

The release of trapped gases from amorphous solid water films. I. “Top-down” crystallization-induced crack propagation probed using the molecular volcano

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Introduction:

In this (Paper I) and the following companion paper (Paper II), they investigate in detail the mechanisms for the release of trapped gases from underneath ASW films.

They have previously reported that the rapid, episodic desorption of a more volatile species, covered by an ASW overlayer, occurs in concert with ASW crystallization.

In a recent paper, the desorption of O₂ in the molecular volcano was exploited to demonstrate that crystallization-induced cracks propagate from the outer surface of the ASW.

These cracks were found to have a finite length and a method was developed to determine the vertical length distribution of cracks through ASW.

They further explore the mechanisms for the release of gases trapped in ASW films.

Experimental section:

Experiments were performed on a 1-cm diameter Pt(111) substrate cooled to a base temperature of ~ 25 K in an ultrahigh vacuum system (UHV), with a base pressure of $< 1 \times 10^{-10}$ Torr.

The Pt(111) substrate was cleaned by Ne⁺ ion sputtering at 1.5 kV followed by O₂ exposure and subsequent UHV annealing at 1000 K.

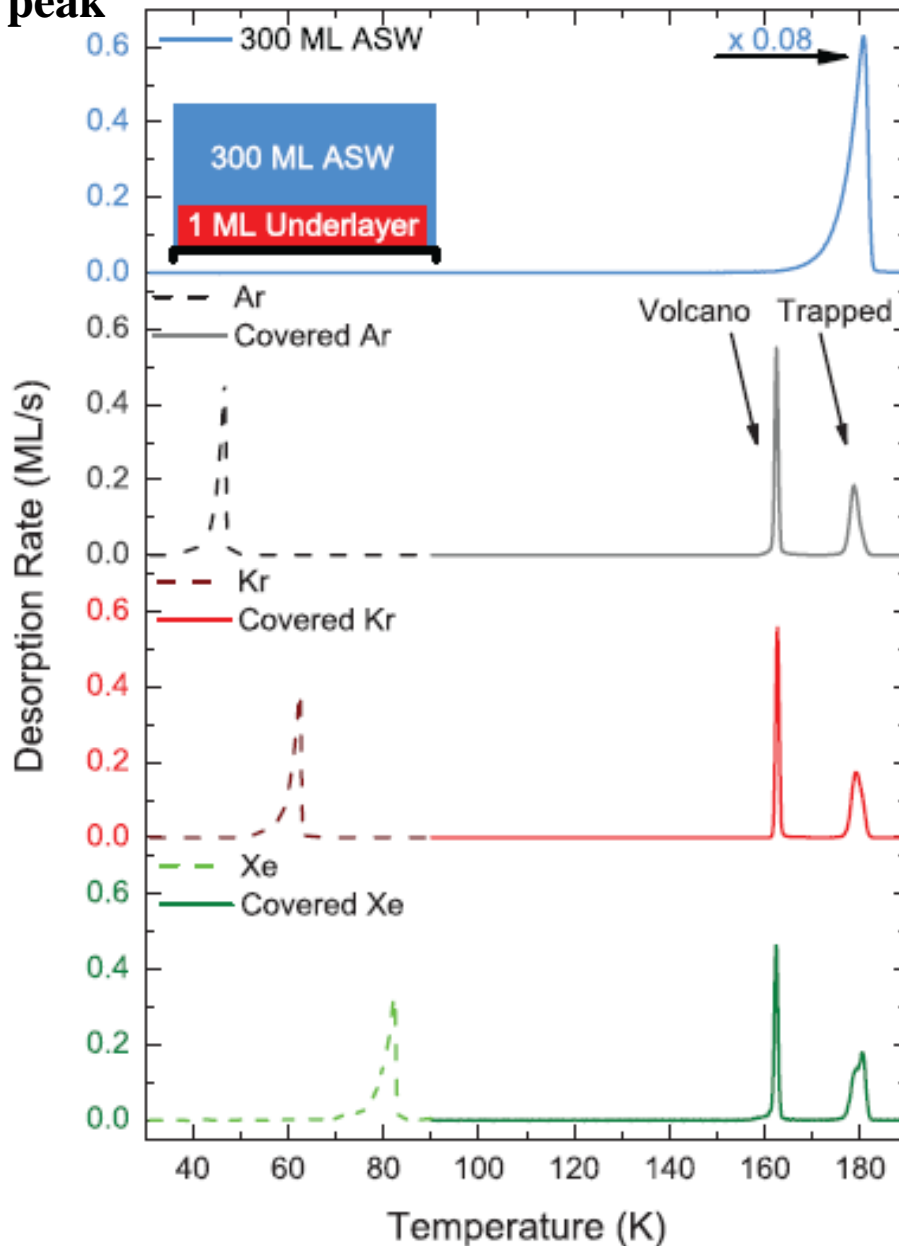
Graphene was deposited by heating the Pt(111) substrate to 1100 K in the presence of decane.

The species were deposited at normal incidence via quasi-effusive molecular beams.

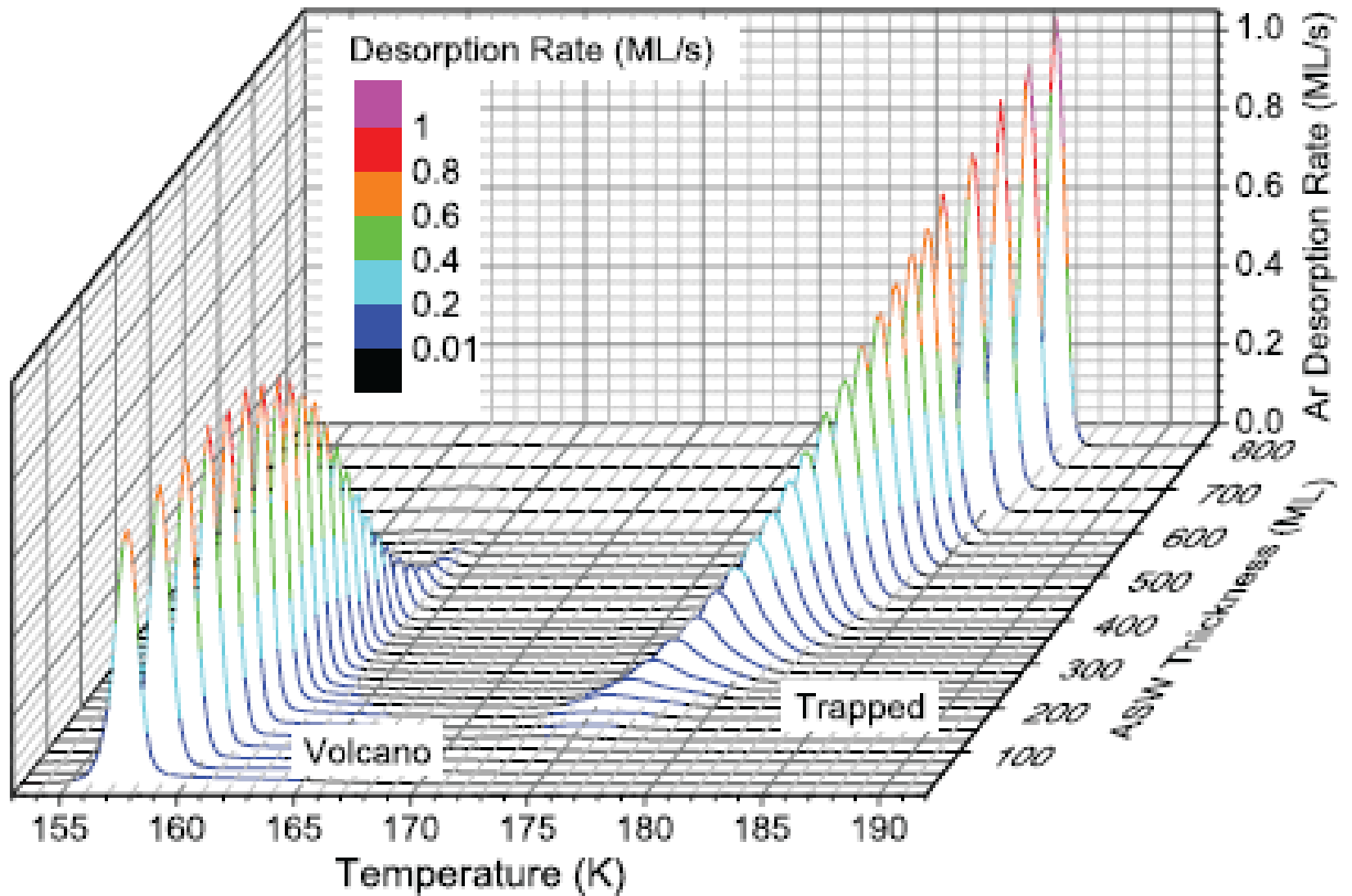
TPD spectra were collected at heating rates ranging from 0.1 to 5 K/s utilizing an Extrel quadrupole mass spectrometer.

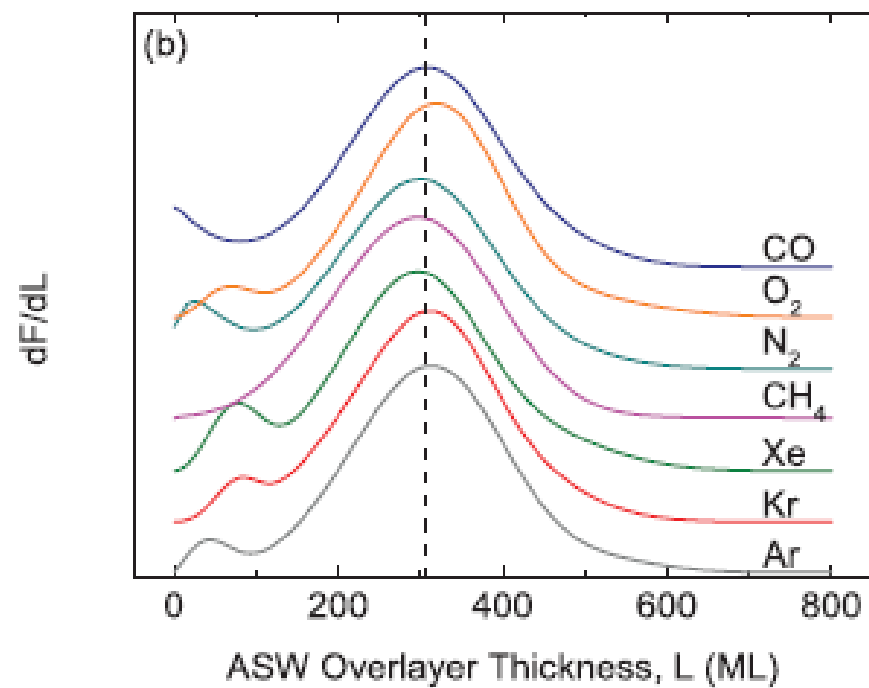
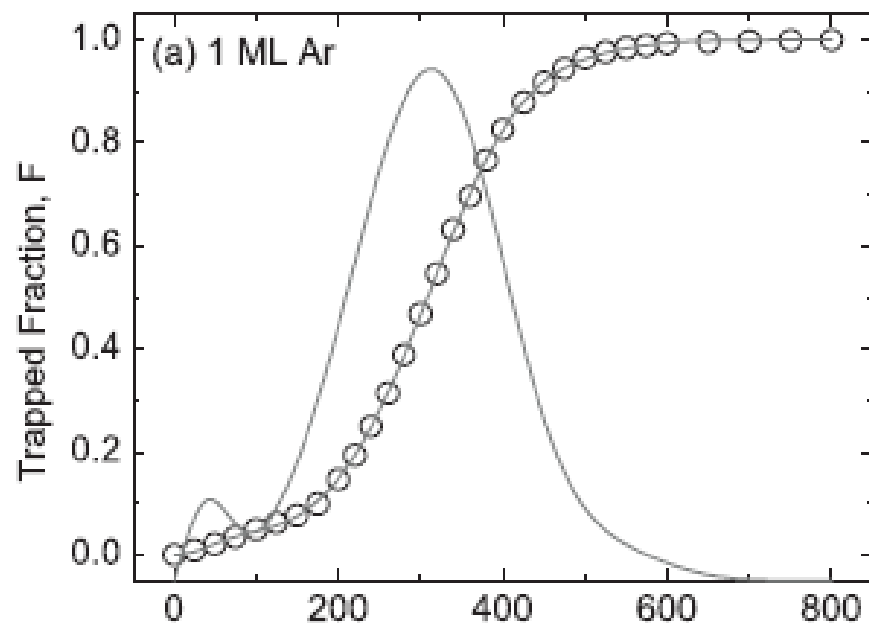
Results and Discussion:

A. Characterization of crystallization-induced crack formation in ASW using the molecular volcano desorption peak

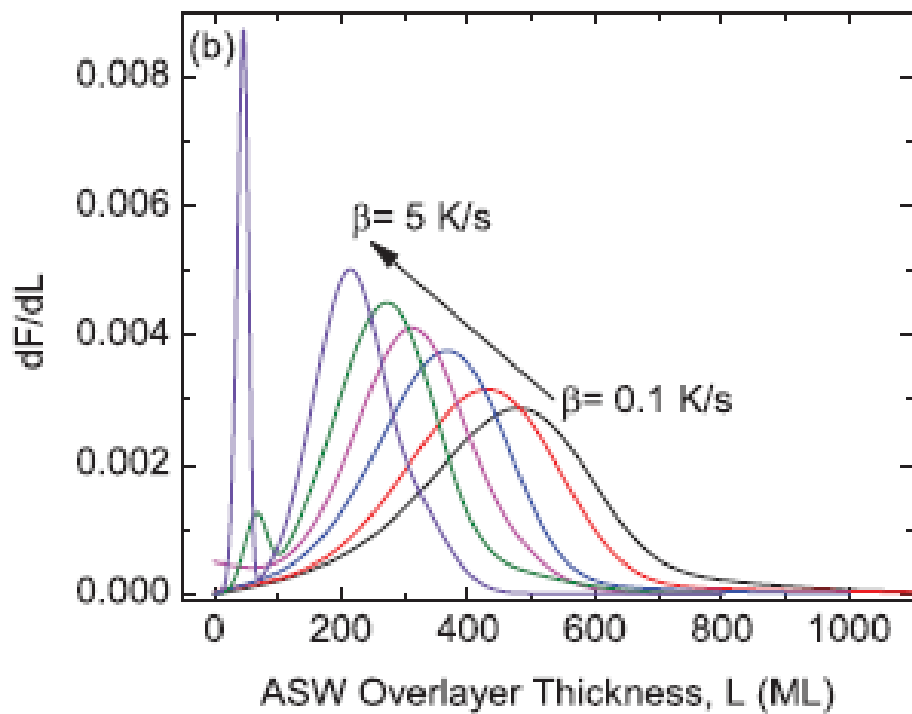
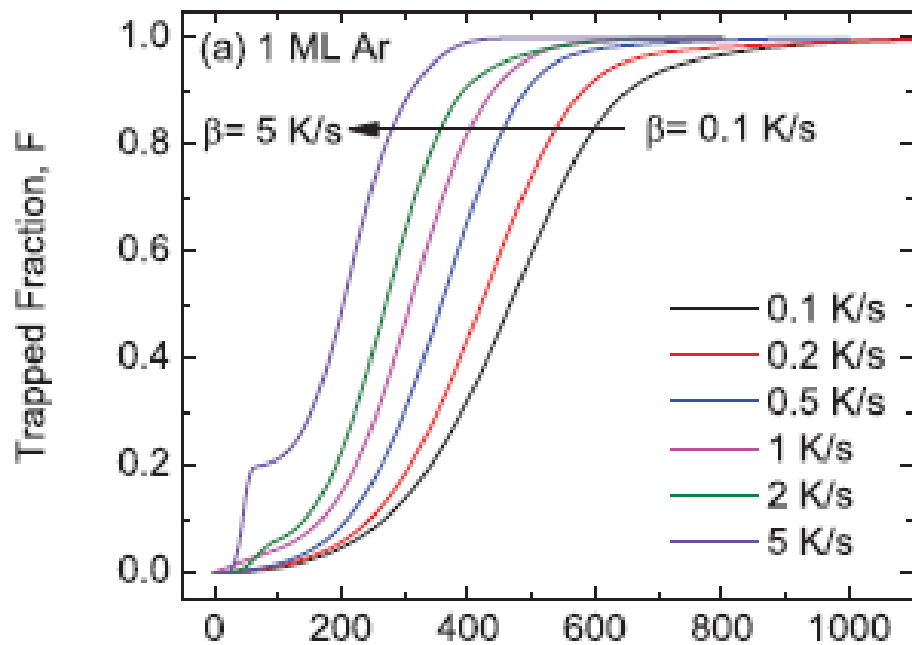


heating rate of 1 K/s

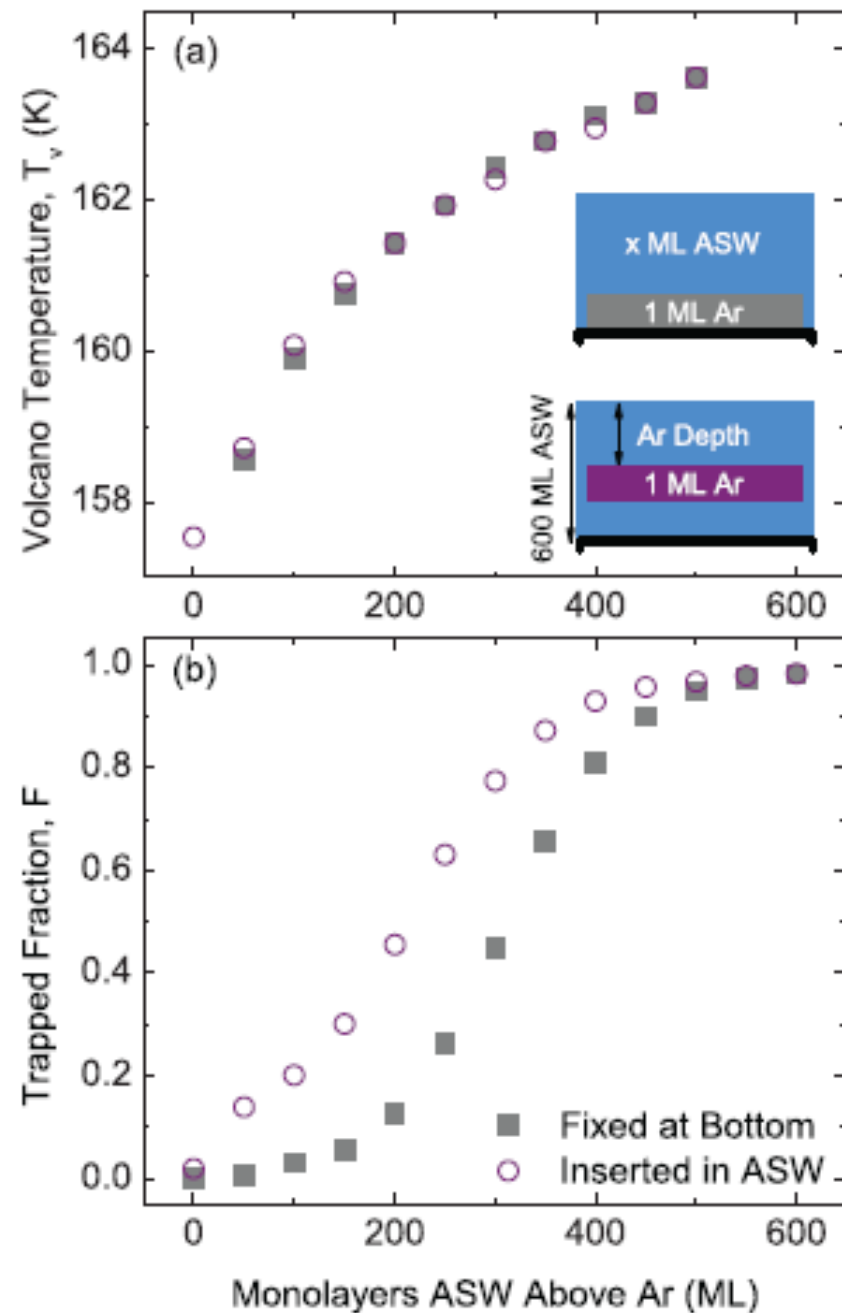


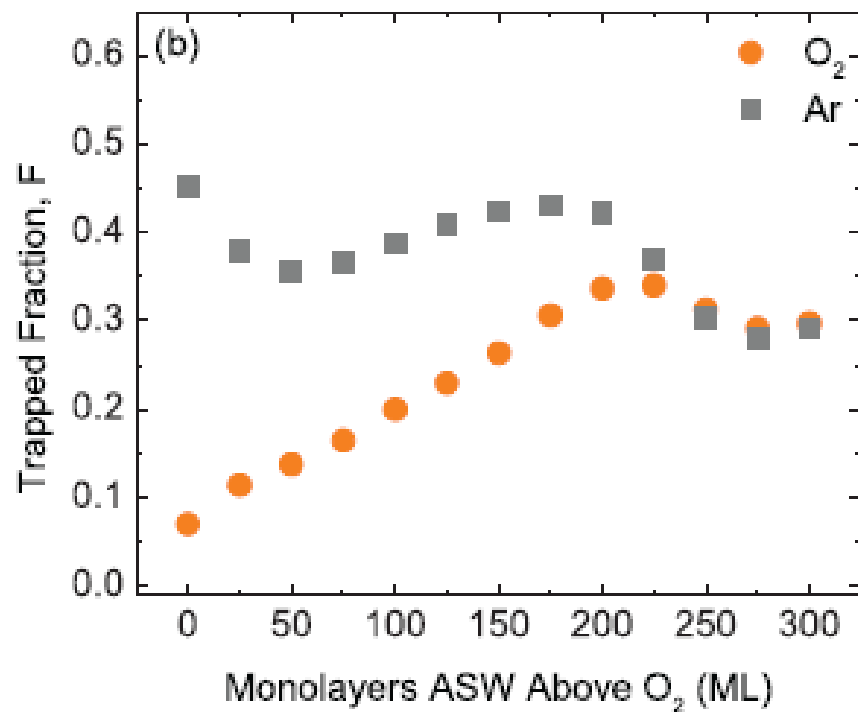
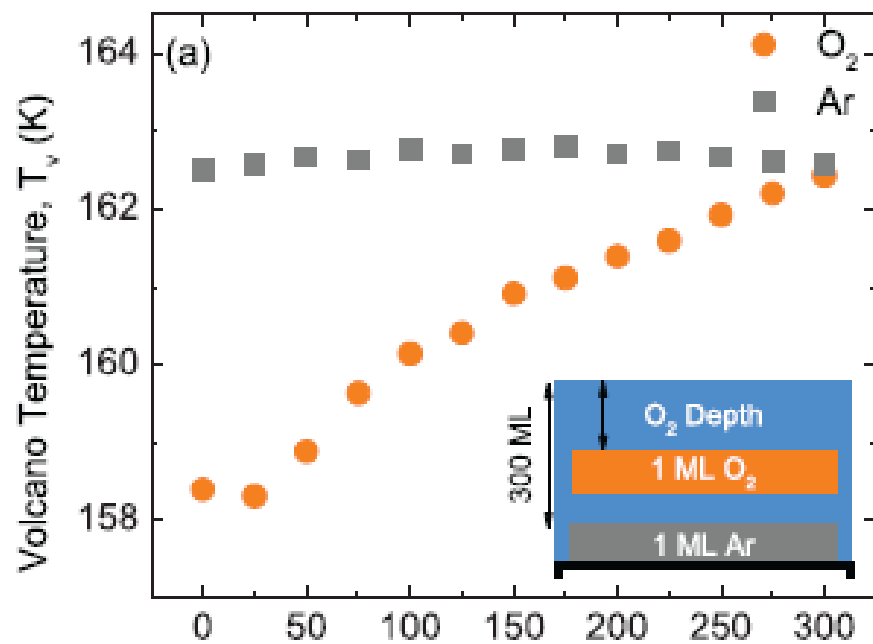


$$F(L) = 1 - \sum A_i e^{-(L/\Lambda_i)^{n_i}}, \quad (1)$$

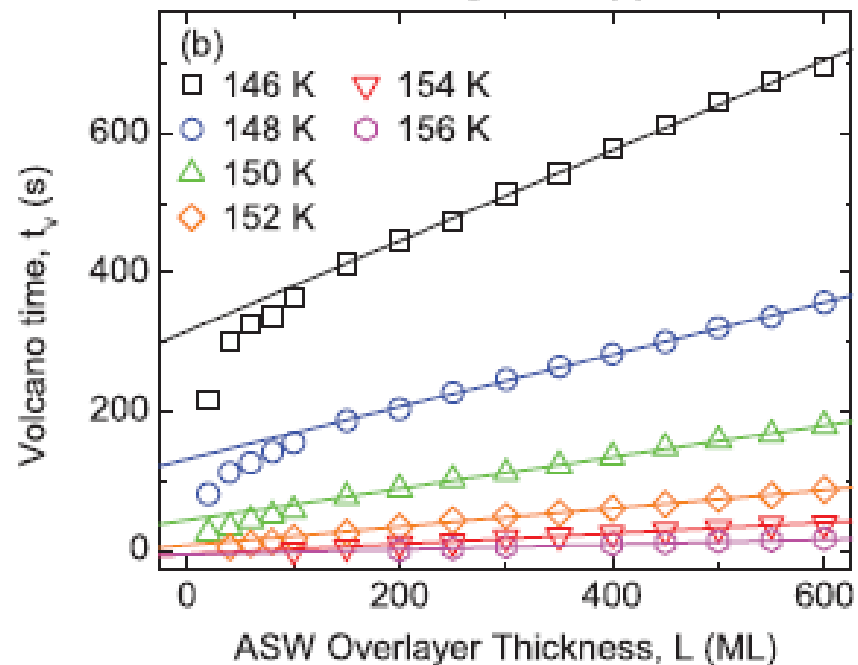
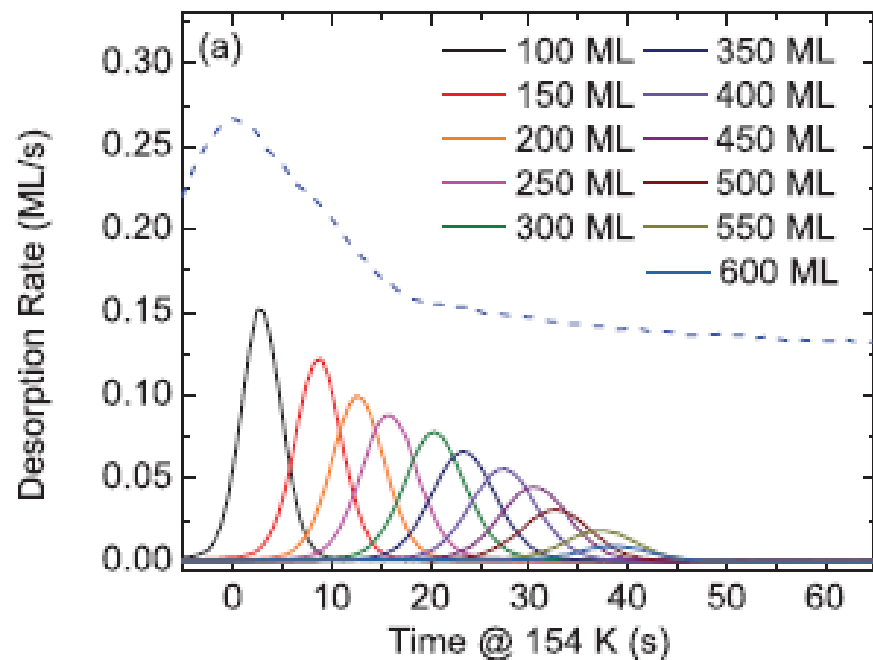


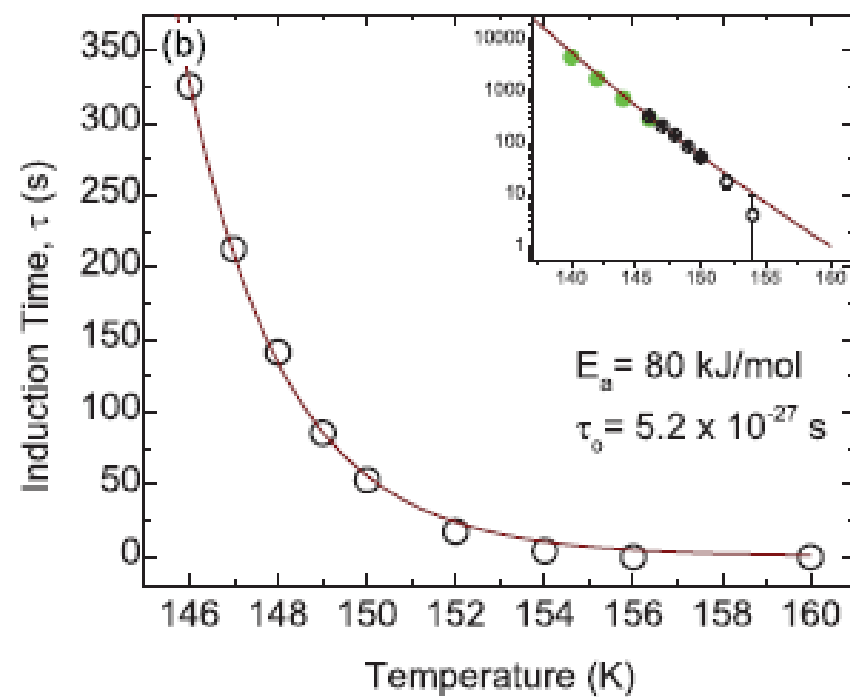
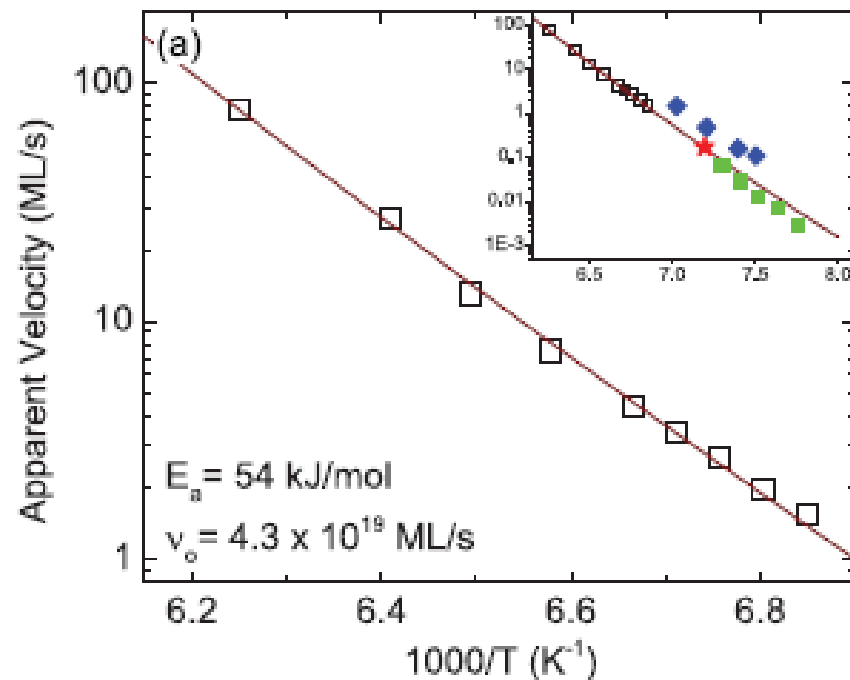
B. “Top-down” crystallization and crack propagation in amorphous solid water





C. Top-down crystallization-induced crack propagation kinetics





Conclusion:

The mechanisms for the release of gases from ASW films have been examined.

They focused on the monolayer coverage regime where the primary release mechanism is due to crystallization-induced cracks in the ASW overlayer, i.e., the so-called “molecular volcano”.

The relative fraction of gas that desorbs via the molecular volcano mechanism versus the gas that remains trapped (“trapped fraction”) have been used to characterize the crystallization-induced cracks.

The results showed that the crack length and distribution were independent of the gas species for Ar, Kr, Xe, CH₄, N₂, O₂, or CO. They also observed that the trapped fraction increased with heating rate indicating a competition between crack propagation and healing.

Together these results established that the release mechanism was due to changes in the ASW overlayer itself and was independent of the particular trapped gas.

The selective placement of the gas layer and the molecular volcano desorption peak were used to conclusively show that cracks form near the top of the ASW film and propagate downward.

In this case, the molecular volcano peak served as indicator of the arrival of the crack propagation front.

They expanded upon this idea and used the molecular volcano peak as a time marker for the crack propagation kinetics.

Isothermal experiments revealed that above ~ 100 ML, the volcano peak time was linear with overlayer thickness indicating a constant crack propagation velocity.

The activation energies for crack propagation (54 kJ/mol) and induction (80 kJ/mol) are nearly the same as those reported by others for ASW crystallization growth and nucleation, respectively.

Thank you

They have studied only with small molecules which have no or less interaction with ASW. But the molecules like CH_2Cl_2 , CCl_4 , CFC, etc. have sufficient interaction with ASW. Will crack length distribution be the same for these molecules also?

Crack length distribution can be studied using different underlying composition.

Ions like H^+ or OH^- may play significant role in the crack length distribution.