Dielectric Response of Water and Ice in Frozen Soils

N. Maeno*, T. Araki**, J. Moore*** and M. Fukuda*

∗Institute of Low Temperature Science, Hokkaido University, Sapporo 060, Japan
∗∗Hokkaido Gas Co., Kita-4, Higashi-5, Sapporo 060, Japan
∗∗∗British Antarctic Survey, Natural Environment Research Council, Madingley Road, Cambridge CB3 0ET, UK

ABSTRACT: Dielectric constants and conductivities of frozen soils were measured as functions of frequency, water content, and temperature. The measurements were conducted at frequencies from 20 Hz to 300 kHz, degrees of water saturation (fractions of pore volume occupied by water) from 0 to 100 % and temperatures from +10 to -100 ^{o}C. In the two kinds of soil samples examined, Fujinomori clay and Tomakomai silt, large dielectric responses were observed in a wide frequency range. The dielectric dispersion at temperatures above about -80 ^{o}C was of 'universal' type; with increasing frequency the dielectric constant and conductivity steadily decreased and increased respectively. The activation energy for 100 kHz conductivity was 35.4 and 38.2 kJ/mol for Fujinomori clay and Tomakomai silt respectively. At temperatures below about -80 ^{o}C the dielectric response associated with water molecules and ions was small and the activation energy was 17.0 kJ/mol for Tomakomai silt.

1. Introduction

Frozen soils are complex mixtures of soil particles, ice, and unfrozen water, each fraction depending on their material compositions, water contents, and temperature. Most of previous electrical measurements of frozen soils have been carried out only at D.C. or a few high frequencies (1-4) since their main objectives were to obtain numerical data for practical water content sensing and electric sounding.

Frequency and temperature dependencies of dielectric properties of frozen soils were first studied by Olhoeft (5). He measured dielectric constants and conductivities of natural permafrost samples at frequencies from 5 mHz to 100 MHz and at two temperatures -10 and -27 ^{o}C, and showed the existence of at least five dielectric dispersions. Then Araki and Maeno (6) conducted a systematic dielectric measurement of sand and clay in wide ranges of frequency, temperature and water content. In the first paper they reported a characteristic feature of frozen soils, especially its dependence on water content; it was concluded that water molecules exist in frozen soils in three modes depending on water content; they are water molecules strongly adsorbed on surfaces of soil particles, those weakly bound, and those solidified in bulk ice filling pores. The present paper, the second report of the study, is specially concerned with the temperature dependencies of the dielectric properties.

2. Measurements

Dielectric measurements were carried out for two kinds of soils, namely Fujinomori clay and Tomakomai silt. Their general physical properties have already been studied (7); the average particle densities of Fujinomori clay and Tomakomai silt are 2610 kg/m^3 and 2650 kg/m^3 respectively; their relative compositions of particle diameters 2 mm-7

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μm, 7-5 μm and less than 5 μm are 15 %, 61 % and 24 % for Fujinomori clay, and 39 %, 32 % and 29 % for Tomakomai silt, respectively. The amount of water-soluble chemical components involved is about thirty times larger in Fujinomori clay; A dry sample (20 g) of Fujinomori clay or Tomakomai silt was mixed in pure distilled water (80 ml), stirred and left one hour. The electrical conductivity of the top solution was 5.895 mS/cm (Fujinomori clay) and 0.200 mS/cm (Tomakomai silt) at 25 °C, which correspond respectively to NaCl concentration of 3200 ppm and 100 ppm if NaCl is assumed to be a sole chemical component dissolved.

Soils were carefully packed in a circular plastic insulation box with 104-mm in diameter and 8-mm in thickness; The dry bulk density achieved was 1000±150 kg/m^3, that is the bulk porosity is roughly 0.62. The bottom of the box is a 5-mm thick chrome-plated copper electrode. An 80-mm diameter electrode was in contact with the upper surface of the soil sample with a weak spring; sometimes a thin aluminum foil was also used to keep better electric contact (8). A guard ring electrode was also used.

Considerable time (two to five days) was spent to achieve a homogeneous distributions of water in a sample. After dielectric measurements the water content of each sample was estimated by measuring its weight before and after baking at 120 °C for 24 hours.

The sample-electrode system loaded in a 10-mm thick stainless steel vessel (300-mm diameter) was installed in a cryostat bath, the temperature of which could be cooled to -150 °C by circulating liquid nitrogen. Dielectric measurements were mostly carried out at temperatures from +10 to -100 °C.

Electric measurements were conducted at frequencies from 20 Hz to 300 kHz. Main electric devices used are an AC bridge (Ando Denki TR-10C), LF impedance analyzer (Hewlett Packard 4192A) and multi-bridge (Wayne Kerr 6425). Numerical data of capacitance and conductance measured at each frequency were stored in a microcomputer. All the data were corrected for stray and residual impedance in the electric circuit. More details of samples, devices and experimental procedure are reported elsewhere (6).

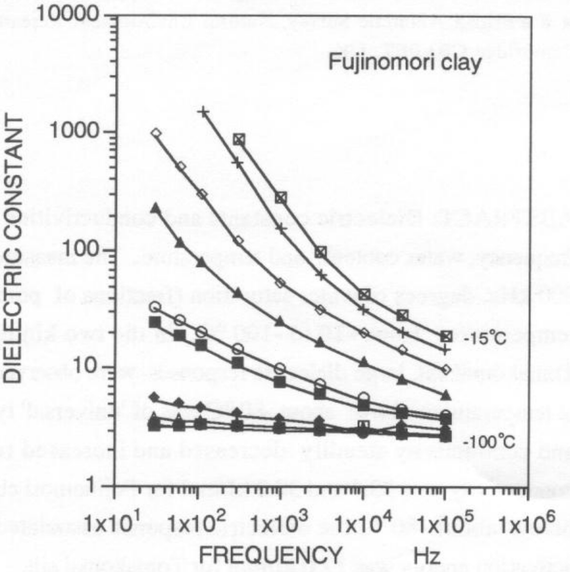

Fig. 1 Dielectric constant of Fujinomori clay versus frequency. The degree of water saturation is 11.1 %. Temperatures are -15, -20, -30, -40, -50, -60, -70, -80, -90 and -100 °C (from above).

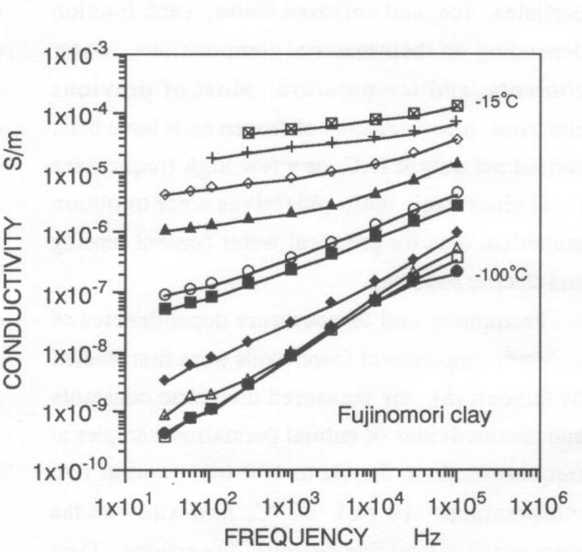

Fig. 2 Dielectric conductivity of Fujinomori clay versus frequency. The degree of water saturation is 11.1 %. Temperatures are -15, -20, -30, -40, -50, -60, -70, -80, -90 and -100 °C (from above).

3. Results

As reported previously (6) the dielectric dispersions of dry Fujinomori clay and dry Tomakomai silt are small and their dielectric constants and conductivities only vary in narrow ranges, 2.3-3.6 and 10^{-11}-10^{-7} S/m for Fujinomori clay and 2.9-4.8 and 10^{-10}-10^{-7} S/m for Tomakomai silt, respectively. These figures imply that both of the dry soils can be regarded as electric insulators or dielectrics; The small dielectric dispersions measured are not intrinsic but caused by a small number of ionic charge carriers remaining within the soils.

Figs. 1 and 2 give typical frequency dependencies of dielectric constant and conductivity of Fujinomori clay (degree of water saturation 11.1 %) at ten temperatures from -15 to -100 °C. Here the degree of water saturation is defined as the volume fraction of pores occupied by water in a soil sample. Figs. 3 and 4 give the frequency dependencies of Tomakomai silt at a similar degree of water saturation (10.3 %) and temperatures. It is then evident that the distinct dielectric response of frozen soils shown in Figs. 1-4, which are much larger than those of dry soils, are caused by the presence of water molecules. However, the mechanism of the dielectric dispersion is not simple since varieties of electric charge carriers are formed and activated in association with added water molecules in frozen soils.

The increase in dielectric constant with rising temperature (Figs. 1 and 3) is the result of additional polarization caused by mobile charge carriers liberated; the polarization does not mean only that due to the rotation of water molecules in ice and unfrozen water but also that due to various ions migrating and piling up at many electrically discontinuous boundaries in the soil samples; the former polarization is the intrinsic property of ice and water, and the latter is extrinsic in nature and considerably influenced by kinds and amounts of chemical components involved. The result that the dielectric constants and conductivities of Fujinomori clay are roughly by an order of magnitude larger than those of Tomakomai silt can be explained by the larger amount of dissolved ions which is roughly thirty times more abundant in Fujinomori clay as mentioned in the preceding section.

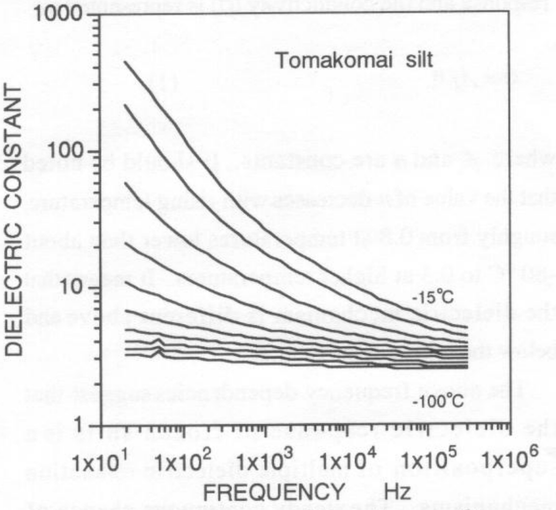

Fig. 3 Dielectric constant of Tomakomai silt versus frequency. The degree of water saturation is 10.3 %. Temperatures are -15, -20, -30, -40, -50, -60, -70, -80, -90 and -100 °C (from above).

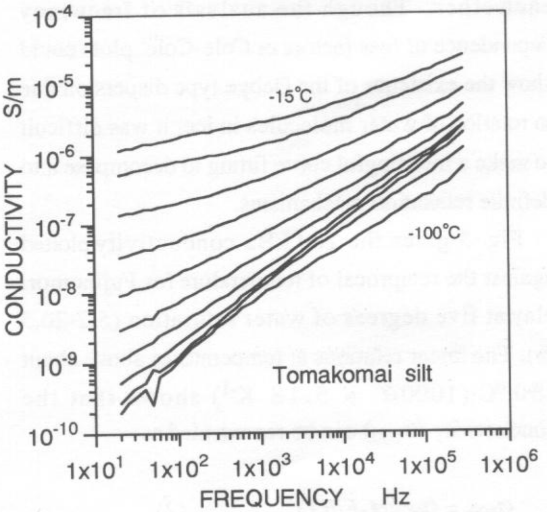

Fig. 4 Dielectric conductivity of Tomakomai silt versus frequency. The degree of water saturation is 10.3 %. Temperatures are -15, -20, -30, -40, -50, -60, -70, -80, -90 and -100 °C (from above).

The observed frequency dependence of conductivity in Figs. 2 and 4 is a 'universal' type response and the conductivity (σ) is represented as

$$\sigma = Af^{n} \qquad (1)$$

where A and n are constants. It should be noted that the value of n decreases with rising temperature, roughly from 0.8 at temperatures lower than about -80 °C to 0.3 at higher temperatures. It means that the dielectric mechanism is different above and below the critical temperature.

The above frequency dependencies suggest that the dielectric response of frozen soils is a superposition of multiple dielectric relaxation mechanisms. The steady continuous change of dielectric constant and conductivity with varying frequency implies that many dielectric mechanisms are involved and their relaxation times are close to each other. Though the analysis of frequency dependence of loss factors or Cole-Cole plots could show the existence of the Debye type dispersion due to rotation of water molecules in ice, it was difficult to make a meaningful curve fitting to decompose into definite relaxation mechanisms.

Fig. 5 gives the 100 kHz conductivity plotted against the reciprocal of temperature for Fujinomori clay at five degrees of water saturation (5.2-20.3 %). The linear relations at temperatures above about -80 °C ($1000/T = 5.18$ K^{-1}) shows that the conductivity (σ_{100}) can be represented as

$$\sigma_{100} = \sigma_{0}\exp(-E/RT) \qquad (2)$$

where σ_0 is a constant, R is the gas constant, T is the absolute temperature, and E is the activation energy for the dielectric conduction. The activation energy estimated as the slope of each straight line increases with the degree of water saturation, from 18.6 kJ/mol at 5.2 % to 35.4 kJ/mol at larger degrees than about 10 %. At temperatures lower than about -80 °C the measured data are not accurate enough but it seems that σ_{100} is roughly constant or even decreases again with lowering temperature.

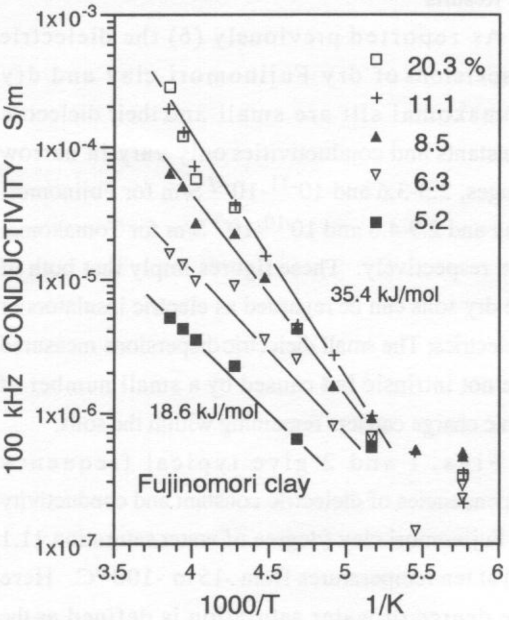

Fig. 5 100 kHz conductivity of Fujinomori clay versus reciprocal of temperature. The degrees of water saturation are 5.2, 6.3, 8.5, 11.1 and 20.3 %.

Fig. 6 gives a similar but clearer trend of σ_{100} for Tomakomai silt at three degrees of water saturation (5.7, 7.7 and 10.3 %); with lowering temperature σ_{100} decreases steadily, shows a plateau between about -60 °C ($1000/T = 4.69$ K^{-1}) and -80 °C, and then decreases again. The straight-line fitting showed that the activation energy at temperatures above -60 °C increases with water content from roughly 14.8 kJ/mol to 38.2 kJ/mol, while that at temperatures below -80 °C was 17.0 kJ/mol.

4. Discussion

The dielectric contribution associated with the three modes of water molecules in frozen soils is clearly seen in Fig. 7 for Fujinomori clay at -30 °C. In the figure the increase in dielectric constant due to the addition of water, that is the measured dielectric constant from which that of the dry sample is subtracted, is plotted against the degree of water saturation at frequencies of 3, 10 and 100 kHz. The gradual increase in a region from 0 to 5 % is caused

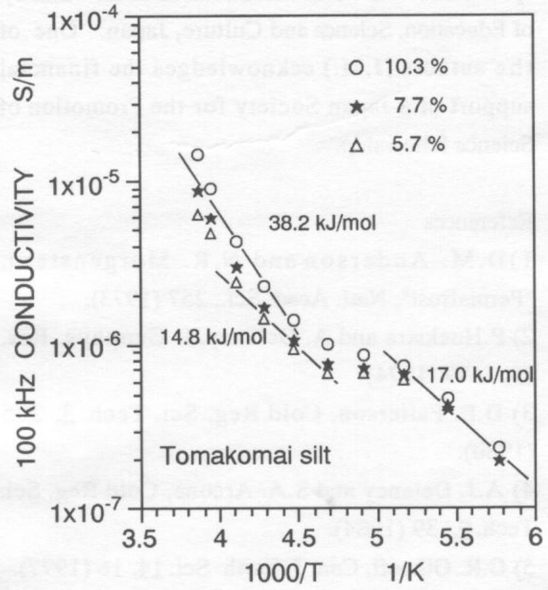

Fig. 6 100 kHz conductivity of Tomakomai silt versus reciprocal of temperature. The degrees of water saturation are 5.7, 7.7 and 10.3 %.

by strongly absorbed water molecules on surfaces of soil particles. The absorption is considered to form a monomolecular layer since the number of molecules (molecular thickness) of the absorption layer at 5 % water saturation is calculated as 1.1 if the specific surface area 9.0 m^2/g measured by the BET absorption isotherm method (9) is taken into account.

The rapid increase in the region from 5 to 10 % is considered to be caused by the development of multi-molecular layers (weakly bound water molecules to soil particles), namely unfrozen water. Water molecules and ions in this mode are mobile and play active roles as effective charge carriers to give rise to large dielectric polarization and conduction. Above 10 % water saturation, which roughly corresponds to the four-molecular thick layer, bulk ice begins to appear in pores. The contribution of the bulk ice to the general dielectric dispersion is generally weak and cannot be detected unless the water content is appreciably large.

The measured activation energies 35.4 kJ/mol (Fig. 5) and 38.2 kJ/mol (Fig. 6) are essentially attributed to the conduction and polarization associated with motions of protons and other ions in unfrozen water layers. Similar energies have been reported by other researchers; Weiler and Chaussidon (10) measured dielectric losses (1 kHz) of montmorillonite clay gels saturated with lithium, sodium potassium or cesium, and gave the mean activation energies 48.2 and 24.0 kJ/mol above and below a critical temperature -73 °C respectively; Hoekstra and Doyle (11) obtained 50.8 kJ/mol for the conductivity at 100 kHz of Na-montmorillonite containing absorbed water of roughly three molecular layers on each clay surface, though they could not detect a break in their temperature range studied(-15 to -75 °C). It is thus concluded that the measured activation energies ranging from 35 to 50 kJ/mol are related to the formation and migration of charge carriers such as protons and ions activated in weakly bound or unfrozen water layers.

Below the critical temperature, that is about -80 °C for Fujinomori clay, -60 °C for Tomakomai silt and -73 °C for montmorillonite (10), unfrozen water cannot exist and all water molecules and chemical impurities are frozen in a solid phase. The lower critical temperature of Fujinomori clay than that of Tomakomai silt might be attributed to the

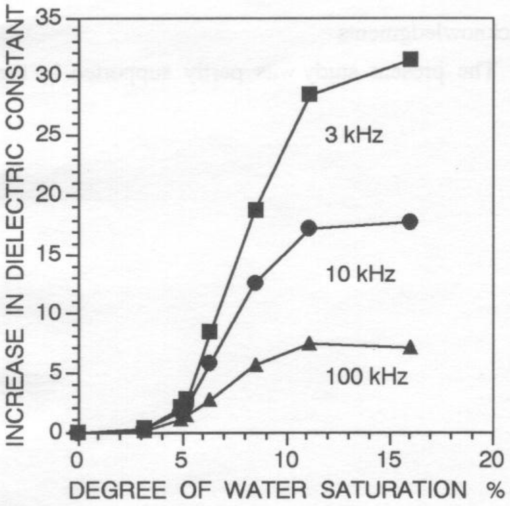

Fig. 7 Increase in dielectric constant of Fujinomori clay due to water added. Temperature is -30 °C.

larger amount of chemica impurities in the former soil as mentioned above. At this stage of study it is not possible to give a clear physical explanation to the dielectric conduction at these temperatures and to the activation energy of Tomakomai silt (17.0 kJ/mol). However, it might be reasonable to consider that the freezing-in of mobile charge carriers proceeds and finishes in the temperature range of about 20 degrees, that is a plateau in Figs. 5 and 6, between -60 and -80 °C (Tomakomai silt) and -80 and possibly -100 °C (Fujinomori clay).

5. Conclusions

Dielectric properties of two kinds of frozen soils were studied as functions of frequency, temperature and water content. It was found that water molecules bound weakly to soil particles, that is unfrozen water, give rise to large dielectric polarization and conduction; the dielectric conduction was described by the activation energies ranging from 35 to 50 kJ/mol. These mobile charge carriers are completely frozen in a critical temperature range (about -60 to -80 °C for Tomakomai silt and about -80 to -100 °C for Fujinomori clay), and the activation energy at lower temperatures is much smaller, 17.0 kJ/mol for Tomakomai silt.

Acknowledgments

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