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# GEOLOGIC HISTORY OF SEA WATER: AN ATTEMPT TO STATE THE PROBLEM

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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  $\text{CO}_2$  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  $\text{H}_2\text{O}$  and  $\text{CO}_2$  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.

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