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Extraterrestrial Life: Some Organic Constituents of Meteorites and Their Significance for Possible Extraterrestrial Biological Evolution

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EXTRATERRESTRIAL LIFE;
SOME ORGANIC CONSTITUENTS OF METEORITES AND THEIR
SIGNIFICANCE FOR POSSIBLE EXTRATERRESTRIAL BIOLOGICAL
EVOLUTION

Melvin Calvin and Susan K. Vaughn

December 7, 1959

EXTRATERRESTRIAL LIFE:
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SIGNIFICANCE FOR POSSIBLE EXTRATERRESTRIAL BIOLOGICAL EVOLUTION*

Melvin Calvin and Susan K. Vaughn**

Department of Chemistry and Lawrence Radiation Laboratory
University of California, Berkeley

Abstract

December 7, 1959

In order to decide the value and type of information to be obtained from outer space with regard to its pertinence for the evolution of life, a brief review is presented of the current status of our thinking on the origin of life on earth. This points up the particular kinds of chemicals whose presence, or absence, on other astral bodies might be significant.

Heretofore, the only data available are the result of telescopic spectroscopy. We report here information indicating the presence in meteorites of complex organic materials, some of them apparently uniquely pertinent to life processes.

* To be presented at COSPAR First International Space Sciences Symposium, Nice, France, January 1960.

** The preparation of this paper was sponsored by the U.S. Atomic Energy Commission.

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The mere fact that the subject of extraterrestrial life was deemed suitable to be included in this meeting seems to me is evidence enough that the interest of men in the possible living population of those bodies they see above them is still alive, as it has been ever since men first looked and thought about those bodies.

Before trying to review for you what it is that we know (or think we know) about the possible existence of living organisms on other astral bodies than the earth, it seemed worthwhile to review the current thinking about the way in which life may have originated on the surface of the earth in order that we may know for which data to seek when we look out from the earth.

It has recently become rather popular to think about this in a way which was not popular thirty or forty years ago, and part of the reason for

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respectability of thinking in terms of the question of the origin of life on earth is due, of course, to the enormous advances which our knowledge of the physics and chemistry, and particularly genetic behavior of living material, has taken in the last twenty or thirty years. I shall not try to review in great detail the arguments for the present, or current, conception. What I would like to do now is simply to review the current conception (at least what is current in my mind and what is generally accepted in its broadest terms) so that we may, from this basis, try to decide what kind of data we should seek in trying to determine the nature, or the existence, of extra-terrestrial life which presumably, ultimately, one day we can take a trip out there and find in the most direct manner possible.

REVIEW OF THE THEORY OF ORIGIN OF LIFE ON EARTH

Backward Extrapolation to Period of Chemical Evolution

Let us review, then, the sequence of events which we now believe may have occurred, leading to the appearance of living cells on the surface of the earth. There are two principal notions upon which this sequence of events which I am going to review is based. The first of these is perhaps most easily expressed as a backward extrapolation of the essential Darwinian principle, which, again, is most simply described by the title of the first Darwin and Wallace paper, namely, 'On the Tendency of Varieties to Depart Indefinitely from Original Types, Leading to New Species.'¹ If we extrapolated this tendency backward, it is quite clear that eventually we would come to a period in which the first type, or first organism, appeared. We can extrapolate right back through that period of time into a region when

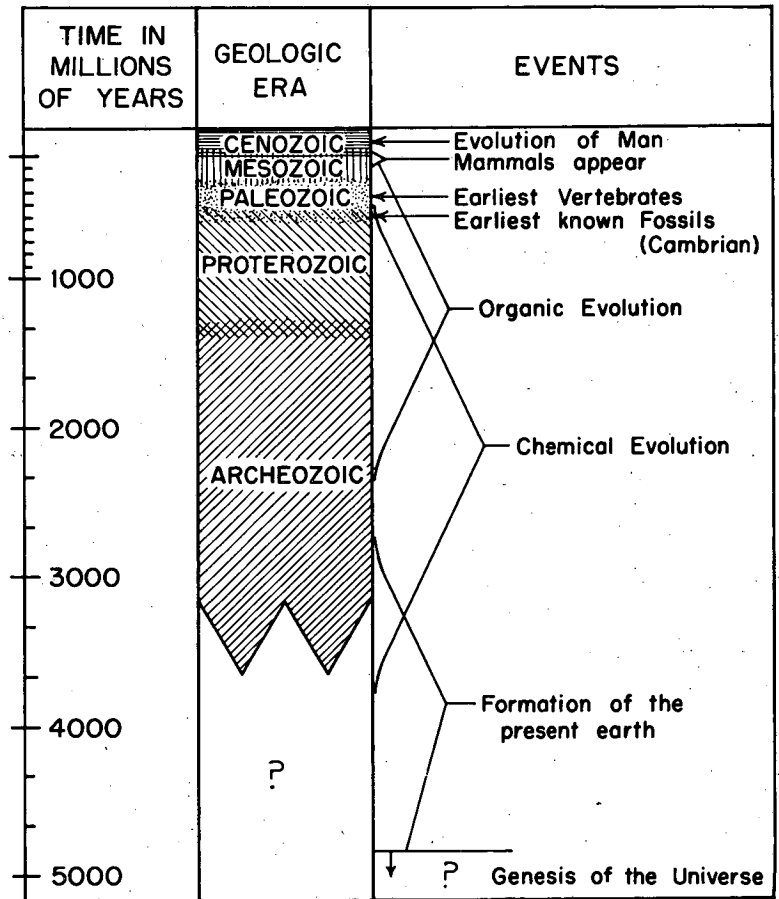
there were no things which we today could (or would) call alive; and we thus enter the period of Chemical Evolution.²

The Primitive Atmosphere

The second principle depends upon the concept of the nature of the primitive atmosphere on the surface of the earth in which the processes giving rise to living things must have occurred, or had to occur. Today, we believe (in a more or less acceptable fashion with most of the astrophysicists) that the atmosphere of the original earth was essentially a reducing atmosphere in which those atoms which were in it were attached largely to hydrogen rather than to oxygen.^{3,4} These are the two basic notions, then, upon which are based our concepts of the sequence of events which I am going briefly to review for you.

The Time Element

The time element that we have available for this sequence of events which have occurred is a rather long one, and Figure 1 indicates how that time sequence is divided. We have roughly 5 billion years (perhaps a little more). Prior to and during the early part of this period the earth was formed. Then, somewhere along 4 or 5 billion years ago, the crust was formed, then the atmosphere, and then began the period which we have labeled here Chemical Evolution. (I have tried to bracket those areas during which the generation of more complex chemicals from the simple ones which were present in the primeval atmosphere took place.) Somewhere in this Archeozoic period, presumably, arose the essential features of a living organism, and then organic evolution began; this is fairly well described and I am not going



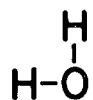
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Fig. 1. The time scale for total evolution.

to take time to go into that aspect of it. Of course, as organic evolution took over, the chemicals that were available decreased in number and variety until we arrive at the period where the earliest known fossils occurred. By this time there were no more of the complex chemicals left. About this time (roughly half a million years ago), photosynthetic organisms based on carbon dioxide appeared⁵ as well as the oxygen-using organisms.

Random Organic Synthesis - Beginning of Chemical Evolution

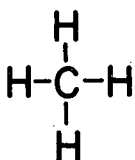
With this long time interval available, let us have a look at what the beginning of Chemical Evolution might have looked like on the surface of the earth. Figure 2 shows in the first row the primeval molecules of the earth's atmosphere (water, methane, hydrogen, ammonia and perhaps some carbon monoxide and carbon dioxide). Presumably, by the action of both ultraviolet radiation from the sun and the action of ionizing radiations, from outer space as well as radioactivity from the rocks of the earth, these simple molecules could be torn to bits -- that is, bonds were broken; the hydrogen-hydrogen bond, the carbon-hydrogen bond in methane, the hydrogen-oxygen bond in water, the nitrogen-hydrogen bond in ammonia. Those fragments which were made by such violent breaking processes would then recombine in a random fashion to give other more complex molecules, particularly those molecules in which carbon-carbon bonds had been formed, as in acetic acid, succinic acid and glycine (Figure 2, row 2). This notion had occurred to a number of people back in the middle twenties,^{6,7} and one of the first trials was made by E.C.C. Baly⁸ using, with water, not one of these carbon compounds but a carbon compound in which the carbon was partly reduced, that is, formaldehyde,



Water



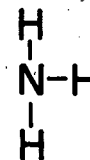
Carbon dioxide



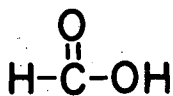
Methane



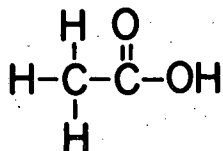
Hydrogen



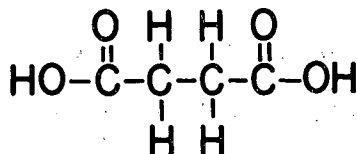
Ammonia



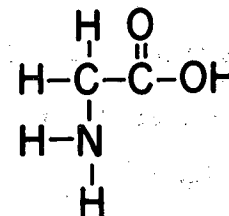
Formic acid



Acetic acid



Succinic acid



Glycine

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Fig. 2. Primeval and primitive organic molecules.

lying in between carbon dioxide and methane. Baly illuminated the solution with ultraviolet light and he did observe the formation of what appeared to be reduced compounds in which the chain length had been increased, that is new carbon-carbon bonds had indeed been formed.

That was in the middle twenties, after which there was a hiatus of about twenty-five years in which nothing was done to test out the possibility of Chemical Evolution, until about 1951 when in the course of our work on photosynthesis we couldn't help but wonder which came first, photosynthesis or respiration. This was a rather obvious question to come to us, working as we did very deeply in the chemical mechanisms of photosynthesis. We thought that possibly the construction of complex compounds occurred using radiation other than visible light first, and particularly radiations which could break these carbon-hydrogen, nitrogen-hydrogen, and hydrogen-hydrogen bonds. We tried such an experiment using carbon dioxide (because our attention had been focused on carbon dioxide in our photosynthetic studies) and water, and indeed we were able to make from these substances this molecule, formic acid, by irradiating a solution of CO_2 and water with ionizing radiation of high intensity in the Berkeley cyclotron.⁹

Shortly thereafter, Urey and his student Miller,^{3,4} reached their conclusion, from quite a different point of view, that the primeval atmosphere of the earth was a reducing atmosphere. They began with methane, ammonia, water and some hydrogen, passed an electric discharge through it. Not only were some of these carbon-carbon bonds formed, such as are shown in Figure 2 (acetic acid and succinic acid), but, more importantly (because they had ammonia in the reaction) amino acids were formed, the first of which

is glycine. If we replace one of the hydrogens attached to the first carbon atom of this amino acid with other groups, we can produce all the amino acids which are today the building blocks of the basic material of all living matter, the proteins.

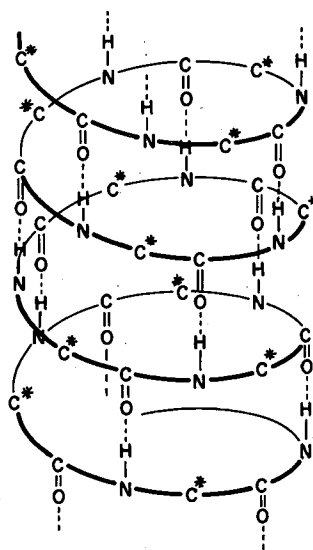
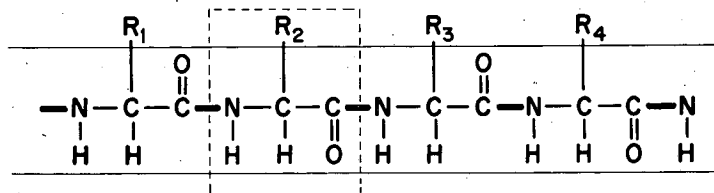
This experiment of Miller's, in which he was able to demonstrate the direct formation of amino acids by random synthesis (I describe this type of synthesis as random synthesis because it involves the indiscriminate breaking of carbon-hydrogen, hydrogen-hydrogen, hydrogen-nitrogen bonds, with the random resynthesis of other molecules from the resulting fragments) constituted an important step forward in our ability to think in these terms. Since then, using other types of high-energy radiations -- not only the gaseous discharge but ionizing radiation from the cyclotrons, or radioactivity -- the same kind of syntheses have been demonstrated.

Complex Molecules in Living Systems

Thus, one can get from the simple molecules of the primeval atmosphere to more complex molecules. It becomes necessary, however, in our thinking to devise ways and means of getting from these primitive molecules (Figure 2, row 2) to more complex substances which are really the foundation of living material as we know it today. The two principal types of complex natural molecules with which we will be concerned (not exclusively these two, but these are the two we are focused on most closely as they are involved in the mechanism of energy conversion and chemical conversion in cells today) are the proteins, which are made up by hooking together amino acids such as glycine and its relatives, on the one hand, and the nucleic acids, which are made up by hooking up the nucleotides in long chains, on the other.

We will see examples of these in a moment, but I first want to describe briefly the two kinds of function which these type types of macro-molecules have in living systems. The first of these, that one due to the protein, is a catalytic function; that is, a function of accelerating, or permitting, the general chemical transformations which living organisms must be able to make in order for them to reproduce themselves. The nucleic acid, on the other hand, contains within it the information necessary to direct the proteins into what they shall synthesize, that is, what they shall make. The proteins are involved in the catalytic processes which are required for the synthesis of living material. But, in general, the proteins will do rather simple things, and the organization of what the proteins will make, in the ultimate sense, is determined by the polynucleotide, or the nucleic acids.

Figure 3 shows a polypeptide, or protein type. A single amino acid is represented by the dotted block, with the R groups varying from one to another another amino acid. This is a simple sequence of amino acids tied together, and one of the principal configurations which they take is shown in the helical structure below the simple chain. The principle of protein construction is rather simple. The formation of a peptide link, that is the elimination of a water molecule between the carboxyl group and the amino group, is all that is required. But this structure has an enormous variety of chemical reactivity, depending on the nature of the R_1 , R_2 , R_3 etc. groups and their sequence and the way in which the chains are folded. These things determine the speed with which the chemical reactions, which the living organism must be able to undertake, may take place.¹⁰



PROTEIN STRUCTURE

Simple structural principles — Variety of chemical reactivity

MU-16147

Fig. 3. Protein structure. Simple structural principles and variety of chemical reactivity.

On the other hand, the organization of those chemical reactions, and actually the putting together of this protein (in other words, what order shall the R groups have) is determined by the genetic material, the nucleic acids, and Figure 4 shows the basic, fundamental structural elements which are found in that genetic material. These structures consist of four different ring compounds (thymine, adenine, guanine and cytosine) attached to a sugar (ribose) phosphate chain. The stripe on each side is a desoxy-ribose phosphate chain, and the chain is a continuous one. According to the Watson-Crick model, these molecules are constructed, in the case of desoxy-ribonucleic acid (DNA) of paired bases -- the thymine paired with the adenine and the cytosine paired with the guanine -- and the big, long molecule which is made up of a sequence of these four bases in some order is then twisted into a double helix.¹¹

I want to call your attention to these four bases which are rather important elements which we will discuss later. Two of them which we call purines have a six-membered ring fused to a five-membered ring, and the other two are pyrimidines, each of which are six-membered rings containing three carbons, two nitrogens and another carbon. Keep in mind that these molecules -- these two pyrimidines which have one six-membered ring in them and the two purines, which have one six-membered ring fused to a five-membered ring -- are also what we call the aromatic type, that is, in the ring, at least, there is a sequence of multiple bonds which gives rise to the aromatic type of structure.

This nucleic acid chain is twisted into a double helix and we see that kind of structure in Figure 5, turned sideways. The bars above and below the

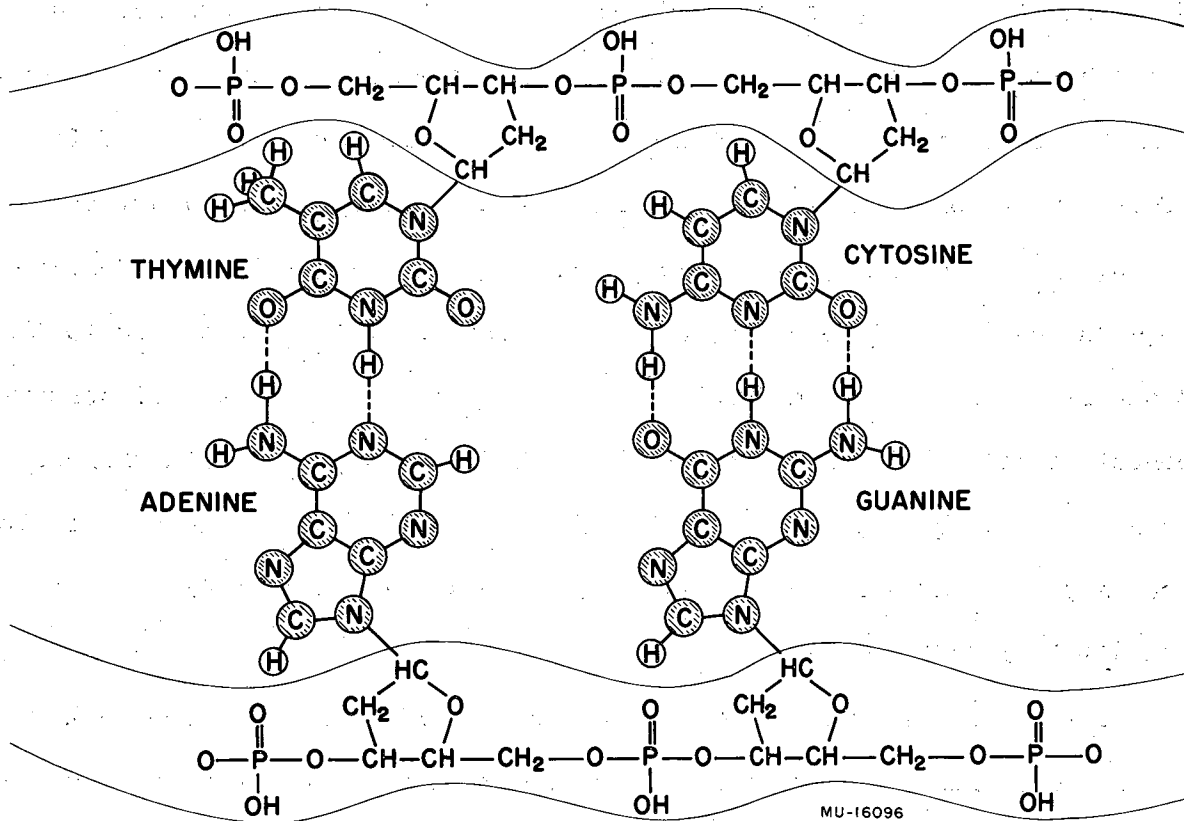
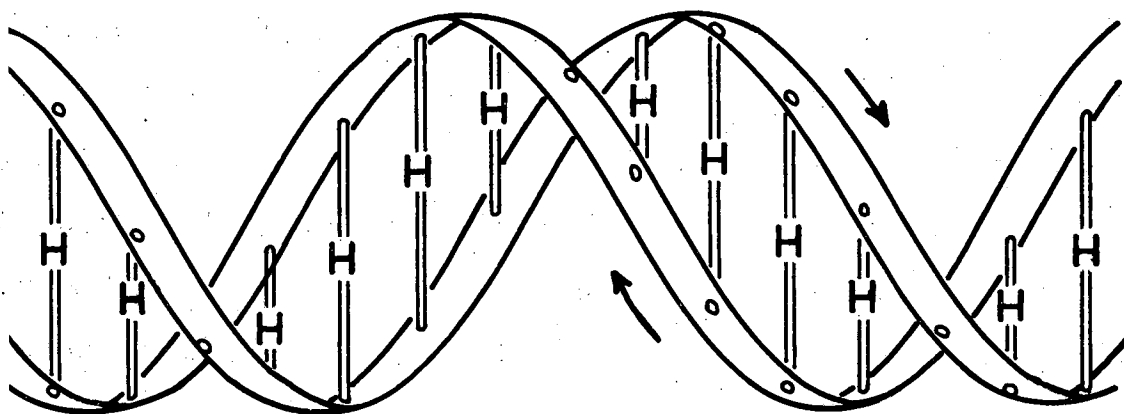


Fig. 4. Molecular drawing of the components of desoxyribonucleic acid (genetic material).



MU-16095

Fig. 5. Double helix model for desoxyribonucleic acid.

H's represent one purine and one pyrimidine ring and the H is the bond holding them together. The ribbons are the sugar phosphate chains which you saw a moment ago in detail. Presumably it is the order of these four bases (thymine, adenine, guanine, cytosine) which, arranged in a linear array, determines the characteristics of an organism, and this determination is, at least in part, made by deciding how a protein, such as an enzyme, is put together; for example, in what particular order the amino acids are put together. Thus we have a complementary relationship between these two principal types of macromolecular substances which are contained in living organisms. The information contained in the nucleic acids and the catalytic ability contained in the protein, which is made up of a sequence of amino acids, are the things which enable the living organisms not only to make the nucleic acids but the protein as well.

Nucleic Acid and Protein Development

We have now come to the point in our discussion at which I want to raise the question of which came first in the course of Chemical Evolution, the polynucleotide or the protein helix; these are two different kinds of substances. You will remember that in the course of testing what happened in the prebiological synthesis of complex molecules from the primeval ones⁴ we saw that we could make amino acids quite easily from methane, ammonia and water. As a matter of fact, Miller has not only shown that it was possible to make glycine, but also alanine and many others,¹² and I am sure that all of the substances that he got out of his reaction mixture have not yet been identified. However, so far no one has demonstrated the random synthesis of such things as these purine or pyrimidine bases, which are also required as a special feature of many organisms. I shall not go any

further into the development of the ideas of the origin of life on the earth than this: simply to say that we are presuming now that there was a sequence of events leading to more complex proteins by autocatalysis, and, at the same time, these proteins at some point were coupled to the synthesis of the polynucleotides in a manner as yet unknown to us.¹³ This is, perhaps, one of the principal problems of modern biophysics -- the relationship between the sequence of bases in the polynucleotide and the sequence of amino acids in the protein which exists today.

In the course of our thinking we have been trying to see if we could not invent some evolutionary sequence of events which could tie these two things together. So far, we haven't really succeeded in doing anything useful in this direction, except to try and extrapolate the experimental facts that the biophysicists are finding in the laboratory to a more theoretical basis. We are quite sure, however, that there is a very close correspondence between these two things, and eventually we will know something about how the two sequences were developed and evolved and how they are related to each other. We have already gotten to the point that we can be quite confident that on the present earth we will not find any of these primitive molecules. By this time they have all gone through biological transformations and have been changed by life as it has developed.

METEORITE ANALYSIS

Existence of Complex Molecules on Other Astral Bodies

However, it may very well be that on other astral bodies, in other parts of the solar system, Chemical Evolution may not have gone as far as it has here, and when we get out there we may find these prebiotic molecules still evolving, still existing. This is one purpose, of course, for sending our rockets to the Moon and Mars, or wherever we can succeed in getting them. In order to determine whether there are living things on bodies other than the earth, the ideal situation would be, of course, to take a space ship, go there and inspect them. Perhaps one day we will do this, or perhaps we can send a ship and bring back a sample. In the meantime, what kind of evidence have we that such complex molecules as we have been talking about exist elsewhere in the solar system? I don't want to talk about other forms of life that we can imagine, or believe we can imagine, but only about the kinds of life that we know about which are based on carbon, hydrogen, nitrogen, oxygen, and on nucleic acid information and protein autocatalysis. What can we do about determining whether such things exist on other bodies?

The first aspect of this is to know that carbon and hydrogen and nitrogen, and fragments of them, are widespread throughout the universe.¹⁴ In the comets we see fragments (CH, CN, C₂, etc.) which we can suppose, as they cool down, will condense into a variety of complex molecules in much the same way as the fragments which are formed by an electric discharge, or in the methane-ammonia-water-hydrogen system used in our laboratories. But we don't know that this is the case. The other bit of information we have to go by, as to whether or not there may be living material elsewhere, is

also a bit of spectroscopic evidence. This is the work of Sinton¹⁵ in which he focused the 200-inch telescope alternately on the light and dark areas on the surface of Mars, and examined the light reflected therefrom in the infrared region of absorption due to carbon-hydrogen bonds. He records that there are bands in the dark regions of Mars in the 3.5 micron spectral range, which correspond to carbon-hydrogen bonds, which are absent, or at least less, in the light areas of Mars. This is a piece of spectroscopic evidence which is very suggestive that the dark areas have C-H bonds (for whatever that may imply) and that the light areas have fewer, or none, of them. You will note that both of these bits of evidence are spectroscopic, that is, we have gotten the information by examining the light that comes to us from the otherastral bodies. Ultimately, one can see how, with our rocketry, we may send instruments out to have a closer look at the Moon, Mars and Venus, but without landing, and these vehicles would bring back spectroscopic, or photographic, information.

Elemental Analysis

Probably the best kind of information would result from a trip out there to get a piece of material from the Moon, or other astral body, and bring it back, but we can't wait for that. It turns out, however, that we don't have to wait for it. In fact, there are pieces of material coming to the surface of the earth every day -- as a matter of fact, there are tons of it coming to the earth every year -- in the form of meteorites. It was called to my attention that some of these meteorites had carbon in them. What form is the carbon in? The men with whom I was speaking at the time didn't know what form the carbon was in, so we decided to find out. Here we have

a gift from heaven, so to speak, something which we don't have to go out and get -- it comes down -- and all we must do is to analyze it, which seemed a pretty obvious thing to do.

We looked in the catalogs and found some 1500 meteorites listed, and of these 1500 meteorites there were about a dozen that were described as containing carbon. (This doesn't mean that these were the only ones that contained carbon; it means simply that these were the ones that had been analyzed and shown to contain carbon. We have since found several others that were not listed as containing carbon, in the catalog.) I just wanted to show how relatively rare the carbonaceous meteorites are; roughly a dozen out of 1500 listed in the 1950 meteorite catalog.

A small sample of one of these meteorites, Murray, which fell in Calloway County, Kentucky in 1950 was sent to us through the kindness of Dr. E. P. Henderson, the associate curator of minerals at the Smithsonian Institution. As we often do, we started the analysis quite blindly. Fortunately, just as we started this work, I took the trouble to hunt up the literature and found that actually a good many meteorites had been analyzed, not only for their carbon content but also to a small extent for the nature of the organic material in them. It was quite a popular sport, about forty or fifty years ago, to analyze a meteorite and find out what kind of carbon compounds it contained. However, at that time organic chemistry was not very well developed, so one finds in the literature of the 19th century that oily materials are present in the meteorites, and that is about the extent of it.

The most recent analysis, which I found, and the first of the ones that are really significant in terms of modern organic chemistry, was an analysis by Mueller¹⁶ performed in England on the Cold Bokkeveld Meteorite (which fell in South Africa in 1838). He reported some 2-3% carbon, of which 50% was extractable by organic solvents. He discussed the nature of these compounds in terms of their carbon content and of their solubility. The carbon content was rather low and they were soluble in alkali and several alcohols but insoluble in acid. Mueller said these compounds resembled hydrocarbons and contained acidic material.

This was already a very exciting business. It is clear that there are, floating around in outer space, already rather complex carbon compounds in these meteorites before they come to the earth. One does not have to wait for the ionization processes which I described earlier as the only way in which the prebiotic compounds might be synthesized. In the meantime, our own analysis of the meteorite fragment (Murray) was proceeding. We also found, by a sequence of organic extractions, that we were able to take out some 30% of the carbon in this meteorite which contained a total of 2% carbon by weight. Today we have available analytical tools which Mueller did not have and which none of the earlier meteorite analysts had. We used on the extracts of this meteorite the very powerful spectroscopic methods, both infrared and ultraviolet (devices which are now quite routine in most organic laboratories) and the techniques of chromatography, mass spectroscopy, etc.

Figure 6 shows the elemental analysis of the meteorite itself. You can see that it is a meteorite containing 2% carbon, about 1% hydrogen, a

CONSTITUENT ANALYSIS OF METEORITE "MURRAY"

A. CARBON-HYDROGEN COMBUSTION ANALYSIS

B. ELEMENTAL ANALYSIS

ELEMENT OR GROUP	% OF TOTAL METEORITE	ELEMENT	% OF TOTAL METEORITE
C	2.07	Fe	24.0
H	0.90	Mg	10.1
N	0.08	Si	15.8
S	0.375	Al	1*
P	0.02	B	0.3
SO ₄ ²⁻ , inorganic	5.72	Ca	0.5
Residue	87.0	Cu	0.5
		Cr	0.5
		Mn	0.5
		Ni	1

* THE FOLLOWING VALUES ARE ACCURATE ONLY WITHIN A FACTOR OF TWO.

MU-18466

Fig. 6. Constituent analysis of meteorite "Murray".

little nitrogen, sulfur, phosphorus, etc. It (Murray) is mostly an iron-magnesium silicate, which is typical of most of the stony meteorites.¹⁷ A mass spectrometer analysis of the small amount of gas produced when some of the ground meteorite was dissolved in HCl showed it to be primarily CO₂ and H₂S in the mole ratio 2:1. The absence of H₂ and such gases as CH₄, C₂H₂, etc. indicate the absence of free metal and of metallic carbides. We extracted a sample of the meteorite, by a sequence of organic solvents, and the nature of the extraction procedure is shown in Figure 7. We then proceeded to make an analysis primarily on the carbon tetrachloride and water extracts.

Spectroscopy

It is interesting to examine the infrared spectrum of the CCl₄ extract (Figure 8). Here the presence of carbon-hydrogen bonds is clearly seen. The shoulder at 2960 wavenumbers is due to the presence of methyl groups and the main peak, at 2930 cm⁻¹, is due to the methylene groups. From this ratio of methyl-methylene, by comparing it with standard, we were able to estimate that there were hydrocarbon chains in this carbon tetrachloride extract, in which we have one methyl group for every 10 to 15 methylenes -- the chains were probably fifteen carbon atoms long, or more. In addition to that, the absorption in this region of 1700 wavenumbers corresponds to the carbon-oxygen double bond, a carbonyl bond. The two bands at 1380 and 1460 wavenumbers are also methyl and methylene bands, and the one at 800 wavenumbers is a very peculiar thing in the region of what are called the 'wagging' frequencies of the benzene or aromatic hydrogens. Figure 9 shows the highly-resolved infrared spectrum of the CCl₄ extract in the 1700 wavenumber region. Here also are seen bands at about 1713 and 1740 cm⁻¹

WEIGHT OF MATERIAL EXTRACTED
BY EACH SOLVENT FROM A
NINE GRAM SAMPLE OF METEORITE

SOLVENT	WEIGHT IN mg
1. CCl ₄	20.1
2. CHCl ₃	3.3
3. BENZENE	3.9
4. WATER	541.1, containing 8% carbon
5. ETHANOL	9.3
6. BENZENE	0.0

MU-18457

Fig. 7. Weight of material extracted by solvents from meteorite "Murray".

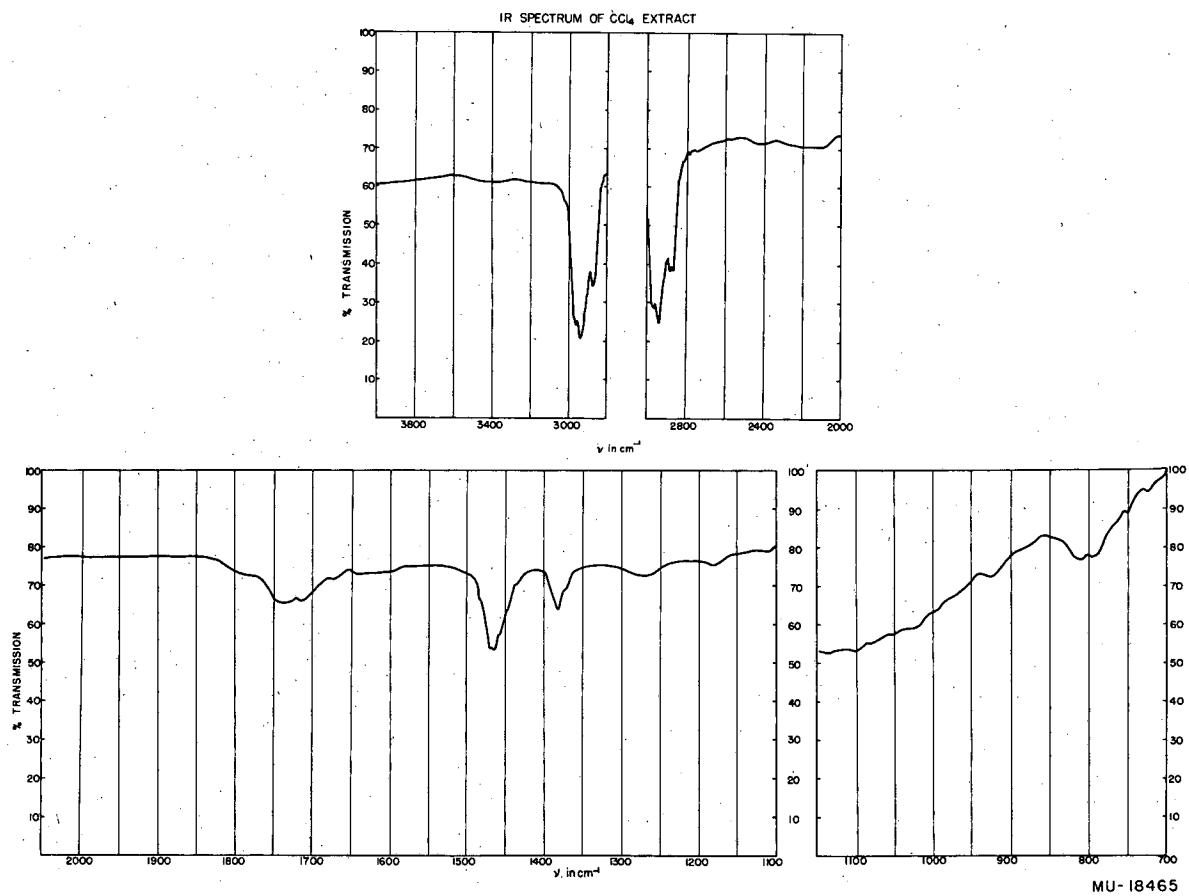


Fig. 8. Infrared spectrum of carbon tetrachloride extract of meteorite "Murray".

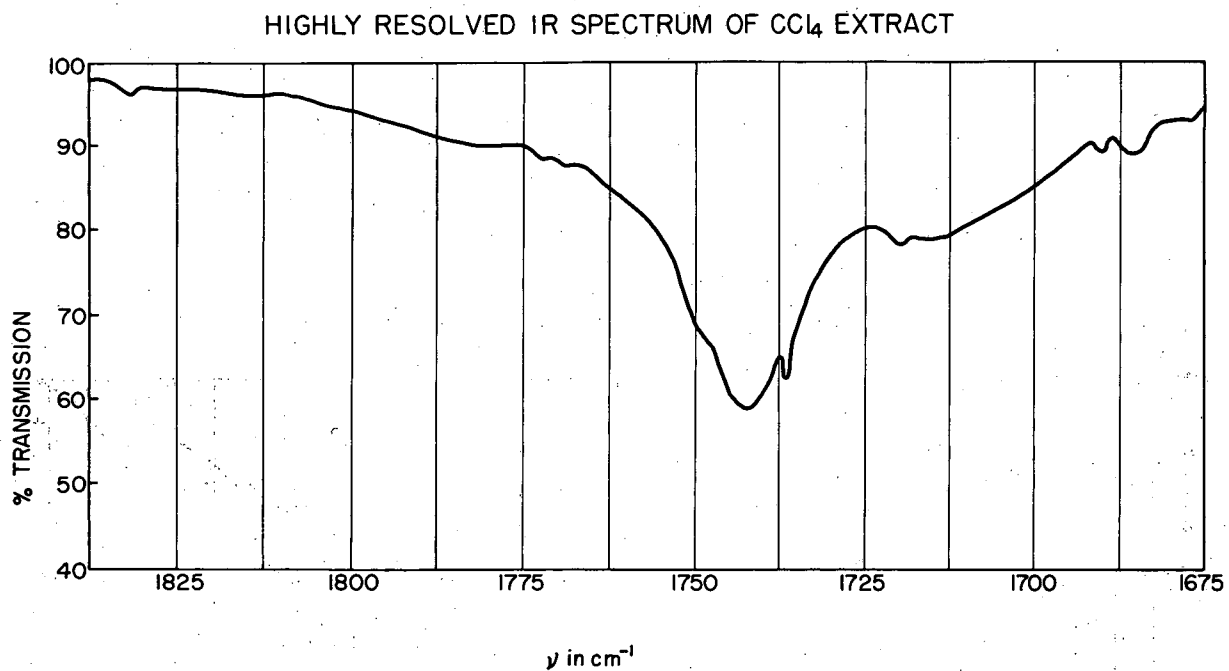
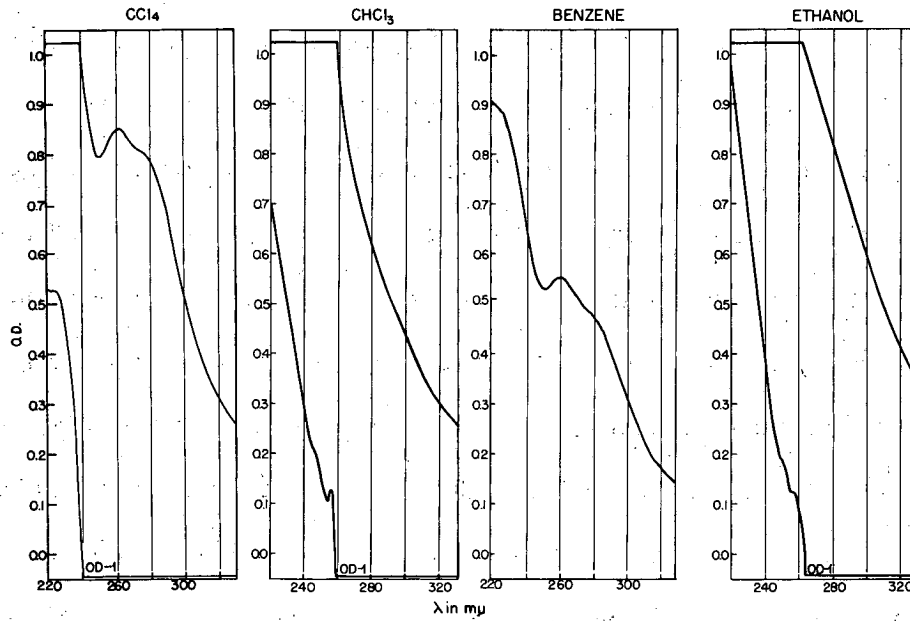


Fig. 9. Highly resolved infrared spectrum of carbon tetrachloride extract of meteorite "Murray".

and other features which are probably significant, but about which we are not in a position to say anything more. The absorption in this region is very complex since several different types of carbonyls are present. The absorption by the water extracts in this region shows acid, acid salt and amide types.

Let us now have a look at the ultraviolet absorption spectra of the whole series of meteorite extracts (Figure 10). Here you have the UV absorption of the carbon tetrachloride extract, the chloroform extract, the benzene extract and the ethanol extract. The most outstanding thing is the presence of a sharp absorption between 2500 A and 3000 A. This can be identified with elemental sulfur.¹⁸ Figure 11 shows the spread-out ultraviolet absorption of the water extract, the 500 mg containing 8% carbon. This blurring is probably due to the presence of a large amount of magnesium sulfate and perhaps other ultraviolet-absorbing materials. In order to get rid of the inorganic salt we put the material on ion exchange resins (Dowex 1 anion resin) and eluted it with hydrochloric acid. This fractionation procedure removed the inorganic salts, giving the first crude extract of the organic material separated from the inorganic. In Figure 11 one can begin to see the absorption at 2700 to 2800 A beginning to show up. If this organic material is again put on a Dowex 1 (anion exchange resin) column and fractionated with different concentrations of hydrochloric acid, two different components separate out -- one with a peak just short of 2700 A and another one with a peak just beyond 2700 A.

UV SPECTRA OF METEORITE EXTRACTS
SOLVENT: METHYLCYCLOHEXANE
CONC: 0.15 mg/ml



MD-18462

Fig. 10. Ultraviolet spectra taken in methylcyclohexane of meteorite extracts.

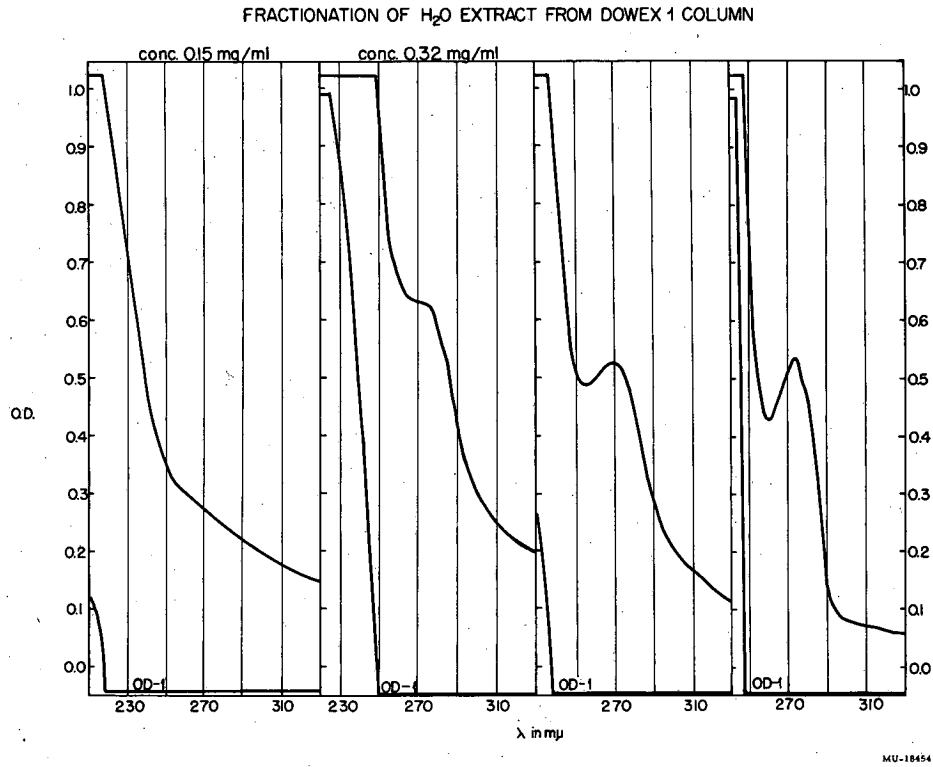


Fig. 11. Fractionation of water extract of meteorite "Murray" from Dowex-1 column.

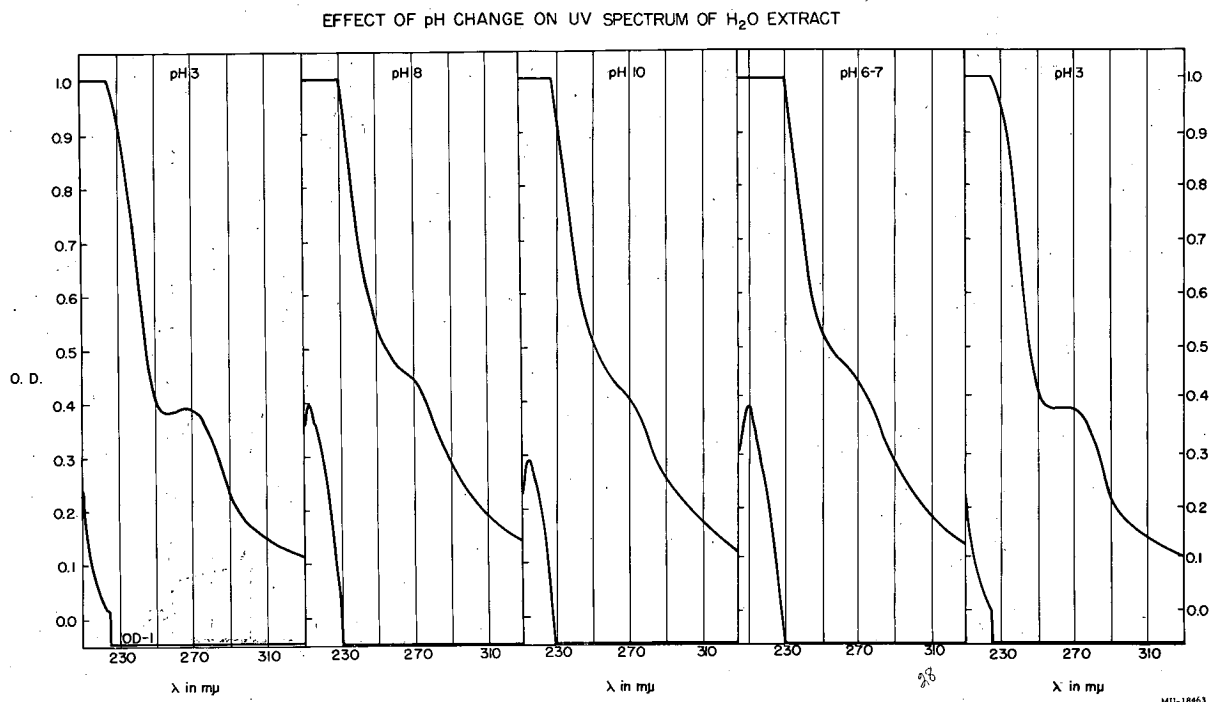


Fig. 12. Effect of pH change on ultraviolet spectrum of water extract I of meteorite "Murray".

Effect of pH

We now tried to characterize more definitely the nature of the absorption of the water extract, which was sensitive to changes in pH (Figure 12). We called the first component of the water extracts, Water Extract I, and the other, Water Extract II. Figure 12 shows what happens to Water Extract I at different pH's. As the pH is increased, the principal band disappears or at least becomes considerably smoothed out, and reappears as the pH becomes acid again; it is^a perfectly reversible change. Figure 13 shows what happens to Water Extract II -- a much more spectacular change. The 2750 and 2800 A bands disappear between pH 4 and pH 7, which indicates that an acidic group is present with a pK in between pH 4 and 7. There is a slight change even beyond, at pH 9 to 10, and these changes are reversible. The behavior of the absorption at 2300 A indicates that something was occurring there also, so the operation was repeated with a more dilute solution, with results as shown in Figure 14. Again, the peak at 2750 A appears and disappears as the solution changes from acid to alkaline.

Discussion of Data

These changes show the presence of some sort of aromatic type material which is pH sensitive (sensitive to acid). One can, in examining the available absorption spectra and without going into the details of the analysis of the spectra themselves, conclude that the spectra of this material are evidence for the presence of an aromatic heterocyclic type molecule which has a pK value somewhere between 4 and 7. There is one group of compounds which we know -- and one particular compound in which

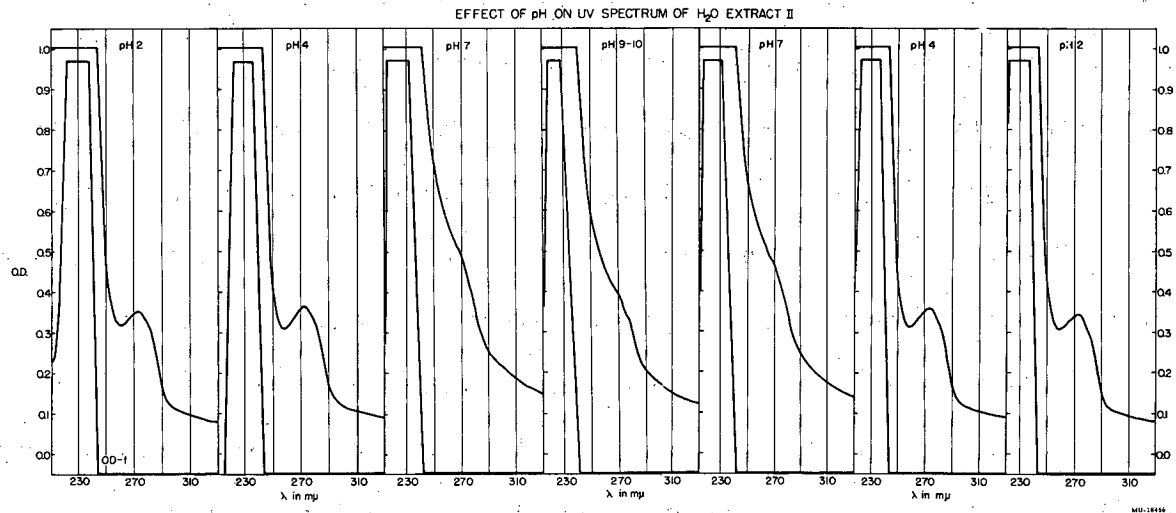


Fig. 13. Effect of pH on ultraviolet spectrum of water extract II of meteorite "Murray".

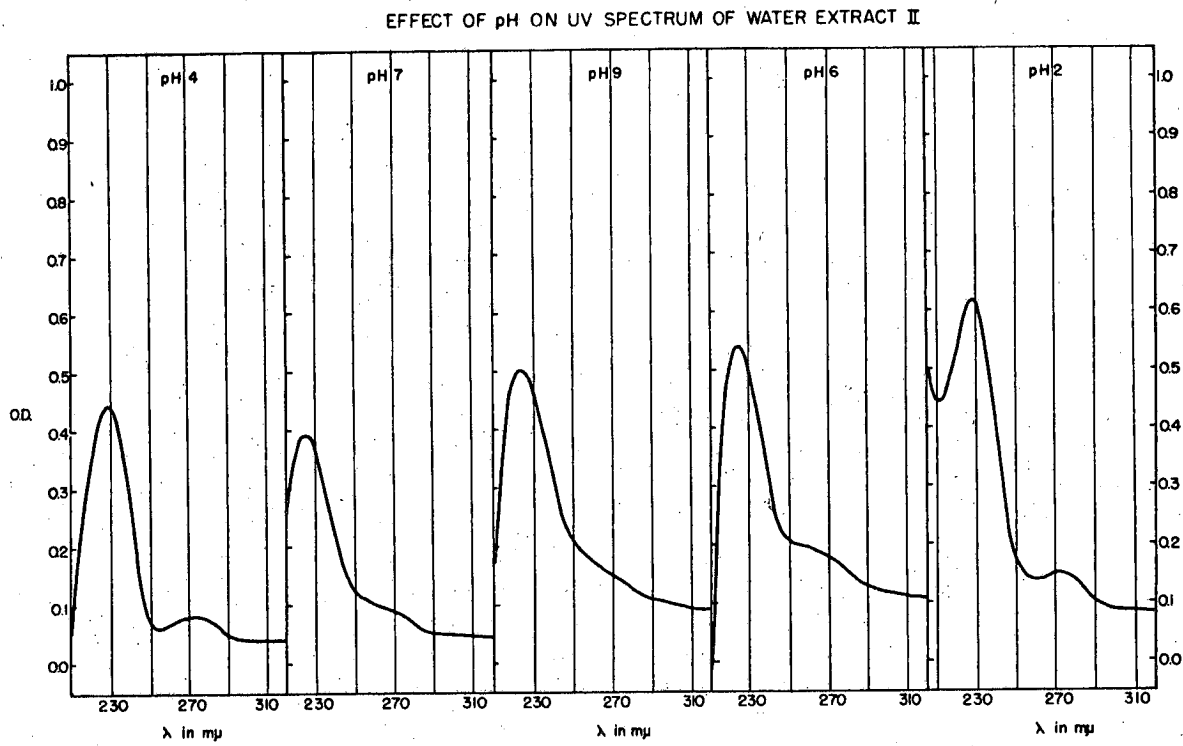


Fig. 14. Effect of pH on ultraviolet spectrum of more dilute solution of water extract II of meteorite "Murray".

we are interested -- which has an absorption spectrum very similar to this. We do not identify the contents of the water extract of the meteorite with that particular material, but we simply say that its spectrum and behavior are very similar to the spectrum and behavior of cytosine, one of the bases which is part of the structure of nucleic acid.

Perhaps the most interesting observation concerning the meteorite extracts, apart from the unequivocal evidence for a relatively long hydrocarbon chain, a carbonyl function and aromatic type molecules (not simple benzenoid hydrocarbons) is the sharpness of the ultraviolet absorption, particularly in the amion fractionated water extracts. This sharpness dictates that relatively few types of chromophoric groups which absorb in this region can be present. First observations on the extracts of another meteorite (Al-Rais, 1957) give similar types of ultraviolet spectrum. The CCl_4 extract spectrum confirms the presence of elemental sulfur in this meteorite as well.

Let me say, in conclusion, that we made tests, which should have been as sensitive on a molar scale as these spectroscopic ones for the presence of amino acids in the meteorite material and were unable to detect amino acids. On the other hand, we were able to demonstrate the presence of hydroxy acids and reducing materials in the aqueous extract by an ordinary reduction test. A mass spectrometric examination of the carbon tetrachloride extract showed the presence of hydrocarbon chains of various sizes and absence of fragments stemming from simple benzenoid hydrocarbons. There was also evidence of something which could give rise to an NO fragment.¹⁹

CONCLUSION

One can begin to think, now, of what the meaning of all this might be. We accept for the moment that what we have found in the meteorite, since the amounts of it are rather large, was indeed present before the meteorite fell to earth. (Although this is something we cannot guarantee, we can take all possible measures to prevent contamination by materials from the earth.) Then, what is the possible significance of this and also the possible significance of the absence of amino acids in the presence of what appear to be sugar acids and reducing compounds as well as heterocyclic aromatic bases?

The point I want to leave with you is one which you undoubtedly have discerned; namely, that the question which we raised earlier, as to whether or not there were possibly prebiotic forms out on astral bodies other than the earth, seems to be answered, at least tentatively, in the affirmative. Moreover, if this meteoritic material is any evidence for prebiotic or chemical evolution, it suggests that for some reason, as yet unknown to us, the formation of the bases takes place more readily and specifically than that of the amino acids, under the conditions that occurred in the meteorite. Whatever that may mean with respect to Chemical Evolution and its consequences on the surface of the earth remain to be seen.

REFERENCES

1. C. Darwin and A. R. Wallace, Journ. Proc. Linnean Soc. London (Zoology), 3, 35 (1858).
2. M. Calvin, American Scientist, 44, 248 (1956).
3. S. L. Miller, J. Am. Chem. Soc. 77, 2351 (1955).
4. S. L. Miller and H. C. Urey, Science, 130, 245 (1959).
5. M. Calvin, Science, 130, 1170 (1959).
6. A. I. Oparin, The Origin of Life, 3rd English Edition, Oliver and Boyd, London, England (1957).
7. J.B.S. Haldane (1958), in collection of essays on The Origin of Life, New Biology No. 16, Penguin Books, Ltd. London, England (1954).
8. E.C.C. Baly, Ind. and Eng. Chem. 16, 1014 (1924).
9. W. M. Garrison, et al., Science, 114, 416 (1951).
10. F.H.C. Crick. Soc. Exptl. Biol. G.B. 12, 138 (1958).
11. J. D. Watson and F.H.C. Crick, Nature, 171, 964 (1953).
12. S. L. Miller, International Symposium on The Origin of Life on the Earth, Akad. Nauk. S.S.S.R. p. 73 (1957).
13. M. Calvin, Evolution, 13, 362 (1959).
14. F. G. Watson, Between the Planets, Harvard University Press, Cambridge, Massachusetts (1956).
15. W. W. Sinton, Science, 130, 1234 (1959).
16. G. Mueller, Geochimica et Cosmochimica Acta, 4, 1 (1953).
17. H. C. Urey and H. Craig. Geochimica et Cosmochimica Acta, 4, 36 (1953).
18. J. E. Baer and M. Carmack, J. Am. Chem. Soc., 71, 1215 (1949).
19. D. P. Stevenson, private communications: July 6 and August 10, 1959.

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