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COMMUNICATION

Prebiotic Synthesis at Impact Craters: the Role of Fe-Clays and Iron Meteorites

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Besides delivering plausible prebiotic feedstock molecules and high-energy initiators, extraterrestrial impacts could also affect the process of abiogenesis by altering the early Earth's geological environment in which primitive life was conceived. We show that iron-rich smectites formed by reprocessing of basalts due to the residual post-impact heat could induce the synthesis and accumulation of important prebiotic building blocks such as nucleobases, amino acids and urea.

Isotopic analysis and study of fossil microstructures tentatively suggest that emergence of life on our planet dates back to the first few hundred million years of Earth's history (i.e. 4.56 – 3.8 Gya) associated with a decrease of extraterrestrial impact activity.^{1–3} This might suggest that chemical and physical processes connected to high energy density plasmas could serve as an important driving force of early chemical evolution.⁴

In our previous works we have shown that high-energy-density events could directly induce a unique radical chemistry that could challenge energetically unfavoured steps in the prebiotic synthesis.⁵ Furthermore, impact activity could indirectly influence the direction of these synthetic processes through the enormous mechanical energy of the impacting

extraterrestrial bodies. Heat liberated upon hitting the planetary surface could be comparable to that of volcanic activity. It could thus significantly re-shape the geological environment by inducing serpentinization of the surrounding basaltic rocks leading to the formation of iron containing clays.⁶ So far, most of the prebiotic chemistry-related studies reported utilization of montmorillonite clays. However, recent works⁷ suggest that formation of montmorillonites on the early Earth was likely preceded by that of iron-rich smectites. This indicates that the latter clays could be more relevant targets for prebiotic chemistry studies.

The synthetic potential of formamide as a prebiotic feedstock molecule is exemplified by a series of studies by the Saladino and Di Mauro groups.^{8–10} Formamide may serve as an important intermediate in various other synthetic pathways as well.^{11, 12} This amide is compatible with the ancient geochemistry of our planet¹³ and its chemistry can be tuned by the addition of diverse minerals.⁸ In particular, it has been demonstrated that rock serpentinization processes could be coupled with the formamide-based synthesis of a series of important compounds relevant to prebiotic chemistry.^{14, 15} In our previous study we have found that •CN radicals created during extraterrestrial impacts, when reacting with the cold formamide environment, are able to trigger the formation of all four canonical RNA nucleobases in a one-pot chemistry.^{5, 16} The yield of these reactions can be enhanced by clays.⁵ In the current work we show that a post-impact formamide chemistry involving iron-rich smectites could follow this direct impact plasma-induced prebiotic synthesis. These processes could be enabled by the residual heat liberated in the impact event in the presence of a suitable catalytic material formed by alteration of basaltic rocks or iron-rich impact structures.

We have designed 10 different experiments (see Table 1) combining various clays (for description see the Electronic Supplementary Information), the Ni/Fe meteorite Campo del Cielo, and Fe₂O₃. A particular emphasis was put on the choice of the clay form. We have considered an Fe-smectite as well as Na- and H-form montmorillonites. The structure of the selected

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Electronic Supplementary Information (ESI) available: detailed description of the experiments, characterization of the clays used, description of the analytical techniques used for detection of reaction products. See DOI: 10.1039/x0xx00000x

Fe-clay fundamentally differs from the two montmorillonites because it contains iron incorporated in octahedral framework positions, essentially substituting for Al atoms. Montmorillonites were chosen because prior to us most of the prebiotic chemistry experiments were mainly conducted with this smectite clay family.¹⁷⁻²⁰ In some of the experiments we have considered various mixtures of clays with the Ni/Fe meteorite and Fe₂O₃ powder in order to see the combined effect of terrestrial/extraterrestrial materials on the studied chemistry.[†]

When treating 0.1 g of clay with 2 ml of formamide at 160 °C for 24 hours (see the Electronic Supplementary Information for details on the experimental setup) a wide palette of prebiotically relevant substances has been detected by GC-MS and capillary electrophoresis: all the canonical RNA nucleobases, as well as non-canonical nucleobases (like hypoxanthine and purine), the amino acid glycine, urea and guanidine (see Table 1). It is noteworthy to mention that among nucleobases Fe-containing catalysts particularly promote the synthesis of purine and adenine hinting at the operation of a massive HCN-based reaction channel. Further, Ni/Fe catalysts alone or to a lesser extent in combination with Fe₂O₃ seem to support the formation of cytosine and uracil. In contrast, the above two catalysts exert an inhibitory effect on thymine formation, whereas clays act in the opposite way. In all experiments HCN, ammonia, and CO were detected among the gas-phase reaction products.

As documented in preceding studies,^{5, 18} clay minerals, in general, promote the synthesis of nucleobases. For example, the Na- and H-clays considered in this study lead to a 6-10 fold increase of purine formation as compared to the uncatalyzed case. For guanine, whose thermal synthesis is notoriously inefficient in the absence of catalysts (see experiment 1 in Table 1), catalysis by the Na-clay (see experiment 2 in Table 1) is even more apparent. In general, the catalytic effect of clays is most likely associated with their ability to concentrate the precursor molecules in the interlayer between the aluminosilicate platelets. Our new results point out that Fe-smectites are even better catalysts for nucleobase formation, whereas the overall catalytic effect of Ni/Fe meteorites or Fe₂O₃ on the synthesis of nucleobases is negligible. The latter catalysts, on the other

hand, exhibit an unusually high activity at the formation of urea and guanidine, in line with previously reported results.^{21, 22} This is at variance with Fe-clays, which clearly inhibit formation of urea and guanidine.

Overall, the product compositions observed in the presence of various iron-containing materials seem to be determined by a subtle balance between three main competing reaction channels shown in Figure 1. As our new data (discussed above) and previous studies on formamide thermolysis^{22, 23} illustrate, to a limited extent, these channels are also operational in the

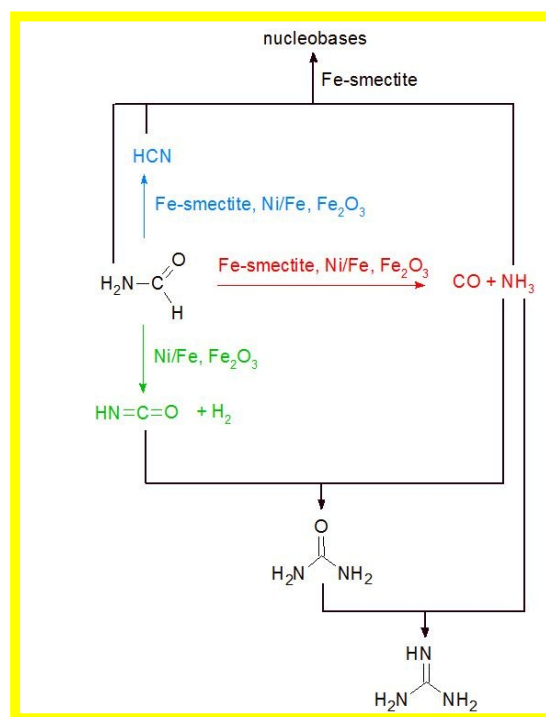


Figure 1. Reaction network of formamide treated at 160 °C for 24 hours in the presence of Fe-clay, Ni/Fe meteorite and Fe₂O₃. The three main dissociation channels (referred to in the text) leading to HCN, CO+NH₃ as well as HNC=O+H₂ are highlighted with blue, red and green colors, respectively.

Table 1: Product compositions after thermal treatment (160 °C, 24 hours) of formamide in presence of various clays, Ni/Fe meteoritic material, Fe₂O₃ and various mixtures thereof. For the gas-phase decomposition products (HCN, NH₃ and CO), we show % vol. as calculated based on the intensity of the absorption lines using calibration standards. Concentration of nucleobases, adenine (A), guanine (G), cytosine (C), thymine (T), uracil (U), purine (P), urea, hypoxanthine (H-X), guanidine (GN), and glycine is expressed in vol. ppm. Products were identified using Fourier transform high resolution infrared spectrometry (FTIR), gas chromatography mass spectrometry (GC-MS) and capillary electrophoresis (CE). Missing number means that the compound was not detected in the analysed sample.

Experiment	1	2	3	4	5	6	7	8	9	10	Detection Method
	Formamide	Fe-Clay	Na-Clay	H-Clay	Fe-Clay + NiFe	Na-Clay + NiFe	H-Clay + NiFe	NiFe	Fe ₂ O ₃	Fe ₂ O ₃ + NiFe	
HCN	3%	8%	1%	1%	8%	1%	3%	8%	10%	7%	FTIR
NH ₃	63%	75%	69%	76%	74%	39%	68%	83%	76%	89%	FTIR
CO	34%	16%	30%	23%	17%	60%	29%	10%	14%	5%	FTIR
A	9	433	30	67	173	159	0.5	23	11	14	GC-MS, CE
G	0.6	11	17	10	7	3		0.2	0.4	0.1	GC-MS
C	10	0.2	16	5	5	12		60	20.0	80	GC-MS
T	19	45	50	51	2	72	56.6				CE
U	41	8	9.5	28	20	16		164		82	GC-MS, CE
P	338	4582	1930	3416	3391	1283	150	531	395	443	GC-MS, CE
H-X	10	56	13	12	21	4.0	2	28	17	15	GC-MS
GN	114		1	8	10		0.5	877	475	1052	GC-MS
Urea	>10000	517	2380	4100	9470	2950	255	25455	19366	20799	GC-MS
Glycine	1	1	0.5	3	0.6	0.3	0.6	2	2	3	GC-MS

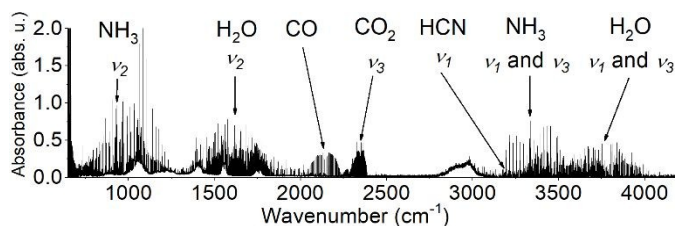


Figure 2. FTIR spectrum of the gas phase reaction products formed when heating formamide (160 °C, 24 hours) in the presence of an Fe-smectite.

absence of catalysts. Our new data suggest that all three iron-containing catalysts (i.e. Ni/Fe meteoritic materials, Fe₂O₃⁸ and Fe-smectites) favour the dehydration of formamide to HCN^{55, 24} (blue reaction channel in Figure 1; see Table 1 and the gas-phase spectrum in Figure 2) as well as the parallel formation of NH₃ and CO (red reaction channel in Figure 1). The formidable amount of urea formed in experiments **8**, **9** and **10** (see Table 1) reveals that the third reaction channel, i.e., the dehydrogenation of formamide to HNCO (green reaction channel in Figure 1), is significant only with Ni/Fe meteorites and Fe₂O₃. Accordingly with the latter finding, literature data also support the fact that the Ni(111) surface may catalyse the decomposition of formamide to HNCO.²⁵ Fe-smectites, on the other hand, are more compatible with a subsequent HCN-related chemistry, which is illustrated by the accumulation of purine and other nucleobases in experiment **2** (see Table 1 and Figure 3).

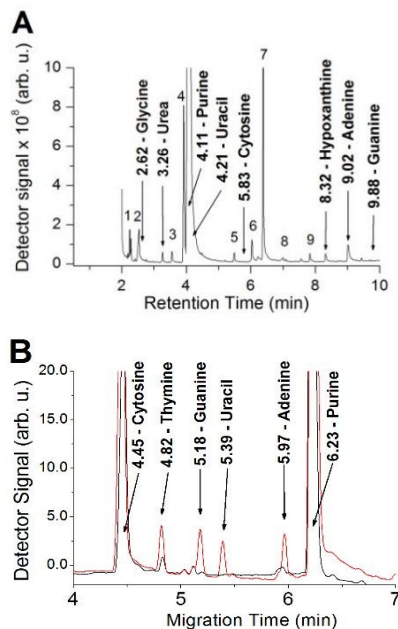


Figure 3. Detection of nucleobases, glycine and urea formed upon thermal treatment of formamide (160 °C, 24 hours) in the presence of Fe-smectites using GC-MS (panel A) and capillary electrophoresis (panel B). Red curve: standard, black curve: sample. For more analytical data see chapter SIV in the Electronic Supplementary Information. The numbered low intensity signals correspond to non-specific by-products of the derivatization reaction.

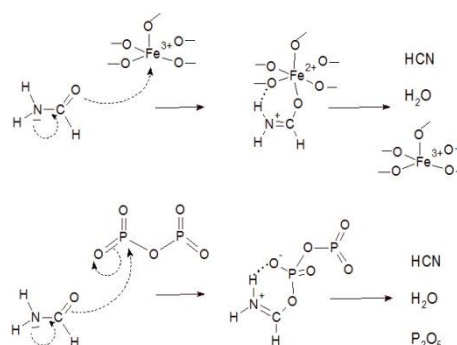


Figure 4. Suggested mechanism for the dehydration of formamide to HCN catalysed by Fe-defects present in the octahedral sheets of Fe-smectites (upper row) and P₂O₅ (lower row, based on Ref. ²⁶).

Remarkably, formation of nucleobases seems to be more compatible with Fe-smectites than with Na- or H-montmorillonites. Indeed, it has been suggested that the latter two clay forms were much less common in the Earth's crust by the time when life emerged on our planet.⁷

When mixing various forms of montmorillonites with Ni/Fe meteoritic materials, the product composition is determined by the competition of the three above-listed reaction channels. Thus, adding Ni/Fe-meteorites to Fe-montmorillonites clearly shifts the product composition towards urea. By contrast, the overall reactivity is nearly lost when mixing Ni/Fe-meteorites and H-form clays together, most likely because the H-form clays readily bind NH₃ and make the conversion of HNCO to urea impossible. Thus, whilst Ni/Fe meteoritic materials do not seem to directly participate in the synthetic processes leading to the first biological building blocks, they could be involved in the synthesis of guanidine, a prebiotically highly relevant condensing agent derived from urea (see the reaction scheme in Figure 1).

In general, iron-containing clays, Ni/Fe meteorites or Fe₂O₃ exhibited higher catalytic activity in the studied reactions than the iron-free clay forms. Our data clearly demonstrate that the direction of prebiotic synthetic processes is dependent on the binding mode of iron inside the catalytic material. Cationic iron incorporated in the octahedral sheets of Fe-smectites seems to be especially well-suited to catalyse prebiotic synthesis leading to nucleobases, which may be associated with the advantages arising when combining the rich chemistry of the Fe²⁺/Fe³⁺ redox system⁷ with the unique three-dimensional architecture of clay minerals. The latter enables Fe³⁺ centers incorporated in defects of Fe-smectites to behave as Lewis-acidic sites which, similar to P₂O₅²⁶ or other P-containing organocatalysts,²⁷ may catalyse the dehydration of formamide to HCN according to the tentative mechanism shown in Figure 4. The clay structure may then catalyse the subsequent reaction steps leading to nucleobase formation due to concentration of the key reactants, i.e. formamide, HCN and NH₃. While HCN does form

in comparable amounts also over Ni/Fe meteorites as well as over Fe₂O₃, due to the lack of the above-mentioned concentration effects, these catalysts fail to structurally support the chemistry required to synthesize more complex molecules than urea or guanidine.

Data presented above clearly suggest that impact reprocessing of the geological environment could finely tune the composition of the prebiotic broth: whilst Ni/Fe meteoritic materials and iron-oxides favour the formation of urea from formamide, Fe-smectites formed upon serpentinization of basaltic rocks⁷ are better suited to catalyse an HCN-mediated formamide chemistry. Thus, the change of the geological milieu and the temporary availability of various energy sources could have determined the sequence of synthetic events in the early ages of our planet.

The robustness of a prebiotic synthetic scenario is highly dependent on the versatility of energy sources and reaction routes leading from the reactants to the products.²⁸ The current results provide a striking example for this variability through the synthesis of nucleobases. This process can be triggered by a radical chemistry⁵ in an extraterrestrial impact event as well as by a simple thermal chemistry using impact-altered rocks containing Fe-smectites. Fe-smectites could have been widespread on the early Earth also from rock serpentinization driven by geothermal energy. All these findings point out the importance of mineral catalysis in a formamide-based abiogenesis on our planet.

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Conflicts of interest

There are no conflicts of interest to declare.

Notes and references

‡ Note that extraterrestrial impacts inevitably led to a massive mixing of terrestrial and extraterrestrial materials during the Late Heavy Bombardment period.

§ Note that metal-oxides are highly relevant to serpentinization processes as well. A recent study illustrates that silica metal-oxide vesicles formed in serpentinizing rocks possess unique catalytic properties and could contribute to the synthesis of a vast range of important prebiotic building blocks, such as nucleobases, amino acids and carboxylic acids.¹⁵

§§ Note that a popular industrial process used for HCN-synthesis from formamide also utilizes iron salts as a catalyst²⁴.

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