

## Nanoscale, in-situ investigations of fluoranthene surfaces

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Over the past few years there has been a number of studies showing the effect of changing ion hydration properties on dissolution and precipitation [e.g., 1 & 2]. Thus far the systems examined at the nanoscale have been ionic materials that readily interact with polar solvents such as water. However, there are many organic molecules that are non-polar, i.e. have an evenly distributed charge or are uncharged. This includes polycyclic aromatic hydrocarbons (PAHs), environmental contaminants that are produced by burning organic matter. PAHs have decreased solubility in saline solutions [3], producing a salting out effect related to the change in the structure of water [4]. Therefore, their dissolution rate and thus mobility is expected to be intrinsically linked to the presence of different cations in water, as observed for minerals.

Here we examine fluoranthene crystal surfaces, a small PAH composed of three benzene rings attached via a five-membered ring. Atomic force microscopy is employed to examine the sublimation and dissolution of fluoranthene *in situ* in air and aqueous solutions respectively. The experiments show removal of material from the macromolecular crystals occurs via step retreat and etch pit formation in both types of media. Sublimation in air is faster than dissolution into pure water. Interestingly, the presence of salts (NaCl and MgSO<sub>4</sub>) with different water structuring properties had minimal influence on the dissolution rate. Instead it is the surface topography that has the most significant effect on material removal rate from the crystal surface. Therefore, mobilisation of PAHs from the solid state will be kinetically controlled by their interactions with other organic molecules in the solid phase, rather than the properties of the aqueous solution.

[1] Ruiz-Agudo et al. 2010 *Geochem. Cosmochim. Acta*, 74, 1256. [2] Kowacz et al. 2007 *Geochim. Cosmochim. Acta*, 71, 5168. [3] Jonker & Muijs 2010 *Chemosphere*, 80, 223. [4] Marcus 2009 *Chem. Rev.* 109, 1346.