

The Role of Mineral Surfaces in Miller's Experiment

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Abstract

We have designed a set of experiments to test the role of mineral surfaces on the yielding of the Miller-Urey type of experiment. Two experiments were performed in borosilicate flasks, two in a Teflon flask and a third couple in a Teflon flask with pieces of borosilicate submerged in the water. The experiments were performed in CH₄, N₂, and NH₃ atmosphere either buffered at pH 8.7 with NH₄Cl or unbuffered solutions. The Gas Chromatography-Mass Spectroscopy results show important differences in the yields, in the number of products and in their structural complexity. In particular, a dipeptide, complex dicarboxylic acids, PAHs, and a complete panel of biological nucleobases form more efficiently or exclusively in the borosilicate vessel. Our results suggest the crucial role of mineral catalysis in Miller-Urey synthesis.

Introduction

The 1953's publication of the Miller-Urey experiment opened the door to the scientific investigation of the origin of life¹. In this brilliant experiment, Miller and Urey demonstrated that electrical sparking a mixture of methane, ammonia and hydrogen in the presence of water produces amino acids within a variety of organic compounds. The impact of these results was so high, that its mind opening relevance hardly fades over time². Different gas mixtures have been explored³⁻⁶, and the yielding and molecular diversity were confirmed with modern analytical techniques⁷, including original sample remnants of early Miller experiments^{8,9}. Variations of the original Miller apparatus have been used but the experiments were always performed within borosilicate flasks. Interestingly, the initial pH of most of the canonical mixtures aiming to mimic the early Earth atmosphere in Miller-Urey experiments are highly alkaline. Under these alkaline conditions, silica dissolves: the higher the pH, the higher the solubility of silica (Fig. S1). Therefore, it could be expected that upon contact of the alkaline water with the inner wall of the borosilicate flask, even this reinforced glass will slightly dissolve releasing silica, and offering silanol groups to the gas phase and to the liquid water and vapor. Motivated by the biomimetic role of silica in mineral self-organized structures, such as silica-carbonate biomorphs¹⁰⁻¹² as well as its catalytic role in prebiotic chemistry^{13,14}, we designed a set of experiments to test the possible influence of silica on the yielding of the classical Miller experiments.

Results

Figure 1 shows the experimental concept. Three types of experiments were carried out under two different chemical conditions, one unbuffered with a starting pH value of ca. 11, the other buffered at pH 8.7. One of the experiments was performed in a borosilicate reactor (hereafter BSR) as used in Miller-type experiments. A second was performed in a Teflon® reactor (TFR), a third in a Teflon reactor with centimeter pieces of borosilicate glass submerged in the water (TFBSR). After proceeding with the electrical discharges, the differences in color of the collected samples were visually evident (Fig. S2). In what follows, we describe the results of these experiments.

We used a single flask Miller apparatus where electrodes, water, and the components of the atmosphere were joined in one single reaction flask made either of borosilicate or of Teflon. The borosilicate flask (Duran ®) had a volume of 3L, the Teflon flask of 1,5L (Fig. S3). A Tesla coil provided the 30 kV to ignite the electric arc between the tungsten electrodes. The flasks were filled with water to a volume of 200 mL, so the sparking took place in the gas phase (Figure S4 and S5). All the experiments were performed at room temperature, with a water vapor pressure of ca. 24 mbars, in order to remove thermal effects for a more effective comparison (see further details in SI# 1). We selected one of the most effective Miller atmospheres made of ammonia (200 ± 20 mbar), methane (200 ± 20 mbar), and nitrogen (100 ± 20 mbar). Ammonia and nitrogen are considered ubiquitous components of the early atmosphere^{15,16}. The initial pH value of the water was ca. 11.1 and it decreased during the run by almost two units in the borosilicate flask and one unit in the Teflon reactor. The experiments with the NH_4Cl buffer were aimed to keep the pH constant in the region where the speciation is not only H_4SiO_4^- silicic acid but also has a small contribution of H_3SiO_4^- . They also mimic the presumptive presence of the ammonium ion NH_4^+ in the primitive ocean¹⁷ and optimize the synthesis of amino acids by the Strecker condensation¹⁸. The crude was analyzed by gas chromatography associated to mass spectrometry (GC-MS) after derivatization of the sample to corresponding trimethylsilyl ethers (TMS), the yield of reaction products was calculated as micrograms of product *per* 1.0 mg of crude (SI#1). The most abundant reaction products are described in Fig. 2 and Table S1 (buffered condition) and Table S2 (unbuffered condition), the mass to charge (m/z) ratio values and relative peak abundances of products are in SI #2 (Table S3), while GC chromatograms and original m/z fragmentation spectra are in SI #3 and SI #4, respectively. As shown in Fig. 2 and Tables S1-S2, a large panel of elemental prebiotic chemical precursors (ECP) **1–4**, amino acids and alkyl amines **5–24**, carboxylic acids **25–35**, RNA and DNA nucleobases **36–40**, and aromatic and heteroaromatic derivatives **41–48** were synthesized in different yield and selectivity depending on the specific experimental conditions. The total yield of compounds **1–48** grouped per chemical class similarity is reported in Table 1.

Overall, these results confirm the visual assessment that the brown broth obtained in the borosilicate experiments contained much more organic compounds than those of the Teflon experiments, irrespective of the buffering (Fig. S2; Table 1, entry 7). A larger panel of reaction products was obtained in borosilicate with respect to Teflon alone (48 compounds versus 31; Tables S2-S3), and several amino acids, a dipeptide, carboxylic acids and aromatic miscellanea (for a total of 17 compounds) were produced only in the presence of borosilicate (Tables S2-S3) (Fig. 3A).

Borosilicate increased the yield of ECP **1–4** relative to Teflon alone (Table 1, entry 1). Ab initio atomistic simulation of the Miller-Urey experiment postulated the barrier-less formation of **1** and **2** from a reducing atmosphere¹⁹, and traces of these compounds of key importance in prebiotic chemistry²⁰ were recently detected by mimicking a meteoritic impact in the pristine atmosphere²¹. DAMN **4** is a common intermediate in the synthesis of nucleobases from HCN and **1**, while **3** is a component of the organic pool in the primitive Earth²². A total of 17 amino acids **5–21**, a dipeptide **22**, and two simple amines **23–24**, were detected in the crude (Fig. 2). The total yield of amino acids was higher in the borosilicate flasks

than in Teflon alone (Table 1, entry 2). In addition, amino acids **6–7**, **12–13**, and **17**, and the dipeptide **22**, formed exclusively in the presence of borosilicate (Fig. 2, Tables S1-S2).

Table 1

Total yield of products grouped for chemical class: ECP elemental prebiotic chemical precursors compounds, amino acids, carboxylic acids, nucleobases, aromatic miscellanea, amines.

Entry	Class	BRSB	TFLB	TFLB*	BRS	TFL	TFL*
		Yield (μg product/1.0 mg of crude)					
1	ECP	122,96	31,29	100,91	129,64	35,46	90,18
2	Amino acids	159,45	27,1	60,53	111,19	51,20	87,41
3	Carboxylic acids	36,65	11,91	26,49	46,3	28,21	80,89
4	Nucleobases	14,01	7,34	5,83	16,3	4,69	14,02
5	Aromatic miscellanea	26,95	7,14	10,86	23,07	48,25	33,58
6	Amines	33,80	33,50	34,79	77,07	78,19	69,06
7	Total amount	393,82	118,28	239,41	403,57	246	375,14

BRSB: borosilicate in buffer. TFRB: Teflon® in buffer. TFBSR: Teflon® in buffer in the presence of pieces of borosilicate. BRS: borosilicate without buffer. TFL: Teflon® sin buffer. TFBSR: Teflon® sin buffer in the presence of pieces of borosilicate. ECP: elemental prebiotic chemical precursors

The synthesis of **22**, as well as that of formylated amino acids **20–21** (Fig. 2), is of prebiotic relevance and was probably favored by the formation of carbodiimide from **1**, a borosilicate-catalyzed process²³. Once formed, carbodiimide can activate amino acids towards the formation of the peptide bond with contemporaneous release of urea²⁴. Carboxylic acids **25–35** (from C-1 to C-9) were also identified in the reaction mixture (Fig. 2), the highest total yield being obtained in the presence of borosilicate (Table S3, entry 3). Carboxylic acids **25**, **30–31**, **32** and **35** were absent in the experiment performed in Teflon alone (Tables S1-S2). The beneficial role of borosilicate was further confirmed in the synthesis of nucleobases. In this latter case, borosilicate systems afforded the complete set of nucleobases **36–40**, while only **36**, **39** and **40** were detected in the Teflon flask (Tables S1-S2). Again, the total yield of nucleobases was highest in the presence of borosilicate (Table 1, entry 4). A slightly different behavior was observed in the formation of aromatic miscellanea **41–48**, including polycyclic aromatic derivatives **45–48** (PAHs) (Fig. 2, Tables S1-S2). PAHs are important contributors to the overall pool of organic carbon in the universe, and potential candidates in the “aromatic world” hypothesis²⁵. Aromatic derivatives prevailed in the borosilicate flask under buffered conditions, but this trend was reversed in the absence of the buffer, in which case the highest total yield was obtained in Teflon alone (Table 1, entry 5). The effect of the buffer in the selectivity of the reactions, and possible reaction pathways for the formation of compounds **1–48** are discussed in Supplementary text SI#5.

The key role of the borosilicate reactor in the diversity and yielding of the molecules forming in the discharge experiment is likely due to the existence of silanol groups on the surface of the glass²⁶. The

presence of Si-O-H groups enhanced by the alkaline conditions facilitates the absorption of the organic molecules synthesized in the gas and in the liquid water in contact with the glass²⁷. This explains the formation, few hours after sparking, of a thin brown film covering the inner surface of the borosilicate flask. This film, which was noticed by Miller in his early experiments (1,3), does not form in the Teflon reactors. The film appears as a translucent orange matrix under the optical microscope (Fig. 3B-C). The infrared spectra of the fresh formed film show the characteristic absorption bands for HCN oligomers²⁸. GC-MS confirms that the film is mainly made of HCN oligomers, in accordance with previously reported data. It also shows that it works as a matrix embedding and concentrating organic molecules, including urea **3**, glycine **5**, lactic acid **28**, adenine **36**, cytosine **39**, guanidine **49**, succinic acid **50**, 2,4-diamino-6-hydroxypyrimidine **51**, hypoxanthine **52**, and four polycyclic aromatic hydrocarbons, namely anthracene **53**, chrysene **54**, pyrene **55**, and dibenz(*a,h*) anthracene **56** (Fig. 2, Table S5). Among them, **49–56** were not previously detected in the liquid fraction of the experiment. As a general trend, the total yield of these latter compounds was found to increase after acid hydrolysis²⁸, highlighting the possibility that the treatment favored their extraction from the solid matrix (See supplementary information Table S5 condition A vs condition B). The EDX analysis of the film reveals the existence of a significant amount of silica (Fig. 3F-H and Figure S8). The formation of organosilicon compounds is most likely responsible for the incomplete mass-balance relative to the crude (Table 1). In addition, the highest total yield for the reaction products observed under unbuffered condition is in accordance with a possible role of borosilicate as catalyst for prebiotic processes (Table 1, entry 7).

Discussion

We conclude that the understanding and relevance of the Miller-Urey discharge experiment for the origin of life require extending the classical purely gaseous phase scenario to one including mineral surfaces. This conclusion is especially important in the framework of the new ideas about the Hadean Earth in which the concomitance of a reduced atmosphere, electrical storms, silicate-rich rocky surfaces, and liquid water is expected^{29,30}. Our results demonstrate that mineral surfaces, particularly silica and silicates, drastically enhance known prebiotic synthetic routes in diversity and yielding. In addition, they also trigger the formation of porous insoluble organic matrices that serve as niches for preservation and concentration of forming prebiotic molecules. These abiotic organic films can form during the early stages of Earth-like planets and moons as in the case of Mars and several moons of the solar system^{31–33}.

Declarations

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Author contributions: J. Criado and J.M. García-Ruiz conducted experiments and perform analysis. B. Bizzarri and R. Saladino perform organic chemistry analysis by GC-MS. J.M. García-Ruiz, R. Saladino and E. Di Mauro write the text. J.M. García-Ruiz conceive the work. All authors discussed the results and agreed on conclusions.

Competing interests: Authors declare no competing interests;

Data and materials availability: All data is available in the main text or the supplementary materials.

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Figures

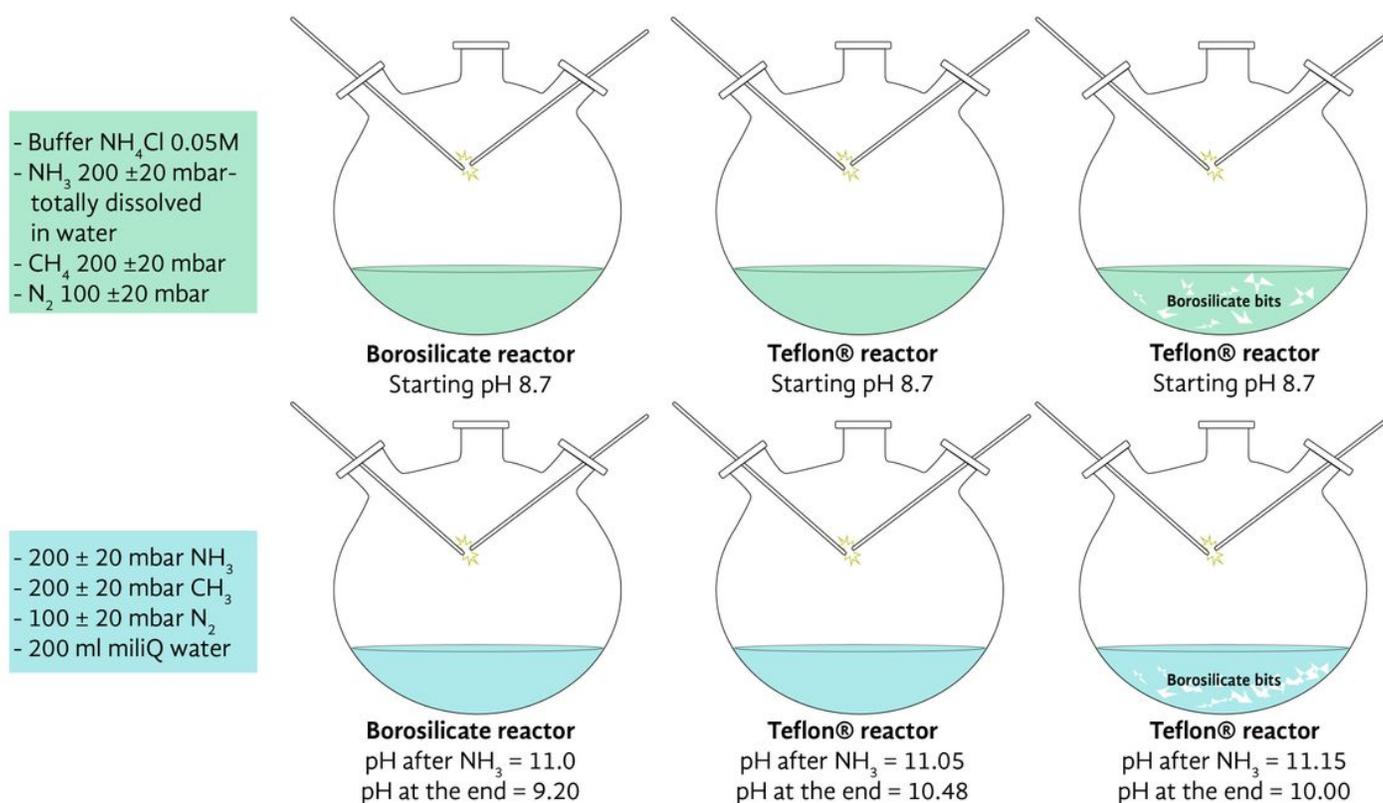


Figure 1

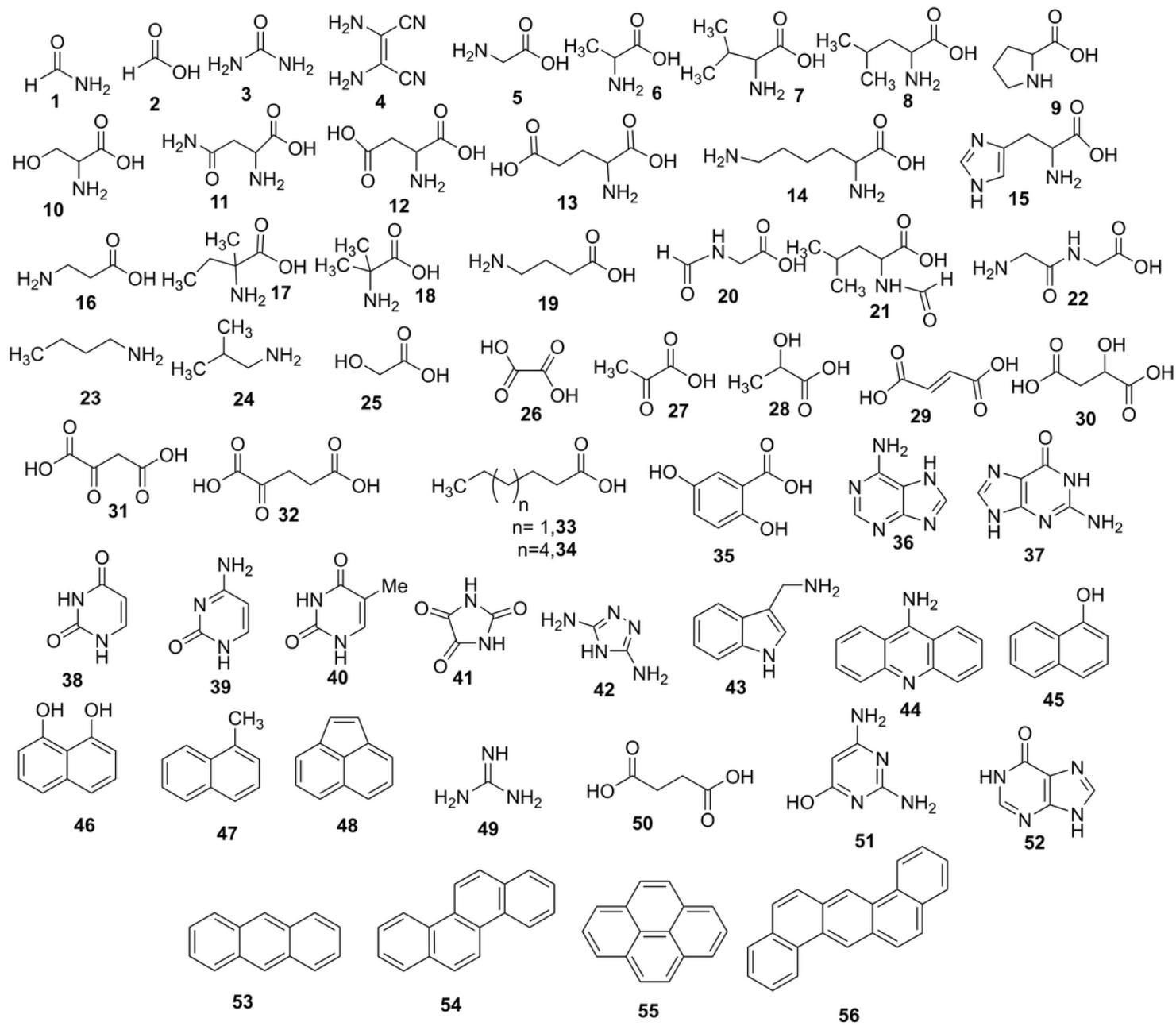


Figure 2

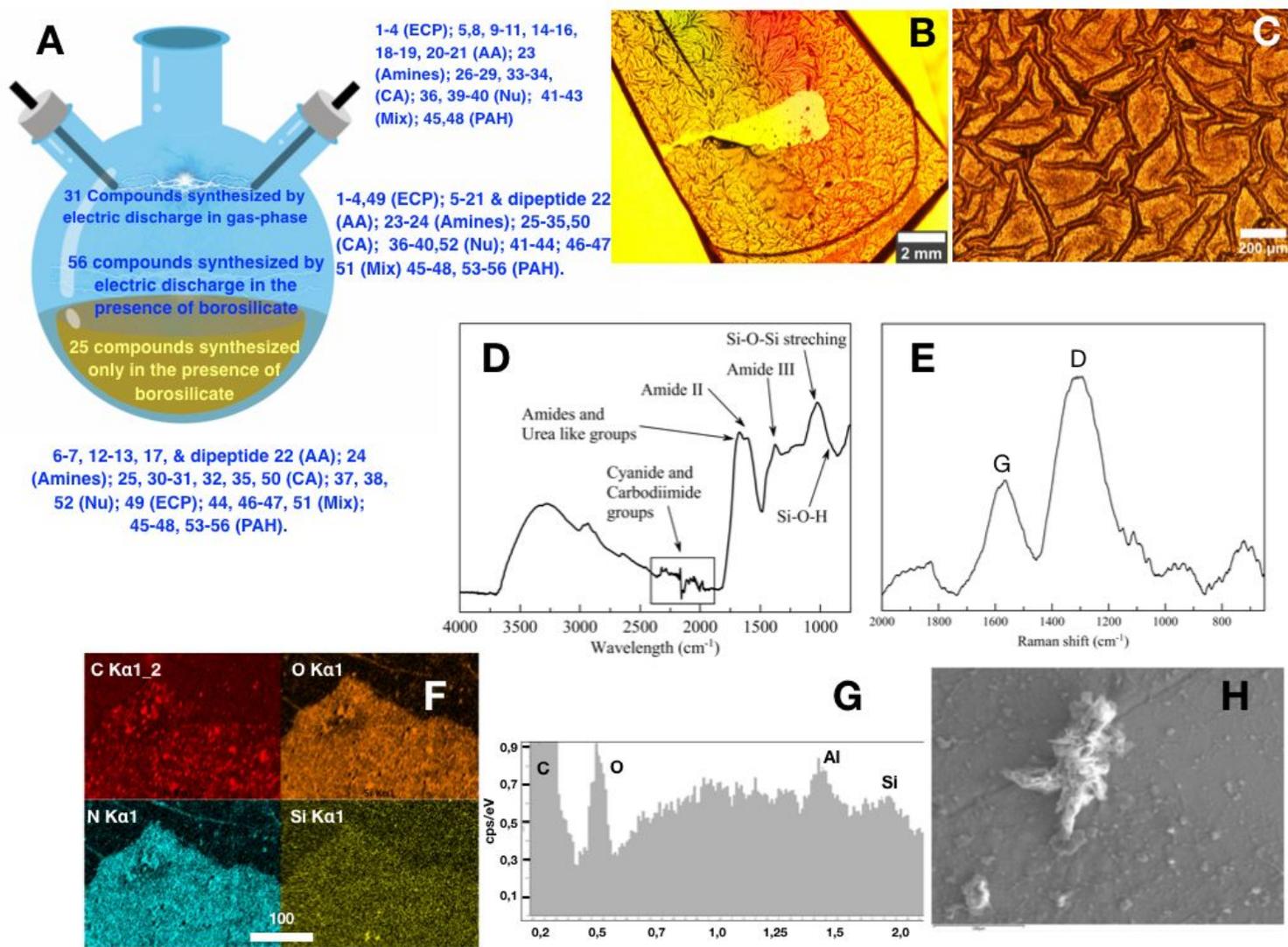


Figure 3

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