

An experimental study of the thermolysis of hydrogen cyanide: the role of hydrothermal systems in chemical evolution

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Research Article

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Abstract

Hydrogen cyanide (HCN) is considered a fundamental molecule in prebiotic chemistry experiments due to the fact that it could have an important role as raw material to form more complex molecules, as well as it could be an intermediate molecule in chemical reactions. However, the primitive scenarios in which this molecule might be available have been widely discussed. Hydrothermal systems have been considered as abiotic reactors and ideal niches for chemical evolution. Nevertheless, several experiments have shown that high temperatures and pressures could be adverse to the stability of organic molecules. Thus, it is necessary to carry out systematic experiments to study the synthesis, stability and fate of organic molecules in hydrothermal scenarios. In this work, we performed experiments focused on the stability and fate of HCN under a simple hydrothermal system scenario: the thermolysis of HCN at 100°C, at acidic and basic pH and in the presence of Mg-montmorillonite. Furthermore, we analysed the products from HCN thermolysis and highlighted the role of these chemical species as prebiotic molecules under a hydrothermal scenario.

Introduction

Hydrogen cyanide (HCN) is suggested as a central molecule in chemical evolution because it is proposed as a ‘chemical block’ of the three pillars of the prebiotic chemistry (Islam and Powner, 2017). Several experiments have shown that HCN is an important precursor of organic molecules such as carboxylic acids, amino acids, purines, pyrimidines and other carbonyl compounds (Sanchez *et al.*, 1967; Draganić and Draganić, 1980; Niketić *et al.*, 1983; Ferris and Hagan, 1984; Schwartz *et al.*, 1984; Draganić *et al.*, 1985a; Borquez *et al.*, 2005; Matthews, 2005; Ruiz-Bermejo *et al.*, 2013; Sutherland, 2016).

However, one of the biggest problems in considering any primitive conditions is the availability of raw material in the environment and its concentration (Miller, 1987). These are fundamental criteria to consider any primitive scenario and the kind of reactions that could have happened on the primitive Earth. Regarding this, several mechanisms could have contributed to the inventory of HCN on early Earth by the action of different energy sources (*e.g.* photolysis, shock waves, electrical discharges of lightning and volcanism; Ferris and Hagan, 1984; Holm and Neubeck, 2009; Tian *et al.*, 2011; Parkos *et al.*, 2016; Ferus *et al.*, 2017; Rimmer and Rugheimer, 2019). Likewise, the extraterrestrial input from meteorites and comets was possibly an important source of HCN (Matthews and Minard, 2006; Colín-García *et al.*, 2009; Mumma and Charnley, 2011; Pizzarello, 2012). In general, the mechanisms for the synthesis of HCN are based in reactions between an oxidizing agent (*e.g.* CO, CO₂), a source of nitrogen (*e.g.* NH₃, N₂) and a reducing agent (*e.g.* H₂, H₂O) (for more details, see Ferris and Hagan, 1984). In addition, cyanide species in the form of complexes with sulphur/ferrous ions could have been present in the primitive oceans or in the vicinity of hydrothermal systems (Mukhin, 1974; Arrhenius *et al.*, 1994; Keefe and Miller, 1996; Dzombak *et al.*, 2006; Holm and Neubeck, 2009).

The concentration of HCN is a critical parameter. High concentrations (>0.1 mol l⁻¹) could have favoured the polymerization of the molecule, while lower concentrations (<0.01 mol l⁻¹) might have favoured its hydrolysis (Sanchez *et al.*, 1968; Miyakawa *et al.*, 2002). Besides, these mechanisms are highly dependent on pH.

There is no agreement about the concentration of HCN on early Earth. For instance, it has been proposed that it was possible to reach high concentrations of HCN at the surface of the water (floating HCN patches >1 mol l⁻¹; Fábíán *et al.*, 2014). Other models propose

that concentration *per se* in the primitive oceans was very low (10^{-10} – 10^{-13} mol l⁻¹) (Stribling and Miller, 1987; Miyakawa *et al.*, 2002). Hence, it is necessary to consider primitive environments where the production of HCN was continuous and then chemical reactions could have taken place to increase the chemical complexity. One plausible scenario may be the hydrothermal systems.

Holm and Neubeck (2009) suggested a possible mechanism for HCN production under hydrothermal conditions from CH₄, NH₃ and other dissolved species (*i.e.* N₂, CO). The main reactions are as follows:

- (1) CH₄ + NH₃ → HCN + 3H₂
- (2) 2CH₄ + N₂ → 2HCN + 3H₂
- (3) CO + NH₃ → HCN + H₂O

In the same way, based on theoretical models, it has been proposed that HCN can coexist with their precursor molecules (*e.g.* CO, CO₂, H₂ and N₂) under hydrothermal conditions (Shock, 1992; Schulte and Shock, 1995; LaRowe and Regnier, 2008). Such species may be available in these environments (Table 1) when the hydrothermal fluids are mixed with seawater. Particularly, alkaline fluids, resulted from the serpentinization processes, could have an essential role in the release of several dissolved species and consequently in the formation of organic compounds (Konn *et al.*, 2015; McDermott *et al.*, 2015). Brandes *et al.* (1998) showed that N₂ could be transformed into NO₂, NO₃ and ammonia in the presence of minerals under hydrothermal conditions. Additionally, abiotic nitrogen reduction could have taken place within primordial hydrothermal vents, supplying some ammonia for the synthesis of C-H-O-N compounds *via* abiotic processes (Schoonen and Xu, 2001).

Consequently, if HCN can be produced under hydrothermal conditions, it is crucial to study its stability and reactivity considering some of the available geochemical variables in hydrothermal systems, such as different pH values, high temperatures and in the presence of inorganic surfaces.

On the one hand, it is well known that both hydrolysis and polymerization of HCN are pH-dependent (Sanchez *et al.*, 1967; Ferris and Hagan, 1984). Besides, it has been proven that some minerals adsorb HCN and/or increase its hydrolysis. This has been demonstrated theoretically and experimentally using ferrierite (Nanba *et al.*, 2000), double-layered hydroxides (Zhao *et al.*, 2015), zeolites (Kotdawala *et al.*, 2008; Demir *et al.*, 2012), titanium oxides (Ma *et al.*, 2017) and serpentinite and clays (Colín-García *et al.*, 2010; Colín-García *et al.*, 2014). Nonetheless, it is necessary to consider all these variables together.

Here, we present an experimental approach of the HCN thermolysis under a simple hydrothermal scenario. In this study, it was considered that it is possible to find relatively warm fluids, generated by the hydrothermal fluids upwelling in chimneys and their diffusion within the medium. The selected temperature (100°C) could be very likely present surrounding the hot chimneys; since it has been reported a temperature difference (50°C) on fluids in a centimetre scale, result of turbulent mixing and venting activity (Fornari *et al.*, 1998; Bates *et al.*, 2010; Mittelstaedt *et al.*, 2012). In the study of the reactivity and fate of HCN and its decomposition products, it is important to consider some prebiotic scenarios, such as the surroundings of submarine and subaerial hydrothermal systems (Colín-García *et al.*, 2018), and to explore their potential implications for chemical evolution.

Materials and methods

Synthesis of HCN

HCN solution (0.1 M) was produced *in situ* by the reaction between KCN and H₂SO₄. HCN gas was dissolved in Milli Q water into an Ar atmosphere (Azamar and Draganić, 1982). The concentration was determined by titration with an aqueous solution of AgNO₃ (Draganić *et al.*, 1973).

Preparation of Mg²⁺-montmorillonite

Mg-montmorillonite (Mg-Mont) was prepared from SWy-2cNa-Mont Crook County, Wyoming, USA (Na-Mont), according to the following procedure: 40 g of Na-Mont was washed with a saturated solution of MgCl₂·6H₂O (2 N) for 24 h. The suspension was then centrifuged for 30 min at 20 000 rpm and washed with deionized water by shaking for 24 h. The suspension was centrifuged and lyophilized. This procedure was repeated three times. The dry powder sample was analysed by X-ray diffraction to quantify the differences of the interlamellar space of the clay. It was corroborated that Mg²⁺ had completely replaced Na⁺. Mg-Mont was used as magnesium was a common element on early Earth and because it is present in a wide variety of minerals in hydrothermal systems (Holm, 2012; Colín-García *et al.*, 2016, 2018).

Thermolysis

Thermolysis experiments were carried out in a static system at ≈100°C (Fig. 1). Aliquots of the HCN solution (0.1 M, 5 ml) were placed in glass tubes of 8 ml with stopcocks; the headspace was air. A ball flask with wells was filled up with toluene. Toluene was heated until boiling; samples were heated for different periods of time by conduction. All tests were carried out in triplicate. Controls and experiments including Mg-Mont were performed with 100 mg Mg-Mont by 5 ml HCN (0.1 M) at acidic and basic pH. The pH was modified and adjusted to 2 or 8.5, adding drops of HCl or KOH solution (0.1 M), respectively. The greater time exposition to heat for each sample was HCN_{acid}: 141.5 h, HCN/Mont_{acid}: 160 h, HCN_{basic}: 143 h and HCN/Mont_{basic}: 159.5 h. The aqueous phase of the samples was analysed to quantify changes of the organic molecule.

Analysis of samples

The treated samples were analysed by different analytical techniques:

Gas chromatography (GC)

The remnant HCN was followed by GC (Varian Series 2400 with flame ionization detector) on a stainless-steel column (1/8 inch and 4 m length) packed with Chromosorb-102 (100/120 mesh). The carrier gas was N₂ with a flow rate of 30 ml min⁻¹. The temperature regime was 60–250°C, with a heating rate of 6°C min⁻¹. The detector temperature was 200°C. A volume of 2 µl was injected.

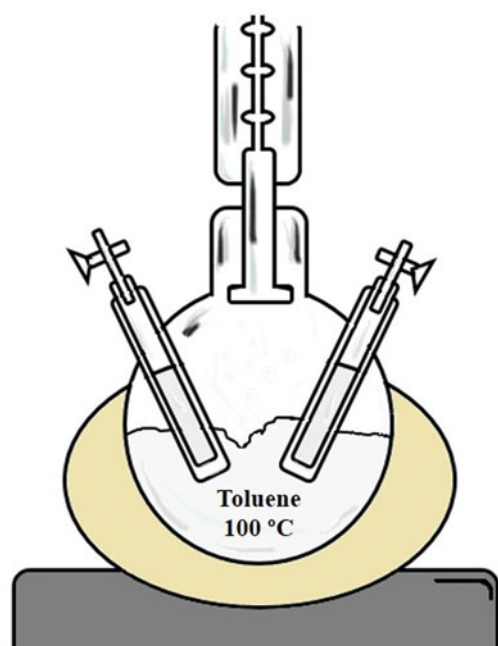
GC-MS

The GC-MS analysis was done in a 6859 network GC system coupled to a 5975 VL MSD with triple-axis detector operating in electron-impact mode at 70 eV (Agilent). HP-5 MS columns (30 m × 0.25 mm i.d. × 0.25 µm film thickness) were used; the analysis was carried out using the method developed by Ruiz-Bermejo *et al.* (2012) to detect polar organic compounds. After thermolysis,

Table 1. Temperature, pH and dissolved species in fluids of some hydrothermal systems and seawater

Physicochemical conditions	Environment				
	Hydrothermal system				Seawater*
	Lucky Stricke [§]	Menez Gwen [§]	Lost City*	Rainbow*	
Temperature (°C)	172–324	275–284	40–93	365	7
pH	3.5–3.7	4.2–4.3	9–11	2.8	8
Chemical species (mmol)					
H ₂	3.3–725	44.2	0.25–0.43	16	–
CO ₂	15.0–26.6	22.6–28.8	–	16	2.3
CH ₄	0.30–0.88	1.2–1.49	0.13–0.28	2.5	–
N ₂	0.5–2.1	1.2–1.49	–	–	–

Based on: [§]Charlou *et al.* (2000); *Schrenk *et al.* (2004) and references therein.



Static system at $\approx 100\text{ }^{\circ}\text{C}$ Heated by conduction

Fig. 1. Static heating system. A ball flask with wells is filled up with toluene; the system is heated until boiling, and samples are heated by conduction.

samples were freeze-dried to remove H₂O. Then, 100 μl of BSTFA + TMCS [N,O bis(trimethylsilyl)trifluoroacetamide with Me₃SiCl, Thermo Scientific Co, Waltham, MA, USA] was added to dry material and heated for 3 h at 80°C. Next, 2 μl of derivatized sample was injected (injector temperature 220°C, detector temperature 300°C and flow rate 1.1 ml min⁻¹; He as a carrier gas).

Ultra-high performance liquid chromatography (UHPLC)

The aqueous component was analysed by UHPLC (UltiMate 3000 UHPLC chromatograph, Thermo Scientific Co) with a UV-Vis

detector (Dionex UltiMate 3000 VWD). For carboxylic acids, we used an Alltech anion exclusion column (7.8 \times 300 mm) and 1.5 mmol⁻¹ of H₂SO₄ as a mobile phase, with a flow rate of 0.6 ml min⁻¹. The detection wavelength (λ) was $\lambda = 210\text{ nm}$. For diaminomaleonitrile (DAMN) detection, a Waters Cortex 2.7 μm , 4.6 \times 150 mm column was used; the mobile phase was (A) ammonium acetate 0.1 mol l⁻¹ and (B) methanol:water 50:50, with a 90 A:10 B ratio and a flow rate of 0.5 ml min⁻¹. The detection wavelength was $\lambda = 293\text{ nm}$.

UV-Vis spectroscopy

Urea was identified using the DAM method. The detection wavelength was $\lambda = 526\text{ nm}$ (Negrón-Mendoza *et al.*, 1986).

Results and discussion

Thermolysis

Figure 2 shows the thermolysis of HCN at acidic (2) and basic (8.5) pH, as well as in the presence of Mg-Mont. According to the species distribution diagram of HCN (Fig. 3), at pH = 2, HCN is the dominant species. However, at pH = 8.5, there is a considerable amount of cyanide ($\sim 20\%$). The availability of cyanide ions is crucial because, as we will discuss below, it is directly related to the polymerization process.

It is possible to identify some trends about the behaviour of HCN in both acidic and basic conditions (Fig. 2). It is noticeable that in acidic pH, the decomposition of HCN is low, but the presence of Mg-Mont increases its decomposition. Some experiments have shown that the half-life time for the hydrolysis of HCN is only a few minutes (Sanchez *et al.*, 1968; Stribling and Miller, 1987; Miller and Bada, 1988). However, Schäfer and Bonn (2000) demonstrated that hydrolysis of HCN_(g), as a function of temperature and in the presence of H₂O and N₂, is relatively slow until 700°C. It is well understood that hydrolysis of HCN yields formamide and, eventually, formic acid (Sanchez *et al.*, 1967; Ferris *et al.*, 1973; Schwartz *et al.*, 1984; Miyakawa *et al.*, 2002; Borquez *et al.*, 2005).

Some experiments have used inorganic surfaces to investigate the hydrolysis of HCN and suggested that this could be the result of the participation of acid sites at catalysts (Nanba *et al.*, 2000; Ma *et al.*, 2017). The catalytic activity of clay minerals may result from Brønsted acidity, Lewis acidity, presence of redox-active

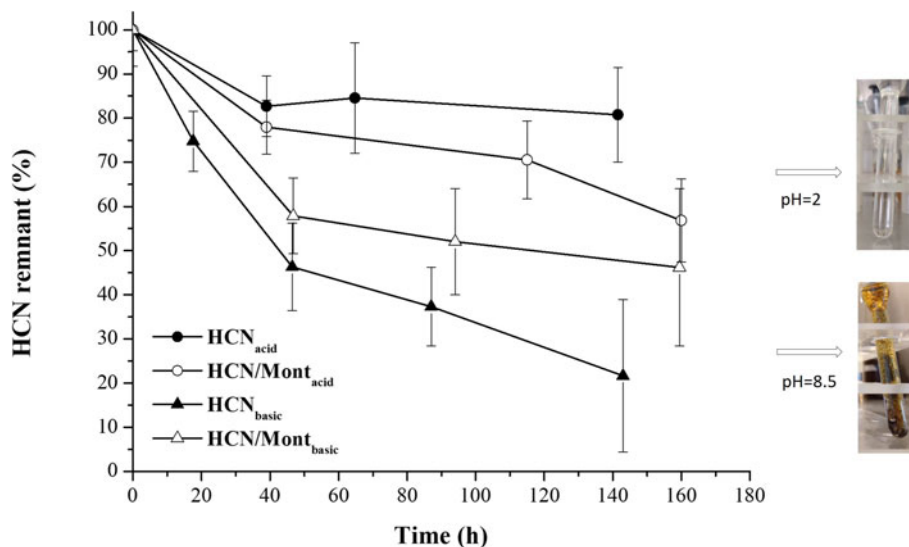


Fig. 2. Thermolysis of HCN at 100°C. Under acid conditions (pH = 2) the HCN remains relatively stable, but in the presence of Mg-Mont, the decomposition increases. At basic pH values (pH = 8.5) and in the absence of clay, the transformation of HCN is more efficient.

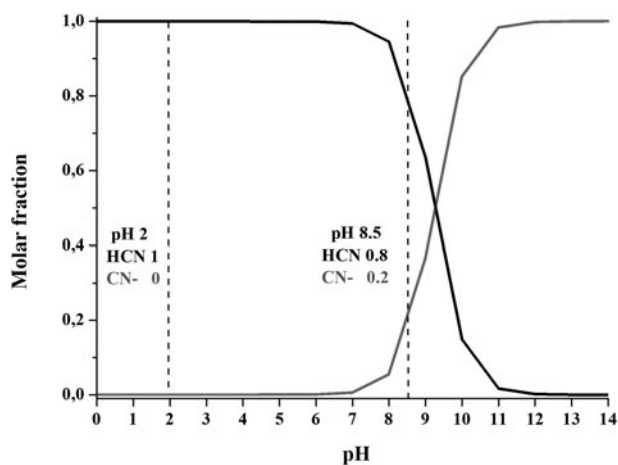


Fig. 3. Species distribution diagram for HCN.

species and/or introduction of catalytic species along the crystal structure (Adams and McCabe, 2006). In addition, the acidity at the surface of Mg-Mont may be the result of terminal hydroxyl groups, the bridging of oxygens and exchangeable cations. Likewise, Mg²⁺ has greater polarizing ability and, in consequence, it can dissociate the water in the interlamellar channel, releasing a proton to the medium (Frenkel, 1974; Nikalje *et al.*, 2000). In addition, the interaction of HCN with the Brønsted acid sites by hydrogen bonding in the lattice of clay would increase the hydrolysis of HCN (Cruz, 1974; Jamis *et al.*, 1995). Although one experimental report suggested that HCN at acidic conditions may be sorbed onto montmorillonite (Colín-García *et al.*, 2014), the HCN:Mont relationship in our experiments suggests that hydrolysis is the predominant mechanism, rather than sorption.

At basic pH, the decomposition of HCN is lower in the presence of clay. Although HCN hydrolysis at basic pH is possible, it has been demonstrated that polymerization until tetramer, DAMN, is the dominant mechanism (Miyakawa *et al.*, 2002; Borquez *et al.*, 2005).

Ferris *et al.* (1979) showed that in the presence of montmorillonite, the oligomerization of HCN is inhibited, suggesting an interaction with HCN oligomers, and not with HCN itself. In

other words, they found that clay catalysed the decomposition of tetramer, DAMN, to form diiminosuccinonitrile (DISN); consequently, the degradation of DAMN involves the release of HCN to the medium. According to this hypothesis, our results are congruent with the greater concentration of free HCN in the presence of clay (Fig. 2). The decomposition of tetramer could be the result of oxidation reactions, mediated by the hydrolysis process and/or the presence of Fe³⁺ in the clay lattice (Ferris *et al.*, 1982).

In summary, the results suggest that the hydrolysis process, at acidic pH and at 100°C, is the dominant mechanism of transformation of HCN. However, at basic pH and at 100°C, the polymerization of HCN is the dominant reaction (Fig. 2). In addition, the change in colour (yellow to brown) of basic samples, after treatment, is evidence of the polymerization process. The presence of Mg-Mont has two effects: on the one hand, it increases the hydrolysis of HCN (at acidic pH) and, on the other, it inhibits the oligomerization of HCN at basic pH. In order to evaluate the effect of pH on HCN-thermal products, several analytic studies were performed to identify organic molecules in the aqueous component.

Products of HCN thermolysis

Some intermediate species with great prebiotic importance can be formed from HCN under several experimental conditions (Ruiz-Bermejo *et al.*, 2013). In this work, only the aqueous phase from HCN thermolysis, the supernatant, was analysed. The organic richness of this aqueous phase will determine the best geochemical conditions in which the products of HCN thermolysis can undergo subsequent reactions in a dynamic environment. The nature, availability and reactivity of the organic molecules dissolved in the medium will determine the importance of HCN on hydrothermal environments. The supernatants of each experiment, with the greater time exposition to heat, were analysed by different qualitative methods.

Aldehydes

Only in the acidic sample heated without clay, a small peak associated with formaldehyde (HCHO) was detected by GC, both by retention time and co-injection of the standard (Fig. 4). Although

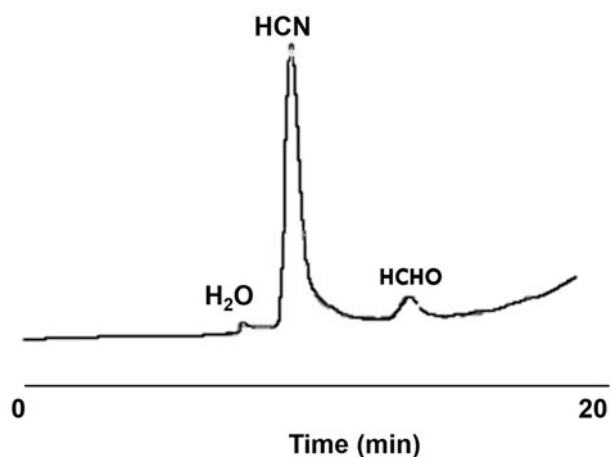


Fig. 4. Gas chromatogram of volatile products from the sample of HCN thermolysis at acidic pH without Mg-Mont. The formation of formaldehyde (HCHO) is shown.

the decomposition of formic acid – formed by hydrolysis of HCN – under hydrothermal conditions has as major products CO_2 and H_2 (Yu and Savage, 1998), it has been suggested that formaldehyde can also be a reaction product (Nelson and Engelder, 1925). In addition, the production of formaldehyde from the radiolysis of HCN has been reported (Negrón-Mendoza *et al.*, 1983). Even if derivatization by Brady's method (in which carbonyl groups are identified by the formation of 2,4-dinitrophenylhydrazones) (Shriner *et al.*, 1982) was performed for all samples, none of them showed positive results; this may be associated with a very low concentration of produced aldehydes in the samples.

Urea

Several researches have shown that urea is a product of HCN oligomerization. Specifically, it may be a product of oxidation/hydrolysis of DAMN (Ferris *et al.*, 1973, 1974b; Ferris and Ryan, 1973; Ferris and Edelson, 1978; Ferris and Hagan, 1984). Our experiments showed that urea is formed only by thermolysis of slightly basic HCN solutions (pH = 8.5) and even in the presence of Mg-Mont (Fig. 5). In addition, urea concentration was greater in the sample without clay. This is consistent with the HCN polymerization mechanism previously mentioned. In other words, and in agreement with Fig. 2, HCN polymerizes better in the absence of clay mineral; and, in consequence, the formation of the tetramer should be higher. Hence, the oxidation/hydrolysis reaction of DAMN at high temperatures led to the formation of an important amount of free urea ($\approx 40\%$ higher concentration than the sample with mineral).

Urea has been considered an important prebiotic molecule due to its participation in synthesis reactions of pyrimidines (Robertson and Miller, 1995; Menor-Salván *et al.*, 2009), and its role in hydrothermal scenarios was highlighted (Holm, 1992). Likewise, it has also been found in HCN-radiolysis experiments (Draganić *et al.*, 1985a, b; Vujošević *et al.*, 1990; Colín-García *et al.*, 2009).

Carboxylic acids

The formation of some carboxylic acids by thermolysis of HCN was confirmed (Fig. 6). Among the main carboxylic acids identified are: oxalic, maleic, glycolic and formic acid, which were also identified by GC-MS. The formation of formic acid corroborates that, at pH = 2, hydrolysis is the main reaction. In addition, the

peaks of oxalic and maleic acid may be a result of the decomposition of formic acid along thermolysis; in other words, they are secondary products.

The samples under basic pH show more production of carboxylic acids than in acidic conditions. The main reaction involves the formation of oxalic acid, which could be the result of oxidation of DAMN and the reaction between DISN with water and other nucleophiles (Ferris *et al.*, 1982; Schwartz *et al.*, 1984). Additionally, the presence of Mg-Mont seems to affect the reaction products (a predominant unidentified peak, with $R_t \sim 8.5$ min, was detected on the sample without mineral). Moreover, the sample with clay showed a higher remnant of HCN, which is consistent with Fig. 2. Clay mineral inhibits the polymerization process, and hence, a higher amount of free HCN is available. Negrón-Mendoza *et al.* (2001) reported that the presence of Na-Mont in HCN radiolysis significantly affects the amount and diversity of carboxylic acids formed.

Other options to explain the formation of carboxylic acids may be by reactions between aldehydes (e.g. formaldehyde) and the cyanide ion through the formation of cyanohydrins as intermediates; as well as the formation of other nitriles (e.g. cyanate, cyanogen, cyanoacetylene, glyconitrile), which are produced from decomposition (*i.e.* hydrolysis, oxidation) of HCN (Kemp and Kohnstam, 1956; Brotherton and Lynn, 1959; Ferris *et al.*, 1968; Wang *et al.*, 1987).

Diaminomaleonitrile

Among oligomers of HCN, DAMN has drawn great attention because it has been pointed out as a gateway for the synthesis of purine and pyrimidines (Zubay, 2000). The analysis of the aqueous phase of heated samples shows that DAMN is present only in the basic solutions (Fig. 7), as previously mentioned (Miyakawa *et al.*, 2002; Borquez *et al.*, 2005). Even though Yuasa and Ishigami (1977) showed that DAMN is also formed in the presence of Mg oxides, which suggests that divalent metals would favour the HCN oligomerization, the presence of a clay mineral seems to inhibit the synthesis of DAMN (the sample with clay showed a considerably lower amount of this oligomer). As mentioned above, the decomposition of DAMN may occur by its hydrolysis and/or oxidation by Fe^{3+} in the clay lattice (Begland *et al.*, 1974; Ferris *et al.*, 1982). Another possibility is that the lower amount of free DAMN in the sample with Mg-Mont may be the result of surface retention of this oligomer, as this has been reported to happen with other surfaces (Thissen *et al.*, 2015; Toh *et al.*, 2019). This is an important result because, although the HCN thermolysis under alkaline conditions yields DAMN, eventually, its interaction with the available clays in the medium would constrain the oligomerization process.

CG-MS analysis

To corroborate some of the species that we characterized and some free amino acids, a derivatization of samples, without the common hydrolysis procedure, was performed. Hydrolysis can affect the original amount and nature of the soluble fraction, and this procedure is focused on HCN-derived polymers (Ruiz-Bermejo *et al.*, 2013). As we mentioned above, this study is only focused on the soluble fraction of samples.

Glycine and alanine traces were detected only in the acidic sample without clay by GC-MS (data not shown). In both basic samples, it was also possible to corroborate the presence of urea, oxalic and glycolic acid by GC-MS. In addition, intermediate species such as carbamic acid, ethanolamine, glycerol, succinic

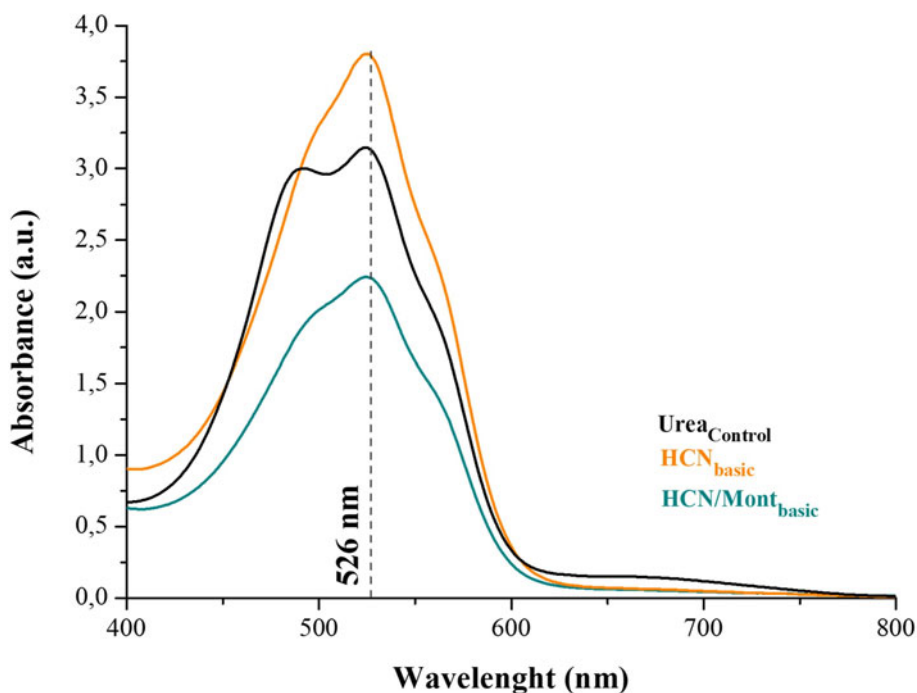


Fig. 5. Urea is a product of the thermolysis of HCN under slightly basic solutions. The spectrum UV-Vis shows the specific absorption band of the complex formed by the reaction of DAM.

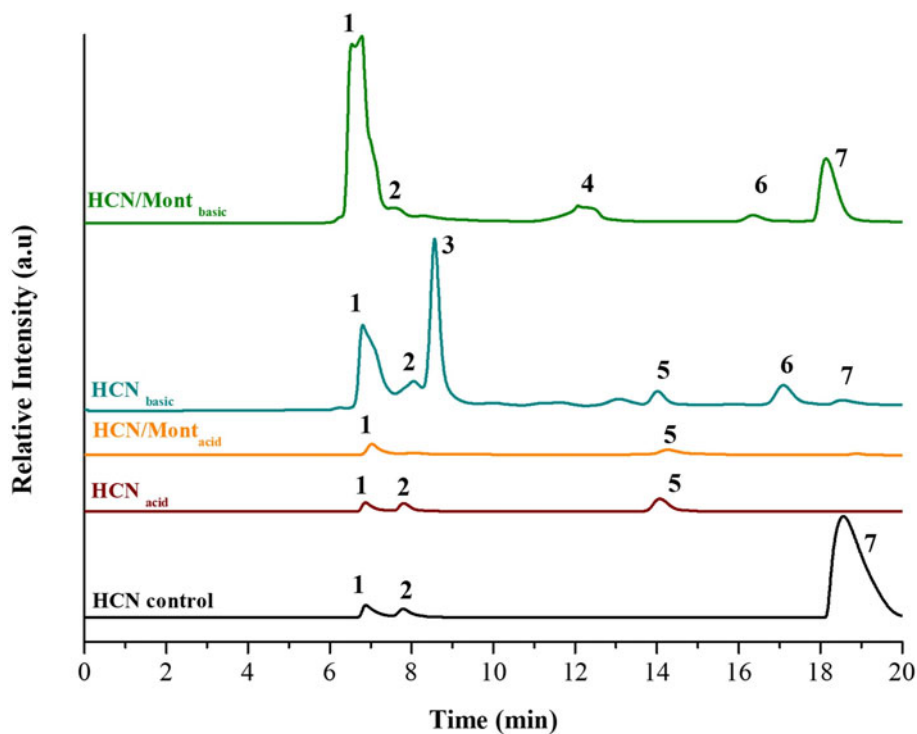


Fig. 6. UHPLC chromatograms of carboxylic acids formed by HCN-thermolysis. Under basic conditions, the formation of carboxylic acids is higher than at acidic pH. Legend: (1) oxalic acid, (2) maleic acid, (3) not characterized, (4) glycolic acid, (5) formic acid, (6) not characterized and (7) HCN.

and propanoic acid were detected in basic solution fractions. It should be mentioned that, in general, free amino acids are not detected in our HCN experiments. Only after acid hydrolysis of HCN oligomers, synthesized either by thermal energy or ionizing radiation, are a significant amount of amino acids released (Ferris *et al.*, 1974a; Draganić *et al.*, 1985a, b; Vujošević *et al.*, 1990; Ruiz-Bermejo *et al.*, 2013; Marín-Yaseli *et al.*, 2016). The

formation of free amino acids can be explained by common Strecker synthesis among HCN, aldehydes and ammonia. Some authors have reported the viability of this mechanism under submarine conditions (Schulte and Shock, 1995; Andersson and Holm, 2000). Other pathways for amino acid production [like the synthesis from ethanolamine (detected in this study by GC-MS) using metal powder and Friedel-Crafts reactions

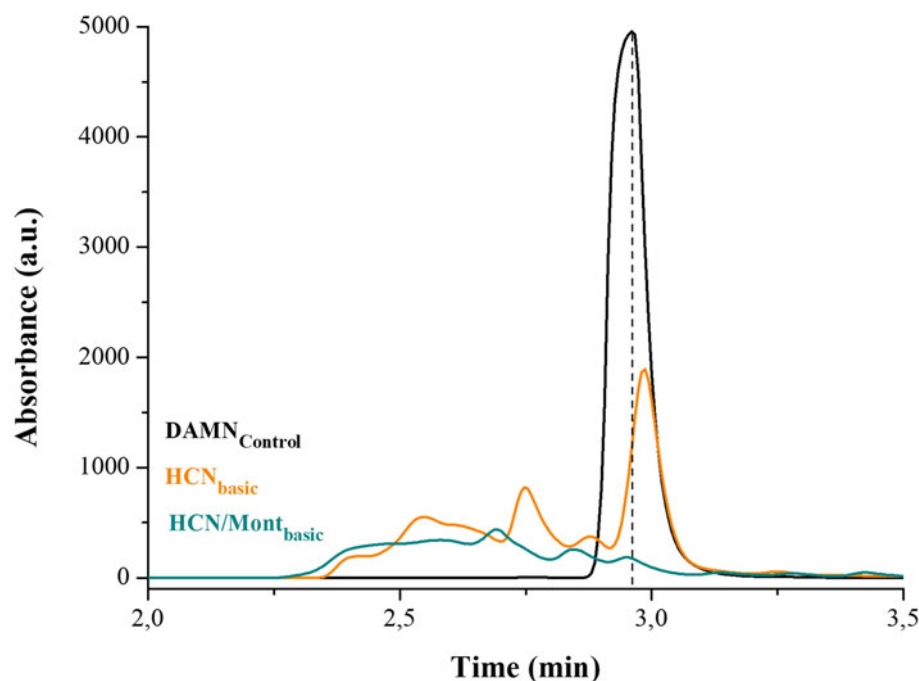


Fig. 7. UHPLC chromatogram of HCN thermolysis samples. Only in basic medium did the HCN thermolysis yield DAMN. However, Mg-Mont may inhibit the polymerization of HCN.

catalysed by minerals] have been proposed under alkaline hydrothermal scenarios (Zhang *et al.*, 2017; Ménez *et al.*, 2018).

In summary, the thermolysis of acidic samples shows that the formation of formic acid by hydrolysis of HCN is the predominant mechanism. In addition, the presence of Mg-Mont increases the transformation of HCN. The formation of formaldehyde and small carboxylic acids, in acidic conditions, may well be the result of decomposition of formic acid. Differently, the thermolysis at basic conditions showed a higher formation of organic molecules. In the case of the sample without clay, the amount of recovered HCN was lower with the consequent high formation of DAMN. Likewise, semi-quantitative analysis showed that a high amount of urea and oxalic acid was present. Finally, the higher amount of free HCN and the lower amount of urea and DAMN in the sample with Mg-Mont corroborate that clay inhibits the oligomerization of HCN at basic conditions.

Relevance for chemical evolution

Our experiments showed that, even considering a simple hydrothermal simulation, HCN thermolysis may be an important starting point for the production of several organic molecules. If the synthesis of HCN under hydrothermal conditions is continuous, these systems could have had a considerable role as ‘abiotic reactors and chemical evolution niches’, as they were originally proposed (Corliss *et al.*, 1980; Baross and Hoffman, 1985). It is important to highlight that geochemical conditions of the environment are crucial because they are directly related to the formation/destruction mechanisms of more complex organic compounds. Although some experiments suggest that both HCN and some thermolysis products are unstable under hydrothermal conditions (Sanchez *et al.*, 1968; Stribling and Miller, 1987; Miller and Bada, 1988; Holm, 1992; Yu and Savage, 1998; Cleaves II, 2008), it is necessary to take into account several points that, according to our criteria, could be underestimated.

The first is that hydrothermal systems are very complex environments with many geochemical variables, and hence, they are more than high-pressure and high-temperature environments. In this way, new approaches are considering the role of several combined parameters (*i.e.* pH, redox state, dissolved gases and/or mineral surfaces) on the stability of compounds. In general, these new approaches have shown that the fate and stability of organic molecules are intrinsically related to these variables (Holm and Andersson, 2005; Colín-García *et al.*, 2016, 2018).

Additionally, the chemical species are not isolated. In other words, the availability of different species in the same environment could favour the subsequent reactions. For instance, the presence of aldehydes and ammonia would favour the polymerization of HCN (Voet and Schwartz, 1983).

Additionally, the molecules are not exposed to the highest temperature all the time. At the moment that the hydrothermal fluids are mixed with seawater, new temperature and/or pH gradients can harbour more suitable conditions (Chevaldonné *et al.*, 1991; Bates *et al.*, 2010) and favour the stability and polymerization of organic molecules (Ogasawara *et al.*, 2000; Ogata *et al.*, 2000; Islam *et al.*, 2003).

This approximation about the role of the HCN thermolysis process in the formation of organic molecules suggests that surroundings of hydrothermal environments (<100°C), such as sub-aerial alkaline environments, could have been an important source of free organic compounds on early Earth. It is necessary to design and carry out more complex experiments that would consider coupled variables present in hydrothermal systems to gain a detailed understanding of the behaviour of organic molecules under several geochemical conditions.

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