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Letter to the Editor

Template-Directed Polynucleotide Synthesis on Mineral Surfaces

Alan W. Schwartz* and Leslie E. Orgel

The Salk Institute for Biological Studies, PO Box 85800, San Diego, California 92138, USA

Summary. Ferric hydroxide, a plausible prebiotic material, strongly adsorbs polynucleotides. We show that adsorption on ferric hydroxide and on several other minerals has no effect, under the conditions studied, on the template-directed oligomerization of guanylic acid on polycytidylic acid.

Key words: Chemical evolution — Template synthesis — Minerals — Polynucleotides — Nucleotide oligomerization

Introduction

An important feature of many scenarios for chemical evolution is the role of mineral surfaces in concentrating reactants, catalyzing polymerizations, and protecting the products of such processes from destruction, for example by ultraviolet radiation or heat. We have shown (Gibbs et al. 1980) that the template-directed synthesis of oligoadenylates in the presence of polyuridylic acid [poly (U)] is not affected by adsorption of the poly (U) on hydroxylapatite. Here we report that in addition to hydroxylapatite, ferric hydroxide and several other plausible prebiotic materials that adsorb polycytidylic acid [poly (C)] are without effect, under the conditions studied, on the very efficient and regiospecific template-directed synthesis of long 3′-5′-linked oligomers of guanylic acid.

Experimental

"Ferric hydroxide" was prepared by adjusting a filtered, stirred solution of 0.05 M $FeCl_3$ to pH 8 with 1.0 M NaOH in the presence of air and washing the resulting precipitate by centrifugation in four changes of distilled water followed by four changes of HEPES buffer [0.1 M 4-(2-hydroxyethyl)-1-piperazine-ethanesulfonic acid, sodium salt, pH 8.5]. This material is probably a complex mixture of iron hydroxides (Mellor 1934). Hydroxylapatite (Bio-Gel HTP, purchased from Bio-Rad Laboratories), attapulgite no. 43 (Clay Mineral Standard, purchased from Ward's), and synthetic manganate and β-FeOOH (akaganeite) (gifts of G. Arrhenius) (Arrhenius 1984) were also washed by centrifugation in four changes of HEPES buffer. Poly (C) was purchased from Sigma, and guanosine 5′-phospho-2-methylimidazole (2-MeImpG) was prepared as reported previously (Joyce et al. 1984).

The reaction mixture contained 0.1 M HEPES buffer (pH 8.5), 0.2 M $MgCl_2$, 0.2 M NaCl, 0.05 M poly (C), and 0.15 M ^{14}C-labeled 2-MeImpG (0.5 μCi/μmol). Fifty microliters of reaction mixture was added to a 1.5-ml microcentrifuge tube containing ferric hydroxide (25 mg, wet), and to a second tube without ferric hydroxide. Separate experiments had shown that poly (C) was 99% adsorbed under these conditions. The contents of the tubes were mixed well and allowed to react at 0°C. After 3 days, the tubes were centrifuged and the ferric hydroxide was extracted three times with 50 μl 0.75 M sodium pyrophosphate. Of the radioactive label originally present, 83% was recovered in the combined supernatant and extracts. Analysis was performed by means of paper chromatography and high-pressure liquid chromatography (HPLC) on RPC-5 as reported previously (Joyce et al. 1984).

In another series of experiments, samples of manganate, attapulgite, and β-FeOOH were exposed to poly (C), with adsorption of 68, 77, and 95% of the template, respectively, and the supernatant, containing nonadsorbed template, was removed. Monomer and salts were added to the mineral-adsorbed poly (C)

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* *Present address:* Department of Exobiology, Faculty of Science, University of Nijmegen, Toernooiveld, 6525 ED Nijmegen, The Netherlands

Offprint requests to: L.E. Orgel

Abbreviations: poly (C), polycytidylic acid; poly (U), polyuridylic acid; 2-MeImpG, guanosine 5′-phospho-2-methylimidazolide

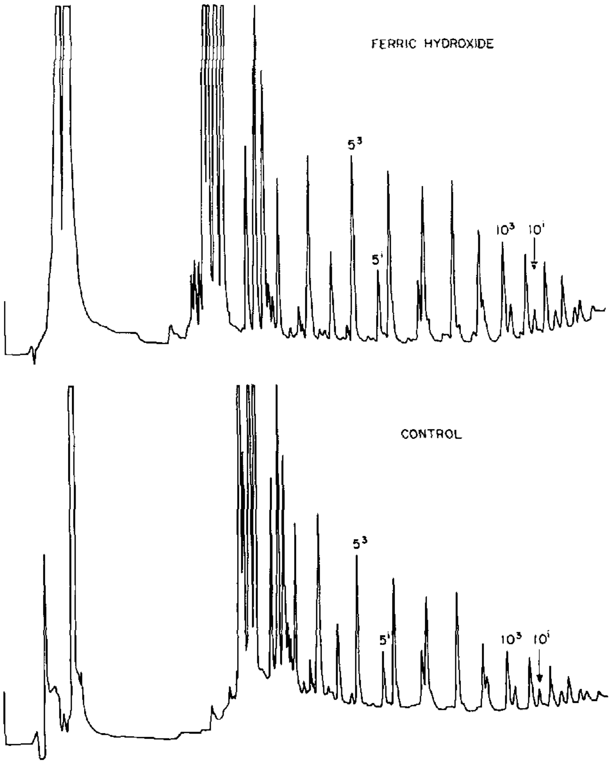

Fig. 1. Comparison of the HPLC separation of the products of the oligomerization of 2-MeImpG on poly (C) adsorbed on ferric hydroxide with that of the products of a control oligomerization in the absence of mineral. For conditions, see text. "5^3" indicates an oligomer five units in length, linked entirely by 3′-5′ phosphodiester bonds. "5^i" is a similar molecule terminated by an unhydrolyzed phosphorimidazolide group

and incubation and analysis were carried out as described for ferric hydroxide.

Results and Discussion

In Fig. 1 we compare the product oligomers recovered from ferric hydroxide with those obtained in a control experiment. Clearly, adsorption on ferric hydroxide has little effect on the pattern of products obtained in the poly (C)–2-MeImpG reaction. The yield of products, as defined by the fraction of radioactive label remaining at the origin in paper chromatography, was 14% after 3 days in the presence of ferric hydroxide and 16% in the control reaction.

Very similar results were obtained with each of the other minerals. Furthermore, under slightly different conditions, poly (C) adsorbed on hydroxylapatite gave products identical to those obtained with poly (C) on ferric hydroxide or in solution. We also found that the template properties of a random copolymer of C and G, poly (C_3G), were unaffected by adsorption on a variety of mineral surfaces.

Our observations do little to support (or contradict) the hypothesis that minerals may have provided a catalytic function in chemical evolution. However, the results presented in this paper, together with those published previously (Gibbs et al. 1980), strongly suggest that concentration and physical protection of polynucleotides could have resulted from their adsorption on minerals, without a significant effect on their properties as templates.

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