

Morphological and Chemical Analysis of Impurities in Ice Using the Environmental Scanning Electron Microscopy and Fluorescence Spectroscopy.

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Accumulated and concentrated impurities can be stored in natural ice or snow. They are found to be rejected from the freezing solution to the ice grain boundaries, free ice surfaces or liquid/brine inclusions. Information about compartmentation and phase speciation in ice is thus essential for the assessment of their fate. The location of impurities and their interactions with the water molecules of ice, still not sufficiently clarified, must be studied at low temperatures because thawing smears the information out. When the impurities keep their location while the surrounding ice sublimates, a 3D morphology of the ice boundaries is revealed. Environmental scanning electron microscopy (ESEM) is one of the few methods allowing direct observation of ice bulk sample with location and compartmentation impurities in dynamically changing conditions of relatively high pressure of gas and stable temperature of cooled sample holder.

For this work, aqueous (aq) samples were frozen under atmospheric pressure on a silicon plate cooled by the Peltier stage. The initial sample holder temperature was above $-1\text{ }^{\circ}\text{C}$, and a droplet of pure water or the uranyl nitrate solution placed on it was frozen. A uranyl nitrate solution (0.01 M) acidified by perchloric acid to $\text{pH} = 1$ was used because hydrolysis of UO_2^{2+} is suppressed, and only a single species (i.e., a hydrated uranyl ion) is present under these conditions. ESEM AQUASEM II equipped with a YAG:Ce³⁺ BSEs detector, an ionization detector of SEs, a special hydration system and a Peltier cooled stage were used [1]. The pressures between 400-700 Pa, 50% water-vapor saturation, and the temperatures above 250 K were utilized in the experiments. The phenomena of etching and subsequent stripping of impurities are largely suppressed at these conditions.

In order to get information about the phase speciation of the uranyl ion and its microenvironment in the ice samples, the corresponding frozen aq solutions were subjected to a luminescence analysis. Crystalline uranyl nitrate hexahydrate provided a luminescence emission spectrum with the emission band maxima located at 488, 509, 533, 559, and 587 nm at 293 K (Fig. 1a). A hydrated uranyl ion in a solution exhibited one additional band at 473 nm besides those observed in the emission spectrum of a crystal. The luminescence lifetime of crystalline uranyl nitrate is known to depend considerably on the degree of its hydration. Uranyl perchlorate was prepared from solid uranyl nitrate by repeated cycles of dissolution in perchloric acid (70%) and evaporation. The luminescence lifetime of uranyl perchlorate crystals was found to be $(283 \pm 10)\ \mu\text{s}$. In addition, the dependence of the uranyl ion luminescence lifetime on the perchloric acid concentration has been reported to be nearly linear at the concentrations between 0.3 and 10 M (0.1 M aq HClO_4 : $\tau = 2\ \mu\text{s}$; 11 M aq HClO_4 : $\tau = 65\ \mu\text{s}$) [2]. We utilized the linear regression equation to estimate the perchloric acid concentration in the brine.

In this work, the mono-exponential lifetime of uranyl aq solutions frozen at 267 K was $(12.3 \pm 0.3)\ \mu\text{s}$ ($n = 5$). Such a slow freezing apparently caused rejection of the solute solution into the veins and on the surface of a polycrystalline ice matrix along with a substantial increase of the perchloric acid local

concentration. Based on the reported linear dependence of the uranyl luminescence lifetime on the perchloric ion concentration, we estimate that the final perchlorate concentration was 1.5 M, see Fig.1b white areas [3].

Figure 1c shows an ESEM image of the ice sample prepared by freezing of pure water under atmospheric pressure inside the specimen chamber. Different shapes and sizes (30–200 μm) of the ice grains can be distinguished. Due to the detection of SEs, sensitive mostly to the surface topography, the ice grain boundaries are visible as black lines with a bright halo. Since emission of BSEs is related to the atomic number of the present elements, ^{92}U -rich regions appear brighter, whereas the regions consisting of water molecules remain dark, see Figure 1b. The difference between pure ice and the frozen uranyl solution is largely manifested in the channels and pools of concentrated UO_2^{2+} solutions (bright) along with the individual ice grains (black). Pools are usually the largest at the triple junctions, although some may also be present on the ice surface. A liquid layer containing UO_2^{2+} was expected to be considerably more concentrated than the parent solution due to the freezing concentration effect.

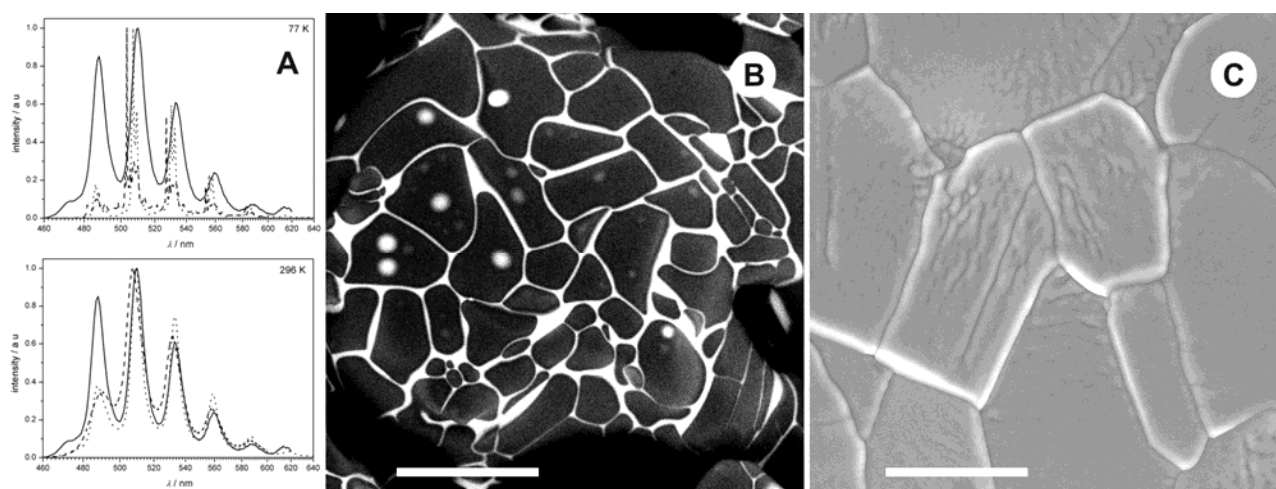


Figure 1: An ESEM image of ice prepared by freezing of a solution inside ESEM chamber: a) the luminescence emission spectra of uranyl nitrate (dotted lines) and uranyl perchlorate (dashed lines) crystals at 296 K (bottom) and 77 K (top); b) uranyl salt solution; c) 10^{-2} M, BSE YAG detector, 254.65 K, 280 Pa (3.9 torr), c) pure water; ionization SE detector; 270 K, 695 Pa (5.2 torr). The spectrum of 0.01 M uranyl nitrate solution in perchloric acid at 296 K (pH = 1; solid black lines) is given for comparison. Bar is 100 μm .

Our ESEM and fluorescence analyses thus provided unequivocal evidence that freezing of the uranyl salt aq solutions causes rejection of a solute solution to the ice grain boundaries to form a more concentrated brine layer at temperatures above the eutectic temperature, regardless of the rate and method of freezing (at 270 or 77 K). However, uranyl ion speciation was largely dependent on the experimental conditions [3]. Acknowledgments go to the grants [4].

References:

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