Science Advances
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Paper presentation

Enabling near-atomic–scale analysis of frozen water

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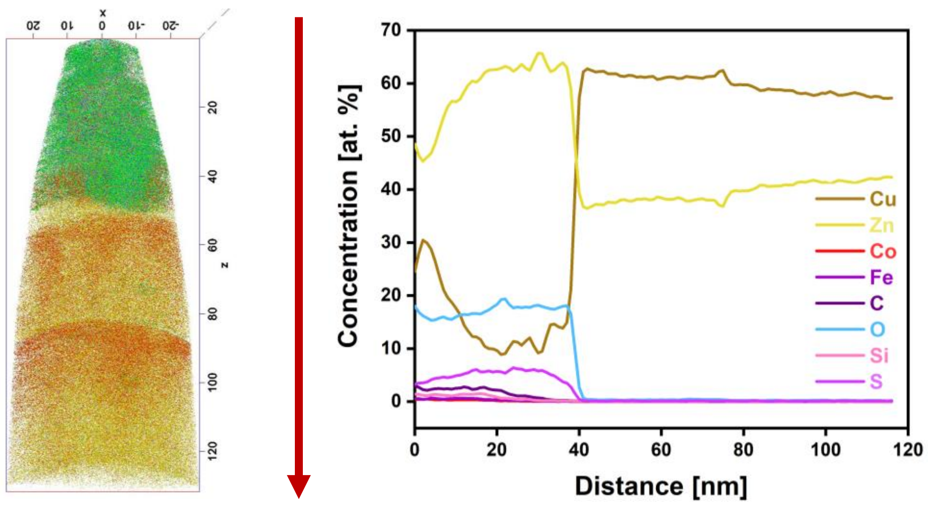
Relevance to our group

- APT analysis of brass-rubber interface

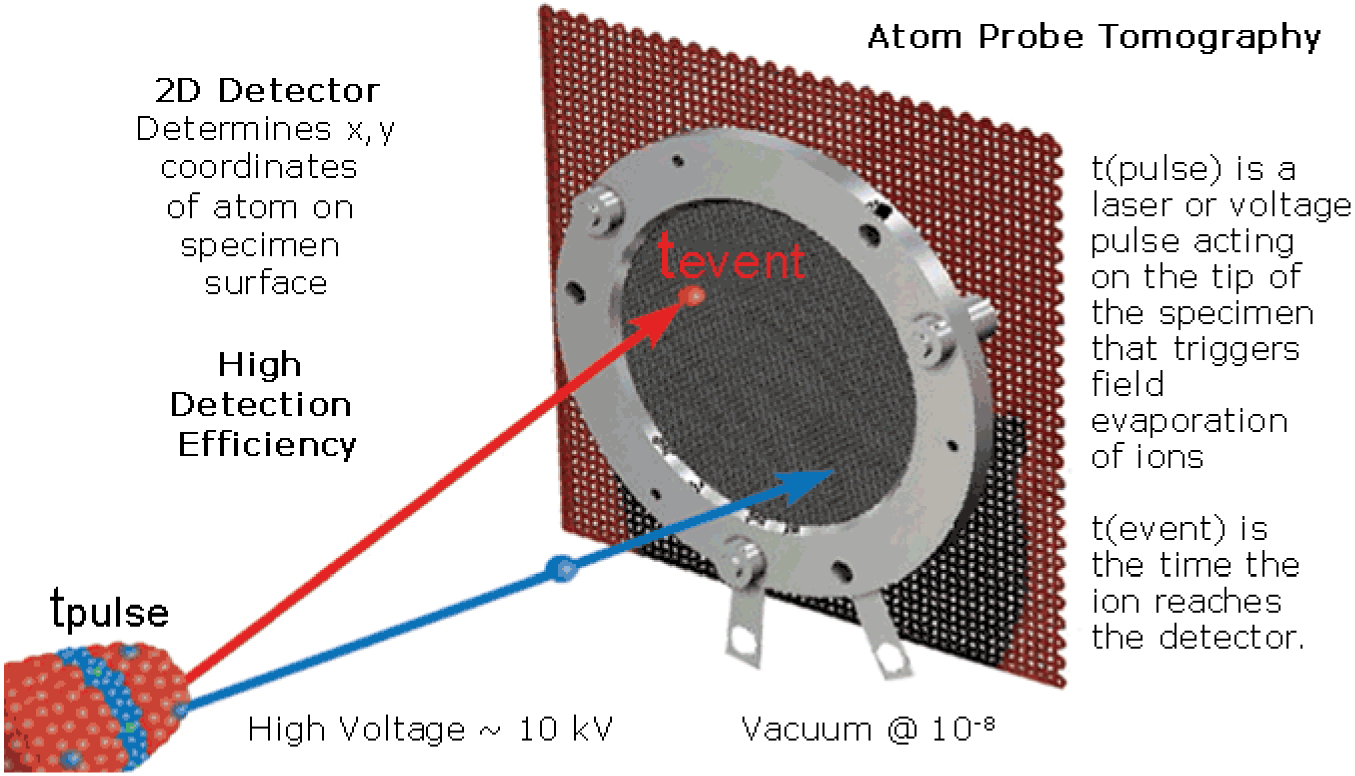


- - APT of clusters

- - Ice chemistry

Terminologies

- Atom probe tomography (APT) and pulsed-laser APT



- Nanoporous gold (NGP)

Background work

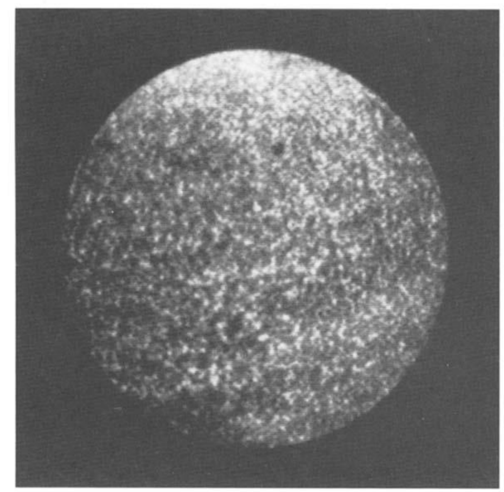
ELSEVIER

Surface Science

Volume 246, Issues 1–3, 3 April 1991, Pages 163-168

Imaging atom-probe analysis of a vitreous ice interface

J.A. Panitz, Andreas Stintz

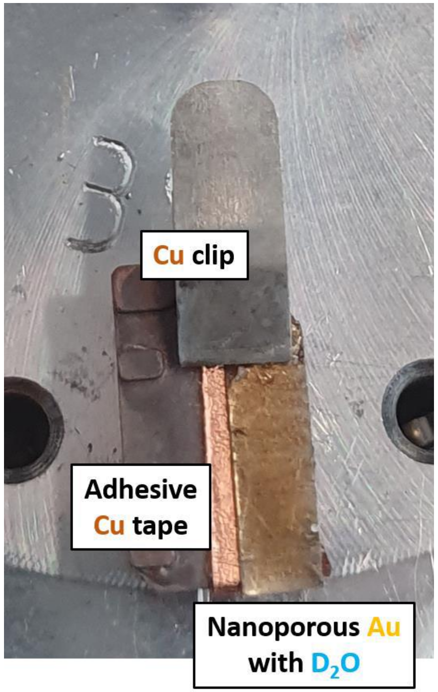


video image of H_2O^+ and K^+ from 1 N KCl in water, frozen on a tungsten tip and field-desorbed from the tip apex. The image shows no order in the liquid indicating that the vitreous state was achieved and maintained during IAP analysis.

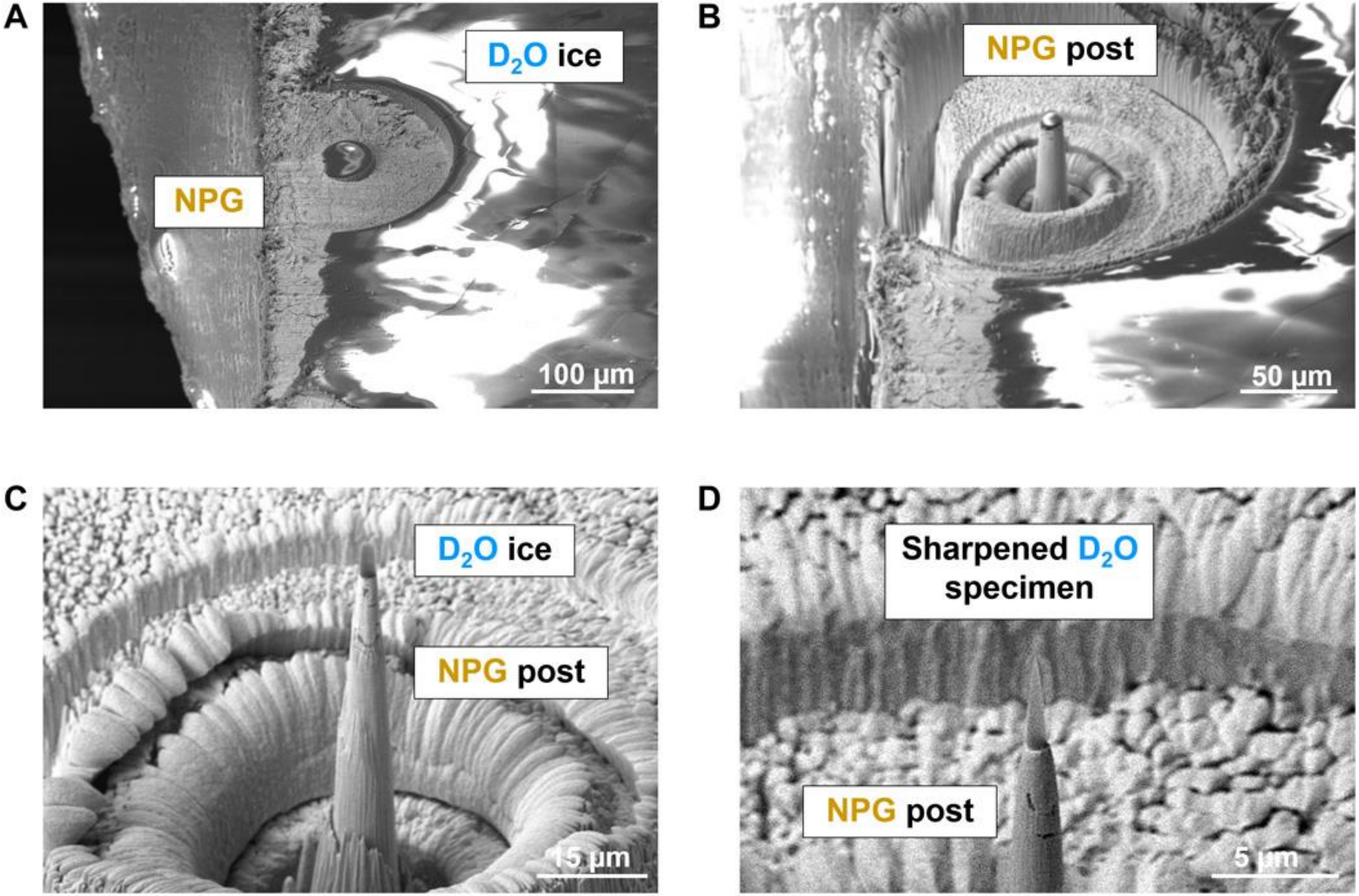
Introduction

- Why APT and the challenges faced while analyzing water.
- Is APT of frozen water known? Why analysis of bulk ice?
- Is APT of silver flake and NGP in ice possible?
- What could be the physics of field evaporation that lead to detection of sets of molecular ions?

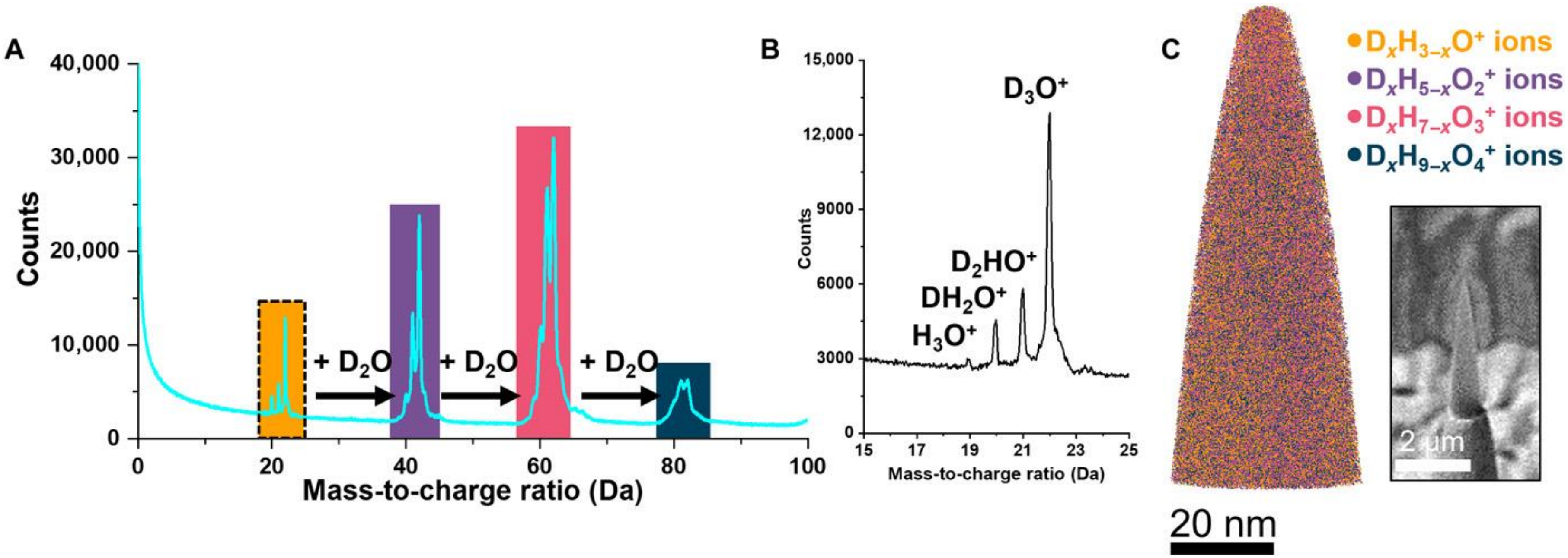
Sample preparation

Dealloying of AuAg foil →  → Cryo-FIB eqiupment

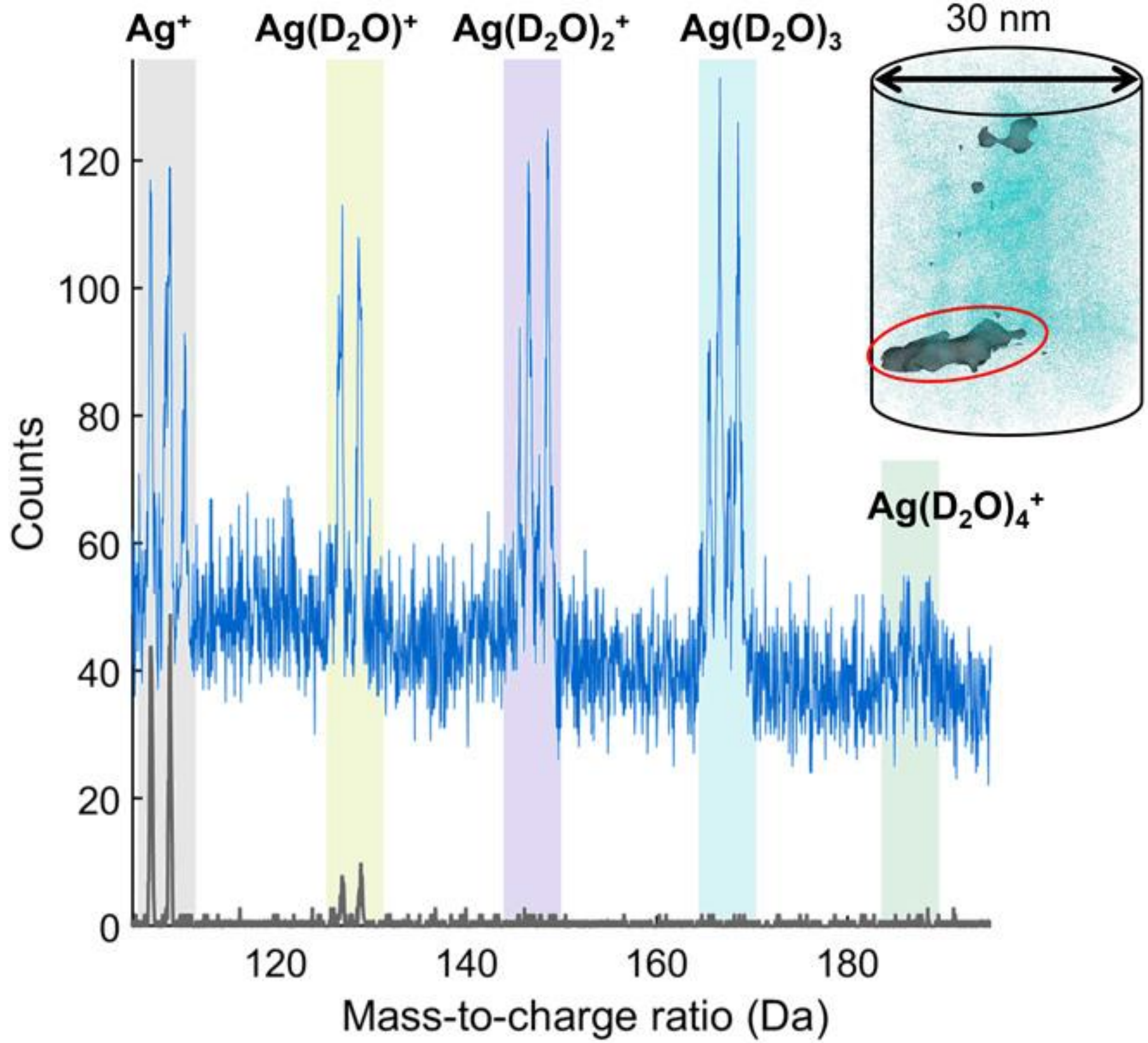
NPG foil mounted on a commercial LEAP system Cu clip with adhesive Cu tape. The NPG foil was immersed into D_2O-based solutions overnight.



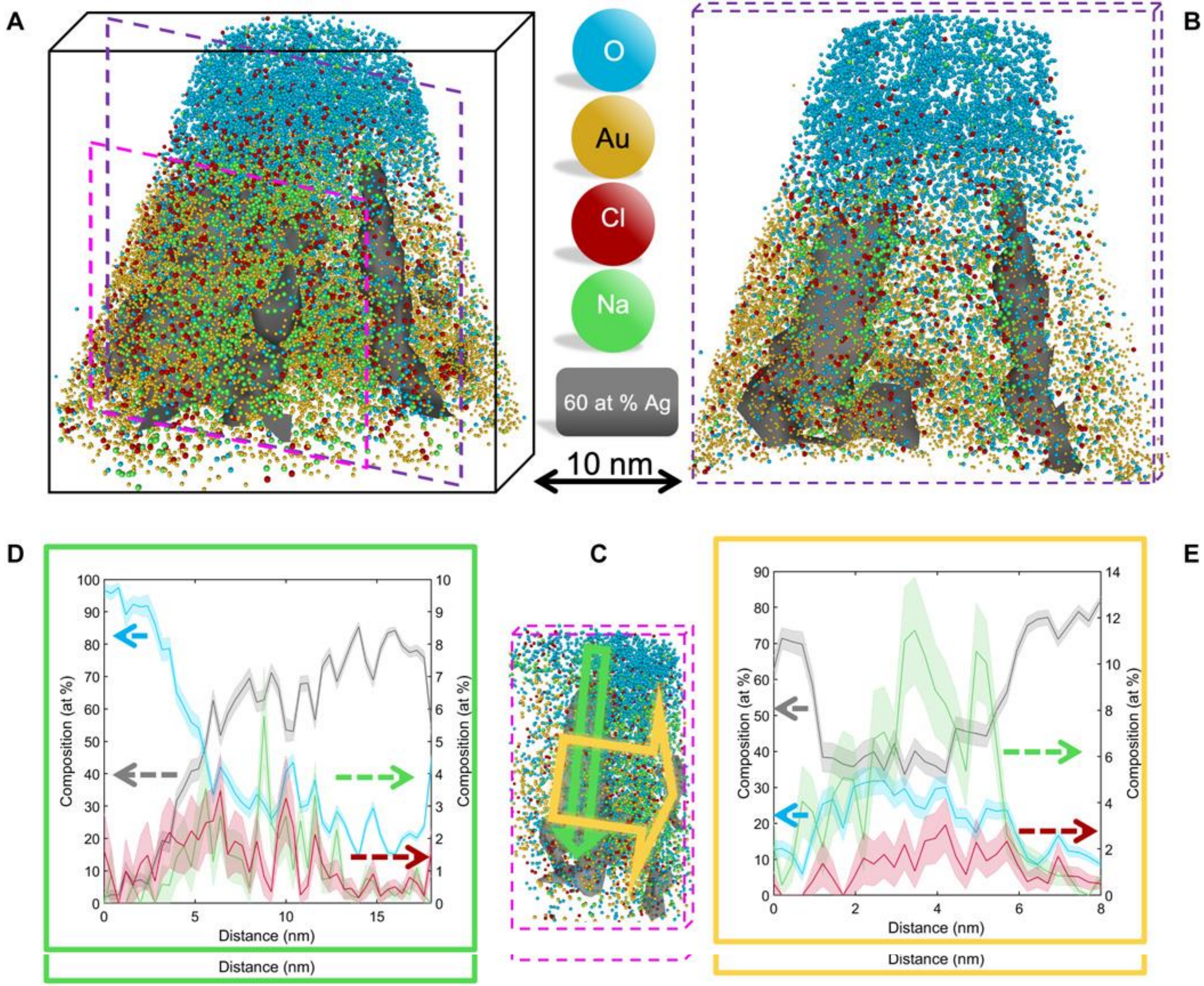
SEM images of in situ APT specimen preparation of an ice sample on NPG. (**A**) The 200- and 75-µm ion beam annular patterns for outer and inner diameters, respectively, were made on the ice/NPG sample. (**B**) The ice/NPG pillar was milled until the height of the Au post reached <50 µm (*83*). (**C**) Ice layer was gradually sharpened along with NPG until the layer reached <5 µm in height. (**D**) Final APT specimen of ice on NPG.



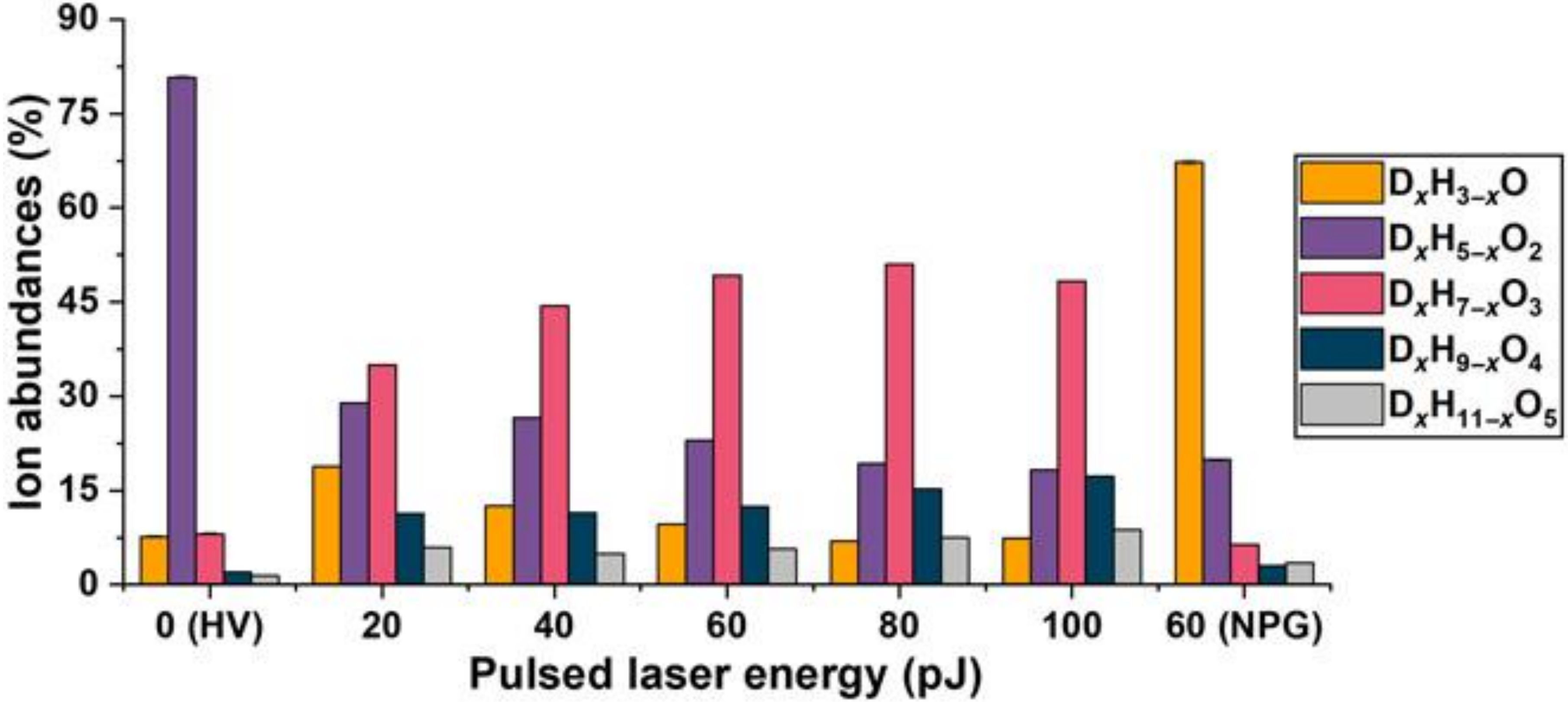
Summary of the atom probe data from a thick layer of ice. (**A**) Mass spectrum of acquired APT dataset of D_2O ice at 100 pJ, 200 kHz, and a detection rate of 0.5%. (**B**) Sectioned mass spectrum from (A) to illustrate $D_xH_{3-x}O$ complex peaks. (**C**) 3D reconstruction map of D_2O. Inset capture shows SEM image of the specimen.



Mass spectra from a floating silver flake and the surrounding ice. Mass spectrum for a 30-nm-diameter and 35-nm-long cylinder, shown in the inset, from within frozen NaCl-containing solution is shown in blue. Inset shows the group of Ag^+ ions surrounded by ice with an isosurface value of 10 at % for Ag. Mass spectrum from within the flake, marked in red in the inset, is shown in gray.

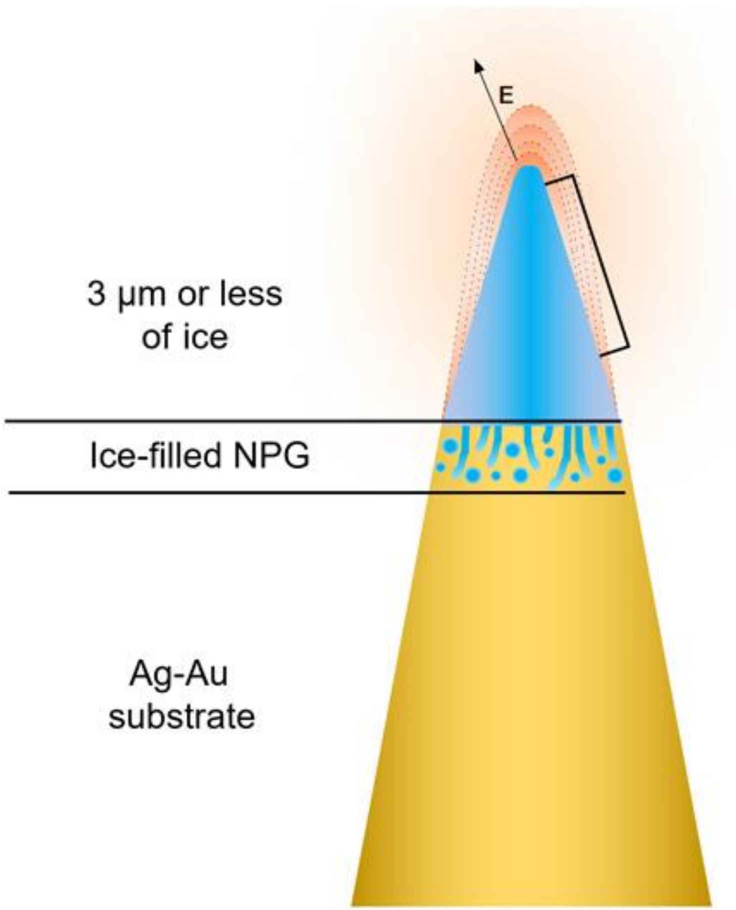


Near-atomic-scale mapping of chemical compositions across frozen gold-water interface. (**A**) 3D reconstruction and analysis of the interface between the NPG substrate and the NaCl-containing ice. (**B**) A 5-nm-thick slice through the tomogram in (A) (**C**) Compositional profile along a 5-nm-diameter cylinder crossing into the interface between a nanoligament and the ice, along the green arrow marked in (**D**), i.e., along the ligament's main axis. (**E**) Composition profile in between two ligaments



Relative molecular ion abundances as a function of the laser pulse energy and in high-voltage pulsing mode. Relative amount of different cluster ions observed in the analysis of D_2O ice at pulsing energies ranging from 20 to 100 pJ. Pulsing fraction for the HV measurement was 15%.

Schematic showing the main parts of the specimen and possible steps involved in the proposed mechanism for pulsed field evaporation of ice.



1. Here, following the departure of a water molecule or molecular cluster from the surface, the rearrangement of charges at the specimen's apex can drive short-range migration of the molecules, which can then combine to form a polymer.

2. Finally, the authors postulate that these mobile, fully or partially charged molecules can flow much more freely on the surface than within the bulk ice, forming a liquid-like layer that acts as a medium between the bulk ice and the vacuum.

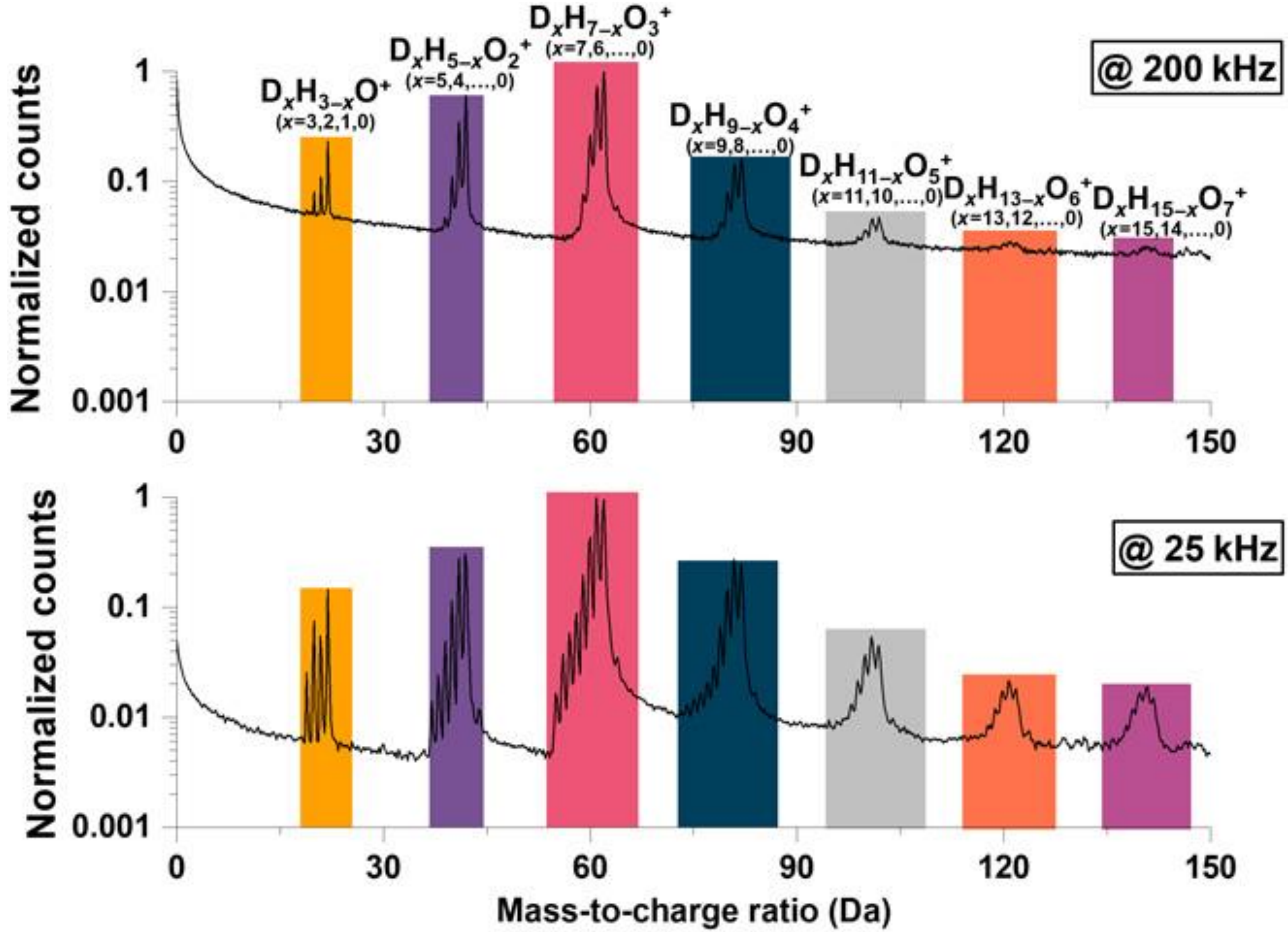
Conclusion

- The approach introduced here has overcome the barriers faced by conventional FIB/APT analysis of liquid layers and nanostructures encapsulated in liquid layers.

- The authors have demonstrated the use of NPG as a substrate for making ice needles in combination with a cryo-PFIB that is suitable for atom probe analysis.

- Within the ice layer itself, there will be opportunities for analyzing the distribution of solutes and the early stage of formation of precipitates, including the possible role of incorporation of impurities.

Thank you ☺



Examples of mass spectra from frozen salt water at different pulse repetition rates. Mass spectra from the NaCl-D_2O water specimen at 200 and 25 kHz—note the difference in scale on the *y* axis.