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Chemical Evolution 40.* Clay-Mediated Oxidation of Diaminomaleonitrile

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Summary. The previously reported inhibition of the oligomerization of HCN by montmorillonite clays was investigated. The inhibition is due to the oxidation of diaminomaleonitrile (DAMN) by the Fe^{3+} in the clay lattice. Fe^{2+} and oxalic acid were shown to be the reaction products. From these reaction products and the previous report that two equivalents of HCN are formed per equivalent of DAMN, it was established that diiminosuccinonitrile (DISN) is the initial reaction product, which is rapidly hydrolyzed to oxalic acid and HCN. The same oxidative transformations are effected by Fe^{3+} bound to Dowex 50, Fe^{3+} in solution and $Ni(NH_3)_6{}^{2+}$. The rate of reaction of DAMN decreased in the order $Fe^{3+} > Fe^{3+}$-Dowex > montmorillonite, indicating no catalytic role for the clay in the oxidation of DAMN. Little reaction of DAMN was observed with montmorillonite in which the bulk of the iron was in the Fe^{2+} oxidation state. The possible significance of these redox reactions to chemical evolution is discussed.

Key words: Cyanide – HCN oligomers – Montmorillonite – Clays – Diaminomaleonitrile (DAMN) – Diiminosuccinonitrile (DISN) – Fe^{3+} – Fe^{2+} – Primitive Earth

Introduction

HCN is formed readily in primitive earth simulation experiments and may have had a central role in the prebiotic synthesis of biomonomers (Oro and Kimball 1962; Ferris et al. 1978 and references therein). The effect of clay minerals on the reactions of HCN was investigated (Ferris et al. 1979) because it has been postulated that clays may have catalyzed prebiotic polymerization reactions (Bernal 1951; Rao et al. 1980). We were surprised by the observation that montmorillonite clays inhibited HCN oligomerization (Ferris et al. 1978). The key step in this inhibition is the decomposition of diaminomaleonitrile (DAMN) (*1*) with the formation of two equivalents of HCN. The mechanism of the clay-mediated decomposition of DAMN and the possible implications of this reaction to chemical evolution are the subjects of this paper.

Experimental

Materials and General Procedures

Montmorillonite 22A (Ward's Natural Science Establishment), which originated from approximately the same location (Amory Miss.) as the clay mineral standard, montmorillonite 22A (American Petroleum Institute, 1951) (R.J. Holmes, personal communication), was used. 10g of the clay were pulverized just prior to use. Diaminomaleonitrile (Aldrich) was recrystallized from boiling water after treatment with Norite decolorizing charcoal. Spectra were recorded on a Cary 219 UV-visible spectrometer and centrifugations were performed on a Sorvall RC2-B refrigerated centrifuge.

Reaction of DAMN with Fe^{3+}-Dowex 50

Dowex 50W-X8 (Biorad 20–50 mesh, H^+, 10g) was converted to the Fe^{3+} form by washing in a 2 cm OD glass column with

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* For the previous papers in this series see Ferris JP, Alwis KW, Edelson EH, Mount N, Hagan Jr J (1980) Origin of Life Wolman Y (ed) Reidel, Dordrecht, p 125–128
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2 N HCl and then with distilled water. A 50 ml solution of 1 M Fe(NO3)3 (pH 3) was passed slowly through the column and the column was washed with 200 ml of distilled water. It was determined that 0.045g (0.8 mmol) of Fe^{3+} was bound per g of Dowex 50 by elution of the Fe^{3+} with 300 ml of 2 N HCl followed by 700 ml of distilled water. The Fe^{3+} in the eluate was determined by spectrophotometric analysis of its SCN-complex at 480 nm (Sandell 1959). The Fe^{2+} form of the Dowex 50 was prepared in the same way using $Fe(NH_3)_2(SO_4)_2$. An average value of 0.021g (0.38 mmol) of Fe^{2+} per g of Dowex was determined by analysis of the Fe^{2+} in the 2 N HCl eluate of the Fe^{2+}-Dowex as the o-phenanthroline complex (Sandell 1959).

A. *Disappearance of DAMN.* Dowex 50 (2g) was washed with 2 N HCl followed by distilled water. The desired amount of Fe^{3+} was bound to the Dowex 50 by stirring the resin with an appropriate volume of $4x10^{-3}$ M $Fe(NO_3)_3$ followed by washing with distilled water. The volume of the Fe^{3+} Dowex suspension was adjusted to 50 ml with distilled water and the mixture was purged with nitrogen. To this stirred solution was added 50 ml of $2x10^{-4}$ M DAMN which had been purged with nitrogen. Aliquots were removed periodically and the DAMN content was assayed by its UV absorption at 295 nm.

B. Formation of HCN. A 5 ml solution of $5.5x10^{-4}$ M DAMN was added to a 3"x3/4" column of Fe^{3+}-Dowex. The column was eluted with 25 ml of H_2O after 20 min. To 4 ml aliquots of the eluate was added 0, 0.3, 0.5 and 0.7 ml portions of $3x10^{-3}$ M CN^- and the solutions were analyzed spectrophotometrically for cyanide (Scoggins 1972). From a plot of absorbance vs. concentration of added cyanide it was determined that 2.1∓ 0.2 moles of HCN are formed per mole of DAMN decomposed.

C. Formation of Fe^{2+}. To 10g of Fe^{3+} Dowex 50 were added 100 ml of $1x10^{-4}$ M DAMN and the mixture was stirred at room temperature for 30 min. All the DAMN reacted as shown by the absence of absorption at 296 nm. The supernant was decanted from the resin and the resin was washed 5 times with degassed water. The iron bound to the resin was then eluted by allowing the resin to stand with 100 ml of 4 N HCl for 1 h. Aliquots of the acid eluate were added to 2 ml of 25% sodium citrate and 1 ml of 0.25% o-phenanthroline. Aliquots (0, 0.2, 0.5, 0.9 and 1.0 ml) of a $5.36x10^{-4}$ M Fe(II) solution were added to the reaction solution and the absorbance of the solutions was measured at 508 nm (Sandell, 1959). From a plot of the absorbance vs. concentration of added Fe(II) it was calculated that 2.0∓0.1 equivalents of Fe(II) are formed per mole of diaminomaleonitrile decomposed.

D. Formation of Oxalic Acid. To 5g of Fe^{3+}-Dowex 50-X8 was added 5 ml of a $5x10^{-3}$ M solution of DAMN. Controls containing 1, 2, 4 and 5 ml aliquots of $5x10^{-3}$ M oxalic acid were also mixed with 5g portions of the Fe^{3+}-Dowex. The reactions were allowed to proceed at room temperature for 24 h and then a 1 ml aliquot was taken from each flask and added to a test tube containing 20 mg of magnesium turnings (Feigl 1954). To each test tube was added 1 ml of 2 N H_2SO_4 and the mixture was allowed to stand at room temperature until the Mg reacted. Then 2 ml of freshly prepared solution of 0.01% 2,7-dihydroxynaphthalene in conc. H_2SO_4 was added to each tube and it was heated at 100°C for 20 min. The absorbance of the solutions were measured at the peak of the broad maximum for the red-violet dye at 530 nm. The intensity of the absorption observed for the DAMN reaction and oxalic acid standard were identical, indicating a 100% conversion of DAMN to oxalic acid by the Fe^{3+}-Dowex. Two control experiments were negative: one in which magnesium was omitted and the second in which the sulfuric acid was not added with the 2,7-dihydroxynaphthalene. The first control established that no formaldehyde was present in the reaction solution before reduction with magnesium and the second control established that no formic acid was present before the magnesium reduction.

Reaction of DAMN with $Fe(NO_3)_3$

Aliquots of a $1.0x10^{-2}$ M solution of $Fe(NO_3)_3$ were added to a 100 ml volumetric flask containing 20 ml of a $5.0x10^{-4}$ M stock solution of DAMN and the mixture was diluted to 100 ml with distilled water (all solutions purged with nitrogen before mixing). The reaction of the DAMN was monitored by the decrease in its UV absorption at 295 nm. The concentration of Fe^{2+} in the solution was determined using phenanthroline (Sandell 1959) after there was no further change in the absorbance at 295 nm. The results are given in Table 1.

Table 1. Reduction of Fe^{3+} to Fe^{2+} with DAMN

Fe(III):DAMN ratio	Fe(II) Formed: DAMN ratio	Determinations	pH
20:1	2.16:1	2	2.7 ± 0.3
15:1	2.01:1	1	
10:1	2.04:1	4	3.0 ± 0.2
5:1	1.98:1	4	3.2 ± 0.1

Reaction of DAMN with Montmorillonite 22A

The total iron in the clay was determined by a modification of the method of Kolthoff and Sandell (1967). Freshly ground clay (0.5g), 5 ml conc. HCl and 5 ml 48% HF were mixed in a polycarbonate centrifuge tube. The mixture was heated in a water bath at just below boiling for 20 min and 15 ml of a saturated solution of boric acid were added to the cooled solution. The solution was transferred to a 250 ml beaker and the polycarbonate tube was washed with 5 ml 1:1 HCl, which was also added to the beaker. The solution was then heated to just below boiling, during which time a yellow color developed. A solution of stannous chloride was freshly prepared by diluting 1.5g $SnCl_2 \cdot 2H_2O$ to 10 ml with 1:2 HCl. The $SnCl_2$ was added dropwise to the sample solution while it was still hot; 2 drops excess were added beyond the decolorization point. The solution was cooled to room temperature, and 10 ml 5% $HgCl_2$ were added; formation of a small amount of white precipitate (Hg_2Cl_2) ensured that an excess of $SnCl_2$ had been added. A solution of Zimmerman-Reinhardt reagent was prepared by weighing 13.3g $MnSO_4 \cdot H_2O$ into a 250 ml volumetric flask, adding 30 ml conc. H_2SO_4 and 30 ml 85% H_3PO_4 and diluting to the mark with water. Twentyfive ml of the Zimmerman-Reinhardt reagent were added to the sample solution. After 1 min, the sample solution was titrated with 0.01 M $KMnO_4$ that had been standardized with $Na_2C_2O_4$ by the method of Fowler and Bright (1935). A blank was determined by performing all the above steps in the absence of clay and the results of the iron analyses reported in Table 2 were corrected for the blank. The Fe^{2+} content of montmorillonite 22A was determined by a modification of the procedure of Kolthoff and Sandell (1967). 1g of clay was weighed into a polycarbonate centrifuge tube. Five ml of 1:1 H_2SO_4 were added and the mixture was heated in a water bath to just below boiling. Five ml of 45% HF were added and the mixture was heated for 10 min. A nitrogen atmosphere was maintained above the liquid during degradation of the clay. The hot solution was added to a chilled beaker containing 150 ml double-distilled N_2-purged H20, 10 ml 1:1 H_2SO_4, 25 ml saturated H_3BO_3 and 10 ml 85% H_3PO_4. Nitrogen was bubbled through the solution as it was stirred and warmed to room temperature. Five drops 0.3% diphenylaminesulfonic acid sodium salt were added and the solution was immediately titrated with standardized 0.001 M $KMnO_4$. The end point was taken as the point at which a purple color was observed to last for longer than 30 s. A blank was determined in the absence of clay, and the Fe^{2+} analyses given in Table 2 were corrected for this factor. A check on the accuracy of the analysis, using $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$, yielded values for Fe^{2+} that were within 1% of the theoretical value.

Table 2. Iron content of Montmorillonite 22A

	Total Fe	Fe^{2+}	Fe^{3+} (difference)
Trial 1	5.77%	0.32%	
Trial 2	5.82%	0.31%	
Average	5.80%	0.32%	5.48%

A. Increase in Fe^{2+} after Reaction with DAMN. A solution of 0.001–0.005 M diaminomaleonitrile was prepared using double distilled water that had been purged with nitrogen for 1 h; the concentration of DAMN was checked by its absorbance at 295 nm (ϵ=13,500) (Sanchez et al. 1967). 10 ml of DAMN solution were added to 1 g of the clay and the mixture was stirred under nitrogen for 1 h. The clay was then centrifuged at 18,000 rpm for 15 min and the concentration of DAMN in the supernant was determined by its absorbance at 295 nm. The concentration of DAMN in a control solution without clay was also measured after 1 h, and the difference between the two concentrations was used to calculate the change in DAMN concentration due to the clay. After centrifugation, the supernant was decanted and the clay was resuspended in 10 ml double-distilled, nitrogen-purged H_2O and again centrifuged. The supernant was decanted and the clay was analyzed for Fe^{2+} as described previously. The increase in ferrous iron was obtained by subtracting the ferrous iron content of a sample of untreated clay (cf. Table 2). The molar increase in ferrous iron was calculated and divided by the molar decrease in DAMN to give the results shown in Table 3.

Table 3. Molar increase in Fe^{2+} per DAMN

[DAMN]	Fe^{2+}/DAMN
0.001 M	1.72
0.002 M	1.74
0.005 M	1.72

B. Reaction of Reduced Montmorillonite with Diaminomaleonitrile. The procedure of Solomon et al. (1968) was used to reduce 0.1–0.25g portions of clay by stirring first for 1h with 5% aqueous hydrazine, centrifugation at 18,000 rpm for 15 min followed by an 18 h treatment with 5% hydrazine. The clay was again suspended in 20 ml H_2O and dilute HCL was added until a constant pH = 6 was obtained. Immediately prior to use, the clay was centrifuged and the supernant was decanted from the clay.

In the comparison of the rate of reaction of the reduced and unreduced clay with DAMN, 0.25g montmorillonite 22A was reduced and washed as described above. A second sample of 0.25 g montmorillonite was not treated with hydrazine but received the same number of washes. A 0.71 x 10^{-4} M DAMN solution was prepared using distilled nitrogen-purged water and adjusted to pH = 6. 30 ml were added to each of the clays; 30 ml served as a control. The solutions were stirred for 1 1/4 h, centrifuged at 18,000 rpm for 15 min, and the absorbance at 295 nm was measured to determine the extent of decomposition of DAMN. The results are given in Table 4.

Table 4. Decomposition of DAMN with reduced clay

Reaction system*	Decomposition after 1.5 h
Control (no clay)	0.8%
Unreduced mont 22A	>90.0%
Reduced mont 22A	2.0%

*0.25 g clay + 30 ml 7.1 x 10^{-5} M DAMN (pH = 6)

The reaction of 1.0 ml of 0.89 x 10^{-4}M DAMN with 0.1g reduced montmorillonite at pH 6 was studied for an extended time period under a nitrogen atmosphere. Nitrogen was continuously passed through the solution at a rate of one bubble per 10 s. At intervals, the reaction mixture was removed and centrifuged at 18,000 rpm for 15 min. The absorbance of the solution at 295 nm was used to calculate the decomposition of DAMN. The clay was then resuspended in the supernant and the mixture was returned to the reaction flask. The results are given in Table 5.

Table 5. Decomposition of DAMN with reduced montmorillonite

Time (h)	DAMN decomposition
15	2.2%
40	2.3%
62	2.5%

A 4.0 x 10^{-4} M solution of DAMN was prepared using double-distilled water which had been purged with nitrogen. The reduced clay was suspended in 25 ml DAMN and transferred to a round bottom flask connected to a water-cooled reflux condensor.The top of the condensor was sealed with a glass tube leading into a flask containing 10 ml 2 M NaOH. The hydroxide solution both prevented air from entering the apparatus and provided a trap for volatile HCN that passed through the condensor. The apparatus was purged with nitrogen and the flask containing the clay suspension was heated with stirring in an oil bath at 80° C for 12–28 days. The apparatus was then cooled to room temperature and the clay suspension was centrifuged. There was no DAMN in the supernant as shown by the absence of UV absorption at 295 nm. There was strong absorption at

245 nm suggesting extensive decomposition of the clay (Banin and Lahav 1968; Chen et al. 1979). The amount of cyanide trapped in the NaOH solution was determined by the method of Scoggins (1972). Values of 2.3 and 1.9 moles of HCN formed per mole of DAMN reacted were obtained after reaction times of 12 and 28 days respectively.

Relative Reaction Rates of Different Forms of Fe^{3+}

Fe^{3+} (3.8×10^{-5} mol) bound to 200 mg Dowex 50, 39 mg of montmorillonite 22A (3.8×10^{-5} mol of Fe^{3+}) and Fe^{3+} (4×10^{-5} mol) dissolved as $FeCl_3$ were reacted in 50 ml with 5×10^{-6} mol of DAMN at pH 2.5 ∓ 0.2. The extent of reaction was determined from the absorption of DAMN at 295 nm. The half life for DAMN decomposition for $FeCl_3$, Fe^{3+}-Dowex and montmorillonite 22A was found to be <1 min, 8 h and 25 h respectively.

Results and Discussion

Previously we established that the exchangeable cations in the montmorillonite were not responsible for the decomposition of DAMN (1) (Ferris et al. 1979), and therefore we undertook an investigation of the reaction of DAMN with the non-exchangeable cations which replace the aluminum and silicon in the aluminosilicate clay lattice. Ferric iron was investigated first, since it is one of the most abundant non-exchangeable metal ions present in montmorillonite 22A based on the analysis of closely related montmorillonite 22 (American Petroleum Institute, 1951).

Ferric iron bound to a Dowex 50 ion exchange resin was used as a simple model for Fe^{3+} within the octahedral layer of the clay lattice. An aqueous solution of DAMN was decomposed rapidly by Fe^{3+} bound to Dowex 50, but a much slower reaction of DAMN was observed with Fe^{2+}-Dowex (experiment not described). The similarity in reactivity of the Fe^{3+}-Dowex and montmorillonite clay systems was demonstrated by the formation of two moles of HCN per mole of DAMN reacted in both. It was established that Fe^{3+} is serving as an oxidizing agent in the Fe^{3+}-Dowex system by the formation of two equivalents of Fe^{2+} per mole of DAMN reacting. Subsequently it was observed that aqueous solutions of Fe^{3+} effected the oxidation of DAMN with formation of two equivalents of Fe^{2+}. A preliminary report which indicated that less than two equivalents of Fe^{2+} are formed has since been found to be incorrect (Ferris et al. 1981).

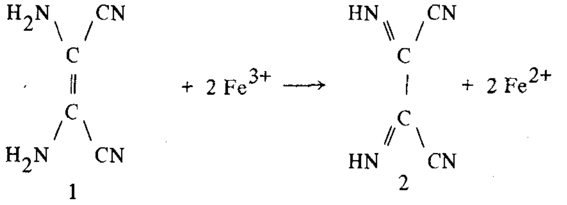
That Fe^{3+} is the principal oxidizing agent in the montmorillonite was established by the observation that 1.7 equivalents of Fe^{2+} are formed per mole of DAMN oxidizied. Since it had been previously demonstrated that two equivalents of Fe^{2+} were formed per DAMN in the Fe^{3+}-Dowex and aqueous Fe^{3+} systems the formation of only 1.7 equivalents of Fe^{2+} with montmorillonite was an unexpected result. We are unable to account for the oxidative loss of the remaining 15% of the DAMN. There does not appear to be any other metal ion present in sufficient quantity in the montmorillonite 22A to act as the oxidant for the remaining DAMN (American Petroleum Institute, 1951). One other possible oxidant is the "crystal edges" of the clay. It has been postulated that coordinatively-unsaturated aluminum ions act as electron acceptors (Solomon et al. 1968). This effect has been postulated to account in part for the oxidation of benzidine by montmorillonite.

DAMN undergoes a very slow decomposition in the presence of montmorillonite that had been reduced with hydrazine. The reaction is accelerated at higher temperatures and an oxidative pathway is suggested by the observation that two moles of cyanide are formed per DAMN. This slow oxidative reaction is understandable in terms of the incomplete reduction of montmorillonite by hydrazine (Tennakoon et al. 1974) and the gradual decomposition of the montmorillonite with the release of Fe^{3+} from the aluminosilicate lattice (Gerstl and Banin 1980; Bar-On and Shainberg 1970). No electron-transfer polymerization of DAMN was observed in aqueous solution with the hydrazine-reduced montmorillonite (Solomon and Loft 1968). This polymerization reaction may be observed in the solid state where there are no competing hydrolytic processes.

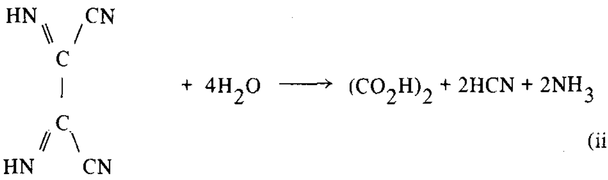
The relative rates of DAMN oxidation were measured to test for catalysis of the reaction by the clay surfaces. The absence of surface catalysis was dramatically shown by the 10^3 fold greater rate of DAMN oxidation by an aqueous solution of Fe^{3+} than by a comparable amount of Fe^{3+} in montmorillonite 22A. The observed 3 fold faster reaction of DAMN with Fe^{3+}-Dowex than with montmorillonite is probably due to the unavailability of some of the iron in the clay to react with the DAMN (Tennakoon et al. 1974). The unreactive Fe^{3+} in the montmorillonite is located in sites which are shielded on the top and bottom by silicon-oxygen tetrahedral layers.

There are other examples of the oxidation of organic compounds by the Fe^{3+} in clays. The oxidation of benzidine to the radical cation benzidine blue (Solomon et al. 1968) is analogous to the first electron transfer step in the oxidation of DAMN. Iron rich clays on Mars are probably responsible for the oxidation of formic acid to CO2 in the Viking Labeled Release experiment (Banin and Rishpon 1979).

The first step in the reaction of DAMN must be its oxidation to diiminosuccinonitrile (DISN) (2) (reaction i) (Webster et al. 1972). DISN reacts rapidly with water and other nucleophiles to form oxalic acid or oxalic acid derivatives and two equivalents of cyanide (reaction ii) (Begland et al. 1972; Ferris and Ryan 1973). The formation of one mole of oxalic acid per mole of DAMN was established by the reduction of the oxalic acid to glycolic acid and the subsequent conver-



$$H_2N(NC)C{=}C(CN)NH_2 + 2\,Fe^{3+} \longrightarrow HN{=}C(CN){-}C(CN){=}NH + 2\,Fe^{2+} \quad \text{(i)}$$



$$HN{=}C(CN){-}C(CN){=}NH + 4H_2O \longrightarrow (CO_2H)_2 + 2HCN + 2NH_3 \quad \text{(ii)}$$

sion of the glycolic acid to formaldehyde (Feigl 1954a). This finding together with the detection of two equivalents of cyanide establishes the stoichiometry outlined in reaction ii.

The facile decomposition of DAMN in the presence of $Ni(NH_3)_6^{2+}$ (Ferris and Edelson 1978) can be understood on the basis of the reaction pathway outlined in equations i and ii. The Ni^{2+}-catalyzed reaction was originally believed to be simply a hydrolytic reaction because an oxidative process requires the reduction of nickel to a less common Ni^+ or Ni0 oxidation state (Huheey 1972). However, the formation of two equivalents of HCN per molecule of DAMN decomposed is good evidence for the oxidation of DAMN to DISN (2) which in turn is hydrolyzed to two equivalents of HCN. Lower valence states of Ni are indicated by our observation that DAMN is decomposed only by $Ni(NH_3)_6^{2+}$ and not uncoordinated Ni^{+2} ions. The lower (less than +2) oxidation states of nickel are stabilized by coordinating ligands (Huheey 1972). In addition, it has been reported that hydrazine reduces the tetracyano complex of nickel from the +2 to the +1 oxidation state (Nast and von Krakkay 1954). Since both hydrazine and DAMN reduce Fe^{3+} it is likely that DAMN will also be able to reduce Ni^{2+} and be oxidized to DISN in the process. The lower oxidation states of nickel formed in the reaction with DAMN would be readily oxidized back to Ni^{2+} by atmospheric oxygen (Nast and von Krakkay 1954).

Our experiments demonstrate that the oxidation state of the metal ions in the clay used in prebiotic simulation experiments can have a profound effect on the course of a reaction. The ratio of Fe^{3+} to Fe^{2+} in clays increased as the atmosphere of the primitive earth became more oxidizing. Clays in which the Fe^{2+} oxidation state predominated were probably formed initially. The release of O_2 by the photolysis of water (Walker 1977) led to the oxidation of some of the Fe^{2+} in the clays to the Fe^{3+} oxidation level. These iron-containing clays may have served as electron transfer agents in primitive forms of life, a process which was eventually taken over by iron porphyrins. The redox properties of the iron in both systems would have provided the bridge (continuity) in the evolution of the clay system to the porphyrin redox systems (Rao et al. 1980).

A mixture of both the Fe^{2+} and Fe^{3+} oxidation states in clays may have been even more effective than Fe^{2+} alone in catalyzing the formation of biopolymers on the early earth. The Fe^{2+} clays may have initiated polymerization reactions by electron donation to olefins (Solomon and Loft, 1968). The Fe^{3+} clays may have effected peptide and nucleotide synthesis and condensation reactions by the formation of high energy intermediates such as DISN - a process similar to the oxidative phosphorylation observed in contemporary biochemical systems (Lehninger 1975). The use of DISN as a condensing agent is currently under investigation in this laboratory.

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References

American Petroleum Institute (1951) Clay Mineral Standards. American Petroleum Institute Project 49 Preliminary Report 7B, Chemical analysis, Columbia University,N.Y.

Banin A, Lahav N (1968) Particle Size and Optical Properties of Montmorillonite in Suspension. Isr J Chem 6: 235-250

Banin A, Rishpon J (1979) Smectite Clays in Mars Soil: Evidence for their presence and role in viking biology experimental results. J Mol Evol 14: 133–152

Bar-On P, Shainberg I (1970) Hydrolysis and Decomposition of Na-Montmorillonite in Distilled Water. Soil Sci 109: 241-246

Begland R W, Hartter D R (1972) Hydrogen Cyanide Chemistry IV. Diiminosuccinonitrile Reactions with Nucleophiles, Acyl Halides and Carbonyl Compounds. J Org Chem 37: 4136–4145

Bernal J P (1951) The Physical Basis of Life. London: Routledge and Kegen Paul, London, pp. 5355–5368

Chen Y, Shaked D, Banin A (1979) The Role of Structural Iron (III) in the Absorption of Smectites. Clay Minerals 14: 93–102

Feigl F (1946) Qualitative analysis by spot tests, Elsevier, New York, p. 186

Feigl F (1954) Spot Tests Vol. II, Organic Applications, translated by R. Oesper, Elsevier, Amsterdam, pp. 249-250

Ferris J P, Ryan T J (1973) Chemical Evolution XIV. The Oxidation of Diaminomaleonitrile and its Possible Role in HCN Oligomerization. J Org Chem 38: 3302–3307

Ferris J P, Joshi P C, Edelson E H, Lawless J G (1978) HCN: A Plausible Source of Purines, Pyrimidines and Amino Acids on the Primitive Earth. J Mol Evol 11: 293–311

Ferris J P, Edelson E H (1978) Chemical Evolution 31. Mechanism of the Condensation of Cyanide to HCN Oligomers. J Org Chem 43: 3989-3995

Ferris J P , Edelson E H , Mount N M, Sullivan A E (1979) The Effect of Clays on the Oligomerization of HCN. J Mol Evol 13: 317–330

Ferris J P, Alwis K W, Edelson E H, Mount N M, Hagan Jr W J (1981) Origin of Life, Y. Wolman (ed.), 218, Reidel, Dordrecht, Holland,pp. 125-128

Fowler R M, Bright H A (1935) J. Research Nat. Bur Standards 15:493 as described in Skoog D A, West D M (1969) Fundamentals of Analytical Chemistry, 2nd ed., Holt, Rinehart and Winston, New York, p. 423

Gerstl Z , Banin A. (1980) Fe^{2+}-Fe^{3+} Transformations in Clay and Resin Ion-Exchange Systems. Clays Clay Min 28: 335–345

Huheey J E (1975) Inorganic Chemistry: Principles of Structure and Reactivity, Harper and Row, New York, p. 443

Kolthoff I M, Sandell A B (1967) Textbook of Quantitative Inorganic Analysis, 3rd ed., MacMillan, New York, pp. 708

Lehninger A (1975) Biochemistry, Worth, New York, p. 514

Oro J , Kimball A P (1962) Synthesis of Purines Under Possible Primitive Earth Conditions II. Purine Intermediates from Hydrogen Cyanide. Arch Biochem Biophys 16: 293–313

Nast R, von Krakkay T (1954) Über ein kalium-tetracyanoniccolat(I)$K_3[NiCN)_4]$. Naturforschg 9b: 798–799

Rao M , Odom D G , Oro J (1980) Clays in Prebiological Chemistry. J Mol Evol 15: 317–331

Sanchez R A , Ferris J P , Orgel L E (1967) Studies in Prebiotic Synthesis II. Synthesis of Cyanide Precursors from Amino Acids and Aqueous Hydrogen Cyanide. J Mol Evol 30: 223–253

Sandell E B (1959) Colorimetric Determination of Traces of Metals, 3rd ed., Interscience, New York, pp. 524–542

Scoggins M W (1972) Ultraviolet Spectrophotometric Determination of Cyanide Ion. Anal Chem 44: 1294–1296

Solomon D H , Loft B C (1968) Reactions Catalyzed by Minerals Part III. The Mechanism of Spontaneous Interlamellar Polymerizations in Aluminosilicates. J Appl Poly Sci 12: 1253–1262

Solomon D H , Loft B C , Swift J D (1968) Reactions Catalyzed by Minerals IV. The Mechanism of the Benzidine Blue Reaction on Silicate Minerals. Clay Minerals 7: 389–397

Tennakoon D T B , Thomas J M , Tricker M J (1974) Surface and Intercalate Chemistry of Layered Silicates Part II. An Iron-57 Mossbauer Study of the Role of Lattice-substituted Iron in the Benzidine Blue Reaction of Montmorillonite. J Chem Soc Dalton: 2211–2215

Walker J C G (1977) Evolution of the Atmosphere, Macmillan, New York, pp. 220–226

Webster O W, Hartter D R , Begland R W , Sheppard W A , Cairncross A (1972) Hydrogen Cyanide Chemistry III. Synthesis of Diiminosuccinonitrile and its Conversion to Diaminomaleonitrile. J Org Chem 37: 4133–4136

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