# THE WATER-AMMONIA SYMMETRY OF AMINO ACIDS: CONSTRAINTS ON PALEOATMOSPHERES

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Összefoglalás - Mindenfajta földi életet három alapvető és közös vonás jellemez: fehérjék alkotják a testet, nukleinsavak hordozzák az információt és víz az oldószer. A fehérjékre, mint a legősibb anyagokra tekintve tudjuk, hogy aminosavakból épülnek fel. Az aminosavak lényeges jellemzője az, hogy a vízre ill. az ammóniára (mint oldószerre) vonatkoztatva számos tulajdonságuk szimmetriát mutat. Ez azt jelenti, hogy ha a vizet ammóniára cseréljük, akkor a fehérjeépítés lényeges vonásai (pl. peptidkötés, fehérjefelépítés) nem változnak meg. Ebből a szimmetriatulajdonságból, ill. abból a tényből, hogy a keletkezéskor az aminosavak környezetében ammóniának is jelen kellett lennie, von le következtetéseket a cikkünk az ősi földi légkörre vonatkozólag.

Abstract - In formation of terrestrial life amino acids played a key role. There is a basic symmetry in amino acids if the solvent liquid is exchanged "behind them" from water to ammonia. This chemical symmetry of solvents behind a characteristic building-block type compound set can give strong constraints when we intend to reconstruct primordial terrestrial atmosphere. Our paper discusses some consequences of the water-ammonia symmetry of amino acids onto the initial conditions of the primordial terrestrial planetary atmospheres.

### 1. INTRODUCTION

The only type of life of which we know anything definite is the life on Earth; all forms of terrestrial life have common building blocks, solvents and processes in their very fundaments. Terrestrial life is characterized by at least 3 fundamental properties:

- 1) The body is built up from *proteins*.
- 2) Genetic information is carried by nucleic acids.

3) The general solvent is water.

Proteins and nucleic acids are macromolecules built up modularly from moderate molecules of limited variety. (It is still an open question if two separate types of macromolecules are really needed, or the fact is merely a historic accident.) Terrestrial life is the action of giant carbon chains in water solvent.

Of the mentioned subsystems of macromolecule families the building blocks of the proteins, the amino acids seem to be the most ancient (Chaps. 2 and 4). Therefore we focus on tracing their origin in connection with atmospheres.

Amino acids form an elementary set of units as building blocks in cellular level terrestrial life. Considering the primordial liquids as solvents where these units could have been developed, the ambivalent characteristics of amino acids might be explained. There are two such liquids: *water* and *ammonia*. Both of them are good solvents but they use up different radicals of amino acids in forming their chemical characteristics in their reactions in the liquids. So amino acids are "Janus-faced" chemicals which have counterpart radicals for both "water-world" and "ammonia-world".

The ambivalency of amino acids in respect of water-world and ammonia-world may represent a kind of symmetry. This symmetry is expressed by the amino acid molecules, when liquid solvent is exchanged from water to ammonia or vice versa "around them". The characteristical radicals of amino acid molecules are carboxyl, hidroxyl, amine and amide ones, too. Therefore they can interact both with water and ammonia in a similar way in many reactions (Chapter 3). Terrestrial life, however, is not W-A symmetric, using W radical at the positive ends and A ones at negative ends and never inversely.

From the ambivalency of amino acids it can be suggested that in the place of their origin both water and ammonia was present. In our previous paper we discussed these regions on a Solar System horizont (*Bérczi and Lukács*, 1995). In this paper we focus our attention to the constraints which arise onto the composition and origin of the primordial terrestrial atmosphere from the Janus-faced chemical character of amino acids.

# 2. EXPERIMENTS AND PREDICTIONS IN SEARCH OF MAIN COMPONENTS OF ANCIENT TERRESTRIAL ATMOSPHERE - CHEMISTRY, GEOLOGY, PLANETOLOGY

The present atmosphere of Earth is clearly the product of billion years of biologic activity, as shown by the free oxygen, impossible without continuous oxygen source (*Koppány*, 1996). The palacoatmosphere is a matter of speculation. *Miller* (1953) was able to produce amino acids in an artificial reducing atmosphere with  $H_2O$ ,  $CO_2$ ,  $NH_3$  and  $H_2$ . While  $H_2$  and  $H_2O$  do not need explanation, and  $CO_2$  is present at Venus and Mars,  $NH_3$  seems to belong to the outer Solar System, and so its original presence is often questioned. Two important definite observations indeed do not confirm the simple schemes.

The situation can be summarized as follows. Abiotic synthesis, and especially that of amino acids, is a very easy and natural process in the presence of  $NH_3$  in a reducing atmosphere. On the other hand, there is no evidence for  $NH_3$  in the palaeoatmosphere, and primordial  $NH_3$  is not expected from Solar System condensation. In this paper we summarize

both scenarios (with and without  $NH_3$ ); the final conclusion will be an alternative. Now first let us see the relevant experiences and planetologic theories.

The *Miller* (1953) experiment used  $H_2O$ ,  $H_2$ ,  $CO_2$ ,  $NH_3$ , substantial temperature, UV radiation and electric discharges. As told above and will be seen below, presence of  $NH_3$  in the palaeoatmosphere is doubtful; all other components and circumstances were characteristic in those times. In such syntheses many organic compounds appeared, in descending order of quantities the first 5 were (*Brooks and Shaw*, 1973)

Formic acid > Glycine > Glycolic acid > Alanine > Lactic acid. Let us remember this sequence. Miller's explanation is that the reaction to amino acids goes in 4 steps:

1) From the simple molecules first an aldehide RCHO is formed. Parallelly HCN is formed too.

2) RCHO and HCN forms RCH(OH)CN.

3) That compound is *aminated* by NH<sub>3</sub>, i.e. the hydroxyle radical is substituted by an NH<sub>2</sub>:

# $RCH(OH)CN + NH_3 \rightarrow RCH(NH_2)CN + H_2O$

Since both  $NH_3$  and  $H_2O$  are present, this reaction does not change the main components of the reaction qualitatively.

4) The amino nitrile takes again  $H_2O$  and gives back  $NH_3$  into the solution:

# $RCH(NH_2)CN + 2H_2O \rightarrow RCH(NH_2)COOH + NH_3$

So the final result is an amino acid; we can see that the reactions are quite natural in the simultaneous presence of  $NH_3$  and  $H_2O$ . No doubt, by complicated catalysers the synthesis may be successful from other sources of nitrogen too, but, as we shall see below, the only possible abundant primordial N source could be  $NH_3$  anyway. We also can see that there is a possibility for bifurcation in the reaction chain. If the amination in Step 3 does not happen, then the final result is not amino acid, but oxiacid, **RCH(OH)COOH**. Indeed, oxiacids are also among the endproducts of the Miller-type syntheses, but with *lower* abundances. Glykolic acid is the oxi-analogon of glycine, and lactic acid is that of alanine.

So primordial  $NH_3$  is welcome for abiotic amino acid synthesis. But let us see observations. Szalay (1975) extracted gases from precambrian sediments. He found  $H_2$ ,  $H_2O$ ,  $N_2$ ,  $CO_2$  and  $CH_4$ , but not  $NH_3$ . And Brooks and Shaw (1973) emphasize that no geologic traces of the often assumed "primordial bouillon" of sugars, amino acids, nucleic acid building stones &c. Then the remainders should be found at least as carbon layers with high nitrogen abundance. However the earliest layers seem to be poor in nitrogen; e.g. the amino acid concentration of such sediments seem to be not higher than  $10^{-9}$  (Schöpf, Kwenvolden and Barghoorn, 1968). This low concentration comes from the Fig Tree layer where the oldest fossil microorganisms were identified (3.7-3.0 Gy old). From this reason Brooks and Shaw (1973) prefer an extraterrestrial origin of terrestrial life and their scenario is that a

microorganism survived a space travel on a meteorite, found an ammonia-free atmosphere and their descendants converted the reducing atmosphere into oxidative. This is a viable solution if there was life somewhere else in the Solar System. However, up to now there has not been found any evidence for such extraterrestrial life. Then it is not uninteresting to see what are the possibilities of appearance of ammonia in the terrestrial palaeoatmosphere.

The Lewis-Barshay model summarizes the most probable precipitates from the Solar Nebula. The original presolar nebula was more or less chemically homogeneous but temperature was dropping outward. When chemical reactions started such compounds precipitated which were in solid state at the specific temperature and pressure. Therefore refractories condensated inside as well as outside but volatiles did it only outside. In the particular calculation only such minerals were incorporated which had well-known geochemical and geological importance according to the state of arts at that time. During the last one and a half decade space probes, mainly the two Voyager missions revealed the satellites in the outer Solar System. So a new emphasis appeared when considering crystalline materials in the solar system. This new emphasis focuses attention to the icy materials, outer cool regions, smaller (cometary, asteroidal, fragmented) bodies in the Solar System.

Now let us see the possible nitrogen sources. N is fairly abundant on Earth; it dominates the present atmosphere, and it is necessary for amino acids. However, N-bearing minerals are rare on Earth, so the original calculations included only  $NH_3$ . According to the Barshay-Lewis model (1976) ammonia could have condensated somewhere outwards from Saturn. Gas evaporation from the bulk of Earth may have seriously contributed to the palaeoatmosphere, but the present Earth litosphere seems to be very poor in ammonia.

In this new perspective the importance of the volatile-metamorphized minerals increased, because of studies on surface geological structures and reflected spectra of asteroids and outer satellites at Jupiter, Saturn, Uranus and Neptune. There the rocky components of satellites may be the hydrated silicates according to the equilibrium condensation model of Lewis and Barshay. But other important constituents of these partly rocky, partly icy bodies may also be relevant, if we pay attention to the other important volatile component,  $NH_3$ . Besides water  $H_2O$ , ammonia,  $NH_3$  can also build into silicates. So ammonium silicates are alternative candidates as precipitation products in this part of the Solar System. Being N almost as abundant as O and C in the cosmic set of chemical elements, the "ammonized"-variants of known terrestrial silicates may also be represented considerably among volatile-metamorphized silicates.

For clarity we must distinguish two kinds of minerals affected by ammonia. The first kind is ammonium silicate. the  $NH_4$  radical acts as a pseudo-alkali ion (similar to rubidium), so in the presence of  $NH_2$  and excess H ammonium can substitute potassium or sodium in their compounds. There are different known members of this group of ammonium-silicates: the ammonium feldspar BUDDINGTONITE (*Erd et al.*, 1964), the ammonium muscovite TOBELITE (*Vedder*, 1964; *Hiyashi et al.*, 1982), the AMMONIOLEUCITE (*Hori et al.*,

1986), the AMMONIUM-ILLITE (Juster et al., 1987), and AMMONIUM PHLOGOPITE (Bos et al., 1987).

The other kind of ammonia-altered minerals is still practically unknown outside of laboratories, and even in laboratories such *silicates* are rare. They are called ammins or ammoniates: salts with crystallic ammonia instead of crystallic water. Hundreds of ammin salts are known, e.g.  $FeSO_4 \cdot 6NH_3$ , but for our purposes data of ammoniated *silicates* would be needed, e.g. the ammoniated analogon of serpentine. We note that generally one expects lower temperatures for an ammoniate analogon than for the hydrated crystal. Such ammoniates (i.e. crystals with structural ammonia) may have contributed to the composition of primordial Earth, and then lost the ammonia when the bulk of the planet was being heated up.

If the possibility of ammoniates is ruled out in later studies (no serious theoretical predictions exist now for the ammonia content in the inner Solar System) but there will be evidence for the atmospheric presence of ammonia in the far past, then a possible source would be extraterrestrial origin, e.g. a collision with an ammonia-rich planetesimal during the formation of Earth. A planetesimal of cca. radius of 1000 km from beyond Uranus could have filled up the terrestrial palaeoatmosphere to 1 atm partial pressure. Of course, there remains the problem that no geologic remnant of this ammonia is found. (Gradual delivery of ices - with ammonia content - by comets might also be considered.)

Other N sources are improbable. Molecular  $N_2$  condensated somewhere at Pluto. For oxides and cyan one can only guess the conditions for condensation, because they have not been incorporated into LB schemes. However, first, the H surplus is overwhelming, so one expects mainly molecules with H, not with O and C. Second, by comparing freezing points, crude estimations for the condensation distances can be made. Observe that  $H_2O$  starts to condensate at Jupiter. Now, at 1 atm freezing points are as follows:

Molecule	Freezing point, °C at 1 atm
NO	-163
N <sub>2</sub> O <sub>4</sub>	-10
C <sub>2</sub> N <sub>2</sub>	-34
HCN	-15
NH <sub>3</sub>	-33

One can see that no possible N source condensated much more inside than ammonia, and, as told, their quantity was probably much less.



Fig. 1 The simplest organic acids and bases in the waterammonia mirror. The simplest amino acid, glycine, (together with most amino acids) is "just on the mirror" although is not mirror symmetric. Glycinamid is "in the ammonia world", but has some minor role in terrestrial (aquatic?) biochemistry. Its mirror image, glykolic acid, is completely aquatic, but has no role in terrestrial biology, it is simply a rare by-product.

Now, one may derive the present N from ammonia, ammonium silicates and ammoniated silicates; the final result will be anyway  $NH_3$ . Namely, inside proto-Earth,  $NH_3$  was driven out of the silicates. So, according to planetology terrestrial proto-atmosphere must have contained  $NH_3$ , otherwise we would not have had  $N_2$  now. However,  $NH_3$  dissociates quite easily, so it is possible that this primordial  $NH_3$  was short-living.

## 3. THE BEGINNING OF ORGANIC CHEMISTRY

Our goals are: guess if to biochemistry is possible in A-chemistry (A for ammonia as solvent), and to see how natural is it in the presence of substantial NH<sub>3</sub> in Wchemistry (W for water as solvent). Let us see first the connection of biochemistry with Aand W-solvents. Some parts of biochemistry are immensely complicated. However, as it will be demonstrated, biochemistry originates quite from the basement of organic chemistry. These initial steps are simple and can be easily understood. Afterwards we may relegate the task to selection, survival of fittest, enzyme effects, and so on.

For a methodical introduction to organic chemistry it is usual to start from methane, or more generally, from the paraffine series  $C_nH_{2n+2}$ , and to enumerate the other fundamental compounds simple and as derivatives. substituting Η atoms. Not everything fits smoothly into this "classification", but one can go far enough in this way.

Now, at each step we shall give the

"mirror" formulae for the hypothetic organic A-chemistry. It is necessary to state that the ammonia-based organic chemistry is still in a not too evolved status, and our detailed knowledge about it is even less so. However, all the mirror molecules we will mention do exist and are chemically well-known. Reaction velocities, equilibrium ratios &c. in -40°C liquid NH<sub>3</sub> are another matter.

Our rules to get the mirror molecules will be simple enough. Only the basis and organic acid radicals will be changed as

$$-\text{OH} \rightarrow -\text{NH}_2$$
$$-\text{COOH} \rightarrow -\text{CONHH}$$

We will call these simultaneous operations in this paper the WA mirror reflection (see *Fig. 1*). The idea is the analogy with the "C-reflection" of particle physics, where some quantum numbers as electric charge, baryon charge etc. are changed to their opposite, while some other data (e.g. mass) are unchanged to get antiparticles from particles and vice versa. The first rule is obvious and has been mentioned in the previous Chapter. The second needs some explanation. An organic acid in terrestrial aquaeous chemistry has generally not the simple -H radical of anorganic chemistry but the carboxyl radical -COOH, since the paraffine chains are rather apolar, and so an H ion is not expected to dissociate from a paraffine carbon atom. Now this group has the approximate structure

0 -С-О-Н

with the easily dissociable -H. It is definitely outside of the scope of the present paper to discuss why just this complicated radical is an effective H donor in carbon sequences; it obviously has its proper quantum many body reasons, and we definitely will not try to recalculate the problem in liquid ammonia. However, the most natural mirror molecule is -CONHH or



Later we will mention examples that such molecules exist indeed. We leave the second O atom unchanged; anyway oxygen is abundant everywhere. The quantum mechanical and chemical analogies between the O atom and the NH imino radical are often mentioned in chemistry.

In this paper we choose such a presentation in which the mirror symmetry between W and A-chemistries is explicit. However, note that the nomenclature of organic chemistry has been established in W-chemistry. Therefore in names the analogons are not the aquo and

amino molecules but rather C and N atoms, or methane and ammonia. So some names do not fit into the scheme, which must be kept in mind.

We note that some molecules are known in which oxygen is completely substituted with the imino radicals. Sometimes we will just mention these analogons.

Now let us start with methane. It does not contain either O or N, therefore it is independent of the solvent; and neither water nor ammonia solve it efficiently. Further members of the paraffine sequence would do similarly; however, for simplicity we remain at the first member.

We may form an (aquatic) organic basis from methane by substituting one H with an OH. It is an alcohol, the first member is the methylalcohol,  $CH_3OH$ . Alcohols do not dissociate too much in water, so their basical nature is not too explicit. However, they perform neutralisation with acids.

The ammonic analogon is  $CH_3NH_2$ . It is a well-known molecule called methylamine, which appears in plants (Mercurialis perennis & annua) and in the juice of processed herring. With aquatic acids it produces some organic salts soluble in water. (For compound properties see e.g. *Römpp* (1958) and *Bailar* (1973).)

By substituting one -H of a paraffine with a carboxyl radical organic (aquatic) acids are obtained. The 1<sup>st</sup> member is the acetic acid, CH<sub>3</sub>COOH. However, now there exists a 0<sup>th</sup> member as well, HCOOH, the formic acid. The mirror molecules are, respectively: CH<sub>3</sub>CONHH, acetamide, and HCONHH, formamide. These compounds are artificial industrial products. (If O is completely substituted, one gets acetamidin, CH<sub>3</sub>C(NH)(NHH), which exists too.)

Now one could try neutralisation reaction of an organic acid and an anorganic basis. In water a simple reaction is sodium hydroxide + acetic acid, giving sodium acetate. With the mirror basis and acid we end in sodium acetamide,  $CH_3CONHNa$ . The molecule may be represented by



Sodium salts of this type were indeed observed when a carbonic acidic amid reacted with sodium amide in aether; that they are unstable in water via hydrolysis is irrelevant in Achemistry.

As for an organic acid and an organic basis (i.e. alcohol), that reaction is again a neutralisation; only it is slow in W-chemistry and generally needs a small amount of anorganic acid for stimulation. The reason seems to be the low dissociation rate of alcohols. Since methylamide possesses the same  $-NH_2$  radical as sodium amide does, by any chance the reaction follows the same pattern.

### 4. THE BEGINNING OF BIOCHEMISTRY

Organic acids and alcohols are improper as building stones of larger, versatile molecules. For that we would need a molecule which is an organic acid on one end and basis or alcohol on the other. Such molecules could repeat themselves in neutralisation steps. With solvent loss at the touching ends the product is a longer molecule again with an acid radical on one end and a basic one at the other; and then the new molecule can enter the process in the same way. In addition, the only by-product is the solvent itself. Therefore the solution will be more diluted but the environment does not change qualitatively. In this case the end-products do not inhibit the reaction. The scheme will be shown immediately.

Now, such an amphoteric molecule can be obtained by doing both substitution steps mentioned above. So take a paraffine and substitute one H with one radical, and another with another. In W-chemistry the 0<sup>th</sup> and 1<sup>st</sup> members of these oxyacids would be



formic and acetic oxyacids. The first molecule does not exist according to the established fact that two -OH radicals cannot be carried by the same C atom. The explanation is of quantum many-body origin and we will not go into details. But a remark is needed. Generally, the -O-H of the carboxil group is not considered to be a hydroxil radical and is not working as one such; the carboxil group has the tendency to lose -H, not -OH. However, the hypothetic formic oxyacid would be so mirror symmetric that there would not be any way (other than spontaneous symmetry breaking) to distinguish the two ends. Therefore in this special case even if the empirical rule did not hold against two hydroxiles, the molecule would not be an acid. The said molecule is sometimes called formaldehyde hydrate, and its polymer is known by the name of poly-oxymethylene hydrate. It seems that this 0<sup>th</sup> oxyacid can exist in aquaeous solution, at least transiently.

Without doubt acetic oxyacid (alias glykolic acid) does exist, and can be found in some grapes. But generally it is not a building stone of the terrestrial life, probably, because it has no tendency to duplicate into a double oxyacid; rather one of its duplication reaction results in the twin molecule diglykolacid:

# HOOC-H<sub>2</sub>C-O-CH<sub>2</sub>-COOH

with one molecule  $H_2O$  lost. So it seems that, from some quantum mechanical reasons, it would be hard to build up versatile macromolecules from oxyacid modules, in spite of their amphoteric nature.

The mirror molecules of 0<sup>th</sup> and 1<sup>st</sup> oxyacids in A-chemistry are, according to the rules,

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The first molecule again would be symmetric and therefore would not be amphoteric; however it is the carbamide, a key molecule of higher terrestrial animal metabolism. This shows, at the same time, that some caution is needed when sketching the mirror chemistry; contrary to the W-chemistry, two amino radicals may attach to the same C atom. (If O is completely eliminated, instead of carbamide we get guanidine, again a completely stable molecule.)

The second A-molecule is called glycinamide, and it is a rare but important building stone of terrestrial biology: glycinamide has been found in the hormone-type peptides oxytocine and vasopressine. We return to the problem of the -CONHH radical at the end of this Chapter.

Now, oxyacids do not work properly as building blocks of W-macromolecules; and of course the terrestrial biology cannot have been built on their A-mirror molecules, being the solvent water. But maybe something in between is still possible.

And it is definitely so. There are two possible hybride WA amphoters originating from methane. Either the hydroxile of the acetic oxyacid can be substituted by an amino radical, or its carboxile is substituted by the "A-carboxile". For practical reasons we turn to the first possibility and shortly comment the second at the end of the Chapter.

The corresponding WA hybride is the molecule

called acetic aminooxyacid, or by shorter name, glycine. And it definitely exists, and is one of the 20 standard amino acids which build up the proteins. The 0th member of this series,  $H_2N$ -COOH is called amino formic acid, or carbamine acid. It is unstable in W-chemistry, but some of its derivatives are familiar, as e.g. polyurethanes. Its potassium salt is found in the urine of horses.

Although glycine is formally not an amphoteric compound in any solvent, it forms "twin ions" in most aquatic environments. Between the pH's 2.34 and 9.60 its usual ionisation type is

and, at least formally, two such glycine twin ions can form a double molecule by water loss. The new molecule will be

# H<sub>2</sub>N-CH<sub>2</sub>-CONH-CH<sub>2</sub>-COOH

which exists and is called glycilglycine. Its slightly more detailed structure can be written as



and the link between the C and N is called the peptide link, the characteristic way of binding together polypeptides and proteins. Here remember that this link automatically appeared above, in Chap. 3, in a simple neutralisation reaction of A-chemistry. The chain can be repeated without any limit because the two ends of glycilglycine are the same as of glycine. For all of the present knowledge, this is the way of building terrestrial proteins. The building process is not too simple and needs catalyser enzymes in W-chemistry.

At this point we stop and recapitulate that the first 5 products of Miller-type synthesis are, in descending order, formic acid > glycine > glycolic acid > alanine > lactic acid. Lactic acid is the W counterpart of the WA alanine. So the yield is decreasing with molecular weight (which is natural), and WA molecules are more abundant than W ones (which is interesting and important).

There is a process called *spontaneous amination* (*Bailar*, 1973). Having solved molecules with hydroxile radicals in water contaminated by ammonia, in a substantial part of molecules -OH is substituted with  $-NH_2$  without any catalyser. We have seen this reaction in Sect. 2 as a step of the Miller synthesis. Therefore in the presence of ammonia the occurrence of *amino* acids is inevitable indeed.

Now some comments on the existence of "A-carboxyl" and the possibility of the "inverse WA hybride".

- As we have seen, organic acid amides do indeed neutralize with alkali amides even in some terrestrial situations. Therefore they behave as acids, i.e. the terminal H indeed dissociate from (CO)NHH.
- 2) The more complicated amino acids may have extra hydroxile, carboxyle or amino radicals on some branches. Two such examples are asparagine acid and glutamine acid, having two -COOH radicals; only one is participating in the peptide link when forming proteins. Now, both of them have their near relatives, asparagine and glutamine, with the only difference of possessing -CONHH instead of the second carboxyle. No surprise that this arm does not form peptide link; from this peptide link could form with NH<sub>3</sub> loss, not the most natural one in W-chemistry.

3) As for the possibility of an inverse hybride, oxyacidamides, having -CONHH for "acidic" and -OH for "basic" end, they are not used, to our knowledge, in terrestrial life. However two analogous compounds do appear. The 1st member of a simpler series, oxyamides, is methanolamide, HO-CH<sub>2</sub>-NHH. It is not used in terrestrial life. However the 2nd member, ethanolamide, is called also cholamine, and it appears in some biological phosphatides. Another analogy is oxytocine (see *Fig. 2*). It is not exactly a polypeptide, since it is cyclic at

the amino end. However the -OH radical of tyrosine is free, and the other end is free, with glycinamide in the beginning, i.e. a -CONHH radical.



Fig. 2 The structure of oxytocine, a hormone-like polypeptide of terrestrial biochemistry. It utilizes glycinamid, an "ammonia-world amphoteric" compound, and, except for the cyclic form of its end, models an "ammonia protein" in small.

The practical absence of biological oxyacidamides in terrestrial life does not need too much explanation. Amino acids and oxyacidamides would be alternative solutions for the same problem. One in itself can do the work, and mutual presence would originate in compounds which would be not amphoters but double acids or double "amino bases". In some sense the elimination of one of them helps and is a spontaneous symmetry breaking.

We close this Chapter by returning to Fig. 1, showing the "mirror symmetry" between some simple organic molecules of W- and A-chemistry. The scheme displays the acids and bases (alcohols) derivated from methane.

The hexagon above the horizontal line is not a compound but the set of building stones. The vertical dashed line separates the W- and A-worlds. Observe the mirror symmetry of the structure.





Fig. 3 The 20 canonical terrestrial amino acids in a so far cyclic peptide chain. Glycinamid is not among them.

Methane (Row 1) is a vertical line on the dividing line. It is common in both worlds. All the other compounds considered here are triangles. Row 2 contains bases or alcohols (outside), and organic acids (inside). Row 3 gives the amphoteres ("oxyacids"). Finally, Rows 4 and 5 are the logically possible amphoteric WA hybrides. They are not mirror symmetric in themselves, but the reflection carries one hybride to another. They are "on the dividing line", with equal areas in both worlds. The upper such hybride is just glycine, the simplest existing terrestrial amino acid.

In this scheme glycine is one of the simplest organic compounds. Therefore not too much explanation is needed for its formation and for amino acids, the building stones of proteins, if water, ammonia and simple carbon compounds are simultaneously present, with some energy transfers.

Even the more complicated amino acids are "half way between W and A worlds". Namely, some of them contain extra basic or acidic radicals above the one pair of  $-NH_2$  and -COOH. In the 20 usual amino acids of terrestrial living organisms (*Fig. 3*) there are 8 such extra radicals, and of them 4 are of the W-chemistry (-COOH and -OH), while 4 are of the A one (-CONHH, -CNHNHH and -NH<sub>2</sub>).



Fig. 4 The scheme of uracil acid synthesis (after Csányi, 1976). Uracil acid is one of the 4 building stones of RNA, the non-peptide fundament of life. Observe that the initial steps of synthesis use amino acids and other aminated compounds, and one peptide link can be seen even in the final product

The water-ammonia symmetry of amino acids: constraints on paleoatmospheres

We close this Chapter with a very brief note of nucleic acids. Terrestrial life uses them for genetic information. They seem very different from proteins; their building stones, the nucleotides, have a -PO(OH)OH radical for acid and an -OH for basis. However in the beginnings there was some connection between the building stones of amino acids and nucleotides. The details are complicated and we mention only one example for demonstration. Uridil acid, UMP, one of the four building stones of RNA, starts to be biosynthetized from carbamile phosphate and aspartate. (For a scheme of the synthesis see *Fig. 4.*) The second is a canonical amino acid, while the first is synthetised from ATP, carbon dioxide and ammonia. Indeed, in the basis of UMP one peptide link can be seen.

### 5. THE ESSENTIALS OF PROTEIN STRUCTURE

The structure of proteins is very complicated, not always known in details, and important for enzyme functions. However, it seems that there are 4 major factors determining the spatial form of the protein. (*Dickerson and Geis*, 1969) These factors will be listed here in decreasing order of occurrence and strength. So the terms primary &c. in this Chapter are not to be confused with the usual biochemical terms. (The items can be seen on *Fig. 3.*)

- The peptide link. It builds up the polypeptide chain of the protein; all the chain-forming links are peptide links with the slight modification at the N of proline, which does not bear H. The peptide link is not a straight line, so there appears a zigzag in the chain, and a tendency to spiral up. In terrestrial biochemistry in each amino acid only one -COOH can form the link, so there is no branching in the chain. This link is covalent and as strong as any usual valence link.
- 2) The S bridges. The -SH radicals in two cysteines can bound. So if 2 such amino acids get near, then an S-S bridge links the two parts of the chain. This link is covalent and as strong as any usual valence link.
- 3) The H bridges. For quantum mechanical reasons an H in valence link with an O or N atom can make a weak (E ~ 0.03 eV) link with another O or N atom too (*Pimentel and McLellan*, 1960; Biczó et al., 1966). This is just the situation if by zigzag or spiralling two peptide links get near (with the exception of the N of proline.); then H bridges can alter the spatial structure. This link is weak and can break down well below the decay point of the chain.
- 4) *Electrostatic interactions*. Some radicals, e.g. -COOH, -OH and -SH may dissociate, and then the free charges establish attraction or repulsion. This link is not too strong; its strength depends on the solvent, via dissociation rates and dielectric constants, and of course on the nature of the radicals too.

According to the above statements, one expects a polypeptide chain if the constituents and the solvent are appropriate for peptide link; there is a good chance that the chain and its

primary strength will be practically the same in W- and A-chemistry. Since the S-bridges are covalent, there again the strength may be similar. As for H-bridges the fundamental quantum mechanical effect behind is independent of any solvent, and the solvent is expected to cause only minor disturbing effects at most. Finally, as it was told above, the strength of electrostatic interactions of ions is clearly solvent-dependent.

Therefore, even if the fundamental protein chain can be produced in A-chemistry, then the primary, secondary and tertiary structures will be similar to that in W-chemistry, but the quartiary interactions will be different in degrees, so some denaturalizable structures will be different. In addition, in terrestrial proteins the H-bridges mainly form at the peptidic links; the H coupled to N bridges between the N and the O, with double coupling to the C. So the structure is the same in both chemistries if the peptide link is the same. But, if that O is eliminated too, and exchanged with NH, then the new H would disturb the H of the bridge. I.e. if O were completely eliminated from the mirror images of amino acids, then the tertiary structure and so the spatial form of mirror peptides might be completely different from the terrestrial ones. (For terrestrial amino acids and peptide bridges see *Fig. 3*, and for the alteration of the peptide link see the link at the proline which is amino acid only by courtesy.)

### 6. ON THE POSSIBILITY OF A-PROTEINS

Protein formation in ammonia solvent is a matter of many details, some still unknown. What will be done here is pure guesswork.

However, let us do it. One may try first with the W amino acids as building blocks. In principle two glycines might bind with ammonia loss, resulting in

### H<sub>2</sub>N-CH<sub>2</sub>-COO-CH<sub>2</sub>-COOH

which is an analogon of glycilglycine, but the link is definitely not the peptide link. This molecule is not familiar in W-chemistry; it may or may not be stable in different environment, and H bridges will be absent because of the lack of H in the link. However, let us not spend too much time on hypothetic molecules.

Then let us try with glycinamide. There is no reason to doubt that two glycinamides can react with ammonia loss resulting in

# H2N-CH2-CONH-CH2-CONHH

The reaction is a simple neutralisation process of A-chemistry. Such processes between other but analogous molecules have been observed even in terrestrial situations. We do not know this molecule, but it is the twin of glycinamide, it is again a regular A-amphoter, and it contains the correct peptide link.

The water-ammonia symmetry of amino acids: constraints on paleoatmospheres

What is more, consider the molecules analogous to amino acids, but interchanging -COOH's and -CONHH's. The peptide binding energy will be practically independent of the solvent; the dissociation rates of H in -COOH and -CONHH will differ, but it influences only reaction rates. So di-, tri- and polypeptides seems possible from the mirror molecules too. Now consider the hypothetic polypeptide built up from many glycinamides and nothing else. Its form is

H2N-CH2-CONH-CH2-CONH...-CH2-CONHH

This molecule is exactly the same as the terrestrial poly-glycine, except for the last 3 atoms of the extreme right end. So the bulk properties of this (useless) protein will only infinitesimally differ from those of its W-counterpart, by which the possibility of such chains is demonstrated. (For the existence of peptide chains with a -CONHH end remember the terrestrial oxytocine.)

So amino acid amines (meaning those with a -CONHH "acidic" end) seem to be able to form very similar polypeptides (and so A-proteins) in A-chemistry to those of W-chemistry. Low temperature will not disturb stability, and ammonolysis does not seem for us strong enough to break up the chains (this can be experimentally investigated using W-proteins in liquid ammonia). In addition, A-chemistry is possible on terrestrial room temperature above cca. 10 atm pressure, not impossible on extraterrestrial planets.

To close this Chapter observe that glycinamide is the natural amphoter of Achemistry (while glycine is not in W-chemistry; there glykolic acid = acetic oxyacid would be natural; see Fig. 1, where glycinamide is purely in A-world). In addition, in A-chemistry the peptide link can arise even in simple neutralisation reactions. So: may it be possible that biological macromolecules could build up more easily in A-chemistry than in W-chemistry?

### 7. LIFE WITHOUT NITROGEN?

Our life definitely uses N. However, let us see briefly if N is really necessary. The answer consists of two halves.

First, the 5 most abundant atoms in the Universe are:

Н	valence 1
He	valence 0
0	valence 2
С	valence 4
Ν	valence 3

He is irrelevant; the other 4 have all different valence numbers, so all possible roles in chain formation are represented. Omitting N, valence number 3 would be absent, so the possible chain structures would be highly reduced. P is much rarer, so could not substitute effectively N.

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Second, as it was told above, oxyacids are formally analogous to amino acids, but they cannot act as bases of a biochemistry, because in aquaeous chemistry they do not tend to form larger amphoteric molecules but rather geminate up as double acids. No doubt, the explanation is quantum mechanical, but irrelevant here.

Consequently, primordial N sources ( $NH_3$  or  $NH_3$ - and  $NH_4$ -bearing silicates) are necessary for life. If a planet is formed at a too hot part of the prestellar nebula, there will be serious problems with life on it.

### 8. DISCUSSION

Life needs long carbon chains built up from small modules of great number but moderate variety. If so, then the modules must have some amphoteric or ambivalent nature, one "polarity" on one end, the opposite on the other; then the long chain can build up by simple reactions, and, if it is needed, the chain can be continued without limit.

On Earth, the amphoteric modules are simple molecules of two types. Terrestrial life has a duality of performance and information; the first is done by proteins, the second by nucleic acids. We do not know if this duality is inevitable. The proteins are built up from amino acids which are acids on one end in water chemistry and bases on the other end in ammonia chemistry. (If our chemical naming reference system were to be based on ammonia instead of water, then we would call amino acids carboxile bases.) Therefore the proteinbuilding reaction is almost neutralisation, which would be the simplest chemical reaction. The true amphoters of water chemistry are practically without use in terrestrial life. However, the protein-building reaction, the peptide linking, would be a true neutralization process in ammonia chemistry. The nucleic acids build up from nucleotides. The binding reaction is a simple neutralisation of water chemistry although the acidic end of the modules is not the carboxyl radical of organic chemistry but the analogon with phosphor instead of carbon. However, the synthesis of the nucleotides needs amino acids and ammonia too.

Therefore it seems that even in aquaeous environment the emergence of life would need or would be speeded up by substantial amount of ammonia. Ammonia seems not too abundant in the internal part of the aquaeous belt because of the high temperature of the ancient solar nebula. So for life in water solvent chances seem best near to the outer boundary of the belt where liquid water can exist on planets in the Solar System, in the vicinity of Earth and Mars.

As for ammonia solvent, it seems that the natural building stones are amino acid amides (amino acids with -CONHH instead of -COOH). The simplest of them, glycinamide, does have a role, albeit minor, in terrestrial biochemistry. The ammonia neutralisation reaction of these molecules would result in a pepride link, and the peptide chain would be identical with the terrestrial protein, except one radical at the very end. 1

It is obvious from the whole presentation that here we did not restricted ourselves to atmospheres, but to the whole volatile sphere of planets, containing the gaseous and liquid spheres plus all volatiles bound in litosphere. The reason is that during planetary evolution volatiles take part in circulation, so all these molecules can interchange roles. Planets are open thermodynamic systems with the only restrictions that the energy flux going through is roughly stationary, prescribed by solar distance, solar luminosity and albedo (of which the latter two can, however, moderately change) and that there is practically no incoming matter after the era of great bombardments (cca. 600 My after Solar System formation).

Applying all these to the Solar System, Venus is almost in the water belt, but in her present status the high greenhouse effect evaporated water. For primordial life we note that Venus must always have been poor in ammonia.

For Earth there is a problem. Earth is and seems to have always been in the water belt. However, at 1 AU not too much ammonia must have been in the solar nebula. To be sure, ammonium silicates have been suggested for ammonia source (*Eugster and Munoz*, 1966), and they could have taken part in the formation process of proto-Earth (albeit in this temperature zone even ammonium silicates seems to have been rare), or Earth may have got an impact of an ammoniated planetesimal from the outer system. Then the most appealing story about terrestrial proto-life would go as follows. First ammonia appears in water as a solved gas, aminates oxyacids and then appear amino acids. They build up proto-proteins. Slightly later from similar compounds nucleotides start to be formed; but these processes, thermal decay and some other processes are eating up ammonia, so in nucleic acids the amino radical is no more operative, only a relict; RNA and DNA build up by usual W acid-basis neutralisation. The only problem is that the earliest known deposits are N-poor, even in the neighbourhood of the first known fossil procariotes. This controversy needs an explanation, not available yet.

Neither water nor ammonia is liquid on present Mars. Some 2 Gys ago Mars had some liquid because riverbeds can be seen. Then Mars may have had either liquid ammonia with abundant water ice, partly solved, or liquid water, with abundant gaseous ammonia, partly solved; Mars may have got substantial amounts of both hydrated and ammoniated and ammonium silicates. We only note that *King et al.* (1993) found ammonium saponite on Ceres by spectroscopy. Therefore there is a chance that ancient Mars generated life, either W or A.

Outwards from Mars liquid water is impossible; liquid ammonia is improbable in the outer system.

Now, let us see what conclusion is possible from the data above for the ammonia content of the primordial atmosphere of Earth.

Planetology tells that in the beginning  $NH_3$  must have been present in the atmosphere, because  $NH_3$  or  $NH_4$ -containing silicates seem to be the most effective condensates carrying N into the proto-Earth; other sources are improbable or very minor ones.

However  $NH_3$  might have dissociated very early. So we have 2 possible scenarios. Atmospheric  $NH_3$  either still existed at the emergence of life, or not. If not, the atmosphere

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may have contained NO, NO<sub>2</sub>,  $N_2O_4$  and  $N_2$ , maybe with smaller amount of  $C_2N_2$  and derivatives. (NH<sub>3</sub> dissociates to N and H, but NO and relatives are created in the *present*, oxidizing atmosphere by lightnings.)

Now, let us assume first that  $NH_3$  was abundant at the emergence of life. Then abiotic synthesis of amino acids, proteins and nucleic acids was very easy, see the Miller experiment and later improvements. We have seen that the simpler amino acids are indeed simple and abundant organic compounds and their appearance is inevitable in the presence of  $NH_3$ .

However, then the very early minerals would have had N content, in two ways.  $NH_3$  can be built into silicates either as crystallic ammonia or as ammonium ion substituting alkalies, and these silicates are fairly stable at temperatures permitting life. Now, *Szalay* (1975) did not find  $NH_3$  in Precambrian gas inclusions, but those samples, although Precambrian, did not go back to the beginning of life. However *Shöpf et al.* (1968) did not find N either in layers of ~3.4 Gy age, with microfossils (of course, outside the organic matter). Then there is an alternative. Either life on Earth is much earlier than 3.4-3.7 Gy, or not.

If it is much earlier, then it may have appeared from the "primordial bouillon", waters containing very abundant amino acids. Then the layers synchronous with primordial life do contain N abundantly, but these layers are not yet unearthed. This bouillon, then, came into existence under the heavy influence of atmospheric NH<sub>3</sub>, still present.

If life on Earth is not much earlier than the Fig Tree and Onverwacht layers, then the absence of N in the minerals is an evidence against substantial atmospheric ammonia concentration at the emergence of terrestrial life. What is more, then it is an evidence that in that time the atmosphere contained only *molecular* N. Namely, nitrogenic oxides react with  $H_2O$  and form nitric acids. These acids attack and alter minerals. Only molecular N is inert enough not to enter minerals even for aeons, as it can be seen in the present atmosphere. In addition, since no trace of primordial bouillon is seen (*Brooks and Shaw*, 1973), then there was no slow and long accumulation of amino acids.

So, if no microfossils were to be found later older than  $\div 3.4$  Gy, then spontaneous terrestrial abiotic amino acid synthesis would be ruled out. Then one should turn to the scenario preferred by *Brooks and Shaw* (1973): the transport of extraterrestrial, evolved microorganisms to Earth, where they utilized the atmospheric N (which was already pure N<sub>2</sub> according to the lack of N in minerals).

Indeed, some C chondrites do contain biomolecules, quite similar to the terrestrial ones. For example, *Brooks and Shaw* (1969) found a component in the Orgueil and Murray meteorites (C1) which was undistinguishable from terrestrial sporopollenine, a biocompound of terrestrial plants.

Now, there remains the question, *where* did then happen the primordial abiotic synthesis of amino acids? For moderately short meteoritic travel only the Solar System is worth discussing. Now, the only major planet whence meteorites can come and where primordial  $H_2O$  and  $NH_3$  were present according to the Lewis-Barshay scheme is Mars.

The water-ammonia symmetry of amino acids: constraints on paleoatmospheres

As it was told earlier, in the condensation of Mars, which planet is farther out than Earth, hydrated, ammoniated and ammonium silicates must have played more substantial role than in the formation of Earth. Now Mars is without liquid water and atmospheric ammonia, but we know that some 2-2.5 Gy rivers existed on the planet. So the early atmosphere may have been good for abiotic amino and nucleic acid synthesis.

Martian meteorites, although rare, are well known. A group of meteorites, called SNC (shergottite, nakhlite and chassignite) meteorites, are identified as Martian ones (*McSween and Stolper*, 1980). SNC's are mafic and ultramafic rocks, and do not go far beyond 1.3 Gy age. However if an impact can dislodge Martian rocks now and can send them to Earth, then it was possible 3.5 Gy ago as well.

So until one does not find substantial N in layers with early microfossils, the  $NH_3$  content of atmosphere at the time of emergence of life and the terrestrial abiotic amino acid synthesis is not proven. Alternatively, manned Martian expeditions may settle the question by checking the N content of early *Martian* layers. But, according to planetology, in the primordial atmosphere  $NH_3$  must have been present at least in the beginning.

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#### APPENDIX: ON THE PROPERTIES OF SOME KEY COMPOUNDS

Here we give some important properties of the simplest molecules used in the text when comparing W- and A-chemistries. The main reason is to demonstrate that the simple fundamental molecules of A-chemistry (both anorganic and organic) are not at all exotic, missing or self-contradictory. Densities, colours and odours are meant at room temperature and pressure.

### The Paraffine series

 $CH_4$ : Methane. Colour: -. Odour: -. Freezing & Boiling Points, K: 89 & 109. Density, g/cm<sup>3</sup>: - (Gas). Characteristic Reaction: With free oxygen detonates, giving CO<sub>2</sub> and water. Interesting Property: Apolar. Appears: Marshes, decaying organic matter.

### Alcohols W & A

 $H_3OH$ : Methylalcohol. C: -. O: alcoholic. Fr. & B.: 179 & 338. D: 0.81. Ch. R.: Neutralization with organic acids resulting in esthers. I. P.: Affecting neural systems of higher animals. A: Aromatic oils, some grapes, spontaneous fermentation.

CH<sub>3</sub>NH<sub>2</sub>: Methylamine. C: -. O: Fishy. Fr. & B.: 194 & 267. D: - (Gas). Ch. R.: With W-acids gives salts solvable in water. I. P.: -. A: Maratiales perennis & annua; in juice of processed herring.

### Organic acids, W & C

**HCOOH**: Acidum formicum. C: -. O: acrid. Fr. & B.: 282 & 374. D: 1.22. Ch. R.: Thermal decay to CO and H<sub>2</sub>O. I. P.: -. A: Ants, bee poison.

**HCONHH**: Formamide. C: -. O: -. Fr. & B.: 275 & 470. D: 1.15. Ch. R.: Good solvent. I. P.: Very viscous. A: Artificial.

CH<sub>3</sub>COOH: Acetic acid. C: -. O: acrid. Fr. & B.: 290 & 391. D: 1.06. Ch. R.: Neutralization. CH<sub>3</sub>COOH+NaOH = CH<sub>3</sub>COONa+H<sub>2</sub>O. I. P.: -. A: Wines, &c. spontaneously formed.

CH<sub>3</sub>CONHH: Acetamide. C: White. O: -. Fr. & B.: 355 & 595. D: 1.16. Ch. R.: Forms from ammonium acetate. I. P.: -. A: Artificial.

### Anorganic bases W & A

**NaOH**: Sodium hydroxyde. C: white. O: -. Fr. & B.: 591 & 1663. D: 2.13. Ch. R.: Very strong basis, neutralization, e.g. NaOH + HCl = NaCl + HOH. I. P.: Very hygroscopic. A: Artificial. **NaNH<sub>2</sub>**: Sodium amide. C: -. O: ?. Fr. & B.: 481 & decay. D: 1.39. Ch. R.: NaNH<sub>2</sub> + HOH = NaOH + NH<sub>3</sub>. I. P.: Reacts with water. A: Artificial.

### Organic salts W & A

CH<sub>3</sub>COONa: Sodium acetate. C: -. O: -. Fr. & B.: 592 & decay. D: 1.39. Ch. R.: Forms in neutralization of acetic acid with sodium hydroxyde. At low temperatures accepts 3 molecules of crystallic water. I. P.: High specific heat. A: Artificial.

CH<sub>3</sub>CONHNa: Sodium acetamide. C: ?. O: ?. Fr. & B.: ? & ?. D: ?. Ch. R.: Forms in reaction of acetamide and sodium amide, in other solvent, but not in water.. I. P.: Unstable in the presence of water. A: Artificial.

Observe the high analogy between the reaction of sodium hydroxyde with HCl and that of sodium amide and HOH (water). The reaction is observed in terrestrial environment without any solvent if water vapour is ejected on solid sodium amide. In ammonia the sodium amide happens to be a weak basis because of its low solubility. This shows that the analogies are sometimes only qualitative; in water sodium hydroxyde is very soluble.

As for sodium acet-amide, the instability in water is no argument against analogy. Water has the tendency to react vehemently with available sodium.

There is a well-known tendency in the paraffine series that both the freezing and the boiling points are increasing with the chain length. The same is true for simple (W) alcohols. Now, *Fig. 5* displays the respective temperatures for the A-alcohols too, according to the available data. (Some points are interpolations.) The tendency is clear: the boiling points of A-



Fig. 5a Boiling and freezing points of paraffine chains and of their alcohole derivatives in the two solvents

alcohols are lower than those of the W-alcohols. So, at least for boiling points, some compounds of the Achemistry follow the solvent into the cooler temperature regions.

Here we compare compounds shown the schematically in Rows 3 and 4 of Fig. 1. They all can be derived from the first member of the paraffines, i.e. from methane, by replacing one H with an organic acid radical, and another with an organic basis one. So all these 3 molecules are amongst the simplest possible molecules of organic chemistry. According to their structures, all of them have some amphoteric properties.

*WW amphoter*: HO-CH<sub>2</sub>-COOH, glykolic acid or acetic oxyacid.

Freezes at 351 K; decays before boiling. Appears: in some grapes. With itself it gives dimers as anhydrides, but the product is not amphoteric.. E.g.:

 $2 \text{ HO-CH}_2\text{-COOH} = HOOC-CH}_2\text{-O-CH}_2\text{-COOH} + H_2O.$ 

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Fig. 5b A very schematic T-p diagram of paraffine chains and the two solvents.



Fig. 6 A peptidisation reaction of terrestrial biochemistry using glycinamid in the presence of chimotripsine katalyser. The link is formed by ammonia loss. The reaction is an analogy of possible peptidisation in ammonia solvent (After *Csányi*, 1976 and *Straub*, 1958).

*AW* amphoter: **H<sub>2</sub>N-CH<sub>2</sub>-COOH**, glycin or amino acetic acid.

Freezes at 505 K; decays before boiling. Appears: in proteins or glues. With itself, at least in the presence of some enzymes, gives an amphoteric dimer, glycilglycine, which is a dipeptide: 2  $H_2N-CH_2-COOH =$  $H_2N-CH_2-CONH-CH_2-COOH + H_2O$ . Here CONH stands for the peptide link. Glycilglycine is a colourless crystall; liquefies at 530 K, then decays. Solvable in hot water, weakly in alcohol.

*AA amphoter*: **H**<sub>2</sub>**N-CH**<sub>2</sub>-**CONHH**, glycinamide.

Freezing point is unknown for hormones us. Appears: in the oxytocine and vasopressine, at the C end of the chain instead of glycine. In presence the of the enzyme chimotripsine reacts in peptidisation: sav bensoil-L-thyrosinamide glycinamide = bensoil-Lthyrosilglycin-amide + NH<sub>3</sub> (Fig. 6). Now, this process would be just an elementary neutralisation process in ammonia: an A-acid radical reacts with an A-basis radical, with ammonia loss. This reaction could build up Aanalogons of proteins.

The WA amphoteric compound, HO-CH<sub>2</sub>-CONHH, glykolic acidamide, is not used anywhere in terrestrial life. The possible reason is that in the simultaneous presence of WA and AW hybrides the module



Fig. 7 The roles of the 4 major elements of terrestrial biochemistry. The correct picture is obtained if the figure is cut and glued into a tetrahedron with N at the top. More details in the text.

building of long chains would be disturbed.

Fig. 7 tries to compare the role of 4 main elements of biochemistry, H, C, N and O. The Figure is a tetrahedron, bent into the plane of the paper. Restoring the tetrahedron, C, H and O are at the 3 points of the triangle of the basis and N is at the top point. Some simple molecules of life are on the basis plane, but not all. Two very important gases of terrestrial metabolism, oxygen and carbon dioxide, are there, the terrestrial solvent, water, too, and hydrocarbons (up to this point all on the edges) together with sugars (in the interior of the basis triangle). But the summed formula of glycine, the simplest amino acid, is  $C_2H_5O_2N_1$ . This molecule is, of course, nearer to the O peak than to the N one; but for glycinamid the relationship is opposite.

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