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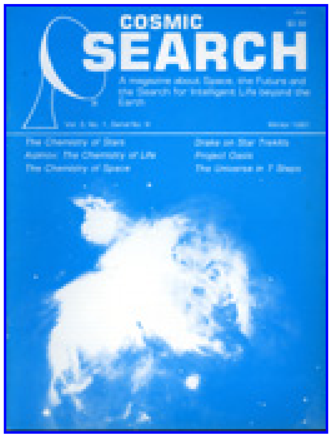

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Universal Chemical Evolution
The Chemistry of Space

By: Robert H. Rubin

Introduction


Robert Rubin

When wondering what extra terrestrial intelligent life — or just life — will be like, we must consider its chemistry. Here on earth life is based on organic chemistry — that is carbon chemistry. In our assessments of what may be elsewhere in the universe it is necessary to consider other possible cosmic bio-chemistries than the one case we know here at home. Many aspects of the other-life-in-the-universe issue turn out to produce criteria that are surprisingly similar to those on earth. By considering the stable lifetimes of stars and the potential habitable zones around them, it turns out that the best candidate stars for life bearing planets are stars very similar to the sun. (See **COSMIC SEARCH**, Vol. 1, No. 3, Summer 1979, page 36).

Another case in point arises when we consider the best way to communicate with Extra-Terrestrial Intelligence (ETI). Many workers feel the answer is by radio waves in the frequency range between 1.42 and 1.72 gigahertz (see **COSMIC SEARCH** Vol. 1, No. 1, page 35). This is the so-called "water hole" since it is flanked by lines of hydrogen (H) and the hydroxyl radical (OH), the combination of H and OH being H_2O or water. On the earth water is inextricable from life. Without arguing the merits of the conclusion that the water hole is the best region, here too we see, as in the case of the sun-like star of the first example, an anthropocentric view is sustained, that life elsewhere should be like it is here. While speculation in this field is certain, a careful scientific examination is necessary to limit the multitudinous possibilities and enhance our chances of success in searching for ETI. It is in this spirit that we shall address the issue of cosmic chemistry.

The Elements from Hydrogen through Oxygen
An introduction to the elements

Atomic number	Element	Symbol	Electrons	Atomic weight*	Nucleons**
1	Hydrogen	H	1	1.008	1p
2	Helium	He	2	4.003	2p + 2n
3	Lithium	Li	2 + 1	6.940	3p + 4n
4	Berylllium	Be	2 + 2	9.013	4p + 5n

5	Boron	B	2 + 2 + 1	10.82	5p + 5n
6	Carbon	C	2 + 2 + 2	12.011	6p + 6n
7	Nitrogen	N	2 + 2 + 3	14.008	7p + 7n
8	Oxygen	O	2 + 2 + 4	16.000	8p + 8n

*Based on atomic weight of oxygen equal to 16.
****Nucleons**: constituents of the nucleus of the atom (protons, p, or neutrons, n).

In the last decade or so much new information has been learned that has a direct bearing on universal chemistry. This has come from various astronomical observations. The chemistry laboratory now includes meteoroids, comets, and interstellar gas and dust clouds.

Meteorites

For over a hundred years it has been suspected that complex organic matter is present in meteorites. When the Orgueil meteorite that fell in France in 1864 was claimed to contain amino acids (the building blocks of proteins), the scientific community was not sympathetic, claiming it was contaminated by earthly organics. Since the meteorite had been displayed many years in the Museum of Natural History in Paris probably undergoing a regular dusting that necessitated touching (and since finger prints transfer amino acids) the stone surely was not a good case for extra-terrestrial amino acids. In fact, the percent of the various amino acids in finger prints and the meteorite were similar!

The modern era of meteorite analysis was ushered in with the work of Cyril Ponnamperuma and his associates. This was aided greatly by "clean room" techniques developed for the analysis of returned lunar rocks. The type of meteorite of particular interest is the carbonaceous chondrite. The former part of the name is due to the fact they are the richest of the meteorites in carbon content (as high as 5 percent by weight). The latter part is because they have glass like spheres called chondrites about 1 to 10 millimeters in diameter. They are also copious sources of water, some containing more than 10 percent by weight. Ponnamperuma and his collaborators, then working at NASA Ames Research Center in California, first analyzed the Murchison meteorite, a carbonaceous chondrite, which fell September 28, 1969 near Murchison, Victoria, Australia. Stones were picked up soon after the fall, those least cracked were culled out, and an interior piece pulverized and analyzed within a few months after its fall. The chemical identification was performed using a gas chromatograph combined with a highly sensitive mass spectrometer. In their initial publication they report finding 5 amino acids that are also found in living things and 2 not found in biological systems. Additional work and a later report increased these to 6 and 12 respectively. This is supportive of the hypothesis that the amino acids must have been synthesized non-biologically. The researchers also were able to determine for several the percentages of left-handed (L) and right-handed (D) amino acids. The terms right and left handed refer to the fact that the amino acids differ only in that they are mirror images of each other like a left and right hand. All the amino acids with the exception of the simplest, glycine, show this effect. Glycine's mirror image can be rotated to superimpose exactly with the original. In living systems on earth, all amino acids other than glycine are L type (except the case of a class of single cell organisms that are made of D type in their cell walls). In the Murchison meteorite they found about equal amounts of both L and D type. Together with the above fact that most of the amino acids in the meteorite are not of the type associated with living things strongly suggests *all* of the amino acids present were produced before they arrived on earth. The final clincher was the ratio of carbon 13 to carbon 1 [sic; should the latter be "12" instead of "1"?] was significantly higher in the organic matter in the Murchison than in terrestrial organic matter. All the evidence points to the indigenous nature of the hydrocarbons and amino acids in the meteorite.

In the early morning hours of February 8, 1969 the Allende meteorite put on a spectacular display appearing brighter than a full moon as it plummeted to the ground near the northern Mexico village for which it is named. Within days much material was collected from this fall. An analysis similar to that performed on the Murchison produced similar results. The experimenters also did not have the word "contamination" thrown up as a criticism as in the early days of meteorite analyses, since the stones were found so soon.

Most recently, Ponnamperuma (now at the University of Maryland) and his colleagues have examined two carbonaceous chondrites from Antarctica — one called Yamato 74662 and the other called Allan Hills. Again they found lots of amino acids (both proteinaceous and non-proteinaceous) containing roughly equal amounts of D and L type. These meteorites appear to be uncontaminated by organic matter from the Earth. Indeed, they show less contamination than did the Murchison even though they fell about 200,000 years ago! This is deduced from the fact that there are equal amounts of amino acids in samples taken from the interior and the exterior. Specifically, in Yamato 74662, 15 amino acids were detected including 9 biological and 6 non-biological while the Allan Hills meteorite had 6 biological and 5 non-biological amino acids. As with the other analyses, the most recent research on the Antarctic meteorites suggests the organic matter including the amino acids are of extra-terrestrial origin.

Meteorites are rocks probably from the asteroid belt or comet remnants that fall to the earth. They are believed to be as old as the solar system having formed about 4.6 billion years ago from the solar nebula. The substances found in meteorites give clues to the kind of chemical reactions that are possible in a system other than Earth's. In addition they may provide vital clues to what processes occurred here on Earth prior to the beginning of life. As far as cosmic chemistry is concerned, the complex molecules that evolved in the meteorites are organic molecules that evolved also on earth. The complex molecules contain for the most part the elements carbon, hydrogen, nitrogen, and oxygen — precisely those atoms most abundant in living things. These are also, in terms of number of atoms, the most abundant elements in the universe — with two exceptions. Helium is the second most abundant element and neon is close to carbon, nitrogen and oxygen in rank. However both helium and neon are inert as a result of full outer electron shells and they don't form molecules (except in rare cases).

Comets

Comets are another source of clues to the understanding of cosmic chemical evolution. Comets, even more than meteorites, provide a sample of the solar nebula which is well preserved. We estimate that the mass of a comet is not very large, perhaps typically the mass of an earth mountain. We have yet to visit a comet although NASA would like to do so when Halley's comet returns in 1985/1986. Still, the chemical analysis can be done remotely from earth by spectroscopy. Optical astronomers have known for many years that comets contain relatively simple diatomic and triatomic molecules (see Table 1). Some are organic since they contain carbon. More recently radio astronomers have been able to extend the list of these molecules by identifying additional substances from their radio lines.

TABLE 1
MOLECULES IDENTIFIED IN COMETS

Name of molecule	Chemical Symbol
Hydroxyl radical	OH
Methylidyne	CH
Cyanogen radical	CN
Ionized hydrogen	H_2^+
Ionized nitrogen	N_2^+
Carbon	C_2
Carbon monosulphide	CS
Amide	NH_2
Ammonia	NH_3
Carbon monoxide	CO
Carbon dioxide	CO_2
Water	H_2O

Hydrogen cyanide	HCN
Methyl cyanide	CH_3CN

Comet Kohoutek in 1973/1974, which turned out to be such a disappointment to the general public after an unprecedented TV and press build up, actually proved to be very fruitful for scientists. Radio molecular spectroscopists believe they have indentified hydrogen cyanide (HCN) and the most complex compound yet found in comets, methyl cyanide (CH_3CN), being emitted by this comet. Calculations of the orbit of comet Kohoutek show that it spends most of its time well beyond the orbit of Pluto in the frozen depths of space. As it approaches the sun under the influence of gravity, the frozen substances can vaporize. It is this gaseous component (often called the coma that surrounds the solid head) that radio astronomers look for with their telescopes. Most probably organic compounds like methyl cyanide are present in the comet throughout its journey around the sun. Comets most likely formed from the nebulosity creating the sun, the planets, and the asteroids and are therefore as old as the solar system itself. It is possible that the molecules in Table 1 are decomposition products of larger parent molecules which break down when exposed to the intense solar radiation.

Astronomers are anxiously awaiting the appearance of a very bright comet. A bright optical comet also will likely be the best candidate to identify molecules by their radio lines. As will be discussed in the next section, there are many complex molecules radio astronomers have found in the interstellar medium. These undoubtedly would be high on the list of priorities to look for in bright comets. Whether Halley's comet will be bright enough for such observations in 1985/86 is not certain. There is also a proposal of a second mission to rendezvous and follow comet Temple II in 1988/89 while close to the Sun. This would provide a dynamic picture of the changing chemistry as the solar radiation and wind vary. There is even the exciting possibility of landing on the head and making direct chemical analyses! Or eventually the "comet of the century" will appear that is bright enough for detection and analysis of many more substances. The indication is that, like meteorites, the complex molecules will be organic and composed of predominantly C, H, N, and O.

The Interstellar Medium

On a much grander scale than comets or meteorites we are now able to say quite a lot about the chemistry of interstellar space, that is the region of the galaxy that is between the stars. It is mainly gas and dust. Just a little over a decade ago it was thought that nothing more complicated than a diatomic molecule would be found in these regions. The reasoning then was that collisions between atoms in the extreme vacuum of the nebulae (clouds of gas and dust in space) would be so rare that gas phase reactions would build molecules of no more than two atoms. The revolution began with the radio astronomy detections of ammonia and water by their microwave spectral lines. In just over a decade, the list of molecules found in the interstellar medium has grown to over 50, and this does not include isotopic variations of the molecules. In Table 2 we list those species detected up until August, 1979, the time of the International Astronomical Union symposium on interstellar molecules. Ozone, O_3, was discovered after that meeting. It's addition makes Table 2 complete as of January, 1980. Most of these are carbon containing organic molecules. Many of these molecules will be recognized as having appeared in comets — CH, CN, OH, CO, C_2, CS, H_2O, HCN, NH_3, and CH_3CN. The heaviest molecule and also the one with the most atoms yet found in interstellar space is cyano-octatetra-yne HC_9N. It contains 11 atoms and has a molecular weight of 123. It is interesting that although no amino acid has yet been found in space, the simplest one, glycine, has less atoms (10) and is lighter (molecular weight of 75) than HC_9N. By far the largest number of compounds in Table 2 contain, H, C, N, and O; ten contain sulfur, and two have silicon. Even though the list of molecules is not a random sample, the picture is quite clear that the most abundant elements in these molecules of interstellar space are the same as in living things on earth. Sulfur also is essential for all terrestrial life forms. It is the only element besides H, C, N, and O that is incorporated into amino acids needed for life — cysteine and methionine.

TABLE 2
MOLECULES DETECTED IN INTERSTELLAR CLOUDS
The order is approximately by time of discovery.

Name of molecule	**Chemical Symbol**
Methylidyne	CH
Cyanogen radical	CN
Methylidyne ion	CH^+
Hydroxyl radical	OH
Ammonia	NH_3
Water	H_2O
Formaldehyde	H_2CO
Carbon monoxide	CO
Hydrogen cyanide	HCN
Cyanoacetylene	HC_3N
Hydrogen	H_2
Methyl alcohol	CH_3OH
Formic acid	HCOOH

Ionized formyl radical	HCO^+
Formamide	NH_2COH
Carbon monosulfide	CS
Silicon monoxide	SiO
Carbonyl sulfide	OCS
Methyl cyanide	CH_3CN
Isocyanic acid	HNCO
Methylacetylene	CH_3C_2H
Acetaldehyde	CH_3CHO
Thioformaldehyde	H_2CS
Hydrogen isocyanide	HNC
Hydrogen sulfide	H_2S
Methanimine	H_2CNH
Sulfur monoxide	SO
Protonated nitrogen ion	N_2H^+
Ethynyl radical	C_2H
Methylamine	CH_3NH_2
Dimethyl ether	$(CH_3)_2O$
Ethyl alcohol	CH_3CH_2OH
Sulfur dioxide	SO_2
Silicon sulfide	SiS
Acrylonitrile	H_2CCHCN
Methyl formate	$HCOOCH_3$
Nitrogen sulfide radical	NS
Cyanamide	NH_2CN
Cyanodiacetylene	HC_5N
Formyl radical	HCO
Cyanoethynyl radical	C_3N
Acetylene	C_2H_2
Cyanotriacetylene	HC_7N
Ketene	H_2C_2O

Nitroxyl	HNO
Ethyl cyanide	CH_3CH_2CN
Carbon	C_2
Cyano-octatetra-yne	HC_9N
Methane	CH_4
Nitric oxide	NO
Butadiynyl	C_4H
Methyl mercaptan	CH_3SH
Isothiocyanic acid	HNCS
Ozone	O_3

What allows these complex molecules to form in the seemingly harsh environment of space? What the astrochemists of the pre-molecule explosion had overlooked was the important role of dust grains in the formation of molecular hydrogen. Also in regions of much higher than average density, the densest clouds, collisions in the gas phase are not so infrequent that more complicated molecules could not be formed. This is aided greatly by reactions between ions and molecules. The energetic radiation present can ionize some of the atoms and molecules in the cloud. It is much easier then for a positively charged atom or molecule to interact with a neutral one than if both were uncharged. The reason is that as two neutral atoms or molecules approach each other, they first feel the electrostatic repulsion of their electrons. This acts as a sort of shield to ward off the advance of the other. When one of them is an ion however, this shielding is much reduced and could even be an electrostatic attraction of a net positive to a negative charge.

Carbon Chauvinism

Why does carbon play such an important role in cosmic chemistry? Could another element serve the same function and be the basis of life elsewhere? An important reason for the ability of carbon to form molecules is that is has four chemical bonds, the most possible for any atom. We say carbon has a valence of four. The only other element with the same capability that is at all cosmically abundant is silicon. Silicon is about 25 times less abundant than carbon (by number of atoms) in the universe, but it is more than 100 times as abundant on earth. Strictly from this standpoint certainly the earth would be a good candidate for a silicon rather than a carbon based life.

In terms of chemical bonding there are several arguments that make the case for a silicon-based life extremely weak. The Si-Si bond (42 kilocalories mole)* is only about half that of the C-C bond (80 kilocalories/mole) which means it is easier to break. (*A **mole** equals the gram molecular weight which equals the weight (in grams) of the total of the atomic weights of the atoms making up the molecule. Thus, a mole of carbon monoxide (CO) is 12.011 + 16.00 = 28.011 grams. — Ed.) Also silicon bonds very strongly with oxygen. In the presence of hydrogen, oxygen, or other silicon atoms, silicon will overwhelmingly choose oxygen. Since oxygen is about 25 times as abundant as silicon cosmically, the chances are most of the silicon will be used up in combining with oxygen. This is supported by the silicon compounds present on earth as well as those observed in interstellar space — SiO and SiS (sulfur is below oxygen in the periodic table so is chemically similar). Also the Si-Si bond is unstable in the presence of liquid water or ammonia. On the other hand for carbon, the C-C bond is of comparable strength to the C-O and C-H bond allowing the formation of carbon ring structures that are characteristic of important pre-biotic molecules and appear in the bases of DNA. Since the Si-O bond is stronger than the Si-Si bond, the formation of Si ring structures is improbable. Furthermore, silicon does not usually make multiple bonds while carbon often does, leaving carbon free to react with other atoms while hanging onto the structure it already has.

Another important comparison is between the oxides CO_2 and SiO_2. Carbon dioxide is gaseous (and thus free to associate with many other substances) for any reasonable temperature for which we believe life will exist, while silicon dioxide is a solid quartz at these temperatures. CO_2 is soluble in water and relatively easy to dissociate while SiO_2 is insoluble in water or most anything and is ultra hard to break up. Imagine the difficulty the photosynthesis process, vital to life on earth, would have with SiO_2. Finally, we introduce perhaps the most decisive evidence of all. For whatever reasons, carbon does make more compounds by far than all of the other elements combined do in non-carbon compounds! This is the case not only in the earth laboratory but also in meteorites, comets, and interstellar clouds.

What might happen or have happened elsewhere in the Universe regarding the subsequent evolutionary steps — let's say the biochemical evolution — is another story. Right now this is a more speculative area than what we have discussed here. Probably most of the experts would say that the omnipresence of DNA in life on earth would not extend to the Universe. Nature could more than likely create other self replicating molecules that would play a surrogate role for DNA elsewhere. However, most workers in the field would most certainly bet that the overwhelming majority of extraterrestrial life forms are C, H, N, and O-based.

Robert Rubin

Robert H. Rubin is a member of the physics faculty of the California State University at Fullerton. Dr. Rubin received his Ph.D. degree from Case-Western Reserve University (Cleveland, Ohio).

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