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PRELIMINARY MEASUREMENT OF HIGH-FREQUENCY ELECTRICAL CONDUCTIVITY OF ANTARCTIC ICE WITH AC-ECM TECHNIQUE

Ken SUGIYAMA[1], Shuji FUJITA[1], Shigeru SUEOKA[1], Shinji MAE[1] and Takeo HONDOH[2]

[1]*Department of Applied Physics, Faculty of Engineering, Hokkaido University, Kita-13, Nishi-8, Kita-ku, Sapporo 060*
[2]*Institute of Low Temperature Science, Hokkaido University, Kita-19, Nishi-8, Kita-ku, Sapporo 060*

Abstract: We measured the high-frequency electrical conductivity of solid ice samples collected in the Antarctic ice sheet with a new technique called "AC-ECM (AC Electrical Conductivity Measurements)". The purpose was to establish a new convenient technique to detect variation of impurity content in ice cores with high spatial resolution and with high reproducibility for repetitive measurements. For this purpose, the conductance of the ice sample was measured with 2-terminal electrodes and with parallel-plate electrodes at 16 frequencies between 40 Hz and 1 MHz. Then both results of the conductance measured by these two different pairs of electrodes were compared to discuss the physical meaning of the signals measured with the new technique. The preliminary measurements were successful. We could measure conductance, which is proportional to the conductivity of ice, at frequencies above 100 kHz at $-20\,^{\circ}$C. The relaxation frequencies of Debye dispersion were higher when values of conductance were measured with the new technique, which suggested that surface conduction was dominant.

1. Introduction

Ice-core analysis technique to measure solid electrical properties is essential for ice core studies, especially for rapid analysis at the coring site. It is very important for the whole coring project to identify depths of past climatic events in ice and to identify impurities rapidly. Therefore it is important to develop and to improve the relevant measurement techniques. So far, two powerful techniques exist. They are the Electrical Conductivity Measurements (ECM) (HAMMER, 1980, 1983; HAMMER *et al.*, 1985; NEFTEL *et al.*, 1985) and the Dielectric Profiling Technique (DEP) (MOORE and PAREN, 1987; MOORE *et al.*, 1989; MOORE, 1993). These two methods have been used as powerful tools in recent deep ice core studies (*e.g.* GRIP Members, 1993; TAYLOR *et al.*, 1993).

As the third method, a new method "AC-ECM" was tested in this study. Electrodes such as ECM are used in this method but the electrical current is AC with frequencies from 40 Hz to 1 MHz. The experimental temperature is $-20\,^{\circ}$C. The system is based on the electrodes and the precision LCR meter. A similar method was also tested by MINKIN and KIPFSTUHL (1992) at a temperature of $-10\,^{\circ}$C, at frequencies up to 250 kHz. The purpose of this study is to develop a new technique which has the advantages of both ECM and DEP in order to: 1) obtain high spatial resolution (ECM); 2) to detect AC high-frequency conductance which is free from the space charge effect and from conductance components due to Debye dispersion (DEP). The new method still requires the preparation of a smooth flat surface of ice specimens, like ECM and unlike DEP. The two advantages are important to detect climatic signals that exist like sharp spikes in ice cores and to interpret the physical/chemical meaning of the signals easily. The preliminary measurements were successful. We could detect the conductance by the AC-ECM technique and conductivity by the parallel-plate electrode technique, and found that both were proportional to one another at frequencies between 100 kHz and 1 MHz at about $-20°C$. It was also found that the relaxation frequencies of the Debye dispersion measured by AC-ECM were higher than the conductivity in ice. However, to establish this technique it is necessary to test it more and to solve several problems.

2. Measurement Method and Procedure

2.1. System and electrodes

The AC-ECM system consists of the electrodes and the precision LCR meter (Hewlett-Packard 4284A) (Fig. 1). This system can measure conductance at a point of the ice core surface at arbitrary frequencies between 40 Hz and 1 MHz in about 10 s. Hence the 50 cm-long ice core can be measured in about 20 min when measurements are carried out at every 1 cm in the ice-core. In addition, measurements at a given frequency (for example 1 MHz) can shorten the measurement period to a few minutes. Because the

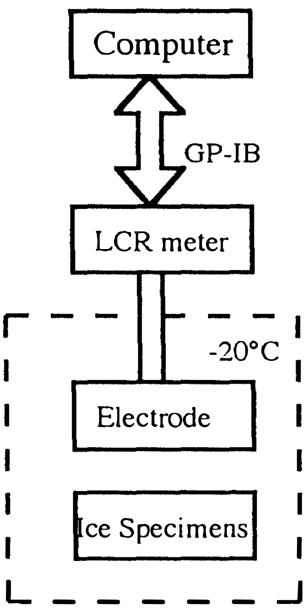

Fig. 1. Schematic diagram of the AC-ECM technique. The system consists of the electrodes and a Precision LCR meter (Hewlett-Packard 4284A). The system was controlled by computer. The experimental temperature was $-20(\pm 1)$ °C.

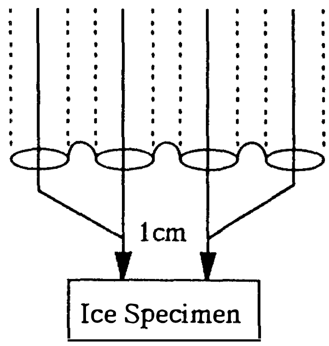

Fig. 2. Diagram of the AC-ECM electrodes. These electrodes form a 4-terminal network. However only two terminals are contacted directly to the ice surface, the other two outer terminals are connected to the inner terminals near the ice surface. The two inner terminals were stainless-steel rods of diameter 3.0 mm. The radius of curvature at the edge of each terminal is 1.5 mm. The distance between the inner terminals is 1 cm.

LCR meter automatically corrects the floating admittance and the residual impedance in the circuit, accurate values of the conductance can be measured. We focused on only conductance and not on capacitance because the electrodes we used was not suitable for accurate measurement of capacitance.

The electrodes which we used for the AC-ECM basically has 4 terminals (Fig. 2). The 4-terminal network was used to prevent interference of the electromagnetic signals in the circuit. However, in the electrodes, only the two inner terminals contacted directly to the ice surface. The other two outer terminals are connected to the inner terminals near the ice-core surface (Fig. 2). Normally, for the conductivity measurement of conductive materials (*e.g.* metals), 4 terminals are used to avoid small resistivity in the circuit, mainly at junctions between the circuit and the measured materials. However, in the case of ice measurement, because impedance in ice is much larger than the resistivity component at the terminal/ice interfaces, the resistivity component could be ignored in the circuit. Therefore only the two inner terminals were contacted to the ice. The electrodes consists of two stainless-steel rods diameter 3.0 mm. The radius of curvature at the edge of each terminal was 1.5 mm. The distance between the inner terminals is 1 cm. The electrodes were scanned by hand along the smooth flat surface of the specimen. The precision LCR meter was controlled by, and the measured data were stored in a

Fig. 3. Photograph of the thin section of the used specimens. This specimen is ice collected from Nansen Icefield near the Sør Rondane Mountains during the search for Antarctic meteorites (NARAOKA et al., 1991).

computer.

Another pair of electrodes which was used for the reference measurements is a pair of parallel plate electrodes (Hewlett-Packard 16451B) of diameter 5 mm. With this pair of electrodes, the conductivity of ice sandwiched between the electrodes was measured accurately. The conductance measured with the electrodes for AC-ECM was compared with the conductance measured with the parallel plate electrodes. In all measurements, the applied voltage was 3 V and the experimental temperature was $-20\pm1\,^{\circ}\mathrm{C}$.

2.2. Specimens

We used two specimens for the test measurements. One is Antarctic ice containing volcanic ash and an adjacent clean layer. Here, the word "clean" means only that it does not contain volcanic ash. The photo of the thin section is shown in Fig. 3. These specimens were collected on the Nansen Icefield near the Sør Rondane Mountains during the search for Antarctic meteorites (NARAOKA *et al.*, 1991). The ice was about 20 cm deep in the bare ice field. A boundary between two ice layers; *i.e.* a layer containing volcanic ash and adjacent ice layer which do not contain volcanic ash; is clearly seen where the crystal size changes at the center of the thin section. The mean concentration of impurity ions in each layer is shown in Table 1. Another sample is

Table 1. Concentration of impurity ions in ice from the Nansen Icefield.*

Ice	Density (kg/m^3)	Cl^- conc. (ng/g)	NO_3^- conc. (ng/g)	SO_4^{2-} conc. (ng/g)	Na^+ conc. (ng/g)	Ka^+ conc. (ng/g)
Ice layer containing volcanic ash	870	1040($\pm$86)	408($\pm$5)	328	815	73
Adjacent layer	889	368($\pm$96)	46($\pm$6)	126	196	0

* Cited from FUJITA *et al.* (1992).

artificial ice that was grown from deionized water. Each sample was prepared as a slab of thickness about 5 mm. A Flat prepared surface was used for the AC-ECM. In the reference measurement, the slab was sandwiched by the pair of parallel plate electrodes. Thus, conductivity which was measured with these electrodes were that of an ice cylinder of thickness 5 mm and diameter 5 mm. In contrast, it can be deduced that the conductance measured by the AC-ECM is that of the ice surface or in the vicinity of the surface.

3. Results

3.1. Pure ice

Figures 4a, b show the conductance measured at a point of the ice specimen with the parallel-plate electrodes and with the AC-ECM electrodes, respectively. Values at 16 frequencies between 40 Hz and 1 MHz in artificial polycrystalline ice are shown. Both electrodes clearly detected the Debye dispersion due to the polarization of water molecules. The difference in measured values between these methods is caused by the

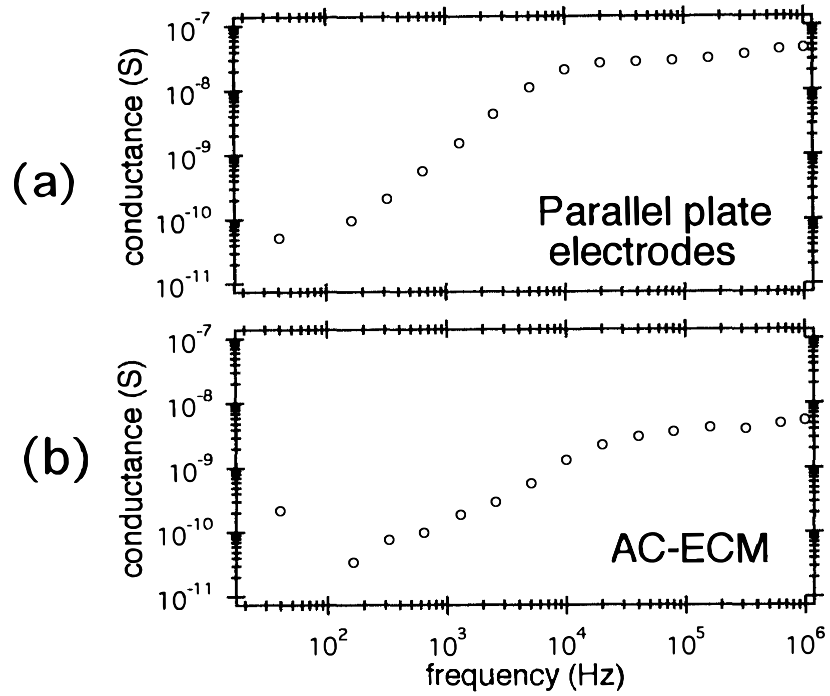

Fig. 4. A schematic representation of the behavior of the conductance of pure ice as a function of frequency near −20°C. The result in (a) is measured by the AC-ECM technique. The result in (b) is measured with parallel plate electrodes.

difference in both distance and area between the electrodes. Note that the measured values at frequencies less than 100 Hz are not reliable in this study because the values were often below the detection limit.

The common features and the differences between the two results are as follows. The common features are: the values measured by both methods have similar frequency dependence at frequencies 100 Hz and 1 MHz; conductance slightly increased at frequencies near 1 MHz. In contrast, the main difference is the frequency at which relaxation occurs. Conductance reaches the high frequency limit value (of Debye dispersion) at higher frequencies for values measured by the AC-ECM (Fig. 4b) than those measured with parallel plate electrodes (Fig. 4a). We will discuss this observed tendency later.

3.2. Ice layer containing volcanic ash and adjacent layer

Figures 5a, b show an example of the conductance measured with the parallel-plate electrodes and by the AC-ECM, respectively, at 16 frequencies between 40 Hz and 1 MHz at a point in the ice layer containing volcanic ash and at a point in the adjacent layer. It was clearly observed that the conductance is larger in the ice layer containing volcanic ash than in the adjacent layer. In addition, the relaxation frequency is higher in the ice layer containing volcanic ash. These tendencies are qualitatively the same as those that are observed in signals measured by DEP. To show the relaxation frequency, conductance in Fig. 5a was converted to the imaginary part of complex permittivity using the relation between the imaginary part (ε'') and conductivity (σ),

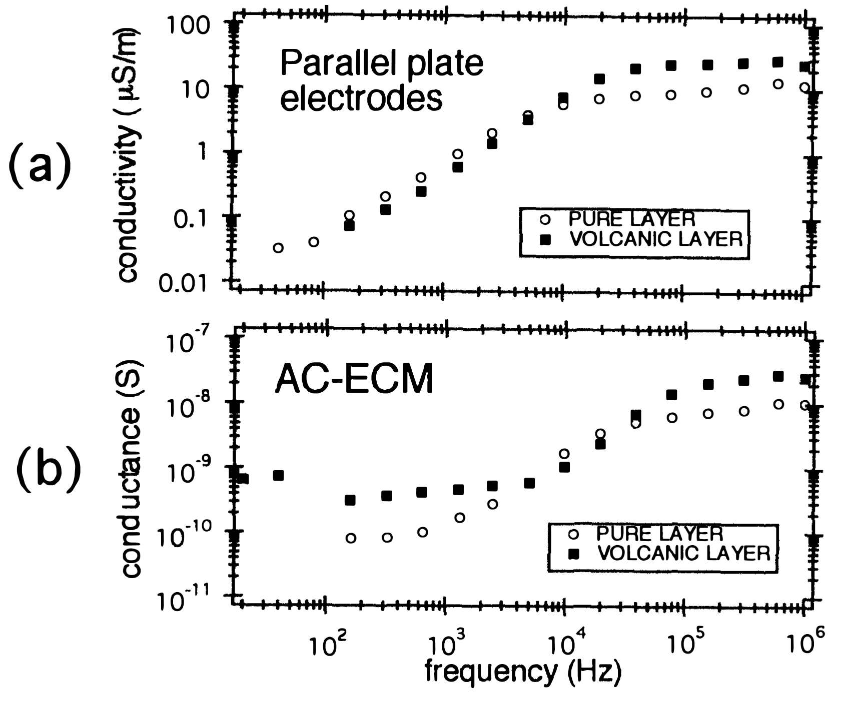

Fig. 5. A schematic representation of the behavior of electrical conduction of Antarctic ice measured with two electrodes; (a) conductivity (μS/m) measured with parallel-plate electrodes and (b) the conductance (S) meausred by the AC-ECM; at a point in the ice layer containing volcanic ash at a point in the adjacent layer.

$$\varepsilon'' = \frac{\sigma}{2\pi f \varepsilon_0} . \tag{1}$$

Here, ε_0 is the permittivity of vacuum. The conductance in Fig. 5b was also converted to values proportional to the imaginary part, $G/2\pi f\varepsilon_0(\propto\varepsilon'')$. Here, G is the conductance. The calculated results are shown in Fig. 6. In this figure, one can clearly see that the relaxation frequency is higher in the ice layer containing volcanic ash than in the adjacent layer. Moreover, as was observed also in pure ice, conductance reaches the high frequency limit values again at higher frequencies in values measured by the AC-ECM (Fig. 5b) than in those measured with parallel plate electrodes (Fig. 5a). This tendency is more clearly seen in Fig. 6 in the relaxation frequencies. The relaxation frequencies were clearly higher when conductance was measured with the AC-ECM than when it was measured with the parallel plate electrode.

We measured at 27 points in all. The relations between the high frequency limit conductance measured with the AC-ECM electrodes and the high frequency limit conductivity measured with the parallel plate electrodes are shown in Fig. 7. This is the result at 1 MHz. Although the points are scattered to some extent, the figure clearly shows that the conductance measured with the AC-ECM is proportional to the conductivity measured with the parallel plate electrodes. This proportional relation was observed only at frequencies well above the Debye dispersion (above about 100 kHz). At frequency range near the relaxation frequencies of the Debye dispersion (below about 100 kHz), such a simple relation cannot be seen because the measured values are

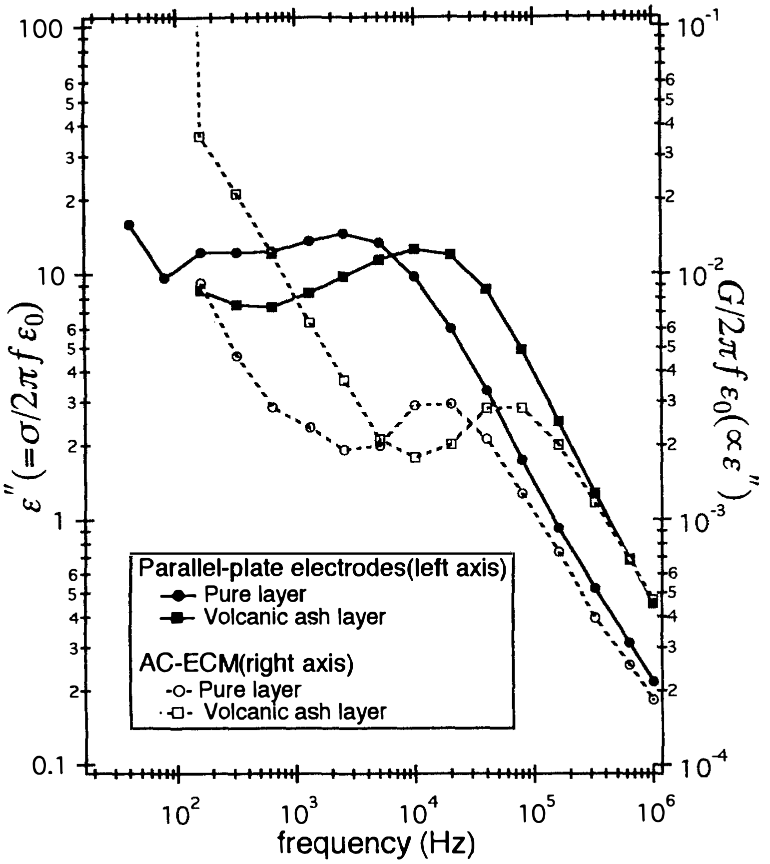

Fig. 6. The results in Fig. 5a were converted to values of the imaginary part of the complex permittivity. The results in Fig. 5b were converted to values proportional to the imaginary part. For the conversion, the relation between the imaginary part (ε'') and the conductivity (σ) in the text was used. The relaxation frequencies of Debye dispersion can be observed clearly in the figure as peaks. The approximate relaxation frequencies are as follows: 1.2×10^4 Hz for ice containing volcanic ash and 2.3×10^3 Hz for adjacent ice when measurements were carried out with the parallel plate electrode; 6.0×10^4 Hz for ice containing volcanic ash and 1.3×10^4 Hz for adjacent ice when measurements were carried out with the AC-ECM electrode.

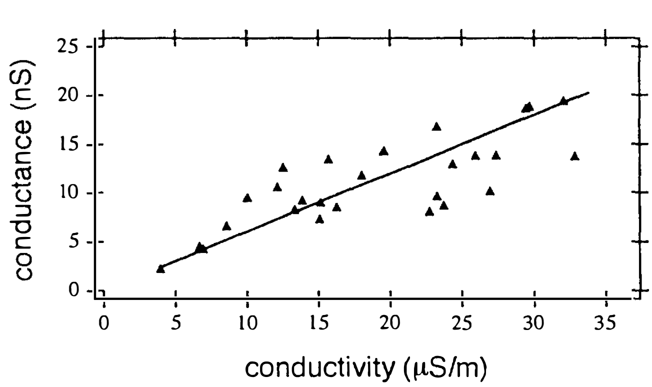

Fig. 7. Relationship between conductivity (μS/m) measured by the parallel plate electrode to conductance (nS) measured by the AC-ECM technique.

affected by the dispersion. We will discuss the physical mechanism that contributes electrical conduction and the data point scattering in the next section.

4. Discussion

4.1. Physical mechanism of the electrical conduction

We first discuss the physical mechanisms which contributed to the observed electrical conduction. It can be deduced that electrical conduction occurs at the ice surface and in the vicinity of the ice surface when conductance is measured by the AC-ECM. However, it is important to confirm this from the data because in actual ice core analysis the relation between electrical properties and location of impurity components should be clear.

Based on the experimental results, we can conclude that the observed data suggests that surface conduction is dominant in the values measured by the AC-ECM. The reason is as follows. The electrical conduction values measured with the two methods are related clearly to the orientational polarization of water molecules in ice because the observed conductance had Debye dispersion. Such phenomenon cannot be explained by other mechanisms. The big difference between the values measured by AC-ECM (Figs. 4b, 5b) and the values measured by parallel plate electrodes (Figs. 4a, 5a) is the relaxation frequency. This is clearly seen in Fig. 6. In other words, in values measured by the AC-ECM, dispersion occurs at higher frequencies than the dispersion frequencies in ice. A plausible explanation is that water molecules that are at the surface of ice contribute the orientational polarization in the case of the AC-ECM. Unlike water molecules in an ice lattice, the molecules at the surface are not restricted completely in the crystal lattice. Consequently, orientational movement of the molecules can occur easily there. This was observed at the higher relaxation frequencies. The explanation above suggests that the AC-ECM measures surface conduction whereas DEP measures conduction in bulk ice.

It should be noted that the discussion above is a qualitative one. To understand the physical mechanism exactly, the quantitative analyses should be done in the future, on the relation between the difference in relaxation frequencies in ice and on the surface, on the quantitative effect of impurity ions, and on the roles of both movement of charge carrier (ions) and orientational rotation of the molecules. And also, the thickness of the surface layers that contribute to the electrical conduction cannot be discussed only from our data. These should be investigated by additional experiments.

4.2. Optimum frequency and temperature for AC-ECM

In order to measure high-frequency conductivity which is not affected by the Debye dispersion, a good combination of experimental temperature and frequency should be chosen. At our experimental temperature ($-20°C$), it is clear that the frequency should be above 100 kHz. At higher temperatures and/or at lower frequencies, it is impossible to measure signals that are simple functions of impurity contents in ice. Therefore care should be taken for both temperature and frequency in the field analysis in summer. The temperature dependence of the dispersion should be investigated more in the future. When frequencies higher than the frequency range of Debye dispersion is considered, the signals are completely free from the space charge effects which is a problem in DC measurement.

Conductance slightly increased at frequencies near 1 MHz in all results. This phenomenon was observed in the results measured by both types of electrodes. This small increase in conductance may be a low frequency tail of the dispersion which JOHARI (1976) reported in the MHz range. However, from a practical point of view, this small increase does not affect ice core analysis because it is much smaller than the increase of conductance due to impurity ions in ice. MOORE and FUJITA (1993) showed that there was no evidence of significant dispersion in electrical conductivity arising from the presence of acid impurity at frequencies between microwave and LF. This also supports the idea that signals are not affected by additional dispersion.

4.3. Reproducibility for repetitive measurements

It was confirmed from our measurements that conductance values measured by the AC-ECM had high reproducibility, unlike the cases of ECM. This fact means that neither AC-current nor the applied voltage, 3 V, changes the state (location and distribution) of impurity ions in ice. This is an advantage of the AC-ECM technique because we can repeat the measurement using the same surface and because we can save very valuable ice cores.

4.4. Comparison between values measured with two electrodes

As for the data point scattering in Fig. 7, there are two plausible causes. One is the fact that both types of electrodes did not measure the exactly same point in ice. With the AC-ECM electrodes, we measured the surface between two terminals 1cm apart. In contrast, conductivity which was measured with the parallel plate electrodes was that of an ice cylinder of thickness 5 mm and diameter 5 mm.

Although the conduction mechanisms are not exactly the same, we try to calculate AC conductivity (μS/m) in ice from the conductance measured by AC-ECM. This procedure can be tentatively justified because we can observe the proportional relation between them (Fig. 5). We choose data at 1 MHz. The relation between AC conductivity σ (μS/m) and the conductance G (S) measured by AC-ECM is expressed by

$$\sigma = G \times 10^6 \times d \times S^{-1}. \qquad (2)$$

Here d is the distance between the terminals in the electrode (here 1 cm) and S is the coefficient which is equivalent to the contact area between ice and electrode. S is determined from the values in Fig. 7. In our case, S was 6.0×10^{-6} m^2 with the standard error of 5%. Therefore we can calculate 1 MHz conductivity from the data by AC-ECM. The validity of this conversion should be further investigated by the comparison between the data by AC-ECM and that by DEP in the future.

5. Conclusion and Further Work

We demonstrated that AC-ECM is a technique with which one can measure surface conductance which is free from both the space charge effect and Debye dispersion at frequencies higher than 100 kHz at $-20°C$. Although a smooth flat surface is still necessary, this ice-core analysis technique can give the same spatial resolution as ECM. To establish this technique, we need to clarify several unknowns. One is the species of ion which contribute to the signals. Although the cause of electrical conduction can be attributed at least to acidity in ice, like ECM and DEP, the role of salt, which is also a cause of conductivity detected by DEP, should be investigated. Knowing the temperature dependence of electrical conduction will help to understand the conduction mechanism in the future. The spatial resolution of the ice core profiling is not finally determined yet because we do not know the extent of the electric field at a measurement point in this study. It should be investigated by additional experiments. The aging effect has not been investigated yet, either. The preliminary application to ice core studies was successful. We are measuring acidic layers which originated from past volcanism, those results will be published elsewhere.

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