

ELECTRICAL PROPERTIES OF ICE AND IMPLICATIONS FOR SOLAR SYSTEM EXPLORATION.

David E. Stillman and Robert E. Grimm, Department of Space Studies, Southwest Research Institute, 1050 Walnut Street, Suite 300, Boulder, CO 80302, dstillman@boulder.swri.edu, grimm@boulder.swri.edu.

Introduction: Electromagnetic (EM) geophysical exploration can be used on many planetary bodies to detect and characterize subsurface ice. Low-frequency EM induction in the icy satellites is sensitive to DC conductivity from which linked bounds may be inferred on temperature, acid and salt content, and the presence of brine channels. Broadband dielectric spectroscopy is useful for detailed characterization extending the factors above and including the fraction of ice buried at the lunar poles or on Mars [1] and whether the ice ever was temperate. Attenuation coefficients in surface-penetrating radars also will be sensitive to many of these factors, although they cannot be recovered as uniquely.

To better understand ice in the planetary environment and geophysical means for detection, we have been conducting low frequency (1 mHz – 1 MHz) laboratory measurements of pure ice, doped ice, salt hydrates, and regolith-ice mixtures at temperatures ranging from 180 – 273 K [see 2 for apparatus details]. Previous measurements performed by other researchers concentrated on single-crystalline ice and at small (<100 ppm) doped levels of HCl and NaCl [see 3 for review]. Our measurements are made on polycrystalline ice slowly frozen and annealed from liquid solutions. The results of this study will be used to optimize future EM geophysical instrument designs to search for or characterize subsurface ice throughout the solar system.

Electrical Properties of Ice: The electrical properties of ice are created by protonic defects in the lattice [3]. There are two types of protonic defects: ionic, which include H_3O^+ and OH^- , and Bjerrum where the hydrogen bond either has two (D defect) or zero (L defect) H atoms. When an external electric field is induced into ice, protonic defects move to cancel this field [3]. Ionic defects move by sliding H to the other side of a hydrogen bond. Bjerrum defects move by jumping an H from its current hydrogen bond to another. Since the latter move takes more energy, Bjerrum defects are more temperature dependent than ionic defects.

Impurities in the ice lattice are limited to Cl^- , F^- , and N^{3-} as these are the only elements soluble in ice. Cl^- is soluble in the ice lattice up to 10 ppm and substitutes with an H_3O^+ to keep ice at a neutral charge [4,5]. At low impurity concentrations, Bjerrum defects outnumber ionic defects. Therefore, at high temperatures, Bjerrum defects are responsible for dielectric relaxa-

tion. However, as temperature decreases and the mobility of the Bjerrum defects is reduced, ionic defects become responsible for dielectric relaxations. At high impurity concentrations, ionic defects outnumber Bjerrum defects and thus ionic defects control the dielectric relaxation.

Dielectric Relaxation of Ice: A dielectric relaxation or frequency dependence in ice occurs because protonic defects move at a finite speed. At low frequency, protonic defects fully separate and wait, creating the maximum dielectric constant. At high frequency, protonic defects cannot separate and the dielectric constant is at a minimum. At an intermediate (relaxation) frequency, the protonic defects are always in motion, covering their maximum range. This relaxation frequency is also temperature dependent because protonic defects with more thermal energy can overcome energy barriers faster and thus polarize faster.

The relaxation frequency of CaCl_2 and NaCl ices was measured and compared to that of previously measured deionized ices (Fig. 1). At low Cl^- impurity levels and high temperature the relaxation frequency varies with temperature with activation energy of ~ 0.57 eV (proportional to the slope in Fig. 1) indicative of Bjerrum defects. As the impurity levels are increased and/or temperature is decreased, ionic defects exceed Bjerrum defects, called a crossover. This is manifested in Fig. 1 by the change in activation energy to ~ 0.3 eV. At high impurity levels ionic defects dominate the entire temperature range. NaCl ices show that Cl^- saturates the ice lattice at >35 ppm Cl^- . At 35 ppm Cl^- the ice is still not saturated and only had a concentration of ~ 0.35 ppm because of ice's distribution coefficient [5]. We expected that CaCl_2 would produce similar results to the NaCl . However, we believe the differences are due to impurities in our reagent-grade anhydrous CaCl_2 that raised the pH of the liquid solution used to create the ice. Serendipitously, the increase in relaxation time with increasing solution pH may indicate a lack of H_3O^+ cosubstitution required for charge balance with Cl^- .

The relaxation frequency of MgSO_4 was also measured. The temperature dependence of the relaxation frequency was directly related to the Cl^- impurity content of the MgSO_4 solution. This Cl^- impurity is present in the reagent-grade anhydrous MgSO_4 .

Ice-silicate mixtures showed no Maxwell-Wagner effects (interfacial polarizations) and had a relaxation

frequency that was based solely on the Cl^- content of the sample (Fig. 1). A power law mixing model $\epsilon^{1/2.25} = f_{\text{ice}}\epsilon_{\text{ice}}^{1/2.25} + f_{\text{sand}}\epsilon_{\text{sand}}^{1/2.25}$ of the low frequency limit of dielectric constant ϵ was used to estimate the concentration of ice f_{ice} in a mixture.

The measured dielectric relaxation is consistent with an origin in the ice alone, without any contribution from hydrates that are significant at higher salt concentrations, or from brine channels. Hydrates and brine channels do dominate the DC conductivity.

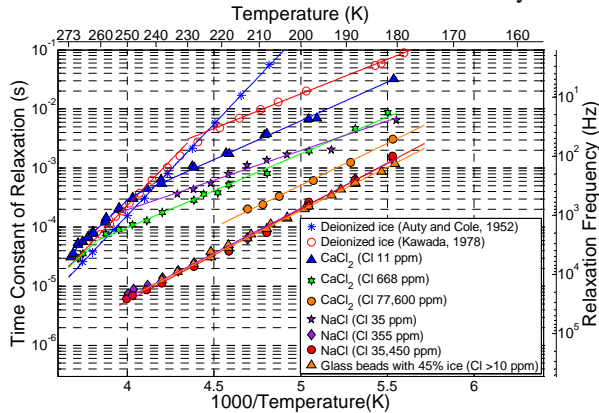


Figure 1. Relaxation frequency versus temperature.

DC Conductivity of Ice and Hydrates: The static conductivity of pure ice is extremely small ($<10^{-9}$ S/m). However, even with a small amount of impurities, ice still has a greater conductivity than dry rock or regolith. At low impurity concentrations (<70 ppm Cl^-), previous measurements of single-crystalline ice [3] indicate that polycrystalline ice is more resistive than single-crystalline ice. We believe this is because the protonic defects do not efficiently transfer from one ice grain to another. At such low concentrations, excluded impurities do not form brine channels, but rather brine pockets. Since these pockets are not connected, they do not increase the DC conductivity.

At high impurity concentrations (>70 ppm Cl^-) and above the eutectic temperature, brine channels do form and dominate the DC conductivity (Fig. 2). As it takes little energy to move ions in brine, this form of conductivity has the lowest activation energy of ~ 0.25 eV.

At high impurity concentrations (>70 ppm Cl^-) and below the eutectic temperature, brine channels freeze forming hydrate channels. The hydrates are much more resistive than brines, but still more conductive than ice. Different hydrates also seem to have different conductivities as $\text{CaCl}_2 \cdot 6 \text{H}_2\text{O}$ (Antarcticite) is the most conductive, followed by $\text{NaCl} \cdot 2\text{H}_2\text{O}$ (Hydrohalite) and $\text{MgSO}_4 \cdot 11 \text{H}_2\text{O}$ (Meridianiite). Because hydrate conductivity is still likely controlled by protonic point defects, the conductivity of meridianiite is probably also due to Cl^- impurity.

Ice-silicate mixtures with low specific surface areas and large pore diameters have the same DC conductivity characteristics as the ice mixtures previously described.

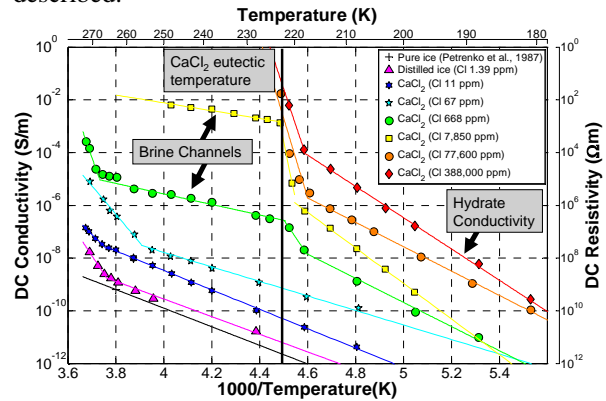


Figure 2. DC Conductivity versus temperature.

Conclusion: The dielectric relaxation of water ice is dependent on ice soluble impurities and temperature. Measurements of ice-silicate mixtures showed that the dielectric relaxation of ice is easily detectable and a power law mixing model can determine the concentration of ice. Observation of the DC conductivity revealed the following: polycrystalline ice is more resistive than single-crystalline ice, brine channels only form at concentrations >70 ppm Cl^- , and hydrate channels are more conductive than ice.

These results show that the following problems can be solved using EM geophysics:

- On the Moon, extrapolating from our measurements down to 180 K, dielectric spectroscopy could find subsurface ice on the Moon if it was >100 K and saturated with impurities.
- On Mars, ground ice could be mapped to determine concentration, temperature, and Cl^- impurity content (0-10 ppm).
- On Enceladus, the temperature profile of impurity rich ice could be found.
- On Europa, Enceladus, and Titan, ice containing brine channels could be detected using GPR and/or EM induction.
- On a comet, dielectric spectroscopy along with GPR could be used to estimate the water content as well as temperature gradients on the surface.

References: [1] Stillman D.E. and Grimm R.E. (2007) *LPSC*, 1944.pdf. [2] Stillman D.E. and Grimm R.E. (2007) *7th Intern. Conf. Mars*, 3311.pdf. [3] Petrenko V.F. and Whitworth R.W. (1999) *Physics of Ice*, 373 pp. [4] Domine F. et al. (1994) *Geophys. Res. Lett.*, 21, 601-604. [5] Gross et al. (1975) *J. Chem. Phys.*, 62, 3085-3092. [6] Auty, R.P. and Cole R.J. (1952) *J. Chem. Phys.*, 20, 1309. [7] Kawada, S. (1978) *J. Phys. Soc. Jpn.*, 44, 1881-1886. [8] Petrenko V.F. et al. (1983) *Philos. Mag.*, B47, 259-78.