**THE ROLES OF ENERGY LOCALIZATION AND BURIED INTERFACES IN ELECTRONIC SPUTTERING OF PRISTINE AND MIXED LOW-TEMPRATURE ICES.**

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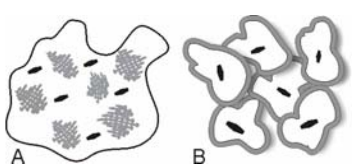
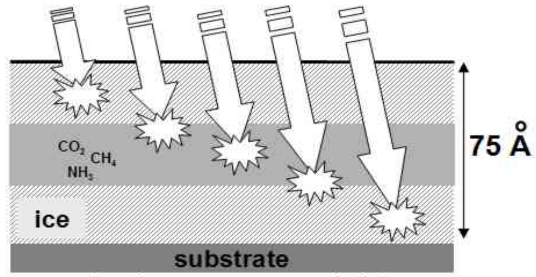
**Introduction:** The radiolysis and sputtering of ice is intimately tied to the electronic structure of condensed water. Throughout the energy regime of 0-100 eV, ice can undergo a number of distinct excitations and/or scattering resonances [1]. These excitations are made mobile by a variety of mechanisms. For example, an exciton can migrate by resonant energy transfer mediated by the hydrogen bond. A "hole" or ion embedded in a highly polar matrix is greatly stabilized due to solvation interactions [2]. This lowers the ionization potential of an embedded molecule by an amount comparable to the ion solvation energy (2-3 eV). Since excitations are mobile in ice, the overall reaction probabilities with adsorbed or embedded inclusions in ice are relatively high. *Hence, excitations that migrate through the ice matrix will preferentially deposit on the organic or embedded "contaminant."*

**Approach**: Icy grains (i.e. precursors to comet nuclei) can form in many possible ways. In diffuse media, the system is thermally equilibrated to very low temperatures and condensation is limited by encounter frequency. Here, particles will tend to form on surfaces of rocky dust particles, but will accumulate in a relatively uniformly mixed distribution, as depicted below in A. In cooling regions of space, the formation of icy grains follows the sequence of sublimation temperatures as the grains cool. The rocky dust particle is formed at high temperature, and upon cooling first condenses the stickiest molecules (water, methanol etc.) then later cools enough to adsorb volatiles and finally gas molecules, resulting in layered grains shown in B. Later, these grains can begin to coalesce and form larger heterogeneous masses. Thermal cycling of these ordered masses can anneal them and cause spontaneous phase segregation and redistribution of the materials throughout the particle, leading from a situation like B back toward one like A




Experimentally, we simulate these two scenarios by controlled deposition. Co-deposition of organics will disperse hydrophilic molecules through the ice, while hydrophobic molecules tend to pool into clusters and pores. Alternatively, organic inclusions can be encased between layers of ice, resembling B. This is shown below where we systematically control the depth of the capping ice layers. We also control the penetration depth of the radiation. The combination allows us to deconvolute the effects of direct irradiation from that of energy migration through the ice.




a. ice / precursor sandwich

In addition, there may also be distinct differences in the products of direct irradiation, and those generated by energy delivered through excitation hopping in the ice. Interfaces such as grain boundaries, hollow pores or embedded silicate or carbonaceous dust grain nuclei can also act as alternate points of energy localization within "ices". We have therefore examined the relative importance of pore collapse and grain boundaries on the radiation-induced production and thermal release of gases such as $H_2$, CO, $CO_2$ and $O_2$ from mixed ices containing methane inclusions and from water covered graphite surfaces. These radiation products can be trapped and released at a later time during thermal cycling and pore collapse [3]. Molecules such as $H_2$ can be released at temperatures up to 50 K, whereas $O_2$ can be retained within clathrate hydrates until the ice sublimates. We discuss an important link between the physical morphology of ice and the yields of direct and delayed release of molecular fragments from ice and ice covered grains.

**References:**

[1] R. E. Johnson, P. D. Cooper, T. I. Quickenden, G. A. Greives, and T. M. Orlando, *J. Chem. Phys*. 123, 184715 (2005). [2] J. Herring-Captain, G.A. Grieves, A. Alexandrov, M.T. Sieger, H. Chen and T.M. Orlando, *Phy.l Rev. B.* 72, 035431-1 (2005). [3] G.A. Grieves and T. M. Orlando (2005), *Surf. Sci.* 593, 180-186.