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From thrown away beer bottles to a bio-integrated nanomaterial with possible future applications

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Iridescent glass objects are well known from archeological sites and are traditionally explained by an internally-layered surface cover that leads to the interference of releflected light in the range of the visible wavelengths. Here we focus on glass bottles that were thrown away only a few decades ago and show spectacular play of colors. Most of the studied objects were dug up in South Australian opal fields, where they were thrown away by earlier opal miners. The locals take these bottles as evidence that the opal still forms, and by recent miners they are believed to be a guide to occurences of precious opal.
The structure of the weathered surfaces was studied by FIB-FEG-SEM (focused ion beam – field-emission gun scanning electron microscopy). They consist of layer stacks of an opal-like substance with layer thicknesses typically in the 120 to 200 nm range. Compared to the original bottle glass the surface layers are strongly depleted in Na2O, K2O and CaO, whereas FeO is retained and SiO2 and especially Al2O3 are enriched. These layers are build up by irregular granules in the tens nm range that appear amorphous both by X-ray and electron diffraction, like opal-A. The surface layers contain about 1 wt% Cl that is not present in the glass substrate and show shifts compared to the fresh glass in the Sm-Nd and the Rb-Sr radiogenic systems, which can be explained by reaction with salinar soil fluids.
The weathering glass surfaces are a substrate for microbes, probably cyanobacteria, that are present as singular cells or colonies dissolved into the opal-like surface layers. Some of them produce Al-enrichment halos as seen by XRD-imaging. Raman spectra indicate the presence of organic molecules throughout the surface layers. This organic material most probably is located on the extremely porous interlayers between the dense opal layers. These interlayers are about 25 nm wide near the interface towards the unaltered glass and widen to about 150 nm before the surface layers tend to chip off. By EELS mapping fluorine is found to be enriched in these interlayers. A possible source are environmental contaminations with fluorinated hydrocarbons. Adsorption into the opal-like surface layers is obviously very effective due to their high interface:volume ratio - similar to activated charcoal, but in a spatially perfectly layered arrangement of interfaces.
The self-organised formation mechanism of such iridescent glass alteration layers is a matter of debate. The well-known effects of organic ligands on silicate dissolution suggest that the organic component in the alteration layers might play an active role in their formation. Favorable methods for further characterisation of the adsorbed interlayer molecules include confocal Raman spectroscopy and NEXAFS. We speculate that weathered glass surfaces or analog materials might become a useful future material for the detection and monitoring of environmental contaminants.