PHASE BOUNDARY WATER IN FROZEN SOILS

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PREFACE

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PHASE BOUNDARY WATER IN FROZEN SOILS

by

Duwayne M. Anderson

INTRODUCTION

It is now widely recognized that water at phase boundaries plays an important and in some cases the dominant role governing heat and mass transport, electrical conduction, transmission of compression waves and other processes of importance in frozen soils. There is also an increasing recognition of the contrast between the complexity of the phenomenology of freezing and thawing and the crudeness of the concepts and models that so far have been available. This report summarizes presently accepted concepts and information and sketches an area where significant advances in knowledge are to be expected.

THE ICE/ICE INTERFACE

Interfacial regions in frozen soils may be classified as of the following types: ice/ice (II, grain boundary); ice/water/air (IWA); silicate/water/silicate (SWS, primarily interlamellar); and silicate/water/ice (SWI, extralamellar). The notations employed imply that the IWA, SWS and SWI interfaces possess a component with liquid-like characteristics, whereas the II interface does not. Let us consider the basis for this distinction.

If liquid-like behavior were associated with the II interface it surely would be manifest in sintering and grain boundary migration phenomena. The concept of sintering can be understood by visualizing a collection of close packed spheres in contact. Their free surface areas define void boundaries. Surface tension at the solid/vapor interface tends to decrease the interfacial areas, leading to reduction in size of the voids. During this process matter is transported to points of contact between spheres from the adjacent surface. Grain boundaries are formed in this way as the centers of the original particles slowly approach one another and the voids reduce in size. The macroscopic result is that shrinkage occurs. In other words, in response to the tendency toward surface energy reduction, the voids disappear by first forming lattice vacancies in the surrounding crystals. The lattice vacancies, one by one, then migrate by diffusion to grain boundaries where they are annihilated by the coalescence of the original spheres. In this description the voids visualized contain only water vapor; when air is present they do not disappear completely. They either remain as air bubbles located at grain boundaries, in which case further migration seems to be facilitated, or they become separated from the boundaries and remain virtually trapped within grains.

The most recent discussions of sintering and grain boundary migration emphasize the rapidity of migration at the boundaries of small grains and the effect of bubbles or foreign particles in retarding grain boundary migration. Under favorable conditions migration rates up to 0.35 mm/hr have been observed.) Two principal driving forces apparently are involved although others may
remain to be discovered: the tendency toward a reduction of the interfacial free energy and the alleviation of intracrystalline stresses created during freezing. However, the factors governing grain boundary migration in ice are not well known and it is apparent that they will be difficult to isolate and study experimentally.

When, as is common, sintering and grain boundary migration occur simultaneously, another complexity is added. At present, it is generally accepted that where no ice/air (IA) interface junction is involved grain boundary migration occurs via lattice vacancy diffusion and it has not been suggested that liquid-like properties are associated in any way with the II interface.

**THE ICE/AIR INTERFACE**

In the case of the IA interface the existence of a transition layer possessing liquid-like properties has been proposed by a number of investigators. The history of this controversial subject and a discussion of the evidence concerning it was given by Jellinek. Proponents of the idea point to the classical study of Nakaya and Matsumoto, who showed that two spheres of ice suspended from threads, when brought into contact at temperatures above \(-7^\circ C\), will adhere to each other and will then rotate and slide in response to an applied torque. This, it is argued, can be explained only by assuming the existence of a liquid-like surface layer. Subsequently these observations were meticulously confirmed by Hosler et al.

Also cited are the ice adhesion results of Jellinek and of Raraty and Tabor in which it appears that above about \(-13^\circ C\) adhesive breaking is characteristic of ice bond failure whereas below \(-13^\circ C\) cohesive breaking of the ice occurs. Note, however, that the interface involved here is a substrate/ice interface and not the ice/air interface in question. Kuroiwa's experiments on the coalescence of ice spheres in contact and the sintering experiments of Jellinek and Ibrahim can be interpreted as indicating the existence of a liquid-like layer; the theoretical calculations of Fletcher support this view. In summary, Jellinek concludes that the existence of a liquid-like transition layer is "very likely" and that a thickness of about 100 A near the melting point, diminishing to practically zero near \(-30^\circ C\), is indicated. From the adhesion data, the viscosity of the liquid-like layer appears to be at least several hundred poises at \(-4^\circ C\), and it is believed that the properties of this layer vary continuously from one side of the film to the other.

Although many are skeptical of the idea, only Hobbs and Mason and Itagaki in recent years have disputed the existence of a liquid-like transition layer at ice/air interfaces. Hobbs and Mason reexamined the rate of neck growth between spheres brought into contact. The data were analyzed by means of the corrected theoretical expressions for growth derived by Kuczynski. Hobbs and Mason concluded that for very clean ice an evaporation-condensation mechanism was predominantly responsible for neck growth. They found surface or volume diffusion to be only \(\frac{1}{1000}\) as effective in mass transport to the growing neck area; therefore, they maintained that the existence of a liquid-like surface layer need not be invoked. Itagaki also failed to be convinced that a liquid-like layer played an important role in neck growth between ice surfaces or in the migration of particles on a subliming ice surface. He also concluded that an evaporation-condensation mechanism was responsible for neck growth and that mass transport by ordinary bulk diffusion and somewhat enhanced surface layer diffusion, possibly aided by local temperature gradients, best accounts for the observed particle migrations.

When ice surfaces are contaminated, especially with solutes excluded from the ice during freezing, the situation is obviously different. Hobbs and Mason noted that neck growth was accelerated on NaCl-contaminated ice surfaces. They believed that if solutes or other contaminants
were present liquid-like transport phenomena on ice surfaces could be expected. This, it seems, is the crux of the matter. For practical purposes, it can be assumed that the ice/air surface will always present a liquid-like transition layer whose thickness and properties vary with temperature down to about -15°C unless the ice surface is kept scrupulously clean. Moreover, infrared and other incident radiant energy could make an additional contribution in bringing about a melted layer, unless scrupulous care is taken to shield the ice surface.

An observation during a recent nuclear magnetic resonance (NMR) investigation is of interest in this connection. Figure 1 shows the wide-line proton NMR spectra of a sample of fresh snow (the curve shown is the first derivative of the absorption curve).* It is evidently made up of a narrow component, roughly 2.6 Gauss wide, superimposed on a very broad component, 17.3 Gauss wide. The wide component (making allowances for possible instrumental broadening) is attributable to polycrystalline ice. The narrow component almost certainly must be attributed to protons on the ice crystal surface and/or perhaps at grain boundaries, since when the sample was stored overnight at about -30°C and scanned at the same settings and temperature, the narrow component, although still present, had diminished considerably in intensity. During successive scans at higher temperatures the narrow component disappeared entirely, whereas the broad component remained until the sample melted. If, as is presently thought to be the case, the narrow component arises from surface protons, disappearance of the narrow component is best ascribed to sintering. As the surface area was reduced continually, the quantity of surface protons was reduced below the number detectable by this technique.

In concluding this section, apparently more often than not the ice/air interface contains a component layer possessing liquid-like properties. Only when scrupulous care is taken in preparation of the ice and when precautions are taken to shield it from all radiation and contaminants can the liquid-like component be reduced to negligible proportions or eliminated. To emphasize the liquid-like properties usually exhibited by the ice/air interface the term ice/water/air interface will be employed unless there is sufficient reason to believe that precautions have been taken to ensure the absence of a liquid-like component.

*The sample was taken outside the Division of Physical Chemistry Laboratory, Royal Institute of Technology, Stockholm, Sweden, 25 January 1967, during (but some hours after commencement of) the snowfall. The sample was packed into the sample container at liquid N₂ temperature and introduced immediately into an NMR Dewar probe at -23°C. Preliminary measurements were taken to optimize the spectrometer settings. The measurements were taken at 3.5 kilogauss (kG), 14.8 MHz, and an RF field of 100 μs, in a 50-min scan with a Varian Model V4230 Low-Proton (LP) (proton-free) probe. Some saturation effects were present and the high sweep modulation (L-6) required contributed some instrumental broadening, but not enough distortion was present to impair the qualitative value of the spectra.
THE SILICATE/WATER/SILICATE INTERFACE

SWS interfaces are obtainable at temperatures above freezing when they include extralamellar capillary water. Water of this type has been much studied. Interest in its nature and properties has been widespread and discussions are available in several recent reviews. The main controversies dominating the discussions in recent years involve the extent to which the electrostatic and electrical double layer theories are adequate to explain soil-water interaction and whether or not clay-water forces facilitate the buildup of hydrogen-bonded water structures on clay (and more generally on soil mineral) surfaces. The main participants are identified and connected with their respective points of view in the papers cited. Evidence on the density, viscosity and thermodynamic properties of clay sorbed water diffusion coefficients, etc. has been brought to bear; but many questions remain more or less unsettled and to some extent poorly defined.

Recent work makes it clear that soil colloids are very much more complex than has been assumed by most investigators, particularly those advancing models of the diffuse electrical double layer. Although reasonably successful when applied in other colloidal systems, it is becoming ever more evident that the double layer theory is not yet developed to the extent required to deal successfully in quantitative terms with soil-water systems. This is not to suggest that the approach has been unfruitful or that problems of clay-water interaction are not amenable to attack from first principles. What have become clear, however, are the formidable difficulties. For example, the presence of significant quantities of hydroxy iron and aluminum complexes, adsorbed gases and other surface moderating substances, and the well known fact that clay-water systems are dynamic and nearly always in a state of dissolution or recrystallization, must be taken into account.

After all the arguments and indirect evidence in support of the possibility, it seemed that the discovery of a threshold pressure gradient below which water movement in colloidal soil-water systems did not occur was proof of the existence of a quasi-crystalline water structure on clay surfaces. Reexamination of this point by Peverly and Miller, however, indicates that in clay-water systems free of hydroxy-aluminum complexes no threshold gradient exists. What appeared to be the weightiest evidence in favor of quasi-crystalline, hydrogen-bonded water structures in clay-water systems has thus been removed.

On the other hand, deductions based on conductometric and NMR data indicated that water in closest proximity to silicate surfaces is not hydrogen bonded but is characterized primarily by water dipole interactions. It seems to have been firmly established by Mortland et al. with similar techniques that water adsorbed by montmorillonite has a "degree of dissociation" some 10′ higher than that of free water and the increased proton concentration thus implied has been termed a strong "surface acidity." Infrared absorption data support this conclusion and indicate less, not more, hydrogen bonding in the clay adsorbed water than in free water. An enhanced surface acidity should be reflected in protonation reactions carried out at the SWS interface. Observations on the conversion of chemisorbed NH₄ to NH₃⁺, the decomposition of Co(NH₃)₆³⁺ on exchange sites, the transformation of triphenyl carbino into triphenyl carbonium, the protonation of pyridine on slightly hydrated Mg-montmorillonite, and the degradation of s-triazines have confirmed the existence of this surface acidity.

An important point established in these studies is that proton availability increases as the degree of mineral hydration decreases. Apparently, the closer the reaction site is to the hydrated ions and the strongly adsorbed water, the more acidic is the environment. It follows, therefore, that in terms of its physical and chemical properties the interfacial water is continually changing its characteristics as the interface changes in thickness. Regions closest to the mineral surface generally are characterized by an interplay of electrostatic and adsorption forces so strong that water molecules are
distorted to the degree that the protons become delocalized. Instead of being filled by a quasi-crystalline, hydrogen-bonded water structure, the SWS interface appears to be a zone of great orientational heterogeneity amid intense, competing electrical forces.

The belief that water sorbed by soil minerals might exist in an ice-like structure, hydrogen bonded to mineral surfaces, was advocated by clay mineralogists and soil scientists many years ago. Recognizing that such a surface configuration could serve as a condensation template for water vapor, atmospheric scientists went to some lengths to determine the nucleating efficiency of representative mineral species. The results were disappointing. Although it was established that clay minerals are common atmospheric nucleation agents, it was found that they are not nearly as effective as they would be if they were covered with a layer or with patches of adsorbed water in an ice-like configuration.

Calorimetric studies, water vapor adsorption isotherms, and many other kinds of evidence show that the water-silicate interaction is exceedingly intense at low surface coverages. The adsorbed water is surely perturbed in this environment; if, as seems established by the foregoing arguments, the effect is not such as to stabilize the regions so that hydrogen-bonded structures can form, the opposite view is the only alternative. Parenthetically, attempts to test for the presence of \( \text{OH}^- \) or the \( \text{OH} \) free radical by chemical methods have yet to be reported. Until experiments of this kind are carried out, the true nature of the surface acidity implied by protonation reactions, and by the high apparent dissociation constant calculated from dielectric and NMR investigations for the interfacial water, must remain obscure. The role of hydroxyl groups as catalysts for reactions involving sorbed molecules is currently receiving attention as is the electron acceptor-donor role of clay minerals in the polymerization of styrene, and hydroxyethyl methacrylate.

Accelerating activity of this kind is expected shortly to generate models of the SWS interface applicable to specific chemical reactions and substrates.

A model given recently to describe ice nucleation by soil minerals portrays a zone in which long-range, clay-water forces stabilize and promote the enlargement of the hydrogen-bonded flickering clusters that are postulated as one of the components in the flickering cluster mixture model of water. The model implies an extension of the lifetimes and an enlargement in the sizes of hydrogen-bonded domains that facilitate the formation and growth of embryo ice nuclei. This concept is illustrated in Figure 2. In Figure 2, shown attached to a negatively charged substrate surface are some adsorbed water molecules (open circles) and some specifically adsorbed anions, both of which are probably highly distorted. It may be assumed that specifically adsorbed anions and possibly other molecular species are sometimes bound to the mineral surface.

Slightly removed from the surface, hydrated cations are encountered. These are shown symmetrically surrounded by water molecules although it is taken for granted that asymmetrical arrangements are more likely. Farther out is the transition region separating the strongly adsorbed water from that which can be said to exhibit the properties and configuration of water in bulk. It is shown as possessing bulges that fit in between domains of cationic perturbation. These bulges 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 are 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 why, as has often been observed, subsequent freezings may require little or no undercooling. The diagram is highly oversimplified to emphasize the latter points. The fact that the anions are shown completely dehydrated and the hydrated cations are shown completely separated from the mineral surface, for example, while perhaps true in certain instances, is not to be taken literally.

So far the discussion has involved extralamellar interfaces in the main, or very widely expanded, interlamellar space. Specific interlamellar structures have often been sought but the attempts have
failed except in the case of vermiculite. Mathieson and Walker and later Mathieson alone succeeded in identifying a two-water-layer hydrate in which the water molecules were arranged in groups of six around each possible cation site. As the water content and temperature were varied, however, other geometrical arrangements were observed. It appears even here that when quasi-crystalline structures can be identified the geometrical arrangements are more obviously related to exchangeable cation and charge site position than to the mutual locations of water molecules; hence hydrogen-bonded water networks even in this system appear very improbable and have been discounted by Graham et al.

THE SILICATE/WATER/ICE INTERFACE

Until recently, of the four interfaces discussed here, the SWI interface was the least understood; recently, however, a number of significant points have been established. From x-ray diffraction studies of frozen montmorillonite-water mixtures it was shown that interlamellar water is not involved in the SWI interfaces in that system. When expanding lattice clay-water systems are frozen, the interlamellar spacings collapse immediately to about 9 Å and with further cooling to about 6 Å at -10°C and
Figure 3. The change in D(001) spacing for several homoionic Wyoming bentonite (montmorillonite) clays during the warming portion of a freeze-thaw cycle. The dotted vertical line indicates the temperature at which the diffraction pattern of ice was last seen.

below. When the temperature is raised in increments between -10°C and 0°C, lattice reexpansion occurs even though the normal diffraction pattern of ice persists (Fig. 3). This is proof of a progressive melting of ice and the concomitant migration of the meltwater back into the interlamellar space. This, together with the fact that the unfrozen water content of these clay-water mixtures corresponds, with only a slight excess, to the volume of the interlamellar space, indicates that when expanding lattice, clay-water systems are frozen the ice crystallizes in extralamellar spaces. Two types of interfaces in frozen soils are thus defined: SWS interfaces in the interlamellar space and SWI interfaces surrounding individual micelles.

The temperature dependence of the SWS interface thickness has been determined directly for various frozen uni-ionic derivatives of montmorillonite: this relationship is shown in Figure 3. A direct determination for the SWI interface thickness in these frozen systems has not been possible. Due to present uncertainties in unfrozen water content determinations and in the partition of the unfrozen water among the interfaces, even an indirect estimate must be assigned a low reliability. However, it is believed that if they differ, the SWI interface must be the thicker of the two. This conclusion follows from the relationship shown in Figure 4, where average interfacial thicknesses (calculated for kaolinite and montmorillonite by dividing their respective total unfrozen water contents by their respective specific surface areas) are plotted against temperature. The data shown are those of Nersesova and Tsytovich but they have been verified recently in this laboratory (unpublished data of Anderson, D.M. and Tice, A.R.). Of the two, kaolinite seems to have the thicker interface at temperatures down to about -5°C. The SWS interface, even at liquid N₂ temperatures, never becomes thinner than about 6 Å.
The liquid-like characteristics of the interfacial water in frozen soil materials have been well established. The evidence bearing most directly on this point was summarized in an earlier paper. In brief, electrical conductance measurements have established the high mobility of charge carriers in the interfacial water. The fact that electrical and thermal osmosis of water is easily accomplished has established the high molecular mobility and the continuity of the interfacial water. Finally, the observation that soil particles suspended in ice migrate through the ice along thermal gradients shows that the mineral particles are free of any but the most tenuous and transitory connections to the ice phase.

As in the case of the SWS interface, NMR spectra of a variety of clay-water systems at temperatures far below the normal freezing point of water have confirmed the high proton mobility (compared with that of ice) of SWI interfacial water. Qualitatively, protons of the interfacial water can be easily differentiated from those in either the mineral lattice or ice. By varying the ice content and type of clay mineral present, it can be shown that the protons of the interfacial water are associated with the narrowest component of the absorption spectrum, whereas those of the mineral lattice or ice are associated with the widest component.
It is well established generally that wide lines are characteristic of solids and that narrow lines are characteristic of gases and liquids. This may be traced to differences in the interaction intensity of the nuclear spin systems with the locally fluctuating magnetic fields. In liquids and gases, the coupling between the nuclear spins and the local magnetic field is greatly reduced by translational motion, rotational tumbling of individual molecules, migrations of atoms or groups of atoms from molecule to molecule, etc. The result is a narrow absorption line width compared with that of solids. In general, the absorption line width can be regarded as a qualitative index of proton mobility in the system. A typical relationship for silicates is shown in Figure 5.

In a rough sense the distinctions shown are sharp enough. On close examination, however, problems appear, especially at very low hydration levels or at low temperatures; it then becomes a somewhat delicate task to differentiate the protons in the interfacial or adsorbed water from those in the silicate lattice. The data of Hecht et al.\textsuperscript{14} indicate rapid exchange of protons among adsorbed water molecules, but Graham et al.\textsuperscript{13} have shown that proton exchange with the lattice hydroxyls does not readily occur. It is thus possible to detect a certain fine structure associated with changes in water content and the type of exchangeable ion present in the spectra, but the picture is still far from complete. With calcium as the exchangeable cation, it is possible to verify the presence of water in a coordination number of 4 around the cations and in magnesium vermiculite relatively clear-cut evidence of water coordinated around Mg\textsuperscript{2+} has been obtained.\textsuperscript{13} Usually, however, in clay-water systems an indication of shifts in the electrical and magnetic environment caused by changing the water content or the exchangeable ions is obtained, but distinct differentiations usually are not possible.

To aid in assessing the differences between SWS and SWI interfaces, the proton NMR spectra of Na-montmorillonite have been obtained.* Figure 6 shows how the absorption line width changes

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*Measurements were taken with a Varian wide-line spectrometer using a V4230 Low-Proton probe at 3.5 kG and 14.8 MHz. RF field strengths and sweep modulations were selected for each measurement to avoid instrumental distortion of the spectra. The sample was contained in a sealed ampoule suspended in a Dewar tube within the probe. Temperature was controlled within ±0.1°C at each measurement.
with temperature for a sample containing two molecular layers of interlamellar water (0.26 g H₂O/g clay) and no ice compared with that containing two layers of interlamellar water and a rather substantial amount of ice (2.0 g H₂O/g clay).*

The following conclusions are obvious: 1) above 0°C the absorption lines are narrow and characteristic of an aqueous solution; 2) from 0°C to -20°C there is a perceptible but gradual increase in line width, with a slight hint of a change in inflection near -15°C, for the sample containing interlamellar water only; 3) the line width for the ice-containing sample increases abruptly, more than fivefold over that of the ice-free sample near 0°C, and it shows a much smaller change as the temperature is lowered. Below -20°C the line width increases more or less exponentially with temperature, with no sharp discontinuities indicative of phase changes in the interfacial water. Conclusive evidence of phase changes at about -35°C and -45°C for the interfacial water in an identical system has been obtained. Evidently these are not of sufficient significance in altering the local electrical and magnetic environment to yield prominent features in NMR spectra.

Figure 6 gives the relationship between absorption line width and temperature for the narrow component: that associated with the liquid-like interfacial water of the NMR spectra. The differences, which are so apparent, surely are indicative of the differences prevailing in the protons of the interfacial environment. However, although the resonance line width is proportional, through∗

*Recall, as mentioned earlier, that when Na-montmorillonite is frozen at temperatures below -10°C all except two layers of the interlamellar water is expelled from between the individual lamellas where it crystallizes to ice in the exaltalamellar space.
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the correlation time to the time scale of molecular motion, it also depends upon the local magnetic field inhomogeneity. Inasmuch as the samples were identical in mineralogical composition, they would be expected to possess about the same degree of line broadening due to ferromagnetic constituents. But ice segregation and concomitant particle rearrangement in the ice-containing sample, by changing the distribution of magnetic material, might have contributed to the observed abrupt increase in line width. It is hardly likely, however, that this possibility can account for all of the broadening nor does it explain the plateau in the curve extending to about \(-40^\circ\text{C}\).

Graham et al.\(^\text{13}\) contrasted the viscosity of the interfacial water in vermiculite, montmorillonite and hectorite with that of the pure bulk liquid by comparing resonance line widths. Free water has a line width of 0.05 milligauss (mG); however, allowing for broadening due to field inhomogeneity and ferromagnetic constituents, Graham et al. found the line width of the interlayer water to be about 30 mG. Assuming a direct proportionality, with appropriate reservations, they concluded that at ambient temperature the viscosity of interlamellar water at large interlamellar spacings was perhaps 600 times greater than that of free water, or roughly equal to that of glycerol. Using the same index of mobility, Figure 6 suggests that the viscosity of the SWI interface might be as much as five times more than that of the interlamellar water. The value obtained in this manner probably is not accurate but it does emphasize the conclusion that the SWI interface has a lower fluidity than the SWS interface. This is of some interest when it is recalled that the SWI interface, with the reduced fluidity, in all probability is the thicker of the two.

The nature of the water/ice interface has been considered in relationship to the development of freezing potentials by Drost-Hansen. Figure 7 gives a schematic illustration of this interface as it advances through a dilute electrolyte. As Drost-Hansen visualizes it, six zones, ranging from normal structure water (consisting of clusters of clathrate cages and monomers) of bulk liquid shown on the left, to normal ice, shown on the right, may be distinguished. Separating these boundary phases there is, from left to right, a disordered transition layer akin to Frank and Wen's\(^\text{10}\) region of "enhanced structure breaking around a hydrated ion." Next is a highly ordered layer of four coordinated water, termed "polar ice" or "pseudo ice" inasmuch as the protons in this region are thought to be directed predominantly toward the interface. The existence of the latter was postulated solely to account for selective ion incorporation in ice during freezing; in the absence of any argument or evidence against this concept, it will be accepted for the present. Differences in shading of adjacent regions to the right mean that the dipole orientations are relaxing and the selectively incorporated anions are being gradually neutralized by migrating protons.

Not shown in Figure 7, but possibly of local importance in defining order-disorder domains at the interface, are boundaries of the characteristic hexagonal microstructure in ice first described by Workman and Truby.\(^\text{8}\) This microstructure, consisting of coordinated hexagonal prisms ranging in width from 0.5 to 20 \(\mu\) and in length from 1 to 10 \(\mu\), with a hollow strain core 0.05 to 1.0 \(\mu\) in diameter, and grain boundary intersections, adds yet another dimension of complexity to an already complicated picture.

Borrowing from the model of Drost-Hansen, Figure 8 illustrates the SWI interface depicted as the ice advances toward the silicate surface. The main features of this figure are understandable from Figures 2 and 7, but an explanation of the terms order and disorder is desirable. The preferred models of liquid water are the mixture models involving monomers and either hydrogen-bonded clusters, or clathrate cages; this is the extent to which pure bulk water is thought to be structured or ordered. The zone of embryo formation as shown in Figure 2 and the zone of enhanced order of Figure 8 are believed to be more structured than free water in the sense that the rapidity of formation and dissolution of the clusters or cages is thought to be reduced, and the size of the clusters or the number of cages is thought to be increased, as compared with the flickering cluster-mixture model of free liquid water. On the other hand, clusters or cages in general must be fewer in the
regions shown as disordered. Monomers probably predominate there and clusters that do exist must be short lived and deformed compared with those normally existing in bulk water. Moreover, because of the intensity of locally fluctuating surface forces, the monomers closest to sites of high surface charge, or those coordinated around ions, must suffer perturbations and stresses that increase their susceptibility to ionization. Hence, as in the SWS interface, proton activity in this zone may be many orders of magnitude higher than in free water. As mentioned earlier, there is abundant evidence of the increased viscosity of water in the SWS interface; the NMR data available indicate that the viscosity of the SWI interface, if anything, is higher. Therefore, although proton mobility may be much higher, the water in this zone cannot be regarded as having more fluidity than normal water.

These remarks reveal the difficulty created by using the terms order and disorder. The fact that they are not defined precisely and are being used to describe a situation that is far too complex to be satisfactorily dealt with in this fashion must be recognized. We are confronted with having to take into account all the steric factors that apply to clusters, molecules and ions on a time scale that varies through several orders of magnitude, and at the same time deal with proton mobility that varies through perhaps six orders of magnitude, depending upon location. Clearly, it is not possible to describe such a situation adequately by the use of such relative terms as order and disorder. The use of these terms should be regarded as a somewhat desperate attempt to make language serve a useful purpose. The terms ought not to be taken so literally as to become a stumbling block to further developments.
Protonation reactions have not yet been attempted at the SWI interface. On the basis of experience with the SWS interface, the model postulated here predicts that attempts to carry out such reactions will be successful. This conclusion follows from the facts that: 1) freezing soil-water systems is equivalent in this respect to drying them (in both cases, water is removed from the mineral surfaces to form a different phase); and 2) proton delocalization is greatest at the lowest hydration states so that protonation reactions seem to be facilitated by a thin interfacial region. Then, even though the total water (ice) content may be high enough to inhibit these reactions at temperatures above freezing, protonation reactions may become possible at temperatures below freezing. Moreover, because the SWI interface is thinnest and proton delocalization presumably greatest as the temperature is lowered, judging from Figure 6 one might predict that such reactions may be possible at temperatures as low as -50°C.

Figure 8 shows two zones in which monomers are believed to predominate. The opinion that monomers predominate in the zone adjacent to silicate surfaces rests on evidence against hydrogen-bonded water networks and on the indications of enhanced proton activity in this region. For the zone adjacent to the ice surface, this opinion rests largely on the principle of microscopic reversibility, which requires that the addition of water molecules to the ice lattice during interface advance must occur by the same mechanism as the removal of water molecules during melting. If
groups of water molecules are believed to add on in ice-like units, it is difficult to explain the phenomena of supercooling and the large entropy of fusion. If it is suggested that the units are not ice-like, but are clusters or cages of some different geometry, it is difficult to incorporate simultaneously large numbers of the units into a continuous hexagonal lattice. It follows that the dominant mechanism must be the addition or subtraction of water in monomeric units.

According to the nuclear magnetic resonance (NMR) data, the SWI interface seems to be more structured than either bulk water or the SWS interface. Yet other evidence and the preceding argument suggest the presence of two separate zones in which monomers must predominate. Thus, it is concluded that in the region separating these two zones clusters or cages must predominate. In a static interface, dynamic equilibrium must prevail on the molecular level; consequently, there must be a constant exchange of water molecules within and between zones. The species that appears to be most compatible with all phases present seems to be the monomer; therefore, the melting and freezing of monomeric units constitute the most probable mechanism by which the interface is thickened and thinned. This view is supported further by the observation that ice crystals grown from the melt and ice formed by vapor condensation commonly show identical morphological features. Also, negative ice crystals produced in a large piece of ice by the removal of water vapor from the interior of the ice through an embedded hypodermic needle show familiar ice crystal morphology. Similar mechanisms seem to be involved in crystal formation and growth even under widely different environmental conditions and constraints.

Earlier measurements of the partial specific volume of water in an SWS interface indicate a water density less than that of free water. At that time, it was pointed out that this was in harmony with the concept of increased hydrogen bonding in the clay-adsorbed water, although this result was not advanced as proof of the existence of such a structure. Since it now appears that hydrogen bonding proximate to clay surfaces, if anything, is less well developed than in free water, it is appropriate to reconsider the significance of a reduced interfacial water density.

It has been postulated that monomers predominate in numbers in the disordered zones, and it might be argued that this would be an important factor in causing an increase in the average interfacial water density. Offsetting this to a certain extent, however, would be the tendency toward a volume increase arising from proton delocalization there. Based on the preceding arguments, it is now hypothesized that separating the two disordered zones is a zone of enhanced order where hydrogen-bonded clusters and/or cages predominate. The presence of this zone is responsible for reducing the average density of the interfacial region below that of free water. On this point, however, it must be remembered that, although the density determinations of Anderson and Low are reliable, measurements were made on only one type of SWS interface. In cases where the technique is appropriate it ought to be extended to other interfaces, including SWI interfaces, if the needed modifications can be made.

Another point that should not be overlooked in considering the SWI interface is that cations predominate in numbers over anions at the silicate surface. During advances of the ice/water boundary, anions probably predominate in numbers next to and within the pseudo ice transition layer; at other times this region probably is polarized to a lower degree. On the whole, cations and most anions tend to be structure breakers while $\text{F}^-$ and $\text{OH}^-$ seem to be net structure makers in water. It is thus possible that $\text{OH}^-$ may play an important role in promoting orientational order if, as may be the case, delocalized protons tend to reside near the silicate surface freeing $\text{OH}^-$ some distance outward.

As pictured by Frank and Wen, a concentric zone of immobilization, followed by one of orientational disorder, surrounds ions in water; outside this, another zone is pictured in which water is dielectrically polarized by the electrical field, which at this distance becomes relatively weak. This idea is compatible with the view presented here and, to some extent, bolsters the
concept of zonation illustrated in Figure 8. In this instance, as in electrophoresis, individual clay micelles are seen to be analogous to large anions.

Although during freezing there is some selective incorporation of ions in the solidifying mass, foreign substances are rejected from ice and must therefore become concentrated in the SWI interface. Aside from an obvious tendency toward segregation according to the polarity of the surface charge, it is difficult at this stage to specify much more concerning the location of the ions and other solutes and their roles except to reiterate that conductance measurements made on frozen clay-water systems establish their high mobility. However, one further observation may be made. Figure 4 shows that the thickness of the interface changes very rapidly with temperature near the freezing point, but rather slowly at lower temperatures. This suggests that insofar as freezing is concerned, the interfacial zone behaves very much like a brine at temperatures near 0°C but that, at lower temperatures and thinner interfacial regions, surface forces dominate. The roles of the exchangeable ions and solutes, therefore, must shift in response to their changing environment as the interface thickens or thins.

SUMMARY

The purpose of this discussion has been to outline in broad strokes the main characteristics of the various interfaces to be found in frozen soil-water systems and to sketch a model that will serve for a time as a working hypothesis for the SWI interface. To this end, the conceptual approach has been employed exclusively and a number of points of interest, but not central to the discussion, have been omitted. For example, the SWS interface shown in Figure 2 and that of Figure 8 resemble in principle the Stern model of the electrical double layer with its Stern layer, inner and outer Helmholtz planes, etc. Double layer theory and the interfacial models proposed, therefore, are viewed as compatible and complementary. Elaboration of this point, however, will be attempted at another time since necessarily it would require a lengthy consideration of the various degrees of influence to be assigned to chemical as opposed to purely electrical forces in various circumstances.

The observation that mineral particles generally migrate along thermal gradients in ice and that mineral surfaces are not particularly good ice nucleating agents has been used as an argument against hydrogen-bonded water networks. Eventually, mineral particles that do not migrate may be identified and the results of ice adhesion studies now in progress may show how hydrogen bonding may be induced in situations where it does not now occur. Possibilities of this sort are not to be unexpected but for the sake of brevity are passed over for the moment. When they do appear, it may be observed, such findings will permit refinement of the model. Part of the value of the models proposed is that they are subject to refinement. Meanwhile, they can serve for a time to guide future investigation of the SWS and SWI interfaces.

LITERATURE CITED

PHASE BOUNDARY WATER IN FROZEN SOILS

LITERATURE CITED (Cont'd)


PHASE BOUNDARY WATER IN FROZEN SOILS

LITERATURE CITED (Cont'd)


Interfacial regions in frozen soils are of the following types: ice/ice (grain boundary) ice/water/air, silicate/water/silicate (interlamellar) and silicate/water/ice (extra-

lamellar). For the last, the mid portion of the interfacial region should be regarded as a liquid-like solution of the ionic and undissociated substances sorbed by the interface and expelled from the ice during freezing. The interfacial forces operative in these regions result in distinct differences in the properties and behavior of the interfacial water, compared with water in bulk; but, in spite of strong interfacial forces, the interfacial water exhibits liquid-like mobility in its response to many kinds of driving forces. From the evidence and arguments considered, it is concluded that distinctly different zones of orientational order can be distinguished within the interfacial regions. For an advancing silicate/water/ice interface it is proposed that there is a zone of strong perturbation and disorder immediately proximate to silicate surfaces in which the protons of water molecules are partially delocalized; this makes them more easily dissociated. Two or three molecular diameters removed from the silicate surface the interfacial forces operative there combine to create a zone of enhanced order in the molecular configurations. At some farther distance, depending upon the temperature below freezing, it is suggested that there exists a disordered transition zone proximate to the ice surface as portrayed in Drost-Hansen's model. It is suggested that future investigations will contribute refinements in the model and will uncover still further complexities in the various interfaces mentioned.
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