

Spontaneous NaCl-doped ice: Focus on the mechanisms of ion inclusion

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Ice-doping processes are of great interest in fields such as atmospheric chemistry, astrophysics and geophysics. In recent years, various studies revealed the existence of sub-surface salty oceans and the presence of high-pressure ice polymorphs in the interior of some planetary bodies such as Jupiter's satellites or exoplanets such as Proxima b [1, 2]. These ices, stable over several gigapascals and hundreds of Kelvin, can contain a significant amount of small ions in their structure. The presence of doped ice suggests a plausible explanation for the behaviour and different physical properties observed in the interior of these icy bodies.

Sodium chloride in water is the most common aqueous solution present in nature. The maximum amount of salt dissolved in water at equilibrium is given by solubility. The value of the solubility depends on the salt, the solvent, and the thermodynamic conditions (i.e., temperature and pressure). When it is added to ice, the salt first dissolves in the liquid water layer that is always present on the surface, thereby lowering its freezing point below the ice coexistence temperature. Moreover, when water freezes from aqueous salty solutions, the salt ions are rejected from the solid phase and saturate the liquid phase giving rise to the appearance of the phenomenon known as brine rejection. Pockets of brine form inside the polycrystalline blocks of ice. Below the melting point the rejected brine phase is liquid until the eutectic temperature of the salt. At temperatures below the eutectic point the salt begins to precipitate.

In addition to the brine phase, during the ice growth a small amount of ions can be accommodated in the solid lattice causing ice doping [3, 4]. The ice-doping process raises fundamental questions concerning the mechanisms by which ions are incorporated into the ice structure, and what their positions and effects are once they get there. While the properties of pure ice have been extensively studied, this has not been so for doped ice. Experiments evidenced that the presence of Na⁺ and Cl⁻ ion dopants in the lattice modifies the properties of ice, as the incorporation of ions causes the appearance of extrinsic defects in the lattice that increase the static conductivity of the system and affect the dielectric properties of doped ice. A small amount of doping impurities is sufficient to induce considerable changes in these properties [5].

The detailed mechanisms for the doping processes in ice have not yet been fully explored. It is in fact still not clear where exactly the impurities are located in the lattice, and the location is important because it affects the concentration of defects that cause conduction.

In this work molecular dynamics simulations on microsecond time scale have been performed on an aqueous solution of TIP4P/2005 water and NaCl by using the direct

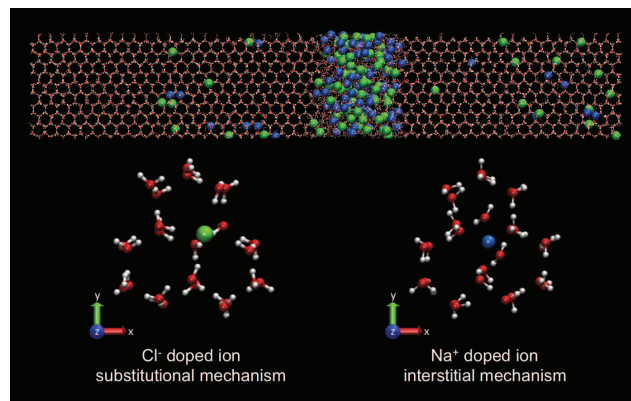


Fig. 1. Final snapshot for the ice/NaCl(aq) system after 2 microseconds (top). Frontal view of a doped ice lattice portion containing a Cl⁻ ion (bottom left) and a Na⁺ ion (bottom right).

coexistence technique to study the ice growth and the interface ice/liquid water. At different pressures, for temperatures above the eutectic point of the salt and at several concentrations the brine rejection phenomenon and the spontaneous growth of a ice slab doped by the salt are obtained, as found in natural terrestrial and planetary environments. Experiments indicate that Cl⁻ goes substitutional to ice sites. In line with these evidences we find a new result: the Cl⁻ ion included in the lattice always substitutes not one but two water molecules leaving the ice structure around not distorted. The Na⁺ ion shows lower probability to be included in the ice and it occupies an interstitial site, causing a local distortion of the lattice. No sign of significative ions diffusion is observed in the lattice [6].

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