

The Coloration of Salty Ices

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1. Context

The Voyagers (flyby during the seventies) and Galileo (operating during the nineties) missions observed the surface of icy Galilean Moons to decipher their composition. It was highly suggested and then confirmed that two of the main components were water ice and a highly hydrated salty phase. The nature of the refractory contaminants is still under debate and an important laboratory initiative is necessary to reproduce these data and better understand the chemical composition of these surfaces. We prepared ices from brines of NaCl and MgSO₄ to characterize further the particles formed through a flash-frozen process.

2. Blue Ices

Ice particles with an averaged diameter of ~70- μ m were produced with our Setup for the Preparation of Icy Planetary Analogue (SIPPA) [2, 3] by flash freezing liquid particles of saturated brines of NaCl (30wt%) and MgSO₄ (29wt%) into liquid nitrogen. The particles are then placed under an optical microscope inside a freezer at -40°C. We recorded the evolution of the shape and colour of particles during their warming up from liquid nitrogen to freezer temperatures. Fresh particles (Figure 1a) appear mainly translucent. With increasing temperature, the particles become blue and then opacify and turn white. We calculate and plot the spectral slopes of the samples in the VIS range to study their change of color quantitatively.

Figure 1b shows the evolution of the slope (calculated between 455nm and 800nm) with the temperature. The particles of pure water ice show a constant blue slope at all temperatures. In contrast, salty ices show a maximum of blue slope at about -65°C for both NaCl and MgSO₄. The values of blue slope for the two salts are very different at lower temperature but very similar at higher temperature until the eutectic points (-20.8°C for NaCl, -3.6°C for MgSO₄[1]).

The reason for this evolution is unclear and currently under investigation. The effects observed are potentially linked to the crystallisation of the salt inside the particles of ice produced by flash-freezing process.

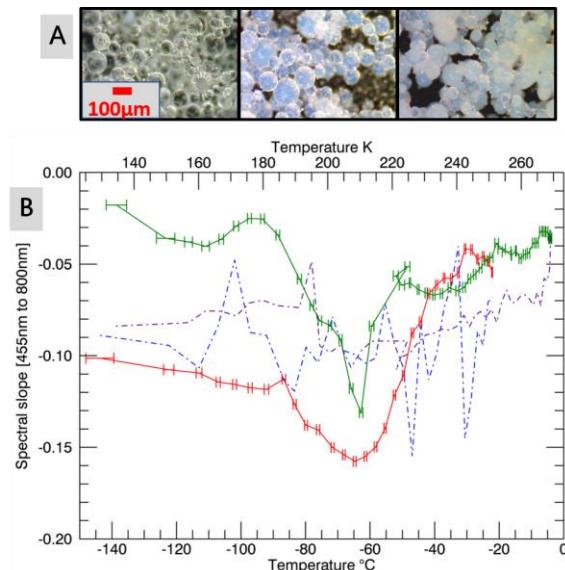


Figure 1: (a) Microscope pictures of salty ices through time. (b) Evolution of the spectral slopes of pure water ice (blue and purple) and ice made of saturated brines (green [NaCl], red [MgSO₄]) with temperature.

Indeed, salts are very soluble in liquid water but not in crystalline ice. The ice Ih, which is the one crystallized at one atmosphere, is not able to incorporate salt in its structure [7, ref. therein]. A slow crystallisation expels the salts outside the water ice particles but in our case, a flash-freezing process at the contact with liquid nitrogen produces the ice. Therefore, as the crystallisation progresses from the outside to the inside, the ions dissolved in the solution are concentrated toward the centre of the particle while a shell of pure water ice is forming around. In the center, an oversaturated brine forms

that finally freezes at temperatures below the eutectic. The ice and salts formed at that point must have a very low crystallinity. With raising temperature, reorganisation and re-crystallisation probably occur and scattering by small crystals probably produces the transient blue coloration.

3. Yellow Ices

F and M-centres are well-known defects in alkali halides crystals [4]. They form through the replacement of anions by electrons in crystal lattice and have already been suggested recently in conditions representative of Europa [5, 6]. We irradiated ices made of a solution with 1wt% NaCl and a saturated solution of NaCl (~30wt%). As a result, the reflectance spectra of the sample show a strong absorption in the visible. The ice containing 30wt% of salt exhibits the F-centre (~460nm) only, whereas the ice containing 1wt% of NaCl shows an absorption complex over the entire visible spectral range.

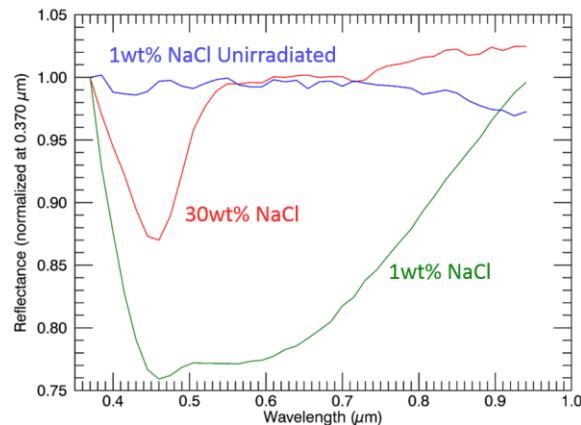


Figure 2: Reflectance spectra of irradiated ices containing 1wt% (green) and 30wt% (red) of NaCl. The blue spectrum is of a non-irradiated ice containing 1wt% of NaCl.

A possible explanation is related to the number of available sites to replace a Cl^- ion by an electron. In the sample saturated with NaCl, there is, in comparison with the sample containing 1wt% of NaCl, a lot more Cl^- emplacements. It therefore requires more electrons to replace all Cl^- ions in a saturated sample than in one with lower salt concentration.

To form M-centres, two electrons must take place in a Cl^- site [8], which could be easier to do when the

number of sites is reduced because of a lower concentration of salt in the sample. Some of the electrons are certainly back-reflected whereas others are included in the lattice crystal to form M-centres. In the case of a saturated sample, it would be necessary to irradiate much longer to generate M-centres via a saturation of the Cl^- sites. Consequently, with the intensity and time of irradiation, we were not able to produce M-centres, or not as much as we did during the irradiation of 1wt% NaCl sample, and then only observed the F-centres.

4. Summary and Perspectives

Preliminary work has been performed on salty ices to better understand the physical reasons for the coloration of the samples appearing in two different cases. These experimental results will be helpful for the preparation of observations and then interpretation of data coming from the JUICE and Europa Clipper Missions. These results will be detailed at the conference as well as the progress made until then.

Acknowledgements

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