Protogenetic coding bypass fixation selectively robust to early earth alkalinity

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Abstract

Alkali-resistant phosphoramidic bonds could have provided an originally selective bypass to the alkalo-deficient acidophilic ribophosphoesterasic fixation of the prospective genetic code.

Keywords: *coding, protogenetic, alkaline, fixation, bypass*

Résumé

Fixation alcaline court-circuitante du codage protogénétique biogène. - *L'alcalinité tellurique originelle pourrait avoir sélectionné les robustes liaisons phosphoramidiques pour la fixation du codage protogénétique des nucléobases, court-circuitant ainsi les liaisons ribophosphoestérasiques alcalo-déficientes du prospectif code génétique.*

Mots-clés: *codage, protogénétique, alcalin, fixation, court-circuit*

Introduction

The precursors of the present-day genetic code, variously quoted as protocode(s) (Kay 2000), first code (Wills & Bada 2000) or original code (De Duve 2002), to which we substitute "protocoding" in a more dynamic connotation, also consist of a list of correspondences between aminoacids specifically encoded by doublets or triplets of nucleobases either fixed stochastically by "frozen accident" (Crick 1968) or by preferential physical-stereochemical complementarity (Woese 1967; Mellersh 1993). We endorsed this last opinion in our anticodonic chart (Turian 1998), using the inversed base-paired letters of transfer-RNAs rather than those outstandingly deciphered by biochemists of the 60ties (Nirenberg & Mattei, 1961, in Kay 2000), namely C + C = G + G for glycine; C + G = G + C for alanine, etc.

What was then the environmental setting for the necessary validating fixation of such protogenetic coding? "The importance of being alkaline", as recently advertised by Russell (2003), confronted to both the original telluric alkalinity and to the necessary high pH robustness of a "pre-RNA world" coding fixation bond, sparked our evolutionary answer.

Primordial alkalinity of the early Earth rocked crust

Igneous rocks predominated in the primitive terrestrial lithosphere, among which silicate alkaline salts (Mg^{2+} - feldspars, Al^{3+} - kaolinite clays, etc.). The surface of these rocks might have been covered with microscopic pits with a probable high pH watery content, selectively favouring resistant intermolecular coding reactions.

In the vent systems of primitive oceans, mineral-catalyzed reduction of molecular nitrogen and oxides of nitrogen, suggested that hydrothermal environments and surrounding waters would have been the ammonia-rich and therefore alkaline. These conditions were most favourable to high pH serpentinization of olivine basaltic rocks of the early Earth crust (for references, see in Holm & Andersson 1998 and Zubay 2000) and, consecutively, to trigger the robustness of the protocoded processes.

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Selectively bypassed ribodefective fixation of the protogenetic coding by alkaline-robust phosphoramide bondings

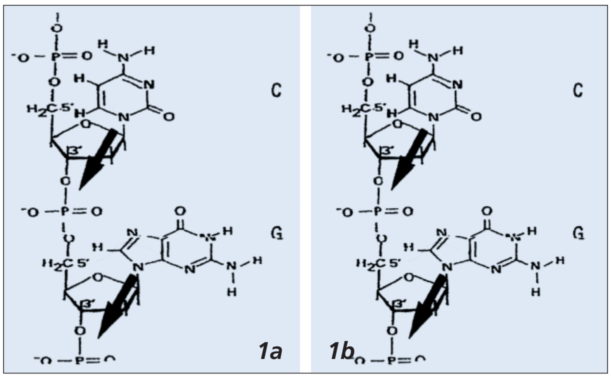
Fixation of the protocode on the ribophosphoesterasic of transfer RNA could not have occurred because of serious difficulties in the primordial synthesis of the sugar D-ribose (Shapiro 1988; Joyce & Orgel 1999), among which its lability in alkaline media (see Lahav 1999), even though possibly alleviated by boric acid present in interstellar space (Ricardo et al. 2004).

Consequently, among the predominant alkalinity of the original telluric environments, available protocoded nucleobases would have been deprived of ribose for their phosphorous fixation. This leads us to propose that the nucleotidic steps of pre-RNA synthesis would have been evolutively bypassed by phosphoramidic N → P bonds (Fig. 1), known to be selectively robust at high pHs (Lohrmann & Orgel 1973; Corbridge 1978), as confirmed for our nucleobase-phosphates (Turian et al. 1999; Turian & Rivara-Minten 2001). These bonds could thus have been the selective pressure factor for the chemical fixation of the protogenetic code.

Acidic transition to ribonucleotide fixation (RNAs)

The high pH dependance of protocoding would have been relevant in prebiotic to biotic evolution, following an environmental switch to acidic media such as the CO_2-enriched surface layers of the oceans (see Russell 2003). Such acidification would have provided the necessary acidic opening of the N → P bondings by electric repulsion (Turian 2001). This would have permitted the median insertion of the hydroxylated precursors of ribose, glycolaldehyde and glyceraldehyde (see Eschenmoser's team work, 1997), produced by formose reaction in alkaline media, before an environmental acidic pH transition to bridge the opened bondings by the acidic pH-solid ribose.

Fig. 1. Protogenetic coding alkaline-selected bypass fixation of pre-RNA.
(a) Phosphoramide bondings (N à P) alkaline-selected (pH 8-10) bypasses of a phosphodiester linked ribopolynucleotide chain.
(b) Previous modellization (Turian, 2001) of protocoding nucleobase doublets, examplified by: A (alanine) for C (cytosine) + G (guanine) riboselessly N – P fixed on the polyphosphate pre-RNA tape.



Conclusion

Transition from N → P to N – C – P (C = ribose) bondings would have stabilized the proceedings from protogenetic to "modern" genetic code. Such biogenic filiation originating from geochemical alkalinity might have commanded protocoded "Protolife" before sparkling into the acidophilic RNA-DNA-genomics-proteomics Life systems.

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