The daguerreotype was named after the French artist and chemist Louis J.M. Daguerre who, in collaboration with the inventor Nicéphore Niépce developed this first successful form of photography in the 1830s [1-3]. Once Daguerre had perfected the process in the early 1840s, this process became a popular technique for portraiture, until it was replaced by the wet collodion process towards the end of the nineteenth century [4]. To produce a daguerreotype, a highly polished, silver-clad copper plate is exposed to iodine and bromine vapor, creating a light-sensitive, mixed silver halide layer. Exposure of the sensitized plate to light causes a photodecomposition process, resulting in the formation of metallic silver particles on the plate surface: the latent image. The plate is then developed by exposure to mercury vapor, which results in the formation of silver mercury amalgam particles. The amalgam particles constitute the image highlights and are of sufficient size to produce the visible image. The darkest areas on the developed plate are due to areas of polished silver surface with a low surface density of light-deflecting amalgam particles. The image is fixed with sodium thiosulfate to remove the residual silver halides, rinsed with water, and subsequently gilded using a solution of gold chloride or gold thiosulfate. The gilding helped the silver mercury amalgam particles to adhere to the plate and also improved image contrast.

Unfortunately, daguerreotypes do not age well unless kept in strictly controlled environments, which most museums now do. The Smithsonian’s National Portrait Gallery, for example, has over 110 daguerreotypes in its collection. However, many of the images have suffered from exposure to the atmosphere and show varying amounts of discoloration and numerous blemishes. While there have been a number of attempts to study the chemistry and morphology of the corrosion and tarnish, there is no systematic study of the various phases and compounds that form on the daguerreotype surface during aging and how they affect the appearance of the image [5-8]. Additionally, there has been little study, to date, of the feasibility of selectively removing the corrosion products to restore the quality of the image.

The aim of this project is to identify the various different corrosion products that exist on daguerreotypes, and to determine whether they maybe selectively removed by either a focused ion beam or by ultrafast laser ablation. The sample daguerreotype chosen for study (see Fig. 1), shows a considerable amount of discoloration across the whole surface. Initial studies focused on the region of the right eye, as outlined in Fig. 1. Fig. 2 shows the eye at higher magnification. The small black dots on the optical image, which appear white on the SEM image, are determined to be part of the brownish cast that is seen in the center of Fig. 1. XEDS maps of these features reveal that they are copper rich islands (see Fig 3.). The origin of these features is under investigation.
References:

![Fig. 1. Image of whole daguerreotype, subject unknown. Red box marks analysis area in subsequent Figs.](image1)

![Fig. 1. Image of right eye. (a) optical, (b) SEM. Note the lines of features to the right of the angled line](image2)

![Fig. 3. SE and XEDS images of dark islands near the figure’s eye. Surface is predominantly silver rich and the islands are copper rich.](image3)