

Some chemical aspects of the evolution of the terrestrial atmosphere¹

By HANS E. SUESS, *University of California, San Diego, La Jolla, California*

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ABSTRACT

At the time of formation of the solar system an almost quantitative separation of gases from solids must have taken place. An upper limit for the amount of gas that could have followed the solids when they accumulated into the planet Earth can be derived from the amount of neon present in the terrestrial atmosphere. This upper limit shows immediately that most of the nitrogen and other volatiles have been derived from the solid matter during, or after, its accumulation. The relative amounts of rare gases show that most, if not all, of the rare gases have undergone a separation process prior to the formation of the Earth. The probable nature of this process is interesting from the point of view of a theory of the origin of the solar system.

The free oxygen in the terrestrial atmosphere cannot have been present at the time when the Earth formed, but must have evolved during geologic time. The escape from the Earth of hydrogen, produced by photolysis of water vapor, was important for the formation of an atmosphere containing free oxygen. It has been shown experimentally that photolysis of water vapor yields hydrogen even in the presence of oxygen. Charged particle reactions in the ionosphere are probably also important for the maintenance of ~ 0.5 ppm of the H_2 present in the atmosphere. The amount of oxygen produced by photolysis was presumably increased by oxygen produced by plant photosynthesis combined with incomplete re-oxidation of the organic plant material formed by this process. The amount of oxygen produced over geologic time, and used up by the oxidation of surface material of the Earth, presents a fascinating geochemical problem that cannot yet be solved in an unambiguous way.

In recent times the problem of the origin of the atmosphere of the earth has elicited renewed interest, partly as a specific geochemical problem and partly in connection with questions concerning the chemical composition of the atmospheres of other planets. It is, in general, agreed that the terrestrial atmosphere is secondary, i.e., that it formed through degassing of the solid earth and, also, that the atmosphere had been reducing in composition at an early stage and had become oxidizing during its geological history. Yet, many questions concerning the general course, as well as the details, of these events cannot yet be answered.

There are only a small number of observational facts allowing conclusions regarding the evolution of the atmosphere, and I would like to review here some of these facts and also mention some important questions that cannot yet be answered without further empirical data.

Specifically, I would like to refer to the following four points which, in my opinion, deserve special attention and which, in the past,

have not been discussed exhaustively at the various recent conferences on the subject: (1) The composition of primordial solar matter as compared with that of the terrestrial atmosphere. (2) Composition of exhalation products that one might expect from the solid parts of the earth. (3) Production of hydrogen by photolysis of water vapor and escape of hydrogen from the atmosphere. (4) Plant photosynthesis and

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² See, for example, the proceedings of the conference held at the Goddard Institute for Space Studies, NASA, New York, April 8-9, 1963, on "The Origin and Evolution of Atmospheres and Oceans", P. J. Brancazio and A. G. W. Cameron, Eds., and also papers presented at the National Academy of Science meeting, April 29, 1964, NAS Proc. 52, 387-397, 1964. References to all the pertinent literature not quoted here can be found in these publications.

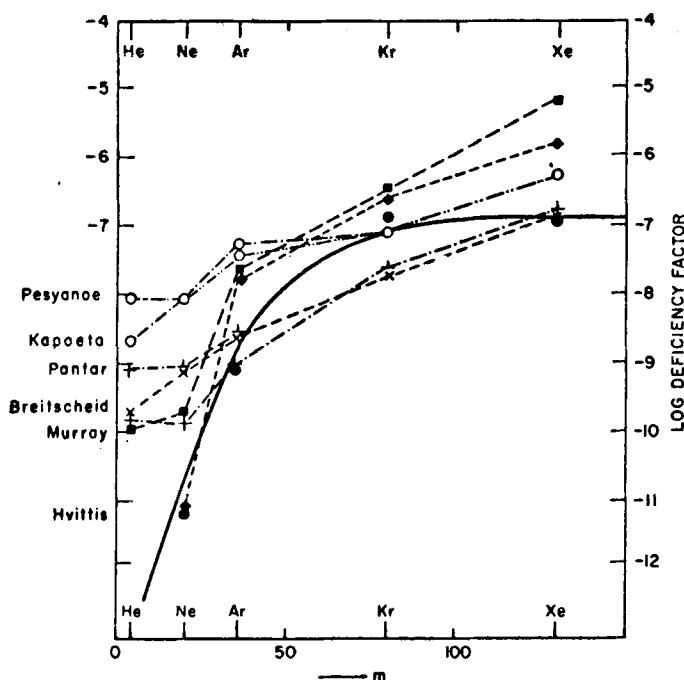


FIG. 1. Deficiency factors of rare gases in meteorites and in the atmosphere (solid line) plotted against the atomic weight, according to SIGNER & SUESS (1960).

the oxidation or preservation of organic compounds formed by it.

The main problem concerning the origin of the terrestrial atmosphere is, of course, how it is possible that in a world of highly reducing chemical composition, in which hydrogen is almost one thousand times more abundant than oxygen, a planet can have an atmosphere containing a large proportion of free O_2 .

Composition of the atmosphere as compared to that of primordial solar matter

The rare gases are excellent tracers for geochemical events in general, and in particular in connection with the question of how effective the separation of solids from gaseous material was at the time when the earth formed, and to what an extent gases were present in solids. A comparison between solar and terrestrial abundances shows that only about one 10^{-11} parts of the neon originally present can have been retained by the earth when it formed. (For further details and literature see, for example, SIGNER & SUESS, 1963.) The fraction of an ele-

ment retained is commonly expressed as its deficiency factor. This factor is not the same for all the rare gases; about ten thousand times as much xenon was retained, compared to neon. The deficiency factor of the other rare gases lie between neon and xenon. The rare gases were not only separated very effectively from the solids, but also a different separation process has separated them from each other.

It seems most remarkable that many meteorites contain rare gases, not only in concentrations of comparable order of magnitude as the earth as a whole, but also in relative amounts similar to those present in the terrestrial atmospheres (Fig. 1). It has been suggested occasionally that the fractionation of the rare gases from each other occurred through diffusive losses from small, solid objects. If this were the case, then the relative amounts of rare gases present in the atmosphere, as well as in the meteorites, would strongly support the view that the earth formed from chondritic material. However, it is also possible that the separation of rare gases from solids occurred prior to their incorporation into the meteorites and prior to

the retention of the rare gases by material from which the earth formed. The rare gas distribution in the individual mineral phases of meteorites, and peculiar variations in the isotopic composition of the rare gases in them may eventually clarify these questions, although the presence of radiogenic and of cosmic-ray-produced rare gas isotopes complicates the situation.

The question of whether or not the rare gases were part of a thin primordial atmosphere, or were derived by degassing of the mantle, could perhaps be answered by further studies of excess xenon-129 in basaltic material and in gases from the interior of the earth. REYNOLDS (1963) found such excess xenon-129, but it seems as yet uncertain whether this xenon isotope was derived from iodine-129 produced by a nuclear reaction during the geologic history of the earth, or, as is the case for meteorites, from iodine-129 produced prior to the time when the earth accumulated.

A comparison of the abundance of nitrogen in the atmosphere with that in the sun shows that its deficiency factor is about an order of magnitude smaller than that for krypton and xenon. This shows conclusively that nitrogen, just like water, was chemically retained together with the condensed material from which the earth formed.

The amounts of carbon present on the surface and in the mantle of the earth provide interesting boundary conditions for the redox state and temperature at the time of separation of the gases from the solids (Suess, 1962).

The possible composition of exhalation products of the earth

At present, volcanic gases appear to be free of truly juvenile material. This was not the case during the early history of the earth. The question of what kind of boundary conditions for the chemical composition of the mantle are provided by the assumption that the water masses of the oceans were derived from it, has, in my opinion, not been discussed exhaustively. A mantle composed of chondritic material contains some 10 weight per cent of metallic iron. In general, it is assumed that the metallic iron gradually settled out to form the core of the earth, while at the same time water-vapor reached the surface of the earth to form the

oceans. At temperatures prevailing in the interior of the earth, the water will undoubtedly react with iron until a certain P_{H_2}/P_{H_2O} ratio is reached. Little is known about what this ratio may be. UREY (1952) pointed out, because of the solubility of H_2O in silicates, the water activity may be considerably decreased so that the equilibrium ratio may be smaller than expected. The possibility of the presence of carbon, of elementary metallic silicon, of sulfur, and perhaps other reducing compounds in the primitive mantle has been also considered. Therefore, it seems probable that together with water, relatively large amounts of hydrogen have reached the surface of the earth.

The escape of hydrogen from the atmosphere and the photolysis of water vapor

It has been known for a long time that helium escapes from the atmosphere of the earth. The rate by which it escapes is difficult to estimate, either from observed data on the flux of radiogenic helium to the atmosphere or from our knowledge of the constitution of the upper atmosphere and the rate of escape calculated from it. The problem is further complicated by the fact that comparable amounts of helium enter the atmosphere of the earth through the low-energy plasma streaming from the sun. In any case, a residence time of both helium-3 and helium-4 in the terrestrial atmosphere of the order of, or smaller than, one million years can be estimated. A detailed quantitative discussion was recently published by Macdonald (see BRANCAZIO & CAMERON, 1964). The atmosphere of the earth contains about 0.5 ppm of hydrogen and it is obvious that hydrogen will leave the atmosphere at a rate equal to or larger than that of helium-3 and helium-4. From the isotopic composition, in particular from the tritium content, it was shown that the hydrogen in the atmosphere was certainly produced by photolysis of water vapor (HARTECK & SUESS, 1949; HARTECK & FALTINGS, 1950).

For a long time it appeared strange that photolysis of water vapor in the presence of large quantities of oxygen could lead to a steady-state concentration of H_2 of the order of 0.5 ppm. However, the fact that this was indeed the case was experimentally confirmed by laboratory experiments which were carried out

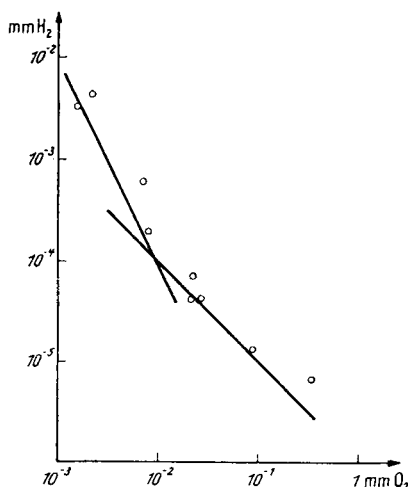
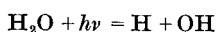
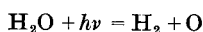


FIG. 2. Steady-state concentrations of hydrogen obtained by irradiating H_2O vapor at one mm pressure in the presence of oxygen, plotted against P_{O_2} according to BARTH & SUESS (1960).

by BARTH & SUESS (1960). It was expected that atomic hydrogen formed by the reaction:



should then immediately react with molecular oxygen to O_2H and, further, back to H_2O . The explanation for the formation of molecular hydrogen in the presence of oxygen, however, is given by the fact that the photolysis of H_2O also takes place according to the equation:



(MARTELL & GROTH, private communication; for literature references see McNESBY & OKABE, 1964).

The presence of large amounts of oxygen will decrease the rate of photolysis of water vapor because of the shadowing effect of the O_2 molecules, but a small steady-state concentration of molecular hydrogen will always be present. This makes it possible to understand the presence of H_2 in the atmosphere in a qualitative way; however, it is still impossible to account for it quantitatively because of the extreme dryness of the upper atmosphere and because of other complicating factors such as the presence of methane of comparable order of magnitude to that of H_2 , the influx of hydrogen atoms from the sun, and the occurrence of charged-particle reactions at high altitudes.

The steady-state concentration of H_2 , found by Barth and Suess in their particular laboratory system, was inversely proportional to P_{O_2} or $P_{\text{O}_2}^2$, depending on the range of partial O_2 pressure of the experiment (see Fig. 2). Clearly, an escape of hydrogen at the present rate cannot have contributed significantly to the formation of molecular oxygen in the atmosphere, but in an atmosphere containing only 1/10 to 1/100 of the present level of oxygen, the hydrogen concentration may have been between 10 to 1000 times higher than at present. The escape of the hydrogen from such an atmosphere could then perhaps account for much of the oxygen in the atmosphere, in particular, if the atmosphere had been different and the water vapor content of the upper stratosphere had been higher than at present.

The effect of plant photosynthesis on the oxygen content of the terrestrial atmosphere

Under the present conditions, the biosphere is essentially in a steady state at which the organic matter produced by plant life is reoxidized again so that practically all the oxygen that has been produced by photosynthesis is re-consumed. This was probably true for a large part of the geologic history of the earth. The known coal and oil deposits correspond to only a very small fraction of the oxygen in the atmosphere. However, the total amount of carbon in shales and in other sedimentary rocks, although in low concentration, exceeds that present in coal deposits by a large factor and corresponds to many times the oxygen in the atmosphere (see, for example, Rubey, in BRANCAZIO & CAMERON, 1964). It is probable that photosynthesis by terrestrial plants has never appreciably affected the oxygen content of the atmosphere because the organic matter produced was immediately reoxidized by bacterial or animal life, although the amount of oxygen and organic matter produced per unit of time by land plants exceeds that of marine plants by a very large factor. The carbon contained in marine sediments was deposited mostly under anaerobic conditions and it appears plausible that at time when the oxygen content of the atmosphere was lower than that of today, large parts of the deep water masses of the oceans were free of oxygen. An answer to the question of how large a contribution to the free oxygen content of the

atmosphere was due to plant photosynthesis can only come from a careful study of the carbon content of sedimentary rocks and of the absolute amounts of carbon in these rocks as a function of their geologic age. The oxygen equivalent of this carbon will then have to be balanced against the amount of oxygen used up by the oxidation by the weathering of igneous rocks.

Concluding remarks

Perhaps it would help to answer the many questions concerning the evolution of the terrestrial atmosphere if the chemical composition of the atmospheres of Mars or Venus would be known. The present ideas of how the terrestrial atmosphere developed would undoubtedly be strongly influenced by comparisons of

conditions on our planet with those on Venus, but the composition of the dense atmosphere of this planet is essentially unknown. As far as the free oxygen in our atmosphere is concerned, we know the types of processes responsible for its presence, but neither one of these processes can as yet be described in a quantitative manner. It is impossible to determine whether inorganic photolysis of water vapor and subsequent loss of hydrogen or organic plant photosynthesis was predominantly responsible for the accumulation of the free oxygen. An answer to the question of whether or not free oxygen is present in the atmosphere of Venus would certainly help to decide this problem, although it would be a mistake to draw any conclusions concerning life on that planet from the presence or absence of free oxygen in its atmosphere.

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ХИМИЧЕСКИЕ АСПЕКТЫ РАЗВИТИЯ ЗЕМНОЙ АТМОСФЕРЫ

Во время образования солнечной системы должно было произойти почти полное отделение газов от вещества в твердом состоянии. По количеству неона, содержащегося в земной атмосфере, может быть оценено сверху количество газов, которые имелись при соединении отдельных твердых тел в планету земля. Эта оценка показывает, что большинство азота и других летучих газов выделилось из вещества в твердом состоянии во время или после его соединения в планету. Относительные величины инертных газов показывают, что большинство из них, если не все, выделились во время, предшествующее образованию земли. Вероятная природа этих процессов исследуется с точки зрения теории происхождения Солнечной системы.

Свободный кислород не мог содержаться в земной атмосфере во время образования земли и должен был выделяться в течение

геологического периода. Главным процессом, ведущим к наличию его в атмосфере, была утечка из атмосферы водорода, образовавшегося при фотолизе паров воды. Было показано экспериментально, что при фотолизе паров воды образуется водород даже в присутствии кислорода. Вероятно, что для поддержания 0,5 ppm H_2 в атмосфере важны также реакции заряженных частиц в ионосфере. Количество кислорода, полученное при фотолизе, увеличивалось, повидимому, за счет кислорода, выделявшегося при фотосинтезе растений и неполном окислении образовавшихся при этом органических продуктов. Оценка количества кислорода, израсходованного на окисление веществ поверхности земли за геологический период, является заманчивой геохимической задачей, которая не может быть еще решена однозначно.