The Geochemistry of the Atmosphere and the Constitution of the Terrestrial Planets

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IT might appear as an arbitrary limitation to discuss the geochemistry of the atmosphere in relation to the constitution merely of the terrestrial planets (Venus, Mars, Mercury, and the Moon). However, the giant planets (Jupiter, Saturn, Uranus, and Neptune) stand far apart both for their low surface temperatures (less than 150°K) and the strange composition and vast depth of their atmospheres. The distinction between these two groups is also in evidence among the bulk properties of the planets. The mechanical characteristics of all the planets are given for reference in Table I.

I. COMPOSITION OF THE PLANETARY ATMOSPHERES

The average chemical composition of dry atmospheric air appears to be uniform to a high degree, as regards both its geographical and vertical distribution. Samples taken during balloon flights have failed to show any signs of variation up to altitudes of about 20 km. Above that level a minute prevalence of helium is indicated, marking the incipient change from convective mixing to diffusion equilibrium. This gravitational separation, according to the molecular weight of the several constituents, used to be invoked as the chief argument in favor of the hypothesis that the uppermost stratosphere should be practically pure hydrogen. Modern spectroscopic observations of the light emitted by the Corona Borealis, extending up to 500 km and more, have refuted this contention. Following mainly F. A. Paneth's critical discussion,[1] Table II gives the composition of dry air. The water vapor content is so variable that it must suffice to illustrate the order of magnitude by some data for the Mount Wilson Observatory (cf. Table III). The absorption spectrum of the terrestrial atmosphere, projecting itself upon the spectra of celestial objects as background, shows the bands of O_2, H_2O, CO_2, O_3, N_2O, N_2O_5, and HDO; the last three of these molecules have been discovered recently by A. Adel[2] as the result of a painstaking analysis of the infra-red solar spectrum. The characteristic absorption spectra of nitrogen and the noble gases are hidden from the observer because our atmosphere is absolutely opaque to radiation shorter than about $\lambda 2900$. Here the O_3 absorption makes itself felt, which toward the Schumann ultraviolet merges into the O_2 absorption. In the infra-red terrestrial water vapor and carbon dioxide block nearly all celestial radiation longer than about 13μ.

The spectroscopic analysis of the atmospheres of other planets is interfered with by the Earth's atmosphere in two ways. First, as just explained, wide continuous ranges of wave-lengths are permanently inaccessible. Second, the discrete bands of the terrestrial atmospheric constituents impair the spectroscopic test for the same gases on other planets, but fortunately they do not frustrate it altogether. For by the relative motion in the line of sight between planet and observer small shifts in wave-length are produced which separate partially the planetary and terrestrial lines, coinciding strictly at relative rest. Gases not represented in our own atmosphere are easily discovered, provided that their bands are accessibly located and their mass surpasses the threshold of sensitivity of the spectroscopic method. For instance NH_3 was detected on Jupiter and Saturn, and CH_4 was found on the same planets and on Uranus and Neptune, too. Very likely the atmospheres of these four giant planets are rich in hydrogen, but H_2 does not admit of direct spectroscopic identification. In fact, the low mean densities of these massive bodies (see Table I) can only be explained on the assumption that the outer zones of their bulk consist of highly compressed hydrogen,[3] but further discussion of that point would go beyond the scope of this paper. In the present context the main interest attaches itself to the constitution of the terrestrial planets Mars,

[1] F. A. Paneth, Quart. J. Roy. Met. Soc. **63**, 433 (1937).

[2] A. Adel, Astrophys. J. **90**, 627 (1939); **93**, 506 and 509 (1941); **94**, 375, 379, 449, and 451 (1941).

[3] R. Wildt, Astrophys. J. **87**, 508 (1938).

TABLE I. Mechanical characteristics of the planets. a, equatorial radius, unit 6378.388 km; M, mass, unit $5.966 \cdot 10^{27}$ g; g, acceleration of gravity, unit 980.60 cm sec.$^{-2}$; V, velocity of escape, unit 11.188 km sec.$^{-1}$; D, mean density, 1 g cm^{-3}; C, moment of inertia.

	a	M	g	V	D	C/Ma^2
Moon	0.273	0.01226	0.1645	0.212	3.33	0.397
Mercury	0.403	0.034	0.2093	0.290	2.86	—
Venus	0.989	0.820	0.8383	0.910	4.86	—
Earth	1.000	1.000	1.00000	1.000	5.52	0.3345
Mars	0.538	0.081	0.3717	0.447	3.84	0.359
Jupiter	11.26	317.1	2.501	5.32	1.30	0.241
Saturn	9.45	95.02	1.064	3.17	0.69	0.235
Uranus	4.19	14.74	0.840	1.88	1.10	0.236
Neptune	3.89	17.27	1.141	2.12	1.62	0.241
Pluto	—	1.0±0.1	—	—	—	—

TABLE II. Composition of the troposphere, F. A. Paneth (1939).

Constituent	μ	Composition of dry air (in percent by volume)	Equivalent path at S.P.T.
N_2	28.016	78.09	6246.5 m
O_2	32.000	20.95	1675.7 m
A	39.944	0.93	74.4 m
Co_2	44.010	0.03	2.4 m
		100.00	
Ne	23.183	$1 \cdot 8 \cdot 10^{-3}$	14.4 cm
He	4.003	$5 \cdot 2 \cdot 10^{-4}$	4.2 cm
Kr	83.7	$1 \cdot 10^{-4}$	0.8 cm
H_2	2.016	$5 \cdot 10^{-5}$	0.4 cm
Xe	131.3	$8 \cdot 10^{-6}$	0.06 cm
O_3	48.000	variable	3 mm
N_2O	44.016		several mm
N_2O_5	108.016	approximately	0.03 mm

(Equivalent path at S.P.T.) $\cdot (22411.5 \text{ cm})^{-1} = \text{mole cm}^{-2} = \text{g cm}^{-2}\,\mu^{-1}$; height of the homogeneous atmosphere: $H^* = kT/g\mu m_A = 7.999$ km; mean molecular weight of dry atmospheric air: $\mu = 28.966$.

Venus, and Mercury. The Moon has almost the same mass and dimensions as Mercury, and must be regarded as a twin planet rather than a satellite. The spectra of Mercury and the Moon are identical with that of the illuminating sun light, and their surfaces, having a very low reflectivity, are evidently bare rock devoid of any trace of atmosphere. Such small bodies lack indeed the gravitational pull necessary to retain an atmosphere. There is another pair of planets with nearly equal masses and dimensions, namely Venus and the Earth, which also have in common the predominant turbidity of their atmospheres. The study of the intensity of the earthshine, visible in the dark part of the Moon's phase, affords a measure of the average state of cloudiness of our globe as a whole, which turns out to be quite high. Venus' brilliantly white surface is a perennial stratum of clouds that has never been pierced, though on photographs taken in ultraviolet light Ross discovered transitory diffuse markings which may have been partial clearings. Hence spectrum analysis applied to Venus can fathom only the atmospheric layers above the clouds, the nature of which is still mysterious. The disk of Mars displays a wealth of detail, the exact nature of which in many cases is still somewhat uncertain because of the limited optical resolving power. However, judging by the variable blurring of the major features, there can be no doubt about the presence of a hazy atmosphere undergoing seasonal and ephemeral meteorological changes. The conspicuous polar caps must be composed of frozen water, since the temperature is known to be too high to permit the existence of carbon dioxide snow. The red color of large areas of the surface strongly suggests the presence of ferric iron in minerals, which may be due to weathering in an atmosphere that at one time contained free oxygen.

The outstanding success of spectrum analysis

TABLE III. Atmospheric composition of Earth, Venus, and Mars.

	O_2	CO_2	H_2O
Earth, sum total*	0.49–0.78 kg cm^{-2}	7.3–9.7 kg cm^{-2}	289 kg cm^{-2}
Earth, present atmosphere	230 g cm^{-2}	0.4 g cm^{-2}	
Earth, above Mount Wilson (6000 feet)		extreme	0.2–2.8 g cm^{-2}
		average	0.7 g cm^{-2}
Venus	<2 g cm^{-2}	40–80 g cm^{-2}	<0.1 g cm^{-2}
Mars	<2 g cm^{-2}	<20 g cm^{-2}	<0.05 g cm^{-2}

* From Table IV.

TABLE IV. Basic data of geochemistry, V. M. Goldschmidt (1933).

Masses per cm^2 of the total surface of the Earth (5.10×10^{18} cm^2):	755 g atmospheric nitrogen
	230 g atmospheric oxygen
	2 g oxygen dissolved in sea water
	256–544 g fossil oxygen in sediments*
	0.4 g atmospheric carbon dioxide
	20 g carbon dioxide dissolved in sea water
	6.56 kg fossil carbon dioxide in sediments
	3.1 kg carbon dioxide equivalent to deposits of coal, bitumen, and humus formations, including the carbon of the biosphere
	3.0 g water vapor
	100 g fresh water
	4.5 kg continental ice
	6 kg water in hydrated and colloidal sediments
	278 kg sea water
	160 kg igneous rocks decomposed into sediments (upper bound)

* Goldschmidt calls "fossil" that amount of oxygen which is bound in sediments during their formation at the expense of primary eruptive rocks (oxidation of Fe^{++} and Mn^{++} to Fe^{+++} and Mn^{+++} and of sulphides to SO_3). In a similar manner the term "fossil CO_2" refers to the mass of carbon dioxide of atmospheric provenience which has become deposited in sedimentary carbonates of calcium and magnesium.

as applied to the terrestrial planets was the discovery by W. S. Adams and T. Dunham, Jr. of large amounts of CO_2 in the atmosphere of Venus.[4] The quantitative determination is still beset with difficulties. Preliminary estimates[5] indicate a CO_2 layer of 200–400 meter-atmospheres, surpassing the total mass of this gas in the Earth's atmosphere by a factor of at least 100. An earlier spectroscopic test for O_2 and H_2O, by Ch. E. St. John and S. B. Nicholson,[6] did not give any positive result, but fixed upper limits to the abundance of these gases. In the path traversed by solar light through Venus' atmosphere there must be less than 1 meter-atmosphere of oxygen and less water vapor than would correspond to 1 mm of precipitable water. The scarcity of oxygen is indirectly confirmed by the lack of strengthening of the terrestrial ozone bands in the spectrum of Venus.[7] If there were in the atmosphere of this planet as much oxygen as in our stratosphere above the 20-km level (about 140 meter-atmospheres of O_2), where practically all the ozone is concentrated for photochemical reasons, then Venus' atmosphere could be expected to contain about as much ozone as the stratosphere, and hence the ozone bands should be thrice as strong in the spectrum of Venus. Such an effect could hardly have escaped being noticed. The failure to detect any water vapor becomes suggestive if held against the fact that the huge mass of CO_2 acts like a greenhouse and raises the temperature just above the cloud stratum approximately to the terrestrial boiling point of water.[8] Even at much lower temperatures the tension of saturated water vapor reaches such enormous values that one would expect the absorption spectrum of H_2O to force itself upon the spectroscopist's attention, provided that the clouds observed on Venus are really formed by condensation of water vapor. In the spectrum of Mars the terrestrial water vapor bands are strengthened by 5 percent at most, according to the latest findings.[9] This does not contradict what has been said before about the nature of the polar caps. Because the spectrograph can detect only water vapor, and this may be distributed through a large part of the entire atmosphere, the visual observation of a thin

[4] W. S. Adams and T. Dunham, Jr., Pub. Astronom. Soc. Pac. **44**, 243 (1932).
[5] T. Dunham, Jr., Carnegie Inst. Wash. Yearbook **31**, 154 (1932); see also A. Adel and V. M. Slipher, Phys. Rev. **46**, 240 (1934).
[6] Ch. E. St. John and S. B. Nicholson, Astrophys. J. **56**, 380 (1922).
[7] R. Wildt, Astrophys. J. **92**, 247 (1940).
[8] R. Wildt, Astrophys. J. **91**, 266 (1940).
[9] W. S. Adams, Astrophys. J. **93**, 16 (1941).

sheet of ice covering a limited area provides a more delicate test for water than could the most powerful spectrograph available today. However, Mars does not have large bodies of open water like the terrestrial seas, for such would reveal their existence by a very bright reflected image of the sun, as was pointed out by H. D. Taylor[10] many years ago. Adams and Dunham[11] also searched for oxygen and concluded that the Martial atmosphere cannot contain more than 1 percent of the O_2 above the same area on the Earth. The same astronomers were unable to discern the CO_2 bands on their spectrograms of Mars, but the optical means brought to bear upon this question were insufficient to guarantee the discovery of, say, 100 meter-atmospheres of CO_2 or less. It is highly desirable that further investigations should definitely establish the absence of carbon dioxide, as any quantitative result would contribute to qualifying the chemical problems posed by the surprising abundance of CO_2 in Venus' atmosphere. A summary of the spectroscopy of Venus and Mars is given in Table III, beside certain geochemical data, the origin of which will be explained presently.

The distinction between the atmosphere and the hydrosphere of the Earth is rather irrelevant in some respects. In fact, it did not exist before the surface temperature had dropped below the critical point of water. What is of greater geochemical import than the palpable discontinuity between the gaseous and liquid phase, is an ideal surface of demarkation separating the zone of weathering and sedimentation, together with the incumbent hydrosphere and atmosphere, from deeper lying material that never was exposed to the physical and chemical attack of the combined fluid phases. In assaying the terrestrial atmosphere, it is perhaps appropriate to list with its present constituents the copious masses of once volatile compounds that became fossilized in sediments and also the matter of the hydrosphere. In Table IV we reproduce a condensed version of V. M. Goldschmidt's[12] estimates relating to the basic quantities of geochemistry. The sum total of O_2, H_2O, and CO_2 taken from this table has been entered in Table III as characteristic of the Earth. Although these numbers are obviously not strictly comparable with those given for Mars and Venus, they seem to be preferable to a mere transfer of the contents of Table II.

[10] H. D. Taylor, M. N. R. A. S. **55**, 462 (1895).
[11] W. S. Adams and T. Dunham, Jr., Astrophys. J. **79**, 308 (1935).
[12] V. M. Goldschmidt, Forts. d. Mineral. Krist. u. Petrog. **17**, 140 (1933).

II. GEOCHEMICAL ASPECTS OF THE EVOLUTION OF THE PLANETS

The striking dissimilarities among the terrestrial planets as regards their superficial constitution invite speculation about the causes of their divergent evolution. These bodies are generally presumed to have a common origin, whose mechanism is as mysterious as ever. Fortunately, it is altogether unnecessary here to go into this controversial subject, and attention may be confined to the history of planetary bodies subsequent to the event that endowed them with individual existence. All *empirical* evidence favors the hypothesis that at some time in the remote past the planets were hot enough throughout to keep liquefied the most refractory substances known. Both in the terrestrial and giant planets the density appears to increase considerably from the surface toward the center of the configuration, and more so than would indicate merely the compression under its own weight of a huge mass of homogeneous composition. This points to a segregation of the *specifically* denser material near the center of the planets, as would naturally occur in an aggregate of several fluids of limited mutual solubility. It has become one of the axioms of modern geochemistry that Earth and planets alike were started on their evolutionary course as homogeneous fluid masses at temperatures of many thousands of degrees. The chemical differentiation bound to unfold as the temperature sinks is of such rich diversity that only its principal traits can be sketched here. These follow the investigations of L. H. Adams, N. L. Bowen, V. M. Goldschmidt, G. Tammann, H. S. Washington, and others.

The earliest history of the cooling planet is terminated by the onset of condensation, which initiates the first geochemical differentiation of the amorphous mass into a deep and dense atmosphere and a liquid core formed by coalescing droplets of high boiling compounds. The atmosphere is made up of the chemically inert

elements, like the noble gases, and of other gases with a very low critical temperature. The core consists mainly of the elements heavier than the neon atom, their oxides, and other compounds. The further evolution of the core is determined by the degree of reduction of the whole system, i.e., by the abundance ratio of the metals (silicon included) to oxygen and sulphur. If there is not enough oxygen to combine with all the metals, it will be bound first by silicon and the light metals of the first three columns of the periodic table, while the heavier metals will largely be left free because of their lesser affinity for oxygen. This is the case realized in the Earth. Since the mutual solubility of liquid silicates and iron, the cosmically most abundant heavy metal, is quite small at lower temperatures, the system will separate into two liquid phases, with the silicates floating on top of the denser native metal. In presence of plenty of sulphur a third liquid phase would be formed, consisting primarily of FeS which is intermediate in density between iron and the silicates and hence will tend to occupy an intermediate shell. The selective solubility of the rarer atomic species in the several liquid phases has been studied thoroughly by laboratory methods, and is also manifested in nature by the distribution of these elements among the iron, sulphide, and silicate phases of the meteoritic specimens. According to the phase in which they are concentrated preferentially, Goldschmidt classifies the elements as siderophile (iron core), chalcophile (sulphide layer), lithophile (silicate mantle), and atmophile (atmosphere). The relative mass of the different geochemical phases depends of course on the initial composition of the planet. As mentioned before, the giant planets must be especially rich in the atmophile hydrogen. This suggests that in the hot gaseous matrix of the planets the lighter elements like hydrogen and helium prevailed over the heavier ones. For the gravitational fields of the giant planets are so strong that they would check excessive loss of hydrogen by dissipation into space at surface temperatures of several thousands of degrees centigrade, whereas the atmospheres of the terrestrial planets even at their present temperatures are slowly being depleted of hydrogen. The gravitational effect naturally accounts for the difference in density between the giant planets and the terrestrial ones, but among the latter the sequence Earth-Venus-Mars-Mercury-Moon represents the order both of falling mass and density, i.e., the relation between the larger and the smaller planets is just reversed. A detailed consideration[13] of the probable density distribution throughout their interior shows that the variation is due mainly to the relative size of the iron core, which occupies about half the radii of Earth and Venus, possibly 0.4 of that of Mars, and probably is altogether missing in Mercury and the Moon. The cosmogonic meaning of these differences remains obscure. However, it should be noted in passing that the once widely held theory of the Moon's birth by disruption of the Earth subsequent to the gravitational differentiation into iron core and silicate mantle has more recently been subjected to severe criticism.[14]

The second period of geochemical differentiation is characterized by the large scale process of fractional crystallization of the silicate phase. Some of its products are accessible to inspection at the Earth's surface. These granitic rocks are thought to be the residual products of the solidification of a gabbroid magma, the primary fractions of which were heavy minerals, like olivine, ferrochromite, and magnetite, now found in the deeper layers of the silicate mantle. The majority of the chemical and mineralogical niceties involved are not germane to this paper, but a few words must be said about the behavior of the lithophile elements that are too rare to form minerals of their own. Extensive investigations by Goldschmidt and his school have established the fact that the atoms of the rare elements have entered the lattices of those common minerals whose ionic constituents happen to have the same valency and approximately the same ionic radius. For example, Ni^{++} and Mg^{++} have nearly identical ionic radii, and so have Al^{+++} and Ga^{+++}. In the first case, despite the close coincidence of the ionic radii, the different geochemical affinity of the elements Ni and Mg leads largely to their segregation in different geochemical spheres, i.e., in the siderosphere and

[13] H. Jeffreys, M. N. R. A. S. Geophys. Suppl. **4**, 62 (1937).

[14] H. Jeffreys, *Internal Constitution of the Earth*, edited by B. Gutenberg (McGraw-Hill Book Company, New York and London, 1939), p. 28.

lithosphere, respectively. But in the second case both elements have lithophile character, and hence the rare Ga enters the minerals of the common Al. The closer the coincidence of the ionic radii, as for the pair Zr—Hf, the more perfect is the "camouflage" (Goldschmidt) of the rare element. Elements of unusually small (Be, B) or large (Th, U) ionic radius had no chance of becoming captured in the early fractions of the large-scale crystallization process and accumulate in the mother liquor and in the products of the specifically lighter residual magma. For this reason the elements Th and U, the mother substances of the natural radioactive series, are preeminently concentrated in the uppermost crust of the lithosphere, though their atomic weights are among the highest and their minerals are specifically heavy. Here may be noted a gratifying convergence of the geochemical argument with the conclusions of the geophysicists as regards the generation of radioactive heat in the Earth's interior. The emerging heat flux, compared with the known radioactive content of the surface granitic rocks, indicates that the radioactive material must be restricted to a superficial layer not deeper than 50 km. Some geologists seem to find this concentration near the surface so incredible that they prefer to believe more heat is being generated in the interior than is escaping at the present time. However, this very concentration, while not quantitatively accounted for, is indeed qualitatively to be expected on geochemical grounds, provided that the solidification of the lithosphere proceeded outward from great depth.

An interesting point concerning the mode of solidification of the Earth's crust was first made by L. H. Adams[15] and has been followed up by H. Jeffreys.[16] Since liquids generally contract and become denser on cooling, a continual process of natural stirring must have been maintained throughout the originally liquid magmatic mantle by the combined action of cooling at the free surface and of the force of gravity. Now both the actual temperature and the melting point of the magma increase with depth, as the latter rises under higher external pressure, but the melting point increases the faster. Hence, as the fluid cooled, the melting point was first reached at the bottom and the consolidation proceeded from the bottom upwards. The rate of increase of the melting point depends on the differential compressibility of the liquid and solid phases. Unfortunately, the meager experimental data available do not permit prediction of this rate for the enormous pressures that prevailed at the inner boundary of the magmatic shell. If the gradient of the melting point curve at very high pressures should become less than the liquid adiabatic one, solidification would start at some intermediate depth and would progress from there as if from the bottom. Decision about the actual depth must await further laboratory studies of the melting curve, but a cautious extrapolation of the present data supports the contention that solidification started at a depth of several hundreds of kilometers at least. Even so it appears certain that the original atmosphere, overlying the liquid surface of the young planet, was considerably augmented in mass by discharge of volatile compounds from the solidifying magma. Among the products of this degassing process Goldschmidt counts not only water and carbon dioxide, but also the greater part of the elements B, S, Se, F, Cl, Br, and I now found in the oceans and sedimentary deposits. A small amount of inert gases remained occluded in the igneous rocks. The mass of occluded gases which were released later on by denudation is almost negligible. By combining the determinations of gases in rocks made by the younger Lord Rayleigh[17] with Goldschmidt's estimate that 160 kg cm^{-2} of igneous rocks were decomposed into sediments, one finds the following figures:

	N_2	Ne	A	
Present atmosphere	6250	0.15	75	m-atmos.
Freed by denudation	60	0.00012	0.03	m-atmos.

III. CHEMICAL DIFFERENTIATIONS AMONG THE TERRESTRIAL PLANETS

After having outlined some of the relevant geochemical ideas, the discussion of the peculiarities of the several terrestrial planets may be resumed. The surface temperature and gravity of the planets have an important bearing upon their ability to retain an atmosphere against the

[15] L. H. Adams, J. Wash. Acad. Sci. **14**, 459 (1924).
[16] H. Jeffreys, *The Earth* (Cambridge University Press, 1929), second edition, p. 138.
[17] Lord Rayleigh, Proc. Roy. Soc. **A170**, 451 (1939).

TABLE V. Upper and lower temperature bounds for loss of atmospheres.

		Earth	Venus	Mars
Loss small during geological times	T(°K)	$<230\mu$	$<190\mu$	$<45\mu$
Loss practically complete during geological times		$>260\mu$	$>215\mu$	$>50\mu$
Loss complete within a few years		$>560\mu$	$>465\mu$	$>110\mu$

tendency of the gas molecules to dissipate into interplanetary space. The formula for the rate of escape given by Jeans[18] is widely used, though at best it is only approximative. If applied to the terrestrial planets, it leads to the predictions summarized in Table V, where μ is the molecular weight on the chemical scale. The figures should be correct as far as the order of magnitude is concerned. At the present time Mars could not retain even hydrogen and helium, whereas the Earth would if it were not for the possibly high temperatures in the *F* layer of the stratosphere. Moreover, as H. N. Russell and D. H. Menzel[19] have pointed out, in the upper atmosphere collisions between H_2 or He and metastable oxygen atoms would impart to the former non-thermal velocities higher than that of escape. According to Goldschmidt's latest computations, the total amount of helium now found in the Earth's atmosphere is equivalent to that formed by radioactive decay during 2 billions of years by a layer of 2 kg cm^{-2} of rocks of the total surface, i.e., only about 1 percent of the material which has undergone decomposition into sediments. The difference must have escaped from the atmosphere during geological time.

The relative importance for different gases of thermal dissipation during the earliest history of the planets is more difficult to judge. Russell, in substantial agreement with Jeffreys, concludes that a surface temperature as high as 5000°K could not have prevailed for more than a few years, and that most of the loss must have occurred during the first few years, if not days, of the planet's independent existence. Rather conclusive evidence for the great loss of light elements is afforded by the conspicuous rarity of neon in the Earth's atmosphere, as compared with argon, particularly since Unsöld's[20] quantitative analysis of the *B*0 star τ Scorpii has proved that there neon and nitrogen are about equally abundant and do not fall much short of oxygen. If this evidence be accepted, it would follow that *a fortiori* the water vapor of the original atmosphere must have escaped nearly altogether. Very likely then the water of the hydrosphere is to be regarded as largely discharged from the solidifying magma, for at surface temperatures even considerably higher than the melting point water vapor would be retained indefinitely. The scarcity of water on Mars fits well into this picture. In consequence of the lesser force of gravity on this planet, the loss of water vapor ought to have continued to be appreciable during the period of upward solidification (cf. Table V). Venus presents a baffling problem in view of the apparent lack of water discussed in Section I. With the masses and mean densities of Earth and Venus so nearly equal, one is reluctant to abandon the hypothesis of a similar constitution of their bulk. However, the mass of the terrestrial hydrosphere is exceedingly small held against the lithosphere as a whole, and hence it is perhaps not unreasonable to assume that a rather minute deficiency in the aqueous component of Venus' primordial magma may have prevented the formation of a hydrosphere, i.e., all water may have been bound in hydrated minerals. Naturally such an *ad hoc* hypothesis is unsatisfactory, but it is the best that can be made for the time being. Further progress in the analysis of Venus' infrared spectrum and the ultimate identification of the chemical constitution of the cloud material may shed new light on the chemical evolution of this planet.

The paucity, if not complete absence, of free oxygen on Venus and Mars contrasts sharply with the abundance of this highly reactive element in the Earth's atmosphere. Here the elementary oxygen is commonly held to be the accumulated by-product of the assimilation process in green plants. Some biologists seem to favor the idea that the spontaneous generation of life in the remote past of the Earth has taken place under anaerobic conditions. This requisite

[18] J. H. Jeans, *Dynamical Theory of Gases* (Cambridge University Press, 1925).

[19] H. N. Russell and D. H. Menzel, Proc. Nat. Acad. Sci. **19**, 997 (1933).

[20] A. Unsöld, Zeits. f. tech. Physik **21**, 301 (1940).

is at variance with the consequences of a theory proposed by G. Tammann,[21] who has demonstrated rather convincingly how copious masses of free oxygen must have been developed immediately after the formation of a solid crust. On evaporation of all the water of the oceans and the polar caps, the partial pressure of steam would be approximately 300 atmos. At this pressure and at a temperature not far above the melting point of crustal magma the dissociation degree of steam is great enough to provide for all the free oxygen now found in the atmosphere, while the rate of escape of hydrogen is so high as to guarantee the rapid dissipation into space of the chemically equivalent amount of hydrogen. By the law of mass action the escape of hydrogen entailed a cumulative development of free oxygen. Part of this was consumed by oxidation of the liquid magma, until solidification prevented further chemical loss. While Tammann believed he could provide in this manner for the entire oxygen content of the present atmosphere, Goldschmidt[12] has criticized his quantitative analysis for the reason that through the geological ages great masses of oxygen became "fossil," i.e., deposited in oxidized sediments. Still, there can be no doubt that the process conceived by Tammann has been instrumental in producing an ample initial supply of free oxygen. Later on vast masses of additional oxygen were released by the assimilation in green plants, and so there would not seem to be any serious difficulty in making up the geochemical balance of oxygen. Now the question arises as to the course of chemical events at the surface of a planet which from the beginning was poorer in water than the Earth. On lowering the partial pressure of steam in the primordial atmosphere, the dissociation degree will steadily increase, but there will be an equally steady diminishing return of free oxygen, since the mass per unit area of the surface decreases. Finally, at a rather small partial pressure—of the order of a few atmospheres, presumably—the oxygen freed by dissociation would be consumed without residue in oxidation of the liquid magmatic surface, and after solidification there would remain a tenuous atmosphere of water vapor, entirely devoid of oxygen. This limiting case may represent the state of affairs on Venus. At any rate, in the light of Tammann's theory the simultaneous absence of water vapor and oxygen on Venus appears to be quite compatible. Mars furnishes an example of an intermediate case. Though its atmosphere contains no longer a spectroscopically detectable amount of oxygen, in former ages there must have been enough of this element to enable the formation of those reddish areas which are now commonly interpreted as highly oxidized sediments. From the point of view of Tammann's theory it is significant that the great scarcity of oxygen on Mars is concomitant to a lack of water, manifesting itself most conspicuously by the absence of oceans.

The total mass of carbon dioxide now buried in sediments, including the CO_2 equivalent of the carbon of the biosphere and of coal, bitumen, and humus formations, is of the order 10 kg cm^{-2} (cf. Table IV). Already fifty years ago it was emphasized by A. G. Högbom,[22] that the mass of CO_2 bound in sedimentary carbonates is so enormous that obviously it cannot altogether have existed in the atmosphere right from the beginning. For life would be impossible under a CO_2 pressure of several atmospheres. Hence the greater part of the carbon dioxide now fossil or still circulating through the biosphere has probably been supplied gradually during the geological ages, primarily in the form of volcanic exhalations. Such exhalations as are observed in the present also contain a large percentage of steam, but reliable and comprehensive data about their composition are not available as yet. It should be kept in mind then that possibly large masses of steam have been ejected continually during the past and that the primeval hydrosphere may have been less massive than the oceans of today. On Tammann's theory, this would imply a smaller oxygen yield from thermal dissociation. The abundance of carbon dioxide on Venus, coupled with the absence of water, either suggests that volcanism, of the sort known to be active on the Earth at present, did not play any role during the history of Venus, or it may be advanced as an argument against the view that the supply of juvenile water derived from

[21] G. Tammann, Zeits. f. physik. Chemie **110**, 17 (1924).

[22] A. G. Högbom, Svensk Kemisk Tidskrift **6**, 169 (1894).

volcanic eruptions during the geological ages of the Earth was of the same order of magnitude as the total mass of the oceans.

Before the surfaces of the primitive planets had sufficiently cooled down, say below red heat, the chemical evolution of their atmosphere was ruled by the laws of thermochemical equilibria. Thereafter certain photochemical reactions tended to gain prominence, with the Sun serving as a powerful source of ultraviolet radiation. The only well-understood instance of a photochemical process working on a planetary scale is the ozone equilibrium in the terrestrial stratosphere,[23] but similar photochemical equilibria may prevail in the atmospheres of other planets.[24] Only a few geochemical aspects of these photochemical processes can be touched here. J. H. J. Poole[25] has quite recently advocated the view that the photochemical dissociation of water vapor in the stratosphere has an important bearing upon the geochemical balance of oxygen. His numerical investigations, based on rather uncertain geochemical data, are all but convincing, and he does not seem to be aware of Tammann's highly relevant theory of the thermal production of free oxygen. Since the absorption coefficient of O_2 for the radiations which produce O_3 is exceedingly great, in any atmosphere the maximum of the stationary O_3 concentration will be maintained at a level at which the partial pressure of O_2 is quite small. Hence, in an atmosphere poor in oxygen, as that of Mars very likely was in the past, the "ozone layer" would be closely adjacent to the ground, favoring chemical interaction with the surface material and an increased rate of consumption of the free oxygen by weathering. In absence of a protective screen of O_2 and O_3, water vapor and carbon dioxide may react photochemically and form traces of formaldehyde. For this reason a search was made in the spectrum of Venus for the CH_2O bands between $\lambda 3500$ and $\lambda 3000$. The negative result[7] left still open the possibility that the CH_2O in Venus' atmosphere had rapidly polymerized into a solid of low vapor pressure and thereby had escaped the spectroscopic test. For the chemical literature concerning the solid formaldehyde polymers contained the definite statement that the vapors of the solid polymers did not consist of CH_2O, but were also of a polymeric nature. Unfortunately this claim is not borne out by the unpublished experiments of Dr. J. Frederic Walker (E. I. DuPont De Nemours and Company, Niagara Falls, New York), to whom I am greatly indebted for having communicated his findings to me, only a few weeks ago. What appeared to me as a rather attractive hypothesis, namely, that the mysterious cloud stuff on Venus might be a solid formaldehyde polymer of low vapor pressure has now become untenable. (A note on this subject will be published forthwith in the *Astrophysical Journal.*)

A review of the geochemistry of the atmosphere in relation to the constitution of the planets may appropriately be closed by a brief reference to the far-reaching biochemical implications of this subject. In a stimulating monograph *The Origin of Life* (The Macmillan Company, New York, 1938) the Russian biochemist A. I. Oparin has analyzed the cosmogonic and chemical requisites for the spontaneous generation of life. In view of the wide attention this book appears to have attracted among biologists, it should be mentioned that the astrophysical data on which Oparin has based his speculations are largely obsolete and often incorrectly interpreted. Notwithstanding that, every new advance in the fields of geochemistry and planetary constitution will undoubtedly reveal more clearly the possibly unique concatenation of circumstances to which we owe the spectacle of life.

[23] O. R. Wulf and L. S. Deming, Terr. Mag. **41**, 299 and 375 (1936).
[24] R. Wildt, Astrophys. J. **86**, 321 (1937).
[25] J. H. J. Poole, Proc. Roy. Soc. Dublin **22**, 345 (1941).