

Role of Interfacial Water and Water in Thin Films in the Origin of Life

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Molecular precursors of life probably evolved in a wet environment. Interfacial water and thin water films appear to form environments that are more favorable for precursor generation over a wider temperature range than water in the liquid phase.

It is widely accepted that some, perhaps many, of the abiotic chemical reactions and processes leading to the origin on Earth of replicating microorganisms occurred very early in the history of Earth in close proximity to the surfaces of clay minerals and other inorganic substrates (Bernal, 1967; Fox, 1965; Rutten, 1971; Anderson and Banin, 1975; Shimoyama et al., 1978). The mineral substrate is believed to have had the following functions:

1. Concentration of chemical reactants by adsorption
2. Preferential orientation of precursor molecules
3. Initiation and reaction rate enhancement by catalysis
4. Stabilization of intermediates
5. Suppression of randomness in recombination, addition, polymerization, and condensation reactions.

The last function is of particular significance for, “if the association of amino acids into a polymer were a completely random phenomenon, there would not be enough mass in the Earth — assuming it were exclusively amino acids — to make one molecule of every possible combination of units in a low molecular weight protein” (Dixon and Webb, 1964, as cited by Katchalsky, 1974). In considering these functions it is usually recognized, but not sufficiently appreciated, that the reactions of interest must have occurred in an aqueous environment and that aqueous interfacial phenomena were involved.

It has been observed that since the temperature coefficients of certain destructive decomposition reactions that would tend to inhibit the abiotic

formation of RNA and DNA are quite large, low temperatures would have been advantageous and, in general, the lower the better (Miller and Orgel, 1974). It is of interest therefore to examine the properties of clay-water interfaces at low temperatures from the point of view of their possible involvement in chemical reactions important in abiotic syntheses of chemical precursors to cellular life.

This topic was reviewed by Anderson (1967) and subsequently by Anderson and Morganstern (1973). Anderson and Banin (1975) also covered essential aspects in their review of the role of soil and water in the origin of life. The nature of the various interfacial environments present in clay-water systems will be reexamined here with particular emphasis on their properties and behavior at low temperatures.

At temperatures below 0°C, the normal freezing point of water, five distinct interfacial environments are possible: ice-ice (grain boundaries), ice-air, silicate-water-air (SWA), silicate-water-silicate (SWS), and silicate-water-ice (SWI).

For the ice-ice interface, an order-disorder transition caused by ice lattice mismatch from one crystal to another causes the appearance of a transition zone with liquid-like properties between grains as temperatures approach 0°C. When impurities or solutes are present, they are concentrated at the interface, lowering the freezing point of the residual water and thickening the interfacial zone.

A liquid-like transition layer at the ice-air interface has long been suspected. Estimates of its thickness are as much as 100 Å (10^{-6} cm) near 0°C to about a monomolecular layer at -30°C and below. Again the presence of contaminants and solutes acts to increase the thickness of the interfacial liquid at any given temperature by depressing the freezing point of water in the interfacial liquid. Nuclear magnetic resonance (NMR) spectra of snow indicate the existence of a liquid-like component, but the width of the NMR signal compared to that of pure water indicates that in the interfacial phase it becomes more viscous and less free to move as a consequence of its interaction with the solid phase.

Silicate-water-silicate and silicate-water-air interfaces have been relatively well characterized at temperatures above freezing; they are less well characterized at lower temperatures. Electrical conductance measurements, NMR data, and protonation reactions indicate that the interfacial water in closest proximity to a clay surface and its exchangeable counter ions is dissociated to a much greater degree than normal (Anderson and Morganstern, 1973). This makes the interfacial liquid characteristically highly acidic and explains why protonation reactions are facilitated in this environment. This characteristic is of fundamental significance in considering the influence and possible roles of the SWS interface in primitive abiotic organic reactions.

The silicate-water interface may also be bounded by air at temperatures below freezing, but usually it is bounded by ice. Thus, depending on the quantity of water per unit of substrate surface, one may have distinct silicate-water and water-air interfaces and the SWS, SWA, and SWI interfaces, each with characteristic properties that vary with temperature, pressure, and solute concentration. The range of properties and behavior of these interfaces can thus be very large.

Until recently not much was known about the SWI interface, but certain basic information has now been obtained. When water-containing layer lattice clays (smectites) are frozen, the SWS interface decreases immediately from its initial value to about 9 Å. At about -10°C , the lattice spacing decreases further to about 6 Å, with no further noticeable decline at lower temperatures. For the SWI interface, a characteristic relationship between interface thickness and temperature can be derived from thermodynamic theory, and this has been confirmed by experimental measurements. The relationships for two homoionic forms of montmorillonite and for kaolinite, a nonswelling clay, are given in figure 1.

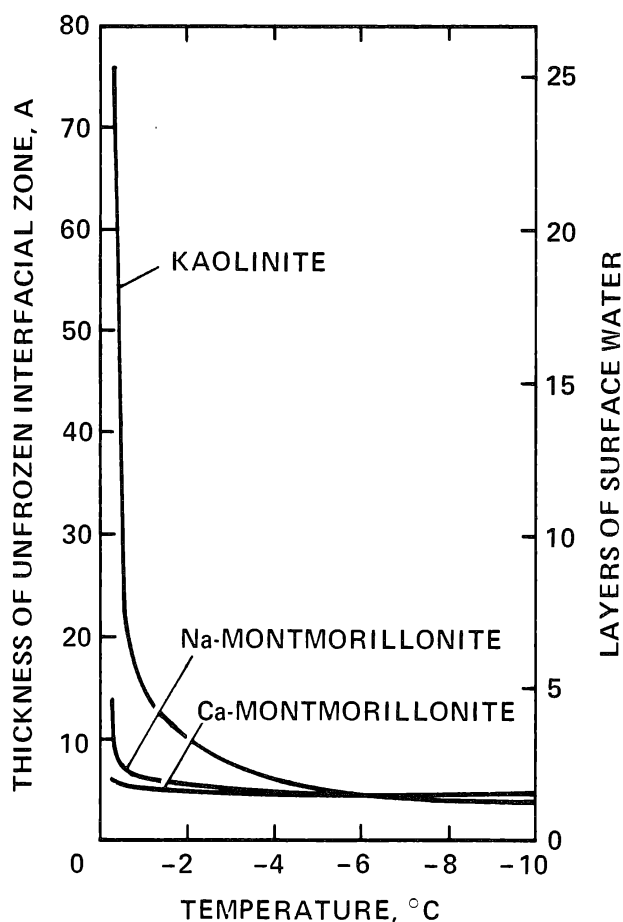


Figure 1. Unfrozen water content plotted against temperature for three representative clays. *Nature*, vol. 216, Nov. 11, 1967.

The nature of the silicate-water interface at temperatures below 0°C is illustrated in figure 2. Adsorbed water molecules (open circles) are shown bound to the clay surface together with some chemisorbed anions. Other specifically adsorbed molecular species and tightly bound cations might also be present. Hydrated cations are found separated from the mineral surface by their hydration sheath (dotted circles). They are shown symmetrically surrounded by water molecules, although asymmetrical arrangements are more likely and proton delocalization must be accounted for. Farther out is

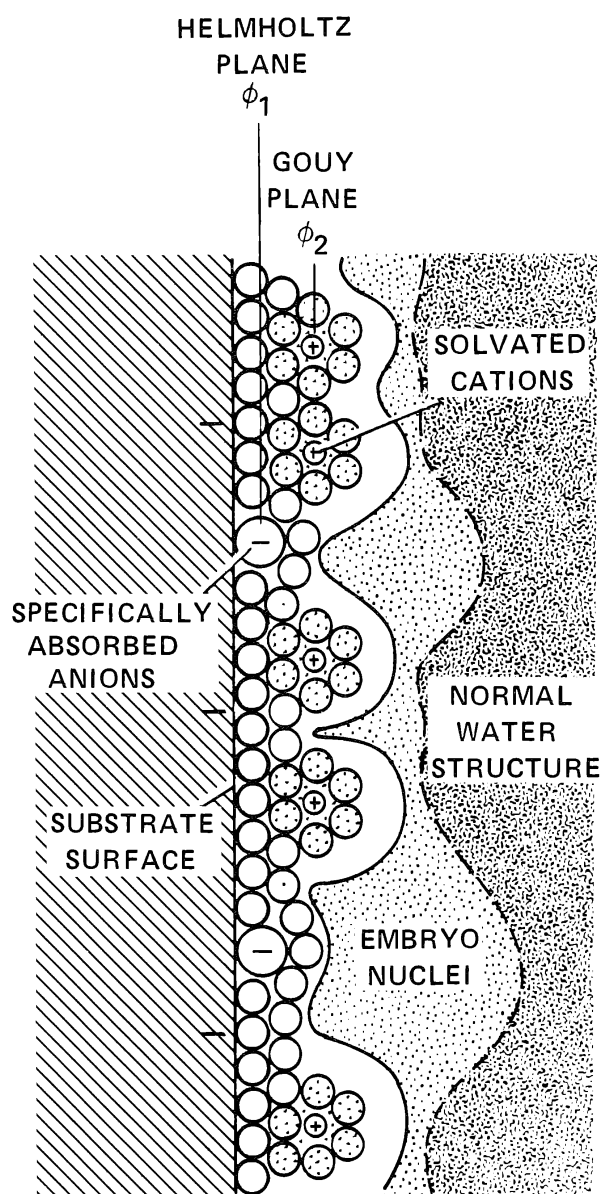


Figure 2. Schematic of the zone of ice nuclei formation in soil water. *Israel Journal of Chemistry*, vol. 6, 1968, p. 350.

the transition region separating the strongly adsorbed water from that which can be said to exhibit the properties and configuration of water in bulk. This zone is shown possessing bulges that fit in between the water domains of cationic perturbation. It is these bulges that are possible natal sites for embryo nuclei; consequently, they are shown as also extending outward into the bulk liquid. Once formed in regions like this, nuclei may be relatively stable. They are easily incorporated into the bulk ice on freezing, and on subsequent melting many may remain intact and active, provided the temperature is not raised too far above the melting point. This explains the common observation that subsequent freezings require little or no undercooling.

Although the influence of surface forces is somehow involved in their formation, the embryo nuclei do not grow by attachment to mineral surfaces, nor are they torn out of an extended network of ordered, chemisorbed water. Initially, adsorbed water is so disrupted by interaction with the surface and its adsorbed ions that embryo ice crystals are not able to form there. At a distance somewhat farther removed from the surface, however, the various adsorption forces may combine to exert a stabilizing influence that allows extensive ordering effects in the interfacial water. Depending on location relative to surface heterogeneities and distance outward from the surface, domains of ordered water, perhaps of more than one type, may exist. The location, extent, and lifetimes of these domains shift as the temperature is raised or lowered. Critical aspects of the environment created in proximity to a substrate surface thus involve reduced molecular motion and a tendency toward more open hydrogen-bonded regions in the fluid. As the temperature is lowered, the coherence and extent of hydrogen bonding must increase. Thus embryos form, and as the temperature is lowered, the favorable environment provided by the interplay of adsorption forces facilitates their enlargement into active nuclei. If one chooses to adopt the flickering cluster, mixture model of water, embryo nuclei may be said to form by the growth to critical size of one of the normal components of the liquid. Viewed in this way, heterogeneous nucleation becomes satisfyingly similar to homogeneous nucleation; it is only a matter of the temperature lowering required, in one case compared to the other, to permit the embryo to grow, by molecular accretion, to critical size.

Drost-Hansen (1967) has explored the nature of the water-ice interface in connection with the measurement of freezing potentials. As he visualizes it, six zones may be distinguished, ranging from the bulk liquid (consisting of clusters of clathrate cages and monomers) to normal ice. Separating these boundary phases is a disordered transition layer. Next is a zone consisting of a highly ordered layer of four coordinated water, termed "polar ice" inasmuch as many of the protons in this region are believed to be aligned perpendicular to the interface. The existence of this zone was postulated primarily to account for selective ion incorporation in ice during freezing.

Immediately adjacent are two zones within the solid phase in which dipole orientations are in various stages of relaxation and the selectively incorporated anions are being neutralized by migrating protons.

The main features of the SWI interface are illustrated in figure 3. The zone of embryo formation mentioned earlier, synonymous with the zone of "enhanced order" in figure 3, is believed to be more structured than free

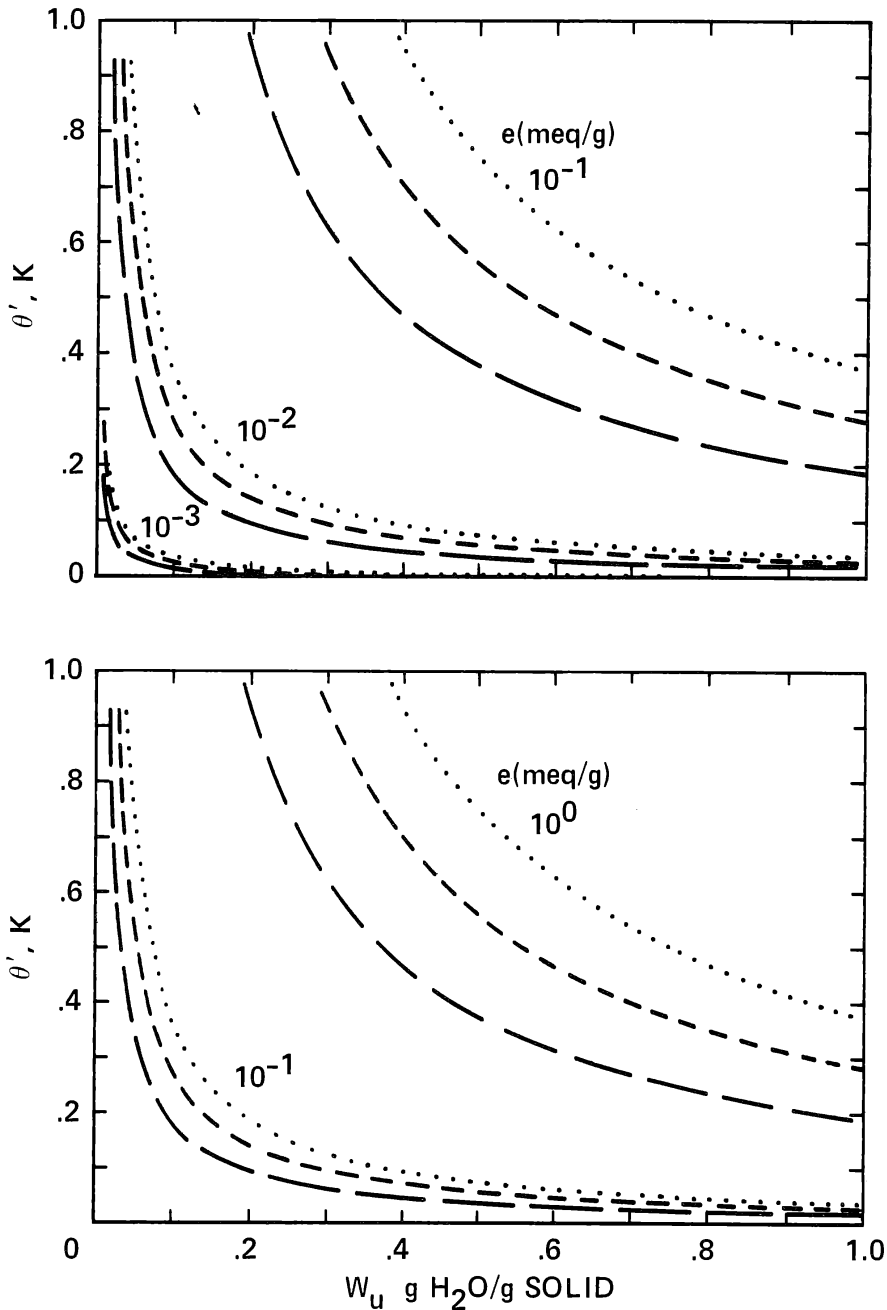


Figure 3. Schematic of silicate-water-ice interface.

water in the sense that the speed of formation and dissolution of the clusters of hydrogen-bonded water cages is thought to be diminished and the size of clusters and number of cages are thought to be larger than for free water. On the other hand, the number of clusters or cages per unit volume is believed to be reduced in the zones of disorder; monomers predominate there. Moreover, monomers closest to sites of surface charge, and the adsorbed cations, and water coordinated to ions located in the interfacial region undergo proton delocalization that, according to conductance and NMR data, leads to a proton activity in this zone many orders of magnitude higher than that of free water. It seems a paradox that, although the viscosity of water in the silicate-water and the silicate-water-ice interfaces is higher than that of normal water, proton mobility is greatly increased; nevertheless the evidence available at present indicates that this is the case.

Two zones shown in figure 3 are termed "disordered." For the zone adjacent to the silicate surface, this is based on the weight of evidence against hydrogen-bonded water networks and in favor of increased proton motion. For the zone adjacent to the ice surface, the argument is based on the principle of microscopic reversibility, which requires that the addition of water molecules to the ice lattice during interface advance must be caused by the same mechanism as the removal of water molecules during melting. If groups of water molecules were added on as "ice-like" units, it would be difficult to explain the phenomena of supercooling and the large entropy of fusion. If the units were not ice-like but clusters or cages of some different geometry, then there would be difficulty in simultaneously incorporating large numbers of these into a continuous hexagonal lattice. We conclude therefore that the dominant mechanism is the addition or subtraction of monomers. Furthermore, on the molecular level there must be continual exchange of water molecules within and between zones. The species most compatible with the phases present is the monomer; hence addition or subtraction of monomeric units is the most probable mechanism by which the interface is thickened and thinned.

NMR data show the SWI interface to be more structured than either bulk water or the silicate-water interface, and the above arguments require the presence of two zones in which monomers are dominant. It follows then that clusters and/or cages predominate in the intervening region. Measurements of the partial specific volume of water in an SWI interface indicate a water density less than that of free water, in harmony with the concept of increased hydrogen bonding, but it appears that hydrogen bonding proximate to clay surfaces is less well developed than that in free water. Since monomers are held to predominate in the two disordered zones, tending to increase the average interfacial water density, a net decrease in the average interfacial water density requires the existence of an intermediate zone where hydrogen-bonded clusters and/or cages predominate.

In exercising this tentative model of the SWI interface, it should be kept in mind that cations predominate in numbers over anions at the silicate surface and that, during advance of the ice-water boundary, anions probably predominate next to and within the polarized "pseudo-ice" transition layer. It is generally conceded that all cations and most anions tend to be water structure breakers, whereas F^- and OH^- seem to be net "structure makers" in water. It is thus possible that OH^- may play an important role in promoting local orientational order if delocalized protons are attracted to and tend to reside near the negatively charged silicate surfaces.

Protonation reactions have not yet been attempted at the SWI interface. However, the evidence cited above leads one to believe that attempts to carry out such reactions will be successful. Freezing soil water is equivalent to drying the soil; in both cases water leaves the mineral matrix. Since proton delocalization is greatest at the lowest hydration states, we conclude that protonation reactions are facilitated by a thin interfacial region. Protonation reactions in the SWI interface therefore may be possible at quite low temperatures in systems where the water (ice) content is high enough to inhibit reaction at normal temperatures.

When electrolytes are present, the general relationship illustrated in figure 1 is shifted to the right due to the freezing point depression effect (Banin and Anderson, 1974). Figure 4 illustrates typical effects.

The effect of a progressive lowering of the temperature of clay-water mixtures is illustrated in figure 5. Each curve represents a different mixture. As the temperature is lowered (moving along a given curve from right to left), nucleation occurs at a characteristic temperature (freezing-point depression) and a large exotherm expressed in electrical units of intensity appears. This exotherm is due to the evolution of the latent heat of freezing; it falls gradually to zero as freezing progresses. For drier clay-water mixtures, this exotherm appears at progressively lower temperatures and is progressively smaller. As the temperature drops further, one or more additional exotherms appear. These are associated in some as yet imperfectly understood manner with individual interfacial water domains. Since kaolinite and halloysite are nonexpandable clays and therefore exhibit only SWA and SWI interfaces, and since they exhibit only one low-temperature phase change at about -40°C , this exotherm is probably associated with a phase change in the SWI interface. The fact that montmorillonite possesses both SWA and SWS interfaces in the unfrozen condition and SWI and SWS interfaces in the frozen state, combined with the appearance of two or three low-temperature exotherms depending on the exchangeable ion present, is indicative of the different characteristics of these interfacial domains and the fact that they are altered to a significant degree by the presence of various ionic species.

The preceding discussion illustrates the great physical and chemical diversity of the interfaces at which various abiotic organic chemical reactions

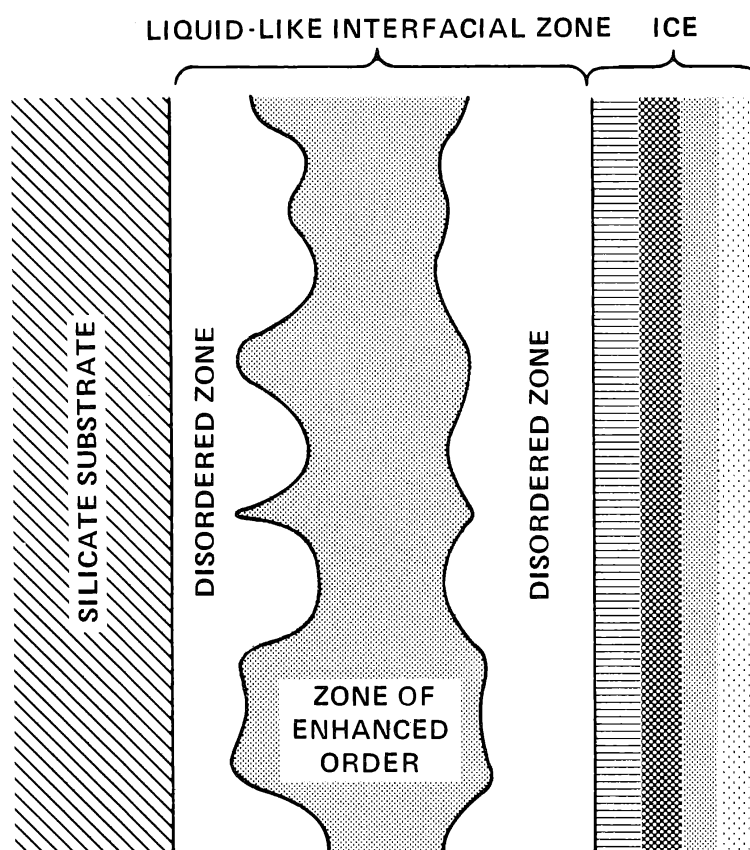


Figure 4. Freezing-point shifts of pore solutions remaining in freezing porous bodies, due to increasing salt concentration of the initial pore solution. (Long dashes represent 1:1 electrolytes; short dashes 1:2 electrolytes; dots 1:3 electrolytes.)

important in chemical evolution could have occurred. Superimposed on this diversity is the heterogeneity of types of clay substrate surfaces made possible by variations in mineralogy characteristic of the many different clay types. It should not be overlooked that curved surfaces as well as planar surfaces exist. Most clays change shape during hydration, dehydration, freezing, and thawing. Halloysite, for example, rolls into tubular configurations and unrolls during such cycles, and single smectite sheets have been observed to fold and unfold during wetting and drying. Curved interfaces such as these may have been crucial at certain stages of nucleotide synthesis. Little work has been done as yet to investigate such possibilities, but recent experimental and mathematical techniques have rendered these once formidable problems tractable.

As Miller and Orgel (1974) have observed, "All of the template-directed reactions that must have led to the emergence of biological organization take place only below the melting temperature of the appropriate organized polynucleotide structure. These temperatures range from 0°C, or lower, to perhaps 35°C in the case of polynucleotide-monomonucleotide helices." They also

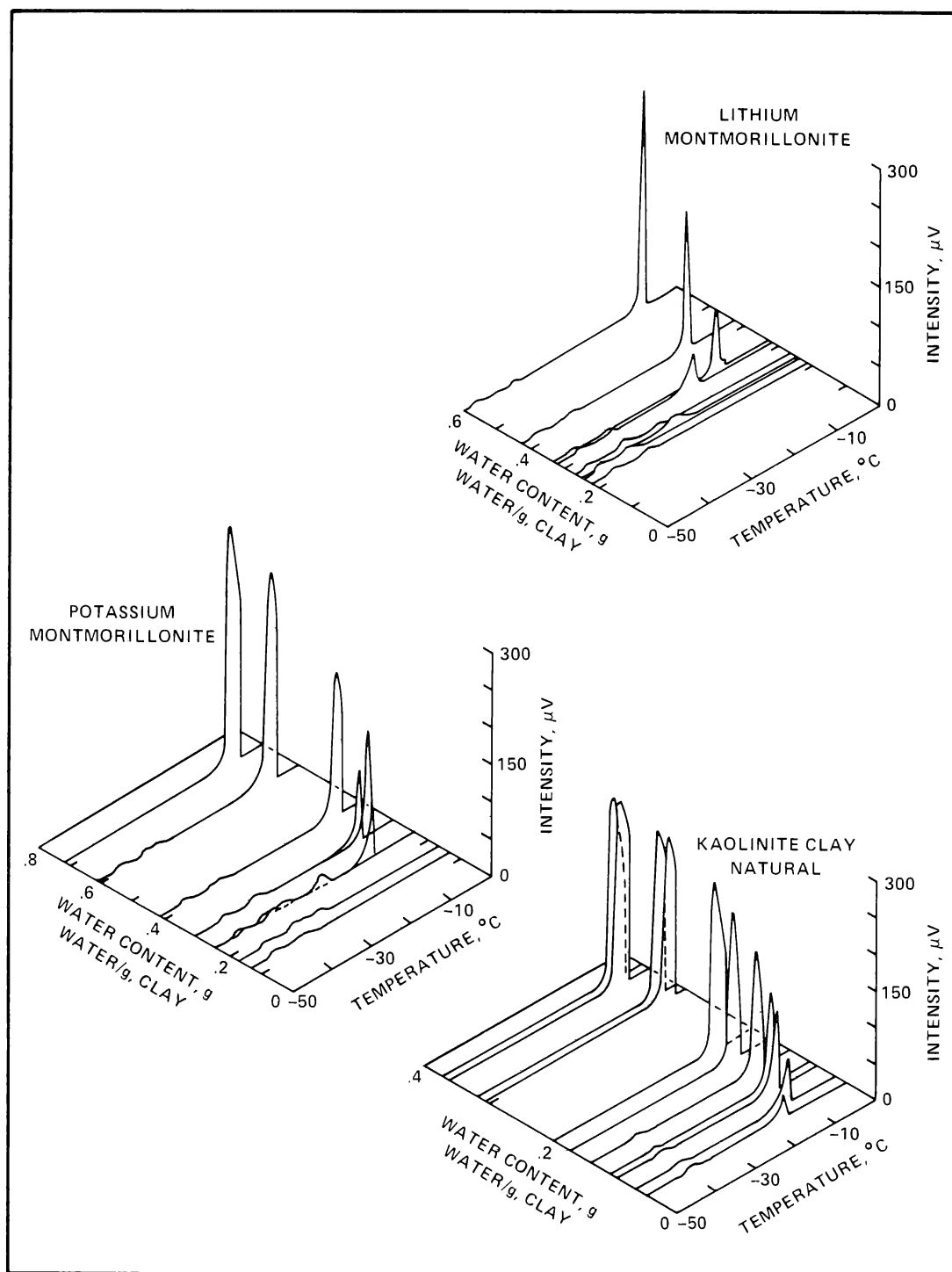
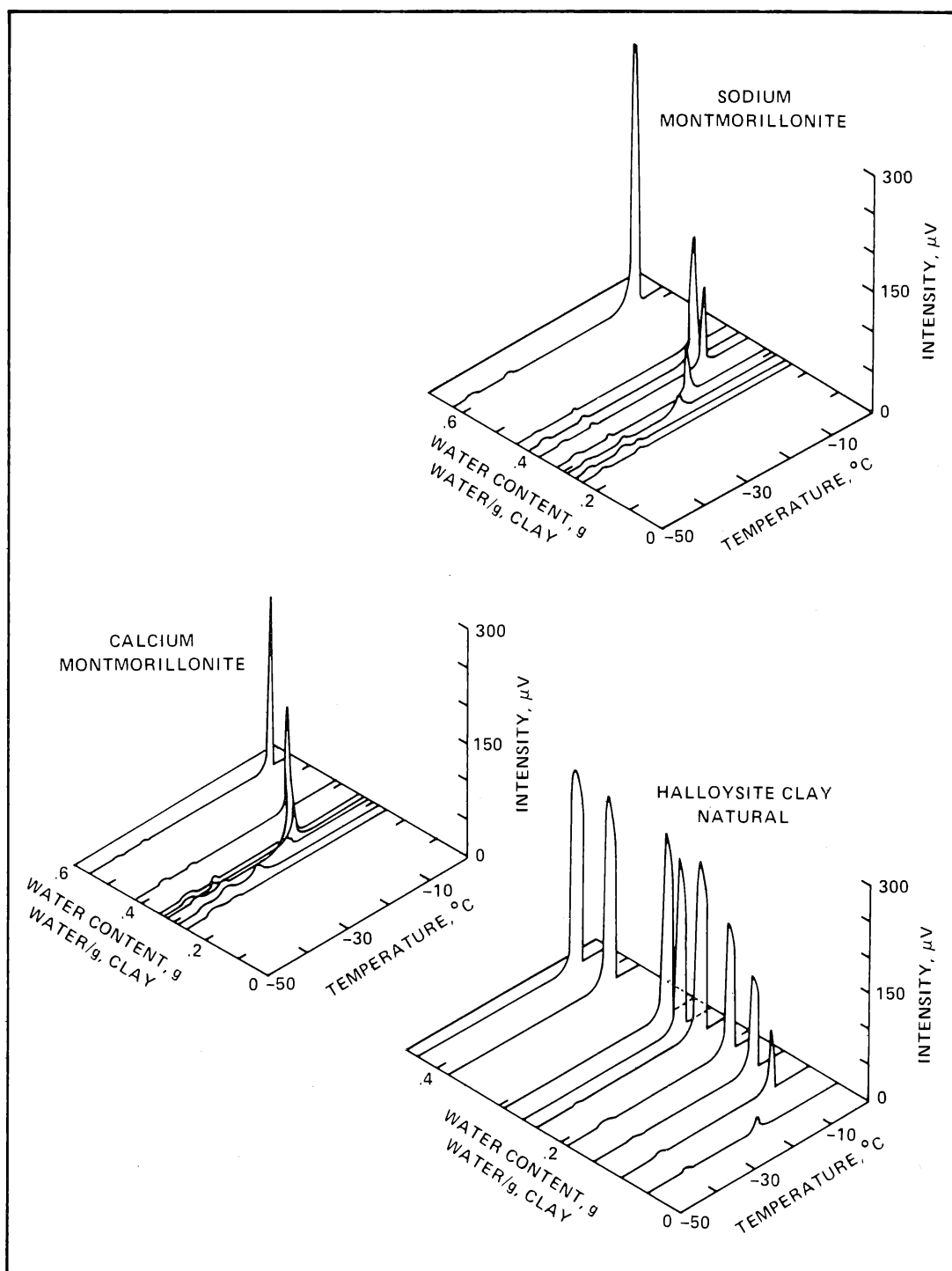


Figure 5. Low-temperature differential thermal analysis data for representative clay-water mixtures (after Anderson and Tice, 1971). *Soil Sci. Soc. America*, vol. 35, Jan.-Feb. 1971.

Figure 5. *Concluded.*

observed that the instability of the various organic compounds and polymers important at other stages "makes a compelling argument that life could not have arisen in the ocean unless the temperature was below 25°C. A temperature of 0°C would have helped greatly and -21°C would have been even better" (-21.8°C is the eutectic point for NaCl solutions).

At more advanced stages, low temperatures would inhibit membrane transport. Kushner (1976) has suggested that the physiological functioning of cells requires a semiliquid state for the lipids within the membrane and suggests that the lowest temperature permitting growth of primitive organisms might be determined by the melting point of the lipids they are capable of producing. Regulation by enzymatic systems is also impaired by temperatures near 0°C, although the work of DeVries (1970) on antarctic fishes has shown that, if ice nucleation can be prevented, cellular process can proceed normally several degrees below 0°C.

Horowitz (1976) has noted the necessity of considering the thermodynamic activity of water whenever one considers the water requirements of living cells. He gives an activity of 0.62 as the probable lower limit to growth as we presently know it. Figure 1 is interesting in this connection since this general relationship has been derived from thermodynamic theory (Low et al., 1968). For montmorillonite clay, the activity of the unfrozen interfacial water approaches 0.62 at a temperature of about -25°C. At this point, the interface is only one or two monomolecular layers thick; therefore it must also be highly acidic in nature. Between -5° and -1°C, the interfacial water activity ranges from 0.95 to 0.99 and the thickness of the interfacial zone varies from two to six monomolecular layers of water. Thus it appears that this interface possesses properties compatible with some living organisms down to temperatures far below 0°C. As indicated in figure 5, the limit is probably reached somewhere between -25° and -30°C, where the first low-temperature exotherms due to a change of phase in the interfacial water appears.

The preceding discussion has been confined to a demonstration that the properties of the unfrozen interfacial water films present in frozen clay-water systems are such that a wide variety of organic reactions of importance in the origin of life could have been facilitated: by the stabilizing presence of clay substrates; by the catalytic properties of the acidic clay surfaces; by the various dynamic geometrical characteristics of the surfaces presented by different clay lattices, which could, for example, have been important in facilitating ordering and coding in primitive polynucleotides; and by the presence of a liquid phase at relatively high water activities at temperatures quite far below the normal freezing point of water. This, in effect, makes the temperature range 0° to -35°C, even without the presence of brines, compatible with the other requirements for the abiotic synthesis of many of the organic molecules required for the natural appearance of life on primitive Earth and

opens up several fruitful new lines of experimentation and theoretical investigation.

Water and ice are known to exist on Mars, Europa, Ganymede, Callisto, and the moons of Saturn. If the abiotic synthesis of organic molecules important in the evolution of life is occurring on any of these planetary bodies, it is likely that a significant portion of the reactions of interest are taking place in interfacial environments such as those described here. Future unmanned landers should include instrumental and sampling capabilities to search for evidence of these processes.

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