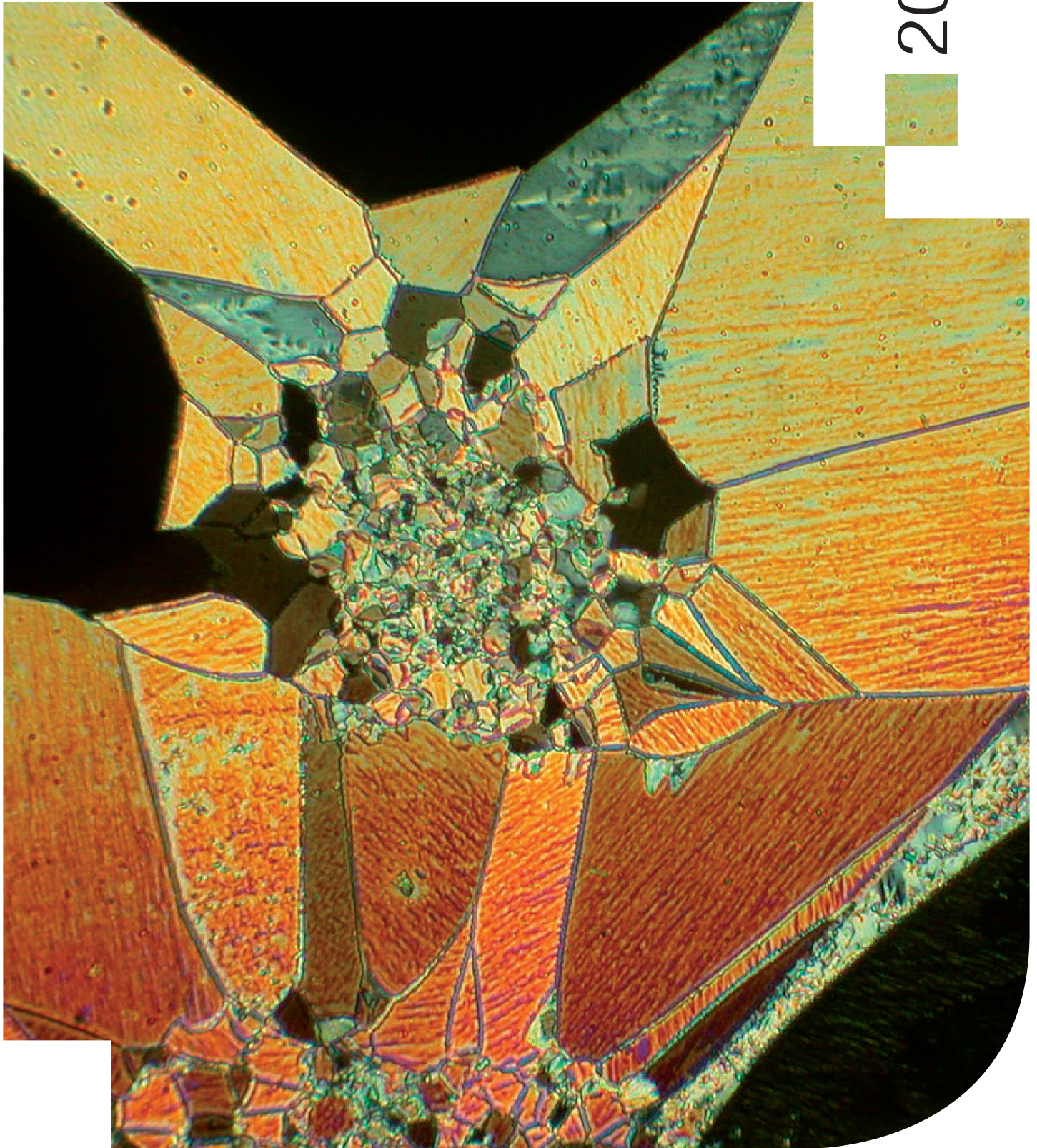# XMaS

NEWSLETTER

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Silver corrosion in real time

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From its veneration above gold in ancient Egypt to modern applications such as the prevention of bacterial growth in clothing and wound dressings (exploiting an antibacterial property known since at least the 8th Century) silver and its alloys remain a central part of human technology, commerce and art after 8 to 10 millennia of use. Yet, the corrosion of silver is a complex phenomenon and is not well understood; fundamental research into the chemistry occurring on surfaces exposed to the environment is needed so that material degradation can be controlled. The most common corrosion products (the sulfides) are black, but we expect to see silver with a lustrous surface often with intricate chasing **(Fig 18)**. Thus, for example, silver museum artefacts, have, been repeatedly cleaned and polished over 100s or even 1000s of years, leading to serious loss of surface detail and other damage **[1]**. In these experiments **[2]** we examined, in real time, the early stages of the corrosion of silver exposed to the anthropogenic gases H_2S and O_3 at various levels of relative humidity (RH). A particular goal was to look for synergistic effects in gas mixtures to closer approach the real environment. Experiments were carried out in an electrochemical /environmental cell (eCell) developed at the universities of Ghent (BE) and Warwick (UK) **[3]** fed by a gas mixing unit designed and built at the Academy of Fine Arts in Vienna **[4]**. Synthetic air containing 500 ppb O_3 and/or 500 ppb or 10 ppm H_2S at 50% or 90% RH was blown through the eCell which contained a high purity silver coupon. In experiments lasting 12-24 hours SR-XRD patterns were recorded every 10 min using the Mar CCD 165 camera with an acquisition time per image of 20 s. Images were reduced to 1D patterns and trends in peak area over time were extracted using the esaProject package.

Overall the effects were neither linear, nor monotonic and the patterns reveal different behaviour for different compounds coexisting on the same surface, changes in rates of corrosion over time, and a strong dependence of the rate of corrosion on the gas mixture. For example, the growth of silver oxides in O_3 at 50% RH was shown to proceed via cubic Ag_2O for 3 hours or so then AgO related reflections appear followed by more complex oxides after 10 hours (polymorphic AgO, Ag_2O_3 and Ag_3O_4). The total coverage is still increasing rapidly after 24 hours. Conversely, when O_3 is replaced by H_2S at the same level **(Fig 19)**, a fresh coupon shows little evidence of corrosion on the same timescale. However, if O_3 is added to the mix after 12 hours, a very rapid increase in coverage of both sulfides and oxides is observed. We conclude that at concentrations close to those found in city centres, synergistic effects between O_3 and H_2S lead to greatly accelerated rates of corrosion.

[1] C. Leygraf, T. E. Gradel, *Atmospheric Corrosion*, John Wiley & Sons, New York, (2000).

[2] R. Wiesinger *et. al.*, presented at SR2A, Paris 2014 and submitted to JAAS.

[3] M. Dowsett, A. Adriaens, *Anal. Chem.* 78 3360-3365 (2006.)

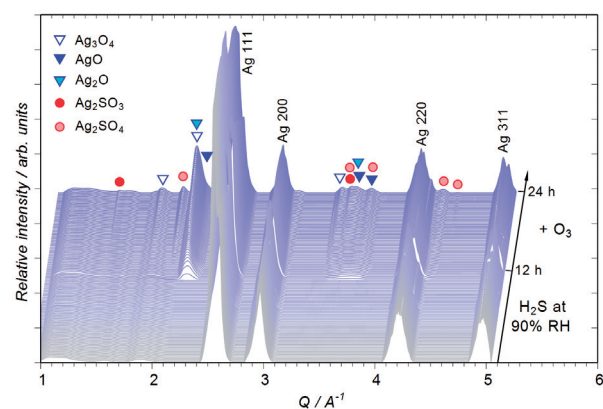[4] R. Wiesinger, M. Schreiner and C. Kleber, *Appl. Surf. Sci.*, 256 2735-2741 (2010).

Fig. 19: *Waterfall plot of extracted and normalized SR-XRD patterns for two part experiment with initial exposure to H_2S at 90% RH with the addition of O_3 after 12 hours. Note the rapid appearance of corrosion peaks upon the addition of O_3*

Fig. 18: *Heavily engraved silver chalice in the Liechtenstein Museum, Vienna, with permission.*