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IONIC MOBILITY IN PERMAFROST

Richard P. Murrmann

U.S. ARMY COLD REGIONS RESEARCH AND
ENGINEERING LABORATORY
Hanover, New Hampshire

INTRODUCTION

The migration of chemicals through unfrozen soil has been extensively investigated in the fields of soil physics and chemistry. The results of these studies have contributed not only to our understanding of fundamental processes in soils but to the solution of diverse yet related problems as well. Information on the migration of chemicals in permafrost and seasonably frozen ground is not available, although the same types of problems occur in cold regions, frequently in even more acute forms.

During the past several years, a series of experiments on the mobility of ions in frozen earth materials has been conducted at the U.S. Army Cold Regions Research and Engineering Laboratory. Approaches have included direct determination of the diffusion coefficients of ions, as well as measurement of electrical conductivity, varying such parameters as temperature, water content, and soil texture. Values for diffusion coefficients have been obtained, the significance of the effects of the parameters on the movement of dissolved substances has been determined, and information on the properties of the interfacial water through which ions diffuse has been derived. The purpose of this paper is to summarize the more significant aspects of these investigations.

ION DIFFUSION

The temperature dependence of sodium ion diffusion in Wyoming bentonite and two silt soils from permafrost regions in Alaska is shown in Figure 1. The diffusion coefficient was determined for salt-free soil materials using a video-tracer technique.¹² Ion diffusion in both the frozen

clay and silts was characterized by a rapid decrease in diffusion coefficient in the temperature range from 0 °C to about -3 °C followed by a much slower decrease to -15 °C. The data for the two silt soils corresponded very closely; however, in the higher temperature range, the ion diffusion coefficient for the soils decreased more rapidly with decreasing temperature than did the ion diffusion coefficient for the clay. The temperature dependence of the ion diffusion coefficients can be accounted for by the properties of unfrozen, interfacial water whose existence has been proved.^{1,15}

The large rate of decrease of the ion diffusion coefficient with decreasing temperature precludes the possibility that observed temperature dependence is primarily caused by a concurrent decrease in thermal energy of the ions. A plot of the unfrozen water content of bentonite and of silt soil against temperature^{3,15} is remarkably similar to the plot shown in Figure 1, indicating a relationship between unfrozen water content and the ion diffusion coefficient. Although the ion diffusion coefficients for the frozen clay and silt soils below -3 °C are about a factor of 10 less than those reported for unfrozen bentonite clay¹⁹ and soils⁶ at low moisture contents, the coefficients for the frozen samples are several orders of magnitude higher than would be expected for solid state diffusion in either ice or minerals. This shows that the water through which the ions diffuse has liquid-like properties relative to those of ice. That ions diffused as far as 5 cm across the samples proves that the films of unfrozen water are continuous throughout the sample matrix. X-ray diffraction measurements for bentonite clay² have shown that most of the unfrozen water is located in interlamellar regions. Moreover, the thickness of the interlamellar water films changes as ice forms or melts

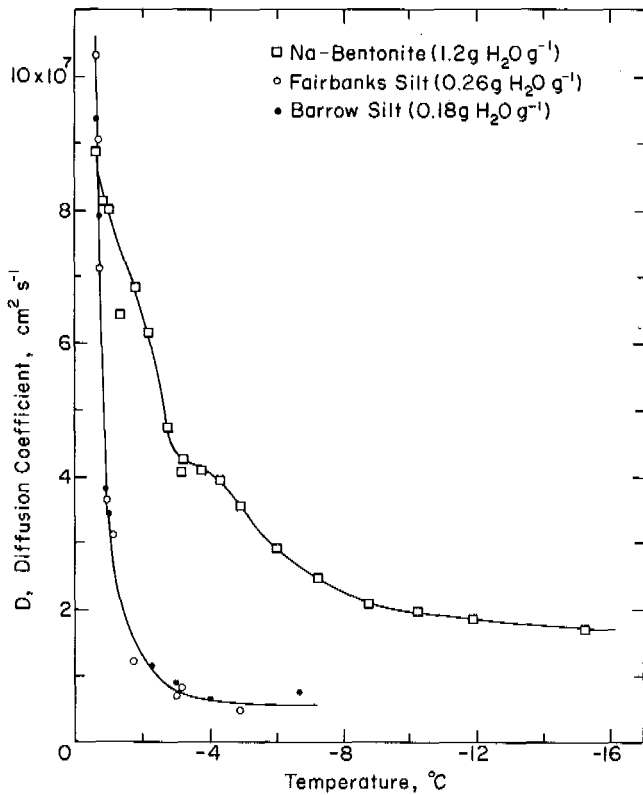


FIGURE 1 Sodium ion diffusion coefficient for frozen Wyoming bentonite, Fairbanks silt, and Barrow silt as influenced by temperature.

in response to temperature variation. Also ion diffusion coefficients for bentonite clay determined after several days as was the case in this study represent values for diffusion in the interlamellar region.⁸ It may be concluded, therefore, that ions in frozen soils are relatively mobile in continuous films of unfrozen, interfacial water.

The initial decrease in ion diffusion coefficient with temperature primarily results from a concurrent decrease in the amount of unfrozen water; however, this initial decrease in ion diffusion is not due to the increasing ice content of the soil since the value of the ion diffusion coefficient is independent of total water content over a wide range (Table I). As the film thickness of unfrozen water decreases with decreasing temperature, ionic mobility is reduced because of the increased electrical interactions of ions with mineral surfaces and/or changes in properties of the interfacial water.

The difference between the temperature dependence observed for ion diffusion in frozen clay and that observed in silts may be explained by first considering the role of the unfrozen water. Unfrozen water per unit weight of soil is higher for bentonite clay than for silt soil at a given temperature, yet the average amount of unfrozen water per unit surface area is actually higher for silts.³ Although this can

TABLE I Sodium Ion Diffusion Coefficient in Frozen Wyoming Bentonite at Different Water Contents^a

Total Water Content (g H ₂ O / g clay)	D _{avg} ^b × 10 ⁷ (cm ² s ⁻¹)
0.8	3.21
1.72	3.41
3.34	2.65
7.07	3.03
AVERAGE	3.08 ± 0.22

^a Temperature, -5.5 °C.

^b Each value represents the average of two determinations.

be interpreted to indicate a thicker film for silts, it has been proposed⁴ instead that silt has a higher proportion of the unfrozen water in pores and capillaries than clay. Hence, the thickness of the interfacial water located adjacent to mineral surfaces is believed to be about the same for both clay and silt. The ion diffusion data support this view in that, if the interfacial films of water were thicker in silt, higher rather than lower diffusion coefficients would be expected at a given temperature. In addition, the more rapid initial decrease in both the unfrozen water content and the ion diffusion coefficient for silt than for clay suggests a higher proportion of pore water in the silt. It is possible that the films of interfacial water are actually thinner in the silt than in the clay. This would account for the lower ion diffusion coefficient for the silt at a given temperature. However, there is no reason to expect that this is the case.

An alternative explanation to account for the difference between the ion diffusion coefficients for the clay and those for silt soils lies in consideration of the matrix characteristics of the two types of materials. To evaluate this, diffusion coefficients were determined for sodium ions in mixtures of bentonite clay and Barrow silt. The diffusion coefficient increased with clay content to about 30 percent clay by weight, remained relatively constant to about 70 percent clay, and then increased to the value of the ion diffusion coefficient for the pure clay (Figure 2). The electrical conductivity of the samples increased with clay content in essentially the same manner as the ion diffusion coefficient.

With the exception of the pure silt soil, the samples were carefully prepared to contain a constant amount of ice phase, even though the ion diffusion coefficient in frozen clay alone is independent of ice content (Table I). Since the mineral phase in the experiment is excluded from the ice upon freezing, the mineral matrix is considered in terms of the volumes of silt, clay, and unfrozen water, rather than in terms of the total volume including the ice phase (Figure 2). Since the silt represents at least 50 percent of the total adjusted volume in samples, with up to 40 percent clay, this region can be considered as a silt matrix to which clay is being added in increasing amounts. At higher clay contents,

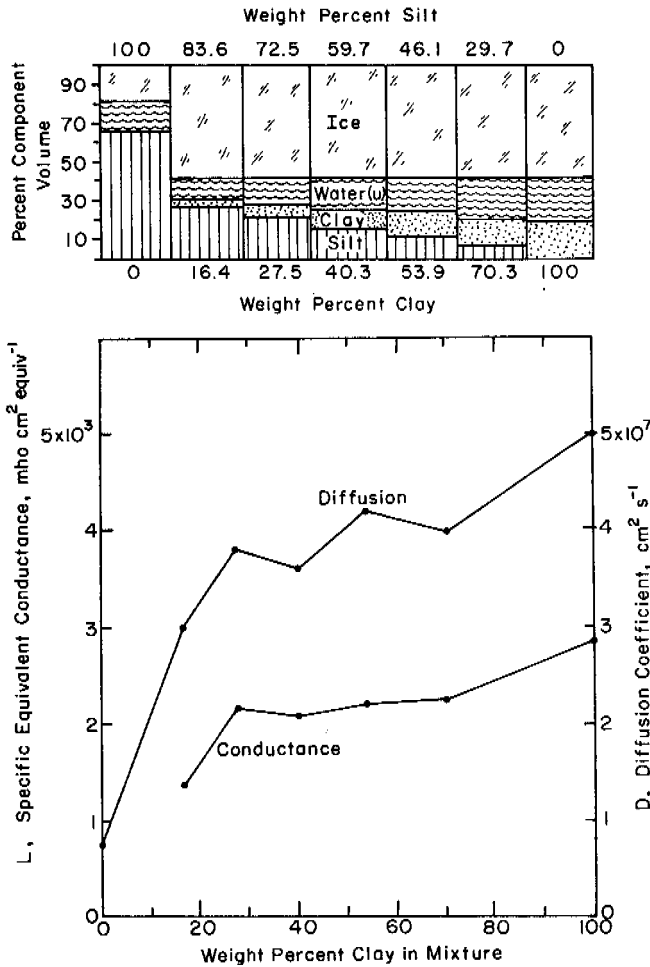


FIGURE 2 Sodium ion diffusion coefficient and specific equivalent conductance for frozen mixtures of Barrow silt and Wyoming bentonite. Temperature constant at -3.0°C .

a transition occurs after which silt can be considered as being suspended in the clay material. Based on this explanation, the ion diffusion coefficient should increase initially because of the increasing particle and film contact as clay is added to the silt. The continued increase in diffusion coefficient after the transition from a silt matrix to a clay paste is thought to reflect shorter diffusion path lengths as the silt content decreases.

Temperature dependence of ion diffusion raises a question about the possible effects of thermal gradients on ion redistribution, since both ionic and thermal gradients exist in permafrost. Experiments were conducted¹⁰ using frozen Wyoming bentonite with a linear temperature gradient of about $0.3^{\circ}\text{C cm}^{-1}$ imposed across samples ranging from -1 to -15°C . A typical ion distribution curve is shown in Figure 3 for a sample in the higher temperature range where the largest effect should occur. In addition to the experimental points, the distribution expected in the absence of a temperature gradient $D(0.5)$ and the distribution computed

using an exact solution¹³ of the diffusion equation with a distance-dependent coefficient $D(x)$ are also shown. The functionality of $D(x)$ was determined using data shown in Figure 1 $[D(T)]$ and the known thermal gradient $[T(x)]$ across the sample. The water content distribution in the sample showed no significant net movement of water toward the cold end, indicating that movement of water did not influence ion diffusion significantly. From the calculated and experimental distribution curves, it is apparent that the effect of thermal gradient on ion movement is small.

Even after 90 days, there should be little effect of a thermal gradient as can be seen by comparing the curves obtained using exact solutions of the diffusion equation, as well as a new approach¹⁴ based on the Monte Carlo method. This approach, which is applicable to true random processes, involves direct construction of random processes rather than solution of the appropriate differential equations as is normally done using the Monte Carlo method. The general approach of this method can be applied to much more complicated problems; for example, soil properties change not only with location but with time under the influence of climatic variation. Predictions of time-dependent phenomena could be made if proper geological and meteorological information were available.

The influence of salt concentration was not investigated, but the mobility of ions at a given temperature should be higher in the presence of dissolved salts because of the in-

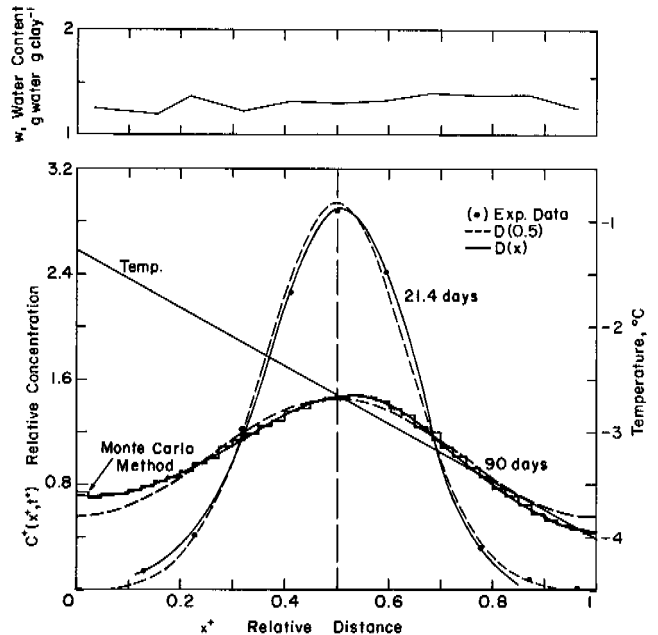


FIGURE 3 Effect of thermal gradient on sodium ion and water content distribution in frozen Wyoming bentonite after 21.4 days and 90 days. Curves were computed using exact solution of diffusion equation or Monte Carlo method as indicated.

creased amount of interfacial water with freezing point depression.⁹ Although the value of the diffusion coefficient differs somewhat for each type of cation or anion, the sodium ion diffusion coefficients shown in Figures 1 and 2 should be generally useful for estimating ion movement in permafrost or seasonally frozen ground under field conditions if temperature and textural characteristics of these soils can be defined. To verify this an ion diffusion experiment was begun in 1970 in a silt section of the CRREL permafrost tunnel.¹⁷ Unfortunately, the results are not yet available for discussion. A similar experiment was recently conducted¹⁸ in Antarctica, but no comparison of data has yet been made.

ELECTRICAL CONDUCTIVITY

Determination of diffusion coefficients is the most direct way to investigate ion migration in frozen soil; such measurements, however, are time consuming and require rather laborious procedures. Consequently, electrical conductivity studies were undertaken with the initial objective of indirectly evaluating ion mobility. The electrical conductance was obtained by measuring the resistance at 1 000 Hz by placing salt-free, Na-Wyoming bentonite samples between stainless steel electrodes in a small, cylindrical Lucite cell. Temperature measurements, accurate to within 0.05 °C, were made using a second identical cell. The electrical conductivity data were expressed in terms of the specific weight conductance to normalize the specific conductance to the number of charge carriers associated with a unit amount of dry clay but independent of the amount of clay per unit volume.

A typical curve of the temperature dependence of the electrical conductance of Wyoming bentonite is given in Figure 4. The decrease in electrical conductivity in the temperature range from 20 to -7 °C is attributed to the decreasing thermal energy of the charge carriers. The sudden drop in conductivity as nucleation occurs (NP) results from decreased film thickness in interlamellar space as water migrates to form ice in extralamellar regions of the clay paste.² Further decrease in electrical conductivity below -7 °C primarily reflects decreased thermal energy of charge carriers, since the unfrozen water thickness in the interlamellar space remains constant.²

Increasing the temperature results in an electrical conductivity curve that is essentially identical to that for ion diffusion (Figure 1). With warming, in addition to an increase in thermal energy of charge carriers, the mobility of charge carriers also increases due to an expansion of the film thickness of interlamellar water as ice melts. The fact that the freezing and cooling curves do not coincide exactly above about 2 °C is thought to reflect changes in internal geometry. It would be expected that because of freezing point depression the two curves would intersect at a temperature (MP) slightly below 0 °C. The fact that this

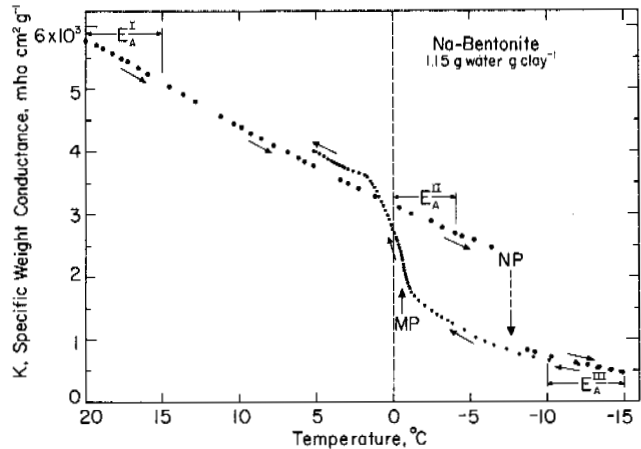


FIGURE 4 Dependence of specific weight conductance of Wyoming bentonite on temperature during freezing and thawing. E_A^I , E_A^{II} , and E_A^{III} refer to data used in calculation of activation energies given in Table II.

did not occur might be explained by the failure of the sample to equilibrate as melt occurs; however, the migration of water back into the interlamellar spaces is known to be rapid.²

A more intriguing explanation is that the melted water, although mobile, may temporarily retain a sufficient number of units with an icelike structure to reduce the mobility of the charge carriers. After warming the frozen samples, even for periods of up to 30 min at 1.5 °C, the electrical conductance generally followed the lower curve in Figure 4 when the temperature was decreased below 0 °C rather than the curve that corresponded to the supercooled condition. This suggests that ice nucleation occurred near the normal freezing point because of the presence of stable ice nuclei as in the concept of heterogeneous nucleation of water.

The temperature dependence of the specific weight conductance for frozen Wyoming bentonite, calculated from the ion diffusion coefficients shown in Figure 1, is shown in Figure 5 in comparison with experimental conductance data. The computation was made using an equation previously derived.¹⁰

Comparison of the experimental and calculated electrical conductance shows that the calculated values are too low by about 60 percent. Although the difference could be due to assumptions made in the computation, it is believed that the higher experimental conductance is largely caused by the presence of charge carriers other than exchangeable ions. It seems likely, however, that exchangeable ions account for a significant fraction of the charge carriers in frozen clay samples with a low ice content. Some investigations^{5,20} have attributed the electrical conductivity of frozen clay almost entirely to protons.

Although the ion diffusion coefficient was found to be independent of ice content in frozen Wyoming bentonite

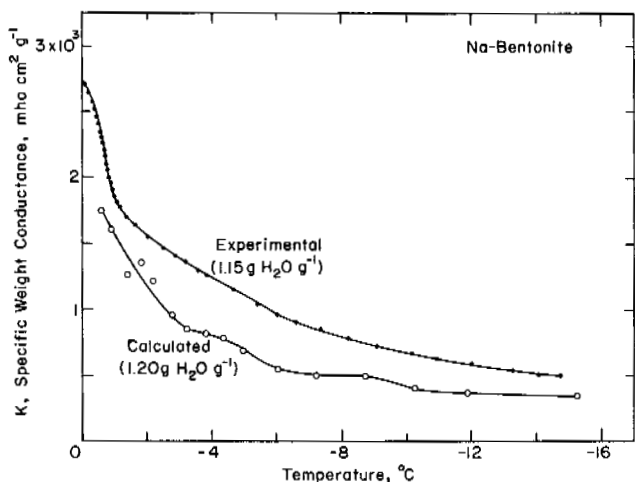


FIGURE 5 Comparison of temperature dependence of experimental specific weight conductance of frozen Wyoming bentonite with that computed from sodium ion diffusion coefficients.

(Table I), close examination of other electrical conductivity data⁷ indicate that this might not be so for the electrical conductance. This was investigated using Wyoming bentonite samples that ranged in total water content from 0.02 to 9.65 g H₂O/g clay (Table 11). Conductivity curves typical of the results are plotted in Figure 6. Clearly, the value of the electrical conductivity at a given temperature increases with ice content, since the amount of unfrozen water is virtually fixed by temperature.¹⁵ The increase in conductivity with ice content may result from several factors, including (1) decreasing tortuosity, (2) higher mobility of a

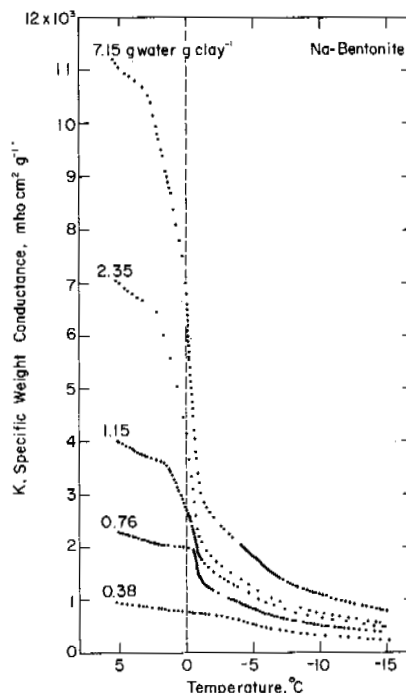


FIGURE 6 Dependence of specific weight conductance of frozen Wyoming bentonite on temperature at selected total water contents.

fixed number of charge carriers, or (3) an increase in the number of charge carriers. However, the fact that the ion diffusion coefficient did not also increase with ice content (Table I) makes the first two alternatives appear unlikely. If tortuosity decreases or more charge carriers are present,

TABLE II Activation Energies for Electrical Conductance of Frozen and Unfrozen Wyoming Bentonite at Different Water Contents

Sample No.	Total Water Content (g H ₂ O/g clay)	Activation Energy (kcal mol ⁻¹)		
		E _A ^I T = 20-15 °C (unfrozen)	E _A ^{II} T = 0 - -4 °C (supercooled)	E _A ^{III} T = -10 - -15 °C (frozen)
1	9.65	4.2	5.2	9.6
2	7.15	4.2	5.1	9.4
3	6.33	4.2	5.1	9.3
4	3.87	4.3	5.1	9.3
5	2.35	4.4	5.4	9.1
6	1.68	4.4	5.3	9.1
7	1.15	4.5	5.5	9.2
8	0.98	3.6	4.6	8.8
9	0.82	4.7	5.6	9.2
10	0.76	4.5	5.6	9.4
11	0.53	4.9	5.9	9.0
12	0.51	4.9	6.0	9.3
13	0.38	5.1	6.3	9.5
14	0.12	6.3	7.4	9.2
15	0.06	6.6	8.0	9.2
16	0.02	8.0	9.0	9.7

the activation energy for electrical conductance should remain constant. However, if ionic mobility increases because of changes in the structure of interfacial water, the activation energy should decrease. Activation energies given in Table II were computed using data in the selected temperature ranges given in Figure 4 (E_A^I , E_A^{II} , E_A^{III}) from a plot of $\log K$ versus $(1/T)$.

The activation energy for the unfrozen samples is included only to illustrate correspondence to previously reported values.¹⁶ For the supercooled samples, the activation energy was consistently about 1 kcal mol⁻¹ less than in the higher temperature range, indicating slight changes in the structure of water in the supercooled state.

The activation energies calculated for frozen samples must be viewed with some caution, because the temperature dependence of conductance reflects not only the thermal energy of the charge carriers but also the effects of the changing amounts of the interfacial water. Since both the total unfrozen water content and the interlamellar spacing remain virtually constant² from -10 to -15 °C, however, calculation of the activation energy seems justified. The activation energy of the frozen sample was about 9.0-9.5 kcal mol⁻¹, higher by a factor of 2 than that of the unfrozen sample except at the lowest water contents in the unfrozen samples. The unfrozen water content in the temperature range -10 to -15 °C is about 0.4 g H₂O/g clay.^{3,15} The activation energy for conductance in the unfrozen samples at an equivalent total water content is only about 5 kcal mol⁻¹. The implication is that the structure of interfacial films of water of equivalent thickness in frozen and unfrozen samples is significantly different. Concerning the increased electrical conductance with ice content, the constancy of the activation energy is inconsistent with the mechanism of increasing ionic mobility. It must be concluded that the enhanced electrical conductivity is caused by an increase in the number of charge carriers.

In recent years, various types of evidence¹ indicating that water adjacent to surfaces in clay systems is highly dissociated relative to bulk water have accumulated. Thus, protons and hydroxyl ions are available to participate as charge carriers. This agrees, in part, with the published results^{5,20} referred to earlier on proton conductivity. Current models² on domains of unfrozen water in frozen clay systems depict differences between properties of water located at silicate-water-silicate (SWS) interfaces and those of the water located at silicate-water-ice (SWI) interfaces. As the ice content increases, the number of SWI interfaces relative to the number of SWS interfaces per unit volume should also increase. The increased electrical conductivity indicates that interfacial water must be more highly dissociated in the SWI domain. It is proposed that, upon spontaneous freezing, the relative number of SWI interfaces that form depends on the structure of the unfrozen clay-water system, which is a function of water content. In this manner,

the number of charge carriers is fixed when freezing occurs. This view is supported by the observation that the change in relative conductance of the frozen clay with total water content is independent of temperature, as defined in Figure 7. Conversely, the relative increase in electrical conductance with temperature is independent of total water content, which primarily reflects the increased mobility of a fixed number of charge carriers.

A plot of total water content versus freezing point depression has been shown⁹ to be equivalent to the temperature dependence of unfrozen water content in frozen soil. It seems worthwhile to make such a comparison based on freezing point depression values obtained from the electrical conductivity curves shown in Figure 6. Although no sharp discontinuity appears in the electrical conductance data as might be expected at the melting point, freezing point depression is thought to be represented by the inflection of the conductance curve as the temperature approaches 0 °C upon warming the frozen samples. This possibility is indicated by the relative rates at which temperature and electrical conductance changed on warming the samples. To test this, the inflection point of the conductance curves was determined with good agreement both by observation and by fitting a curve to the experimental data. The water content of the samples was then plotted against the inflection point temperature as shown in Figure 8. Available unfrozen water content data³ were then added to the graph. The solid lines correspond only to the experimental unfrozen water content. The agreement between the two types of data supports the contention that the inflection point in the conductivity curve does represent freezing point depression. By refinement of experimental

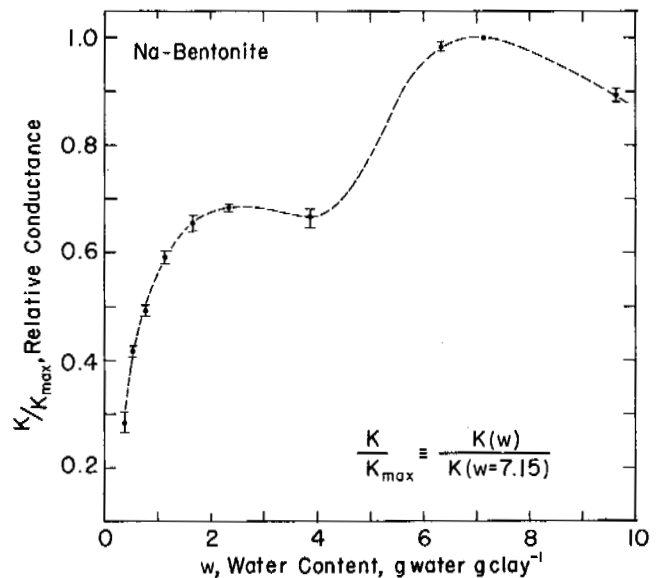


FIGURE 7 Dependence of relative specific weight conductance of frozen Wyoming bentonite on total water content.

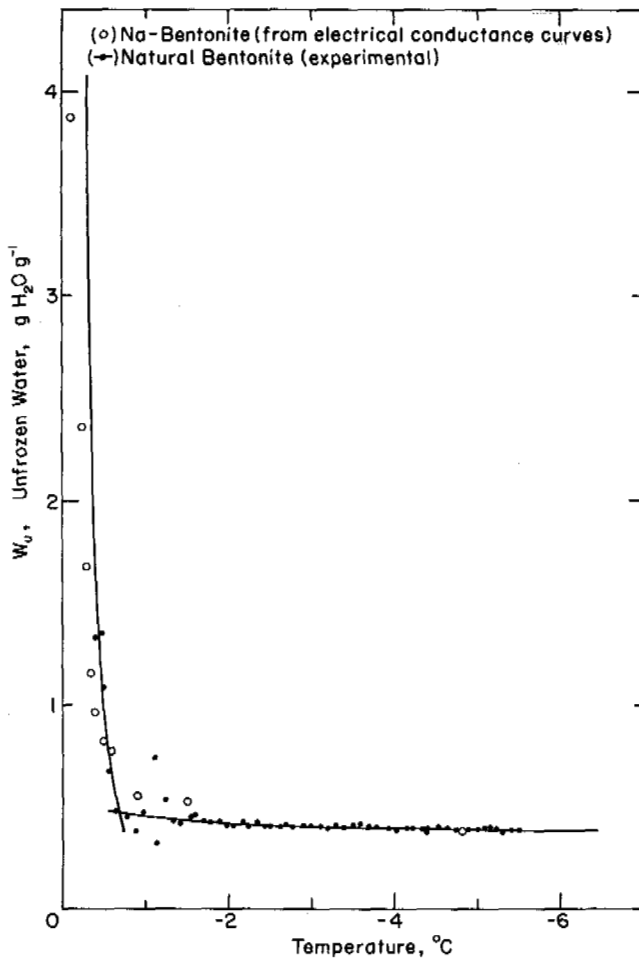


FIGURE 8 Estimate of unfrozen water content in Wyoming bentonite as a function of temperature from inflection point in electrical conductivity curve of samples with known total water content.

procedures, it might be possible to reliably estimate the unfrozen water content of soils near 0 °C where difficulty is encountered using most other methods.

SUMMARY

Despite the significance of the movement of chemical substances in relation to both natural processes and current problems of practical significance, little is known about ion migration in permafrost or seasonally frozen ground. In this work, the mobility of ions in frozen bentonite clay and frozen silts was investigated directly by determining sodium ion diffusion coefficients and indirectly by measuring electrical conductance. The results define diffusion rates, determine how soil parameters influence ion migration, and acquire supportive evidence for current concepts about the nature of unfrozen water in frozen soil.

Although ion diffusion is slower in frozen soil than in unfrozen soil, values of the diffusion coefficients in the temperature range from about 0 to -15 °C are surprisingly

high relative to those of solid state diffusion. For example, the diffusion coefficient for sodium ions in frozen bentonite at -15 °C is $1.7 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$, only about a factor of 10 less than that expected at 25 °C. For typical silt soils the diffusion coefficient for sodium ions is about $1 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ at -3.0 °C. Although the rate of ion diffusion is lower in frozen silt soil than in frozen clay at a given temperature, it increases with clay content because of the decreasing tortuosity of the soil matrix. The values of the diffusion coefficient remain constant with time, and ion diffusion is not affected over a wide total water content range. The most important parameter influencing ion diffusion in a given soil is temperature, but the influence of temperature cannot be accounted for by the changing thermal energy of the ions. Despite the importance of temperature in determining the value of the ion diffusion coefficient, thermal gradients of $0.3 \text{ }^\circ\text{C cm}^{-1}$ have little perturbing influence on ion diffusion in frozen clay, even after 3 months. Generally, data reported should be applicable to any frozen soil whose texture and temperature can be specified.

The temperature dependence for the low frequency electrical conductivity of frozen Na-bentonite is strikingly similar to that for ion diffusion. Although the electrical conductivity of a sample could be reasonably estimated from ion diffusion data, electrical conductance is somewhat higher at a given temperature than can be accounted for from the diffusion coefficient of exchangeable ions in a comparable sample. Unlike diffusion, the specific weight conductance of frozen bentonite clay increases with total water content of the sample. The enhanced conductivity is due to an increased number of charge carriers, since it can not be accounted for by either increased mobility of charge carriers or decreasing sample tortuosity.

The behavior observed for ion diffusion and electrical conductance is completely consistent with current concepts proposed for the nature of unfrozen water in soils. The physical movement of ions through the frozen soil matrix and the relatively high values for diffusion coefficients can be accounted for only by the existence of continuous, thin films of interfacial water in which the molecules are relatively mobile compared with those of ice. The temperature dependence of ion diffusion and electrical conductance largely results from a higher ion mobility as interfacial films of water thicken with the melting of ice with increasing temperature. Differences between the temperature dependence of ion diffusion in frozen silt and that of frozen clay are best explained by the partition of the total unfrozen water within different domains of the soil matrix. A higher electrical conductivity than that expected from exchangeable ions arises from interfacial water, which has a higher degree of dissociation than bulk water. The increase in electrical conductivity with ice content indicates that the water at silicate-water-ice interfaces is more highly dissociated than the water at silicate-water-silicate interfaces.

ACKNOWLEDGMENTS

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SOUND AND SHOCK TRANSMISSION IN FROZEN SOILS

Yoshisuke Nakano

U.S. ARMY COLD REGIONS RESEARCH AND
ENGINEERING LABORATORY
Hanover, New Hampshire

Nilson H. Froula

SYSTEMS, SCIENCE AND SOFTWARE
La Jolla, California

INTRODUCTION

To promote better understanding of the structure and history of the earth and to develop solutions to engineering problems, stress wave propagation in earth materials has been a topic of intensive research in geophysics and geology.

In the past decade, advancements in science and technology have led to two important laboratory experimental techniques in the field of wave propagation: the ultrasonic technique to study dynamic elasticity and the high pressure technique to study shock compression of earth materials, using a gas-gun facility. Although these techniques