

**ELECTRICAL PROPERTIES OF SALINE ICES, SALT HYDRATES, AND ICE-SILICATE MIXTURES: APPLICATIONS TO SOLAR-SYSTEM EXPLORATION.** R. E. Grimm<sup>1</sup> and D.E. Stillman<sup>1</sup>, <sup>1</sup>Dept. of Space Studies, Southwest Research Institute, 1050 Walnut St. #300, Boulder, CO 80302 (grimm@boulder.swri.edu; dstillman@boulder.swri.edu).

**Introduction.** The electrical properties of ices and associated mixtures influence the ability of both radar and low-frequency electromagnetic (EM) soundings to penetrate and recover information on the icy satellites and polar regions of Mars and the Moon. They also have fundamental implications for mechanical properties and habitability.

**Measurements.** Four approaches are used to understand the electrical properties of ices: 1. *Single-crystal laboratory measurements.* These classic studies focused on basic physical chemistry and used low impurity levels (doping) to develop understanding of fundamental solid-state electrical-conduction mechanisms. 2. *Polycrystalline laboratory measurements.* This is our approach for planetary studies, in order to elucidate multiphase relationships (ice, brines, hydrates, silicates). 3. *Ice cores.* Large quantities of natural polycrystalline ices provide rich empirical correlations on the variations of electrical properties with various impurities and environments, but are uncontrolled. 4. *Geoelectrical/EM sounding.* Field studies that recover electrical properties at depths of kilometers or more can be compared to lab and core work.

**Electrical Properties, Dispersion, and DC Conductivity.** The complex dielectric constant  $\epsilon' - i\epsilon''$  describes the storage of electrical energy (capacitance) in  $\epsilon'$  and dissipation (resistance) in  $\epsilon''$ . Below the infrared, frequency dependence or dispersion is caused by dielectric relaxations, where bound charge carriers fail to keep in phase with an applied EM field over some critical frequency range and so convert that energy to heat. This results in a peak in absorption in that region and an increase in real dielectric constant with decreasing frequency. It is important to recognize that causality constraints (Kramers-Kronig relations) require that the real dielectric constant increases monotonically with decreasing frequency. The DC conductivity by definition is added to all frequencies and represents the motion of free charges.

**Water Ice.** Electrical conduction is by point defects, analogous to semiconductors [1]. There are two kinds of protonic point defects in the tetrahedral lattice, each with two states, that allow charge movement. Rotation of a water molecule produces one hydrogen-bond site with no protons (Bjerrum L-defect) and another with two (Bjerrum D-defect). Bjerrum defects are caused by molecular or anionic substitution for H<sub>2</sub>O; NH<sub>4</sub><sup>+</sup> and compounds containing F<sup>-</sup> and Cl<sup>-</sup> can substitute due to their small size. Translation of pro-

tons between molecules transfers ionization state by a charge surplus (H<sub>3</sub>O<sup>+</sup> ionic defect) or deficit (OH<sup>-</sup> ionic defect). Acids and bases easily contribute such ionic defects. Intrinsic Bjerrum defects greatly outnumber intrinsic ionic defects in "pure" ice.

A fundamental feature of ice is its dielectric relaxation, ~1 kHz for pure ice at 252 K and decreasing in frequency with decreasing temperature and increasing impurity content. The "high-frequency" (above the relaxation) conductivity is dominated by most efficient mechanism, i.e., Bjerrum defects. The "low-frequency" (below the relaxation) conductivity requires both mechanisms, and so is controlled by the much-less-abundant ionic defects.

**Conductivity Crossover.** Single-crystal ice grown from solutions with just tens of umol/l impurities have comparable numbers of both ionic and Bjerrum defects; the former eventually dominate due to their higher mobility and effective charge. This results in a crossover of conduction mechanisms where now the ionic defects control the high-frequency conductivity and the Bjerrum defects are dominant at low frequency. However, it has not heretofore been recognized that the modest impurity levels in polar ices (typically 10s-100s of umol/l) should be above this crossover limit, but no crossover is observed: acid alone still controls the low frequency response and the total active impurities—basically hydrogen, chloride, and ammonium—determine the high-frequency limit [2]. The crossover or its absence has profound, still unresolved effects on low-frequency exploration because it is unknown whether measured ice conductivity will be sensitive to acid/base or salt/ammonia. Radar sounding, well beyond ice high-frequency limit, will be affected by sum of both acid/base and salt/ammonia.

**Cation Incorporation.** Salts have been supposed to act exactly as acids with respect to lattice substitution [3], e.g., NaCl dissociates in water and enters the lattice as H<sub>3</sub>O<sup>+</sup> and Cl<sup>-</sup>, leaving Na<sup>+</sup> and OH<sup>-</sup> in solution. Our experiments instead indicate that Na<sup>+</sup> accompanies Cl<sup>-</sup> into the ice, and must be accommodated interstitially instead of as a lattice defect. This follows from calculation of the defect rate as follows: the lattice appears to saturate for initial NaCl solutions >1-10 mmol/l; using our measured relaxation time constant and known Bjerrum L-defect mobility at -20°C [1], ~4x10<sup>-6</sup> defects/H<sub>2</sub>O molecule can be derived, or an equivalent concentration ~0.2 umol/l. The corresponding water-ice partition coefficient for Cl<sup>-</sup> is then ~10<sup>-4</sup>.

In order to supply enough  $\text{H}_3\text{O}^+$  for charge balance using the same partition coefficient, the pH must be  $<2.7$ . Our NaCl solutions were pH  $\sim 5.7$ , consistent with carbonic acid in equilibrium with the atmosphere. The small  $\text{H}_3\text{O}^+$  supply leads to the conclusion that charge balance is achieved by interstitial cations. We have confirmed this by observing that relaxation times do not depend on pH. Longer time constants for  $\text{CaCl}_2$  ices are consistent with a smaller defect rate due to increasing difficulty of substitution.

**Salt Hydrates.** Even HCl has a saturation limit  $\sim 10$   $\mu\text{M}$  in the ice lattice [4]. Excess impurities are rejected during freezing and for a single impurity at concentrations of interest, the amount and composition of liquid follow classic binary eutectic phase relations. The last fluid at maximum freezing-point depression is the eutectic composition and subsequently crystallizes to a mixture of ice and hydrate. For starting concentrations of NaCl less than the eutectic composition of 23 wt%, we found that the electrical-mixing fit describing  $\text{NaCl}\cdot 2\text{H}_2\text{O}$  (hydrohalite) and ice implies that the eutectic mixture (22 vol% hydrohalite) is the conductive phase and is distributed as interconnected shells enclosing the “pure” ice, consistent with the expected binary phase relations. For initial NaCl above the eutectic composition, pure hydrohalite is the conductive phase relative to the excluded eutectic mixture, but the latter now appears electrically as the inclusion phase, i.e., as disconnected shells around the former.

Antarctite ( $\text{CaCl}_2\cdot 6\text{H}_2\text{O}$ ) is a factor of  $\sim 100$  more conductive than hydrohalite as revealed through measurements at supereutectic composition. Moreover, its eutectic mixture (31% antarctite) is  $\sim 1000\times$  more conductive than its NaCl counterpart for  $>10$  mM initial solution. At lower concentrations, the rapid increase in conductivity with concentration evokes a differential mixing rule [5] or percolation threshold, perhaps indicating that antarctite is progressively becoming better connected within the eutectic mixture as concentration increases.

The conductivity of meridianiite ( $\text{MgSO}_4\cdot 11\text{H}_2\text{O}$ ) has been indeterminate to date because the values measured (at relatively low, subeutectic compositions) closely followed those for antarctite for solutions with the same chloride content. Our reagent-grade salts contained up to 1% impurities including Ca and Cl; evidently even minor quantities of antarctite are sufficient to overwhelm any signature of meridianiite. The relevant volumetric ratios indicate that the conductivity of meridianiite must be comparable to or less than that of hydrohalite. This contamination also serendipitously demonstrates that the conductivity of antarctite exceeds any contribution from Cl doping of meridianiite and therefore suggests that hydrate conductivity is dominantly through intrinsic defects.

**Brine Channels.** A well-connected fluid phase is evident in some measurements as a distinct segment of DC conductivity above the eutectic temperature ( $-23^\circ\text{C}$  for NaCl and  $-51^\circ\text{C}$  for  $\text{CaCl}_2$ ). Conductivity decreases regularly with decreasing temperature in good agreement with fluid abundance and composition predicted from equilibrium theory, but with an overall signature determined by Archie's Law, the classic formula for the electrical conductivity of brine-saturated clastic rocks. The exponent  $\sim 2$  indicates welded grain contacts.

Brine channels only appear for initial fluid concentrations  $> 3$  mmol/l. This threshold for brine-channel formation is consistent with the minimum salt concentrations in electrically conductive sea ice [6]. It has the important implication that brine drainage will not occur in icy satellites [7,8] for low bulk impurity levels and it will furthermore cause a discontinuity in bulk viscosity.

**Ice/Hydrate/Silicate Mixtures.** These experiments are aimed primarily at understanding EM exploration and habitability in icy regoliths. We have measured ice/hydrates mixed with silica beads, sands, clays, and JSC-Mars-1. Preliminary results suggest that the dielectric dispersion and DC conductivity are dominated by the  $\text{H}_2\text{O}$  phases. A mixing model indicates that the ice fraction can be recovered from the low-frequency dielectric constant; this is the fundamental principle behind measuring subsurface ice content on Mars and the Moon from surface measurements [9,10]. Interfacial water due to capillary/adsorption forces at subeutectic temperatures has been confirmed by us using NMR, but its DC conductivity is indistinguishable from that of the ice/hydrate. Without useful ionic transport, interfacial water is unlikely to be a viable microbial habitat on Mars unless temperatures are within a few tens of degrees of melting [11,12]. We have observed an additional dielectric relaxation near 1 MHz in JSC-Mars-1 that is likely associated with the material itself [13]. Future work will seek to determine if the interfacial water has a rotational dielectric relaxation at higher frequency, which could then contribute significantly to strong radar attenuation observed for most of the silicate surface of Mars [14].

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