GEOLOGIC HISTORY OF SEA WATER

An Attempt to State the Problem

(Address of Retiring President of The Geological Society of America)

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Abstract

Paleontology and biochemistry together may yield fairly definite information, eventually, about the paleochemistry of sea water and atmosphere. Several less conclusive lines of evidence now available suggest that the composition of both sea water and atmosphere may have varied somewhat during the past; but the geologic record indicates that these variations have probably been within relatively narrow limits. A primary problem is how conditions could have remained so nearly constant for so long.

It is clear, even from inadequate data on the quantities and compositions of ancient sediments, that the more volatile materials—H_2O, CO_2, Cl, N, and S— are much too abundant in the present atmosphere, hydrosphere, and biosphere and in ancient sediments to be explained, like the commoner rock-forming oxides, as the products of rock weathering alone. If the earth were once entirely gaseous or molten, these "excess" volatiles may be residual from a primitive atmosphere. But if so, certain corollaries should follow about the quantity of water dissolved in the molten earth and the expected chemical effects of a highly acid, primitive ocean. These corollaries appear to be contradicted by the geologic record, and doubt is therefore cast on this hypothesis of a dense primitive atmosphere. It seems more probable that only a small fraction of the total "excess" volatiles was ever present at one time in the early atmosphere and ocean.

Carbon plays a significant part in the chemistry of sea water and in the realm of living matter. The amount now buried as carbonates and organic carbon in sedimentary rocks is about 600 times as great as that in today's atmosphere, hydrosphere, and biosphere. If only 1/100 of this buried carbon were suddenly added to the present atmosphere and ocean, many species of marine organisms would probably be exterminated. Furthermore, unless CO_2 is being added continuously to the atmosphere-ocean system from some source other than rock weathering, the present rate of its subtraction by sedimentation would, in only a few million years, cause brucite to take the place of calcite as a common marine sediment. Apparently, the geologic record shows no evidence of such simultaneous extinctions of many species nor such deposits of brucite. Evidently the amount of CO_2 in the atmosphere and ocean has remained relatively constant throughout much of the geologic past. This calls for some source of gradual and continuous supply, over and above that from rock weathering and from the metamorphism of older sedimentary rocks.

A clue to this source is afforded by the relative amounts of the different "excess" volatiles. These are similar to the relative amounts of the same materials in gases escaping from volcanoes, fumaroles, and hot springs and in gases occluded in igneous rocks. Conceivably, therefore, the hydrosphere and atmosphere may have come almost entirely from such plutonic gases. During the crystallization of magmas, volatiles such as H_2O and CO_2 accumulate in the remaining melt and are largely expelled as part of the final fractions. Volcanic eruptions and lava flows have brought volatiles to the earth's surface throughout the geologic past; but intrusive rocks are probably a much more adequate source of the constituents of the atmosphere and hydrosphere. Judged by the thermal springs of the United States, hot springs (carrying only 1 per cent or less of juvenile matter) may be the principal channels by which the "excess" volatiles have escaped from cooling magmas below.

This mechanism fails to account for a continuous supply of volatiles unless it also provides for a continuous generation of new, volatile-rich magmas. Possibly such local magmas form by a continuous process of selective fusion of subcrustal rocks, to a depth of several hundred kilometers below the more mobile areas of the crust. This would imply that the volume of the ocean has grown with time. On this point, geologic evidence permits differences of interpretation; the record admittedly does not prove, but it seems consistent with, an increasing growth of the continental masses and a progressive sinking of oceanic basins. Perhaps something like the following mechanism could account for a continuous escape of volatiles to

the earth's surface and a relatively uniform composition of sea water through much of geologic time: (1) selective fusion of lower-melting fractions from deep-seated, nearly anhydrous rocks beneath the unstable continental margins and geosynclines; (2) rise of these selected fractions (as granitic and hydrous magmas) and their slow crystallization nearer the surface; (3) essentially continuous isostatic readjustment between the differentiating continental masses and adjacent ocean basins; and (4) renewed erosion and sedimentation, with resulting instability of continental margins and mountainous areas and a new round of selective fusion below.

CONTENTS

ILLUSTRATIONS

INTRODUCTION

I trust that all of you recognize that the title of this paper is largely a figure of speech. It would be interesting and even, for some inquiries, useful if we knew the history of the earth's sea water and atmosphere. But that history cannot be told until we have solved nearly all other problems of earth history. My title might much better have been "The problem of the source of sea water and its bearing on practically everything else".

Even with this modification, you still may wonder what qualifications I must think I possess to justify undertaking a subject of such global dimensions. I had originally intended to explain that I am neither an oceanographer, a geochemist, nor a Precambrian geologist, and therefore that I have no special qualifications whatever for undertaking this problem. But after discussions with various colleagues—paleontologists, petrologists, geophysicists, structural geologists, and others—I feel somewhat less modest. It seems that the subject I have selected is one in which all geologists, equally, are experts.

My interest in this general problem grew from a paper on which I began working a number of years ago. Trying to test the possibility that the phosphate rock of western Wyoming may have been laid down by direct chemical or biochemical precipitation from sea water, I began searching for some basis on which to estimate the composition of sea water and the carbon dioxide content of the atmosphere in Permian time.

It soon became evident that this question ramifies almost endlessly into nearly every fundamental problem of earth history and far beyond into the foggy borderlands between

other scientific disciplines. Eventually I began to realize some of the broader implications of the problem I had tackled. I wish to take this opportunity to review what I think I have learned about the probable history of sea water and to indicate what I think this all means in terms of general earth history.

The principal conclusions of this paper were presented orally, in December 1948 and April 1949, before the Geological Society of Washington under the titles, *The problem of changes in composition of sea water and atmosphere during the geologic past* and *A possible mechanism for the continuous supply of volatiles at the earth's surface*. Since then the main thesis has been given before various groups, in successively revised form and with different points of emphasis.

In preparing this paper I have had the unsuspecting collaboration of nearly every geologist and countless others I have talked with during the past few years. Many of my colleagues of the U. S. Geological Survey and the staff members of the Geophysical Laboratory have been most generous with their criticisms and suggestions. K. J. Murata, James Gilluly, W. T. Pecora, and D. T. Griggs have been especially helpful in leading me across some of my worst gaps of data, logic, and understanding. It is only fair to add, however, that none of these many collaborators are to be held in any way responsible for the pattern of conclusions I have tried to weave from the varied threads of our discussions.

COMPOSITION OF SEA WATER AND ATMOSPHERE IN THE PAST

Lines of Possible Evidence

No more than a brief review can be attempted here of the several lines of evidence that afford at least some information about the probable composition of sea water and atmosphere in the past. I cannot refrain, however, from emphasizing the one that seems to me most promising—and most neglected. The intimate dependence of living organisms on the chemical and physical conditions of their environment is so familiar—for example, an adequate supply of oxygen in the air we breathe—that we are inclined to take it all for granted. Were it not for the small amount of ozone in the upper atmosphere, which absorbs most of the deadly ultraviolet radiations, land-living or-

ganisms could not survive in direct sunlight (Poole, 1941, p. 346; Giese, 1945, p. 226, 243–246; Allee and others, 1949, p. 74). Yet, if the amount of ozone were much greater than it is, no anti-rachitic or "sunshine" vitamin, essential to the nutrition of most animals, would be produced (Stetson, 1942, p. 18–19). Likewise, many species of modern invertebrates can tolerate only narrow ranges in the salinity of their environment, largely because of the osmotic pressures that are involved (Dakin, 1935; p. 12, 16, 25–27; Rogers, 1938, p. 670; Gunter, 1947). Many organisms have very specific requirements, on the one hand, and tolerances, on the other, for the amounts of dissolved calcium, sodium, potassium, and other elements in the waters in which they live (Rogers, 1938, p. 430, 680–682). It seems not unlikely that the ancestors of some of these modern forms may have been subject to similarly rigid requirements.

Needless to say, it is hazardous to assume that ancient animals and plants had exactly the same chemical and physical requirements as their modern descendants. Conditions may have changed gradually, and the organisms may have modified their requirements by evolutionary adaptations. Yet precisely this same hazard accompanies any effort whatever to interpret the ecology of ancient plant and animal communities. The considerable measure of success that has been attained in paleo-ecologic interpretations by paleontologists and ecologists, working together and balancing several lines of evidence, shows that, while the problem is difficult, it is not insuperable (Twenhofel, 1936; Vaughan, 1940, p. 457; Ladd, 1944; Lowenstam, 1948, p. 104–114, 140–142; Cloud and Barnes, 1948, p. 31, 58–66).

Paleontologists have given relatively little attention to chemical factors in the environment of ancient organisms. The most noteworthy efforts I know about have been made by a few physiological chemists (Macallum, 1904, p. 561; 1926, p. 317–322, 341–348; Henderson, 1927, especially p. 38–190; Conway, 1942; 1943). Macallum believed that the blood serum and body fluids of many animals reflect closely the composition of sea water at the time when their respective ancestral

lines became established. From this hypothesis he deduced a history of the composition of sea water. However, many physiologists do not accept Macallum's main premise. Many of you are familiar with L. J. Henderson's fascinating volume, *The fitness of the environment*, which presents the thesis that life as we know it today would be impossible if the physical and chemical conditions on the earth were much different from those of the present. All in all, it seems likely that the most definite information about the composition of sea water and atmosphere during the past will come, eventually, from the joint efforts of biochemists, ecologists, and paleontologists.

Another possible line of evidence on the composition of ancient sea water has proved much less dependable than was at first hoped. When A. C. Lane (1908, p. 63, 125) defined *connate waters*, it was with the thought that they represent samples of the original water in which a sediment was deposited. As information about these brines has grown, however, it has become increasingly evident that many chemical and physical processes have been modifying these waters since deposition of the enclosing sediments: adsorption, base exchange, dolomitization, evaporation, sulphate reduction, hydration and recrystallization of clay minerals, and other processes (Mills and Wells, 1919, p. 67–68; Newcombe, 1933, p. 189–196; Piper, 1933, p. 82, 89; W. L. Russell, 1933; Crawford, 1940, p. 1221–1222, 1317–1319; Heck, Hare, and Hoskins, 1940; Foster, 1942, p. 846–851). It now seems likely that most so-called connate waters have been so altered in composition that they do not represent at all accurately the original water of deposition.

Two other lines of evidence that afford some information on the probable composition of sea water and atmosphere in the past may be mentioned briefly: (1) Spectroscopic data on the solar and stellar abundances of chemical elements (Goldschmidt, 1938, p. 99–101, 120–121; Brown, 1949b, p. 625–627) and on the composition of the atmospheres of other planets (Wildt, 1942; Kuiper, 1949, p. 309, 326) set limits to the range of permissible speculation. (2) Sedimentary rocks of certain ages appear to have distinctive chemical or mineral characteristics over wide areas. The iron formations

of the Precambrian (Eskola, 1932b, p. 39–40, 54; Leith, 1934, p. 161–164), the magnesian limestones of Precambrian and early Paleozoic age (Daly, 1909, p. 163–167), the coal beds of the Carboniferous, and other examples (Rutherford, 1936, p. 1212–1214; Landergren, 1945, p. 26–28; Lane, 1945, p. 396–398) have been mentioned as possibly indicating changes in chemical conditions on the earth with lapse of time. However, either the existence of these supposed worldwide similarities or, where their existence seems clear, this particular interpretation of their significance has been questioned (Clarke, 1924, p. 579; Leith, 1934, p. 161; Pettijohn, 1943, p. 957–960; Conway, 1943, p. 174–179, 200–202; 1945, p. 593–601, 603–604; Bruce, 1945, p. 589–590, 601; Miholić, 1947, p. 719). On the whole, it appears likely that there have been some real changes in the composition of sea water and atmosphere with time but that these changes must have been relatively small.

In the interest of brevity, I may summarize by stating that several lines of evidence seem to indicate some actual changes in the composition of sea water and atmosphere with time. Yet, the more closely one examines the evidence, the more these changes appear to be merely second-order differences. Everything considered, the composition of sea water and atmosphere has varied surprisingly little, at least since early in geologic time. This is certainly no startling conclusion to bring to an audience of geologists. It might even be considered as simply one of the underlying facts of geologic history on which the doctrine of uniformitarianism is based. Yet such a relative constancy of the composition of sea water throughout much of the geologic past has far-reaching implications, and these implications are worth a more careful consideration than they have sometimes received.

Method of Geochemical Balances

The most definite information about the paleochemistry of sea water and atmosphere may come eventually from the biologists, but the best evidence now available seems to lie in a comparison of the composition of rocks that have been weathered and of sediments that have been deposited during the geologic past. This general method has been used by Clarke (1924, p. 31–32), Goldschmidt (1933,

p. 131–133), Kuenen (1946), and others (Leith and Mead, 1915, p. 73; Twenhofel, 1929, p. 395–399) to estimate the total mass of rocks eroded and sediments deposited. Using a modification of this method, I have attempted to bring these earlier estimates up to date. But one must still rely on much the same data used by others; and attempted refinements of the method still give pretty much the same answers as before. Suffice it to say that, when this method is applied to rocks of different ages and to each of the commoner rock-forming elements—silicon, aluminum, iron, calcium, and several others—, the results are in surprisingly good agreement with one another. But for another group it is clear, even with present data, that there is no such agreement. All the constituents of this latter group are much too abundant in the present atmosphere and hydrosphere and in ancient sediments to be accounted for as simply the products of rock weathering—the explanation that fits well enough for the commoner elements. Compared with the commoner rock-forming oxides, the members of this group are all relatively volatile[1]. They are the substances which, in the language of the early chemists, we might call the *distillable spirits* of the earth's solid matter.

I had originally intended to present in this paper a detailed statement of the method by which these estimates have been made. The main paper grew out of all bounds in several directions, however, and these estimates and a fuller statement of the method by which they were derived must be reserved for publication in a separate article. The method of geochemical balances, as it might be called, can be outlined only briefly here.

In any given unit of geologic time, the quantity of material weathered and eroded from (*a*) crystalline rocks and (*b*) previously formed sedimentary rocks, plus (*j*) juvenile matter from volcanic gases, hot springs, etc., equals the quantity of material deposited as sediments on (*c*) continental platforms and (*d*) the deep-sea floor, plus (*s*) matter stored in sea water or escaped into interstellar space.

The results of applying this general equation of geochemical balances are the basis for much of the entire discussion that follows. For some elements, such as Si, Al, and Fe, which are relatively non-

volatile and sparingly soluble at moderate temperatures, the juvenile and stored-in-sea terms are probably negligible; so that for these elements the general equation can be simplified considerably. If we have reasonably good estimates of the chemical composition of crystalline rocks, older sedimentary rocks, new continental deposits, and new deep-sea sediments, we can find for each constituent the relationship between *a*, the proportion of crystalline rocks to all rocks eroded, and *c*, the proportion of continental sediments to all sediments deposited. From the percentages of two chemical constituents in each kind of rock eroded and sediment deposited, we can find one expression relating *a* to *c*. From percentages of more than two constituents in each rock and sediment, we obtain several simultaneous equations that permit a fairly rigorous test of the chemical compositions we have used.

This is all simple enough in theory, but it is difficult in practice because accurate and representative analyses of sediments are not available. It is encouraging that a National Research Council committee is now being organized to improve available information on the chemical composition of sedimentary rocks. But, even from present information, it is possible to learn something by means of this general equation (or rather the series of equations derived from it) and to obtain results that are not grossly in conflict with other types of evidence.

It turns out that, for average crystalline rocks and sediments of Mesozoic and later ages, the average chemical compositions now available agree surprisingly well with one another for most of the permanent rock-forming oxides—SiO_2, Al_2O_3, total Fe, CaO, Na_2O, K_2O, TiO_2, and P_2O_5. If the average composition of igneous rock in earlier times was somewhat nearer that of plateau basalt, this statement is also true for sedimentary rocks of Paleozoic and even Precambrian age.

This general equation gives only ratios between the several kinds of rocks eroded and sediments deposited. Three independent estimates (based on the amount of sodium now dissolved in the ocean, the quantity of continental sediments remaining uneroded today, and the mean rate of deep-sea sedimentation) accord reasonably well in their results and thus afford means for converting these ratios into quantities of rocks eroded and sediments deposited. When all is done, the final estimates have at least this to recommend them: for the greater part they fall well within the range of estimates that Clarke, Goldschmidt, Kuenen, and others have made by simpler and more direct methods.

The foregoing statements apply to the major rock-making constituents, which are the ones that agree rather well with one another in the general

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[1] Hence Fenner's convenient term, "volatiles", for the entire group (1926, p. 696–697).

equation of geochemical balances. Collectively they make up from 60 to 95 per cent of all the rocks eroded and sediments deposited. But for the re-

TABLE 1.—ESTIMATED QUANTITIES (in units of 10^{20} grams) of VOLATILE MATERIALS NOW AT OR NEAR THE EARTH'S SURFACE, COMPARED WITH QUANTITIES OF THESE MATERIALS THAT HAVE BEEN SUPPLIED BY THE WEATHERING OF CRYSTALLINE ROCKS

	H_2O	Total C as CO_2	Cl	N	S	H, B, Br, A, F, etc.
In present atmosphere, hydrosphere, and biosphere..	14,600	1.5	276	39	13	1.7
Buried in ancient sedimentary rocks.....	2,100	920	30	4.0	15	15
Total.....	16,700	921	306	43	28	16.7
Supplied by weathering of crystalline rocks..	130	11	5	0.6	6	3.5
"Excess" volatiles unaccounted for by rock weathering	16,600	910	300	42	22	13

maining constituents it is quite a different story. All but two of these latter form relatively volatile compounds at moderate temperatures and pressures; and it is the source of this group of volatile constituents that seems particularly significant in the geologic history of sea water and atmosphere.

Let us look at the way these "volatile spirits" are now distributed on and near the surface of the earth. In Table 1 are summaries of the best estimates I can find or make of the quantities of water, carbon dioxide, chlorine, etc., in today's atmosphere, ocean, fresh water, and organic matter. In the second row are the estimated totals of these constituents that are now buried in sedimentary rocks and that must have been part of the atmosphere and

ocean in earlier times. Next we have the sums of the first and second rows, the quantities that must have come from somewhere and whose source should be accounted for. In the fourth row, we have, from the amount of crystalline rocks that must have been eroded to form all the sediments and from the composition of average igneous rocks, the amounts that must have been released by the weathering of crystalline rocks. Finally, in the last row, the differences between the quantities in the third and fourth rows, we have the "excess" volatiles that cannot be accounted for ² simply the products of rock weathering. ⁷⁰ˣ

For the sake of simplicity, C is shown as CO_2 in Table 1. This arbitrary convention oversimplifies the actual situation, for O does not occur in the right amounts to balance C as CO_2 exactly. Estimating directly (in units of 10^{20} g), the amount of O not combined in permanent rock oxides and in water, we find about 12 units in the atmosphere, 26 in the SO_4 of sea water, and small amounts in HCO_3, H_2BO_3, and elsewhere, giving a total of approximately 39 units of O in the present atmosphere, hydrosphere, and biosphere. In sedimentary rocks, estimates indicate about 490 units in the carbonates, 25 in organic matter, 21 in SO_3, 14 in the oxidation of FeO to Fe_2O_3, and 2 in the interstitial water, giving altogether about 550 units of O in the ancient sedimentary rocks. This, together with that in the atmosphere, etc., makes a total of about 589 units. Approximately 8 units of O have probably been released during the weathering of the small amount of CO_2 in crystalline rocks and 75 units from the Na, Mg, Ca, and K now dissolved in sea and interstitial water, which comes to a total of 83 units from rock weathering. This leaves (589 − 83 =) 506 units of O "unaccounted for" and is to be compared with ($\frac{12}{44} \times 910 =$) 248 units of C similarly "unaccounted for".

If no other complications were involved, these quantities might be explained by the release of 483 units of CO_2 and 271 units of CO from some other unspecified source. But to find a more meaningful balance between the "excess" C and O, one must consider also the probable composition of other gases, besides CO_2 and CO, that may have come from the same unspecified source. Associated with an estimated 68 units of C and 25 units of O in the organic matter in sedimentary rocks, there should be about 9.6 units of H. If this was released originally as H_2O, it would account for 76 of the 506 units of "excess" O in the above calculation. On this assumption, the "excess" of 248 units of C and

(506 − 76 =) 430 units of O would be equivalent to 274 units of CO_2 and 404 units of CO.

It is conceivable, however, that the "excess" Cl, N, S, Br, and F shown in Table 1 were originally released as HCl, NH_3, H_2S, HBr, and HF. If so, the 19 units of H thus required have since lost their identity, presumably by oxidation to H_2O; and this oxidation would have subtracted approximately 150 units of O from the original C-O mixture. On this assumption, the original "excess" of 248 units of C and (430 + 150 =) 580 units of O would have been equivalent to 687 units of CO_2 and 141 units of CO.

In these three hypothetical mixtures of CO_2 and O, the CO_2 ranges between 40% and 83%. If the original gases also contained significant quantities of methane, CH_4 (Poole, 1941, p. 350–351), the percentage of CO_2 would have been correspondingly higher. It is evident that the proportion of "excess" C originally released as CO_2 cannot be estimated, even approximately, unless the original composition of all the "excess" volatiles is known. For this reason, all C is shown by arbitrary convention in Table 1 as CO_2.

POSSIBLE SOURCE OF THE "EXCESS" VOLATILES

Nomenclature[2]

Only two possible sources of the "excess" volatiles occur to me: Either (a) they are largely or entirely residual from a primitive atmosphere and ocean; or (b) they have largely or entirely risen to the surface from the earth's interior during the course of geologic time.

A few years ago an eminent geologist, in discussing magmas, divided those who have views on the subject into the *pontiffs* and the *soaks*. The classification is not directly applicable to those who have views on the origin of the ocean. But here, also, we have two opposing schools of thought, and, with apologies to Bowen (1947, p. 264), his classification may readily be modified to fit the occasion. From the very nature of the problem, there can be no anhydrous pontiffs when the origin of the ocean is considered but only soaks of one persuasion or another. Here, we may say, we have the *quick soaks* who prefer to have the wetness of the ocean there at the very beginning, all of it at once; and then there are the *slow soaks* who prefer to increase the liquor gradually by small increments over a

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[2] Literally, "name-calling".

much longer period of time. The quantities involved are the same by both courses of action, but the effects are conspicuously different: Taken in small drafts and with a proper regard for timing, an astonishingly large quantity of volatile spirits can be handled by the earth without showing it; but taken hastily, even moderate amounts are almost certain to have noteworthy effects.

Dense Primitive Atmosphere—Solution in the Melt

The two contrasting procedures or viewpoints just mentioned afford a basis for discussing the probable source of these "excess" volatiles. In the opinion of some who have considered the problem—those who are of the "quick-soak" school of thought—, the source of these volatiles can be deduced without too much trouble merely from a consideration of the conditions of the primitive earth. Their argument runs something like this: As the earth was probably once molten throughout, it follows that all or a large part of the water, carbon dioxide, etc., would have been volatilized in a primitive atmosphere. On subsequent cooling, the water vapor would condense into a primitive ocean; and the present hydrosphere and atmosphere are thus residual from this primitive ocean and atmosphere.

Yet, when we examine it more closely, this conclusion is not altogether convincing. To begin with, it is by no means certain that the earth was originally molten (R. T. Chamberlin, 1949, p. 252–253; Latimer, 1950; Slichter, 1950). The inert gases—neon, argon, krypton, and xenon—are from 10^6 to 10^{10} times less abundant on the earth than in the atmospheres of the stars, the lighter gases showing the greater discrepancies. Compounds and elements of the same molecular weights—water, nitrogen, carbon dioxide, carbon monoxide, and oxygen— would have been lost in the same proportions if they too had existed as gases when the earth was formed. The fact that water is present in considerable quantity on the earth today is evidence that much of it was bound in chemical compounds or occluded in solid (that is, in relatively cool) matter when the earth accumulated (Aston, 1924; Jeffreys, 1924; Russell

and Menzel, 1933, p. 999–1001; Rayleigh, 1939, p. 463; Brown, 1949a; Gibson, 1949, p. 278; Suess, 1949; Jones, 1950, p. 420, 423–424, 428–429). This leaves us with two alternatives: either the earth remained solid from the beginning, except for local melting; or it was first cold, then heated by some process until molten throughout (Urry, 1949, p. 172, 179) and finally solidified again. Whichever one of these two theories may ultimately prevail, the evidence appears distinctly unfavorable to the concept of an atmosphere that ever contained very much of the earth's total volatiles. Instead, this evidence seems to call for some mechanism by which the volatiles were largely retained within the interior of the earth, to the extent of only a few tenths of 1 per cent of the solid matter. This appears entirely possible, whether or not the earth was ever completely molten.

These interpretations are not new, but neither are they as widely accepted as I think they deserve to be. I shall try, therefore, to show why a consideration of the geologic record leads me to these conclusions.

We might start by attempting to follow through, in a semiquantitative way, some of the consequences of a dense primitive atmosphere. If all the water in today's atmosphere and hydrosphere and in ancient sediments were once present in a primitive atmosphere, and if this atmosphere were in contact with molten silicate rock, then some fraction of the water would dissolve in the melt, the amount depending on the vapor pressure, the solubility of water in the melt, and the total quantity of molten material. Using Goranson's data for the solubility of water in a melt of granitic composition, one finds that, at this vapor pressure, the melt would dissolve $2\frac{1}{2}$ per cent by weight of water.

As the deeper-lying rocks probably now contain considerably less than $2\frac{1}{2}$ per cent water, this must be simply a limiting case. If there were then any considerable quantity of molten material and if this were stirred by convection currents, the water that would dissolve in the melt would materially reduce that in the atmosphere until an equilibrium was reached. Making allowance for the water now in deep-lying rocks, calculation shows that

a primitive atmosphere in equilibrium with a completely molten earth would contain less than one-tenth the amount of water in the present ocean. As the supposed molten earth cooled and crystallized, the water in the remaining melt and in the atmosphere would be unlikely to remain in equilibrium, for the surface would probably crust over with slag long before the interior had fully crystallized. Thus, when crystallization was completed, the primitive atmosphere, even on this hypothesis, would probably contain at that stage, as it had at the very beginning, much less water than the present ocean.

Goranson's data on the solubility of water in a melt of granitic composition at the temperatures and pressures at which crystallization begins (Goranson, 1932, p. 229–231) appear to be the most nearly applicable to the conditions here postulated. I find no data on the solubility of other gases in silicate melts of the required composition. One would expect, from the work of Morey and Fleischer (1940, p. 1051–1057) on the system CO_2-H_2O-K_2O-SiO_2, that the proportion of CO_2 to H_2O dissolved in the melt would be somewhat higher than that in the vapor phase or atmosphere in equilibrium with it, but not enough higher to modify the results of the following calculation significantly.

Under the assumed conditions, the primitive atmosphere would contain 16.6×10^{20} kg of water vapor. Over the 5.1×10^{18} cm^2 area of the earth's surface, this quantity of water would exert a pressure of 325 kg/cm^2. Goranson found that a melt of granitic composition at liquidus temperatures dissolved 3% by weight of water at 400 bars[3] and 2% water at 260 bars (Goranson, 1932, p. 234). Interpolating between these values, it appears that, at a vapor pressure of 325 kg/cm^2, a melt of this composition would dissolve 2.5% water, and the temperature of crystallization would be about 985°C.

If the rock materials of the earth's crust retained after crystallization, and still contained today, an average of about 2.5% water, the results of this calculation would be of greater significance. Actually they now contain much less than this—only 1.15% in Clarke and Washington's average igneous rock (Clarke, 1924, p. 29). On this hypothesis, over half of the calculated 2.5% water in the melt must have escaped to the surface during or after crystallization. This means that some unspecified quantity of the water in today's atmosphere, ocean, and sedi-

[3] 1 bar = 1.01972 kg/cm^2 (Birch, Schairer, and Spicer, 1942, p. 319.)

mentary rocks was not there earlier and so was not present in the supposed primitive atmosphere. Hence the original vapor pressure would have been less than the 325 kg/cm² calculated from today's total of 16.6 × 10²⁰ kg. The amount of this difference depends largely upon the quantity of melt that was involved in the assumed equilibrium.

With present data, the amount of water in the supposed primitive atmosphere can be estimated only within rather broad limits. For purposes of this calculation, the average water content of crystallized rock to a depth of about 40 km may be taken as near 1.15%. This would amount to 6.6 × 10²⁰ kg of water. If this thickness of 40 km of rock were molten, the total water in the primitive atmosphere and melt together would be (16.6 + 6.6 =) 23.2 × 10²⁰ kg. From Goranson's data it may be found that, under conditions of equilibrium, 46% of this total water would be dissolved in the melt; the remainder left in the atmosphere would exert a vapor pressure of 244 kg/cm² at the earth's surface. At this pressure the granitic melt would dissolve 1.9% water, and the melting point would be about 1010°C. If it were true that the rocks of the earth's interior now contain 1.15% water to a depth of 300 km, similar reasoning would show that about 85% of the total water would have been dissolved in the melt; the amount remaining in the atmosphere would have had a vapor pressure of 175 kg/cm², and the melt would have contained about 1.3% water.

It is extremely doubtful, however, that rocks lying more than a few tens of kilometers below surface contain as much as 1.15% water. For the rocks of the deep interior, direct determination of the water content is, of course, impossible; and there is little on which to base an estimate other than the composition of stony meteorites (Clarke, 1924, p. 42–44; Brown, 1949b, p. 627–629). Meteorites contain few if any hydrous minerals; yet an average of 63 chemical analyses, "of the highest grade obtainable", of stony meteorites gives 0.47% H₂O (Merrill, 1930, p. 16–17), and a recent digest of all earlier analyses shows an average content of 0.063% H [equivalent to 0.56% H₂O]. (Brown, 1949b, p. 626). Some of this water, in even the most carefully collected and analyzed samples, may be the result of weathering after the meteorites reached the earth. At least some, however, is probably present as original impurities or occlusions, as seems indicated by the quantities of H₂, CO₂, and other gases in both stony and iron meteorites (R. T. Chamberlin, 1908, p. 26; Farrington, 1915, p. 190–196; Nash and Baxter, 1947, p. 2541–2543). More data on the volatile content of stony meteorites are badly needed; but from present information the best estimate for the siliceous rocks of the earth's interior,

from depths of 40 km to 2900 km, is probably about 0.5% H₂O.

If the iron meteorites are similarly taken to represent the materials of the earth's iron core, from 2900 km to the center, we may assume the water content there is negligible.

For rocks of the deep interior, one should logically have data on the solubility of water in melts of basaltic or peridotitic composition. However, in comparison with the uncertainties about present water content of these rocks at depth, the lack of data on the solubility of water in a more basic melt is no actual handicap. Increasing pressure at greater depth would increase very considerably the solubility of water in silicate melts (Goranson, 1931, p. 492–494). Under the assumed conditions of a molten earth and with the relatively small quantities of water involved, it is probable that nowhere would the amount of water carried down into the interior by convection currents exceed that which could be dissolved in the deeper-lying melt of different composition. The controlling factor therefore would be the solubility of water in the part of the melt that was in contact with the atmosphere.

For the densities of rocks at various depths to the center of the earth, Bullen's values (1940, p. 246; 1942, p. 28), which are calculated from seismic and astronomic data, may be used.

With these various estimates, it may be calculated that, in an earth molten to the base of the silicate mantle at 2900 km, the total water in the primitive atmosphere and silicate melt would have been (16.6 + 207 =) 224 × 10²⁰ kg. Under conditions of equilibrium, approximately 98% of this total would be dissolved in the melt. The remainder left in the atmosphere would have a vapor pressure of 76 kg/cm² at the earth's surface, and the melt would contain about 0.54% by weight of water. In an earth entirely molten to the center of the iron core, approximately 99% of the total water would be dissolved in the melt. The remainder in the atmosphere would have a vapor pressure of 52 kg/cm², and the melt would contain 0.37% H₂O. This water in the primitive atmosphere, about 2.6 × 10²⁰ kg, would be only 16% of the total in today's atmosphere and ocean and buried in ancient sedimentary rocks. If the estimate used here of 0.5% H₂O in the earth's siliceous mantle is too high, the total quantity of water involved in the equilibria would be less, and the remainder in the primitive atmosphere would be even lower than 16% of that today.

For purposes of presentation, this calculation has proceeded through steps of increasing depth of melting from the earth's surface downward to the center of the earth. Actually the hypothesis of an originally molten earth requires the reverse order,

starting with a completely molten condition and solidifying from the bottom or, rather, from the base of the silicate mantle, upward (Adams, 1924, p. 467–468). If, at any stage of cooling, the surface crusted over with slag, equilibrium between the water content of the atmosphere and melt could no longer be maintained, and the primitive atmosphere would end up with some earlier water content, which would be much less than 16.6×10^{20} kg.

If, on the other hand, the surface did not crust over before the earth solidified throughout, heat from the deep interior would continue to escape rapidly; and solidification would probably have been completed within a few tens of thousands of years (Jeffreys, 1929, p. 79, 147–148; Slichter, 1941, p. 567, 582–583). With such rapid freezing, it is improbable that equilibrium could have been maintained between the water content of the atmosphere and that of the immense volume of the melt. Thus, on this alternative also, the primitive atmosphere would probably end up with a water content significantly less than 16.6×10^{20} kg.

Dense Primitive Atmosphere—Chemical Effects

A totally different line of approach also indicates that the fraction of present hydrosphere and atmosphere that might be residual from a primitive ocean and atmosphere is probably very small. Let us assume, for purposes of calculation, that all the "excess" volatiles were once in a very hot atmosphere; that, on cooling, the water vapor condensed to liquid and dissolved all the chlorine, fluorine, bromine, etc.; and that the principal gases— carbon dioxide, nitrogen, and hydrogen sulphide—were dissolved in the water according to their solubilities and partial pressures.

This would mean at first a very acid ocean (pH 0.3). This acid water would attack bare rock with which it came in contact, and the primitive ocean would rapidly take into solution increasing quantities of bases from the rocks, until the solubility product of calcite or dolomite was reached. Thereafter, as more dissolved bases were brought in by streams, carbonate would be deposited, and carbon dioxide subtracted from the atmosphere-ocean system.

Eventually conditions would be reached under which primitive life could exist. Certain mosses have been found to tolerate as much as one atmosphere of carbon dioxide (Ewart,

1896, p. 404, 406–407), an amount more than 3000 times that in the atmosphere today. If we take this value as a basis for estimating when life and the photosynthetic production of free oxygen began, we find that sea water then would have a pH of about 7.3; a salinity approximately twice that of the present; and, because of buffer effects, considerably more bicarbonate than chlorine in solution. The bases required to balance the acid radicals, added to those previously deposited as carbonates, would call for the weathering by that time of considerably more igneous rock than appears, from other evidence, to have been weathered in all of geologic time. And, even worse, more than half the original carbon dioxide would still remain in the atmosphere and ocean.

This hypothesis also calls for the deposition of tremendous quantities of carbonate rocks before the carbon dioxide of the atmosphere was lowered to the point where life could first exist. No such excessively large quantities of carbonates are known in the earliest Precambrian sediments. Compilations of measured thicknesses of sedimentary rocks suggest that the percentage of limestone in sediments of Precambrian age is about the same as (or perhaps lower than) that in later sedimentary rocks. Sederholm's estimate (1925, p. 4) indicates a very low proportion of limestones and dolomites in the Precambrian rocks of Finland. Schuchert's (1931, p. 58, 49) figures (25% limestone in the Precambrian, 20% limestone in Cambrian to Pleistocene inclusive) are heavily influenced by estimates, now known to be excessive (Osborne, 1931, p. 27–28), of the thickness of the Grenville series in southeastern Canada and so should be lowered somewhat. Leith's estimates (1934, p. 159–162) show from 1 to 48 (average about 19%) limestone in sections of Precambrian rocks in North America, Africa, and Asia and an average of 22% limestone in sedimentary rocks of later age. There is thus no indication in the geologic record of the tremendous quantities of early Precambrian limestone that would be required under this hypothesis. These and other semiquantitative tests make the hypothesis of a dense primitive atmosphere appear very improbable.

Under the given conditions of temperature, pressure, and composition (essentially no free hydrogen or oxygen), the quantities of the gases, CH_4, NH_3, and SO_2, that would be stable may be taken as negligible, and therefore the "excess" C, N, and S present as CO_2, N_2, and H_2S. If all the Cl, Br, and F were dissolved in 16.6×10^{20} kg water, they would amount to 0.529 acid equivalents per liter. Initially this amount of acid would be balanced almost solely by hydrogen ions, from which a hydrogen-ion concentration of $0.529 = 10^{-0.277}$ or a pH of 0.277 may be calculated.

This acid water would decompose the rocks with which it came in contact, and in so doing it would dissolve some of the bases. As a result, its acidity would decrease, and the chemical effects of dissolved gases would come to play an important part in the over-all balance. Better data are available for estimating the required coefficients at moderate temperatures than at those near the boiling point of water; and 30°C is here chosen as the basis for calculation. At this temperature and in sea water of normal salinity (35°/₀₀ or a "chlorinity" of 19.4 °/₀₀), the solubility coefficients of CO_2, N_2, and H_2S are estimated at 0.026, 0.0009, and 0.077 mols/liter (Harvey, 1945, p. 66; Sverdrup, Johnson, and Fleming, 1946, p. 191); the first and second apparent dissociation constants of CO_2 at 1.11×10^{-6} and 1.27×10^{-9} (Harvey, 1945, p. 64); the two comparable dissociation constants of H_2S at 3.0×10^{-7} and 2.8×10^{-14} (Latimer, 1938, p. 316); the single dissociation constant of H_3BO_3 at 2.26×10^{-9} (Harvey, 1945, p. 62); and the apparent solubility product of $CaCO_3$ at 1.2×10^{-6} (Revelle and Fleming, 1934, p. 2091; Wattenberg, 1936, p. 176; Smith, 1940, p. 182). Equations that express the relationships between various quantities involved in the CO_2 equilibria of sea water (Harvey, 1945. p. 61–68) may, with some patience, be solved by the method of successive approximations.

The proportions of the different bases dissolved when igneous rocks are decomposed by weathering may be estimated roughly from the average composition of waters of the type that drain from areas of igneous rock (75 stream waters lowest in salinity and highest in silica; Clarke, 1924, p. 111, 74–79, 81, 83, 89–91, 95–97, 103–105, 107–108). After correction for "cyclic salts" (Conway, 1942, p. 135–139, 155), this is found to be, in terms of the four principal bases,

Ca	52%
Mg	11%
Na	27%
K	10%
	100%

Other bases, acid radicals, and colloidal aggregates, including significant amounts of silica and iron, in such waters may be ignored for purposes of the present estimate.

An independent estimate of the relative abundance of the principal bases in such stream water may be made by applying Conway's average percentage losses on weathering of igneous rock (Ca —67%, Mg —18%, Na —41%, and K —26%; Conway, 1942, p. 153) to Clarke and Washington's average composition of igneous rocks (Clarke, 1924, p. 29). This gives, as the expected composition of stream water from igneous areas (in per cent),

Ca	53
Mg	8
Na	25
K	14
	100

The subsequent calculations depend primarily upon the proportion of dissolved Ca to total bases, and these two estimates therefore accord closely enough for present purposes.

As decomposition of rocks proceeded, more and more dissolved bases would be carried to the sea until the solubility product of $CaCO_3$ would eventually be reached, and carbonates would begin to precipitate. Using the foregoing data, it may be found that at this stage the concentration of $[Ca^{++}]$ in the sea water would be about 0.15 mols/l, that of $[CO_3^-]$ about 8×10^{-6} mols/l, and the pH 5.1. Approximately 29% of the total CO_2 would then be dissolved in the sea water, 0.6% of the N_2, and 52% of the H_2S. The gases remaining in the atmosphere would have partial pressures of $P_{CO_2} = 12.2$, $P_{N_2} = 1.27$, and $P_{H_2S} = 0.28$. Summing up the quantities of dissolved acids, bases, and atmospheric gases in the sea water would give a "salinity" of about 46 g/kg. (See Table 2, column 2.)[4]

With further rock weathering and transportation of dissolved bases to the sea, carbonates would continue to be deposited and CO_2 subtracted from the atmosphere-ocean system. At the arbitrarily assumed $P_{CO_2} = 1.00$, at which it is conceivable that living organisms could survive, it may be found that 980×10^{20} g $CaCO_3$ would have been precipitated, leaving 53% of the original CO_2 still in the atmosphere and ocean. The concentration of $[Ca^{++}]$ would then have fallen to about 95×10^{-6} mols/l and that of $[CO_3^-]$ would have risen to about 13×10^{-6} mols/l. The pH would be 7.3, and the concentration of Na in the sea water would be about 12.5 g/kg. Approximately 87% of the CO_2 then

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[4] The full computations would require several pages for adequate presentation; only the results are given here.

remaining in the atmosphere-ocean system would be dissolved in the sea water, 0.5% of the total N_2, and 85% of the H_2S. The gases in the atmosphere the writer has estimated the total amount of carbonate rocks of all ages now remaining uneroded at 1500×10^{20} g and the total amount of igneous

TABLE 2.—COMPOSITION OF ATMOSPHERE AND SEA WATER UNDER ALTERNATIVE HYPOTHESES OF ORIGIN, COMPARED WITH PRESENT-DAY CONDITIONS

	All "excess" volatiles in primitive atmosphere and ocean. (Original P_{CO_2} very high)			Only a fraction of total volatiles in primitive atmosphere and ocean. (Original $P_{CO_2} \leq 1.0$ Life begins early)		Present-day conditions
	Initial stage; before rock weathering	Intermediate stage; $CaCO_3$ begins to precipitate.	Late stage; life begins at $P_{CO_2} = 1.0$	Initial stage; before rock weathering	Intermediate stage; $CaCO_3$ begins to precipitate.	
	(1)	(2)	(3)	(4)	(5)	(6)
Atmosphere (kg/cm²)	14.2	13.8	2.1	<1.1	<1.1	1.0
N_2	9	9	50	7	7	78
CO_2 (% by volume)	89	89	47	90	90	0.03
H_2S	2	2	3	3	3	—
O_2, others	—	—	—	—	tr	22
Ocean ($\times 10^{20}$ g)	16,600	16,600	16,600	<990	<990	14,250
Cl, F, Br	18.3	18.3	18.3	18.3	18.3	19.4
$\Sigma S, \Sigma B$, others	0.8	0.8	1.3	0.1	0.1	
ΣCO_2	14.3	15.8	25.2	<1.1	<1.7	
Ca (g/kg)	—	5.9	tr	—	<5.5	0.4
Mg	—	1.3	5.2	—	<1.2	1.3
Na	—	3.1	12.5	—	<2.9	10.8
K	—	1.2	4.7	—	<1.1	0.4
H	0.5	tr	—	0.5	tr	—
"Salinity" ‰	33.9	46.4	67.2	<20.0	<30.8	35.2
pH	0.3	5.1	7.3	0.3	5.7	8.2
$CaCO_3$ pptd. ($\times 10^{20}$ g)	None	None	980	None	None	1500± 11,000±
Igneous rock eroded ($\times 10^{20}$ g)	None	4200±	17,000±	None	<240	

would have partial pressures of $P_{CO_2} = 1.00$, $P_{N_2} = 1.07$, and $P_{H_2S} = 0.073$. The solids and gases dissolved in the sea water would give a total "salinity" of about 67 g/kg (Table 2, column 3).

If we apply Conway's percentage losses of bases when igneous rock is weathered and use igneous rock of average composition, it may be found that approximately $17,000 \times 10^{20}$ g of igneous rock must have been weathered to account for the Ca, Mg, Na, and K then dissolved in sea water and previously precipitated as carbonates.

It is of interest to compare the results of these calculations with independent estimates of the quantities of some materials that have been weathered, dissolved, or precipitated during the entire course of geologic history. By methods mentioned briefly in an earlier part of this paper,

rock that has been weathered at $11,000 \times 10^{20}$ g (Table 2, columns 3 and 6).

These figures do not accord at all well with those required by the hypothesis of a dense primitive atmosphere. Even after precipitation of 980×10^{20} g $CaCO_3$, 53% of the original CO_2 would still remain in the atmosphere and ocean. To reduce this to its present small amount would mean the weathering of even more than the $17,000 \times 10^{20}$ g of igneous rock required at this stage and the deposition of additional C as $CaCO_3$ and organic carbon. It is thus seen that this assumption of a dense primitive atmosphere requires the weathering of more igneous rock and the deposition of more carbonates than seems likely to have been weathered and deposited in all of geologic time.

The same conclusion may be reached more di-

rectly, without using the estimated quantities of igneous rocks eroded and carbonates deposited. The amount of Na now dissolved in sea water is known within relatively narrow limits of uncertainty. Adding any reasonable estimates that one prefers for the Na in ancient salt deposits and the Na dissolved in the interstitial water of sediments, it still comes out that this hypothesis of a dense primitive atmosphere requires the solution of much more Na in sea water, even before life began, than appears, from other evidence, to have been dissolved in all of geologic time.

Results not significantly different from these are obtained if we assume that the first rocks that were decomposed by the supposed highly acid sea water had a composition quite different from that of average igneous rock. Applying Conway's percentage losses to the weathering of average plateau basalt (Daly, 1933, p. 17) gives, as the probable relative abundance of the principal bases in stream water,

Ca...........................	73%
Mg...........................	12%
Na...........................	13%
K...........................	2%
	————
	100%

Plateau basalt makes up only a small fraction of all the various rocks now exposed and undergoing erosion on the continents of the earth. Yet it just happens that present-day streams (Clarke, 1924, p. 119), after correction for "cyclic salts", are carrying these four bases to the ocean in proportions (per cent) similar to those that would be expected in streams from outcrops of plateau basalt:

Ca...........................	73
Mg...........................	11
Na...........................	9
K...........................	7
	————
	100

If stream water of this composition, instead of that from areas of average igneous rock, is used in the above calculations, it may be found that, at the stage when $P_{CO_2} = 1.0$, not quite so much igneous rock needs to have been weathered (13,000 $\times 10^{20}$ instead of 17,000 $\times 10^{20}$ g) but that even more $CaCO_3$ must have been deposited (1500 $\times 10^{20}$ instead of 980 $\times 10^{20}$ g). With these quantities, as with those calculated from the weathering of average igneous rock, the conclusion remains that this hypothesis of a dense original atmosphere seems to require entirely improbable amounts of rock weathering and of carbonate deposition in the early stages of earth history.

Moderate Primitive Atmosphere and Gradual Accumulation of Ocean

Let us contrast this with an alternative hypothesis that seems much more probable. The difficulties just mentioned—with what might be called the "quick-soak" hypothesis—could be avoided if, instead of all the "excess" volatiles, only a small fraction was ever present at any one time in the primitive atmosphere, and if the partial pressure of carbon dioxide never exceeded, let us say, one atmosphere. Following the same reasoning as before about the accumulation of bases in sea water, one finds that—with the alternative "slow-soak" hypothesis—carbonates would begin to precipitate when the atmosphere and ocean contained less than 10 per cent of the total "excess" volatiles. At that stage, the atmosphere would have a total pressure only one-tenth greater than at present; the salinity of the sea water would be nearly the same as that of today; and its pH would be about 5.7. The fourth and fifth columns of Table 2 show some of the conditions for two stages of this alternative hypothesis. With gradual addition of more volatiles, and as free oxygen accumulated after the advent of plant life (Van Hise, 1904, p. 956), conditions would approach closer and closer to those of today (Table 2, last column). Something of this sort seems a much more likely picture of the earth's early atmosphere and ocean.

The preceding calculation started with all the "excess" volatiles in the primitive atmosphere and ocean and followed through the consequences to be expected if the high initial pressure of CO_2 were reduced by deposition of carbonate sediments to some point where primitive forms of life could survive. This alternative hypothesis starts with the assumption that at no time did the "excess" volatiles in the atmosphere and ocean exceed such an amount that the partial pressure of CO_2 was greater than 1.0. This would permit, as seems to be required by geologic and chemical evidence (Rankama, 1948, p. 390–392, 409–414), the existence of primitive forms of life as early as, or earlier than, the deposition of the first carbonate sediments. From this

alternative hypothesis (assuming that not enough free oxygen had yet accumulated to oxidize the H_2S to SO_4) and from the previous values for the composition of incoming stream water, it is possible to estimate the conditions that would have prevailed when carbonates first began to precipitate from the sea. It may thus be found that, if P_{CO_2} never exceeded 1.0, then not more than 6% of the total "excess" volatiles could have been present in the early atmosphere and ocean; and the volume of the primitive ocean would therefore have been much smaller than at present.

At this stage the concentration of $[Ca^{++}]$ would be about 0.14 mols/1, that of $[CO_3^-]$ about 8.8 $\times$ 10^{-6} mols/1, and the pH 5.7. Approximately 3.2% of the CO_2 in the system at that time would be dissolved in the small ocean, 0.04% of the N_2, and 6.7% of the H_2S. The gases in the atmosphere would have partial pressures of $P_{CO_2} = 1.0$, $P_{N_2} = 0.077$, and $P_{H_2S} = 0.033$. The solids and gases dissolved in the sea water at this stage would give a "salinity" of about 31 g/kg (Table 2, column 5).

Poole (1941, p. 346–347, 359) has suggested that an initial supply of free oxygen, sufficient to support life and permit photosynthesis by green plants, may have been produced by photochemical dissociation of water vapor in the upper ionized layers of the atmosphere and by subsequent escape of hydrogen. In this connection, it is of interest to note that purple sulfur bacteria and certain other present-day forms can synthesize organic matter from CO_2 in an anaerobic environment that contains some H_2S. It is possible that primitive organisms of this type may have helped prepare the way for the advent of green plants on the earth (Rabinowitch, 1945, p. 4, 82–83, 99–106, 124–125). If, as, here assumed, the partial pressure of CO_2 was once as high as 1.0 atmosphere, even the rain water would have been so highly carbonated that it would leach much Fe and Si from exposed rocks, and the streams would transport significant amounts of these elements in solution (Gruner, 1922, p. 433–436; Moore and Maynard, 1929, p. 276, 293–298, 522–527; Cooper, 1937, p. 307), much as seems to have happened in parts of Precambrian time (Leith, 1934, p. 161–164).

The conditions calculated for stream water from average igneous rocks would remain essentially unchanged if we used stream water from plateau basalt instead. If, however, the partial pressure of CO_2 were less than 1.0, the fraction of total "excess" volatiles in the atmosphere-ocean system would be proportionately less than 6%; and several of the other quantities (Table 2, column 5) would likewise be decreased.

I am sure I need not warn you that the results of these calculations are not to be taken too seriously. They are based on inadequate data and laden with many "ifs and ands". Nevertheless I believe they point rather clearly to the right answer. If so, not

TABLE 3.—INVENTORY OF TOTAL C (AS CO_2) IN ATMOSPHERE, HYDROSPHERE, BIOSPHERE, AND SEDIMENTARY ROCKS

	$\times 10^{18}$ g	
Atmosphere........	2.33	
Ocean and fresh water	130	
Living organisms and undecayed organic matter....	14.5	147
Sedimentary rocks (including interstitial water)....		
Carbonates.......	67,000	
Organic C........	25,000	92,000
Coal, oil, etc......	27	

more than a small part of the total "excess" volatiles could be residual from a primitive atmosphere and ocean. The only alternative I can think of is that these volatiles have risen to the surface from the earth's interior.

SIGNIFICANCE OF CARBON DIOXIDE IN THE ATMOSPHERE-OCEAN SYSTEM

Inventory of Carbon Dioxide

Moreover, these volatiles must have risen to the surface gradually and not in a few great bursts. Table 3 is an attempt to bring together an inventory or summary of separate estimates and thus arrive at a figure for the total carbon dioxide and carbon on and near the surface of the earth today. The present atmosphere and ocean contain approximately $1\frac{1}{2} \times 10^{20}$ grams of carbon dioxide—a small part of it in the atmosphere, somewhat more in organic matter, and most of it dissolved in water. It is significant to note that, altogether, this is less than 1 part in 600 of the total carbon dioxide and organic carbon that has, at one time or another, been in circulation in the atmosphere and ocean and is now buried in ancient sedimentary rocks.

The amount of CO_2 in the atmosphere is taken directly from Humphreys (1940, p. 81); that in sea water has been calculated as 129×10^{18} g from data on the solubility and dissociation constants in sea water of $35^0/_{00}$ salinity, at an average temperature of 8°C, and in equilibrium with a partial pressure of 0.0003 atmospheres of CO_2 (Harvey, 1945, p. 59, 62, 64–66). The total quantity of fresh water is here estimated at 335 $\times 10^{20}$ g and, from Clarke's data on average composition of stream and lake waters (1924, p. 119, 138), the amount of dissolved CO_2 is calculated to be 0.9×10^{18} g.

The quantity of CO_2 equivalent to the C in living organisms is estimated at 0.036×10^{18} g in the oceans, using data from Krogh (1934b, p. 433, 436); and at 0.029×10^{18} g on the lands, using data from Krogh (1934a, p. 421, 422), Riley (1944, p. 133), and Rabinowitch (1945, p. 6), and assuming a rough proportionality between the amount of living organic matter and the rate of carbon fixation. Undecayed particulate organic debris is estimated as equivalent to 11.8×10^{18} g CO_2 in the oceans (Krogh, 1934a, p. 422; 1934b, p. 435–436) and, very roughly, as equivalent to 2.6×10^{18} g CO_2 on the land areas, using data from Rabinowitch (1945, p. 6) on the areas of soil types and from Twenhofel (1926, p. 17) on the humus content of soils.

The estimates of carbonates and organic carbon in ancient sediments are those derived from the equations of geochemical balance mentioned above; space does not permit a more complete statement of them here. The estimates for coal, oil, etc., have been taken directly or calculated from the following sources and are here summarized in units of 10^{18} g C: Coal—7.2 (Assoc. for Planning and Regional Reconstruction, Broadsheet No. 10, 1942, p. 4); oil —0.1 (Weeks, 1950, p. 1952); oil shale—0.1; tar sands—0.025; natural gas—0.025 (Hubbert, 1950, p. 174–175); graphite—1.0×10^{-5} (U.S. reserves— Currier and others, 1947, p. 249—multiplied by 10). These total to an amount equivalent to 27.3×10^{18} g CO_2.

Carbon Dioxide Equilibria in Sea Water

If only a small part of this total buried carbon dioxide were suddenly added to today's atmosphere and ocean, it would have profound effects on the chemistry of sea water and on the organisms in the sea. These effects become more evident when we consider the important part played by carbon dioxide in the chemistry of sea water.

Table 4 is presented as a reminder of the composition of sea water and to illustrate several essential points. Sea water varies widely in its total salinity, but scarcely at all in the proportions of its dissolved constituents. The most significant exceptions are the quantities of bicarbonate and carbonate ions, which depend only in part upon salinity but are affected much more by hydrogen-ion concentration and by the amount of carbon dioxide in the atmosphere with which the water is in contact.

Note, in the column to the right, that the positive ions would exceed the negative ions by 2.38 milli-equivalents were it not that the difference between them, the so-called "excess base", is balanced by dissociated ions of carbonic and boric acid. The process of balancing the "excess base" is one of the results of the buffer action of sea water. Note also that, if the amount of sodium in sea water has been increasing continuously through geologic time, as commonly assumed, then some of the acid radicals, such as chlorine, must also have been increasing by the same amounts. Otherwise sea water would have been acid rather than alkaline throughout much the greater part of the past.

The exceedingly delicate balance that prevails between the positive and negative ions in sea water may be appreciated more fully if one considers the consequences of a decrease of only 1 part in 100 of the dissolved Na. For the salinity and temperature shown in Table 4, this would mean reducing the dissolved Na from 480.80 to 475.99 milli-equivs/l and the total of dissolved bases from 621.76 to 616.95. If the acid radicals, other than the carbonic and boric acid ions, remain unchanged, then they will exceed the bases; and the "excess base" becomes a negative quantity of $619.38 - 616.95 = 2.43$ milli-equivs/l. It may readily be shown, using the appropriate constants (Harvey, 1945, p. 59, 61–68), that under these conditions the total concentration of carbonic and boric acid ions, $C_{HCO_3^-} + 2C_{CO_3^-} + C_{H_2BO_3^-}$, would be only 5.6×10^{-6} milli-equivs/l, an entirely negligible quantity by comparison. Chemical balance would therefore be maintained by a concentration of $2.43 \times 10^{-3} = 10^{-2.61}$ mols or gram-ions of hydrogen per liter. That is to say, the pH of the sea water would fall from its present average value of 8.17 to 2.61.

The carbon-dioxide equilibria of sea water are numerous and complex, but related to one

another in such a way that, for a given temperature, salinity, and partial pressure of carbon dioxide, all the other variables are fixed. Published tables (Harvey, 1945, p. 59, 62, 64–66) make it possible to work out, for

the solubility product of $CaCO_3$ was greatly exceeded, carbonate would be precipitated from the sea water, either directly or by organic agencies, and it would continue to precipitate until equilibrium was re-established. If, on the other hand, much

TABLE 4.—COMPOSITION OF NORMAL SEA WATER

(Salinity $35^0/_{00}$, $8°C$, $\rho = 1.025$, pH 8.17)

	Dissolved matter (g/kg)	Milli-mols liter	Milli-equivalents liter	
Cl⁻	19.360	560.70	560.70	
SO₄⁼	2.701	28.88	57.76	
Br⁻	0.066	0.85	0.85	
F⁻	0.001	0.07	0.07	
CO₂ ⎫ H₂CO₃ ⎭	0.001	0.01	—	
HCO₃⁻	0.116	1.90	1.90 ⎫ "Carbonate	
CO₃⁼	0.012	0.20	0.40 ⎭ alkalinity"	
H₃BO₃	0.022	0.35	—	
H₂BO₂⁻	0.005	0.08	0.08	
			619.38 2.38	
Na⁺	10.770	480.80	480.80	
Mg⁺⁺	1.298	54.78	109.56	
Ca⁺⁺	0.408	10.46	20.92	
K⁺	0.387	10.18	10.18	
Sr⁺⁺	0.014	0.15	0.30	
	35.161		621.76 − 619.38 = 2.38 = "Excess base"	

Recalculated for Cl = $19.37^0/_{00}$, $\rho = 1.025$, and pH = 8.17 from Sverdrup, Johnson, and Fleming (1946, p. 173).

any given salinity and temperature, the amounts of dissolved carbon dioxide, carbonic acid, bicarbonate and carbonate ions in equilibrium with different amounts of carbon dioxide in the atmosphere, and also to find the resulting hydrogen-ion concentration in the sea water. In the left-hand diagram of Figure 1, the amounts of carbonate range from high values, which would cause precipitation of calcium carbonate, at low pressures of CO_2, to low concentrations of carbonate, which would cause solution of calcium carbonate, at high pressures of CO_2. The vertical line through the middle of both graphs represents the amount of CO_2 in the present atmosphere.

These values at low and high pressures of CO_2 would not represent stable conditions in nature. If

of the water was significantly unsaturated with $CaCO_3$, carbonate sediments lying on the sea floor would be dissolved, or Ca would simply accumulate from incoming stream water until the point of saturation was reached. From Smith's values of the solubility product for 20° and 30° C and $36^0/_{00}$ salinity (Smith, 1940, p. 182) and from Wattenberg's temperature and salinity coefficients (Wattenberg, 1936, p. 176), the solubility product for 8° C and $35^0/_{00}$ salinity may be estimated at 2.1×10^{-6}.

The right-hand diagram of Figure 1 shows, for comparison, the conditions when sea water is saturated with calcium carbonate. Note that the total carbon dioxide dissolved in sea water increases much more with increase in the partial pressure than on the other diagram.

Also the proportion of bicarbonate is much greater, and the pH varies much less.

These quantities of dissolved carbon dioxide in sea water and of partial pressure in the atmosphere may, if we wish, be converted into

exposed to the atmosphere in a period of from 2000 to 5000 years (Callendar, 1938, p. 224). The solid line in Figure 2 gives the pH values that would follow, perhaps more slowly, as calcium carbonate was precipitated or dis-
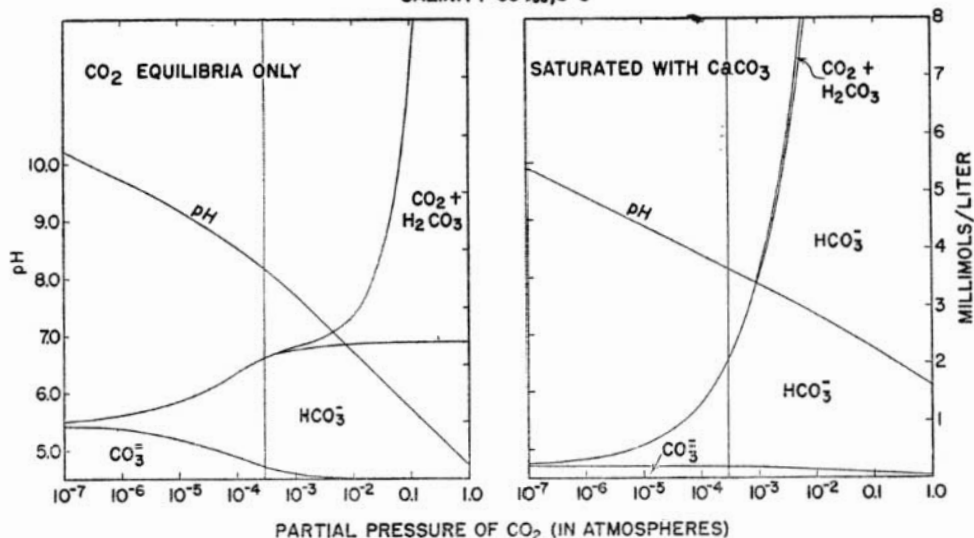
NORMAL SEA WATER
SALINITY 35‰, 8°C

FIGURE 1.—CARBON DIOXIDE COMPONENTS AND HYDROGEN-ION CONCENTRATION OF SEA WATER AT DIFFERENT PARTIAL PRESSURES OF CARBON DIOXIDE

total carbon dioxide of the atmosphere and ocean combined. This can be done simply by multiplying through by the quantities of sea water and of atmosphere on the earth today and then adding these together. We then may see more readily the effects of changes in the total amount of carbon dioxide in the atmosphere-ocean system.

Figure 2 shows the effects that changes in the total CO_2 in the atmosphere-ocean system would have upon the hydrogen-ion concentration. Note that the dashed line gives the pH values based merely on the carbon-dioxide equilibria and that these are the values that would follow relatively soon, geologically speaking, after sudden changes of total carbon dioxide. The rate at which sea water could re-establish equilibrium after a change in atmospheric CO_2 depends mainly on the rate at which the deeper water is brought into contact with the air. From what is known about oceanic circulation, it has been estimated that the entire volume of sea water is

solved. Figure 3 shows the effects that changes in the total CO_2 would have upon the partial pressure of CO_2 in the atmosphere. The values of total CO_2 shown in Figures 2 and 3 are the original ones before the adjustment that would be caused by solution or precipitation of $CaCO_3$.

The relationships shown in Figures 2 and 3 are for the present-day volume of sea water, a salinity of 35‰, and a temperature of 8° C. The effects of reducing the volume of sea water, of decreasing the salinity, or of raising the temperature are to shift the lines for pH in Figure 2 and for P_{CO_2} in Figure 3 somewhat to the left; but the essential relationships are unchanged.

Effects on Organisms

What would be the effects of such changes in total carbon dioxide on organisms living in the sea? We have already considered the narrow tolerance ranges of some animals for total salinity and for composition of the waters

in which they live. For many forms of life, the concentration of bicarbonate and hydrogen ions and the carbon-dioxide tension are among the most critical factors in their chemical environment. A number of higher marine animals (the herring, for example) are extremely sensitive to small changes in the pH of their environment. A large proportion of the eggs of some marine animals remains unfertilized if the acidity of sea water departs more than about 0.5 pH from normal. Lower organisms are commonly less sensitive; but many species of mollusks, sea urchins, Medusa, diatoms, bacteria, algae, and others seem unable to tolerate a range of more than about 1 unit of pH. Recent workers attribute a larger part of these observed biologic effects to the carbon-dioxide tension or to the concentration of bicarbonate ions than to hydrogen-ion concentration directly (McClendon, 1916, p. 148; Shelford, 1918, p. 101–102; Gail, 1919, p. 288, 295, 297; Powers, 1920, p. 381–382; 1939, p. 73; Atkins, 1922, p. 734–735; Legendre, 1925, p. 213; Singh Pruthi, 1927, p. 743; Valley, 1928, p. 215–216, 218–220; Davidson, 1933; Rogers, 1938, p. 97, 285, 286, 294, 430, 653–656, 679, 680; Edmondson, 1944, p. 43–45, 63, 64; Allee and others, 1949, p. 175, 197).

Having thus reviewed in outline the part played by carbon dioxide in the chemistry of sea water and in the environment of marine organisms, let us now return to the inventory of carbon dioxide and to the significance of the fact that more than 600 times as much of it is buried in ancient sedimentary rocks as there is now in circulation in all the atmosphere, hydrosphere, and biosphere.

If only one-one hundredth of all this buried carbon dioxide were suddenly added to today's atmosphere and ocean (that is, if the amount in the present atmosphere and ocean were suddenly increased $\left(\dfrac{600}{100} + 1 = \right)$ sevenfold, from 1.3×10^{20} to 9.1×10^{20} g), it would have profound effects on the chemistry of sea water and on the organisms living in the sea. The first effect would be to change the average pH of sea water from about 8.2 to 5.9 (Fig. 2, a). This acid water would be much less than saturated with calcium carbonate, and thus further changes would follow. Eventually, when equi-

librium was re-established, the partial pressure of carbon dioxide in the atmosphere would be about 110 times its present value, and the pH of the sea water would end up at an average of about 7.0 (Fig. 2, b).

The two values of pH, 5.9 and 7.0, are those for present volume and salinity of sea water and a mean water temperature of 8° C. For three-fourths of the present volume of sea water but with present salinity and temperature, these values are 5.8 and 6.9, respectively. For a salinity of $27^0/_{00}$ instead of $35^0/_{00}$ but with present volume and temperature of water, the corresponding values are 5.8 and 7.1. For a mean water temperature of 30° C but with present volume and salinity of sea water, these values are 5.9 and 6.8.

The effects of these changes on living organisms would be drastic. If the supposed increase of carbon dioxide happened suddenly, it would probably mean wholesale extinction of many of the marine species of today. If, however, the increase were gradual, so that organisms could adapt themselves by generations of evolutionary changes, the effects would be much less disastrous—but perhaps no less clearly recorded in the physiological adaptations of the surviving forms. From the paleontologic record it appears improbable that any change so drastic as an abrupt sevenfold increase of carbon dioxide has happened, at least since the beginning of the Cambrian.

Effects on Composition of Sediments

The conclusion that the amount of carbon dioxide in the atmosphere and ocean cannot have varied widely through much of the geologic past does not rest solely on the narrow bicarbonate and pH tolerances of many organisms. The mineralogical and chemical compositions of sedimentary rocks tell much the same story.

Carbon dioxide is constantly being added to the present atmosphere and ocean by the weathering of limestones and other rocks, by artificial combustion (Callendar, 1940, p. 399), and from volcanoes, geysers, and hot springs. At the same time, it is also being subtracted by the deposition and burial of calcium carbonate and of organic carbon in sediments.

Let us, for the moment, ignore the contribu-

tions of carbon dioxide from artificial combustion and from volcanoes and hot springs, and compare only the rates of addition by rock

this rate of net loss, the total carbon dioxide in the atmosphere and ocean would be reduced to about one-fourth its present value in one
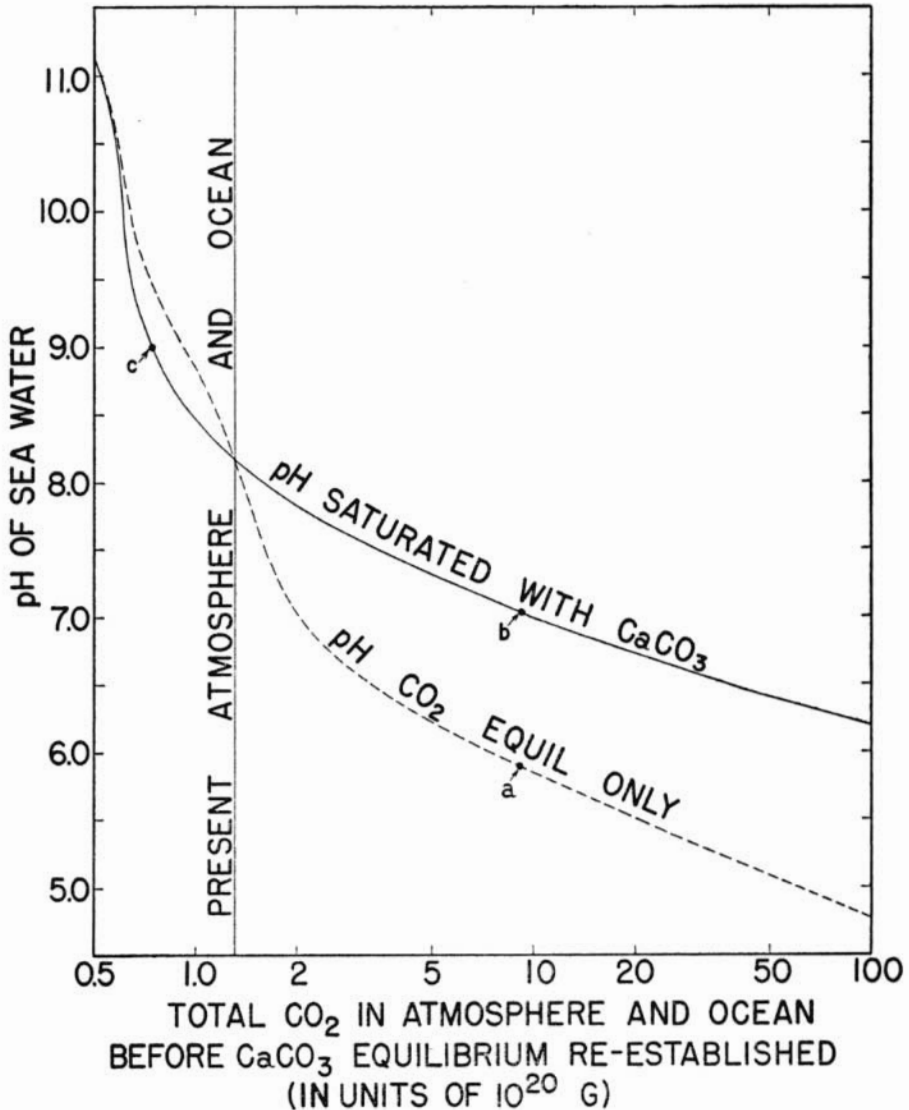

FIGURE 2.—EFFECTS OF CHANGES IN THE TOTAL CARBON DIOXIDE IN THE ATMOSPHERE-OCEAN SYSTEM UPON THE HYDROGEN-ION CONCENTRATION OF SEA WATER (AT 35°/₀₀ SALINITY AND 8° C)

weathering and of subtraction by sedimentation. These rates are not known accurately, of course, but from several lines of evidence it appears that the loss by sedimentation must exceed the gain from weathering by something like 10^{14} grams of carbon dioxide each year. At

million years, and the concentration of hydroxyl ions in sea water would be so high that magnesium hydroxide—the mineral brucite—would be precipitated and almost completely take the place of calcite as a common marine sediment. Even if liberal allowance is made for

a probable slowing down of weathering and of the synthesis of organic matter as carbon dioxide is subtracted from the atmosphere-ocean system, it would still be only about 2 million years until brucite would largely take the place of calcite deposition. No such occurrences of sedimentary brucite are known to me in rocks of any age, and it appears unlikely that this condition was ever reached in the geologic past. It seems much more likely that the net losses by sedimentation have been roughly balanced by a source neglected in the foregoing calculation—that is, by continuous additions of carbon dioxide from volcanoes and hot springs.

It seems clear that the loss of CO_2 from the atmosphere-ocean system by sedimentation must, in the long run, somewhat exceed the gain from rock weathering, but the amount of the difference is uncertain. Sedimentary rocks contain, on the average, roughly equivalent amounts of CaO and CO_2 (Clarke, 1907a, p. 169; 1907b, p. 269; 1924, p. 30). Their decomposition by weathering or precipitation by sedimentation does not disturb this equivalent ratio significantly. But igneous rocks contain many times more CaO than CO_2 (Clarke, 1924, p. 29). Thus the proportion of igneous rocks to all rocks undergoing erosion at any time is a rough measure of the amount of CO_2 that must be supplied from some other source in order to maintain the observed ratio in newly formed sediments. Several different methods of estimation (based on the probable quantities of CO_2, organic C, and Ca in rocks undergoing erosion, in material being transported by streams, and in sediments being deposited, both today and in the geologic past) yield values for the net loss of CO_2 from the atmosphere-ocean system of from 0.3×10^{14} to 4.0×10^{14} g/yr. The estimates of 1×10^{14} to 2×10^{14} g appear somewhat the more reliable, and, for purposes of the following calculations, a value of 1×10^{14} g CO_2/yr has been adopted.

At this rate of net loss, the total CO_2 would be reduced from 131×10^{18} to 31×10^{18} g in

$$\frac{(131-31) \times 10^{18} \text{ g}}{1 \times 10^{14} \text{ g/yr}} = 1,000,000 \text{ years,}$$

and the pH of sea water would then be about 9.0. Wattenberg and Timmermann (1938, p. 87–88) found the solubility product of $Mg(OH)_2$ to be 5×10^{-11} in sea water; and Harvey remarks that "when the hydrogen-ion concentration of sea water falls and the pH rises above circa pH 9, magnesium hydroxide separates as a precipitate with calcium carbonate" (1945, p. 25). If CO_2 subtraction continues after the precipitation of $Mg(OH)_2$ has begun, the relative

amounts of Mg and Ca in sea water and the various CO_2 equilibria cause $Mg(OH)_2$ to accumulate in far greater amounts than $CaCO_3$.

This estimate of the time required to reduce the total CO_2 in the atmosphere and ocean to the point when brucite would be deposited neglects several factors—one that would operate to decrease the time and two that would operate to increase it. The several chemical relations involved require that, as the pH of sea water is raised from 8.2 to 9.0, 70 mg/l of $CaCO_3$ must, on the average, be subtracted by precipitation to maintain the various equilibria. With the present volume of sea water, this would mean the deposition as carbonate of about 43×10^{18} g of CO_2 in addition to the average net subtraction of 10^{14} g/yr based on present conditions. The total subtraction of $(131-31=)$ 100 units of CO_2 is thus made up in part of 57 units lost because of normal sedimentation. If this is not replaced by CO_2 from other sources, this primary loss causes the precipitation, as carbonate, of 43 additional units of CO_2 in order to maintain the various equilibria. Figure 2 shows the effects of primary rather than secondary changes of total CO_2 in the system; and point c (pH 9.0) is therefore plotted at $(131-57=)$ 74 units instead of at 31 units. For purposes of the present calculation, we are interested in the time required for the primary loss of 57 units of CO_2. That is, if there were no other corrections to be considered, the time required to reduce the pH to 9.0 would be only

$$\frac{(131-31-43) \times 10^{18} \text{ g}}{1 \times 10^{14} \text{ g/yr}} = 570,000 \text{ years.}$$

The total rate of loss of CO_2 by sedimentation is the rate of deposition of carbonates and that of organic carbon. Over the years, the mean rate of carbonate deposition depends upon the rate at which streams bring new Ca to the sea, and this in turn depends upon the rate of rock weathering on the lands. It seems reasonable to assume that the rate of chemical weathering is controlled in large measure by the partial pressure of CO_2 in the atmosphere (Van Hise, 1904, p. 465, 476; Clarke, 1924, p. 110–111) and by the quantity of decomposing organic matter (Jensen, 1917, p. 255–258, 267–268) which likewise depends upon atmospheric CO_2, as is discussed somewhat more fully below. As the atmospheric CO_2 would decrease under the assumed conditions of this calculation, the rate of rock weathering and hence the rate of carbonate deposition would likewise decrease.

Similarly the rate of accumulation and burial of organic carbon is probably roughly proportional to the rate at which new organic matter is produced, both on the lands and in the sea. This in turn depends largely if not entirely on the rate of carbon

fixation by photosynthesis which, at optimum light intensities, varies almost directly with the partial pressure of CO_2, up to a P_{CO_2} of about 3, 4, or 5 times that of the present (Brown and Escombe, 1905, p. 40–41; Hoover, Johnston, and Brackett, 1933, p. 10–17; Rabinowitch, 1945, p. 330–331). Thus as the partial pressure of CO_2 decreased under the assumed conditions, the rates of deposition of both carbonate sediments and organic carbon would probably decrease in roughly the same proportion.

From the relationship between CO_2 and P_{CO_2}, it may be found that, when the total CO_2 is reduced to 31×10^{18} g (Fig. 3, d, plotted at 74×10^{18} g to show the effects of primary loss), the P_{CO_2} would be reduced to only one-forty-fourth its present value. Numerical integration indicates that, over this range, the P_{CO_2} would average about 28% of its present value. Thus the mean rate of CO_2 deposition would be only about 0.28×10^{14} g/yr. Combining the effects of these several corrections, a revised estimate of the time required to reduce the total CO_2 to the point where $Mg(OH)_2$ would begin to precipitate would be $\dfrac{(131 - 31 - 43) \times 10^{18} \text{ g}}{0.28 \times 10^{14} \text{ g/yr}} =$ 2,000,000 years. This is a relatively brief interval in geologic time, and it seems necessary to conclude that CO_2 must have been supplied to the atmosphere-ocean system more or less continuously from some extraneous source in order to account for the absence of brucite as a common marine sediment. The foregoing calculations are based on the constants for sea water of normal salinity at a mean temperature of 8°C. The calculated values are somewhat different if other salinities and temperatures are assumed but not enough so to modify this conclusion significantly.

Possible variation in the amount of CO_2 in the atmospheres of the past might be estimated, if sufficiently reliable data were available on the rate at which organic carbon has been deposited during different geologic periods. As stated above, the amount of organic carbon that becomes buried along with sediments and thus removed from circulation at any time is probably roughly proportional to the amount of it then in existence as organic matter. This in turn depends, through a narrow but significant range, on the partial pressure of atmospheric CO_2. The rate of deposition of organic carbon is thus a rough measure of the partial pressure of CO_2 in the atmosphere. For this reason, it is tempting to suppose that the CO_2 content of the atmosphere may have been much greater than at present during those parts of the Carboniferous, Cretaceous, and Tertiary periods when great quantities of coal and other organic deposits accumulated. Available data do not support this possibility,

however. To begin with, the total amount of carbon in all coal, petroleum, oil shale, etc., is negligible in comparison with the carbon that is present (to the extent of only a few tenths of 1 per cent) in the far more abundant ordinary sedimentary rocks (Table 3). Furthermore, local deposits of highly organic sediments do not necessarily mean unusually large accumulations at that same time over the entire earth. Finally, even widespread deposits of highly organic sediments are not in themselves sufficient evidence; the time elapsed during accumulation of the sediments is an essential factor in determining whether or not the rate of carbon deposition was abnormally rapid.

Merely to list the data needed for this calculation is sufficient to demonstrate how far we now are from being able to appraise at all accurately, from this type of evidence, the rates of burial of organic carbon through the geologic past. One needs (a) reliable information on the organic carbon content of different types of sediment of different ages, (b) reasonably good estimates of the relative amounts of different sediment types deposited during a given interval of time, and (c) data on the number of years required for deposition. Of these several categories of essential data, the third is probably now known better than the other two.

Nevertheless, something of interest may still be obtained, even from such data as now exist. The average composition of the principal types of sedimentary rocks (Clarke, 1924, p. 30, 547, 552) affords one of the bases for estimation; the relative abundance of sandstone, shale, and limestone in rocks of different ages may be taken from such compilations as Schuchert's (1931, p. 49); and the estimated durations, in millions of years, of the different periods are available from several sources (for example, Holmes, 1947b, p. 144). When these various estimates are combined, along with estimates of the amounts of contemporaneous deep-sea sediments, one finds no indication whatever that the rate of carbon burial has ever exceeded that of today. In fact this evidence, taken at face value, appears to show that the rate of carbon accumulation has been increasing gradually and rather uniformly ever since the beginning of geologic time.

This apparent evidence of an increasing rate of carbon deposition needs to be viewed with considerable skepticism, however. It may readily be recognized as simply one other aspect of the widely observed relationship that the maximum thicknesses of sedimentary rocks deposited during a unit of time appear to increase progressively as one ascends through the geologic column. This general relationship has been noted and variously interpreted by a number of geologists. Gilluly (1949, p. 574–582)

has clearly pointed out that it does not necessarily *mean any real increase in the rate of sedimentation* with time but may be explained equally well as the result of the accidents of preservation and exposure of ancient sediments. Whatever may be the correct explanation of this commonly observed relationship, one finds no indication from this type of evidence that the average rate of deposition of organic carbon was greater at any time in the past than it is today.

Possible Limits of Variation in the Past

Even if the rate of carbon deposition, averaged over fairly long intervals of time, has remained approximately constant through much of the past, it still seems likely that the rate *would have varied somewhat from this average*, as the result of irregularities of volcanic eruptions and other possible sources of supply. The observed fact that many plants are capable of a higher rate of carbon-dioxide assimilation and *photosynthesis, if the carbon-dioxide content* of the atmosphere is several times greater than normal, is perhaps most simply explained as the result of the adaptation of ancestral forms to an atmosphere that was at times somewhat *richer in CO_2 than at present. If we adopt this* interpretation and take a P_{CO_2} of about 0.0015 (or five times that of the present) as an optimum condition for photosynthesis (Brown and Escombe, 1905, p. 40–41; Hoover, Johnston, and Brackett, 1933, p. 15–16), we have a basis for estimating what may have been the total amount of CO_2 in the atmosphere-ocean system at such times.

With the present volume and salinity of sea water, *a mean water temperature of about 8° C*, and a prevailing P_{CO_2} of 0.00030, the quantity of CO_2 in the atmosphere and ocean is calculated to be 2.33×10^{18} and 129×10^{18} g, respectively. If, with the other conditions remaining constant, the total quantity of CO_2 in the atmosphere and ocean were increased from 131×10^{18} to 157×10^{18} g, the various CO_2 equilibria would distribute the CO_2 between atmosphere and water so that the P_{CO_2} would *rise to the assigned value of 0.00150 (Fig. 3, e) and* the pH would fall to 7.5. This sea water would then be much less than saturated with $CaCO_3$, and, as a result, $CaCO_3$ would, on the average, be dissolved from the ocean floor until equilib-

rium was re-established. At that stage, the total *quantity of CO_2 in the atmosphere and ocean* would be about 177×10^{18} g; the pH would rise to 8.0 (nearly its original value), and the P_{CO_2} would fall back to about 0.00059 (Fig. 3, *f*).

It would probably give a more reasonable *estimate of the limiting conditions to assume* that the arbitrary P_{CO_2} of 0.00150 prevailed *after* rather than before adjustmsnt to $CaCO_3$ equilibrium, which would mean that the P_{CO_2} was at times well above that limit. On this alternative assumption, the total quantity of CO_2 would have increased from 131×10^{18} to 212×10^{18} g, the addition having come from some unspecified source. The CO_2 equilibria alone would distribute this total between the atmosphere (49×10^{18} g) and sea water (163×10^{18} g) so that the P_{CO_2} would rise to 0.00630 (Fig. 3, *g*) and the pH would fall to 6.9. Sea water of this acidity would dissolve $CaCO_3$ from the ocean floor until about 62×10^{18} g of CO_2 had been added to the system, thereby bringing the total to $(212 + 62 =) 274 \times 10^{18}$ g. At that stage, when equilibrium was re-established, the quantity of CO_2 in the atmosphere and ocean would be about 11.6×10^{18} and 262×10^{18} g, respectively; the P_{CO_2} would fall back to the assigned value of 0.00150 (Fig. 3, *h*); and the pH would end up at 7.8. It is worth nothing that, although the quantity of CO_2 in the atmosphere would have increased by a factor of $\dfrac{11.6}{2.33} = 5$, the quantity in the ocean would have increased by only $\dfrac{262}{129} = 2$.

The volume and salinity of sea water and the temperature of the water have been held constant in the foregoing calculation. The probable effects of their variation may be estimated by similar calculations. If the volume of the ocean were only three-fourths as great as at present, the quantity of CO_2 *dissolved in sea water would be only* 194×10^{18} instead of 262×10^{18} g when the P_{CO_2} was 0.00150. For salinity ranges of as much as 20 per cent above and below those of present average sea water, the net effects on the distribution of CO_2 between atmosphere and sea water are almost negligible. If the mean water temperature were 30°C instead of 8°C, the quantity of CO_2 dissolved in sea water would be about 138×10^{18} instead of 262×10^{18} g when the P_{CO_2} was 0.00150. Thus the effects of each of these other controlling variables is such

that, if the P_{CO_2} were 5 times that of today, the total CO_2 in the atmosphere-ocean system would probably not have been much more than about twice the present total of 131×10^{18} g.

photosynthesis, which in turn is proportional to the P_{CO_2} through this range. This would mean that, as the P_{CO_2} increased by a factor of 5, the quantity of CO_2 equivalent to organic carbon in the biosphere
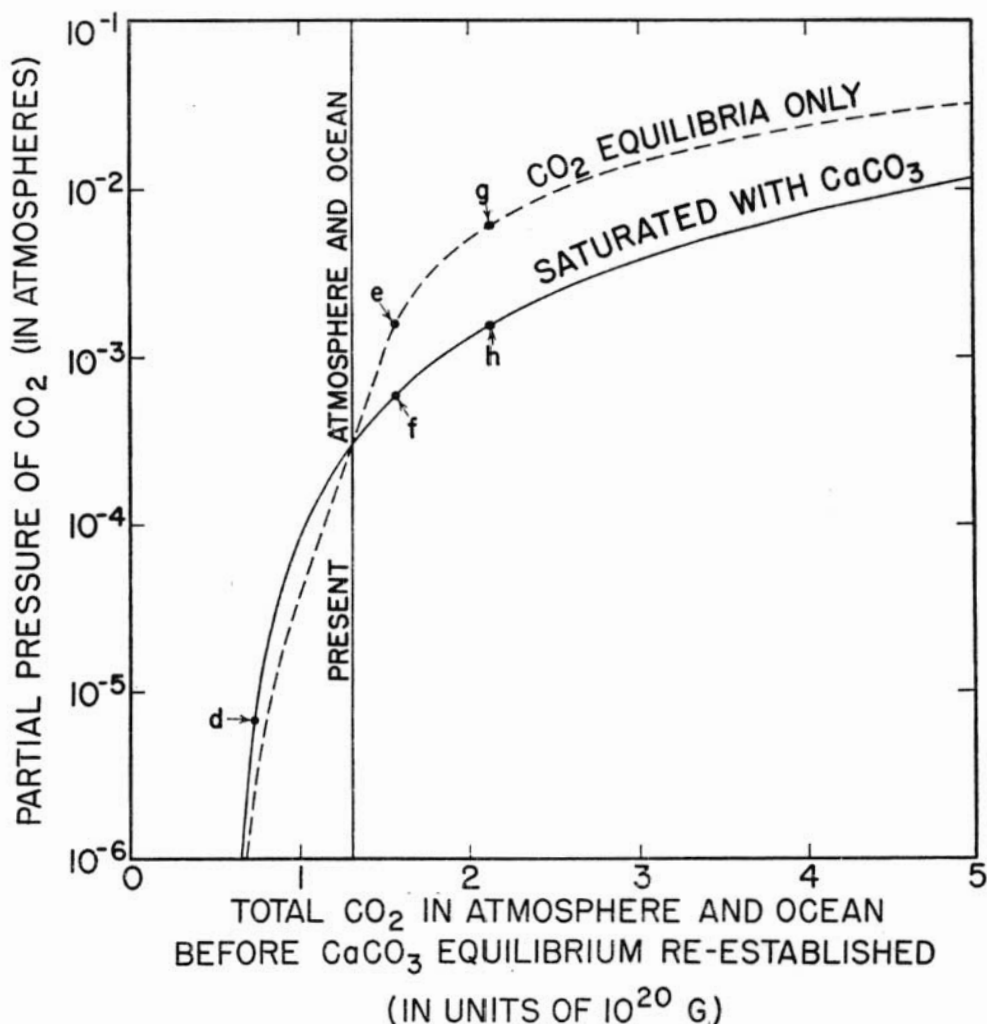

FIGURE 3.—EFFECTS OF CHANGES IN THE TOTAL CARBON DIOXIDE IN THE ATMOSPHERE-OCEAN SYSTEM UPON THE PARTIAL PRESSURE OF CARBON DIOXIDE IN THE ATMOSPHERE (AT $35^0/_{00}$ SALINITY AND 8° C)

All these calculations have considered only the amounts of CO_2 in the atmosphere and ocean and have ignored any changes in the total quantity of living organisms and undecayed organic matter in the biosphere, as the P_{CO_2} increased from 0.00030 to 0.00150. By an extension of the reasoning followed above, in the section entitled Effects on Composition of Sediments, it might be estimated that the quantity of organic matter in the biosphere at any time would be roughly proportional to the rate of

would also have increased from the estimated 14.5 $\times 10^{18}$ g of today (Table 3) to about 72.5×10^{18} g. This would bring the total quantity of C in circulation in the atmosphere, hydrosphere, and biosphere under these limiting conditions to about $(274 + 72 =) 346 \times 10^{18}$ g CO_2. A similar "correction" might be made for organic C in the biosphere in each of the other calculations. None of the conclusions would be modified, however, and the basis

for the "correction" itself seems too uncertain to warrant this refinement.

The possible effect of variation in the CO_2 content of the atmosphere upon world climate has been discussed by meteorologists and others for many years. The hypothesis, developed in some detail by Arrhenius (1896) and T. C. Chamberlin (1897, p. 680; 1899), was that an increase of atmospheric CO_2 would act as a trigger mechanism, retarding radiation of heat from the earth, and thereby starting a train of events that would cause general warming. Physical measurements subsequently indicated that the heat absorption by water vapor far outweighs that by CO_2, and the hypothesis fell into general disfavor (reviews in Clarke, 1924, p. 52–53, 147–149; Humphreys, 1940, p. 584–586, 621–622). Recent work, however, seems to have reopened the question to some extent (Callendar, 1938, p. 231–232; 1941; Dobson, 1942; Elsasser, 1942, p. 64). Callendar's later estimates (1938, p. 231; 1941, p. 32) call for an increase of 20 to 30 fold over the present atmospheric CO_2 in order to account for the warmest climates indicated by Tertiary floras, and they call for a decrease to about one-tenth the present content (corresponding to a decrease to about 0.4 of the present total CO_2 in atmosphere and ocean) to account for the coldest epochs of continental glaciation. Other lines of evidence, discussed elsewhere in this paper, make it seem unlikely that the P_{CO_2} has been 20 to 30 times greater than at present, at least in later parts of geologic time. But it appears possible, if CO_2 has the climatic effects some have claimed for it, that decreases in the amount of atmospheric CO_2 may have been a contributory cause of some of the epochs of glaciation.

From several lines of evidence, it seems difficult to escape the conclusion that, for a large part of geologic time, carbon dioxide has been supplied to the atmosphere and ocean gradually and at about the same rate that it has been subtracted by sedimentation.

Sources of Supply

If the bulk of the carbon dioxide in the atmosphere, hydrosphere, biosphere, and sedimentary rocks cannot have been residual from a primitive atmosphere, one must look for other sources of this gradual and continuous supply. At first glance, the possibility seems tempting that this unidentified source may have been the great reserve of carbonates and organic carbon in the ancient sediments. Crustal movements

bring these older sedimentary rocks to the surface, where they undergo weathering and gradually release their contained carbon to the streams and atmosphere. If sedimentary deposits accumulated only on the continents and continental shelves and if no igneous rocks were eroded, this problem of the supply of carbon would not concern us, for the quantities of older sedimentary rocks eroded from and new sediments deposited on the continents have probably maintained a reasonably close balance through much of geologic time. But igneous rocks have also been eroded, and sediments have accumulated not only on the continents but also in large quantity in the deep-sea basins (Twenhofel, 1929, p. 394, 400; Kuenen, 1937; 1941; 1946). It is evident, therefore, that the weathering of sedimentary rocks alone could not suffice to maintain the supply of carbon dioxide to the atmosphere-ocean system.

If weathering of sedimentary rocks is not sufficient, what about the carbon released by metamorphism or by actual melting of the older sediments? Many of the successive steps in metamorphism of siliceous carbonate rocks involve progressive decarbonation of the mineral species (Bowen, 1940, p. 245, 256–257, 266); and actual melting of sediments would drive off all carbon dioxide or carbon monoxide that could not be dissolved in the resulting melt. In many areas, volcanic rocks and associated schists of Precambrian age have largely been converted into carbonates (Van Hise, 1904, p. 972; Collins and Quirke, 1926, p. 31–32; Macgregor, 1927, p. 159–162), possibly as the result of high concentrations of carbon dioxide driven off from near-by sources.

The extent to which ancient sediments have undergone decarbonation by metamorphism or melting is not known. It seems very improbable, however, that such processes are adequate to account for the continuous supply of carbon dioxide to the atmosphere and ocean. As an outside estimate, we may assume that *all* Precambrian and *half* of all Paleozoic sedimentary rocks now remaining uneroded on the continents have undergone complete (not merely partial) decarbonation and that *all* the resulting carbon dioxide escaped into the atmosphere-ocean system. This would reduce the estimated amount of CO_2 now buried in sedimentary

rocks from 920×10^{20} (Table 1) to about 780 $\times 10^{20}$ g and would mean that the amount now buried is about 530 (instead of 600) times as great as that in circulation in the present atmosphere, hydrosphere, and biosphere. In other words, even if decarbonation of sedimentary rocks has been far more extensive than seems likely, the essential problem of accounting for this huge discrepancy still remains.

It may be worth noting also that, judged by the estimated relative abundances shown in Table 1, the volatile constituents that could be released on complete decarbonation, dehydration, etc., of average sedimentary rock would be very different in over-all composition from the "excess" volatiles.

One other possible source of carbon dioxide may be worth mentioning. Stony and iron meteorites contain an average of 0.04 per cent and 0.11 per cent carbon, respectively (Brown, 1949b, p. 626). Conceivably the supply of carbon dioxide to the earth's surface might have been replenished continuously by showers of meteoritic dust from interplanetary or interstellar space (Van Hise, 1904, p. 970, 973, 974). A brief consideration, however, of the exceedingly slow rate at which meteoritic debris is reaching the earth today (less than 1 mm/billion years—Jeffreys, 1933—to about 10 cm/billion years—Nininger, 1940, p. 461) and the apparent absence of geologic evidence that the rate has been significantly higher any time since sedimentary rocks began to accumulate makes it seem highly improbable that extra-terrestrial sources have made important contributions to the earth's supply of carbon dioxide since very early in the history of the planet.

The conclusion, arrived at so laboriously here, that carbon dioxide has been supplied to the atmosphere and ocean gradually and at about the same rate that it has been subtracted by sedimentation, is not particularly new. The Swedish geologist, A. G. Högbom, clearly recognized in 1894 (summarized in Arrhenius, 1896, p. 269–273) that carbon dioxide has been supplied continuously to the earth's surface since early in geologic history and that the chief source of this supply must have been volcanic or juvenile. Essentially this same conclusion has been restated many times (T. C. Chamberlin, 1897, p. 654–656; Fairchild, 1904,

p. 97, 109–110; Clarke, 1924, p. 58–59; Macgregor, 1927, p. 156–157; Jeffreys, 1929, p. 312; Goldschmidt, 1934, p. 415; 1938, p. 101; Eskola, 1939; Conway, 1943, p. 170–174; Cotton, 1944; Hutchinson, 1944, p. 180, 192; 1947, p. 300–301); but it is a significant fact about the history of the earth that has sometimes been ignored and, as such, it deserves frequent repetition.

SIMILARITY OF "EXCESS" VOLATILES AND MAGMATIC GASES

The evidence bearing on the probable source and rate of supply of carbon dioxide has been emphasized in the preceding discussion because the chemical and physiological effects of carbon dioxide are relatively well known. Perhaps for this reason, carbon dioxide appears to be of particular significance in our understanding of the history of the atmosphere and ocean. Comparable data on the effects of other volatiles are apparently not available; but, from scattered information, approximately the same conclusions are suggested for the source and rate of supply of chlorine, oxygen, and several other constituents of the atmosphere and hydrosphere.

In summarizing the evidence on the source of carbon dioxide, Hutchinson put it succinctly when he stated that "it seems unreasonable to accept juvenile addition in the case of one constituent, and, in the absence of very strong reasons, to deny it in the case of the others" (1944, p. 180). A number of other writers have reached much the same conclusion (Fairchild 1904, p. 98, 103; Evans, 1919; Jeffreys, 1929, p. 147, 312; Eskola, 1932b, p. 66–67, 69–70; Lane, 1932, p. 318; Gilluly, 1937, p. 440–441; Goldschmidt, 1938, p. 17, 24, 101; Wildt, 1939, p. 143; R. T. Chamberlin, 1949, p. 253, 255–256). (See also references regarding the earth's loss of inert gases in section on Dense Primitive Atmosphere-Solution in the Melt.)

Let us now return to the "excess" volatiles we started with and see how they compare in composition with gases that are escaping from volcanoes, fumaroles, and hot springs and with gases that are occluded in igneous rocks. Considering that these gases have come in contact and presumably reacted with diverse rock

TABLE 5.—VOLUME PERCENTAGES OF GASES FROM VOLCANOES, ROCKS, AND HOT SPRINGS

| | Volcano gases from Kilauea and Mauna Loa* (26 samples) | | | Gases from rocks | | | | | | | Gases from fumaroles of the Katmai region† and from steam wells and geysers of California and Wyoming.** (23 samples) | | | |
| | | | | Basaltic lava and diabase* (13 samples) | | | Obsidian, andesitic lava, and granite* (17 samples) | | | | | | | |
	Minimum	Maximum	Median	Minimum	Maximum	Median	Minimum	Maximum	Median			Minimum	Maximum	Median
CO_2	0.87	47.68	11.8	0.89	15.30	8.1	0.08	20.26	2.0	CO_2		0.03	1.24	0.02
CO	0.00	3.92	0.5	0.02	8.28	0.2	0.01	2.22	0.5	CO		—	0.01	tr
H_2	0.00	4.22	0.4	0.38	6.18	1.2	0.08	11.60	0.4	O_2		0.00	0.08	tr
N_2	0.68	37.84	4.7	0.27	7.21	2.0	0.03	3.90	1.2	CH_4		0.00	0.30	0.11
A	0.00	0.66	0.2	0.00	0.04	tr	0.00	0.02	tr	H_2		0.00	0.29	0.15
SO_2	0.00	29.83	6.4	—	—	—	—	—	—	$N_2 + A$		0.00	0.31	0.02
S_2	0.00	8.61	0.2	0.08	1.96	1.1	0.00	2.89	0.2	NH_3		—	0.02	0.01
SO_3	0.00	8.12	2.3	—	—	—	—	—	—	H_2S		0.00	0.10	0.02
Cl_2	0.00	4.08	0.05	0.06	1.33	0.5	0.01	10.59	0.5	HCl		0.01	0.57	0.06
F_2	—	—	—	0.00	14.12	3.8	0.25	7.80	2.3	HF		0.00	0.10	0.03
H_2O	17.97	97.09	73.5	71.32	92.40	83.1	69.44	98.55	92.9	H_2O		98.04	99.99	99.58
			100.0			100.0			100.0					100.00

* Analyses by E. S. Shepherd (1938, p. 321, 326).
† Allen and Zies (1923, p. 126, 142).
** Allen and Day (1927, p. 76; 1935, p. 87).

COMPOSITION OF GASES AND OF "EXCESS" VOLATILES

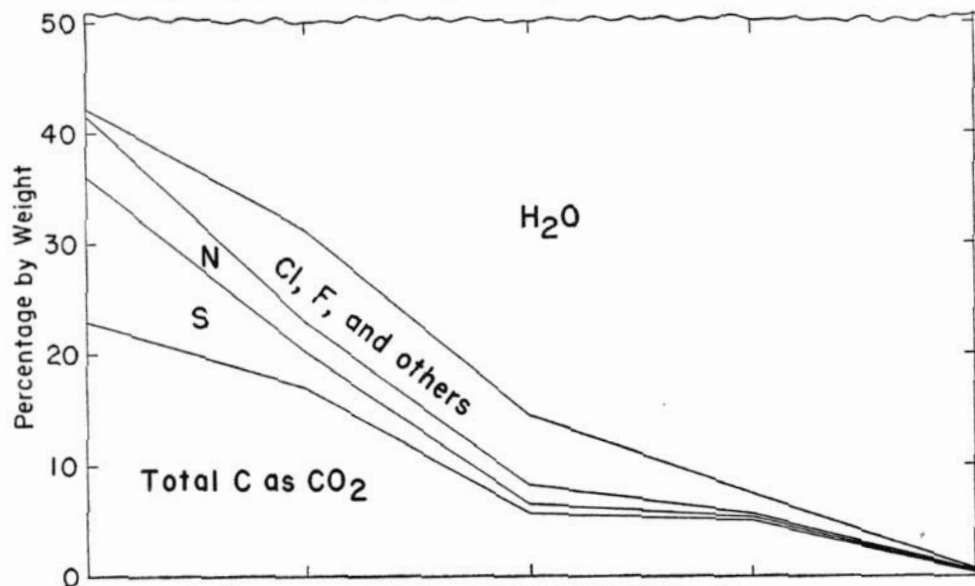| Kilauea (26 samples) | Basalt and diabase (13 samples) | Obsidian andesite and granite (17 samples) | "Excess" volatiles | Hot springs, geysers, and fumaroles (23 samples) |

FIGURE 4.—COMPOSITION OF GASES FROM VOLCANOES, IGNEOUS ROCKS, AND HOT SPRINGS COMPARED WITH "EXCESS" VOLATILES

types and ground waters and that they probably contain at least some recirculated or *resurgent* volatiles that have been absorbed from earlier sedimentary rocks (Shepherd, 1938, p. 312–313), it is to be expected that they will be

TABLE 6.—COMPOSITION OF GASES FROM VOLCANOES, IGNEOUS ROCKS, AND HOT SPRINGS, AND OF "EXCESS" VOLATILES IN ATMOSPHERE, HYDROSPHERE, AND SEDIMENTARY ROCKS

(Median analyses, recalculated from volume to weight percentages)

	Kilauea and Mauna Loa	Basalt and diabase	Obsidian, andesite, and granite	Fumaroles, steam wells, and geysers	"Excess" volatiles
H_2O	57.8	69.1	85.6	99.4	92.8
Total C as CO_2	23.5	16.8	5.7	0.33	5.1
S_2	12.6	3.3	0.7	0.03	0.13
N_2	5.7	2.6	1.7	0.05	0.24
A	0.3	tr	tr	tr	tr
Cl_2	0.1	1.5	1.9	0.12	1.7
F_2	—	6.6	4.4	0.03	tr
H_2	0.04	0.1	0.04	0.05	0.07
Others	—	—	—	—	tr
	100.04	100.0	100.04	100.01	100.04

variable in composition. The extreme ranges of composition of these gases are in fact wide; but median compositions by groups indicate consistent differences in the gases in rocks and lavas of different types (Tables 5 and 6). If we compare these median gas compositions with the relative abundance of the constituents of the "excess" volatiles, we see that an average of the gases in granitic rocks and those from hot springs and fumaroles approximates closely the over-all composition of the "excess" volatiles (Fig. 4). Judged solely by compositions then, it is conceivable that all the hydrosphere and atmosphere may have come from such gases (Allen, 1922, p. 39–42, 52). Several questions must be answered, however, before we may consider such a conclusion.

ESCAPE OF VOLATILES DURING CRYSTALLIZATION OF MAGMAS

Is there some reasonable mechanism by which these gases from the interior could be the source of the "excess" volatiles? In the cooling and gradual crystallization of complex silicate melts, certain minerals crystallize out first and thus enrich the remaining melt in other constituents, such as silica, alumina, and the alkalies (Bowen, 1928, p. 293, 297–298) and water, carbon dioxide, and other volatiles (Allen, 1922, p. 57). As crystallization proceeds, the concentration of the remaining volatiles rises and therefore also their vapor pressures. As Morey (1922; 1924) and others (Goranson, 1931, p. 499; Ingerson, 1940, p. 784) have pointed out, when these vapor pressures become greater than the weight of overlying rocks, escape to the surface may be violent, as in volcanic eruptions; or where the crystallizing melt lies at greater depths, the volatiles may escape more gradually along fractures in the overlying rocks.

How adequate is such a mechanism to explain the quantity of volatiles that must have risen to the earth's surface in the course of geologic time? Probably the total quantity of extrusive rocks that has risen to the earth's surface in all of geologic time, although large, is still insufficient to furnish more than a few per cent of the water of the ocean, unless extrusive rocks bulk larger than the total of all sedimentary rocks and unless they originally contained more than 10 per cent of water. (*See also* Verhoogen, 1946, p. 746.) Intrusive rocks, on the other hand, appear to be a more adequate source. Goranson's experimental work has shown that a melt of granitic composition can dissolve as much as 9.3 per cent of water at 900° C and at a pressure equivalent to a depth of 15 kilometers (Goranson, 1931, p. 493). The amount of water in natural magmas, however, is a subject about which petrologists are not agreed. Gilluly's estimates, which are fairly representative of others[5], are that the water content of many magmas has been "fully 4 per cent for basalts and perhaps as much as 8 per cent for deep granites" (1937, p. 441).

Let us estimate 4 per cent water in an average magma. Then, as igneous rocks now contain an average of about 1 per cent water, this would mean that magmas have commonly given off about 3 per cent of water during crystallization.

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[5] In a paper that appeared after this was written, Ingerson (1950, p. 813–814) has reviewed the estimates made by a number of geologists. Gilluly's estimates lie near the middle of the entire range.

On these assumptions, the crystallization of a shell of igneous rock 40 kilometers thick would account for the entire volume of water in the ocean. In a similar calculation, Gilluly (1937, p. 440–441) estimated that the ocean could have been derived from the escape of 5.8 per cent of water from the sialic rocks of the crust.

HOT SPRINGS AS POSSIBLE CHANNELS OF ESCAPE

How might this quantity of volatiles have escaped to the earth's surface? Hot springs are much less spectacular than volcanoes, but they are more numerous and more widely distributed, and they may be the principal channels by which volatiles escaping from crystallizing magmas have reached the surface. For example, Allen and Day (1935, p. 40, 87; Allen, 1935, p. 6, 12; Day, 1939, p. 328–329) have estimated, from the temperature of escaping steam in Yellowstone Park, that the hot springs of that area are discharging ground water that has been heated by mixing with about 10 or 15 per cent of magmatic steam[6].

Hot springs are much more abundant in the area of the Idaho batholith than in that of the much younger lava flows of the adjacent Snake River Plains (Meinzer, 1924, p. 296–297; Stearns, Stearns, and Waring, 1937, Fig. 11, p. 82). More than 100 hot springs and groups of hot springs are known within the limits of the Idaho batholith, and the discharge and temperature of a number of them have been measured (Stearns, Stearns, and Waring, 1937, p. 136–151). If these springs are heated by the same process of mixing of ground water and magmatic steam that is believed to operate in the Yellowstone, then one may estimate roughly that the average percentage of magmatic water is about $2\frac{1}{2}$ per cent. The Idaho batholith is thought to be of Cretaceous age (Ross, 1936, p. 382–383), yet it is still discharging hot waters. Can it be that batholiths cool much more slowly than is generally supposed? If so, this may be one explanation for the long-continued and relatively uniform supply of volatiles that seems to be indicated by the geologic record.

The average temperature of the hot springs of Idaho that have been measured is about 39°C, and the mean annual temperature there is near 8°C. Making the same assumptions about original temperature and mixing as those used in the similar calculation that follows, we find that 1 g of magmatic steam would be sufficient to heat 35.5 g of ground water to 39°C. This would mean 2.7 per cent magmatic water in the final hot-spring mixture.

A crude estimate of the total quantity of water being discharged today from all the hot springs of the earth may be made from available data on the springs of a smaller area. Stearns, Stearns, and Waring (1937, p. 115–191) list more than 1000 thermal springs or groups of springs within the limits of the continental United States. Undoubtedly some of these are heated by deep artesian circulation, but probably only a small proportion, for many are located in areas of igneous rock. To allow roughly for such artesian heating, the hot springs of the eastern two-thirds of the United States are here omitted from calculation. If the total area of the States, as thus "corrected", is a fair sample of the continents and if the oceans contribute about half as much per unit area, then the annual discharge of all hot springs, multiplied by 3 billion years, gives a total volume somewhat more than 100 times that of the present ocean. That is to say, if hot springs are delivering to the surface an average of only 0.8 per cent of juvenile water, they could, in the course of geologic time, account for the entire volume of the ocean. This is not counting any contribution of water directly from volcanic eruptions.

Stearns, Stearns, and Waring consider only springs with water more than about 8°C above local mean annual temperature. Of the 1059 hot springs they list for the entire United States, 721 show estimated discharges, and 616 show water temperatures. The total discharge of the 721 measured or estimated springs is 511,600 gal/min. The 338 springs for which no discharge is recorded include the 96 hot springs and geysers of Yellowstone

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[6] Rubey and Murata (1941) have investigated a small but apparently typical group of hot springs farther south along the Wyoming-Idaho border. From relations between the compositions of water and of contained gases and the temperatures at different outlets, it appears that approximately 5 per cent of the water of these springs is of magmatic origin. For estimates of the amount of magmatic water in other areas, see Zies (1929, p. 73–74) and White and Brannock (1950, p. 573).

National Park, for which an estimate of 49,400 gal/min is available from another source (Allen, 1935, p. 5). Estimating separately by States for the unmeasured springs, it appears that a total of approximately 800,000 gal/min is a fair approximation for the discharge of all 1059 springs. Comparing the water temperatures with estimated mean annual temperatures and weighting the differences in proportion to the quantities discharged, one arrives at the estimate that the springs are heated, on the average, about 20°C above mean annual temperature.

By the same methods, the hot springs of the western one-third of the country (Ariz., Calif., Colo., Idaho, Mont., Nev., N. Mex., Ore., Utah, Wash., and Wyo.) yield a total of approximately 700,000 gal/min or 1.4×10^{15} g/yr of water. Taking the area of all continental U. S. as one-thirtieth that of all the continents and using the discharge from only these 11 western States would give a total from all continents of 42×10^{15} g H_2O/yr. The rate of hot-spring discharge on the ocean floor is unknown. Presumably it is lower than that on the continents but, to judge by the evidence of extensive lava flows there (Pettersson, 1949, p. 186), it is probably considerable. If the mean rate per unit area from the oceans is taken as half that from the continents, then the hot-spring discharge from the continents and oceans combined is about 66×10^{15} g H_2O/yr. This rate, continued over a period of 3 billion years, the assumed age of the earth (Holmes, 1947a; Bullard and Stanley, 1949; Ahrens, 1949, p. 254, 257–258; H. N. Russell, 1949, p. 11, 12, 15, 20, 24), would yield a total of 2.0×10^{25} g H_2O. The $16,600 \times 10^{20}$ g of "excess" water (Table 1) would be 0.0083 of this amount.

It is of some interest to compare this rough estimate of 0.8 per cent juvenile water with another estimate arrived at in quite a different way. Judged by those measured, the hot springs in the 11 western States have an average temperature of about 29° C, which is roughly 20° above the local mean annual temperatures. For purposes of calculation, let us assume that these springs are heated by deep-seated magmatic steam at an original mean temperature of, let us say, 600° C, and that this steam is cooled to 29° by mixing with ground water at the mean annual temperature of 9° C. In cooling from 600° to 29°, steam and water would release about 1100 gram-calories for each gram of magmatic water (estimated from data in Keenan and Keyes, 1936, p. 79–81). This would be suffi-

cient to heat $\left(\dfrac{1100}{20} = \right)$ 55 grams of ground water from 9° to 29°. On these assumptions, the hot springs of the United States are being heated by mixing with an average of $\left(\dfrac{1}{56} = \right)$ 1.8 per cent of magmatic water.

It would, of course, be rash to attach any great significance to the numerical results of these calculations, for the difference between the two estimates is subject to several possible explanations. Nevertheless, it may be worth reminding ourselves that the estimate of 0.8 per cent is for new *juvenile* water and the 1.8 per cent estimate is for total *magmatic* water of whatever source. It is conceivable that the difference of 1.0 per cent between the two estimates may be a rough measure of the *resurgent* water, not newly risen from the earth's interior for the first time but recirculated water that magmas have resorbed from earlier sedimentary rocks—"second-hand" water that is now being returned to the surface.

GENERATION OF LOCAL MAGMAS

Even if we should grant all that has gone before about the probable juvenile origin of the "excess" volatiles, there still remains the question of why the magmas that released the volatiles have not long since cooled off and crystallized completely. In spite of seismic evidence that indicates the possibility, at least in some areas, of a layer of molten rock at a depth of about 80 km (Gutenberg and Richter, 1939b; Gutenberg, 1945, p. 302–307), serious difficulties restrain us from assuming a world-encircling layer (Daly, 1946, p. 712, 721–722) of slowly crystallizing magma from which volatiles have been escaping continuously ever since the world began. However, the abundant field evidence of local intrusive masses, some of them very large, that have been generated repeatedly throughout the past suggests a possible answer.

If we are willing to adopt the eclectic method of borrowing from various theories those parts of each that we like best, then a possible mechanism suggests itself—a mechanism by which local masses of hydrous magma might be generated more or less continuously throughout geologic time. The geothermal gradient varies

from place to place (Van Orstrand, 1939, p. 132–141; Landsberg, 1946); but probably below a depth of 50 to 100 kilometers rocks are heated to significantly higher temperatures (Holmes, 1915, p. 111; Adams, 1924, p. 468–472; Jeffreys, 1929, p. 154; Gutenberg, 1939, p. 162; Urry, 1949, p. 176; or one may calculate his own thermal gradient from revised data on the radioactive generation of heat in different rock types—Keevil, 1943, p. 299; Birch, 1950a, p. 612–613, 616, 619), temperatures at which they would melt, if the confining pressures were not so great (Holmes, 1916, p. 269; Adams, 1924, p. 462, 468–472; Anderson, 1938, p. 50–51, 56–57, 72–73; Benfield, 1940, p. 157–158; Buddington, 1943, p. 139).

Under these conditions, several processes may operate to cause local melting. As sediments accumulate in a region, their low thermal conductivity makes them act as a blanket to impede the upward flow of heat (Jeffreys, 1930, p. 328). And in geosynclinal troughs, where sediments accumulate to great thicknesses, the entire column of underlying rocks is depressed into zones where the temperature is significantly higher (Eskola, 1932a, p. 456–457, 468–469). Temperatures may thus be reached at which some of the minerals in the deeper rocks are melted. Moreover, as strains accumulate in the earth's crust and the rocks eventually fail by fracture, sudden localized relief of pressure and shearing stresses may, without increasing the temperature, bring some of the minerals above their melting points (Johnston and Adams, 1913, p. 210–223, 248–253; Johnston and Niggli, 1913, p. 602–603, 613–615; Bowen, 1928, p. 314; Holmes, 1932, p. 556; Wahl, 1949, p. 148). As has been shown by Bowen (1928, p. 311–320), Eskola (1932a, p. 474), and others (Holmes, 1926, p. 315–316; 1932, p. 545, 556; Kennedy, 1938, p. 38–39; Buddington, 1943, p. 132–133, 137–139; Wahl, 1949, p. 161–163), such selective fusion of the lower-melting minerals would form magmas more granitic and at the same time richer in volatiles than the original rock.

Fusion would cause increase of volume, and the resulting hydrous, granitic magmas would tend to rise, partially recrystallizing as they moved into higher, cooler zones. This process would "pump" nearly all the volatile materials from the original rock; in recrystallizing these magmas could form suites of intermediate and granitic rocks; and the volatiles would largely escape to the earth's surface. By this mechanism, the volume of granitic rocks would increase near areas of sedimentation and where the crust was for any other reason unstable. As these unstable areas migrated with the continental margins and with the sites of mountain making, the granitic rocks would thus increase progressively in volume (Eskola, 1932a, p. 468–469, 480; Lawson, 1932, p. 358–361; Wilson, 1950, p. 101, 108, 111; Bucher, 1950, p. 500–504; Hurley, 1950).

COROLLARIES AND TESTS OF THE SUGGESTED MECHANISM

Isostatic Considerations

This leads to an important corollary of the suggested mechanism. If granitic rocks have grown progressively in volume through geologic time, then isostatic equilibrium would require more or less continuous readjustments, by which the thickening blocks of lighter, granitic or continental types of rocks would rise higher and higher above adjacent blocks of undifferentiated material. In another terminology, this would mean that the ocean basins must sink deeper as the continental blocks thicken. If the ocean basins have sunk at approximately the same rate as the volumes of granitic rocks and of sea water have grown, then it is no coincidence, but the effects of one single process, that the surface of the sea has oscillated back and forth near the same level on the continental shelves throughout the geologic past.

Isostatic balance between the oceanic and continental blocks affords a basis for estimating the relative quantities of water and granitic rocks and of the original subcrustal matter from which they may have been derived by selective fusion. The area of the earth's surface that rises above sea level is roughly 1.49×10^{18} cm²; but the actual margins of the continental blocks lie much farther oceanward, beyond the continental shelves and near the base of the steep continental slopes. If 3000 meters below sea level is taken as approximately the base of the continental slopes, then the total area of the continental blocks is about 2.32×10^{18} cm² (Sverdrup, Johnson, and Fleming, 1946, p. 15, 19, 21).

The mean elevation of the continental blocks, as thus defined, is about 0.12 km above sea level, and the mean depth of the ocean basins (below the −3000 m contour) is about 4.6 km below sea level. The average density of sea water *in situ* is approximately 1.04 (Sverdrup, Johnson, and Fleming, 1946, p. 219). From independent estimates, mentioned briefly elsewhere in this paper, it appears that the mean thickness of deep-sea sediments may be about 1.3 km and their mean density, when filled with interstitial water, about 2.3. For purpose of this calculation, the average density of rocks to several tens of kilometers below the continents (the sedimentary, "granitic", and "intermediate" shells) may be taken as 2.9, and that of undifferentiated ultrabasic rocks to similar depths below the deep-sea sediments as 3.2.

From these several estimates, the average depth of compensation below the continents may be found to be

$$0.12 +$$

$$\frac{(0.12 \times 2.9) + 4.6(3.2 - 1.04) + 1.3(3.2 - 2.3)}{3.2 - 2.9}$$

$$= 38.3 \text{ km.}$$

This value accords reasonably well with the average depth to the Mohorovičić discontinuity, which is found widely distributed beneath the continents but is not recognized with certainty over extensive areas beneath the oceans (Macelwane, 1939, p. 237–239; Gutenberg and Richter, 1939a, p. 321–322). This major discontinuity is often interpreted as representing the approximate base of the crustal materials that make up the continents.

It seems permissible to assume that these densities of continental and oceanic materials have remained approximately the same throughout the past. It follows then that, if there was a time when the mean depth of the ocean basins and the mean thickness of deep-sea sediments were half their present values, isostatic equilibrium would require that the mean elevation of the continents and the mean depth of compensation below the surface of the continental blocks would, at that time, also be just half their present values. If the total areas of the continental blocks and of the oceanic basins have remained approximately the same (peripheral growth of the continents having approximately balanced subtraction by continental foundering), this strictly proportionate deepening of the oceanic basins and thickening of the continental crust, which is required by isostatic balance, would accord with the suggested mechanism of selective fusion which likewise would require that the volumes of sea water and of continental rocks have grown in strict proportionality.

The total mass of the continental blocks today may be estimated from the results of the previous calculation at $(2.32 \times 10^{18} \text{ cm}^2)(38.3 \times 10^5 \text{ cm}) \times 2.9 \text{ g/cm}^3 = 258 \times 10^{23}$ g. Allowing for the probable quantity of crystalline rocks that has been eroded from the continents in the past and is now represented as deep-sea sediment on the ocean floor, one obtains an estimate of 2.65×10^{25} g for the total mass of crustal rocks that have been formed on and in the continental blocks. It is to be noted that this estimate makes no allowance for any similarly differentiated crustal rocks that may now be lying foundered beneath the sea.

According the the eclectic hypothesis here suggested, this 2.65×10^{25} g of crustal rock has been formed, largely by selective fusion and subsequent recrystallization of the resulting magma, from an unknown quantity of subcrustal rock materials. The total mass of the earth's silicate mantle that lies directly below the continents, to a depth of 2900 km and above the earth's "iron core," may be estimated at about 185×10^{25} g. Much of this subcrustal matter may still be in very nearly its original condition (Birch, 1950b). But that part of it lying above the maximum depth (of about 700 km) to which deep-focus earthquakes are recorded (Gutenberg and Richter, 1941, p. 4–11; Benioff, 1949, p. 1844–1854) may have been worked over and subjected, at one time or another during the course of geologic history, to at least some selective fusion. The total mass of this subcrustal matter below the continental areas and between depths of 38 and 700 km is about 50×10^{25} g.

On the assumption that this is roughly the quantity of subcrustal matter that may have yielded both the "granitic" magmas that became the continental rocks and the volatile substances that have formed the atmosphere and ocean, it is of interest to compare the relative amounts of each. With an average water content of 1.15 per cent (Clarke, 1924, p. 29), the 2.65×10^{25} g of present crustal rocks would contain 3050×10^{20} g H_2O. This, added to the $16,600 \times 10^{20}$ g of "excess" H_2O in the present atmosphere, ocean, and sedimentary rocks, gives a total of $19,650 \times 10^{20}$ g H_2O that has escaped, along with the 2.65×10^{25} g of "granitic" magmas, from the subcrustal matter. Thus the original $(50 + 2.65) \times 10^{25}$ g of subcrustal matter would have yielded, by selective fusion, $\frac{2.65}{52.65} = 5.0$ per cent, or 1 part in 20, of magmas that have risen to form the crustal rocks and $\frac{0.1965}{52.65} = 0.37$ per cent H_2O. If the "granitic" magmas originally held all this water in solution, they would have

contained at that time an average of $\dfrac{0.1965}{2.65} = 7.4$

per cent H_2O, of which $\dfrac{0.166}{2.65} = 6.3$ per cent subsequently escaped to the surface during recrystallization of the magmas.

These estimates are, of course, only crude ones based upon very uncertain foundations. They make no allowance for possible "granitic" rocks now foundered beneath the oceanic depths; to whatever extent any continental rocks now lie beneath the ocean floor, the calculated percentages of water in the "granitic" magmas and of water lost from the subcrustal matter must be reduced proportionately.

A rough but independent check on the reasonableness—or otherwise—of this estimate of the amount of subcrustal matter that has been selectively fused can be made by considering certain substances that may have been concentrated in the crustal rocks or at the surface as the result of the supposed differentiation. In the absence of better information, the average composition of the original undifferentiated peridotitic material may be taken as similar to that of stony meteorites (Bowen, 1928, p. 315–316; 1950. *See also* references in section on Dense Primitive Atmosphere—Solution in the Melt). The silicate phase of stony meteorites contains an average of 0.063% H [equivalent to 0.56% H_2O] and 0.199% K [equivalent to 0.24% K_2O] (Brown, 1949b, p. 626). Thus the calculation that 0.37% H_2O has escaped from the subcrustal matter to a depth of 700 km would mean that, on the average, $\dfrac{0.37}{0.56} = 66\%$ of this mass of material has undergone selective fusion.

If the residual unmelted fraction remaining after selective fusion has an average composition similar to that of dunite, it would contain about 0.04% K_2O (Daly, 1933, p. 20). The average igneous rocks now exposed on the continents contain 3.13% K_2O (Clarke, 1924, p. 29). From these average compositions, we may calculate that the original subcrustal matter has yielded about $\dfrac{(0.24 - 0.04)}{(3.13 - 0.04)} = 6.5\%$, or 1 part in 15, of magmas that have crystallized to form the present crustal rocks. This ratio of 1 part of magma to 15 parts of subcrustal matter, when compared with the previous estimate of 1 part in 20 (based on total material to 700 km), would mean that on the average about 75% of the mass of subcrustal matter to a depth of 700 km has undergone selective fusion.

It is only fair to add that ratios of much more and much less than 1 part in 15 may be obtained by using for comparison other elements than K and other rock types (peridotite instead of dunite and

diorite instead of the average igneous rock now exposed at the upper surface of the continental blocks). Yet when one considers that the process of selective fusion would act unequally on different constituents of the subcrustal matter and would probably remove much larger proportions of the readily volatile substances, such as water, than of the more refractory rock-forming minerals, it is surprising to find even such rough agreements as those just mentioned. About all that may safely be concluded is that the general order of magnitude of the ratio of "granitic" magmas to subcrustal matter appears not unreasonable.

Other Geologic Tests

The least one can ask of any hypothesis is that it be consistent with the known facts. But it is not always as easy as it sounds to apply this test, because much information and hard work are sometimes required to formulate corollaries of a hypothesis so that they can be tested by the known facts. I have thought of a few geologic tests of this suggested mechanism, but I am sure that many others have not occurred to me.

At first thought, the widespread epicontinental seas of the past seem to contradict the suggestion flatly. But areas are not to be confused with volumes. If the ocean basins have been sinking relative to the continental blocks, then one must look largely to the ocean floor, rather than to the continents, for evidence of a growing volume of sea water. Unfortunately, our information about the ocean floor is still very sketchy. The flat-topped sea mounts, or guyots, discovered by Hess (1946) indicate a considerable sinking of the ocean floor, some part of which may mean a general rise of sea level and not merely local deformation. Other lines of evidence, such as submerged terraces and great thicknesses of shallow-water limestones on some oceanic islands (Carsey, 1950, p. 376), suggest, although likewise they do not prove, the same conclusion. It has long been recognized that very few areas that once were part of the deep sea have later risen to become part of the continents (Walther, 1911, p. 60–61). Furthermore, the truncation of structural trends at some continental margins and the geographic distribution of certain animals and plants seem to require that parts of some land masses have broken off and foundered to oceanic depths

(Barrell, 1927, p. 303–305; Moore, 1936, p. 1786). These are all rather obvious, general tests that yield results consistent with, but certainly not proving, an increasing volume of ocean basins through geologic time.

Undoubtedly other and more rigorous tests should be looked for in the stratigraphic and structural record on the continents, where many more facts are available than we yet know about the ocean basins. A gradually increasing volume of sea water and of marine sediments would mean a gradual rise of sea level and relatively slow marine transgressions, modified of course by the effects of local deformation, and interrupted by relatively rapid withdrawals of the sea, when the ocean floor sank to new positions of equilibrium. Such sudden withdrawals of the sea would affect parts of all continents at the same time (Moore, 1936, p. 1803–1805, 1808). On the other hand, if hydrous granitic magmas have formed by the mechanism indicated, then mountain-making movements, as contrasted with emergences of the continental shelves, need not have been even approximately contemporaneous from one continent to another (Gilluly, 1949).

How well or how poorly do the geologic facts bear out such corollaries as these? Or if these are not valid tests of the suggested mechanism, I trust that others will think up much better ones.

As I warned at the beginning, this subject ramifies almost endlessly into many problems of earth history. A satisfactory solution of the problem of the source and history of the earth's air and water depends on the solution of a great many other questions. Because it is so closely related to many others, this problem is likely long to remain one of those hardy perennials that need a new look and reappraisal every few years, as new observations accumulate. Perhaps what I have presented here is simply another case of putting 2 and 2 together and getting 22, instead of 4. But this review and these tentative conclusions will have served their purpose if they help stimulate—or if they provoke—critical observations and critical thinking about the history and significance of sea water.

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