The Search for Life in the Solar System

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The purpose of this account is to review the search for extraterrestrial life in the solar system in the light of present knowledge of the physical state of the planets. It is being written on the eve of the launch (August 1975) by the U.S. of two Viking spacecraft to Mars. These unmanned spacecraft, each consisting of an orbiter and an instrumented lander, are to perform the first biological exploration of another planet. The Viking mission, if successful, will answer many of the questions posed in this paper. Furthermore, since Mars is the most plausible extraterrestrial habitat of life in the solar system, the Viking results are likely to have a strong influence on future explorations of this kind.

The search for extraterrestrial life is inseparable from the problems of the origin and fundamental nature of life and related cosmo- and geochemical questions. These questions are considered briefly in the first part of this Account.[1] The planets are then taken up, with Mars as the object of principal interest.

Life and Carbon Chemistry

Life on our planet is a manifestation of light-element—especially carbon—chemistry. The chemistry of living matter is, in addition, characterized by a high degree of molecular complexity—i.e., a high information content. In this respect there is no difference between the smallest viruses and the most advanced animals: nucleic acids and proteins are fundamental to both. It will be argued here that all life, wherever it may occur in the universe, will be based on carbon chemistry.

All terrestrial cells and organisms are expressions of the information contained in the structure of their genes (DNA). It now appears that all of this information is concerned, directly or indirectly, with the production of protein molecules—their structure, time of appearance, and rate of synthesis. The genetic heritage of each species is thus a set of specifications, encoded in DNA, for the synthesis of an array of enzymes and other protein molecules. From this initial input, all other aspects of the organism follow—its structure, development, metabolism, and behavior—insofar as these are genetically determined.

The information contained in the genes is generated by random mutations in DNA, screened by natural selection. The genetic specifications are thus an evolutionary product—a record of discovered solutions to the problems of survival encountered by the species in the course of its long history. Basic to this evolution is the mechanism—itself perfected ·by mutation and natural selection—that brings about the nearly flawless replication of nucleic acids and their mutants, and through them of proteins and the entire organism. Since it is this *genetic* property that is ultimately responsible for the variety of structures and functions that identify the objects we recognize as "living", it is this property that fundamentally distinguishes living from nonliving matter.[2]

The capacity for generating, storing, replicating, and utilizing large amounts of information implies an underlying molecular complexity that is known only among compounds of carbon. The special properties of the carbon atom that fit it for the construction of large and complex molecules which, although unstable thermodynamically, are kinetically stable have been discussed by Edsall and Wyman.[3] No other element possesses these properties to the same degree. It is sometimes proposed that under conditions different from those that prevail on the earth, elements other than carbon might be as useful, or even superior, for building biological molecules.[4] It is not possible to evaluate these proposals because they have not been developed in detail. In the absence of detailed models, all such speculations must be viewed with skepticism.

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(1) For a more detailed review of recent work on the origin of life, see N. H. Horowitz and J. S. Hubbard, *Annu. Rev. Genet.*, 8, 393 (1974).

(2) H. J. Muller, *Proc. Int. Cong. Plant Sci., 1926*, 1 897 (1929). Excerpted in H. J. Muller, "Studies in Genetics", Indiana University Press, Bloomington, Ind., 1962, p 188.

(3) J. T. Edsall and J. Wyman, "Biophysical Chemistry", Academic Press, New York, N.Y., 1958, p 23.

(4) See, for example, G. C. Pimentel, K. C. Atwood, H. Gaffron, H. K. Hartline, T. H. Jukes, E. C. Pollard, and C. Sagan in "Biology and the Exploration of Mars", C. S. Pittendrigh, W. Vishniac, and J. P. T. Pearman, Ed., National Academy of Sciences, Washington, D.C., 1966, Chapter 12.

Table I
Elementary Abundances in the Solar System

Order of abundance	Element	Atomic no.	No. of atoms per 10^6 Si
1	H	1	2.6×10^{10}
2	He	2	2.1×10^9
3	O	8	2.36×10^7
4	C	6	1.35×10^7
5	N	7	2.44×10^6
6	Ne	10	2.36×10^6
7	Mg	12	1.05×10^6
8	Si	14	1.00×10^6
9	Fe	26	8.90×10^5
10	S	16	5.06×10^5

Carbon in the Universe

Carbon and the other light atoms that make up the bulk of biological material are among the most abundant elements of the universe. Table I shows the ten elements of greatest abundance in the solar system, taken from the compilation of Cameron.[5] These abundances are nominally those of the sun, which contains approximately 99.9% of the mass of the solar system. In fact, more accurate measurements of nonvolatile elements can be made on meteorites, especially carbonaceous chondrites;[6] these measurements are then normalized to solar data. Since the composition of the sun is the same, within the limits of error, as that of most other stars (even stars of other galaxies) and of the interstellar medium, the solar abundance ratios can be said to describe the universe as a whole.[7]

Composition of the Planets. The planets are a different story, since only the giants—Jupiter, Saturn, Uranus, and Neptune—can retain atmospheric hydrogen and helium. Jupiter and Saturn are, in fact, approximately solar in composition, but Uranus and Neptune are much less so.[8] The terrestrial planets—Mercury, Venus, Earth, and Mars—are deficient in the light elements. The earth, for which we have by far the best data, is markedly deficient in carbon, hydrogen, nitrogen, and all the noble gases.[9] The abundance of H_2O, CO_2 and N_2 at the earth's surface is not representative of the bulk of our planet, which is composed principally of metals, metal oxides, and silicates.[10] The volatiles at the surface—found principally in the ocean, atmosphere, and carbonate rocks—were formed secondarily by outgassing of the earth's interior.[11]

Organic Compounds in Meteorites. Not only is carbon abundant cosmically, but carbon chemistry leading to the production of biologically interesting molecules occurs on a large scale in the universe. It has been known since the time of Berzelius (first half of the 19th century) that some meteorites contain or-

ganic matter. Modern investigations have shown that organic compounds are found almost exclusively in the carbonaceous chondrites, a class of meteorites containing examples of what many investigators consider to be primordial, unmetamorphosed condensates from the solar nebula.[6,10,12] These contain up to 5% carbon, largely in organic form.[13] Most of this organic matter is present as an unextractable, condensed aromatic polymer. The smaller, extractable fraction contains hydrocarbons and a variety of oxygen-, nitrogen-, halogen-, and sulfur-containing compounds. Much confusion was engendered in the past by the difficulty of distinguishing between indigenous meteoritic materials and contaminants introduced during entry of the meteorite into the earth's atmosphere, impact with the ground, and subsequent handling and storage. These problems have been resolved in recent years, thanks to improved analytical methods—e.g., gas chromatography–mass spectrometry—and to recognition of the need to minimize contamination by prompt recovery and clean handling of meteorite falls.

Recent investigations[14] confirm that the hydrocarbons of carbonaceous chondrites are indigenous, as shown by their enrichment in ^{13}C relative to terrestrial samples. Of even greater interest is the finding of free amino acids in aqueous extracts of the meteorites, together with precursors that yield amino acids on hydrolysis. The total amino acid content is about 20 μg/g; the identity of the hydrolyzable precursors is unknown. Twenty amino acids have been identified, of which eight are constituents of proteins (glycine, alanine, valine, leucine, isoleucine, proline, glutamic acid, aspartic acid). All of the amino acids with asymmetric atoms whose chirality could be determined proved to be racemic. These results clearly indicate a nonbiological and extraterrestrial origin of chondritic amino acids.

Organic Compounds in Interstellar Space. Complex organic compounds, including known precursors of amino acids, also exist in interstellar space. This remarkable discovery was made by microwave spectroscopy.[15] The molecules are found in association with clouds of gas and dust in regions of the sky where stars and planetary systems are forming. It is possible that the dust grains have a role in the formation of the molecules from the rarefied interstellar gas, and it is certain that they shield them from photolysis by stellar ultraviolet radiation. Carbon monoxide is the most abundant molecule in the clouds,

(5) A. G. W. Cameron in "Origin and Distribution of the Elements", L. H. Ahrens, Ed., Pergamon Press, London, 1968, p 125.

(6) E. Anders, *Geochim. Cosmochim. Acta*, **35**, 516 (1971).

(7) A. Unsöld, "The New Cosmos", Springer-Verlag, New York, N.Y., 1969, p 162; *Science*, **163**, 1015 (1969).

(8) M. Podolak and A. G. W. Cameron, *Icarus*, **22**, 123 (1974).

(9) S. I. Rasool in "Physics of the Solar System", S. I. Rasool, Ed., National Aeronautics and Space Administration, Washington, D.C., 1972, Chapter 12.

(10) B. Mason, "Principles of Geochemistry", Wiley, New York, N.Y., 1966.

(11) W. W. Rubey, *Geol. Soc. Am., Spec. Pap.*, **62**, 631 (1955).

(12) J. A. Wood, "Meteorites and the Origin of Planets", McGraw-Hill, New York, N.Y., 1968; E. Anders, *Anu. Rev. Astron. Astrophys.*, **9**, 1 (1971); R. Lewis and E. Anders, *Proc. Natl. Acad. Sci. U.S.A.*, **72**, 268 (1975).

(13) The organic chemistry of carbonaceous chondrites has been reviewed by (a) J. M. Hayes, *Geochim. Cosmochim. Acta*, **31**, 1395 (1967); (b) J. Oró, *Space Life Sci.*, **3**, 507 (1972); (c) E. Anders, R. Hayatsu, and M. H. Studier, *Science*, **182**, 781 (1973).

(14) K. Kvenvolden, J. Lawless, K. Pering, E. Peterson, J. Flores, C. Ponnamperuma, I. Kaplan, and C. Moore, *Nature (London)*, **228**, 923 (1970); K. Kvenvolden, J. Lawless, and C. Ponnamperuma, *Proc. Natl. Acad. Sci. U.S.A.*, **68**, 486 (1971); J. Oró, J. Gilbert, H. Lichenstein, S. Wikstrom, and D. Flory, *Nature (London)*, **230**, 105 (1971); J. Cronin and C. Moore, *Science*, **172**, 1327 (1971); J. Lawless, K. Kvenvolden, E. Peterson, C. Ponnamperuma, and C. Moore, *ibid*, **173**, 626 (1971); J. Lawless, K. Kvenvolden, E. Peterson, C. Ponnamperuma, and E. Jarosewich, *Nature (London)*, **236**, 66 (1972); W. Pereira, R. Summons, T. Rindfleisch, A. Duffield, B. Zeitman, and J. Lawless, *Geochim. Cosmochim. Acta*, **39**, 163 (1975).

(15) D. Rank, C. Townes, and W. Welch, *Science*, **174**, 1083 (1971); D. Buhl, *Nature (London)*, **234**, 332 (1971); D. Buhl, *Origins Life*, **5**, 29 (1974); F. Gardner and G. Winnewisser, *Astrophys. J.*, **195**, 1127 (1975).

next to H_2. Several orders of magnitude less abundant than CO are NH_3, HCN, HCOOH, HCHO, $CH_3C\equiv CH$, $HC\equiv CCN$, CH_3OH, and CH_3CN. Also seen, in lesser or undetermined abundances, are H_2O, CH_3CHO, $HCONH_2$, and $H_2C=CHCN$.

The assemblages of molecules detected in meteorites and interstellar clouds bear a strong qualitative— and in some respects quantitative—resemblance to those that have been found in laboratory experiments simulating conditions in the solar nebula and on the prebiotic earth.[16] All of the meteoritic amino acids and interstellar organic molecules so far identified have been produced in such experiments. HCN and aldehydes such as those found in interstellar clouds have been shown to react in a Strecker synthesis to yield amino acids in prebiotic simulation experiments.[17] Formaldehyde adds to itself to yield sugars in the well-known formose reaction, which may have prebiotic significance.[18] HCN is the starting point for a possible prebiotic synthesis of adenine;[19] and cyanoacetylene (HC_2CN), also seen in interstellar clouds, is the starting point for a synthesis of cytosine.[20]

The implication of these results is that organic syntheses in the universe have a direction that favors the production of amino acids, purines, pyrimidines, and sugars—the building blocks of proteins and nucleic acids.[21] Taken in conjunction with the cosmic abundances of the light elements, this suggests that life elsewhere will be based not only on carbon chemistry, but on carbon chemistry similar to (although not necessarily identical with) our own.

Prospects for Life in the Solar System

If we are correct in postulating that life must be based on carbon chemistry, then most of the bodies in the solar system can be eliminated as potential biological habitats on the basis of two corollaries. First, the temperature of habitable objects must not exceed the stability limit for complex organic molecules. This limiting temperature is not easily defined, but it is not necessary to know it very accurately for the present purpose. An upper estimate is derivable from the fact that amino acids decompose rapidly at 200–300°C. It is therefore safe to say that no planet whose temperature exceeds 250°C is habitable. The actual temperature limit is probably lower than this.

Second, objects without atmospheres are not habitable. This follows from the volatility of low-molecular-weight compounds of the light elements. It seems inescapable that volatile compounds would be produced by living organisms in the course of their me-

tabolism, as well as by thermal and photochemical processes acting on dead organisms, and that these would enter the atmosphere, and would in fact be an essential link in the cycling of matter that must occur on any life-bearing planet. Gravitational escape of these molecules would deplete the planet of its light elements, and life would then cease. Thus, even if it were possible for life to start on an object incapable of retaining an atomsphere, it could not survive there indefinitely.

It has been suggested that life could exist on an atmosphereless body—specifically, the moon—at some depth beneath the surface where gases might be trapped.[22] This solution only exchanges one problem for another, since the subsurface habitat is cut off from solar energy. Life requires a constant supply of both matter and energy, but whereas matter recycles, energy cannot, for fundamental thermodynamic reasons. Since the sun is, for all practical purposes, the only inexhaustible source of energy in the solar system, life cannot survive without access to solar radiation. The fact that some bacteria—the chemoautotrophs—obtain energy for the reduction of CO_2 by oxidizing sulfur or other inorganic materials—and thus can live in an inorganic environment without sunlight—does not affect this conclusion, since the inorganic energy sources are not renewable except by an input of solar energy. There is thus no possibility for sustained life on, or in, an atmosphereless planet.[23]

Mercury, Venus, Moon, the Asteroids. It can be concluded from the foregoing discussion that life cannot exist on the moon or most of the other satellites of the solar system, nor on Mercury or the asteroids, because none of these objects has an appreciable atmosphere. In the case of the moon, this conclusion has been verified by direct observation of the Apollo samples. Venus is also excluded as an abode of life because of its high surface temperature—in excess of 400°C (Table II). It has been proposed that organisms could live in the clouds of Venus, where temperatures are more reasonable.[24] A major difficulty with this proposal is that the atmosphere of Venus is a convective one; special means must therefore be invoked to maintain the organisms at a safe altitude. In addition, there is the problem of obtaining nutrients and water. The Venus atmosphere is very dry,[25] in agreement with the finding that the clouds of Venus consist of an aerosol of 75% aqueous H_2SO_4.[26] It is worth noting that the arguments advanced to support the idea of life in the clouds of Venus apply with equal or greater force to the atmosphere of Earth. Yet, while our atmosphere swarms with microorganisms of every sort, no true "aeroplankton" in the above sense has been found.[27]

(16) Anders et al.[13c] have carried out Fischer–Tropsch-like reactions in mixtures of CO, H_2, and NH_3 under conditions thought to simulate a cooling solar nebula. To simulate events on the primitive earth, Miller and associates pass an electric discharge through a mixture of CH_4, N_2, and H_2O. See D. Ring, Y. Wolman, N. Friedmann, and S. Miller, *Proc. Natl. Acad. Sci. U.S.A.*, **69**, 765 (1972); Y. Wolman, W. Haverland, and S. Miller, *ibid.*, **69**, 809 (1972).

(17) S. L. Miller, *Ann. N.Y. Acad. Sci.*, **69**, 260 (1957).

(18) N. W. Gabel and C. Ponnamperuma, *Nature (London)*, **216**, 453 (1967); C. Reid and L. E. Orgel, *ibid.*, **216**, 455, (1967).

(19) J. Oró and A. Kimball, *Arch. Biochem. Biophys.*, **94**, 217 (1961); R. Sanchez, J. Ferris, and L. Orgel, *Science*, **153**, 72 (1966).

(20) R. Sanchez, J. Ferris, and L. Orgel, *Science*, **154**, 784 (1966); J. Ferris, R. Sanchez, and L. Orgel, *J. Mol. Biol.*, **33**, 693 (1968).

(21) It should be noted that the condensation of these subunits into proteins and nucleic acids abiologically presents difficulties to which there are as yet no generally accepted solutions. For a recent review, see ref 1.

(22) C. Sagan, *Proc. Natl. Acad. Sci. U.S.A.*, **46**, 396 (1960).

(23) Nevertheless, the fear that organisms from the moon might contaminate the earth was a major consideration in the design of the Lunar Receiving Laboratory, as well as in the quarantine imposed on returning Apollo astronauts. See J. McLane, E. King, D. Flory, K. Richardson, J. Dawson, W. Kemmerer, and B. Wooley, *Science*, **155**, 525 (1967).

(24) H. Morowitz and C. Sagan, *Nature (London)*, **216**, 1259 (1967).

(25) M. Janssen, R. Hills, D. Thornton, and W. Welch, *Science*, **179**, 994 (1973).

(26) A. Young, *Science*, **183**, 407 (1974).

(27) P. H. Gregory, "The Microbiology of the Atmosphere", Leonard Hill, London, 1961; T. D. Brock, "Principles of Microbial Ecology", Prentice-Hall, Englewood Cliffs, N.J., 1966.

Table II
Planetary Data

Planet or satellite	Mass (Earth = 1)	Density, g/cm³	Distance from sun (Earth = 1)	Solid surface		Observed atmospheric constituents	
				Mean temp, K	Mean pressure, mbar	Major (>1%)	Minor (≤1%)
Mercury	0.06	5.5	0.39	440	~0		
Venus	0.82	5.2	0.72	700	10^5	CO_2	CO, H_2O, H_2SO_4, HCl, HF
Earth	1.00	5.5	1.00	288	1013	N_2, O_2	A, H_2O, CO_2, and others
Moon	0.01	3.3		275	~0		
Mars	0.11	4.0	1.52	218	5.5	CO_2	CO, O_2, H_2O, O_3
Jupiter	318	1.3	5.19			H_2, He	CH_4, NH_3, H_2O, C_2H_6, C_2H_2
Saturn	95	0.7	9.53			H_2	CH_4, NH_3
Titan	0.02	2.3		≃80	≥20	H_2(?), CH_4	
Uranus	15	1.3	19.2			H_2	CH_4
Neptune	17	1.7	30.1			CH_4	

The Jovian Planets. The low densities of the giant planets show that they are more solar in elementary composition than are the inner planets of the solar system. Much of our knowledge of the properties of these distant objects is based on theoretical models which, because of the simple compositions of the Jovian planets, can be calculated with reasonable confidence. This is particularly true of Jupiter and Saturn. All of the Jovian planets have deep atmospheres whose compositions must be assumed to be dominated by H_2 and He, both of which gases have been identified spectrally for Jupiter. The additional detection of methane and ammonia (and more recently of ethane,[28] acetylene,[28] and water[29]) in the atmosphere of Jupiter has supported the expectation that complex organic compounds like those formed in laboratory simulations of the primitive earth would be found as a matter of course on Jupiter, and possibly even indigenous life.[30] Unfortunately, these expectations run into several difficulties,[31] the most serious of which has to do with the thermal structures of the giant planets.

Current models of these planets require hot interiors, the temperature increasing linearly with depth (adiabatic lapse rate). In the case of Jupiter, for which the best data exist, the temperature increases from ~135 K at the top of the visible ammonia-ice clouds to temperatures of the order of 10^4 K at the center of the planet.[8,32] A high internal temperature is required by the observation, confirmed by the Pioneer 10 flyby,[33] that Jupiter radiates over twice as much energy as it receives from the sun. If a solid planetary surface exists, which is doubtful, its temperature must greatly exceed the stability limit for organic compounds. Furthermore, as in the case of Venus, the atmosphere of Jupiter is convecting; in fact, the entire planet can be treated, at least to a first approximation, as an adiabatic, convecting fluid.[32] Time constants for convective transport can

be estimated from mixing-length theory.[34] Characteristic times of the order of a day are found for transport of a parcel of gas through a height in the Jovian atmosphere involving a temperature change of 100–200 K. Given this physical situation, it is unlikely that life could evolve or survive on Jupiter.

Saturn, which also has an internal energy source, is qualitatively much like Jupiter in its composition and thermal structure,[8,32] and the biological outlook is the same.

Uranus and Neptune are smaller, colder, and less well understood than the other two major planets. The densities of these remote objects became known accurately only in 1970, and there is still a possibility that these values will be changed.[35] Recent physical models[8,36] suggest that solid planetary surfaces with temperatures suitable for the accumulation of organic matter are not present. Aqueous ammonia clouds at room temperature are a possibility, however. The importance of convection in the atmospheres of Uranus and Neptune is at present uncertain.

Titan. Titan, the largest satellite of Saturn, is the only satellite in the solar system known to have a substantial atmosphere. Titan's atmosphere is more massive than that of Mars. The mean surface temperature of a body with Titan's albedo and distance from the sun is expected to be 82 K, or too low for solution chemistry, either aqueous or ammoniacal. Recent infrared measurements, however, have shown higher temperatures which, if they result from an atmospheric greenhouse effect, would allow biologically interesting models of the surface to be considered. The alternative to a warm surface is a warm layer in the atmosphere caused by absorption of solar radiation by dust particles. A decision on this and other questions about Titan can be expected in the near future.[37]

Mars

Mars fulfills the minimal conditions for a life-bearing planet. It retains an atmosphere of light elements, and its surface temperature is compatible with the

(28) S. Ridgway, *Astrophys. J.*, **187**, 141 (1974).

(29) R. Treffers, H. Larson, U. Fink, and T. Gautier, "Detection of Water Vapor on Jupiter", American Astronical Society Division of Planetary Science, 6th Annual Meeting, Columbia, Mo., 1975.

(30) C. Sagan, *Space Sci. Rev.*, **11**, 827 (1971); T. Owen, *Origins Life*, **5**, 41 (1974).

(31) J. Lewis and R. Prinn. *Theory Exp. Exobiol.*, **1**, 125 (1971).

(32) W. B. Hubbard, *Annu. Rev. Earth Planet. Sci.*, **1**, 85 (1973).

(33) A. G. Opp, *Science*, **183**, 302 (1974).

(34) P. Gierasch and R. Goody, *J. Atmos. Sci.*, **27**, 224 (1970).

(35) R. L. Newburn, Jr. and S. Gulkis, *Space Sci. Rev.*, **3**, 179 (1973).

(36) S. J. Weidenschilling and J. S. Lewis, *Icarus*, **20**, 465 (1973).

(37) D. M. Hunten, Ed., "The Atmosphere of Titan", National Aeronautics and Space Adminstration, Washington, D.C., 1974.

existence of complex carbon compounds. These are necessary conditions for a habitable planet, but not sufficient ones. There is no present evidence suggesting that Mars is in fact an abode of life; neither is there proof to the contrary, although the Martian environment appears to be an extremely hostile one. It is expected that the Viking landers, mentioned in the introduction to this article, will remove much of the uncertainty surrounding the question of Martian biology.

The Martian Environment, Pre-1965. No discussion of Mars as a possible biological habitat would be complete without reference to earlier views, only recently abandoned, concerning the nature of the Martian surface environment. Although now obsolete, these views were current during the early years of space exploration. They influenced attitudes and policy decisions whose effects are still being felt—for example, in the requirement for sterilization of lander spacecraft.

In the early '60s, the accepted value of the atmospheric pressure at the surface of Mars was 85 mbars, based on light-scattering and polarization measurements.[38] It was assumed that N_2 made up over 90% of the atmosphere, since no spectroscopically detectable gas was present in sufficient abundance to account for the pressure. The water-vapor content was variable and uncertain, but spectroscopic evidence seemed to prove that the polar caps were composed of water ice. The seasonal evaporation of the caps was seen to be correlated with a progressive change in contrast over the Martian surface, the dark regions ("maria") becoming darker relative to the bright regions ("deserts"). This so-called "wave of darkening" occurred twice every Martian year, alternately in the two hemispheres. A plausible explanation of the darkening phenomenon seemed to be the growth of vegetation, stimulated by the seasonal availability of water. Supporting this hypothesis were infrared spectra of the Martian surface which showed absorption features in the neighborhood of 3.5 μ in light reflected from the dark areas of the planet, but not from the bright ones. These absorptions were interpreted as arising from C–H bonds—and probably, therefore, vegetation—in the maria.

None of these findings has withstood closer scrutiny. Measurements from spacecraft and by high-resolution spectroscopy from the earth have shown that the Mars surface pressure varies from 3 to 9 mbars, depending on the elevation, with a planetary mean of about 5.5 mbars. The atmosphere is at least 75% CO_2.[39] Radiometric and spectrometric measurements made from the Mariner 7 flyby showed the principal constituent of the polar caps to be frozen CO_2,[39] in agreement with an earlier prediction.[40] The contrast changes on the Martian surface are now seen, by analysis of Mariner-9 photographs, to be explainable by the movements of windblown dust; it is questionable whether a seasonal "wave of darkening" exists.[41]

And the spectral features originally attributed to C–H vibrations on Mars are now known to have had their origin in deuterated water, HDO, in the earth's atmosphere.[42]

The current picture of Mars is thus distinctly less promising biologically than was the pre-1965 view, and that in turn was less favorable than the Martian fantasies of the 19th and early 20th centuries which it had replaced.[43]

Water on Mars. It has been obvious for some time that Mars is a very dry planet. The vapor pressure of water at the triple point is 6.1 mbars, a value that exceeds the total Martian atmospheric pressure. The mass of water vapor in the atmosphere of Mars, as determined by spacecraft and ground-based observations, varies from undetectable to about 6 mg cm^{-2}, depending on the season and latitude,[39] or about three orders of magnitude less than the water abundance in the earth's atmosphere. If water vapor is uniformly mixed in the Martian atmosphere, its partial pressure does not exceed 5.6×10^{-3} mbar at the surface, or if contained in the lowest 2 km of the atmosphere, the maximum pressure is 2.8×10^{-2} mbar.

Because of the dryness of the atmosphere, water on Mars is stable only in the form of vapor or ice. Atmospheric water vapor can condense only to ice under Martian conditions, and this ice cannot melt, even in soil interstices, because of the high evaporation rate.[44] Liquid water could exist on Mars only in the form of concentrated salt solutions. These considerations do not exclude the possibility that large quantities of ice exist beneath the surface of Mars; indeed, this is expected to be the case in a current theory of planetary condensation.[45] The high latitudes of Mars would be the most likely repository of such ice beds.

The dryness of Mars has important biological implications. The water requirements of terrestrial organisms are so high that water is the life-limiting factor over large regions of our planet, despite the fact that over 70% of its surface is covered with water. Even microorganisms, the hardiest of all cells in this as in other respects, share with higher species the need for large amounts of water. All microorganisms grow only in aqueous solutions, and for the large majority of species it is required that the water activity of the medium, a_w,[46] exceed 0.9.[47] A few microbial species are adapted to grow in relatively anhydrous solutions such as saturated sucrose ($a_w = 0.85$) and saturated NaCl ($a_w = 0.75$). Some fungi have been observed to grow very slowly at $a_w = 0.62$. There are no reliable reports of growth at any lower a_w. In the Antarctic dry desert, where local physical evidence indicates that the prevailing relative humidity and a_w have not exceeded 0.45 for thousands of years, no microorganisms capable of growing at or near this a_w have been found. The region is abiotic—i.e., the organisms found in the soil are not growing there, but

(38) Further details of these and the other pre-1965 results described in this section can be found in S. Glasstone, "The Book of Mars", National Aeronautics and Space Adminstration, Washington, D.C., 1968.

(39) C. A. Barth, *Annu. Rev. Earth Planet Sci.*, **2**, 333 (1974).

(40) R. B. Leighton and B. C. Murray, *Science*, **153**, 136 (1966).

(41) C. Sagan, J. Veverka, P. Fox, R. Dubisch, J. Lederberg, E. Levinthal, L. Quam, R. Tucker, J. Pollack, and B. Smith, *Icarus*, **17**, 346 (1972).

(42) D. G. Rea, B. T. O'Leary, and W. M. Sinton, *Science*, **147**, 1286 (1965).

(43) See ref. 38 and N. H. Horowitz, *Bull. At. Sci.*, **27**, 13 (1971).

(44) A. P. Ingersoll, *Science*, **168**, 972 (1970).

(45) J. S. Lewis, *Annu. Rev. Phys. Chem.*, **24**, 339 (1973).

(46) $a_w = p/p_0$, where p is the vapor pressure of the solution and p_0 is the vapor pressure of pure water at the same temperature. a_w is numerically equal to the equilibrium relative humidity.

(47) W. J. Scott, *Adv. Food Res.*, **7**, 83 (1957).

have apparently been carried in by the wind and other sources of contamination.[48]

The relative humidity of the Martian atmosphere (and the a_w of solutions with which it is in equilibrium) can be calculated for any temperature. For −10°C, the lower limit for microbial growth,[49] the maximum relative humidity or a_w at the Martian surface is 0.01. For higher temperatures, the value is lower. It is evident that Mars is by a large factor too dry for the most xerotolerant terrestrial organisms. This does not prove that life cannot exist on Mars, but it suggests that Martian life could not be built on a terrestrial model with respect to its water metabolism. An alternative view, based on cyclic changes in the Martian climate, will be mentioned below.

Gravitational Loss of N and H₂O. No nitrogen, free or combined, has been detected in the Martian atmosphere. The observational upper limit for N_2 is about 1%.[39] Mars does not lose N or N_2 by the usual thermal escape, but it appears that photochemical mechanisms can remove nitrogen at a rate which, integrated over the age of the solar system, would result in the loss of 90% or more of the estimated supply of Martian nitrogen.[50] The most important loss mechanism involves photoionization of N_2, followed by dissociative recombination: $N_2^+ + e \rightarrow N + N$. The N atoms can have sufficient energy to escape from Mars. This process is not important for the earth because of its stronger gravitational field.

The loss of atmospheric nitrogen would sooner or later terminate any Martian life, for reasons already given in discussing the biological role of the atmosphere. If, by analogy with the earth, the bulk of nitrogen outgassed on Mars is, or was, stored in the atmosphere,[10,11] then little nonvolatile nitrogen can be expected in the surface material. Even this, however, would eventually escape, and this escape would be accelerated by biological processes. To what extent Mars is actually depleted of nitrogen may become clear after the Viking mission. This is currently one of the most important questions relating to the chemistry and biology of Mars.

Dissociative recombination reactions involving CO_2^+, CO^+, and O_2^+ allow the nonthermal escape of C and O from Mars as well. The calculated escape rate of O balances the observed thermal loss of H atoms which are produced by photolysis of H_2O. The loss rate, integrated over the age of the planet, amounts to several meters of water since the formation of the solar system. It is probable, however, that significant quantities of water remain on Mars, especially in the polar regions.[51]

Martian Climatic Changes? One of the surprising discoveries made by the Mariner-9 orbital mission to Mars was that of various meandering, braided, and dendritic features strongly resembling dry water-courses.[52] Since liquid water cannot exist on Mars at the present time, the source of the water that cut the presumed channels (not all observers are

agreed on this interpretation of the features) is an interesting question. A possible solution to this puzzle invokes climatic changes—one or more interglacial epochs, during which melting of permafrost could occur.[53] This proposal is supported by Mariner-9 photographs showing laminated terrains in the Martian polar regions.[54] These terrains seem clearly to be the result of a periodic depositional process, with a period estimated to be of the order of 10^6 years.[54]

Recent dynamical calculations show that the obliquity of Mars oscillates, due to gravitational interactions with the other planets, with periodicities of 10^5 and 10^6 years.[55] These oscillations would produce periodic climatic changes which, depending on the assumed thickness of the frozen volatile deposits in the polar caps, could bring nearly earthlike conditions to the Martian equatorial region,[56] or could have only small effects.[51] In the former case, sufficient water might be available to support a terrestrial type of biota which, however, would have to go into a dormant state in order to survive during an ice age, such as the present.[56] Whether such an organism—or any organism—does or can exist on Mars is, for the time being, entirely speculative.

The Viking Mission

Viking is the most ambitious unmanned space mission yet attempted. Scientific experiments and measurements are to be performed from Mars orbit, during entry into the atmosphere, and on the surface of the planet. Orbital instruments include two vidicon cameras having a ground resolution of about 50 m from an altitude of 1500 km; an infrared spectrometer, boresighted with the cameras, designed to map the distribution of water vapor over the planet; and an infrared radiometer, also boresighted with the cameras, which will map the surface temperature.

During its entry into the atmosphere, the Viking Lander will analyze the neutral gases of the upper atmosphere by means of a double-focusing mass spectrometer of mass range 1–50 amu, and it will make measurements on the ionosphere with a retarding potential analyzer. Density, temperature, and pressure profiles will also be obtained during entry.

An additional set of instruments will be deployed on the Martian surface. Two facsimile cameras, with stereo capability and a resolving power of a few millimeters at a distance of 1 m, will observe the area around the landing site and search for objects of geological, biological, and meteorological interest. A mass spectrometer of range 12–200 amu will analyze the atmosphere at ground level and, in conjunction with a pyrolysis oven and gas chromatograph, will perform an organic analysis of the surface material. Three metabolic experiments designed to detect microbial life in the soil will be deployed. One of these measures the light or dark fixation of atmospheric CO or CO_2 into organic matter in the soil, using radioactive gases as tracers. Another measures the production of radioactive gases by a soil sample moistened with a solution containing labeled substrates. The third uses a gas chromatograph to measure gas

(48) N. H. Horowitz, R. E. Cameron, and J. S. Hubbard, *Science*, 176, 242 (1972).

(49) H. D. Michener and R. P. Elliott, *Adv. Food Res.*, 13, 349 (1964).

(50) R. T. Brinkmann, *Science*, 174, 944 (1971); M. B. McElroy, *ibid.*, 175 443 (1972).

(51) B. C. Murray and M. C. Malin, *Science*, 182, 437 (1973).

(52) D. J. Milton, *J. Geophys. Res.*, 78, 4037 (1973).

(53) H. Masursky, *J. Geophys. Res.*, 78, 4009 (1973).

(54) J. A. Cutts, *J. Geophys. Res.*, 78, 4231 (1973).

(55) W. R. Ward, *Science*, 181, 260 (1973).

(56) C. Sagan, O. B. Toon, and P. J. Geirasch, *Science*, 181, 1045 (1973).

exchange above a soil sample moistened with a complex organic medium.

Also on the lander will be an X-ray fluorescence spectrometer designed to analyze the surface material for elements of atomic number greater than 11, a three-axis seismometer, and a set of meteorological instruments.

Detailed descriptions of these experiments have been published.[57]

(57) Various authors, *Icarus*, **16**, 1 (1972); **20**, 153 (1973).

Rydberg States and Rydbergization

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For a comprehensive understanding of atomic and molecular electronic spectroscopy and photochemistry, spectra of Rydberg states must be included. Further, Rydberg states are stepping stones toward ionization. For atoms and molecules of high ionization energy, Rydberg spectra lie in the vacuum ultraviolet, but for those of lower ionization energy, they come in part into the nearer ultraviolet. Many of the higher energy valence-shell excited states occur at similar energies to Rydberg states, with resultant interaction and mixing of their wave functions. Predissociation often occurs with results relevant to photochemistry. Rydberg states are important for reactions in the upper atmosphere.

Rydberg States and Rydberg Series of Atoms. Ordinary atomic states can usually be fairly well described in terms of an electron configuration, telling how many electrons are to be assigned to a series of AO's (atomic orbitals), of decreasing ionization potential in the order written.[1] For example, the ground state of silicon is a $^3P_0$ state of the configuration $1s^2 2s^2 2p^6 3s^2 3p^2$. Any one (or more) of the occupied AO's can be excited. In ordinary Rydberg states, one electron is excited to a relatively large AO, e.g., ns (n = 4, 5, or 6 . . .). If the ground-state configuration is called A, the Rydberg state configuration may be described as $A^+ ns$, where A^+ denotes the *core* configuration and state. If in A^+ an electron is removed from the 3p AO, leaving a ^2P core, the Rydberg state can be $^3P_0$, $^3P_1$, $^3P_2$, or ^1P, or ^3P and ^1P if we disregard the multiplet structure in the ^3P. A series of states with successive values of n constitutes a *Rydberg series*. Each series member is characterized by a *term value T*, $T = E(A^+) - E(A^+ ns)$, where the energies E are usually expressed in spectroscopic units (cm^{-1}). Note that T is largest for Rydberg states of low energy. If it is written in the form Ry/n^{*2}, where

n^* is an *effective n*, and Ry is the Rydberg constant (109679 cm^{-1} for the H atom and a little larger for heavier atoms), T is given to a good approximation by

$$T = Ry/n^{*2} = Ry/(n - \delta)^2 \tag{1}$$

The *quantum defect*, δ, is approximately a constant. (The deviations from constancy normally decrease steadily with increasing n.)

The value of δ is relatively large and positive for Rydberg AO's which have *precursors*, i.e., occupied AO's of the same l value (in the present example 1s, 2s, 2p, 3s, and 3p) in the core; in short, for *penetrating* Rydberg AO's. Here $n^* < n$. However, the value of δ is also appreciably affected by the particular state of the Rydberg configuration, e.g., ^3P or ^1P in our example; δ is larger for the ^3P than for the ^1P state. The two contributions to δ just mentioned may be called *penetrational* and *exchange* contributions. The exchange contribution is positive for the ^3P and negative for the ^1P. For nonpenetrating Rydberg AO's, e.g., nd or nf, δ is much smaller. Here a third, relatively small, positive *polarization* contribution to δ may be decisive. In rare cases for singlet states the negative exchange contribution can make δ slightly negative. In general, there may be a number of Rydberg states of the same Rydberg configuration, e.g., for silicon $A^+ nd$, there are ^3P, ^3D, ^3F, ^1P, ^1D, and ^1F states for a ^2P core. In such a case, one may wish to use a weighted mean energy of the several states to calculate a mean n^* and δ for the Rydberg AO.

The simplest case is that of a closed-shell core as in the ordinary excited states of the Na atom: $1s^2 2s^2 2p^6 X$, where X is ns or np or nd, etc.; here the Rydberg AO determines the overall state. In Na, even the ground state is essentially a Rydberg state (X = 3s). Table I contains illustrative data on some Rydberg states of Na, Rb, and Mg.

Molecular Rydberg States. In molecules, the same general principles apply as for atoms. Usually

(1) For further discussion, cf. R. S. Mulliken, *J. Am. Chem. Soc.*, **86**, 3183 (1964).