THE EVOLUTION OF THE HYDROSHERE.

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ABSTRACT. Thirty years ago, by the medium of quite different approach, Daly and Lane came independently to similar conclusions regarding the interaction and organic life of the composition of the primitive ocean. In the present article, the reasons for assuming that early composition are reviewed and the means examined by which changes of composition have been brought about.

Astronomical, volcanological, and hydrothermal, lithologic, botanical, and isotopic evidences are considered as well as the testimony of the various kinds of extant waters and their presumed effect upon the constitution of the ocean.

The section of the pre-Cambrian of western Canada, as presented to Daly in his work on the "Geology of the Fortieth Parallel," led him between 1908 and 1911 to explain the absence of calcareous fossils.

I was attracted to the same kind of solution of the problem, not merely by Joly's calculation of the age of the earth from the accumulation of sodium, and R. Quinton's speculations, but by the analyses of waters of deep mines and oil wells.

We agreed that the explanation of the scarcity of identifiable fossils was to be found in the interaction of the evolution of organic life and the chemical evolution of the ocean.

In spite of the high salinity of many of the waters struck in deep mines and wells, often greater than that of the ocean, I took, and still take, the original ocean to have been relatively fresh and more acid (pH higher) than now.

Recently, however, Charles Henry White, in his paper "Why the Ocean is Salt," suggested that, before the earth cooled enough to have a hydrosphere, the water vapor was in the atmosphere above a crust of solid chlorides over silicates. Then he suggested that, when the earth became cool enough for air to form, the rain dissolved the chlorides, and the ocean was from the beginning highly saline.

This idea I cannot accept for sundry reasons. During the past thirty years I have assembled data bearing on the problem, furnished by studies and research along various lines: (1) Astronomical studies; (2) Studies as to the character of the earliest rocks; (3) Studies and analyses of the earliest

rocks; (4) Studies and analyses of interstitial waters; (5) Studies of the botanical formation of limestone; (6) Variation in the relative proportion of the isotopes in elements.

ASTRONOMIC SYMPOSIUM ON COSMOGONY AND THE EARTH’S ORIGIN.

Symposia of astronomers agree only in finding serious objection to each theory proposed. There are radioactive minerals that indicate that the earth had a solid crystalline crust some two billion (2,000,000,000) years ago. From the present rate of expansion of the universe estimated by Hubble, it must have been enormously condensed at that distant time, and the universe could not have been much older than the earth, so that Shapley has suggested that the earth should be considered the sister rather than the daughter of the sun.

F. G. Watson has calculated that, at the present rate of accumulation of meteorites, there would, in that time, be only a centimeter added to its radius. Thus, though G. P. Merrill has pointed out that they contain considerable chlorine, the contribution of chlorine to the ocean in that way would be trifling.

Fred L. Whipple² and R. Wild have studied the atmosphere of other planets.

It is not astronomically impossible that the earth’s crust should have had at one time a temperature in which chlorides should be solid and the water a vapor; but to assume most of the present ocean water held in the atmosphere would imply a high temperature at the bottom, and a capacity to dissolve silicates also, and bring us close to T. Sterry Hunt’s crenitic hypothesis. It is also not impossible that there was less water in the atmosphere and that the atmosphere was largely carbon dioxide. That carbon dioxide is very important in the atmosphere of Venus, there is definite evidence.

CONTRIBUTIONS FROM WITHIN.

The loss of volatiles from solidifying silicate magma has been much studied by the geophysical laboratory.³

A silicate magma or jelly may well contain 7 per cent to 9 per cent of “mineralizer,” largely water. If the average depth of the ocean is 4.117 km., the loss of water in forming 21 km. of granite (about the thickness of the sial) could supply the

water of the ocean, assuming the rock to weigh about twice as much as the water per unit volume. Moreover, in two billion years, at the present rate of production of volcanic gases, at least a very large proportion of the present ocean should have been exuded from within.

I do not mean to imply that the gases and water came wholly from a depth of less than 21 km.; certainly much is of deeper origin. Nor do I mean to imply that part of the volcanic water may not be resurgent, returning to the surface, as it was once common to think was true for all. Nor is there any special reason to believe that the present rate of supply of volcanic gases from within represents the average for the past. There is reason to believe the output varies greatly, and the average rate of supply may be less or even greater than the rate now obtaining. There is nothing in the rocks, however, to lead one to suppose that the volcanic emanations differed greatly in amount through the ages.

That is one reason for assuming the original ocean relatively fresh. It would be so if derived mainly from volcanic emanations. The volcanic waters would lack bases to neutralize the acid. The bases would be taken up from rocks exposed to attack. But in the average rock as computed by Daly, the sodium is nowhere near so preponderant as in the ocean.

The juvenile waters, according to Kemp and Lindgren, are, however, alkaline, but there is a large proportion of carbonate and sulphate, and the ratio of sodium to chlorine is much higher than in the ocean—much over 0.55, often over 1.00.

STUDIES AS TO THE CHARACTER OF THE EARLIEST ROCKS.

The earliest rocks show some sediments that obviously settled in water.

That the atmosphere had little or no oxygen is indicated by the absence of saprolites (rocks like beauxite), the result of prolonged chemical weathering. Also ferric- (red) rocks are absent until an era in the pre-Cambrian when there is extra iron in the formation and banded jasper iron ores are abundant. This is after the earliest Kewatin. Cherty iron carbonate, and ferro-dolomite have extra importance. The name “Greenstone schist,” which used to be applied, was significant.

Black and graphitic beds are characteristic of the upper pre-Cambrian in general, and the succession may be explained by the splitting up of carbon dioxide by the early vegetation.
This reaction would give on the one hand possibilities of black shale and petroleum and on the other a more oxidizing atmosphere, able to form and precipitate ferric oxide and salts.

The practical absence of early evaporites like salt, gypsum, and anhydrite, and of sulphur in beds suggests that the ocean was not very saline.

**STUDIES AND ANALYSES OF INTERSTITIAL WATERS—CONNATE WATERS.**

A feature to which I have paid special attention is the interstitial water held between the grains of sediments or igneous rocks.

The term "connate" I introduced in 1908 to emphasize the fact that the circulation of "vadose" water from the surface and "juvenile" water given off by magmas from the interior must first replace the water which generally occupied the original interstices of the rock, if there was any porosity. However, the water now in the interstices practically never has the absolutely unaltered connate composition.

Alteration may be due to: (1) circulation, of course; (2) reaction with the rock grains; (3) chemical instability, especially in the presence of bacteria. For instance, as Daly pointed out, organic matter may reduce sulphates and generate carbonates. The water itself may enter into new hydrated mineral compounds. Magnesium may be extracted out to form dolomite or bentonite or various chloritic minerals. Oil-field waters are often strikingly low in magnesium compared with sea water. Base exchange (i.e. "permutite") reactions occur. But in general they do not seem to lower the ratio of Na:Cl in the interstitial waters as might sometimes be expected.

As strata are laid down, they may be filled with air, as in sand dunes and eolian deposits generally; or filled with pond or river water, that contains varying amounts of air and oxygen; or with lake or playa water; or with ocean water, either of the open ocean or of brackish arms or extra-saline bays; or, in the till or other subglacial deposits, with an extra pure ice water.

All these are connate by my definition, even though the term has been most generally used and applied to those waters whose saline character enables us to recognize a large proportion of marine connate water. In time to come one may be able to identify more surely continental connate waters.
The saline waters and the reduction of sulphates is so often associated with oil that many hundreds of analyses have been made and an excellent annotated bibliography on oil-field waters has been issued.\(^4\) Determination of only five ions is so generally made, however, that the analyses are available for wide correlations. These are the three acid ions: Cl, SO\(_4\), CO\(_3\), or HCO\(_3\) and two bases, Ca, Mg. The alkalies (Na) may be estimated as enough to balance the acids by difference if the water is neutral. Small quantities of bromine and iodine included with the chlorine, or strontium and barium included in the calcium, or possibly selenium and uranium will also prove to be significant if and when they are determined. A spectroscopic analysis of the minor ingredients is desirable beside the customary analysis. Recent work on F is suggestive. Fe is often determined. Determinations of K are not made often enough to justify sweeping statements.

Rock cores from a well, promptly dipped in paraffin to prevent evaporation, contamination, and loss, immersed in boiling hot distilled water when they reach the chemical laboratory to remove the paraffin and other contamination, and then put to soak in a known amount of distilled water (enough to cover them) for a day or more will show in the analysis of that water proportions of elements and ion which are significant of the interstitial and perhaps of the connate water.

The most inclusive generalization I can make is regarding the ratio Na:Cl. In Continental waters and vadose waters, even those which have circulated far underground, the carbonate is usually more characteristic than the Cl, and the Na:Cl ratio is practically always higher than in the ocean (0.55). This may be traced from the Rocky Mountains in the work of Crawford, Renick, W. B. Riffenberg, and others down across the Great plains to the Gulf of Mexico. This statement may also apply to water which circulated from buried land surfaces, now represented by unconformities.

Water in western closed basins may have Na:Cl nearly as high as a salt solution (NaCl), i.e. 0.65, as might be expected if the water came from leaching rock-salt outcrops.

If salt beds are precipitated from the ocean or arms of the sea, the residual brine or bittern will have the Na:Cl ratio increased if it was already above 0.65, lowered if the ratio was originally below. This latter is almost always what seems to

have happened. This is a confirmation of what otherwise appears in the analyses—that the open ocean water has always had NaCl lower than at present, and the tendency in geologic times is for the Na:Cl ratio in the ocean to rise.

In the post-paleozoic waters, the Na:Cl ratio is hardly ever below 0.5. In the upper Paleozoic, 0.45 seems to be more characteristic, though I am bothered with probable circulation from the time of the Appalachian Uplift. In the lower Paleozoic, the Na:Cl ratio seems to get down at least to 0.3.

In the copper mines of the Keweenaw Peninsula, the ratio gets down to 0.07. This might be due to residual magmatic waters; but according to the suggestion of Daly and myself and Quinton, in the earliest rocks without calcareous fossils, the calcium or total salts should be below the physiological optimum, which is some seven parts per thousand.

STUDIES ON THE BOTANICAL FORMATION OF LIMESTONE.

Studies with Charles A. Davis on the marl lakes of Michigan suggest the importance of vegetation like the Chara in forming limestone deposits even in quite fresh water. A similar origin might be ascribed to the Grenville and other pre-Cambrian limestones.

RELATIVE PROPORTION OF THE ISOTOPES IN ELEMENTS.

E. A. Gulbranson and A. O. Nier have found some indication that the proportion of C\(^{12}\) is slightly greater in coal than in the carbonates while meteorite carbon comes between.

The Pb in the early-formed sediments, so far as it was precipitated from the ocean, should have more of the early and more rapidly-formed isotopes of lead (Pb\(^{204}\) and Pb\(^{207}\)) than of the slower (Pb\(^{206}\) and Pb\(^{208}\)). To test this, the proportion of isotopes in the lead ores contemporary with the sediments in which they occur should be determined. Dr. H. Berman had picked out a suite for this purpose for study by Professor A. O. Nier.

A sample of chlorine water from deep in the Calumet and Hecla mine sent by me to Madame Curie, however, gave E. Gleditsch no indication of variation of isotopes.

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