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## Photolysis rate differences of impurities in various frozen matrices, including nature-identical snow crystals

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Chemical compounds can be incorporated into snow crystals during formation, for example by co-deposition with water vapor, or after the crystal is formed, such as by vapor deposition onto the surface of the crystal. As fallen snow crystals consolidate in a snowpack, entrained compounds can remain at the ice-air interface of the snowpack (i.e., in the quasi-liquid layer (QLL) of the disordered interface), or be trapped in liquid-like regions (LLRs) at grain boundaries in the ice matrix. More than just a reservoir for these materials, snow can be an important location for a variety of chemical reactions, such as transformations of pollutants.

Some recent work has suggested that some photochemical reactions proceed faster in surface QLLs than in either internal LLRs or in aqueous solution. This phenomenon has not been well studied. If photolysis at the air-ice is faster, it might have significant implications for our understanding of chemical fate in snow-covered regions.

Laboratory studies have attempted to reproduce the physical reaction environment of snow by a variety of methods, including freezing aqueous solutions in molds, spraying aqueous solutions into liquid nitrogen to form ice grains, or grinding solute-containing ices into small pieces. However, natural snow crystals are quite complex, and while current snow surrogate preparation methods have yielded important insights, they do not accurately mimic the structure and physical properties of newly-fallen natural snow crystals.

Here, we describe our work to study photolysis in various frozen matrices, including nature-identical snow samples. We built a snow-making machine, modeled on earlier efforts from other laboratories, which is based on the principle of nucleating supersaturated water vapor to form snow crystals. We incorporate chemicals into/onto the snow crystals either during the formation process or by treating the snow afterwards. Then, we illuminate this snow (or other samples) using the output from an arc lamp, filtered to approximate polar sunlight.

We have measured photolysis rates for several compounds in both frozen and aqueous matrices. Our results have found similar photolysis rates in aqueous and frozen solutions for all tested compounds, suggesting chemical reactions in internal LLRs proceed similarly as in aqueous solution. However, reaction rates for some chemicals deposited to snow or ice surfaces are up to 20 times faster than in aqueous solution, while other compounds show no enhancement. We will discuss which compounds and freezing conditions lead to an enhancement.

### Significance statement

We have identified some compounds that photolyze faster on snow or ice surfaces than in either aqueous solution or frozen within the ice matrix. Enhanced photolysis rates at the air-ice interface suggest certain chemicals may degrade or transform faster than previously believed.

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