

Surface Analysis at NRC, Ottawa

Sample s6, X-ray Photoelectron Spectroscopy
(XPS)

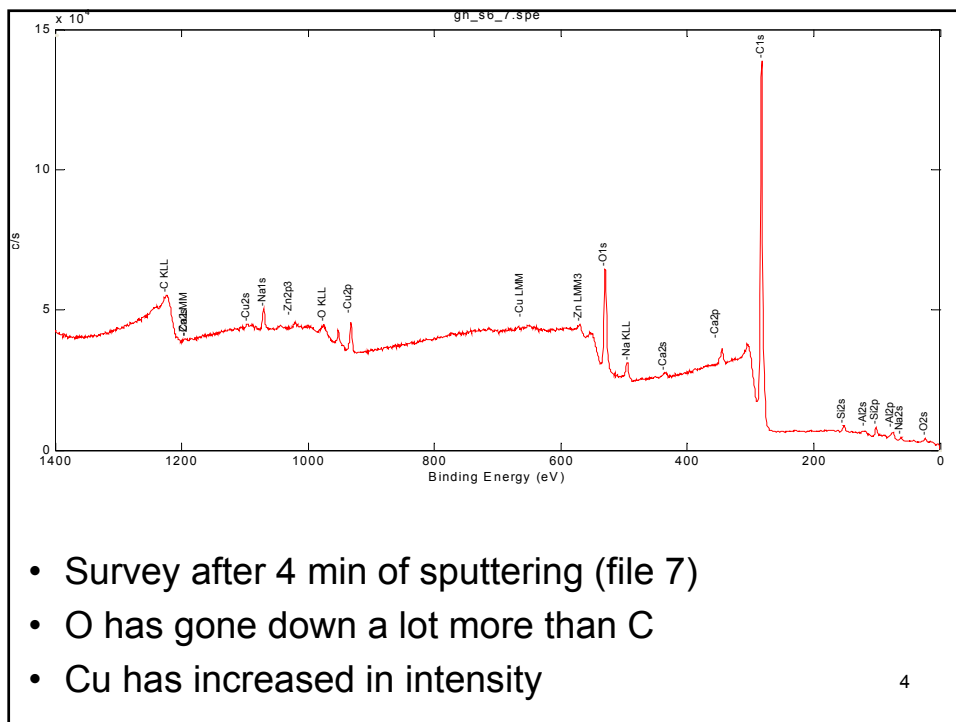
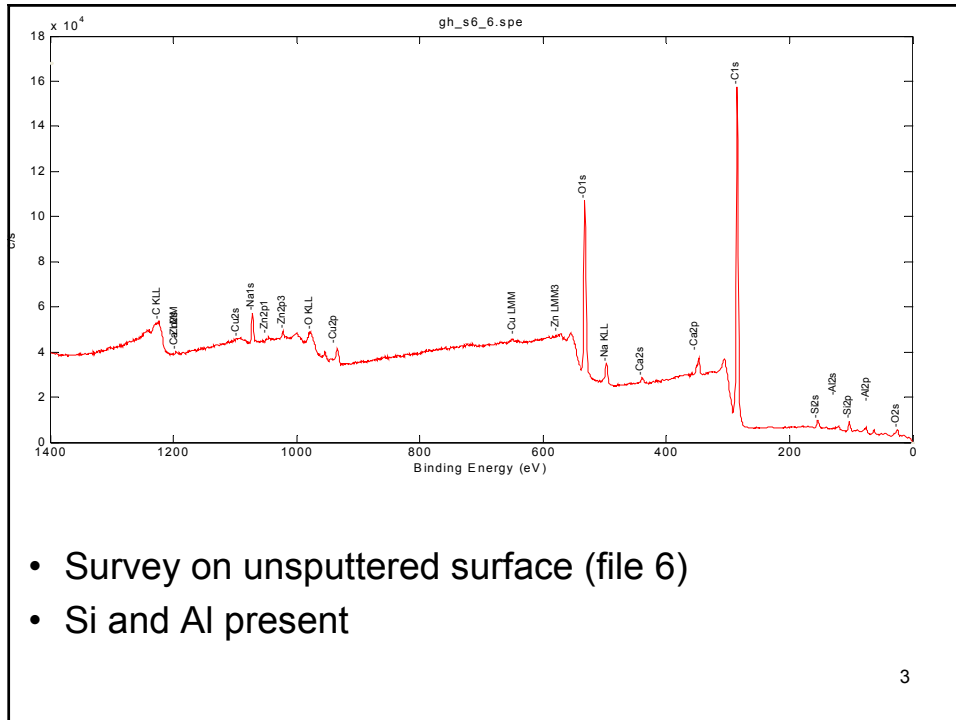
7 year exposure in Oskarshamn, Sweden

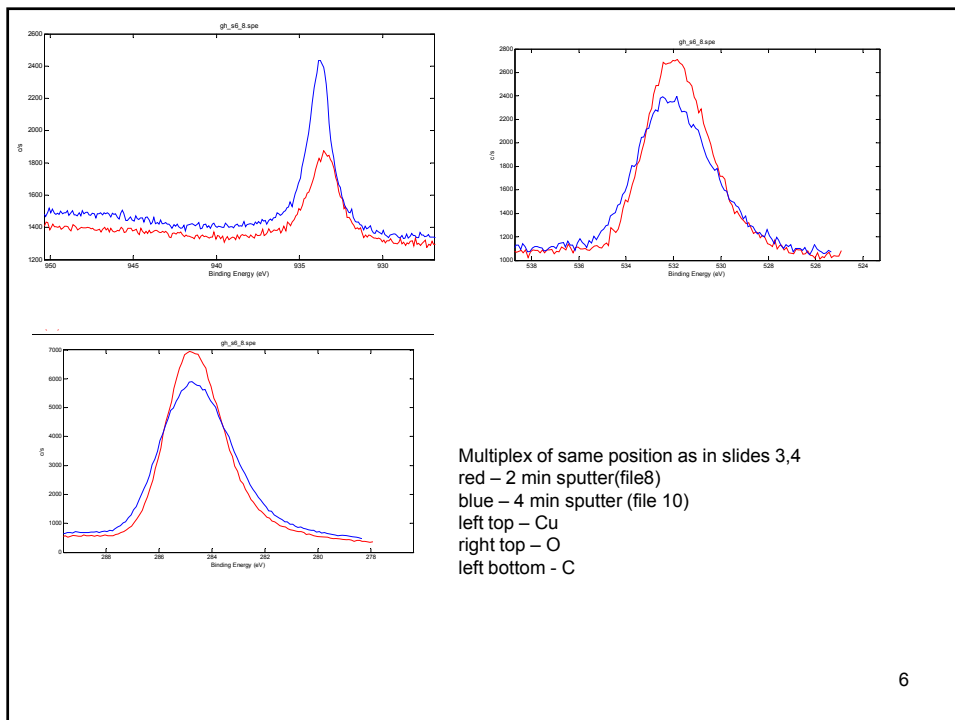
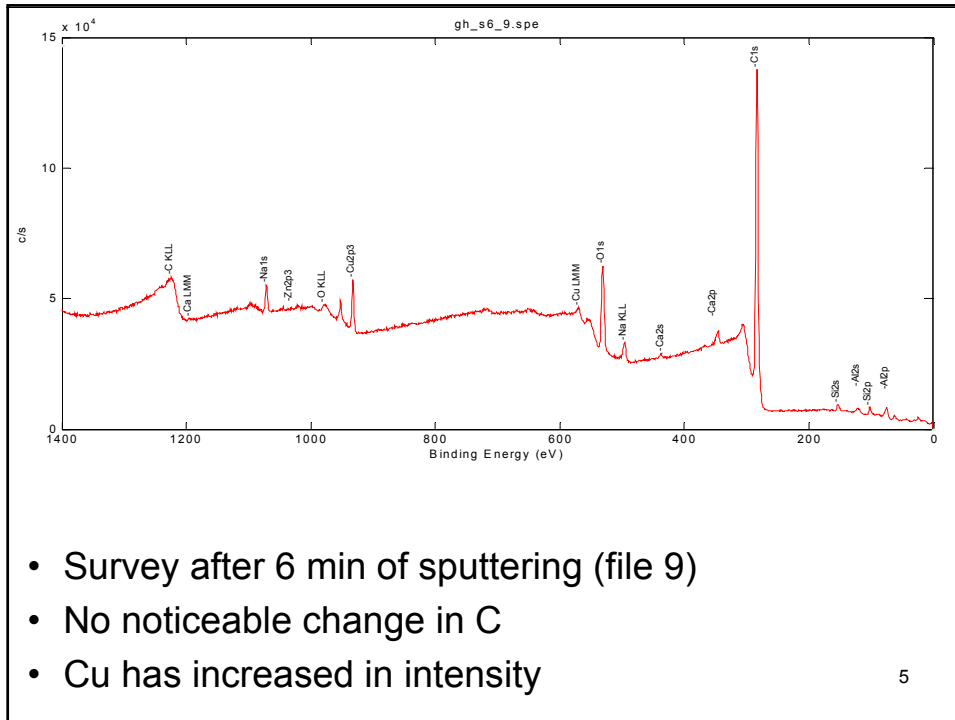
1

Notes

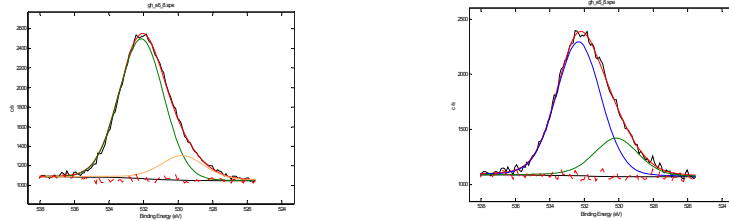
- Spectra were taken in the corners of sample s6
- The sample was not uniformly blackened
- The sputtering was done with Xe⁺ (1kv)
- Sample charged; had to use the neutraliser
- The Al 2s and 2p peaks are in the same position as Cu 3s and 3p peak. However the Cu peaks are very weak compared to the Cu 2p peak

2



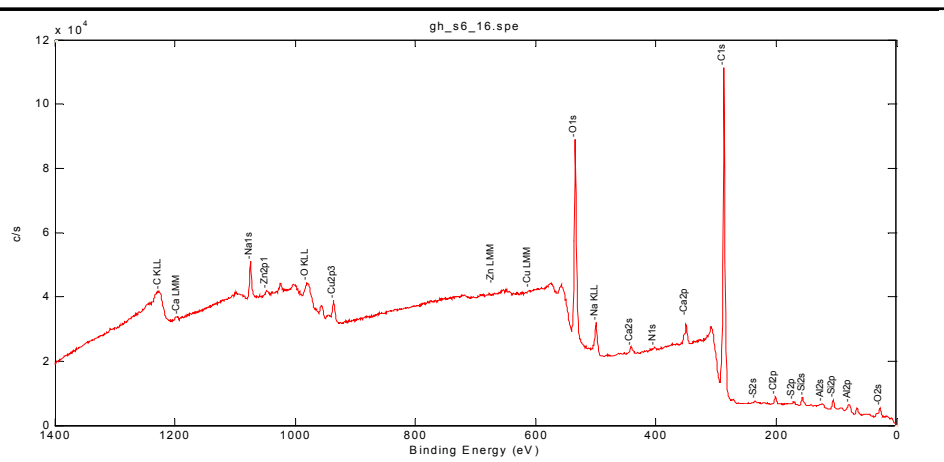


O1s fitted spectra



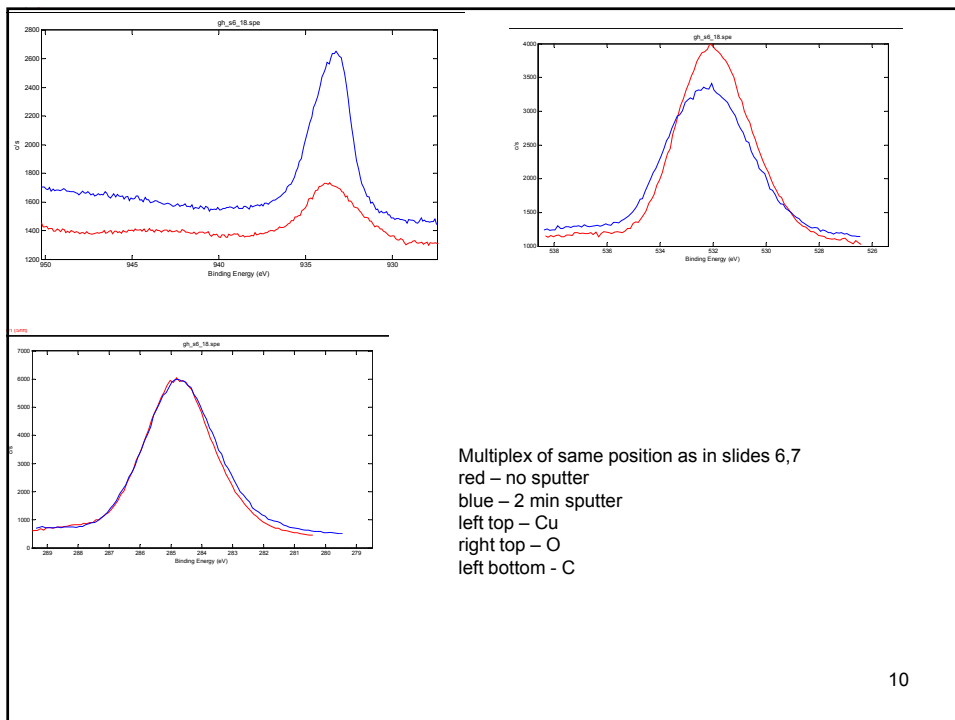
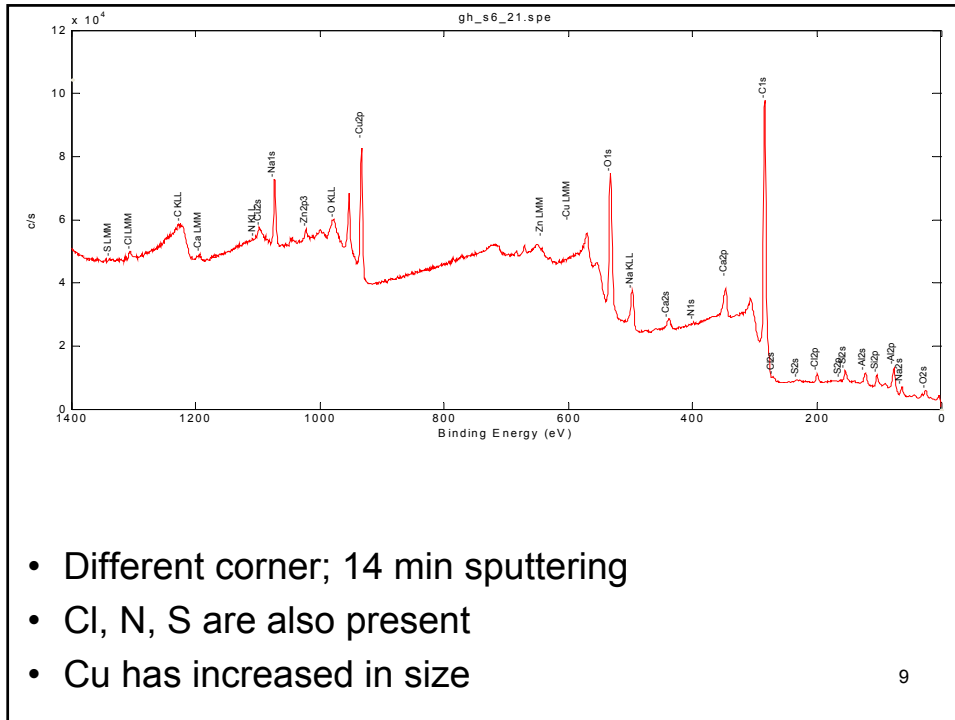
| Sample | Peaks (ev) | Area (cts) |
|---------------------------|------------------------------------|--------------|
| 8 (2 min sputter; left) | 532.1 (hydroxide) 529.8(oxide) | 4697 932 |
| 10 (4 min sputter; right) | 532.3 (hydroxide) 530.2 (oxide) | 4144 1252 |

7

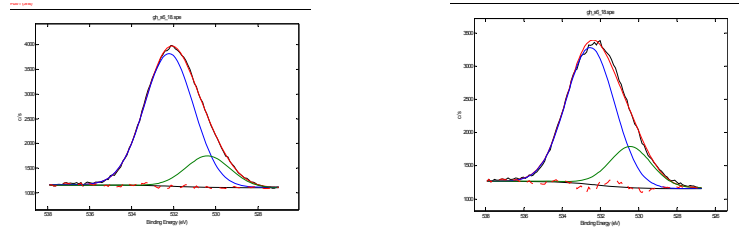


- Different corner; no sputtering
- Cl, N, S are also present

8

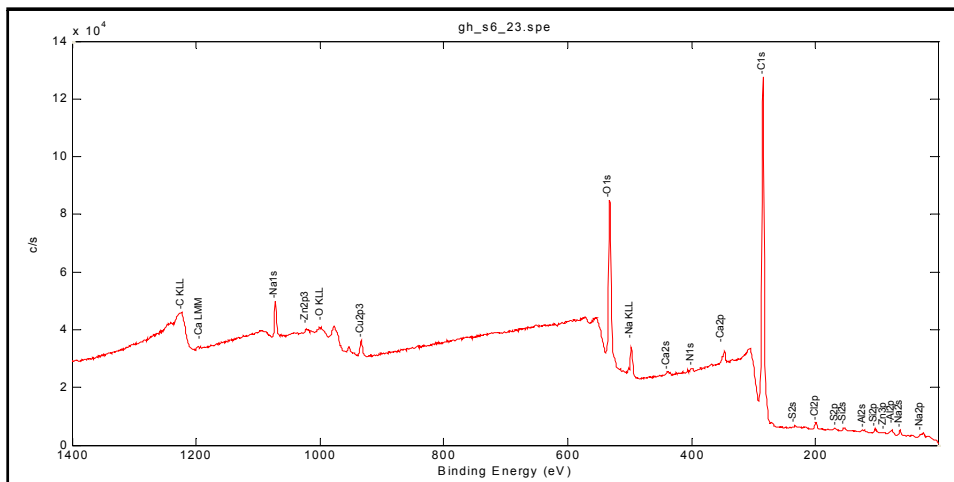


O 1s fitted spectra



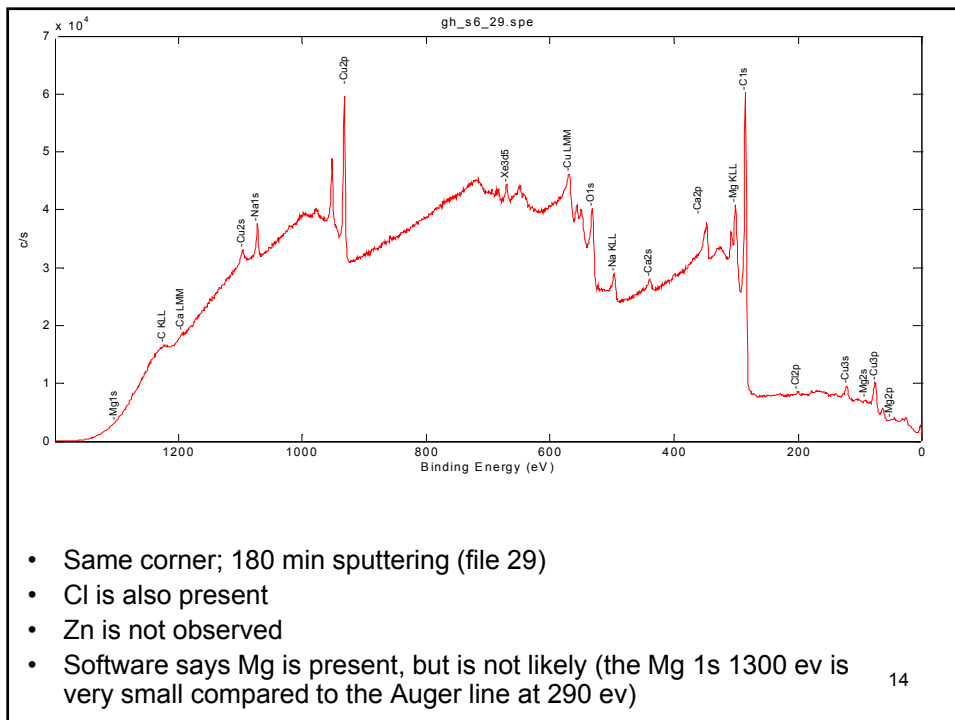
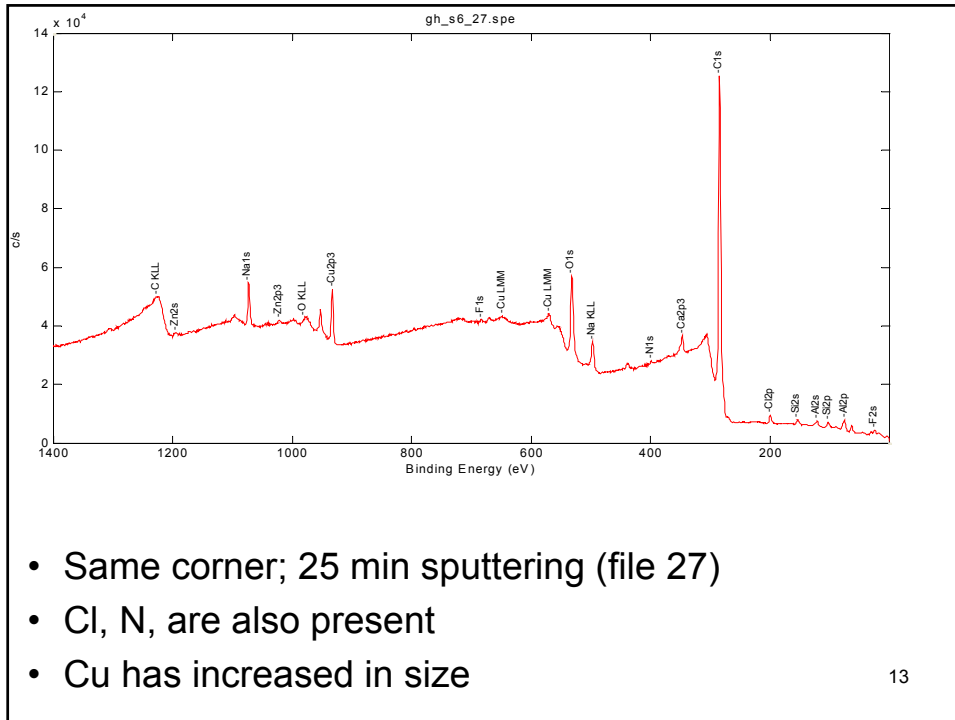
| Sample | Peaks (ev) | Area (cts) |
|---------------------------|------------------------------------|--------------|
| 18 (no sputter; left) | 532.2 (hydroxide) 530.4 (oxide) | 8027 1684 |
| 20 (4 min sputter; right) | 532.5 (hydroxide) 530.4 (oxide) | 6516 1807 |

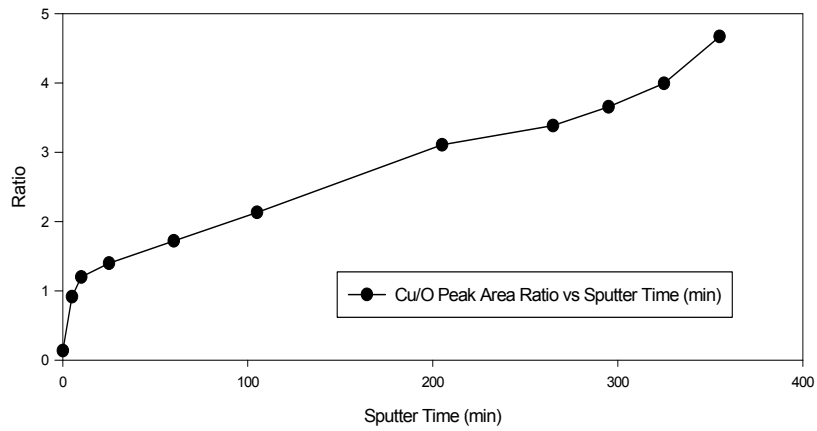
11



- Different corner; no sputtering (file 23)
- Cl, N, S are also present

12





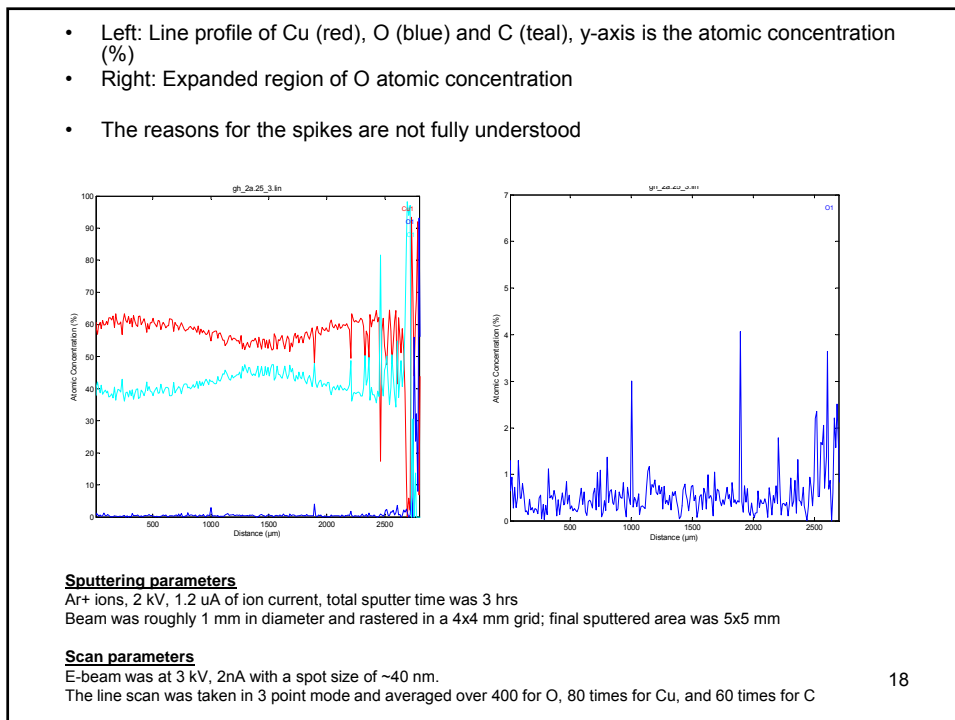
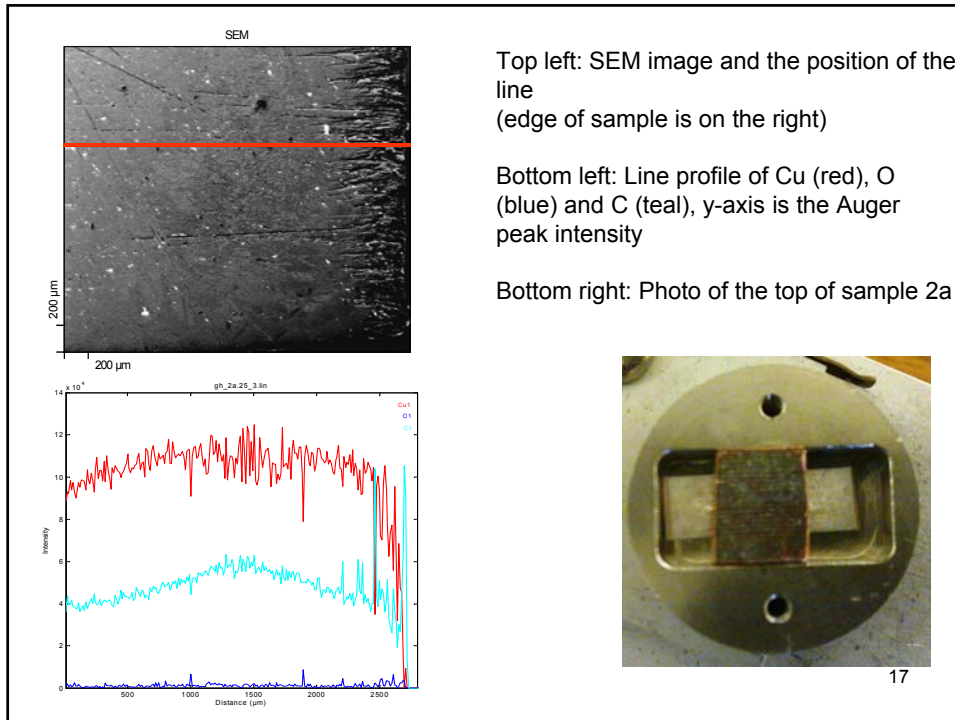
- The peak areas were calculated using a Shirley background on the respective XPS surveys, after different times of sputtering on the same area. Sputter rate is estimated to be ~130 nm / 100 minutes

15

Sample 2a, Auger Electron Spectroscopy (AES)

7 year exposure in Oskarshamn, Sweden

16



Observations

- XPS surveys indicate that the black layer is not uniform, and impurities Si, and Al (and Na and Ca) are likely from clay. Cl, N, and S are sometimes detected in different regions of the black layer
- High resolution O 1s XPS spectra indicate the presence of both copper hydroxide and copper oxide (likely Cu_2O) in the black layer. With no or little removal of the outermost layers by ion sputtering, the hydroxide:oxide ratio is $\sim 5:1$. After 4 minutes of sputtering the ratio is reduced to $\sim 3.5:1$, indicating, as expected, the hydroxide is on top of the oxide.
- Auger line scans to a depth of 2500 μm from the outer blackened surface indicate that oxygen does not penetrate deep into the sample grains (Auger detection limit ~ 0.2 atomic %)