

Research Article

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Micro-impact-induced mechano-chemical synthesis of organic precursors from FeC/FeN and carbonates/nitrates in water and its extension to nucleobases

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Abstract: Much effort was taken to elucidate how organic precursors appeared in early Earth, and attention was paid to two impact experiments: hypervelocity impacts by a propellant gun which simulated meteorite collides to Earth forming fatty acids and amino acids from inorganics, and micro-impacts by a planetary ball-mill which formed ammonium and acetic acid from inorganics. Our extended study on micro-impacts showed the formation of carboxylic acids, amines, and amino acids from Fe₃C/Fe₄N, carbon, and carbonates/nitrates by milling up to 30 h at 40 G. Fe(CO₂)₂·2H₂O accelerated the formation a step further. Cu addition caused superior capability to form amines and amino acids. Two reaction fields were disclosed. In the impact field, the hydration of ferrous materials generated hydrogen which hydrogenated inorganic carbons to organics and ferrous transient materials and, in the maturing field, hydrogenated materials were then transformed into complex organics. Iron and CO₂ were presumably the key components in the Hadean Ocean. Discussions on the mechano-chemical reaction were extended to serpentinization coupled with diastrophism of oceanic crusts and further led to a depiction that organic precursors were formed by micro-impacts and

frictions of rocks and sands (like milling-balls) due to tremors in crusts. It provides a new path on how organic precursors were formed on the aqua-planet Earth.

Keywords: mechano-chemical, micro-impact, precursor, hypocenter, serpentinization

1 Introduction

Much effort has been paid to elucidate how organic precursors, the origin of life, appeared in the inorganic world of early Earth. Simple gears like Miller's synthesis [1,2] were used in the early days. Recently, sophisticated means like the asteroid Ryugu mission in space [3] and hypervelocity impacts by a propellant gun simulating meteorite collides to Earth [4–6] were deployed. The most recent challenge by a ball-milling, an old-fashioned technology, also showed the formation of ammonium and acetic acid from Fe₃C and Fe₄N in water [7]. Based on these findings, new challenges were encountered to form more complex organic molecules and further to clarify effects of the mechano-chemical (MeChem hereafter) reaction, which formed organics from inorganic materials.

As illustrated in Figure 1, there are mainly two reaction fields. One is an impact field where collisions of small milling balls ($\phi = 2$ mm) produce a temperature exceeding 1,000 K and a high pressure [8,9] and transform the starting inorganic materials to new materials, stable or unstable, which are then quenched. The produced energies at the field are moderate and far less than hypervelocity impacts, which generate a high temperature (>2,900 K) and a pressure (20 GPa) [6]. The other is a maturing field where newly formed materials react with each other to form stabler materials, probably enhanced by the friction of balls. It should be noticed that, in both fields, materials are built up to more complex organic materials

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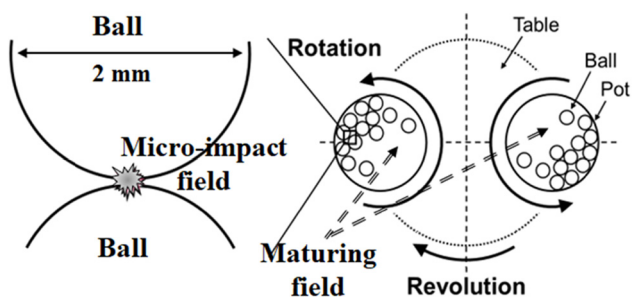


Figure 1: A schematic illustration of micro-impact and maturing fields.

and at the same time broken down to simpler organic materials. Since there is no organic material provided in the beginning, built-up reactions are taking place as a whole.

In the previous experiments, it was frequently observed that pots were too tight to open after milling. It was simply due to the abnormal pressure built up. The excess hydrogen formation was caused in part by a reaction of eroded metal pots with water, and an extremely high hydrogen pressure was seemingly very harmful to obtain organics effectively. Thus, ZrO_2 -coated pots were introduced, and amounts of starting materials were also reduced to prevent excessive hydrogen pressure in this study. As starting materials, solid C, FeS, FeSO_4 , NaNO_3 , and Cu were used in addition to Fe_4C , Fe_3N , $\text{Fe}(\text{NO}_3)_3$, CaCO_3 , and MnCO_3 which were used in the previous experiment. These compounds were assumed to be activated by the versatile MeChem reaction. $\text{Fe}(\text{CO})_2$ was also introduced as a good carbon source since it decomposes to CO, CO_2 , and Fe_3O_4 at about 600 K. The introduction was also expected to prevent pressure build-up and thus larger starting amounts could be applied. Furthermore, it might easily produce HCOOH and enhance the formation of organics at a step higher. Cu was introduced to observe its affinity with NH_3 . The clay, montmorillonite, was expected to enhance reactions, first by increasing viscosities of muddy liquids, second by adsorbing organics as Fuller's earth, and third by catalytic actions like Lewis acidic centers.

Finally, discussions are developed on how starting inorganic materials transformed to organics by the MeChem reaction and extended further; how organic precursors were formed 4 billion years ago with regard to serpentinization, diastrophism of terrestrial crusts, and global carbon/nitrogen cycles on early Earth.

2 Materials and methods

To produce micro-impacts, a planetary ball mill ("High-G" X382; Kurimoto, Ltd., Japan) was used. The mill

accommodated two pots at a time and created a centrifugal acceleration of up to 150 G (rotating in the same planetary direction) continuously for days. Pot temperatures were kept below about 330 K by forced cooling. Zirconia-coated pots were used to avoid undesirable metal erosion causing high hydrogen pressures. Zirconia balls with a diameter of 2 mm were also used as milling balls. The centrifugal acceleration G was estimated using mechanical dimensions such as revolution and diameters based on the equation by Hashishin *et al.* [10].

As starting materials, Fe_4N , Cu powder (Kojundo Chemical Laboratory, Japan), Fe_3C (Rare Metallic, Japan), $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Fe}(\text{CO})_2 \cdot 2\text{H}_2\text{O}$, CaCO_3 , MnCO_3 , $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, FeS (Kanto Chemical, Japan), montmorillonite (Alfa Aesar, UK), and Ketjen black (Nippon Ketjen, Japan) for solid carbon were used. To eliminate possible organic contamination, Ketjen black and Cu powders were fired at 1,073 K and 873 K for 2 h in nitrogen flow, respectively.

Experimental conditions and starting materials are summarized in Table 1. Notice that the total amount of starting materials in this experiment was about 10 g or more; in most cases, it was far greater than the amount of about 100 mg in propellant gun experiments [5,6]. Larger starting amounts resulted in larger amounts of final products, which made chemical analyses much easier. Milling operations were carried out at 40 G (rotating in the reverse planetary direction) for 30 h, except #12–14 (10, 6.5, and 3.5 h, respectively) and #15 and 16 (20 h). After milling, muddy products were separated into liquids and solids by centrifugation. For organic analyses, the liquids were only used although the solids might contain some organics. The solids were dried in a cool box for XRD analyses. Some were dried at 373 K for further XRD analyses.

The amount of organic carbon and nitrogen in liquids was evaluated using a total organic carbon analyzer (TOC; TOC-LCPH; Shimadzu, Japan). The organics were analyzed at the Analytical Institute (Qualtec Co., Ltd., Japan) using a gas chromatograph mass spectrometer (GC-MS; GC-MS-QP2010Ultra, column: DB-5 at MS Scan: 35–300, MS SIM: 26, 27, 28, 29, 30, sphere 31, 32, 42, 43, 44, 45, 46, 58, 60, 73, 76; Shimadzu, Japan) following the standard procedure as described before [7]. Some specimens were evaluated at the Tohoku University using an ultra-high-performance liquid chromatograph tandem mass spectrometry (LC-MSMS; LCMS-8040; UHPLC/MSMS, Shimadzu, Japan) after derivatization with the AccQ-Tag reagent (Waters, USA). The details of the UHPLC/MSMS conditions are described elsewhere [11,12]. Crystalline phases of the solids were identified by powder X-ray diffraction (XRD; D2 PHASER; Bruker AXS, Germany with its XRD software) using Cu $\text{K}\alpha$ radiation. A few

Table 1: Starting materials (weight in g) and milling time

No.	Fe ₄ N	NO ₃	C	Fe ₃ C	FeCO ₂	M*	H ₂ O	Others	Milling time (h)
#1	2.701			2.057		0.503	162.0	FeS 0.105 MnCO ₃ 5.245	30
#2	2.480			2.501	5.020	0.507	161.4	FeS 0.101	30
#3	1.958			1.410		0.510	160.0	FeSO ₄ 12.873 CaCO ₃ 3.768	30
#4						0.502	180.2	FeS 3.018	30
#8	9.953			0.643	11.303	1.070	170.1		30
#9	10.005			1.008	11.358		170.0	*1 NH ₄ C 2.067	30
#10	2.415		0.480			1.000	189.1		30
#11	1.001		0.194				192.0	*2 NH ₄ C 1.029	30
#12	8.339			0.700	9.010	0.301	170.2	*3 FeS 0.498	10
#13	8.340			0.702	8.998	0.300	170.4	*3 FeS 0.501	6.5
#14	8.341			0.699	9.006	0.299	175.9	*3 FeS 0.508	3.5
#15		Na 1.700			7.198		170.0	Cu 11.713	20
#16		Fe 2.699			7.200		170.0	Cu 11.138	20

M*: montmorillonite, FeNO₃: Fe(NO₃)₃·9H₂O, Na: NaNO₃, NH₄C: (NH₄)₂CO₃, FeCO₂: Fe(CO₂)₂·2H₂O; *1 CeO₂ 0.119 La₂O₃ 0.102 YCl₃·6H₂O 0.177; *2 CeO₂ 0.101 La₂O₃ 0.093 YCl₃·6H₂O 0.128 ErCl₃·6H₂O 0.091; *3 AgNO₃ 0.105 ZnCl₂ 0.107 ZnO 0.104 CuCO₃Cu(OH)·2H₂O 0.105 all within ±0.005.

liquids were evaluated by X-ray fluorescence analysis (ED-XRF; Rayny EDX-800; Shimadzu, Japan) to check metal contents.

3 Results and discussion

It was evident that no gas blew out from pots when opened in the course of this experiment as expected. Zirconia coatings of the pots were clearly effective in reducing excessive gas built-up (hydrogen and presumably CH₄). It was also noticed that specimens were generally dark brown or black muds when pots were opened and that some specimens showed light brown or yellow color and turned to black when exposed to air. This was simply due to the fact that the atmosphere in pots was strongly reductive and ferrous Fe was oxidized to ferric. When montmorillonite was present, muddy specimens were very viscous and occasionally bubbles were observed for a while after opening pots. Bubbles probably indicated degassing of CO₂ from muds. Sewage-like odors indicated the formation of some organics. Most liquids were transparent but few showed slight bluish-green color, which was an indication of Fe ions in liquids. The specimen #15 (#15 hereafter) showed a fine blue color. ED-XRF analyses revealed that it contained Cu ions of 860 ppm and Fe of 120 ppm, and #16 showed very slight green color and contained only Cu of 270 ppm.

Typical organics observed by GC-MS measurements were ethanol, acetone, formic acid, and acetic acid as shown in Figure 2. These results are summarized in

Table 2 along with TOC values, magnetization, and pH changes. High TOC values obviously showed the formation of some organics. An increase in pH values was simply due to NH₃ formation from Fe₄N, Fe(NO₃)₃, or NaNO₃ [7,13,14]. Magnetization was a sensible indicator of magnetite formation and most specimens showed its presence, even if its presence was very small.

3.1 Organic analyses of the liquids

Based on the characteristics of starting materials, specimens are assembled into five groups in the following discussion, namely #4 which contained no carbon source, Group1 (#10 and #11) which contained solid C, Group2 (#1 and #3) which contained Fe₄C but no Fe₂(CO₂)₂, Group3 (#2, #8, #9, #12, #13, and #14) which contained Fe(CO₂)₂, and Group4 (#15 and #16) which contained Cu. The assembling clearly visualized features of the observed results in Table 2 as shown in Figure 3 (amount of formic acid and acetic acid vs TOC values). The observed features are as follows:

1. The TOC value of #4, 21 mg·L⁻¹, was the lowest among the specimens. Since the starting materials of #4 (blank specimen) contained no carbon sources, the TOC value of 21 mg·L⁻¹ was mostly due to some organic contaminants. Considering that no nitrogen was detected (Table 4), the organic contaminants were most likely botanical fabrics, cellulose, and not surfactants or proteins which generally contain nitrogen. The TOC values exceeding 21 mg·L⁻¹ were thus proofs of some organic formations. All specimens in Groups 1–4 showed higher TOC values and formed some organics doubtlessly.

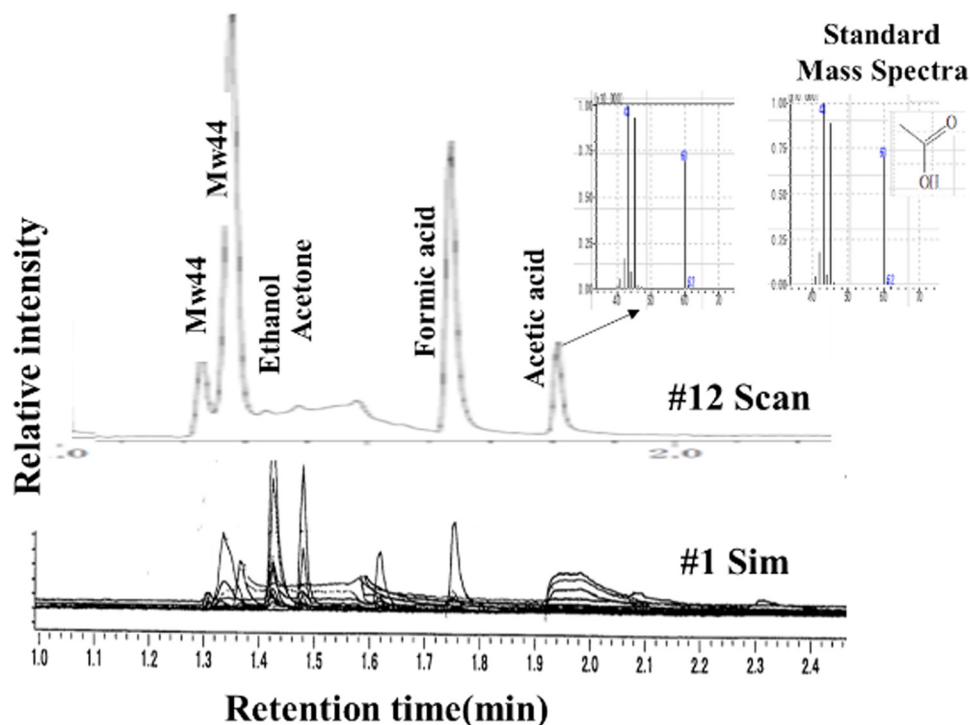


Figure 2: GC-MS chromatograms and spectra of specimens #1 and #12.

- TOC values of any specimens were far greater than total amounts of detected organics by GC-MS measurements. The differences were clearly due to numerous organics which were below the detection limits of GC-MS measurements.
- Three zones (#4 ignored) are observed in Figure 3. It was apparent that TOC values of Group1 < Group2 < Group3 and that amounts of two acids also showed the same behavior; Group1 < Group2 < Group3 as a whole.
- Comparing these behaviors with characteristics of Group1 (contained only solid C), Group2 (contained Fe_3C), and Group3 (contained $\text{Fe}(\text{CO})_2$), it was deduced that activities of carbon were in order of solid carbon < Fe_3C < $\text{Fe}(\text{CO})_2$ to produce organics under these experimental conditions.
- #11 showed remarkably higher amounts of carboxylic acids than #10, although their TOC values did not show such a big difference. This irregularity of #11 is

Table 2: Summary of experimental results of TOC ($\text{mg}\cdot\text{L}^{-1}$), GC-MS (ppm), and pH

No.	TOC	Ethanol	Acetone	Formic acid	Acetic acid	Magnetism	pH change	Group
#1	97	6	7	TR	TR	Y	7 → 9	G2
#2	492	4	7	196	187	Y	5 → 9	G3
#3	114	6	8	BD	TR	Y	4 → 7	G2
#4	21	BD	BD	BD	BD	No	7 → 7	#4
#8	947	BD	21	850	86	Y	5 → 12	G3
#9	648	BD	26	581	101	Y	10 → 11	G3
#10	32	30	20	BD	BD	Y	7 → 12	G1
#11	49	BD	19	57	67	No	10 → 11	G1
#12	402	TR	BD	378	93	Y	10 → 12	G3
#13	334	BD	BD	245	86	Y	10 → 12	G3
#14	255	BD	BD	172	71	Y	10 → 12	G3
#15	1,046	TR	TR	TR	20	No	6 → 7	G4
#16	332	TR	TR	TR	TR	No	4 → 7	G4

TR: trace amount; BD: below detection.

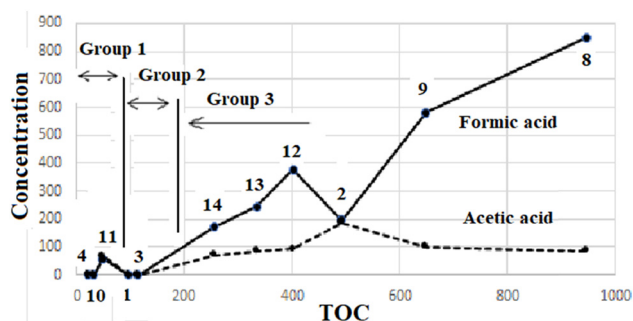


Figure 3: TOC values vs carboxylic acid concentrations of specimens #1 to #14.

discussed with respect to yields of carbon and mass balances later.

An example of LC-MSMS measurements is shown in Figure 4, and measurement results are summarized in Table 3. Simple amino acids like glycine and alanine were mainly observed, and serine, sarcosine, and valine were rarely observed. When amounts of glycine and alanine were plotted against TOC values (Figure 5), the same zone behavior as that in Figure 3 was observed. Implications by LC-MSMS measurements are as follows:

1. Three zones (Group1, Group2, and Group4) showed that amounts of amines and amino acids trailed the same behavior as discussed above. It showed again that the activities of carbon were in order of solid carbon < Fe_3C < $\text{Fe}(\text{CO})_2$ as discussed above.
2. Group4 showed higher amounts of amines and amino acids than other groups. Since Cu was contained only in Group4, Cu might have an unusual effect different from Fe.
3. #4 (blank specimen) showed small amounts of contaminant amines and amino acids. These amounts were so small to be reflected in TOC values.
4. B-alanine showed abnormally large values which were not related to TOC values at all. It was assumed that there was some systematic contamination associated

with the experimental setup. Although the cause of the contamination was unclear, the formation of amines and other amino acids was certain in all specimens of Groups 2–4 as stated just above.

All of the above discussions based on TOC, GC-MS, and LC-MSMS measurements clearly proved that the MeChem reaction was effective to form organic materials like alcohols, carboxylic acids, amines, and amino acids from inorganic materials like Fe_4C , Fe_3N , and carbonate/nitrates.

3.2 Mass balances of carbon, nitrogen, and inorganic materials

Yields of inorganic carbon in starting materials to organics (Yield.C) were calculated based on the data listed in Tables 1 and 2, and summarized in Table 4 along with TOC, Calc.C, Obs.N, Calc.N, and Yield.N. From Table 4, some aspects of the MeChem reaction were elucidated as follows:

1. All Yield.C values except #4 were in a range of 0.01–0.18 which were extremely higher than those reported by Furukawa et al. [6]. This was simply due to numerous micro-impacts, millions of million repetitions of the MeChem reaction.
2. As pointed out above, #11 of Group1 showed remarkably higher contents of carboxylic acids than #10 of the same Group1. #11 also showed a higher Yield.C of 0.03 than 0.01 of #10. Since NH_4CO_3 was only the difference between #10 and #11 (Table 2), NH_4CO_3 was provably more active carbon source than solid C to form carboxylic acids.
3. Among Group2 (containing Fe_3C), #3 showed the second highest Yield.C value of 0.16, while #1 showed a moderate value of 0.09. The second highest value was probably due to the reaction of CaCO_3 and FeSO_4 forming CaSO_4 and Fe_3O_4 as observed in #3 (Figure 6). In the reaction, hydrogen was generated by the

Table 3: Summary of experimental results of LC-MSMS (in μM)

No.	TOC	Methylamine	Ethylamine	Gly	Ala	B-Ala	Ser	Sar	Val
#4	21	0.06	0.07	0.04	0.01	0.2	BD	BD	TR
#11	49	0.07	0.03	0.03	0.01	1.5	BD	TR	TR
#1	97	0.3	0.1	0.1	0.10	0.2	0.03	BD	0.03
#16	332	1.0	0.2	0.3	0.05	0.2	TR	BD	0.01
#15	1,046	0.3	0.3	0.1	0.04	0.2	TR	TR	TR

TR: trace amount; BD: below detection.

Table 4: Amount of carbon and nitrogen before and after milling and their yields

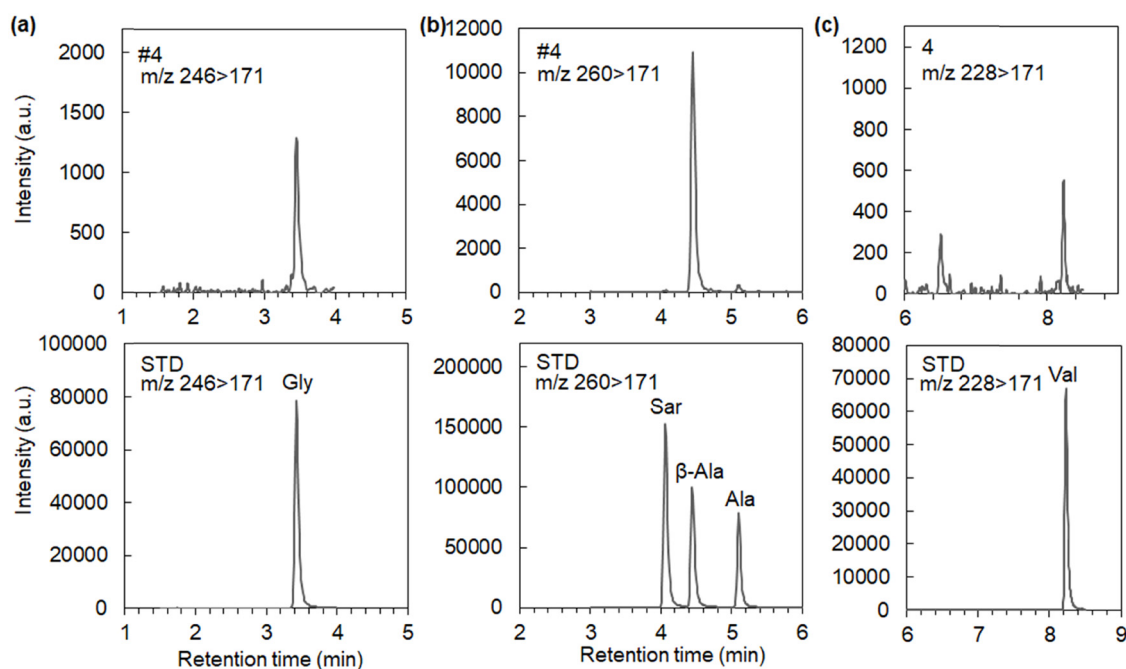
No.	TOC	Calc.C	Yield.C	Obs.N	Calc.N	Yield.N	Group
#1	97	849	0.09	750	984	0.76	G2
#2	492	5,189	0.09	513	907	0.57	G3
#3	114	589	0.16	571	722	0.79	G2
#4	21	0	—	0	0	—	#4
#8	947	9,125	0.1	1,724	3,453	0.5	G3
#9	648	9,317	0.07	3,443	7,018	0.49	G3
#10	32	2,538	0.01	568	754	0.75	G1
#11	49	1,010	0.03	1,670	1,870	0.89	G1
#12	402	7,067	0.05	2,078	4,090	0.51	G3
#13	334	7,051	0.04	1,513	4,090	0.37	G3
#14	255	6,837	0.03	1,048	3,958	0.26	G3
#15	1,046	5,653	0.18	911	1,648	0.55	G4
#16	332	5,655	0.06	622	1,651	0.38	G4

Calc.C: all carbon content of starting materials excluding CO_3 , in $\text{mg}\cdot\text{L}^{-1}$; calc.N: all nitrogen content of starting materials, in $\text{mg}\cdot\text{L}^{-1}$; obs.N: nitrogen content in liquid after milling observed by the TOC measurement, in $\text{mg}\cdot\text{L}^{-1}$; Yield.C: yield of inorganic carbon to organic carbon in liquid, $(\text{TOC}-21)/\text{Calc.C}$; Yield.N: yield of nitrogen, $\text{Obs.N}/\text{Calc.N}$: In this calculation, CO_3 was excluded since strong tendency of C to form CO_2 was assumed.

hydrothermal oxidation of ferrous Fe to ferric and, at the same time, CO_2 was released from CaCO_3 when CaSO_4 formed. Newly generated hydrogen reduced CO_2 to CH_4 and further to simple organics, while CaCO_3 and MnCO_3 without FeSO_4 were rather stable as also shown in Figure 6. The series of reactions is just like the serpentinization reaction that ultramafic

rocks react with carbonated sea water forming H_2 , CH_4 , and Fe_3O_4 [15,16].

4. A Yield.C of 0.18 and also the highest TOC of $1,046\text{ mg}\cdot\text{L}^{-1}$ was realized by #15 in which the liquid uniquely showed a clear blue color. Since the liquid contained high Cu ions of 860 ppm, Fe of 120 ppm (no Na ions observed), and since the solid contained CuCN as

**Figure 4:** LC-MSMS spectra of specimen #4. MRM chromatograms of AccQ-derivatized (a) glycine, (b) C3 amino acids, and (c) valine and their referential standards.

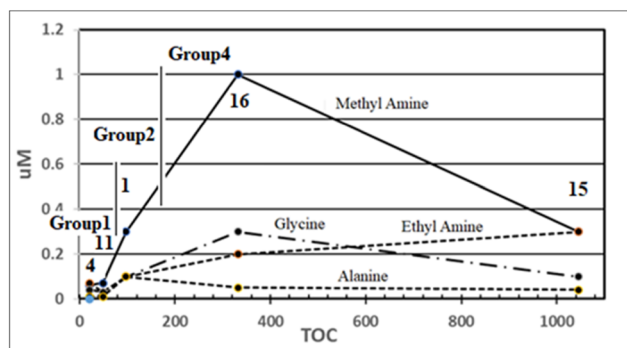


Figure 5: Amounts of amines and amino acids vs TOC values of #4, #11, #1, #16, and #15.

shown in Figure 6, the liquid most probably contained some Cu/Fe/CN/NH₃ complexes and NH₄CN. CN ions in the liquid contributed to high values.

- Group4 (#15 and #16) showed the highest TOC values and higher contents of amines and amino acids. This was apparently due to either Cu or NO₃ (Table 1). More studies are necessary in combination with the CN formation.
- The presence of CN ions reminds us of the well-known reactions, HCN chemistry [17] and Strecker amino acid synthesis [18]. The formation of nucleobases from HCN [19] and HCN with NH₃ [20] and also from formamide in the presence of goethite [21] was reported. Furthermore, extensive discussions have been

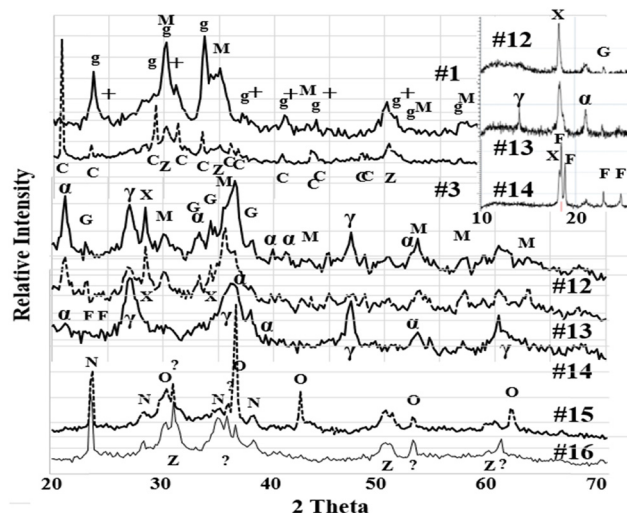


Figure 6: Some XRD patterns of solid products after high-energy ball millings. Note that #1 and #3 were in Group2, #12, #13, and #14 in Group3, and #15 and #16 in Group4. Insets: XRD patterns of #12, #13, and #14 after heat dried at 373 K. M: magnetite, G: green rust, g: pseud-Fe(HCO₃)₂, α: α-FeOOH, γ: γ-FeOOH, F: Fe(CO₂)₂, C: CaSO₄, +: MnCO₃, Z: ZrO₂, N: CuCN, O: Cu₂O, X: Fe glucose.

made whether the traditional HCN-based concept or the formamide-based scenario [22,23] is the most probable hypothesis for the origin of life. These reports strongly suggest that nucleobases like adenine could be formed in #15 and #16, which contained CN⁻ and NH₃. Nucleobase formations by hypervelocity impacts [11] also support this hypothesis.

- XRD patterns (Figure 6) reveal that Fe₄C, Fe₃N, FeS, and Fe(CO₂)₂ in water transformed to mainly magnetite, goethite, and transient-Fe and/or green rust and that, during the transformation, the generated hydrogen hydrogenated carbon and CO₂ to organics as discussed above. XRD diffraction lines marked as “g” correspond to Fe(HCO₃)₂:PDF00-007-0043, the source of which was not reliable. However, considering the unintentional coincidence of patterns and ferrous experimental conditions rich in CO₃, it is not unreasonable to assume compound g as the remains of Fe(HCO₃)₂. It is, thus, expressed as transient-Fe. Nitrogen transformed mostly to NH₃. When Cu was present (#15 and #16), CuCN and Cu₂O were formed as solids, and CN and NH₄ ions were in liquids as stated above. The different effects of Fe and Cu suggest that some other metals might show superior effects and efficiencies to form organics.
- Unaccounted carbons such as TOC were probably in the form of gases like CO₂ and CH₄ and in solid compounds like C and transient-Fe/green rust. Carbon could be produced by the de-hydrogenation of CH₄ with a Fe-based catalyst [24,25].
- The nitrogen in Fe₃N, NaNO₃, and Fe(NO₃)₃ was transformed to mostly NH₄NO₃, some solids, and probably N₂ [7] as well as recovered in liquids by 50–90%. Exceptions were #13, #14, and #16. #13 and #14 were only milled by short milling at 3.5 and 6.5 h, respectively, and thus unreacted components remained in solids. In the case of #16, CuCN formation was the cause of the low nitrogen in its liquid.
- Chemical analyses of solids, which were beyond our capabilities, should have yielded organic formation and might reveal some effects of montmorillonite although any clear effect of montmorillonite was observed in this study.

Phase changes observed in #12, #13, and #14 (Figure 6) disclosed some dynamic aspects of the MeChem reaction. After 3.5 h of milling (#14), Fe(CO₂)₂ almost disappeared. All other starting materials also disappeared and α- and γ-FeOOH were dominant. After 6.5 h (#13), Fe₃O₄, green rust, and/or transient-Fe appeared adding to α- and

γ -FeOOH while $\text{Fe}(\text{CO}_2)_2$ disappeared. However, the XRD pattern of #13 after heat treatment (Insets) still showed a small amount of $\text{Fe}(\text{CO}_2)_2$, which was in amorphous or nanoparticle states before heat treatments.

At this point of 10 h, all starting materials were mostly consumed and the secondary chain reactions with newly formed products were assumed to be formed. In the primary reaction, it was observed that Yield.C and Yield.N of #14, #13, #2, and #8 (corresponding to 3.5, 6.5, 10, and 30 h of milling) increased from 0.04 to gradually 0.06 and from 0.26 to 0.50, respectively. These yields appeared to be saturating and indicated that the primary reaction was saturating. There are still many ambiguities left as follows:

- A phase X in the inset shows a sharp diffraction line. It is actually the highest diffraction line in #12. Although it is indexed as Fe gluconate; PDF00-005-0257, it is not conclusive. There are still many unindexed diffraction lines which may correspond to complex organic or inorganic materials.
- What is the lowest limit of G to form organics? At lower revolutions of mills, the effects of impact fields get weaker and far longer milling times are necessary to achieve enough number of impacts. Considering the effect of serpentinization, milling at above 200°C would be plausible to enhance the reaction and to reduce milling times.
- Trials with materials that were available on early Earth, CaCO_3 , CuFeS_2 , and $\text{Fe}(\text{NO}_3)_3/\text{NH}_3$ in water would be very interesting. Olivine and carbonated water as a carbon source would also be an interesting combination.

3.3 A link; hypervelocity/micro-impacts, serpentinization, and shocks at faults in crusts

There are common features, e.g., starting materials including Fe and CO_3 produce H_2 , CH_4 , magnetite, and organics. Serpentinization is a hydrothermal reaction of ultramafic ferrous rocks with carbonated sea water forming H_2 , CH_4 , and magnetite at faults in crusts [15,26] as shown in Figure 7. Hypervelocity impacts [6,11] create extremely high temperatures at contact edges of Fe/Ni powders, a kind of micro-plasma, and activate nitrogen and other ingredients. Activated gaseous ingredients are quenched and form organics during a cooling process, presumably at about $300\text{--}100^\circ\text{C}$ for a few minutes. The formation of organics in this short time is astonishing since 10–30 h milling times are required in micro-impact experiments. This is probably because

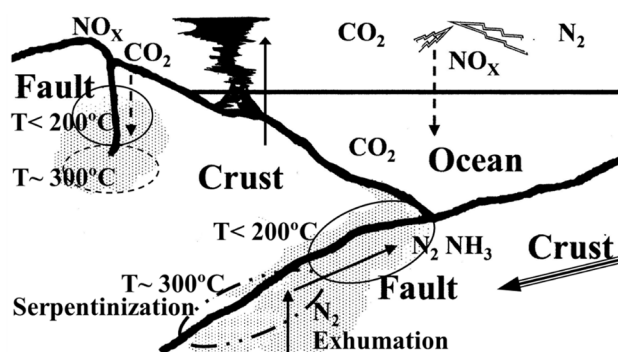


Figure 7: An illustration of carbon and nitrogen transfer at faults where the MeChem reaction should work most effectively.

activated ingredients are well mixed to realize fast reactions at the atomic scale, of 0.1 nm, which is far shorter than the mixing level of 10 nm in ball-milling experiments.

It is quite natural to imagine that the impacts of rocks and sand create the MeChem reaction. Impacts of asteroids, meteorites, and interplanetary dust doubtlessly have great energies and create the MeChem reaction. While vibrations of rocks and sands created by earthquakes, for instance, behave just like milling balls and create the MeChem reaction, big or small. Although impact energies of rocks and sands produced by earthquakes are mostly very small at land surfaces, the energies would be tremendous at faults where stresses are accumulated. Near or at hypocenters, centers of shocks with highest G located at faults in deep crusts, pressures are tremendously high as well as temperatures. Then, the MeChem reactions take place very efficiently there. It is also expected that the impacts more effectively cause the MeChem reaction combined with serpentinization to form organics at faults in deep oceanic crusts. These events occur frequently and organics will be accumulated for a long period of time.

Moreover, faults are ideally positioned in ocean beds as inorganic ingredients are abundant here. More than 1 teramole of carbon per year are subducted as carbonate or carbonaceous materials [26], which are far greater than meteoritic materials of 37,000–78,000 tons every year falling on Earth (<http://curious.astro.cornell.edu/about-us/75-our-solar-system/comets-meteors-and-steroids/meteorites/313-how-many-meteorites-hit-earth-each-year-intermediate>). A great amount of Fe nitrate is also subducted into crusts [27]. Furthermore, it is noted that the MeChem reaction occurs even in the area of temperature below 200°C where serpentinization is assumed to be inactive and should enhance the reaction further in areas of temperature $200\text{--}350^\circ\text{C}$ where serpentinization is assumed to work effectively [15].

This vision is further extended to the following hypothesis. When the CO_2 content in atmosphere was thousand times higher on early Earth [28], subducted amount of carbon was even greater and then the MeChem reaction and serpentinization were probably far more active in the Hadean Ocean. As nitrogen sources, NH_3 and N_2 were built up along with upward movements of mantles [15,29,30] in faults where crusts collided, and the NO_x produced through lightning and photochemical processes dropped down to Hadean Ocean [31]. All of these carbonates and nitrates are deposited as sediments with rocks and sands at sea floors in an anoxic world rich with CO_2 and ferrous irons [32]. The transient materials discussed above, green rust and/or transient-Fe, might have played a big role. At events of seismic tremors due to any diastrophism of crusts, rocks, and sands produced micro-impacts and frictions just like milling balls. Organic precursors were thus formed in sediments. Even small earthquakes might cause violent tremors or impact well enough to form organics in the vicinity of hypocenters located in faults where the MeChem reaction was accelerated by high temperatures and pressures. In Hadean Eon, crusts were unstable, and diastrophism was so vigorous that the MeChem reaction was assumed to be extremely active. Because diastrophism was a universally occurring event on Earth, organic precursors were kept accumulating for billions of years and kept feeding primordial soup [33].

Hypervelocity/micro-impacts and serpentinization are phenomenologically described in short as follows. Hypervelocity impacts by propellant gun experiments (micro-plasma formation and quenching) [6,11] reproduce intense meteorite impacts forming organic precursors and imply further that organics are contained in coronal mass ejections of solar plasma flares. Micro-impacts of balls (fairly low energy and just enough to hydrogenate carbon components) also formed precursors and imply further that the micro-impacts of rocks and sands caused by any seismic activity in the lithosphere work efficiently to form precursors at hypocenters along faults. Serpentinization assisted by the MeChem reaction also forms precursors.

4 Conclusions

Micro-impacts induced by a high-energy ball milling at 40 G and up to 30 h formed organic precursors including amino acids from inorganic materials like Fe_3C , Fe_4N , carbonates, nitrates, and water. Unusually high yields were apparently due to frequent collisions of numerous balls, although the MeChem reaction due to each collision

produced only a fraction of organics. The observed results and some remarks are as follows:

- Yields of inorganic carbons to organic ones (Yield.C) were very high, up to 0.18. As carbon sources, Fe_3C , solid carbon, and $(\text{NH}_4)_2\text{CO}_3$ were effective. CaCO_3 was activated by the FeSO_4 addition. $\text{Fe}(\text{CO}_2)_2$ was a very effective carbon source and greatly enhanced organic formations.
- Starting materials, Fe_4C , and $\text{Fe}(\text{CO}_2)_2$ transferred to organics, magnetite, FeOOH , green rust, and/or transient-Fe in a short milling time of a few hours, and then gradually transformed to organics like alcohols, carboxylic acid, amines, and amino acids. Primary transformations appeared to be saturated at about 10 h under these experimental conditions.
- Fe_3N , NaNO_3 , and $\text{Fe}(\text{NO}_3)_3$ were effective nitrogen sources. The activity of $(\text{NH}_4)_2\text{CO}_3$ as a nitrogen source was unclear. Nitrogen transformed mainly to NH_3 . When Cu was present, CN ions were dominant. Other metals and combinations might offer different results.
- The formation of CN ions and NH_3 strongly indicate the formation of nucleobases according to the traditional HCN chemistry or the formamide-based model.
- The concept of mechanically enhanced serpentinization suggests that millings at lower G and a higher temperature of about 200°C may work to form organics.
- It is expected that combinations of CaCO_3 , CuFeS_2 , $\text{Fe}(\text{NO}_3)_x$, and/or NH_3 which were available on early Earth produce organic precursors including nucleobases.
- It is suggested that CO_2 and Fe were key components to form organic precursors in the Hadean Ocean and that the micro-impact-induced MeChem synthesis was a key process.

Our experiments demonstrated that the micro-impact-induced MeChem synthesis can be regarded as the dynamic crustal hydrothermal reaction or the mechanically enhanced serpentinization and offer a new route to produce organic precursors, the origin of life in early Earth. Over a billion years, great amounts of precursors have been accumulated in crusts as the mechano-chemical cradle on the aqua-planet.

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