

On the role of silica in the formation of insoluble organic matter in Miller-Urey-type experiments.

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INTRODUCTION

Our previous studies on the role of borosilicate in Miller-Urey-type experiments have highlighted the importance of amorphous borosilicate within the geochemical context of early Earth (Hadean) environments and their potential role in the origins of life (1). In a reducing atmosphere in contact with water, our experiments revealed significant quantitative and qualitative differences in the formation of prebiotic organic compounds, depending on the reactor wall material—either borosilicate glass or Teflon. The yield of water-soluble organic compounds, dissolved within the resulting "prebiotic soup," was substantially higher in experiments utilizing a borosilicate reactor. Furthermore, the spectrum of organic compounds obtained in the borosilicate reactor was 55% richer, containing amino acids, nucleobases, and even dipeptides, in contrast to the comparatively "light" soup collected from the inert Teflon reactor. In addition, our prior experiments indicated that the amount of insoluble solid organic matter produced was almost negligible in the absence of borosilicate. The underlying factors driving these notable differences remain hypothetical. Two main possibilities warrant further investigation: (a) a specific influence (potentially catalytic) of silicon-containing groups, such as silanol, present in solution or on solid surfaces, and (b) a catalytic effect of other compounds typically found in borosilicate, such as boron, aluminum, and/or alkali metal ions. Testing these possibilities requires experiments where pure solid silica, i.e., a quartz crystal, is exposed to the alkaline water and the reducing atmosphere within a Miller-Urey-type experiment. This is the primary objective of the present study.

METHODS

Miller-Urey-type discharge experiments were performed in a Teflon cylindrical reactor containing a reducing atmosphere composed of methane (500 ± 20 mbar), nitrogen (250 ± 20 mbar) and ammonia (200 ± 20 mbar). In addition, the reactor contained 200 ml of ultra-pure deionized water. Due to the dissolution of the ammonia into the water reservoir, the initial pH of the aqueous phase was highly alkaline with a pH of 11.7. Two tungsten electrodes connected to a 60.000 volts discharge generator supply energy to the system in 15-minutes on/off cycles to trigger chemical conversion of the precursor gases. Inside the Teflon reactor, we placed pieces of single-crystalline quartz with sized between 0.1-5.0 cm that were either exposed to the reducing atmosphere or submerged in alkaline water. After 14 days of electrical discharging at room temperature (25°C) the reactor was opened and samples of the brownish solid organic film, that has formed on the quartz crystals were taken and analyzed.

RESULTS

After the experiment, a brownish stain and condensed water drops were observed on the reactor walls (Fig. 1A). A strong black coloring directly below the electrical spark and a slight blackening preferably on the left side of the reactor is nota. More interestingly, the formation of the typical solid organic film (SOF) is preferentially located on the surface the quartz crystals as well as the water-air interface as shown in Fig. 1A. This film has the same visual and physical appearance of the SOF from our regular borosilicate Miller-Urey-type experiments (2) and can be easily collected as it detaches from its substrate upon submerging it into water (Fig. 1C). Samples transferred onto a FE-SEM sample holder were analyzed and compared to the SOF of a typical borosilicate reactor experiment in Fig. 1E+F. In addition, samples were taken from the colored Teflon reactor walls and analyzed by the means of FE-SEM and EDX (Fig. 1D). The insoluble organics in this area appear to be highly different in structure and composition.

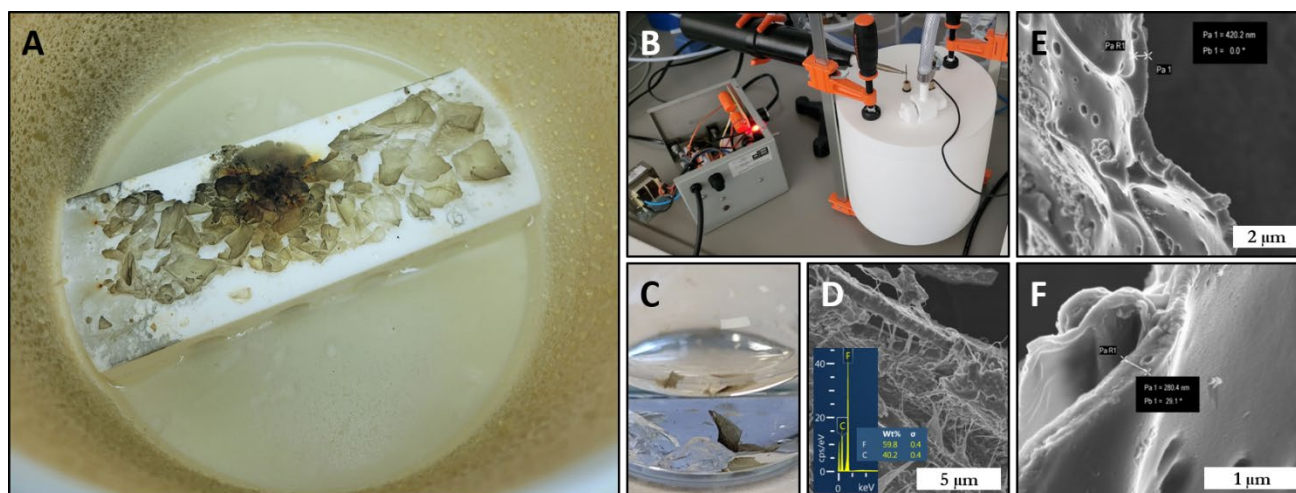


Fig. 1. (A) Photograph of the interior of the Teflon reactor after 14 days (B) Electrical discharge generator positioned near the Teflon reactor, emitting an electromagnetic field during experimentation. (C) SOF fragment floating near a quartz crystal from which it detached after submersion in water. (D) Field Emission Scanning Electron Microscopy (FE-SEM) and Energy Dispersive X-ray (EDX) of the discolored SOF collected from the Teflon reactor walls. (E) FE-SEM image of SOF obtained from quartz, compared to (F) the SOF sample obtained from borosilicate, showing their morphological similarities.

DISCUSION AND CONCLUSIONS

The several key findings can be observed already from the macroscopic photograph taken right after opening the Miller-Urey-type Teflon reactor are discussed briefly. The black coloration observed on surfaces below the electrodes results from elemental carbon particles forming on the electrodes. This effect is commonly seen in Miller-Urey-type experiments. The asymmetric darkening of the reactor is likely due to the attachment of charged particles generated by the spark, moving towards the electric field of the proximately placed generator.

The reactor walls in general are less coated with solid organic film (SOF) the borosilicate reactors (2). Indeed, samples collected from these areas show a distinctly different structure and composition: they are rich in fluorine and have a glue-like appearance (Fig. 1D). We hypothesize that certain organic compounds formed during the experiment may either partially dissolve in Teflon, leading to softening and coloration of the Teflon. Due to the residual Teflon in the wall samples, a direct comparison of the insoluble organic compounds with those obtained at the silica and water-air interface is difficult. Analysis of the insoluble organic matter on the quartz and water-air interfaces through FE-SEM imaging reveals the characteristic structure of SOF typically observed in our reference Miller-Urey experiments using borosilicate (Fig. 1E+F). These findings suggest that the presence of pure silica enables SOF formation. By using quartz instead of borosilicate, we can exclude a substantial contribution from other borosilicate glass components, such as boron, aluminum, and alkali (earth) metals, in the formation of insoluble organic matter. Further analysis of the molecular composition of this SOF and the "primordial soup" will clarify whether these are also unaffected by the change in material, supporting silica as a primary contributor in prebiotic chemistry within the Miller experiment.

Summarizing, SOF formation appears to be preferentially enhanced at silica-containing interfaces (Fig. 1A). We propose that free silanol groups either in solution or on solid surfaces, play a critical role in catalyzing reactions of primary precursor molecules generated by the electrical discharge, such as hydrogen cyanide and formamide (3). These reactions likely contribute to the formation of more complex organic molecules and/or their subsequent polymerization and agglomeration, ultimately resulting in the solid organic film observed in our study (2).

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