

## Introduction

Aluminum is a widely used metal in common materials such as soda cans, tire rims, roofing and, of course, aluminum foil. It is used often because it is a light, ductile metal; however, like other metals such as iron, it is susceptible to corrosion. Thus, it is important to understand the conditions which promote or deter corrosion and, eventually, develop an environmentally safe coating which prevents corrosion of aluminum.

The rate of the reaction is determined by the other species in the environment. Wei, Lee, and Chen discovered that the spectator ions, ions other than the species participating in the redox reaction, can have a substantial effect on the rate of a reaction, specifically, between a copper(II) salt and aluminum. The trio developed a mechanism which described how corrosion takes place in such a system.

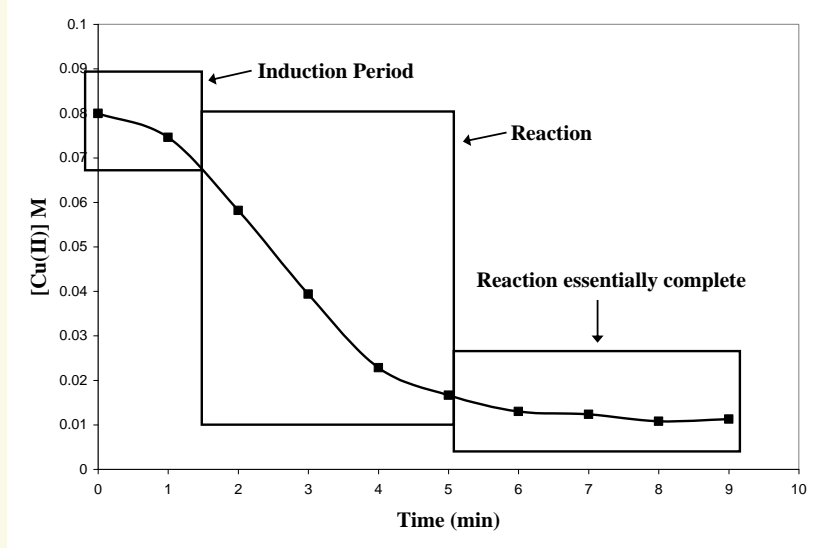
It has been known for some time that aluminum has a natural defense against corrosion; upon contact with air, aluminum is oxidized to form a layer of aluminum oxide ( $\text{Al}_2\text{O}_3$ ) on the surface. This oxide layer is aluminum's protection from corrosion; therefore, the removal of the oxide layer is both the first step and the rate determining step in aluminum corrosion. Wei, Lee, and Chen devised the following mechanism for aluminum corrosion in copper(II) salts: (1) destroy  $\text{Al}_2\text{O}_3$  layer, (2)  $\text{Cu}^{2+}$  diffuses to Al surface, (3)  $\text{Cu}^{2+}$  adsorption, (4) Redox reaction between  $\text{Al}^0$  and  $\text{Cu}^{2+}$ , and (5) desorption and release of  $\text{Al}^{3+}$ . Using this mechanism, Wei, Lee, and Chen determined a rate law for such a reaction. In the rate law, K is the rate constant, A is the area, V is the volume of solution, t is time,  $t_{\text{ind}}$  is the induction time which describes how long it takes to remove the oxide layer. The simplified rate law can exist in two forms: an exponential equation and a linear equation as depicted below.<sup>1</sup>

$$\ln\left(\frac{[\text{Cu}^{2+}]_0}{[\text{Cu}^{2+}]_t}\right) = \frac{KA}{V}t - \frac{KA}{V}t_{\text{ind}}\left[1 - \exp\left(\frac{-t}{t_{\text{ind}}}\right)\right]$$

Exponential Integrated Rate Law

$$\ln\left(\frac{[\text{Cu}^{2+}]_0}{[\text{Cu}^{2+}]_t}\right) = \frac{KA}{V}t - \frac{KA}{V}t_{\text{ind}}$$

Linear Integrated Rate Law



In past research (this group – see table below, and others), copper(II) halides have shown to have a profound effect on the corrosion of aluminum. In fact, corrosion with copper(II) sulfate is about fifty times slower than with copper(II) chloride. Furthermore, addition of dilute concentrations of NaCl to the reaction of copper(II) sulfate and aluminum shows a dramatic increase in the rate of the reaction. **This aspect of the on-going research project highlights efforts to elucidate the interaction of halides with the surface of aluminum during aluminum corrosion, using the copper-aluminum reaction as a model.**

Periodic correlations in acceleration effects have been discovered in this research; bromide causes similar acceleration in aluminum corrosion.

Periodic Table of the Elements																	
1A (1)	2A (2)											3A (13)	4A (14)	5A (15)	6A (16)	7A (17)	8A (18)
1 H	2 He											3 B	4 C	5 N	6 O	7 F	8 Ne
2 Li	3 Be	4 Na	5 Mg	6 Al	7 Si	8 P	9 S	10 Cl	11 Ar								
3 K	4 Ca	5 Sc	6 Ti	7 V	8 Cr	9 Mn	10 Fe	11 Co	12 Ni	13 Cu	14 Zn	15 Ga	16 Ge	17 As	18 Se	19 Br	20 Kr
4 Rb	5 Sr	6 Y	7 Zr	8 Nb	9 Mo	10 Tc	11 Ru	12 Rh	13 Pd	14 Ag	15 Cd	16 In	17 Sn	18 Sb	19 Te	20 I	21 Xe
5 Cs	6 Ba	7 La	8 Hf	9 Ta	10 W	11 Re	12 Os	13 Ir	14 Pt	15 Au	16 Hg	17 Tl	18 Pb	19 Bi	20 Po	21 At	22 Rn
6 Fr	7 Ra	8 Ac	9 Th	10 Pa	11 U	12 Np	13 Pu	14 Am	15 Cm	16 Bk	17 Cf	18 Es	19 Fm	20 Md	21 No	22 Lr	23 Uuo

Salt	Rate Constant (cm/min)	Induction Time ( $t_{\text{ind}}$ )
$\text{CuSO}_4$	$4.7 \times 10^{-4}$	7.9 min
$\text{CuCl}_2$	0.15	1.4 min
$\text{CuBr}_2$	0.11	1.9 min

(from Ref. 3)

## Experimental

Solutions of copper(II) bromide and copper(II) chloride were made at a concentration of 0.10 M. The samples were prepared by exposing a known area on the aluminum foil to copper(II) bromide for a known amount of time. After the allotted time, the foil was rinsed five times with 1 mL aliquots of Nanopure water and left to dry. Samples treated with copper(II) chloride were examined via Scanning Electron Microscopy with Energy Dispersive X-ray Spectroscopy (SEM-EDS) by FEI Co. on a Quanta x50. Samples treated with copper(II) bromide were examined for X-ray fluorescence (XRF) at Brookhaven NSLS beamline X-26A, which is suitable for detecting elements heavier than argon. Samples were mounted on XRF tape, centered using light microscopy, then flyscans of areas of interest at either copper X-ray edge or bromine X-ray edge energies were completed.

## Conclusion

All of the copper(II) halides were investigated; however, due to solubility and stability issues, only the chloride and bromide species could be studied. Copper(II) fluoride aqueous solutions spontaneously precipitate a mixed hydroxide-fluoride, and copper(II) iodide aqueous solutions are unstable with respect to redox disproportionation to copper(I) iodide and iodine. Both XRF and SEM-EDS scans demonstrate the concentration of halides at the margins of corrosion sites. This may be due to the interaction of halide ions with surface aluminum oxide, thus weakening the adherence and coherence of the oxide layer. This would expose aluminum metal to the solution, which would lead to the redox reaction, thus corrosion.

## References

1. Corrosion of Aluminum and Aluminum Alloys; Davis, J. R., Ed.; ASM International: Materials Park, OH, **1999**, 313 pp, Chapter 2.
2. Wei, WY, Lee, C. and Chen, H.J. "Modeling and Analysis of the Cementation Process on a Rotating Disk." *Langmuir* **1994**, *10*, 1980-1986.
3. Sobel, Sabrina G. and Cohen, Skyler. "Spectator Ions ARE Important: A Kinetic Study of the Cu-Al Displacement Reaction." *Journal of Chemical Education*, **2010**, *87*(6), 616–618.

## Acknowledgements

The authors wish to acknowledge the collaborative participation of Freeport High School students, mentored by Dr. Vincent Pereira, District Coordinator for Science, in preparation of samples for analysis at Brookhaven National Labs. Special thanks to Brookhaven's National Synchrotron Light Source, Randy Smith at the U2 beamline, Sue Wirick at the X26A beamline, Scott Bronson, Director of the InSynC program, Lisa Miller for organizing our visit, and the InSynC Program for giving us the opportunity to use Brookhaven's resources. Special Thanks to FEI Co., who donated time and expertise to demonstrate utility of this method for analyzing this type of sample for an NSF-MRI grant application. Partially funded by Hofstra University Provost's Office (student summer research stipend) and HCLAS Faculty Research and Development grant.

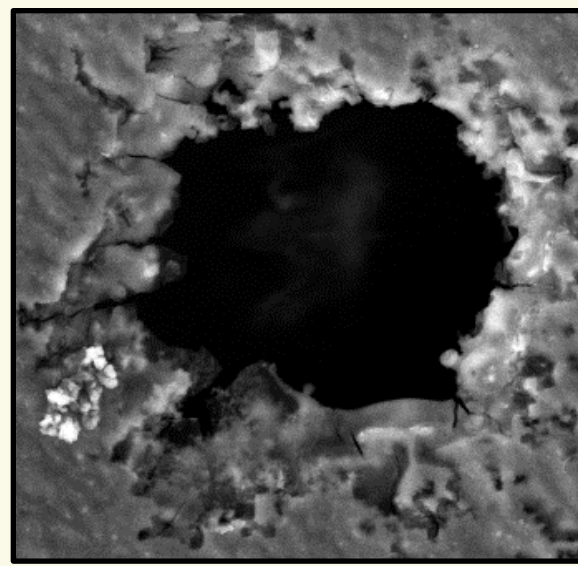
## Results

### Experimental Set-up and Visible Corrosion

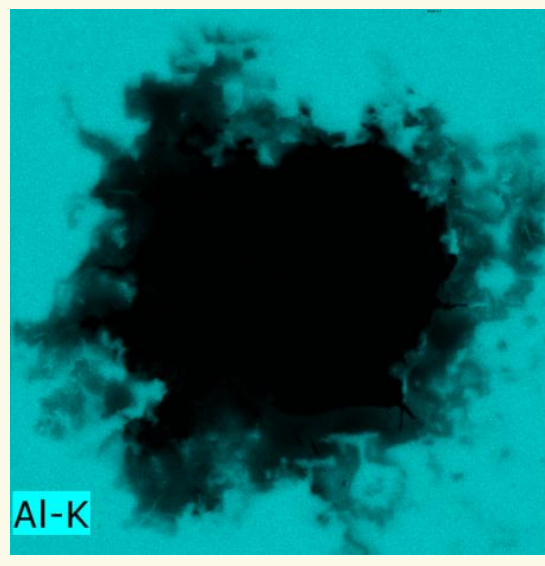


Above Left: One drop of 0.10 M  $\text{CuCl}_2(\text{aq})$  on Al foil photographed immediately after. Note appearance of  $\text{H}_2$  bubbles due to acid side-reaction. Above Right: Reaction after one minute. Note additional dark spots due to Cu(s) deposition.

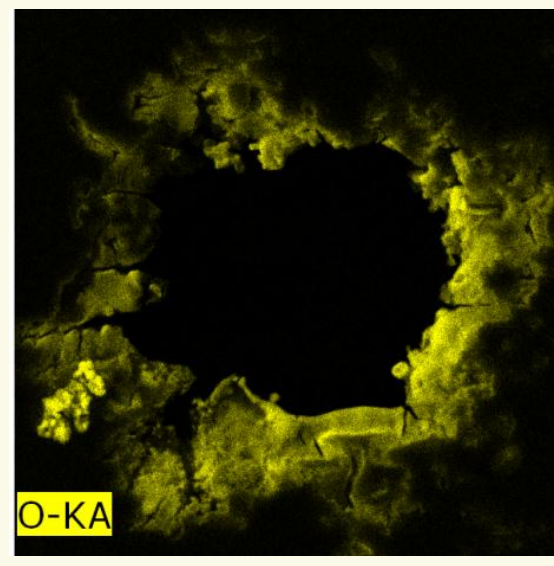
### SEM-EDS of 3.0 min $\text{CuCl}_2$ (aq) Sample



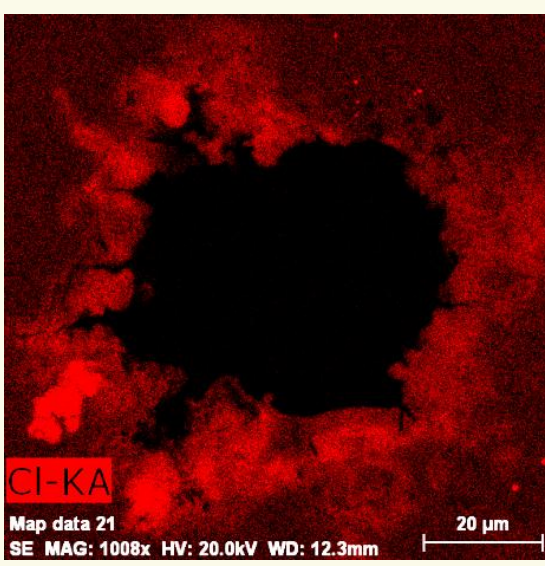
A



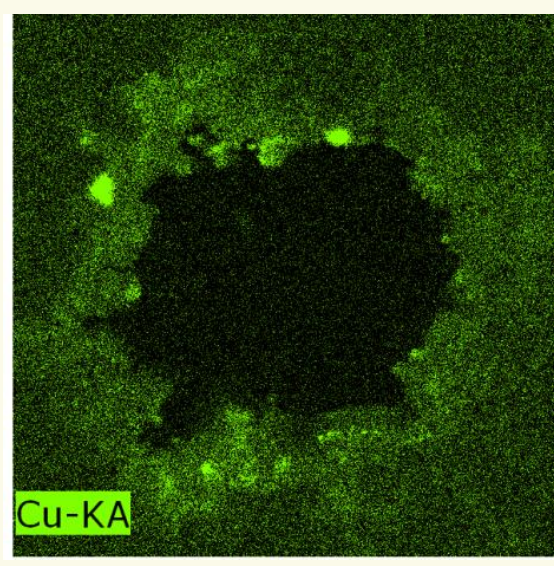
B



C



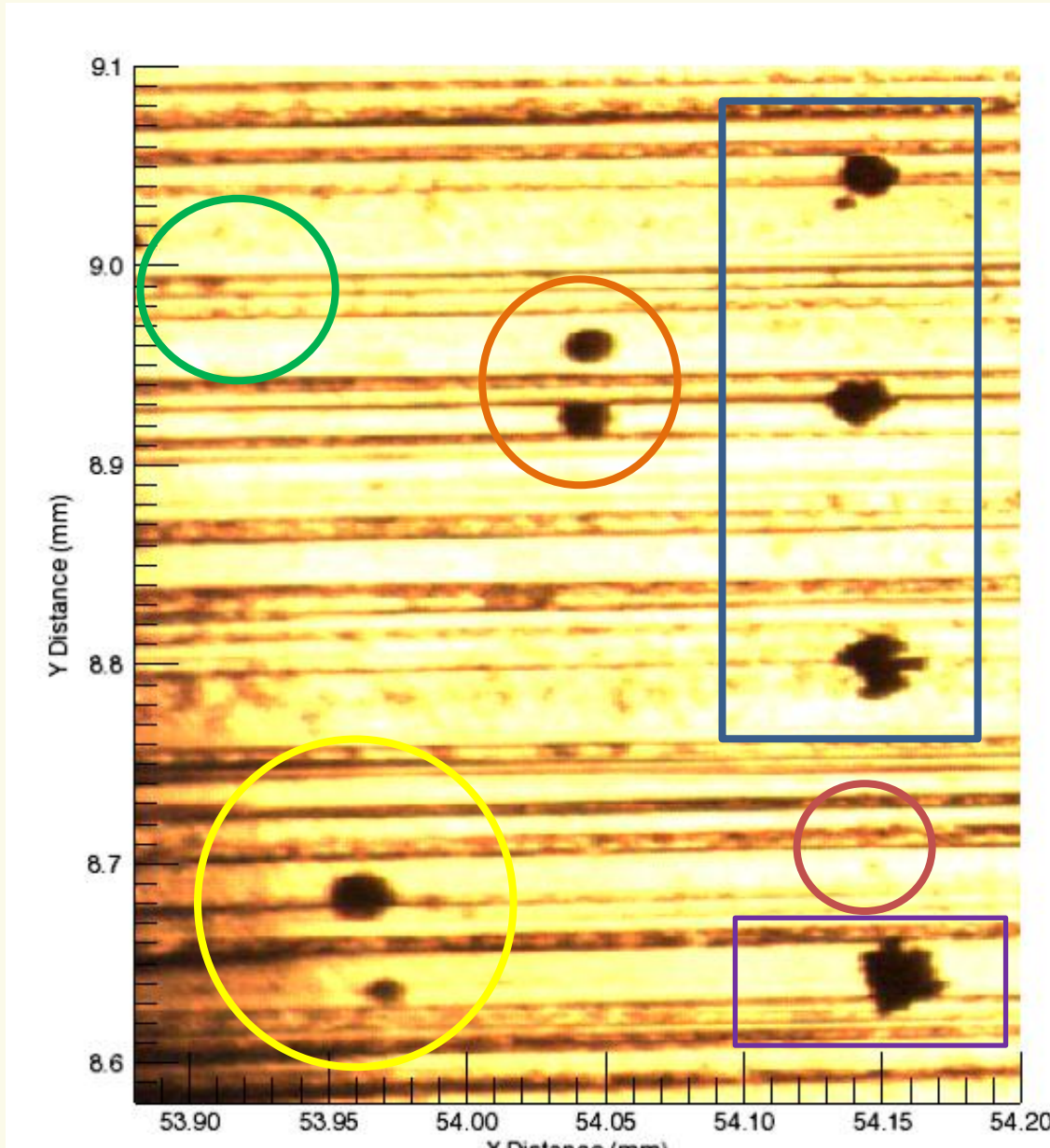
D



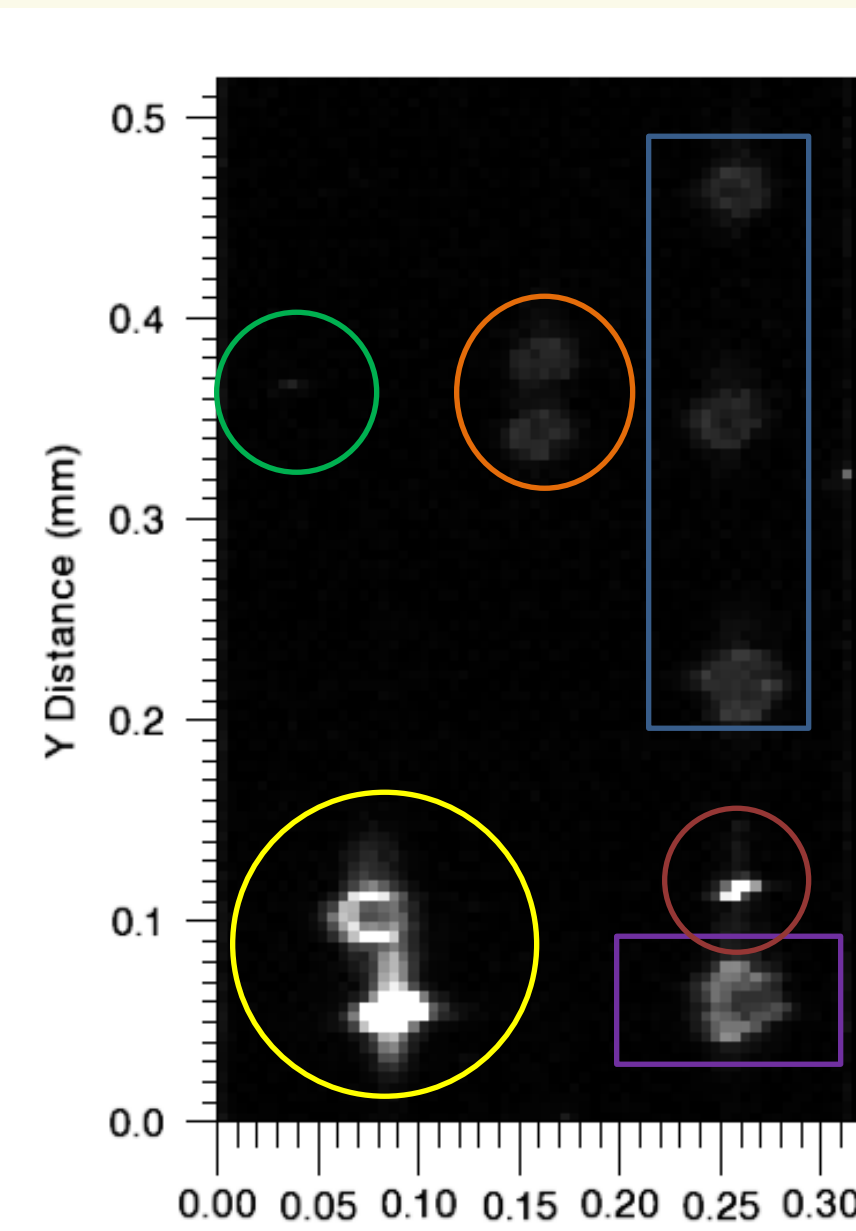
E

A: SEM of a corrosion hole at 20 KeV. B – E: EDS for elements Al, O, Cl and Cu, respectively. Co-location of O and Cl is evident in the lower left quadrant, lending credence to the idea that Cl<sup>-</sup> interacts with the surface  $\text{Al}_2\text{O}_3$  layer. Cu deposition is minimal since this is a hole through the Al foil.

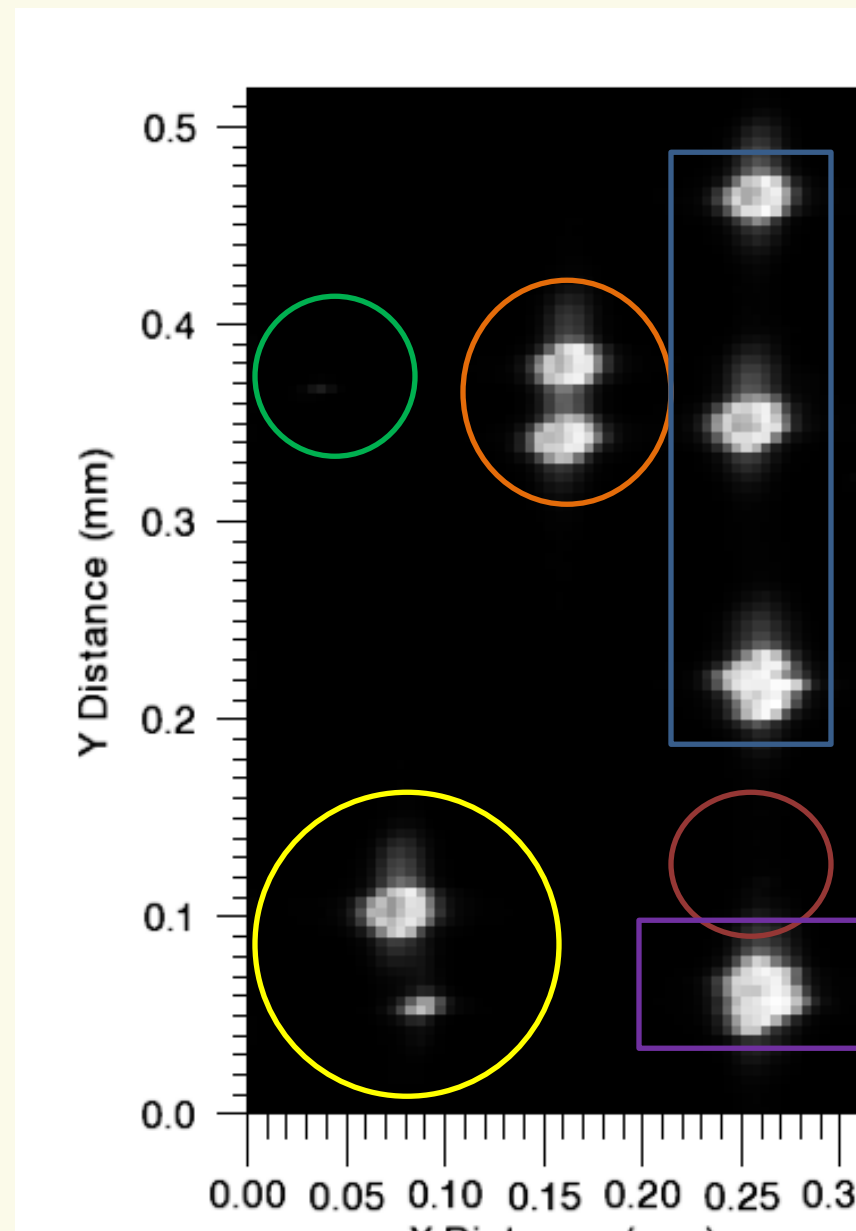
### Surface Studies Using Brookhaven NSLS X-Ray Fluorescence X-26A



1A

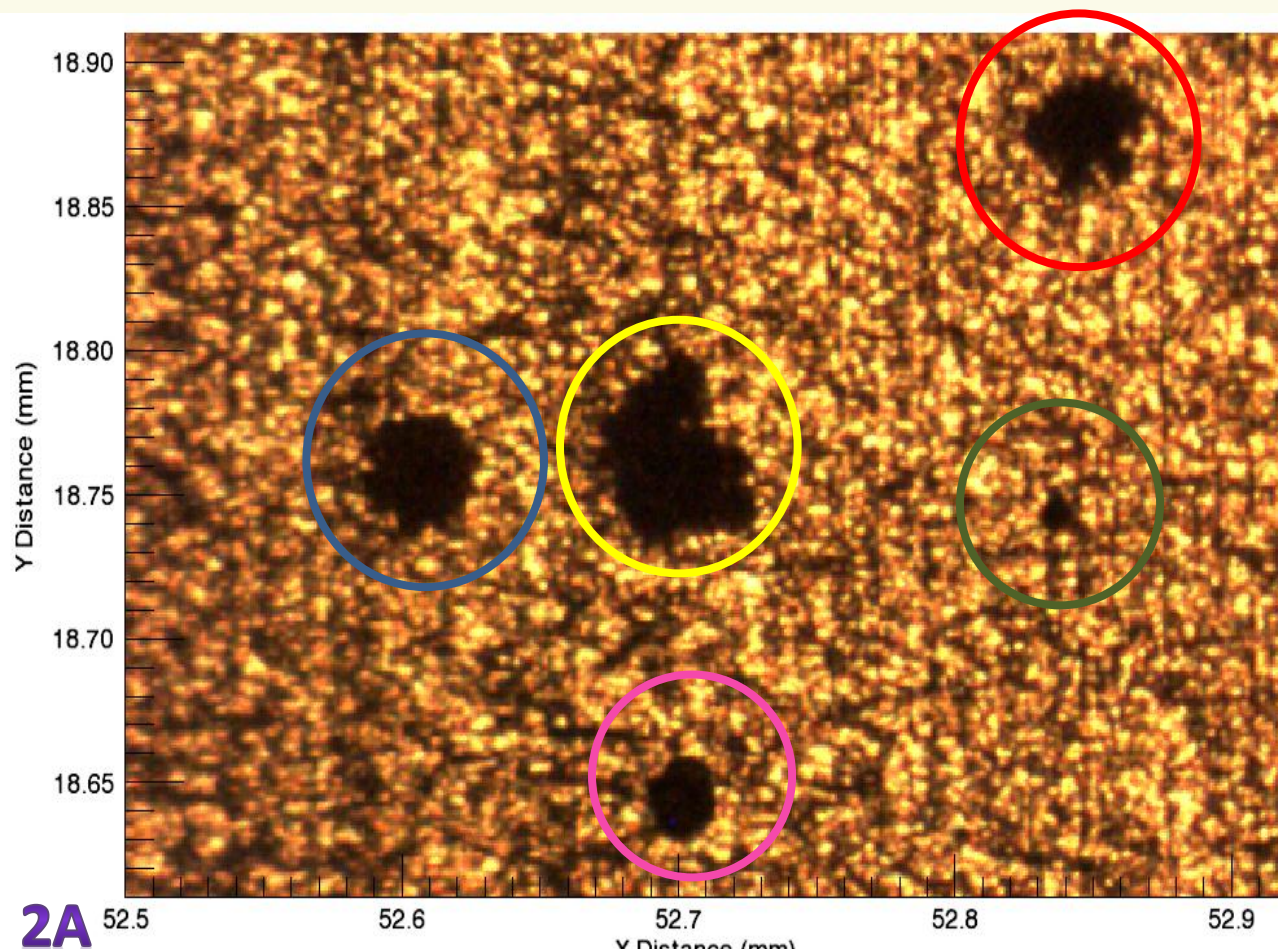


1B

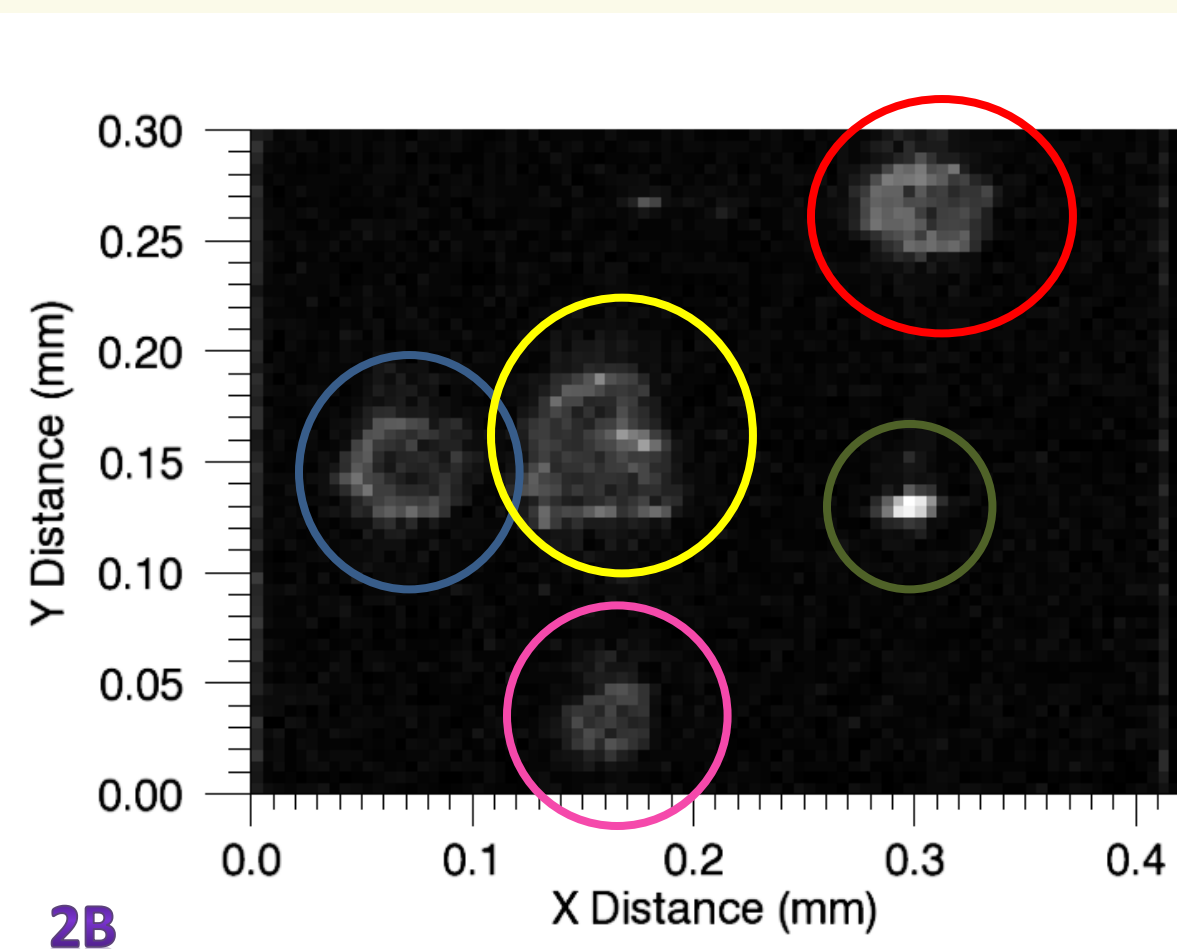


1C

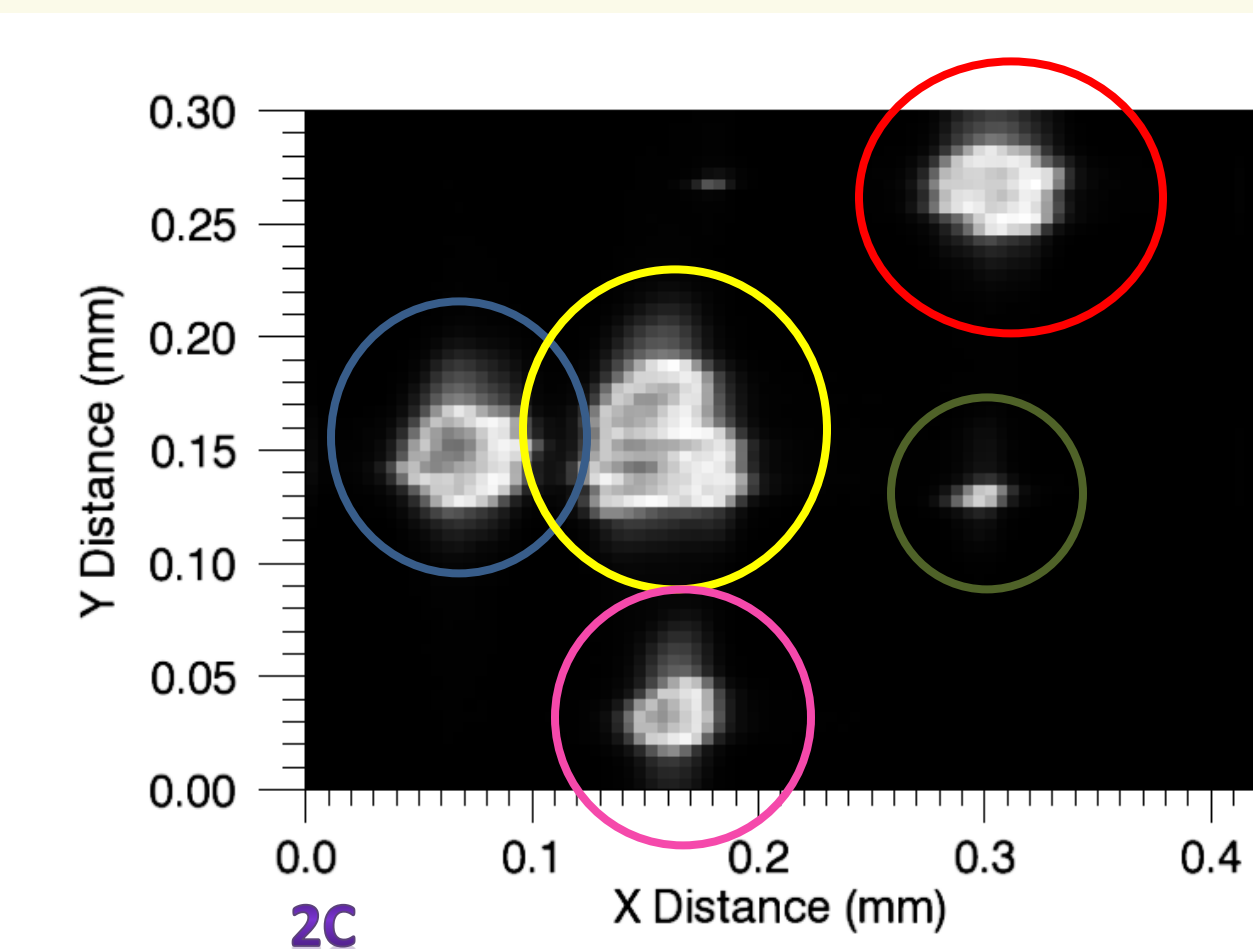
**Figure 1: Aluminum treated with 0.1 M  $\text{CuBr}_2$  for 1.5 minutes.** **1A:** A visible image of aluminum foil which shows well defined corrosion pits and developing corrosion pits. **1B:** XRF image depicting bromide incorporation into the aluminum surface. **1C:** XRF image depicting copper incorporation into the aluminum surface. One striking observation can be found in the red circles. Figure 1B shows intense bromide adsorption and, in the same position, in Figure 1C there is no evidence of copper incorporation, indicative of bromide incorporation before copper deposition.



2A



2B



2C

**Figure 2: Aluminum treated with 0.1 M  $\text{CuBr}_2$  for 3.5 minutes.** **2A:** A visible image of aluminum foil which exhibits both growing and defined corrosion pits. **2B:** XRF image depicting bromide incorporation into the aluminum surface. **2C:** XRF image depicting copper incorporation into the aluminum surface. The green circle shows both intense bromide and copper incorporation into the surface, which suggests that the incorporation of bromide and copper initially can occur together. After significant pit development, bromide intensity is much lower whereas copper intensity is high.