

SOIL AND WATER AND ITS RELATIONSHIP TO THE ORIGIN OF LIFE

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Abstract. Soils of the terrestrial planets form at the boundaries between lithosphere, atmosphere and hydrosphere. Biogenesis occurred in these zones; thus, it is axiomatic that some, perhaps many, stages of biogenesis occurred in intimate association with the mineral constituents of soils. Because of a high surface to mass ratio and, consequently, a high surface reactivity, the layer lattice clay minerals are the most important of these. According to the geological record, clay minerals appeared very early on the primordial Earth. Recent investigations have confirmed their presence in carbonaceous meteorites and have indicated their occurrence on Mars.

In this paper we collect pertinent physico-chemical data and summarize the organic reactions and interactions that are induced or catalyzed by clays. Many clay-organic reactions that do not occur readily at high water contents proceed rapidly at adsorbed water contents corresponding to surface coverages of one or two molecular layers. One or two monolayers of adsorbed water correspond to extremely dry or cold planetary environments. Some consequences of these facts *vis à vis* biogenesis on Mars are considered.

1. Introduction

It now seems certain that the multiplicity of organic compounds required in primitive life forms could have arisen through the 'normal' sequences of abiotic synthesis (Oró, 1972, Ponnamperna and Gabel, 1971). Consideration of the reaction-kinetics that must have been involved has produced general agreement on the necessity of a liquid phase. Beginning with Bernal, it has often been observed that zones where lithosphere and hydrosphere come in contact (or, on the molecular level, where liquid and solid phases join) were critical locations (Bernal, 1967; Fox, 1965; Rutten, 1972). Others, however, have argued from time to time that the entire sequence might have occurred in an essentially open aqueous system. The basic biochemical unity of terrestrial life has fostered the view that surviving life-forms, despite great morphological diversity, evolved from a single primitive precursor. Even though a number of concurrent abiotic sequences originally may have developed, the common view is that eventually one prevailed. In principle, it should be possible to deduce the environmental locale in which the prevailing sequence originated; in actuality, this information probably will never be apprehended.

It is axiomatic in evolutionary thought that complexity has, over time, arisen step by step out of simplicity; thus, research in chemical evolution began with efforts to establish how the building blocks of molecular biology could have arisen through abiotic synthesis from such simple molecules as CH_4 , CO , NH_3 , H_2 , N_2 and H_2O . This has been followed by investigations of abiotic syntheses of organic molecules of increasing complexity. In order to guard against ambiguity in the interpretation of experimental data, most investigators have endeavored to keep the number of the

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reactants and the complexity of the experimental design to a minimum. For this reason, until relatively recently, heterogeneous and imperfectly characterized solid substrates such as clays and other soil constituents were avoided although the possible critical roles of mineral surfaces often implicitly were recognized. Now, sufficient knowledge pertaining to the general aspects of biogenesis is in hand so that an increasing number of systematic experiments involving mineral substrates are being made. In this paper, we collect and examine recent experimental evidence bearing on the involvement of soil particulates in biogenesis.

2. Clays, the Active Constituent of Soil

Soils form where the lithosphere contacts atmosphere and hydrosphere. In the most primitive condition soil consists entirely of mineral matter derived by simple comminution of parent rock together with the products of primary chemical alteration and resynthesized secondary minerals. In the present context, the important processes occur at solid-liquid and solid-gas interfaces. Hence, the extent of these interfaces is of primary importance. Because of an exceedingly large surface area to mass ratio, the smallest particles constitute the most active fraction of planetary soils. By definition, this is the clay fraction. Although seldom, if ever, in true equilibrium with surrounding environments, the clay minerals can be very stable, as indicated by their presence in the oldest known sedimentary rocks and a high abundance throughout geologic history (Ronov *et al.*, 1973). According to one possible sequence (Eitel, 1966) the zeolites appear first, following the late magmatic-hydratogenic state. Subsequent hydrothermal stages and low temperature diagenesis lead to the appearance of the several clay mineral families. Following synthesis and continuing diagenesis, representative species rapidly became distributed throughout the atmosphere, hydrosphere and, much of the lithosphere.

For present purposes, it is permissible to employ the term clay in its most general sense, i.e. materials that exhibit the familiar properties of clays. This includes naturally occurring, fine-grained, heterogeneous mineral matter exhibiting a strong affinity for water, plasticity and base exchange. This includes all the crystalline clay minerals of the kaolinite, halloysite, montmorillonite, vermiculite, illite, chlorite, attapulgite, sepiolite and palygorskite families and, in addition, others present in a state of subdivision sufficiently small to exhibit colloidal properties such as amorphous, allophane. The crystalline clay minerals for the most part are platy aluminosilicates composed of alternating layers of silicon in tetrahedral coordination, and aluminum in octahedral coordination, with oxygen. Stacked in 2:1 or 1:1 sequences these form elementary crystalline sheets; several elementary sheets then stack to form packets (tactoids) or quasi-crystals. Without going into the details, because of isomorphous substitution of metallic ions within the lattice, such as aluminum for silicon and iron for aluminum, a residual net negative charge usually is imparted to each elementary sheet. This charge must be balanced by adsorbed cations, usually sodium, calcium, etc. Taking montmorillonite as an example, the fundamental particle is an aluminosilicate

silicate sheet 10 Å in thickness and up to several thousand Å in length and width. Faces of the sheets consist of planes of oxygen atoms in planar hexagonal array. Tactoids normally contain two to fifteen elementary sheets depending on the exchangeable cation(s) present. The principal effect of variations in tactoid size is to bring about a change in the ratio of external to internal surface area (Banin and Lahav, 1968). Other clay minerals differ in structural detail, but in general possess similar characteristics. A summary of some of the best characterized clay minerals is given in Table I. Interestingly, it is a general observation that regardless of mineralogy, clay-size particles, produced by comminution tend toward platy shapes, even quartz (Krinsley and Smalley, 1973). Clays exist in interstellar space in the form of small (<0.1 μ) 'dust' particles and have been identified as constituents of comets and carbonaceous meteorites (Bass, 1971; Oró, 1972; Rutten, 1972). Clays thus are

TABLE I
Surface characteristics of the major aluminosilicate clay minerals

| Characteristics | Montmorillonite | Vermiculite | Illite | Kaolinite |
|---|---------------------------|---------------------------|---------------------------|---------------------------|
| Lattice stacking units (Si tetrahedral layers: Al octahedral layers) | 2:1 | 2:1 | 2:1 | 1:1 |
| Total specific surface area (m ² g ⁻¹) | 700-800 | 700-800 | 100-200 | 25-50 |
| Percentage of internal surface | 10% to 90% ^a | 80% to 90% | 0 | 0 |
| Cation exchange capacity (meq g ⁻¹) | 0.8-1.2 | 1.2-2.0 | 0.15-0.40 | 0.02-0.10 |
| Average surface charge density (esu cm ⁻²) | 3.3-4.3 × 10 ⁴ | 5.0-7.2 × 10 ⁴ | 4.3-5.8 × 10 ⁴ | 2.3-5.9 × 10 ⁴ |
| Area per elementary charge (Å ²) | 110-150 | 60-100 | 80-110 | 180-200 |
| Free swelling in water (cm ³ g ⁻¹) | 0.5-20 ^a | 0.5-15 ^a | 0.1-1.2 | 0-0.3 |
| Range of interlammellar expansion | 6-240 Å ^a | 6-200 Å ^a | - | - |

^a Depending upon exchangeable cation.

ubiquitous in time and space and have been present at virtually all stages of planetary accretion and subsequent evolution. Interactions between clay particles and the reactants and products of prebiotic sequences of organic synthesis therefore must have been of significance in primordial chemical evolution as well as subsequent stages of speciation and population of the Earth.

3. Clay-Organic Reactions

Not all the interactions possible would have facilitated biogenesis: many would have tended to hinder or interrupt the process. On the other hand, many might have aided and some could have been vital. Concentration of reactants is required at certain steps. Adsorption and preferential orientation of significant precursors by mineral substrates is a process by which this function may have been accomplished. Another crucial process that could have been operative is the juxtaposition of reactants and the catalysis of surface reactions, the stabilization of intermediates and catalysis of

subsequent polymerizations. Clay substrate-organic reactions that can lead to the synthesis of larger and more complex molecules from simple precursors may be categorized as:

- (1) Simple bonding by interaction at the surface (physical and chemisorption)
- (2) Initiation of (or rate enhancement of) reactions, including polymerizations (Catalysis)
- (3) Suppression of randomness in recombination, polymerization, and condensation reactions (Epitaxy)

In many cases, the first may occur without leading to the second and the first and second occur without the third.

Clay-organic reactions investigated to date are summarized in Table II. Organic

TABLE II
Representative known clay-organic interactions

| | Clay type | Mechanism | References |
|--|------------|--|---|
| I. ADSORPTION | | | |
| n-Alkyl-ammonium ions | M | Cationic adsorption | Jordan (1949a, b) |
| | V | | Walker (1950) |
| | V | | Garret and Walker (1962) |
| n-Alkyl-pyridinium ions | M | Cationic adsorption | Raman and Mortland (1969) |
| | M | | Greenland and Quirk (1962) |
| | M | | Greenland and Quirk (1962) |
| Pyridines, purines, nucleosides | M | Cationic adsorption and coordination complex | Lailach <i>et al.</i> (1968a, b) |
| | M | | Lailach and Brindly (1969) |
| | M | | Farmer and Mortland (1966) |
| Diquat and paraquat ions (herbicides) | Soils | Cationic adsorption and coordination complex | Knight and Tomalinson (1967) |
| | M, K, I | | Weed and Weber (1968, 1969) |
| Quinoline | M, K, I | Surface interaction with polar groups | Doehler and Young (1962) |
| Polyalcohols (various) | M | Surface interaction with polar groups | Tettenhorst <i>et al.</i> (1962) |
| | M, N, V | | Brindly (1966) |
| | M | | Greenland (1963) |
| | M | | Dowdy and Mortland (1968) |
| Hystidine | M | Polar groups; coordination | Heller-Kallai <i>et al.</i> (1972) |
| Proteins (various) | M | Polar groups and hydrogen bonding | Ensminger and Giesking (1941) |
| | K | | McLaren (1954) |
| | M, K, I, V | | Harter and Stotzky (1971) |
| | M, K, I, V | | Albert and Harter (1973) |
| NH ₃ adsorption | M, V | Coordination complex formation and cationic adsorption following protonation | Mortland <i>et al.</i> (1963) |
| Urea and urea derivatives | M | Coordination complex formation and cationic adsorption following protonation | Mortland (1966) |
| | M | | Tahoun and Mortland |
| | M | | (1966 a,b) |
| Pyridine, methylamine, 3-aminotriazole | M, S | Cationic adsorption following protonation | Farmer and Ahlrichs (1969) |
| | M | | Farmer and Mortland (1966) |
| Ethylenediamine | M | Protonation and hydrogen bonding | Raman and Mortland (1969) Cloos and Laura (1972) |

Table II (Continued)

| | Clay type | Mechanism | References |
|---|-----------|--|--|
| II. ACID CATALYSIS REACTIONS | | | |
| Ethyl-acetate hydrolysis; sucrose inversion | M | Bronsted acidity (Adsorbed H ⁺) | Coleman and McAuliffe (1955) |
| Trans-alkylation of alkylammonium cations | M | Bronsted acidity | Calvet <i>et al.</i> (1964) |
| | M | (partially dissociated adsorbed water) | Durand <i>et al.</i> (1972) |
| Decomposition of amines | M | Bronsted acidity (partially dissociated adsorbed water) | Chaussidon and Calvet (1965) |
| Decomposition of Co (III) hexamine cations | M | Bronsted acidity (partially dissociated adsorbed water) | Chaussidon <i>et al.</i> (1962) |
| Coloration reactions (benzidine-benzidinium) | M | Lewis acidity (aluminum ions exposed at edges) | Hauser and Leggett (1940) |
| Decomposition of S. Triazines | M | Protonation and | Russell <i>et al.</i> (1968) |
| | M | hydrolysis | Cruz <i>et al.</i> (1968) |
| III. POLYMERIZATION REACTIONS | | | |
| Methacrylates | M | | Blumstein (1965) |
| | M | | Blumstein <i>et al.</i> (1969) |
| | M | | Solomon and Loft (1968) |
| | M | | Malhotra <i>et al.</i> (1972) |
| Vinyls | M | | Dekking (1967) |
| Styrene | M, K, A | | Solomon and Rosser (1965) |
| IV. CATALYSIS AND POLYMERIZATION REACTIONS OF BIOLOGICAL SIGNIFICANCE | | | |
| Amino acid formation from NH ₂ , | M | | Yoshino <i>et al.</i> (1971) |
| H ₂ , CO ₂ and ND ₂ , D ₂ , CO ₂ | M | | Hayatusu <i>et al.</i> (1971) |
| Amino acids and purines | Z | | Fripiat <i>et al.</i> (1972) |
| formation from CO and NH ₃ | | | |
| Formation of trioses, tetroses, pentoses and hexoses from formaldehyde | K | | Gabel and Ponnampereuma (1967) |
| Polymerization of amino acid phosphate anhydrides | M | | Paecht-Horowitz (1971) |
| Polymerization of amino acids | M | | Cloos <i>et al.</i> (1966) |
| Formation of polypeptides from amino acid adenylates | M | | Fripiat <i>et al.</i> (1966) |
| | | | Paecht-Horowitz <i>et al.</i> (1970) |
| Oligonucleotide formation from thymidylic acid | M | Pentanucleotides formed in the presence of montmorillonite | Ibanez <i>et al.</i> (1971) |
| ADP synthesis | K | | Steinman <i>et al.</i> (1965) Steinman (1966) |

M = Montmorillonite A = Attapulgit
 S = Saponite K = Kaolinite
 N = Nontronite Z = Zeolites
 I = Illite

adsorption on clays involves direct, electrostatic adsorption and ion-dipole and coordination bonding to adsorbed inorganic ions on the clay. Also of importance are van der-Waals attraction, hydrogen bonding, covalent bonding and entropy effects (Mortland, 1970). Possible combinations of these bonding mechanism explain the observation that for large organic ions of the same valence, organic cations are more strongly adsorbed than inorganic cations.

The catalytic activity of clays and zeolites derives in part from the moderation of molecular displacements by adsorption forces and the ability of clays to exchange ionic species and expose adsorbed molecules to strong electrostatic forces at a variety of localized charge sites. Naturally occurring surfaces are heterogeneous with regard to sorption sites, but the density of sites of surface charge and sites of potential catalytic activity is surprisingly uniform, the total number per unit weight depending principally on the specific surface area. Thus it can be suggested in passing that in many in-vitro syntheses, surface catalysis by the apparatus may have contributed significantly to the results, especially in reactions of low yield, requiring relatively high temperatures. In media such as beach sand and basalt, moreover, clays usually are present to some extent unless specifically removed. In such experiments, the question of reaction rates and yield should be addressed keeping the total surface areas exposed by both apparatus and media in mind.

Catalysis of reactions by clay surfaces in most cases is related to a 'surface acidity' resulting from one or more of the following mechanisms:

(a) Protons donated from the adsorbed, exchangeable hydrogen ions (Coleman and McAullife, 1955); Bronsted acidity.

(b) Protons transferred from adsorbed water molecules polarized by the electrostatic fields of exchangeable, metallic cations; e.g. protonation of pyridine to pyridinium cation on partially hydrated montmorillonite (Farmer and Mortland, 1966; Touillaux *et al.*, 1968); Bronsted acidity.

(c) Protons transferred from other adsorbed ions or molecules; e.g. proton transfer from adsorbed NH_4^+ to 3-Aminotriazole forming 3-Aminotriazolium cation (Russel *et al.*, 1968); Bronsted acidity.

(d) An adsorbed ion or molecule acting as an electron acceptor; e.g. electron transfer from benzene, xylene, etc. to Cu (II) on montmorillonite; (Donner and Mortland, 1970); Lewis acidity.

(e) The clay lattice acting as an electron acceptor; e.g. electron transfer to lattice aluminum exposed at an edge, transforming colorless benzidine to blue, monovalent benzdinium cation; (Hauser and Leggett, 1940); Lewis acidity.

Mechanisms (b) and (c), commonly referred to as 'protonation' reactions, are now well characterized. Regarding mechanism (e), Lewis basicity may operate in some circumstances. It has been suggested that a lattice component in a relatively low oxidation state, such as Fe^{+} , may act as an electron donor (Solomon, 1968); experimental confirmation of this mechanism, however, presently is lacking.

Polymerization on clay substrates has been demonstrated in a number of cases. According to Solomon (1968) and Solomon *et al.* (1971) polymerizations involving

free radicals generally are catalyzed by clay surfaces only if a suitable 'initiator' is present; otherwise they are inhibited. Reactions involving cationic radicals generally are catalyzed, but reactions involving anionic radicals are catalyzed only if certain conditions involving polymer type, expandability of the clay, and the presence of a transition metal of low oxidation state in the lattice (e.g. Fe^{+2}), are fulfilled. Consequently, most anionic-radical polymerizations appear to be inhibited by clay mineral surfaces. The polymerization of hydroxy methacrylate on montmorillonite surfaces, however, is an exception (Solomon, 1968). It is of particular interest to note that 'insertion polymers' produced from methyl methacrylate monomers sorbed by montmorillonite (Blumstein, 1965; Blumstein *et al.*, 1969), formed aggregates, "... the architecture (of which) is reminiscent of the elementary crystallite of montmorillonite." (Blumstein *et al.*, 1969). An example of the ability of mineral substrates to confer orientational order on condensed surface phases is the orientation of the nematic phase of p-azoxyanisole on glass. This 'liquid crystal' displays sensitivity both to crystallographic orientation of the substrate and to subtle variations in surface topography (Bikerman, 1970). The full range of such epitaxial phenomena is immense but undefined; it merits systematic evaluation.

4. Clay-Water-Organic Interactions

Clay surfaces are commonly hydrophilic; isosteric heats of water vapor adsorption of the order of 75 kcal mole⁻¹ characterize the first increments. Values for subsequent increments decline with increasing surface coverage to the normal latent heat of liquefaction. The presence of water in a definite quantity and position is essential for some of the processes discussed above, particularly those in the category of acid catalysis. Optimal water contents for acid catalysis are in the range of 5–10% by weight for montmorillonite (Durand *et al.*, 1972). This corresponds approximately to a monolayer of water separating adjacent lamella. The enhanced catalytic activity can be attributed to a perturbation of water molecules by the electrostatic fields surrounding the exchangeable ions and covering the silicate surfaces that results in localized increases in proton activity. Higher water contents interfere by decreasing the rate of interaction between the reacting species and the finite number of perturbed water molecules, reducing conversion rates. On the other hand, desiccation of the surface below the optimum value reduces conversion rates because of reductions in the number of perturbed water molecules.

At high water contents, clays can form gels that, in many significant respects, mimic the gels that constitute portions of intracellular media. Depending on clay and electrolyte concentration, these gels exhibit thixotropy, and syneresis, and have water activities and rheological properties comparable to those required for biochemical processes and characteristic of present day intracellular fluids. Although mere rheological mimicry cannot be advanced as proof that inorganic gels played essential roles in the origin of life, neither is it without significance. It is highly probable that many adsorbed organic molecules were conveyed by this means into aqueous

environments, complete with electrolytes, like those characteristic of living cells.

5. Expanding Clay Lattices

The possible role played by clay substrates in orienting organic molecules and bringing about juxtapositions favorable for charge or proton transfer reactions or effective in reducing randomness in addition reactions and polymerizations is a particularly striking possibility in the case of the expanding-lattice clay minerals montmorillonite and vermiculite. In these minerals, individual lamella separate, expand and contract according to the degree of hydration. A full treatment is precluded but a brief discussion of an expanding vermiculite is given for purposes of illustration.

Vermiculites exist as powders, small flakes and large single crystals. As shown in Table I, they have high ion exchange capacities. When saturated with lithium or butylammonium ions and subsequently exposed to water, they expand by imbibition in the (001) dimension. The rate and extent of expansion of lithium saturated Kenya vermiculite in water is illustrated by the time-lapse photographs presented in Figure 1. It is seen that the crystal expands in the (001) direction to about 20 times its original dimension. Since expansion is uniform and the initial thickness of the swelling units is about 10 Å, it follows that the thickness of the imbibed interlamellar water layers averages about 200 Å. Gradual dehydration brings about collapse of the expanded crystal and complete dehydration is only partially reversed. Semiclosure of the interlamellar space can also be accomplished, without dehydration, by freezing. In the case of the various ionic forms of montmorillonite (a comparable mineral) the interlamellar space contracts on freezing to about 9 Å at -5°C and to about 6 Å at -10°C (Anderson and Hoekstra, 1965). On subsequent thawing of this mineral, re-expansion occurs. The lamellar ice crystals are preferentially oriented, presumably due to interaction with the mineral surface; the same effects have been observed with lithium-vermiculite. It is significant that from -10°C to -180°C the thickness of the interface separating adjacent lattice layers remains nearly constant, at 6 Å. Calorimetric investigations of both pure and mixed clay substrates has shown that this 6 Å thickness of interlamellar water remains liquid-like down to at least -30°C (Anderson and Morgenstern, 1974). The interface thickness as a function of temperature is shown in Figure 2. The ordinate, given in $\text{g H}_2\text{O m}^{-2} \times 10^2$, is equivalent when multiplied by 100, to interface thickness in Å (thus $0.10 \text{ g H}_2\text{O m}^{-2} \times 10^2 \approx 10 \text{ Å}$ thickness). Specific data for lithium-vermiculite are not yet available, but inasmuch as its other properties parallel those of montmorillonite it is safely concluded that its interface thickness vs. temperature relationship is encompassed by the curves shown in Figure 2. It is seen then that liquid-like interfaces separating lamellar ice sheets from the silicate surfaces range in thickness from 5 or 6 Å to more than 80 Å. Due to solute exclusion during ice crystallization, the concentration of solutes can change over wide ranges during freezing and thawing. At about -40°C the interface undergoes a secondary exothermic phase change, perhaps due to solute precipitation or a transition to the glassy state (Anderson and Tice, 1971) with no perceptible change in

clay lattice spacing. Because of these characteristics, expanding lattice clay minerals exhibit properties and behavior well adapted to perform the functions of concentration, orientation and positioning of reactant molecules. The process may be regulated by such ordinary environmental phenomena as flocculation, sedimentation, coagulation, wetting and drying, or freezing and thawing.

With respect to systematic experimental investigations designed to demonstrate or clarify the possible roles of substrates at various stages of biogenesis, the system just discussed has much to recommend it. Expanded lithium or butylammonium vermiculite has a very large specific surface; its interlamellar space is easily opened to more than 100 Å; potential reactants may be introduced during imbibition of water or by diffusion after the mineral has been expanded by exposure to aqueous media; and crystal sizes are completely adjustable from macroscopic to submicron

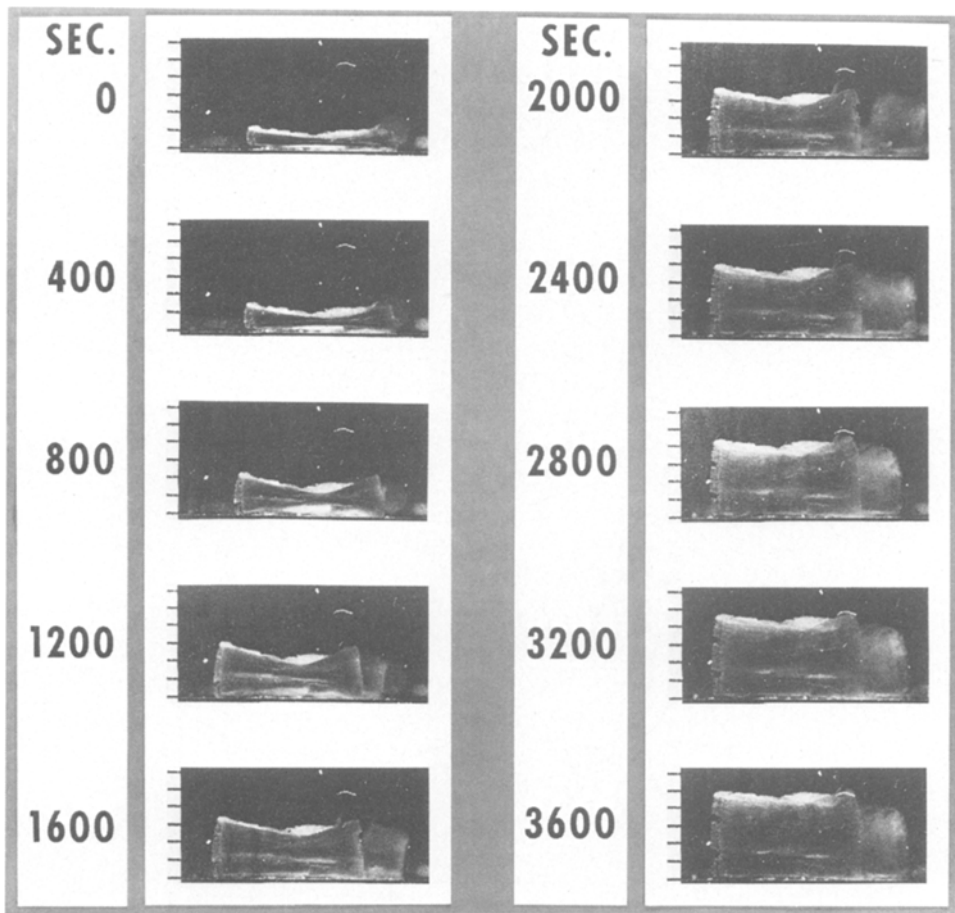


Fig. 1. Selected time-lapse photos following the process of swelling in Li-Vermiculite freshly immersed in water. Scale in mm on left-hand side of each photo gives relative sizes. Initial thickness of the dry vermiculite particle was about 1 mm.

dimensions. The possibility of molecular manipulations by means of controlling changes in interlamellar lattice spacing by wetting and drying or by freezing and thawing is useful and by transforming portions of the interfacial liquid phase to ice, concentration to nearly any desired degree can be accomplished. Thus it should be

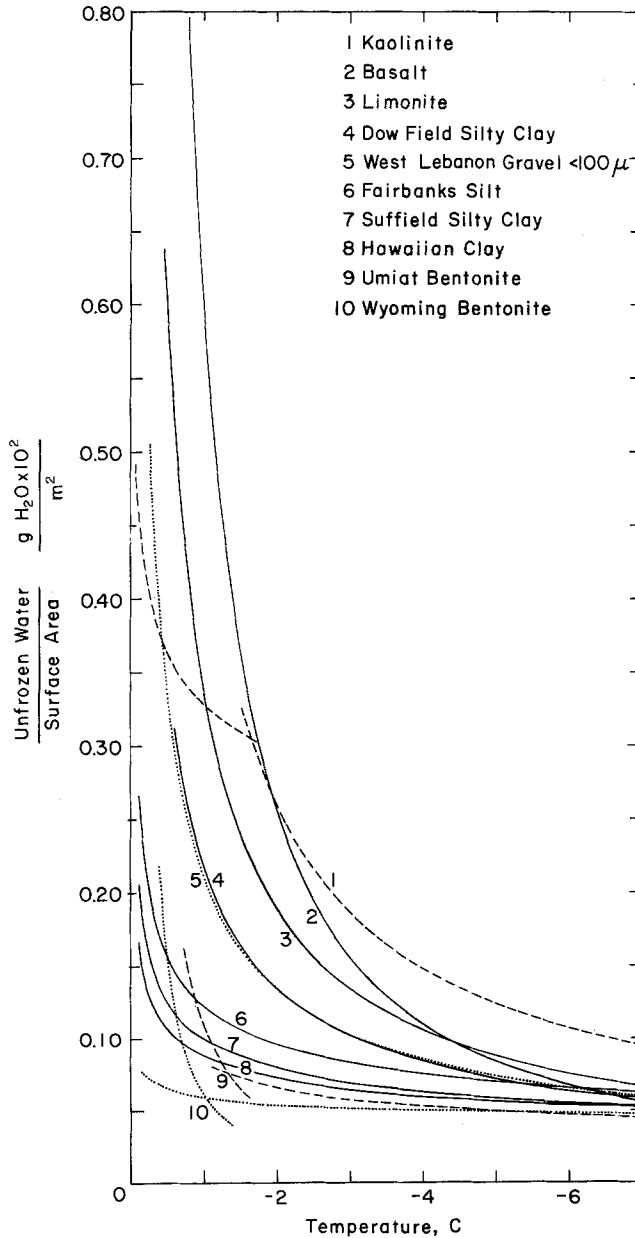


Fig. 2. The amount of water remaining unfrozen in partially frozen clay-water suspensions as a function of temperature for ten representative substrates. (Generalized from published data, Anderson and Tice, 1972.)

possible to bring reactants sufficiently near sites of surface and ionic exchange and active protons to accomplish protonation and acid catalysis and preferred ordering due to epitaxy becomes a possibility not only on the silicate surfaces but on the sandwiched ice surface as well (Anderson and Morgenstern, 1974). Evidence of a characteristic preferred orientation of the proton-proton vector of the water molecules in the interfacial regions seems to be conclusive (Woessner, in press). Thus claywater systems offer favorable environments for a multiplicity of prebiotic reactions.

6. Biogenesis on Mars

We turn briefly now to some remarks *vis à vis*, the possibility of biogenesis on Mars. Assuming that the planet was formed by low temperature accretion from cosmic dust, each submicron particle would have had, let us say, a monomolecular layer of adsorbed molecules representative of those present in the primordial gaseous envelope. Among these are water, ammonia, formaldehyde, hydrogen cyanide, methyl alcohol, formic acid, formamid, acetonitrite, methyl-acetylene, acetaldehyde, thioformaldehyde and larger organic molecules yet to be positively identified. Assuming, for simplicity, spherical particles of radius 1μ , a density of 3, and taking the average density of the adsorbed monomolecular complex as unity, a rough estimate of the total quantity of organic and inorganic volatiles that could have been collected by this means of about 2×10^{24} g for a planet such as Earth (planetary mass $\approx 6.0 \times 10^{27}$ g) is obtained. For Mars, the estimate is about 2×10^{23} g (planetary mass $\approx 6.4 \times 10^{26}$ g). Rubey (1955) estimates the total excess volatiles in the present terrestrial atmosphere, hydrosphere and sedimentary rocks to be about 1.7×10^{24} g. This agreement is intriguing.

These estimates could be as much as an order of magnitude smaller if the adsorbed phase consisted originally of less than a monomolecular layer due to degassing prior to or during accretion; on the other hand they could be as much as a factor of three larger if chemisorption was active and as much as an order of magnitude larger if the original particles were as small as 0.1μ in radius. In this connection, recent evidence has shown that the hydroxylation and subsequent production of water from oxygen in the silicate lattice occurs in the solar wind (Cadenhead and Buerger, 1973). Carbonaceous meteorites contain relatively large amounts of hydrated platy silicates, mainly magnesium and iron silicates, similar to terrestrial clay minerals. Bass (1971) claims, for example, to have identified montmorillonite and serpentine as constituents. Carbonaceous meteorites thus are of interest not only because of the relatively high amount of carbon contained in them but their relatively high water contents as well. According to Wiik's classification, type I carbonaceous meteorites contain 3–7% carbon, up to 22% water bound up in laminar magnesium and iron silicates. Isotope ratio studies of the meteorites (mainly of the Orgueil meteorite) have shown beyond reasonable doubt that the carbon compounds in them are of extraterrestrial origin. It is still debated whether or not the organic compounds found in them are of biotic or abiotic origin; however, the evidence more and more favors the latter view

(Kvenvolden *et al.*, 1971; Oró *et al.*, 1971). Without debating this long argument (see for example the review of Baker, 1971), we point out that accompanying these compounds and making up the most prominent group of mineral constituents (constituting up to 50% of it) are flakey, silicate minerals closely resembling terrestrial clay. This combination graphically portrays the intimate relationships possible between the platy silicate minerals and the abiotic precursors involved in biogenesis.

Allowing for considerable latitude in estimates, the quantities of volatiles that could have been 'gettered' as adsorbates are large. Whereas on Earth, it is possible that many, if not all, the significant steps in abiotic synthesis and biogenesis may have occurred in the hydrosphere with only sporadic and possibly insignificant contact with particulates, the situation is greatly different on Mars where the present hydrosphere is composed principally of ice and subsurface water. Although a number of geomorphic features revealed by Mariner 9 have been interpreted as indicative of the possibility of a liquid hydrosphere in the past, its existence surely was very limited in aerial extent and brief. Aeolian processes predominate and the atmosphere for aeons has been combed by circulating and sedimenting dust. Thus, extensive deposits of fine grained particulate matter whose surfaces have no doubt equilibrated with successive atmospheric environments, have been laid down. If biogenesis is proceeding at the present time, the focus of activity is in the martian soil at soil-water interfaces. The dimensions of the adsorbed water interface in which the vital reactions must occur if they are to be accomplished were computed in an earlier paper (Anderson *et al.*, 1967). Adsorption isobars for montmorillonite were given for possible partial pressures of water vapor in the martian atmosphere. For a time, these were regarded with some scepticism because the possibility of montmorillonite on Mars was not generally accepted. This has changed since Hunt *et al.* (1973) showed that infrared spectra returned by Mariner-71 provide evidence for the presence of montmorillonite on Mars. The water vapor adsorption isobars show that under present conditions of temperature and pressure, the quantity of water adsorbed normally does not exceed a monolayer. In circumstances where frost or ice is in contact with mineral surfaces, an unfrozen liquid-like interface may approach 5–6 Å, as shown in Figure 2. Thus, the situation is not favorable. However, the presence of salts and other soluble substances at this interface may increase the thickness, d , at a given temperature by (Banin and Anderson, 1974):

$$d = \frac{ae}{10^{-4} S \theta} \quad (1)$$

where d is in Å, e is the salt content, meq g⁻¹ soil, S is the specific surface area of the soil (m² g⁻¹), θ is the temperature in °C below zero and a is a coefficient that depends on the salt type. The latter is 3.72, 2.79 and 1.86 deg meq⁻¹ ml, for the 1-1, 1-2 and 2-2 salt types, respectively. Because of this effect it is conceivable that circumstances might exist on Mars in which the activity, P/P_0 , of the interfacial water and the thickness of the unfrozen, liquid-like interface might exceed 0.5 and 6 Å, respectively. In exotic, or ephemeral environments where the water vapor

pressure might rise to, or even exceed 10 millibars, more favorable situations might exist and the reactions vital to biogenesis become correspondingly more favored. On a planet-wide basis it must be concluded that if biogenesis has proceeded to the stage of bringing forth organisms, it is virtually certain that most are now sustained in aqueous interfaces of the types discussed above. If biogenesis is now occurring, the probability that its vital processes are proceeding in these locations is high. If biogenesis has been initiated, but temporarily interrupted by hostile environmental conditions, its remains and dormant fragments must be present there.

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