of the present paper.

If we take a quart of clear water from the river and proceed to evaporate it slowly over a gas lamp in a glass beaker—that is to say, to drive off the water in the invisible form of steam—we shall find, if we watch the process closely, that at a certain stage, probably when about $\frac{1}{4}$ to $\frac{1}{5}$ of the original volume of water remains, a thin, clear pellicle begins to form on its surface, which as the process goes on breaks up and floats freely in the remaining liquid, and finally goes to the bottom as a considerable precipitate. The same sort of pellicle, I daresay, you will have observed—in fact it is the same substance—forming on the surface of lime water when it is freely exposed to the air. Gradually, too, you will see the sides and

bottom of the beaker become encrusted with a whitish, limy-looking substance. Continuing the evaporation to nearly dryness, you will find when only a few drops remain if you taste the liquid that it is at least brackish, if it be not even decidedly salt. Carefully transferring what remains of clear water to another vessel for further examination, we proceed to examine the deposit in the beaker. If we pour a little dilute acid into it we find that the precipitate effervesces briskly, and so does the crust on the sides. We therefore infer that it is a carbonate. Neutralising the excess of acid with a little ammonia, and then adding a little oxalate of ammonia, we get in time a copious white precipitate which we know to be oxalate of lime. The original substance must therefore have been carbonate of lime. If we now pass on to examine the liquid portion, we shall find dissolved in it a host of other substances. Two experiments may be made to show that there are other substances dissolved in it, and at the same time determine the character of some of them. Dividing the liquid into two parts, to both I add a few drops of nitric acid, then to the one barium chloride, when we get a white precipitate, indicating the presence of sulphates. To the other I add nitrate of silver, when a curdy, white precipitate is thrown down, and indicates that chlorides are present in abundance. Now, we shall not go further into this question experimentally, but take for granted that we have worked through the analysis, determined and noted all the substances present. Among these, if we examine a list of the substances to be found in natural waters, we shall find a selection from the following:—

Carbonates of Lime, Magnesia, Soda, and Potash.
 Sulphates of Lime, Magnesia, Soda, and Potash.
 Chlorides of Lime, Magnesia, Soda, and Potash.
 Nitrates of Soda and Potash (traces).
 Phosphates of Soda and Potash (traces).
 Oxides of Iron, Aluminium, and Manganese.
 Silica and Silicates of Soda and Potash.
 Organic matter and traces of Ammonia Salts.

As to the amount of saline substances dissolved in natural waters, we may take, according to Bischof, 21 parts in 100,000 parts as a very fair average. More than one-half of this quantity is in almost all cases carbonate of lime. In the remainder, sulphate of lime usually bulks largely, while chlorine, present as chlorides, and by far the most important ingredient from our present point of view, may be put down as about 9 parts in 1,000,000.

Now, what is the origin of these substances, and how do they come to be present in river water? Almost all of them have been derived by the action of the atmospheric agencies or the action of the acids derived from decomposing organic matter on certain minerals present in the rock-system of the earth. Thus we know that there exist in the earth's crust great bands of limestone—that is carbonate of lime in a state of greater or less purity—and it is also matter of common knowledge that carbonic acid and moisture, both of them at all times present in the atmosphere, bring a portion of this carbonate of lime into solution. But it is not the only source of this substance. Hornblende, among other substances, contains lime, and I shall now show, by the help of a diagram, the changes that take place in this mineral under the action of a moist atmosphere.

Thus, hornblende, which contains lime, magnesia, iron, alumina, and silica, under the atmospheric influences—that is, in consequence of the action of carbonic acid, oxygen and moisture gives carbonate of lime, carbonate of magnesia, oxide, or hydrate of iron, alumina in combination with silica and water, and possibly also some free silica.

Take again the mineral labradorite—a felspar present in many igneous rocks, which consists of lime and soda in combination with alumina and silica. Under the action of the atmosphere it gives carbonate of lime, carbonate of soda, alumina in combination with silica and water as kaolin, and some free silica.

The common felspar—orthoclase gives rise, on similar decomposition, to carbonate of soda, carbonate of potash, kaolin, and free silica.

These will suffice to show the possible origin of the carbonates which we find in natural waters.

Now, as regards sulphates, take the mineral nosean which is present in some recent volcanic rocks.

This mineral contains soda and alumina, the former in combination, partly as a double silicate with the alumina, partly as sulphate. On decomposition, carbonate of soda and kaolin are formed as before, with liberation of the sulphate of soda.

Sulphates also take origin from the oxidation of naturally occurring sulphides. Take, for example, iron pyrites. By the action of oxygen and water, this is converted into hydrated oxide of iron (rust) and sulphuric acid.

Sulphuric acid also results from the oxidation of organic matter containing sulphur, and the acid so formed decomposing the naturally occurring carbonates, gives rise to the corresponding sulphates.

Again, as regards phosphates and chlorides, the mineral apatite, which is a double phosphate and chloride (or fluoride) of lime, under atmospheric agencies breaks up into carbonate of lime, phosphoric acid, and chloride of lime. The phosphoric acid so liberated meeting with alkaline carbonates will give rise to the corresponding alkaline phosphates.

Sodalite is also another chlorine-containing mineral which is found in some recent volcanic rocks. Another source of chlorine is from the liquid present in the pores of the quartz of such rocks as granite. In such quartz grains countless numbers of minute cavities are seen filled, or partially filled, with fluid. This fluid is known to contain chlorides—in fact, it is often saturated with sodium and potassium chlorides, and in some cases we even find small cubes of these salts lying loosely in these little interspaces. Where that occurs we know the fluid has once been supersaturated with chlorides, and the excess has crystallized out on cooling. Then, again, in the case of volcanoes, we have hydrochloric acid vapours given off at certain stages of their action. These are no doubt derived from the decomposition of chlorides, but as to whether these are of cosmic origin or derived from the decomposition of inflowing sea water, which, according to one theory, is an element in the cause of a particular phase of volcanic action, must needs remain an open question.

Of nitrates, more than one source may be found. By actual experiment in the chemical laboratory, we find if we pass an electric spark through air that the oxygen and nitrogen unite to form nitrogen pentoxide, and this in the presence of water becomes nitric acid. The acid so formed, acting upon alkaline carbonates, gives rise to the corresponding nitrates. Of course it will be easily seen that all the conditions exist in Nature for the formation of nitrates in this way, and insignificant possibly though the amount be that is so produced, one has always greater faith in what can be actually demonstrated in the chemical laboratory. It is, nevertheless, certain that nitrates are also formed by the oxidation of nitrogenous organic matter. In proof of this we have only to cite the methods adopted by the French chemists for the preparation of nitre for making gunpowder at a time when, being at war with this country, the French nation was cut off from the natural supplies. In much the same way probably most of the nitrates existing in Nature have been produced, as, for example, in the nitre beds of India and Chili.

Analyses of surface waters always show more or less organic matter, which, though variable both in kind and quantity, is almost always less in amount than the inorganic salts present.

The functions of organic matter from a chemical point of view are no doubt important, and will be referred to in another connection.

Ammonia salts in traces are present in natural waters, and are derived from the decomposition of nitrogen-bearing organic matter.

In this way may be explained the origin of most of the substances existing in natural waters, but the question will now naturally be asked, "What bearing has all this on the saltiness of the sea?"

I think we shall probably best attack this problem by taking salt lakes on our way. There we shall be dealing with like conditions on a smaller and perhaps, if anything, more comprehensible scale. Salt lakes, as is well known, receive rivers of fresh water, but give none out except by evaporation. Most of the lakes of this class exist under warm and arid climates, and we have thus practically repeated, on a vastly larger scale, our initial beaker experiment. Ordinary fresh water containing, as we have seen, a small proportion of salts in solution, runs in. Evaporation continuously goes on. None of the salts can pass off by evaporation, while the water does. In this way the waters of the lake get gradually salter. At last, after saturation of the water left, the saline constituents come to be deposited in solid form on the bottom or along the shores of the lake, just as we saw they were deposited on the sides and bottom of our beaker. Most of these lakes are salter than the sea, and contain their salts in different proportions, both relatively and absolutely, from those existing in the rivers which supply them, as well as from those existing in the waters of the sea. I shall now show you the differences that exist among them by placing side by side typical analyses of the three classes of waters*—

* Besides the ingredients in sea water tabulated here, there have also been found in it traces of iodine, fluorine, silica, phosphoric acid, ammonia, carbonate of magnesia, barium, strontium, iron, nickel, cobalt, zinc, manganese, aluminium, silver, lead, copper, arsenic, and gold, &c. The latter has been lately (in 1896) ascertained by Professor Liversidge to exist in sea water off the coast of New South Wales in the proportion of $\frac{1}{2}$ to 1 grain per ton, which is equal to 130 to 260 tons per cubic mile of sea water. There is nothing new in this discovery. As early as 1872 E. Sonstadt ("Chemical News," October 1872, vol. xxvi. p. 159), had announced the interesting fact that the sea water of the British coasts contains, in addition to silver, about 1 grain of gold per ton. That being so, if only suitable means of extraction could be devised, the ocean would prove to be the richest gold mine extant.

RIVER WATERS—Salts in 100,000 parts.

	Dee, Aberdeen	Danube, Vienna.	Rhine, Basel.	Rhone, Lyons.	Thames, Ditton.	Seine, Paris.	Averages.	Sea Water, English Channel.
Sodium Chloride.....	.96	Traces	.15	.1	1.57	2.5	.88	2705.9
Potassium ,,	—	—	—	—	—	—	—	76.5
Magnesium ,,	—	—	—	—	—	—	—	366.6
,, Sulphate.....	.46	1.37	.39	1.6	—	1.7	.92	229.5
Calcium ,,17	.29	1.54	1.4	4.37	3.9	1.95	140.6
Magnesium Bromide.....	—	—	—	—	—	—	—	2.9
Calcium Carbonate.....	1.22	8.37	12.79	14.1	16.84	17.4	11.78	3.3
Magnesium ,,20	1.50	1.35	—	1.81	6.2	1.84	—
Silica.....	.11	.89	.9	1.	2.61	1.4	1.15	9. (about)
	3.12	12.42	17.12	18.2	27.2	33.1	18.52	3534.3 *

SALTS IN SALT LAKES—*Parts in 100.*

	Great Salt Lake, Utah.	Elton Lake, Kirghes Steppes	Indertsh Lake.	Dead Sea.	Mediterranean.
Sodium Chloride.....	9.74*	7.4	23.9	11.003	2.9424
Potassium „	1.89	—	.01	.166	.0505
Magnesium „ ..	.74	16.3	1.7	1.696	.3219
„ Bromide.....	—	—	—	—	.0556
Calcium Chloride.....	—	—	—	.680	—
„ Carbonate.....	—	—	—	.953†	.0114
„ Sulphate.....	.20	—	—	.233	.1357
Magnesium „745	2.2	.30	—	.2477
Potassium „	—	.04	.04	—	—
Silica	—	—	—	.200	—
	13.315	25.94	25.95	14.931	3.7652

* Calculated from an Analysis by H. Bassett, "Chemical News," vol. xxviii., 1873.

† This is far above the solubility of carbonate of lime under any circumstances. There must be some error in the calculation of the analysis; other analyses of Dead Sea water give no carbonate of lime whatever.

CHARACTER OF SALTS IN VARIOUS KINDS OF WATER COMPARED.

	Salts in Fresh Water.	Salt Lakes.	Sea.
CARBONATES	Usually more than half total.	Variable or absent.	Trace of Lime.
CHLORIDES.....	Poor in quantity.	Often up to saturation.	Moderate in quantity.
SULPHATES	Relatively high.	Poor or absent.	Moderate in quantity. ∞
LIME SALTS.....	More than half total.	Variable, sometimes present as Chlorides.	Under saturation as Sulphate.
MAGNESIA SALTS.....	Fairly rich.	In very large amount.	Moderate in quantity.
POTASH ,	Poor in quantity.	Poor.	Poor.
SODA ,	Compared with Potash, relatively high	Very abundant.	Abundant.

From this comparison it will be seen that sea water as regards the salts dissolved, both quantitatively and qualitatively, lies between river waters and the water of salt lakes. Some of the latter have no doubt at some period of their history been connected with the sea, and hence has arisen a certain similarity in their saline constituents. From this initial similarity they have of course diverged in proportion to the length of time that has elapsed since their separation. Others, such as the Dead Sea and the Salt Lake of Utah, we know, from a study of their geological history, have started as lakes of transmission, and hence as sheets of fresh water. But even these have become much salter than the ocean. This, it will be seen on a little reflection, is due to the fact that the proportion of water, and consequently of salts, entering them must relatively to the volume of water which they contain be greater than the proportion which the volume of the water of all the rivers with their salts entering the ocean bear to that enormous volume of water. Consequently a very much shorter time has been required to saturate the waters of salt lakes, and render them even salter than the sea.

What, however, strikes one is the marked difference in the proportion of salts relatively to one another in river waters, compared with the proportions present in the other two.

Thus carbonates count for more than half the salts of river waters, while they exist in the waters of salt lakes and in the sea in mere traces. Chlorides again, which are present in river water in small amount, and much subordinate in quantity to the carbonates, are in large excess in salt lakes and the sea. These two groups have, as it were, changed places. Again, the proportion of sulphates in river water in the examples given, count as more than three times the chlorides. In the sea the sulphates count as less than 1-7th of the chlorides, while in salt lakes the proportion is still less. In all of the waters soda salts are in excess of the potash. In river water in the determinations I have been able to make and the analyses I have been able to consult, potash counts as about 1-7th of the soda present. In sea water it counts for less than 1-20th, while in the salt lakes it is variable in amount running from as low as 1-180th or less to $\frac{1}{4}$ in the Salt Lake of Utah. Differences, of course, are to be expected in waters of the latter class. The rivers entering them, necessarily draining different geological formations, convey different salts and different proportions of their salts. These on concentration will give different results in the different lakes. A river like the Dee, in Aberdeenshire, draining as it does an eminently granitic country, will carry very little

saline substance in solution, and this, such as it is, will differ both in quantity and quality from the salts in the Thames, which drains an eminently calcareous country. A river draining a basaltic region again will contain in its waters considerable proportions of lime and magnesia, and so on. Further, I do not think it would be difficult to demonstrate the fact that differences of climate make an immense difference to the quality and quantity of the salts dissolved in natural waters.

All over, however, there are fairly marked differences as regards the salts dissolved among the three classes of waters. Now, how have these differences been brought about? As has been already intimated, the evidence that the salts of salt lakes have been derived from river salt is complete, and my argument will now be that as these have been derived from the river salts, so in like manner the salts of sea water, which differ from river waters less widely, have either wholly or in part been derived from the same source. To complete the case, it will now be necessary to show how the differences observed have arisen. As a general answer to the question, How has the one been changed into the other during the process of concentration? we may say that—

1. Some substances have dropped out of solution by reason of their relative insolubility, e.g., carbonate and sulphate of lime.
2. Others have been reduced by the action of the organic matter present, and have so been changed into substances which are either themselves insoluble or which by reactions with other substances present have formed insoluble compounds, e.g., sulphates and nitrates.
3. Others have been precipitated by the accumulation of substances which form insoluble compounds with them, e.g., soluble lime salts.
4. Still others have been extracted by the agency and used up in the processes of plant and animal life, e.g., lime, potash, phosphoric acid, silica.

These points may now be illustrated in detail. Take the case of the salts of lime first. Carbonate of lime* dissolves in water to

*In presence of ammonia and carbonate of ammonia, its solubility, according to Fresenius, is 1 in 65,246.

the extent of only 1 part in about 10,600. In the presence of excess of carbonic acid, however, it may reach to about 1 in 1100. So that it will at once be seen that in sea water the amount of carbonate of lime dissolved must lie below the latter limit. As a matter of fact it lies below the former limit, and in the analysis of sea water given is equal to 1 in about 30,000. Further, carbonate of lime is being eliminated from the water of the sea by innumerable marine organisms, which extract it to form their skeletons and shells. But the sufficiency of this agency at the present time to keep down the proportion of lime in sea water to its present limits may be reasonably doubted.

When concentration passes beyond the limits indicated above, precipitation must inevitably follow, even in the absence of life,* and this may have taken place, for aught we know, at different periods in the history of the ocean. In fact the presence in deep sea deposits of carbonate of magnesia, which is not extracted by animal life, points to the high probability of at least a portion of the lime being deposited by simple concentration. In the case of the Dead Sea and other salt lakes where the amount of lime is kept in due bounds and there is no animal life, this has probably been the efficient cause.

Sulphate of lime, again, is soluble up to the extent of 1 in 400, so that where both sulphate and carbonate of lime are present, the former will have the chance of being in excess. In sea water its amount lies between 1-600th and 1-700th, or only just under the limit of its solubility, and in the presence of excess of soluble sulphates, such as sulphates of the alkalies or magnesium, no soluble lime salts can exist in a water above the limit indicated. Even under that limit the sulphate of lime itself may be precipitated as carbonate by the action of carbonate of magnesia or carbonate of the alkalies, thus:—Calcium sulphate plus magnesium carbonate, gives magnesium sulphate and calcium carbonate; and again, calcium sulphate plus sodium carbonate, gives sodium sulphate and calcium carbonate; when, of course, soluble sulphates of magnesium or the alkalies take its place.

Again, sulphates as a class, and among them, of course, sulphate of lime, get reduced by the action of organic matter to sulphides, which readily form insoluble substances with other compounds, and hence through this cause alone they may totally disappear from a water in which they were formerly plentiful. In

*Similar positions taken up by T. P. Blunt, "Chemical News," vol. xxvi. p. 172.

fact the presence of sulphides in the mud of the sea bottom is ascribed by J. Y. Buchanan, of "Challenger" expedition fame, to the reduction of its sulphates to sulphides by its repeated passage through the bodies of innumerable sea worms.

The more soluble salts of lime as the chloride are not now present in sea water, but it is to be found in the waters of many salt lakes, and notably in the waters of the Dead Sea. Sterry Hunt, from numerous analyses of natural waters rising through the Laurentian and Cambrian rocks of Canada and New England, and many of which showed large proportions of calcium as well as magnesium chlorides, formed the theory that the waters of the primeval ocean, in which, of course, the rocks in question were deposited, were rich in chlorides of calcium and magnesium. The former salt, as already stated, has probably long vanished from the waters of the ocean, while a considerable proportion of the latter still remains in it.

It is, of course, very easy to show by chemical equation that calcium chloride would in time be eliminated from the waters of the primeval sea by the continual inflowing of alkaline carbonates which we have seen exist in river waters. These would precipitate the lime as carbonate of lime, with at the same time the formation of sodium chloride, thus:—Calcium chloride plus sodium carbonate, gives calcium carbonate and sodium chloride. But while it is highly probable that this hypothesis is correct, I think it is possible that calcium chloride in the cases observed may have originated in other ways. We have seen that this salt is liberated in the decomposition of the mineral apatite, and among the formations where Sterry Hunt made his observations the occurrence of beds of massive apatite is a noteworthy phenomenon.

Further—and the operation of this cause applies more particularly to local occurrences, such as the case of the Dead Sea—volcanic action is accompanied at a certain stage by the evolution of free hydrochloric acid, and this acid, naturally attacking carbonate of lime as the most available and most susceptible substance, would of course form chloride of calcium. The fact that the Dead Sea region is an eminently volcanic one favours this idea, while the derivation of the same salt from apatite, usually present in volcanic rocks, is not to be altogether excluded in this case.

Salts of magnesium, particularly the sulphate and carbonate, are present in natural waters, but the former only appears in sea water.

From what has already been said in speaking of calcium sulphate, it will be manifest that sulphate of magnesium could

not have accumulated in the water of the ocean so long as soluble salts of lime existed in it above the level of the solubility of sulphate of lime, which is about .2 per cent. The fact that a considerable quantity of sulphate of magnesium, as well as sulphate of soda and potash, above this limit is present in sea water, will go to show that it is at least some time since calcium chloride vanished from the waters of the ocean. Carbonate of magnesia naturally precipitates soluble lime salts as carbonate, hence, perhaps, its almost entire absence from sea water. It is, of course, itself precipitable on concentration to a point exceeding its natural solubility, which is not markedly high.

Magnesium chloride also exists in sea water in some quantity, and its presence will be referred to in due course.

The alkali bases are present in river water as bicarbonates and chlorides, and possibly also as sulphates. The first, as we have already seen, precipitates the soluble salts of calcium and magnesium as carbonates, replacing them by their respective alkaline soluble salts. If these have been chlorides, as in the equations given below, alkaline chlorides take their place in the waters of the ocean, thus:—Calcium chloride plus sodium carbonate, give, as before, calcium carbonate and sodium chloride; and magnesium chloride plus sodium carbonate, give magnesium carbonate and also sodium chloride. In this way alkaline chlorides tend to replace both the calcium and magnesium salts, while the chlorides of the alkalies already present in river water of course go directly to swell the amount of chlorides resulting from these reactions, and the same may be said of the sulphates, subject always to possible changes in the latter salts from the causes already noted.

Now, as regards the several acid radicles, something may be said regarding the several groups of these.

Carbonates of lime and magnesia are eliminated in the way indicated on account of insolubility, while carbonates of the alkalies react with the soluble salts of these bases and produce the corresponding alkaline salts, e.g., sulphates or chlorides.

Phosphates are insoluble generally, and are extracted from sea water by animal life.

Sulphates are reduced in the way indicated, and hence they are in relatively less quantity proportionally to the other salts in sea water than in river water. Their precipitation as sulphate of lime has also to be remembered in this connection.

Nitrates again exist in small amount in most ordinary river waters, and unless there were some means by which they undergo chemical change there would be a tendency to their accumulation

in the waters of the sea. Mr Buchanan might very well have extended his theory of reduction to these, for their cannot be much doubt, I think, that they are reduced by the action of organic matter. We have already seen that they owe their origin to the oxidation of nitrogenous organic matter, but in Nature such processes are often reversed under different conditions. By organic matter of another kind a process of reduction takes place, with the result that they are finally converted into carbonates of the corresponding bases with the formation of carbonate of ammonia at the same time, thus:—Potassium nitrate, by reduction, would give potassium carbonate and ammonium carbonate. Both of these products reacting on the soluble calcium and magnesium salts present would naturally precipitate them as carbonates. Further, where in enclosed seas or salt lakes there is necessarily a higher proportion of organic matter, I think it is possible that some such compound as oxalate of ammonia may be formed during its decomposition. This substance would have the effect of precipitating the last trace of lime salts, and this, as the analyses of the saline residue of the salt lakes would seem to suggest, has actually happened in some cases.

Chlorides as a class are very soluble salts, and the chlorine radicle is incapable of further change either by oxidation or reduction. Hence chlorides once formed tend to persist. We have further seen that the precipitation of the chlorides of the earth metals by alkaline carbonates result in the formation of chlorides of the alkalis. From both these causes chlorides have come to be in marked excess in sea water, as indeed in most saline waters. But why should the sodium be in such marked excess of the potassium salt? Relatively to the potash salt it is only slightly more soluble, and consequently, so far as that goes, might reasonably be expected to appear in relatively not much greater amount. The potash, not as chlorides probably, but as carbonate—which we have just seen is a readily convertible salt—is eliminated both on the land surface and in the sea by the action of plant life, and also it is said by filtration through natural soils. These causes to some extent account for the relatively low proportion of potash salts in sea water. But, further, I think I can demonstrate the fact that there is a very great difference in the relative amounts of these substances originally dissolved out of the rocks of the earth's crust.

In tabular form below are placed the average results of a series of rock analyses, so far as the substances present in water are concerned. First are given the original proportion of lime,

magnesia, potash, and soda present in a number of igneous and metamorphic rocks, and, second, of the same bases in a series of clastic rocks. The average of the former afford a measure of what might be expected in the latter if no solution of these substances had taken place during denudation. The average of the latter gives the proportion of the substances remaining in the waste of such rocks, while the balance in each case may be taken as fairly representative of the proportions of bases dissolved and which by implication must have finally found their way to the sea. It will be seen that there is nearly twice as much soda as potash dissolved, while the lime and magnesia together are in marked excess of the total alkalies.

AVERAGE PERCENTAGE OF LIME, MAGNESIA, POTASH, AND SODA
IN VARIOUS ROCKS.

<i>Crystalline.</i>				
	Lime.	Magnesia.	Potash.	Soda.
Average of 13 Granites.....	1.50	.47	4.27	2.81
" 15 Metamorphic Rocks....	2.56	1.63	2.41	2.21
" 6 Diorites.....	7.12	5.40	1.18	1.83
" 1 Diabase Porphyrite....	1.35	1.76	3.72	2.55
" 1 Quartz Porphyry.....	.23	.10	4.02	2.16
<i>Clastic.</i>				
Average of 3 Torridon Sandstones....	.24	1.06	4.25	.36
" 5 L.O.R. "63	.19	2.87	.67
" 8 U.O.R. "67	.32	1.58	.29
" 5 Reptiliferous "96	.17	1.22	.44
" 5 Glacial and Post Glacial..	1.14	.56	2.34	1.03
" 5 River Sands.....	1.28	.53	1.93	.95
" 2 Sea Sands.....	—	—	1.25	.60
" 1 Blown Sand.....	—	—	1.19	.70
Average of 36 Crystalline rocks above..	2.94	1.85	2.98	2.26
" 34 Clastic " " ..	.98	.42	2.08	.61
Loss—presumably by solution....	1.96	1.43	.90	1.65

Whatever may have been the composition of the salts of the primeval ocean, I do not think it can be doubted that sodium chloride has been and probably is now being formed by the process of double decomposition suggested by Sterry Hunt. Alkaline carbonates, as we have seen, are constantly flowing into the ocean. There by their cumulative action they can have only one effect,

and that is to precipitate the soluble calcium and magnesium salts as carbonates. If these salts were originally present as chlorides, chlorides of the alkalies, particularly of sodium, would take their place as soluble constituents of the ocean salts. Now, chloride of calcium, if originally present, has been eliminated by this process, and also it should be noted by its probable precipitation as sulphate by the action of the inflowing soluble sulphates, and now only so much of calcium salts remains in sea water in the form of sulphate and carbonate as just falls within the limits of solubility of these salts. Further, it is evident that the accumulation of sulphates of other bases could not have taken place till this limit was reached. We may therefore conclude that it is some time, even geologically speaking, since calcium chloride vanished from the waters of the ocean. At the present time the addition of sodium bicarbonate to sea water throws down a bulky precipitate of carbonate of lime, and if in excess of the hydrated carbonate of magnesia also.* As magnesium salts, both sulphate and chloride, which are also precipitable by alkaline carbonates, still remain in quantity in sea water the legitimate inference must therefore be that sufficient sodium carbonate has not yet been found to precipitate these salts; in other words, the proportion of chlorine now united with magnesium in sea water has not found its equivalent of soda, and so has failed as yet to produce its equivalent of sodium chloride, or, to put it differently, the sum of the waste of chlorine throughout geological time has been and continues to be in excess of the waste of soda.

That it is likely that sufficient alkaline carbonates have not been available for the decomposition of the magnesium and calcium salts entering the sea throughout geological time, will be evident from the results of the analyses already tabulated. Thus the loss from the sedimentary waste was found to average—Lime, 1.96 per cent.; magnesia, 1.43 per cent.; potash, .90 per cent.; soda, 1.65 per cent. Supposing the first two to exist in a water as chlorides, the latter in the form of carbonates would not in that case be sufficient to precipitate them as carbonates, for actual calculation shows there would be sufficient alkaline carbonate to just precipitate the calcium salt and no more. This calculation, too, is based on the supposition that the whole of the potash is used up for that pur-

* If the magnesium carbonate is filtered off and the filtrate heated to 68 deg. Fah., a further precipitate of the carbonate takes place, and is not entirely redissolved on cooling. This fact may account for some of the peculiarities of distribution of magnesium carbonate in deep sea deposits.

pose, and takes no note of the fact that the lime total given above does not include carbonate of lime derived from the solution of previously existing carbonate of lime, but only what formerly existed as silicate in the rocks from which it was derived.

To the suggestion that the saltness of the sea is due to the solution in its waters of substances extracted from the rock-system of the crust, and that the present relations of these substances, quantitative and other, have resulted from the various reactions that have taken place during the concentration of its inflowing waters, the question of how long time it has taken the waters of the sea to reach their present degree of salinity will come as a natural corollary.

Supposing for the present that all the chlorine in sea water has been derived from the land surface in the way indicated, we may take the amount of chlorine entering the sea in the river water as the basis of our calculation. The chlorine, calculated from the averages of the sodium chloride in the river waters previously tabulated, which amounts to .88, gives .534 of chlorine in 100,000 parts of water; while sea water contains about 1.92 per cent. of chlorine, that is to say about 3600 times as much. If the sea started as a body of fresh water, derived from river water similar to the present, the volume of the ocean would have to be evaporated 3600 times to attain its present saltness. Now, if we take the average depth of the ocean to be 13,000 feet, and suppose that evaporation takes place at the rate of 2 feet (and it is probably nearer 1 foot) a year, it would take 6500 years to one evaporation. We thus get 6500×3600 , or 23,400,000 years* (or twice that if 1 foot is taken), for the sea to reach its present salinity.

But everything goes to show that our chlorine average is probably very much too high. If you look into that wonderful book, "Air and Rain," by the late Dr Angus Smith, you will find all sorts of tables bearing on the substances dissolved in rain-water. Among these is chlorine. Now, Dr Smith found that the nearer the place of observation to the sea the more chlorine was found in the rain. He also found that chlorine increased in the rain-water as we approach large cities, where it was believed to be derived from the combustion of coal. The explanation in the former case lay in the fact that chlorine was caught up from the sea in the form of tiny, light vesicles of sea-water which were car-

* The average rain-fall over the land surface may be taken as the measure of efficient evaporation from the surface of the ocean. This has been placed at about 30 inches annually, which would mean something less than a foot (9-10ths) from the surface of the ocean; so that twice the above estimate would be nearer the mark.

ried inland by the winds. So that you will see by including some of the rivers in our average, we have simply been carrying back coals to Newcastle and have actually been adding chlorine to sea water which originally came from it, and which for that reason could not contribute anything towards its increasing saltness. The same might be said of chlorine derived from the combustion of coal and from the salt used in the kitchen. In this respect civilisation is probably only accelerating the rate at which sodium chloride originally taken from the ocean is finding its way back thither. The chlorine derived from volcanic action, too, according to one theory, is simply taken from the waters of the ocean, and, of course, in that case its return to the ocean cannot add anything to its saltness. All such sources of salt must therefore be discounted, with the result that our average must come down to a corresponding degree. Smith found that the rain of continental areas far from the sea contained the least amount of chlorine. Hence such rivers as the Danube contain only traces of chlorine. If therefore we take the average of the eight lowest determinations of chlorine in river water we can find which happens to be .145 in 100,000, and even that is probably not all carried to the sea for the first time, we shall probably be still including some proportion of chlorine derived from the rain, and therefore by implication really from the sea. Correcting our former result by substituting the latter figure, we get a correspondingly longer period for the ocean to reach its present saltness, the corrected period being 86,000,000 years, which probably is much nearer the truth.

But on the supposition that the sea started as a body of fresh water, the most reliable calculation *ought* to be made on the basis of the amount of chlorine actually present in the rock-rind of the earth. From a series of 18 determinations I deduce the average of .06 per cent. as the average amount of chlorine in the rocks of the crust, thus:—5 granites gave an average of .054 per cent.; 4 diorites an average of .105 per cent.; 5 metamorphic rock, .04 per cent.; 1 diabase, .05 per cent.; 1 serpentine, .1 per cent.; 2 sandstones, .02 per cent.—giving an average over all of .06 per cent. From this it appears that sea water contains 32 times as much chlorine as the rocks all over weight for weight, but taking 2.5 as the average specific gravity of rocks it follows that it would take 12.8 volumes of rock to make up the salt in one volume of sea water. Now, the ocean basins would probably hold the continental masses above their level 40 times over. This figure is obtained from the following calculation:—The average depth of the ocean is taken as 13,000 feet; the average height of the con-

tinents above the level has been put down as 900 feet (though some estimates make it more than twice this amount); the surface of the ocean is 2.8 times the land surface— $13,000 \div 900 \times 2.8 = 40$ nearly. Now, $40 \times 12.8 = 512$ continents required to yield sufficient salt. Converting this into time, we get $512 \times 5,000,000$ years (the time for denudation of one continent), or a total of 2,560,000,000 years for the ocean to reach its present saltness. That is surely an age sufficiently hoary to gratify the keenest appetite for the antiquity of the earth, but it is one which certainly is in marked excess of all estimates of geological time. Therefore the calculation on the basis of the amount of chlorine present in the crust of the earth ends in a manifest *reductio ad absurdum*. Wherefore we may safely conclude that at the dawn of life upon the earth the sea had already reached a degree of saltness, and that in virtue of the solution in its waters of chlorine compounds derived from sources other than the rock-rind of the earth.

Reasons have already been given for believing that sufficient soda has not been dissolved out during the denudation of the crust to unite with all the chlorine present in the sea. In that case calculation on a soda basis might be expected to give a different result, and one which might be accepted with greater probability of its being nearer the truth. As the average loss of soda from the rocks of the crust is 1.65 per cent., and sea water contains soda equal to 1.50 per cent., we have, on the foregoing data, a period of only 72,500,000 years required,* a result which would probably be accepted by most geologists as a fair average for the lifetime of the earth as the scene of the operations known to them.

These calculations are no doubt very interesting! They are founded on data, some of which are perhaps impossible of exact determination. But making all due allowances, we may say that if they prove anything at all, it is that if the sea started as a body of fresh water it has, by any of these calculations, taken a very long time indeed to reach its present degree of saltness. I say *if*, for I think it is abundantly evident, both from the results of calculation and from the consideration of the substances now present in solution in sea water, and the relative proportion of the substances that have passed into it during geological time, that the sea had become salt—and that by the operation of causes other than those now observed—at a period that would generally

* It is interesting to note that Professor J. Joly, of Dublin, has since reached a very similar period for the age of the ocean from calculation on a sodium basis. His method of attacking the problem is very different from the above, and it is certainly remarkable that the results should be so nearly concordant.

be considered long prior to the dawn of life upon the globe. The same result is borne out by theoretical considerations. On the hypothesis of an originally molten globe, it will be manifest on a little reflection that the first drops of water that condensed on its surface were not in all probability at the ordinary summer temperature of 60 deg. Fahr., or under the normal atmospheric pressure of 30 in. of mercury. At such temperature and pressure as then existed, water would be in what is known as a superheated state, and by implication would have the power of dissolving in large amount substances not soluble in it at ordinary temperatures and pressures, as well as large quantities of such substances as are freely or only faintly soluble at such temperatures and pressures. In fact, one very convenient theory of the origin of some of the older rocks—what we call the metamorphic rocks—is that they were simply deposited one after the other from the waters of the primeval ocean as they slowly cooled under a gradually decreasing pressure. But if we accept the theory of the gradual cooling down of the earth from a state of incandescence and regard the water of the ocean itself as simply so much burned up hydrogen—water which we know cannot be resolved into its elements again at a temperature less than 2000 C.—I do not see that it is possible to get away from the necessity of believing that there must have been some such stage in the history of the earth, though it is very certain, I think, that it must have been long antecedent to the formation of the metamorphic rocks as we know them. At this time the atmosphere, along with the elements of water, and at a later stage the actual vapour of water would also hold chlorine, first, possibly in the free state, later combined as hydrochloric acid. This, as the cooling process went on, would be condensed with the aqueous vapours, and so from the beginning charge the waters of the primeval ocean with hydrochloric acid. There, attacking the substances with which it came in contact, the acid would form chlorides which would thus from the first be an integral part of the waters of the ocean. Whether Sterry Hunt is right or not as regards the presence of calcium chloride, we do not know for absolute certainty, but there cannot be a doubt that chlorides were present in the first water that collected on the surface of the earth, and there is every probability that calcium chloride was one of them. But whatever the composition of the salts of the primeval ocean may have been, I think it is equally evident that great changes have taken place in these salts, both qualitatively and quantitatively, since then. There are good reasons for believing, on theoretical grounds, that the sea is getting salter, and for the same reasons we know that it will continue to get salter while there remains

land above its level and the elevatory forces of the crust and the denuding agencies on its surface continue to operate.

To take a broad view, we may say that the bed of the ocean is the dumping ground of Nature's bye-products. Some of these products, such as the carbonate of lime, the phosphoric acid, the silica, and the potash salts, she uses over and over again and makes subservient to higher ends. But for the sodium chloride she has no further use, at least on a scale commensurate with the largess with which it has been produced. It is therefore to that extent a waste product in the economy of Nature.

To many minds the suggestion of "waste in Nature" will come as a sort of nightmare. While the physicist may prove in abstract the truth of the principle of the conservation of energy, and the chemist demonstrate the indestructibility of matter, there cannot, I think, be a doubt that, so far as the earth is concerned, energy has been dissipated and substances have accumulated which in the present state of things are final and irreversible. What to the eye of the chemist is the water of the ocean itself but so much deflagrated hydrogen—so much hydrogen and oxygen which have satisfied their chemical affinities and long dissipated the heat generated by their union into space? So with the sodium chloride of its waters. In the process of denudation substances have been dissolved out of the rocks, these meeting in the waters of the ocean have reacted and produced sodium chloride, which has gradually accumulated by reason of its being at once the most soluble salt, the least susceptible of further change and the least available for further use in the economy of Nature. It is true that the chemist can decompose water by processes which practically mean the restoring of the energy that was dissipated on its formation and bring you out hydrogen and oxygen again, but what avails his art in relation to the immensity of the ocean? In the same way some relatively infinitesimally small proportion of sodium chloride may be used over again, but out of all measure the enormously preponderating balance remains, and must remain, the everlasting and unchangeable salt of the sea.

The paper was illustrated by lime-light views, mathematical calculations, and chemical experiments. It was listened to with great interest and evoked discussion.

Dr Mackenzie, in proposing a vote of thanks to the lecturer, discussed the subject from his point of view, and the discussion was continued by Mr Wilson Reid, Mr Thomas Wallace, Mr John Mackenzie, and Canon Brook. Dr Mackie suitably replied, and explained various points that had been raised. The vote of thanks was seconded by Canon Brook, and cordially awarded.

