Amino Acids (2004) 27: 113–118
DOI 10.1007/s00726-004-0106-4

Amino Acids
Printed in Austria

A review of adsorption of amino acids on minerals: Was it important for origin of life?

Short Communication

D. A. M. Zaia

Departamento de Química-CCE, Universidade Estadual de Londrina, Londrina-PR, Brazil

Received November 11, 2003
Accepted May 31, 2004
Published online July 19, 2004;

Summary. Minerals more readily adsorb amino acids with charged R groups than uncharged R groups, so that the incorporation of amino acids with charged R groups into peptides would be more frequent than for amino acids with uncharged R groups. However, 74% of the amino acids in the proteins of modern organisms contain uncharged R groups. Thus, what could have been the mechanisms that produced peptides/proteins with more amino acids with uncharged R groups than precursors with charged R groups? Should we expect the composition of amino acids adsorbed on minerals to be similar to those of present proteins? Was the adsorption of amino acids on minerals important for the origin of life? The lipid world offers an alternative view of origin of life. Liposomes contributed to elongation of peptides as well as select hydrophobic amino acids and peptides. These experiments could be showing the mechanism, which hydrophobic amino acids have been selected. However, liposomes have no influence on the stereoselectivity in the oligomerization of amino acids. In the present paper, several other mechanisms are also discussed that could produce peptides with a greater proportion of amino acids with uncharged R groups.

Keywords: Adsorption – Minerals – Amino acids – Proteins – Side chain

Introduction and hypothesis

Numerous studies have been undertaken since Bernal (1951) first suggested that mineral clays could have played an important role in the origin of life, because they took part in processes such as the selection and concentration of key monomers from dilute solutions and their subsequent condensation to form biopolymers (Bernal, 1951). The adsorption of biomolecules on minerals has been studied by several investigators: amino acids on minerals (sand, clays, sediments, hematite) (Lahav and Chang, 1976; Henrichs and Sugai, 1993; Bentaleb et al., 1994; Zaia et al., 2002); amino acids plus transition metals on clays (Gupta et al., 1983; Fu et al., 1996); ATP/ADP/AMP/TMP/TTP plus metals on clays (Odom et al., 1979; Rishpon et al., 1982); ATP and AMP on pyrite (Tessis et al., 1999; Pontes-Buarque et al., 2001); nucleic acid bases on clays (Prabahar and Ferris, 1997; Sowerby et al., 2001) and cyanide on minerals (Boclair et al., 2001). There are also several papers showing the formation of biopolymers on mineral surfaces, whereby peptides and polynucleotides are commonly studied polymers (Ferris et al., 1996; Zamaraev et al., 1997; Hill Jr. and Orgel, 1999; Ferris, 2002).

The main goal of this paper is to discuss the implications of the adsorption of amino acids on mineral surfaces with regard to the origin of life. A review published by Lahav and Chang (1976) shows the results of adsorption coefficients for several amino acids binding to various clays. The apatite adsorption coefficients for glutamate and aspartate (both with negatively charged R groups) are twice that for glycine (non-polar aliphatic R group) with the same mineral and can be three times higher depending on the method of measurement (Lahav and Chang, 1976). That review (Lahav and Chang, 1976) also listed adsorption coefficients of illite for amino acids. Similarly, a large difference in adsorption was observed between glycine/alanine (non-polar aliphatic R groups) and histidine (positively charged R group), and the same was described for the adsorption coefficients of montmorillonite for alanine/leucine/glycine (non-polar aliphatic R groups) and

arginine/histidine/lysine (positively charged R groups) (Lahav and Chang, 1976). Paecht-Horowitz (1978) observed that histidine (positively charged R group) was adsorbed four times more than alanine-adenylate on montmorillonite. Tanaka et al. (1989) observed that hydroxyapatite showed a high affinity for aspartic acid (negatively charged R group) and lysine (positively charged R group), whereas a low affinity for alanine (non-polar aliphatic R group) which was almost independent of the solution pH. Henrichs and Sugai (1993) showed that the adsorption of lysine (positively charged R group) was greater than alanine or leucine (non-polar aliphatic R groups) in sediments from Resurrection Bay, Alaska. Bentaleb et al. (1994) studied the adsorption of amino acids (glycine, lysine, glutamic acid) on hematite (α-Fe_2O_3), and they observed that lysine (positively charged R group) and glutamic acid (negatively charged R group) are adsorbed much more than glycine (non-polar aliphatic R group). Polyadenylic acid binds to silica gel, and it was observed that from a pool of 18 amino acids only L-lysine and L-arginine (both with positively charged R group) were bound by silica/polyadenylic acid (Mellersh and Wilkinson, 2000). A study of the adsorption of alanine (non-polar aliphatic R group), tyrosine (polar aromatic R group), glutamic acid (negatively charged R group) and lysine (positively charged R group) by sea sand was carried out by Zaia et al. (2002), and only lysine (positively charged R group) showed adsorption on sea sand. Churchill et al. (2004) used atomic force microscope (AFM) to measure the point of zero charge (pH_{pzc}) of several minerals (quartz, calcite, silica glass and albite). They observed that the amino acids adsorb most strongly on minerals when pH_{pzc} and pI differ significantly. So, quartz ($pH_{pzc} = 2.8$) adsorbs strongly lysine ($pI = 9.74$) and calcite ($pH_{pzc} = 9.5$) adsorbs a variety of amino acids with a range of pI.

There is no doubt that clays, sand and many minerals can concentrate amino acids as well as catalyze their reaction in the formation of peptides. However, the results described above raise some questions about the role of minerals in providing a concentration mechanism for amino acids. A study was published by Klapper (1977) on the average occurrence of amino acids in over 200 proteins. This study showed that proteins have the following composition: 40.1% amino acids with non-polar aliphatic R groups; 8.1% amino acids with aromatic R groups; 25.9% amino acids with polar uncharged R groups; 11.7% amino acids with negatively charged R groups; and 13.8% amino acids with positively R charged groups (Klapper, 1977). It should be pointed out that the proportion of amino acids with different side chains in peptides and proteins is very important for the conformation of those molecules and consequently for the biochemistry of the organisms of today (Darnell et al., 1990). Minerals adsorb much more amino acids with negatively or positively charged R groups. Thus, this mechanism will produce peptides with much more amino acids with charged R groups than uncharged R groups. However, 74% of the amino acids of today's proteins are comprised of amino acids with non charged R groups. Thus, what were the mechanisms involved in producing peptides/proteins with more amino acids with uncharged R groups than charged R groups? Should we expect the composition of amino acids adsorbed on minerals to reflect that of present-day proteins? Was the adsorption of amino acids on minerals important for the origin of life? An attempt to answer the above questions is made in the following section.

Experimental work supporting hypothesis

We should search for substances or mechanisms that preconcentrate more amino acids with uncharged R groups than amino acids with charged R groups from dilute solutions for their subsequent condensation to peptides, in more close agreement with the composition of today's peptides. We should also look for mechanisms that produce more peptides with an amino acid composition of uncharged R groups more than with charged R groups. In spite of the little attention paid so far to these possibilities by investigators of prebiotic chemistry, there are several mechanisms that could produce peptides with the incorporation of a large proportion of amino acids with uncharged R groups.

Sowerby et al. (2002) studied the modulation of the adsorption of amino acids by adenine and hypoxanthine preadsorbed on bare graphite. Although graphite cannot be considered as a dominant prebiotic material, but these authors presented some interesting findings. The amino acids that showed the highest interaction energies with bare graphite were: $His > Glu > Arg \cong Asp > Met > Cys$. On the other hand, when graphite was preadsorbed with adenine or hypoxanthine the highest energy interactions were observed for Asp/Glu (negatively charged R group), and the base-modified graphite surface showed a sharp decrease in affinity for His (positively charged R group). The importance of this kind of study is that it demonstrates that a simple pre-RNA amino acid discrimination mechanism could have existed on primitive Earth. The results of the latter study showed a mechanism that selected more amino acids with negatively charged R groups (Asp, Glu)

with one mineral surface and two nucleobases; however, other materials (silicas, zeolites, etc) should be investigated, and in combination with other bases as well.

The use of wetting/drying cycles for the synthesis of peptides has been studied by several research groups. However, the main goal of these studies was to show the formation of peptides as well as the yields obtained for each molecular weight range. As far as we know, there are only a few experiments describing the amino acid composition of formed peptides from different starting amino acid solutions. Yanagawa et al. (1990) studied the formation of polypeptides in wetting/drying cycles using microwave heating, with the following starting amino acids (0.1 mol L^{-1} each): glycinamide (non-polar aliphatic R group), alaninamide (non-polar aliphatic R group), valinamide (non-polar aliphatic R group) and aspartic acid α-amide (negatively charged R group) plus kaolin. The amino acid analysis of the peptides showed that the incorporation of glycinamide (non-polar aliphatic R group) into polypeptides was about 1.5 times that of alaninamide (non-polar aliphatic R group), valinamide (non-polar aliphatic R group) or aspartic acid α-amide (negatively charged R group), which were incorporated into polypeptides almost in proportion to their starting concentration (Yanagawa et al., 1990). Suwannachot and Rode (1999) studied the catalytic influence of amino acids and peptides (Gly_2, DKP, Ala_2) in the formation of the dipeptides Val_2 (non-polar aliphatic R group), Leu_2 (non-polar aliphatic R group) and Lys_2 (positively charged R group) using wetting/drying cycles with 0.5 mol L^{-1} of NaCl/0.040 mol L^{-1} of Cu^{2+} (salt-induced peptide formation-SIPF). The best yield was obtained for Val_2 using Gly, His, Gly_2 or DKP as catalyst (Suwannachot and Rode, 1999). Plankensteiner et al. (2002) studied the formation of dipeptides in wetting/drying cycles with 0.5 mol L^{-1} of NaCl/0.040 mol L^{-1} of Cu^{2+} (salt induced peptide formation-SIPF) plus glycine or diglycine (catalytic factors), using the following combinations of amino acids (each 0.040 mol L^{-1}): aspartic acid/proline, aspartic acid/leucine, leucine/proline, valine/aspartic acid, valine/proline and valine/leucine. It should be pointed out that leucine, valine and proline are amino acids with non-polar aliphatic R groups and aspartic acid is an amino acid with a negatively charged R group. Using diglycine as a catalyst, dipeptides with the highest yields were: Pro-Pro > Pro-Val = Asp-Val > Leu-Pro. When glycine was used as catalyst the yields were not much different than those with diglycine. The wetting/drying cycles should be investigated with different starting solutions of amino acids, because the results shown above suggest that this process concentrates more amino acids with uncharged R groups than charged R groups. A review published by Rode (1999) pointed out that one of the important features of the SIPF reaction is the preferential formation of certain dipeptides, which implies the preference of certain amino acid sequences.

The polymerization of amino acids in aqueous solutions has been studied by several investigators using different reaction conditions, such as minerals as catalysts or a pre-concentrator, activating agents for oligomerization, etc (Ferris et al., 1996; Liu and Orgel, 1997; Hill Jr. et al., 1998; Imai et al., 1999; Ogata et al., 2000; Alargov et al., 2002; Yokoyama et al., 2003). However, as far as I know, there have been no reports of studies on the polymerization of amino acids in aqueous media using a mixture of several amino acids in the starting solutions.

The thermal polymerization of amino acids in solid state with and without minerals has been described by various authors, indicating in general an increase in the incorporation of amino acids with charged R groups (Philips and Melius, 1974; Saunders and Rohlfing, 1974; Rohlfing and McAlhaney, 1976; Hartmann et al., 1981). Thus, this process of peptide synthesis probably did not contribute to the formation of peptides with a large proportion of amino acids with uncharged R groups.

Quartz or sand was not used in many experiments to study the adsorption of amino acids because of their small surface-area-to-volume ratio compared to clays. The adsorption of amino acids on bare silica and modified silica (octadecyl, zirconium phosphate, aminobenzenesulfonic groups) was studied by Basiuk (2002). With bare silica, most of the α-amino acids were found to have positive ΔG^{θ} values, meaning that their concentration on silica was lower than in the bulk of solution. Some of the ΔG° values for the adsorption of amino acids on modified silica were negative, indicating that the amino acid concentration in solid phase was greater than in the liquid phase (Basiuk, 2002). However, modified silicas cannot be considered prebiotic materials. For the adsorption of amino acids on bare silica, Basiuk (2002) observed that the imidazole side-chain of His (positively charged R group) and carboxylic groups of Asp (negatively charged R groups) and Glu (negatively charged R group) accounted for the greatest increase in ΔG^{θ} values and correspondingly the decrease in adsorption. In general, Basiuk (2002) observed that amino acids with uncharged or non-polar R groups were adsorbed more by bare silica, than were amino acids with charged R or polar groups. The adsorption of amino acids on bare silica is very complex and depends on several factors such as:

hydrophobic interactions due to the hydrophobic properties of the silica surface (–Si–O–Si– siloxane groups); ionic interactions with silanol groups (≥Si–O^-); and hydrogen bonding interactions with silanol groups (≥Si–O–H) (Basiuk, 2002). Alternatively, Zaia et al. (2002) determined that only lysine (positively charged R group) was adsorbed on sea sand, probably because of the silanol groups (≥Si–O^-) of sea sand. However, in both the study of Zaia et al. (2002) and of Basiuk (2002), the experiments were carried out in distilled water without controlling for pH and the effect of sea water salts. These type of experiments could be helpful in clarifying whether sand can concentrate more amino acids with uncharged R groups than amino acids with charged R groups.

As seen above, there are several mechanisms that could play an important role in the formation of peptides with a large number of uncharged amino acids in their composition. However, all the experiments cited above are based on a ''mineral origin of life,'' because of the influence of minerals in the production of biomolecules and biopolymers. However, we should also look for mechanisms that probably could have existed, where minerals did not play an important role.

Segré et al. (2001) proposed a lipid world instead of an RNA world as an alternative view of the origin of life. These substances were probably very easily found on prebiotic Earth (McCollom et al., 1999; Rushdi and Simoneit, 2001). Several advantages can be cited for this lipid world: self-assembly of amphiphilic molecules into complex supramolecular structures is spontaneous, the supramolecular structures have the capacity to act as catalysts, to contain compositional information and to undergo evolution (Luisi et al., 1988; Bachmann et al., 1990; Bachmann et al., 1991; Wick and Luisi, 1996; Oberholzer et al., 1999; Fisher et al., 2000; Segré et al., 2001). The polymerization of glycine on or inside lipid vesicles in hydrothermal environments was studied by Tsukahara et al. (2002). They obtained greater yields of di- or triglycine with lipid than without lipid, and it was possible to synthesize even heptaglycine (Tsukahara et al., 2002). The polymerization of amino acids inside of lipid vesicles under hydrothermal conditions is a very attractive idea, because no catalyst is necessary for the reactions and inside these vesicles the peptides would be protected from the environment and further chemical changes. Therefore, experiments with different amino acids in the starting solutions should be carried out to determine the amino acid compositions favored in the peptides synthesized. Using the lipophilic condensing agent 2-ethoxy-1-ethoxycarbonyl-1,2-dihydroquinoline (EEDQ), Blocher et al. (1999) and Luisi et al. (2000) have been shown that membrane of liposomes can contribute to elongation of peptides as well as select hydrophobic amino acids and peptides operating as a selection tool in the polimerization. They also showed when the membrane is negatively charged oligomers containing Arg (positively charged R group) and His (positively charged R group) were obtained (Blocher et al., 2000). By the other hand, when membrane is positively charged (cetyltrimethyl ammonium bromide) charged oligomers containing Asp (negatively charged R group) and Glu (negatively charged R group) were obtained (Böhler et al., 1996). These experiments could be showing the mechanism which hydrophobic amino acids have been selected. However, Hitz et al. (2001) and Blocher et al. (2001) reported that liposomes have no influence on the stereoselectivity in the oligomerization of racemic NCA-amino acids.

There are several experiments showing that chiral selection of L or D amino acids occurs. However there are some reports involving minerals that it should be pointed out as follow. Hazen et al. (2001) observed that when calcite ($CaCO_3$) was immersed in a racemic aspartic acid solution it was possible to obtain a chiral selectivity of D- and L-enantiomers on crystal surfaces. Viedma (2001) showed when aspartic acid and glutamic acid were crystallized from free solutions, the result was always crystals of racemic compounds DL-aspartic acid and DL-glutamic acid. However, when those amino acids were crystallized from solutions inside porous media (brick and paper), the result was always crystal of conglomerates D- and L-enantiomeric aspartic acid or glutamic acid. Hitz and Luisi (2002) obtained that the oligomerization of racemic NCA-leucine in the presence of quartz in aqueous solutions yields peptides with a high degree of homo chiral sequences on the quartz surface. They also observed a similar effect (lesser extent) for oligomerization of NCA-glutamic acid on hydroxylapatite. Hitz and Luisi (2004) also reported that polymerization of NCA-amino acids (Try, Leu, Ile) racemates in aqueous solution yields oligopeptides with a high degree of homochiral sequences. They also showed that quartz selectively adsorbs the more stereoregular oligopeptides from an aqueous solution of oligo-D, L-leu. Besides, the paper published by Shinitzky et al. (2002) did not use any mineral to select an enantiomer, it is very important, and should be cited in this review. They reported a difference in the solubilities of D- and L-tyrosine in water. They observed that a supersatured solutin of 10 mM of L-tyrosine at 20°C crystallized much more slowly than D-tyrosine, so the satured solution of L-tyrosine was more concentrated than that of D-tyrosine. They

also observed that supersatured solutions of DL-tyrosine in water formed precipitates of predominantly D-tyrosine and DL-tyrosine, resulting in an excess of L-tyrosine in the satured solution.

All the experiments cited above are not conclusive about which one was the most important for the selection of the chiral amino acids, because mostly of those experiments were performed with single amino acid and in distilled water. So the results described above raise some questions about the role of minerals in providing a chiral selection mechanism for amino acids. What will set of amino acids be selected in a mixture of them? If one mechanism works for the selection of one enatiomer this mechanism will work for all amino acids? It should also be also pointed out that many of those experiments were carried out in distilled water, so what will the effects of salts of seawater be on the selection of enantiomers?

Implications

Minerals adsorb amino acids with charged R groups much more than with uncharged R groups. Therefore, the subsequent polymerization of these amino acids would produce peptides with large proportions of amino acids with charged R groups. However, the proteins of modern living beings are comprised of 74% amino acids with uncharged R groups. It was proposed in this report that there are several mechanisms that could be involved in the synthesis of peptides with an incorporation of a larger proportion of amino acids with uncharged R groups. The ''mineral basis for the origin of life,'' resulting from mineral-based synthesis of amino acids and peptides has been more thoroughly investigated than any other idea for the origin of biomolecules and biopolymers. However, it should be pointed out that lipids (as suggested in the lipid world) in the hydrothermal environment could be a very promising alternative mechanism for the synthesis of peptides, because of its simplicity in which there would be no need for catalysts or any specific minerals for adsorption. It should be also pointed out that liposomes selected hydrophobic amino acids and peptides, this could be explain why the 74% of the amino acids of today's proteins are comprised of amino acids with non charged R groups. However, liposomes have no influence on the stereoselectivity in the oligomerization of racemic NCA-amino acids.

Acknowledgements

The author is greatly indebted to Dr. Cássia T. B. V. Zaia from the Departamento de Ciências Fisiológicas-CCB, UEL, for stimulating discussions about this paper.

References

Alargov DK, Deguchi S, Tsujii K, Horiloshi K (2002) Reaction behaviors of glycine under super and subcritical water conditions. Orig Life Evol Biosph 32: 1–12

Bachmann PA, Walde P, Luisi PL, Lang J (1990) Self replicating reverse micelles and chemical autopoiesis. J Am Chem Soc 112: 8200–8201

Bachmann PA, Walde P, Luisi PL, Lang J (1991) Self replicating micelles: aqueous micelles and enzymatically driven reactions in reverse micelles. J Am Chem Soc 113: 8204–8209

Basiuk VA (2002) Adsorption of biomolecules on silica. In: Encyclopedia of surface and colloid science. Ponisseril Somasundaran (ed) Marcel Dekker Inc., New York, p 277

Bentaleb A, Vera P, Delgado AV, Gallardo V (1994) Electrokinetic studies of monodisperse hematite particles of inorganic electrolytes and amino acids. Mater Chem Phys 37: 68–75

Bernal JD (1951) The physical basis of life. Routledge and Kegan Paul Ltd., London

Blocher M, Liu D, Walde P, Luisi PL (1999) Liposome assisted selective polycondensation of α-amino acids and peptides. Macromolecules 32: 7332–7334

Blocher M, Liu D, Walde P, Luisi PL (2000) Liposome assisted selective polycondensation of α-amino acids and peptides: the case of charged liposomes. Macromolecules 33: 5787–5796

Blocher M, Hitz T, Luisi PL (2001) Stereoselectivity in the oligomerization of racemic tryptophan N-carboxyanhydride (NCA-Trp) as determined by isotope labeling and mass spectrometry. Helvetica Chimica Acta 84: 842–848

Boclair JW, Braterman PS, Brister BD, Jiang J, Lou S, Wang Z, Yarberry F (2001) Cyanide self-addition, controlled adsorption, and other processes at layered double hydroxides. Orig Life Evol Biosph 31: 53–69

Böhler C, Hill AR Jr, Orgel LE (1996) Catalysis of the oligomerization of o-phospho-serine, aspartic acid or glutamic acid by cationic micelles. Orig Life Evol Biosph 26: 1–5

Churchill H, Teng H, Hazen RM (2004) Correlation of pH-dependent surface interaction forces to amino acid adsorption: implications for the origin of life. American Mineralogist 89: 1048–1055

Darnell J, Lodish H, Baltimore D (1990) Molecular cell biology. Scientific American Books, New York, p 48

Ferris JP (2002) Montmorillonite catalysis of 30–50 mer oligonucleotides: laboratory demonstration of potential steps in the origin of the RNA world. Orig Life Evol Biosph 32: 311–332

Ferris JP, Hill A Jr, Liu R, Orgel LE (1996) Synthesis of long prebiotic oligomers on mineral surfaces. Nature 381: 59–61

Fischer A, Oberholzer T, Luisi PL (2000) Giant vesicles as models to study the interactions between membranes and proteins. Biochim Biophys Acta 1467: 177–188

Fu L, Weckhuysen BM, Verberckmoes AA, Schoonheydt RA (1996) Clay intercalated Cu(II) amino acids complexes: synthesis, spectroscopy and catalysis. Clays Miner 31: 491–500

Gupta A, Loew GH, Lawless J (1983) Interaction of metals ions and amino acids: possible mechanisms for the adsorption of amino acids on homoionic smectite clays. Inorganic Chemistry 22: 111–120

Hartmann J, Brand MC, Dose K (1981) Formation of specific amino acid sequences during thermal polymerization of amino acids. BioSystems 13: 141–147

Hazen RM, Filley TR, Goodfriend GA (2001) Selective adsorption of L- and D-amino acids on calcite: implications for biochemical homochirality. Proc Nat Acad Sci USA 98: 5487–5489

Henrichs SM, Sugai SF (1993) Adsorption of amino acids and glucose by sediments of Resurrection Bay, Alaska, USA-Functional Groups effects. Geochimica et Cosmochimica Acta 57: 823–835

Hill A Jr, Orgel LE (1999) Oligomerization of L-γ-carboxyglutamic acid. Orig Life Evol Biosph 29: 115–122

Hill A Jr, Bohler C, Orgel LE (1998) Polymerization on the rocks: negatively-charged α-amino acids. Orig Life Evol Biosph 28: 235–243

Hitz T, Blocher M, Walde P, Luisi PL (2001) Stereoselectivity aspects in the condensation of racemic NCA-amino acids in the presence and absence of liposomes. Macromolecules 34: 2443–2449

Hitz T, Luisi PL (2002) Enhancement of homochirality in oligopeptides by quartz. Helv Chim Acta 85: 3975–3980

Hitz T, Luisi PL (2004) Spontaneous onset of homochirality in oligopeptides chains generated in the polymerization of N-carboxyanhydride amino acids in water. Orig Life Evol Biosph 34: 93–104

Imai EI, Honda H, Hatori K, Matsuno K (1999) Autocatalytic synthesis of oligoglycine in simulated submarine hydrothermal system. Orig Life Evol Biosph 29: 249–259

Klapper MH (1977) Independent distribution of amino acids near neighbor pairs into polypeptides. Biochem Biophys Res Comm 78: 1018–1024

Lahav N, Chang S (1976) The possible role of solid surface area in condensation reactions during chemical evolution. J Mol Evol 8: 357–380

Liu R, Orgel LE (1997) Efficient oligomerization of negatively-charged β-amino acids at -20°C. J Am Chem Soc 119: 4791–4792

Luisi PL, Giomini M, Pileni MP, Robinson BH (1988) Reverse micelles as hosts for proteins and small molecules. Biochim Biophys Acta 947: 209–246

Luisi PL, Walde P, Blocher M, Liu D (2000) Research on the origin of life: membrane assisted polycondensations of amino acids and peptides. Chimia 54: 52–53

McCollom TM, Ritter G, Simoneit BRT (1999) Lipid synthesis under hydrothermal conditions by Fischer-Tropsch type reactions. Orig Life Evol Biosph 29: 153–166

Mellersh A, Wilkinson AS (2000) RNA bound to a solid phase can select an amino acid and facilitate subsequent amide bond formation. Orig Life Evol Biosph 30: 3–7

Oberholzer T, Nierhaus KH, Luisi PL (1999) Protein expression in liposomes. Biochem Biophys Res Commun 261: 238–241

Odom DG, Rao M, Lawless JG, Oro J (1979) Association of nucleotides with homoionoc clays. J Mol Evol 12: 365–367

Ogata Y, Imai EI, Honda H, Hatori K, Matsuno K (2000) Hydrothermal circulation of seawater through hot vents and contribution of interface chemistry to prebiotic synthesis. Orig Life Evol Biosph 30: 527–537

Paecht-Horowitz M (1978) Clay catalyzed polymerization of amino acid adenylates and its relationship to biochemical reactions. Origin of Life 289–295

Phillips RD, Melius P (1974) The thermal polymerization of amino acids. Int J Prot Res 6: 309–319

Plankenseiner K, Righi A, Rode BM (2002) Glycine and diglycine as possible catalytic factors in the prebiotic evolution of peptides. Orig Life Evol Biosph 32: 225–236

Pontes-Buarque M, Tessis AC, Bonapace JAP, Monte MBM, Cortés-Lopez G, de Souza-Barros F, Vieyra A (2001) Modulation of adenosine 5′-monophosphate adsorption onto aqueous resident pyrite: potential mechanisms for prebiotic reactions. Orig Life Evol Biosph 31: 343–362

Prabahar KJ, Ferris JP (1997) Adenine derivatives as phosphate-activating groups for the regioselective formation of 3′, 5′-linked oligoadenylates on montmorillonite: possible phosphate activating groups for the prebiotic synthesis of RNA. J Am Chem Soc 119: 4330–4337

Rishpon J, O'Hara PJ, Lahav N, Lawless JG (1982) Interaction between ATP, metal ions, glycine, and several minerals. J Mol Evol 18: 179–184

Rode BM (1999) Peptides and the origin of life. Peptides 20: 773–786

Rohlfing DL, McAlhaney WW (1976) The thermal polymerization of amino acids in the presence of sand. BioSystems 8: 139–145

Rushdi AI, Simoneit BRT (2001) Lipid formation by aqueous Fischer-Tropsch type synthesis over a temperature range of 100 to 400°C. Orig Life Evol Biosph 31: 103–118

Saunders MA, Rohlfing DL (1974) Inclusion of nonproteinous amino acids in thermally prepared models for prebiotic protein. BioSystems 6: 81–92

Segré D, Ben-Eli D, Deamer DW, Lancet D (2001) The lipid world. Orig Life Evol Biosph 31: 119–145

Shinitzky M, Nudelman F, Barda Y, Haimovitz R, Chen E, Deamer DW (2002) Unexpected differences between D- and L-tyrosine lead to chiral enhancement in racemic mixtures. Orig Life Evol Biosph 32: 285–297

Sowerby SJ, Cohn CA, Heckl WM, Holm NG (2001) Differential adsorption of nucleic bases: relevance to the origin of life. Proc Natl Acad Sci USA 98: 820–822

Sowerby SJ, Petersen GB, Holm NG (2002) Primordial coding of amino acids by adsorbed purine bases. Orig Life Evol Biosph 32: 35–46

Suwannachot Y, Rode BM (1999) Mutual amino acid catalysis in salt-induced peptide formation supports this mechanism's role in prebiotic peptide evolution. Orig Life Evol Biosph 29: 463–471

Tanaka H, Miyajima K, Nakagaki M, Shimabay S (1989) Interactions of aspartic acid, alanine and lysine with hydroxyapatite. Chem Pharma Bull 37: 2897–2901

Tessis AC, Penteado-Fava A, Pontes-Buarque M, de Amorim HS, Bonapace JAP, de Souza-Barros F, Vieyra A (1999) Pyrite suspended in artificial sea water catalyzes hydrolysis of adsorbed ATP: enhancing of acetate. Orig Life Evol Biosph 29: 361–374

Tsukahara H, Imai EI, Honda H, Hatori K, Matsuno K (2002) Prebiotic oligomerization on or inside lipid vesicles in hydrothermal environments. Orig Life Evol Biosph 32: 13–21

Viedma C (2001) Enantiomeric crystallization from DL-aspartic and DL-glutamic acids: implications for biomolecular chirality in the origin of life. Orig Life Evol Biosph 31: 501–509

Wick R, Luisi PL (1996) Enzyme containing liposomes can endogenously produce membrane-constituting lipids. Chem Biol 3: 277–285

Yanagawa H, Kojima K, Ito M, Handa N (1990) Synthesis of polypeptides by microwave heating I. Formation of polypeptides during repeated hydration-dehydration cycles and their characterization. J Mol Evol 31: 180–186

Yokoyama S, Koyama A, Nemoto A, Honda H, Imai EI, Hatori K, Matsuno K (2003) Amplification of diverse catalytic properties of evolving molecules in a simulated hydrothermal environment. Orig Life Evol Biosph 33: 589–595

Zaia DAM, Vieira HJ, Zaia CTBV (2002) Adsorption of L-amino acids on sea sand. Journal of the Brazilian Chemical Society 13: 679–681

Zamaraev KI, Romannikov VN, Salganik RI, Wlassoff WA, Khramtsov VV (1997) Modeling of the prebiotic synthesis of oligopeptides: silicate catalysts help to overcome the critical stage. Orig Life Evol Biosph 27: 325–337

Author's address: Dimas A. M. Zaia, Departamento de Química-CCE, Universidade Estadual de Londrina, 86051-990, Londrina-PR, Brazil, E-mail: damzaia@uel.br