Exploring the Use of Covellite as a Proxy for Corrosion of Native Copper by Sulphur Reducing Bacteria (SRB)

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➢ Thank you to **Ivan Barker** and **Surface Science Western** for helping with the carbon coating and optical scan procedure

Outline

The NWMO Deep Geological Repository

- Spent nuclear fuel rods contain several potentially harmful radioactive isotopes which must be isolated until they naturally decay away over thousands of years.

- Canada must find a way to safely isolate spent nuclear fuel produced over the last few decades, and future fuel since nuclear energy will play a role in transitioning from a carbon economy

- A Deep Geological Repository (DGR) is an underground facility designed to isolate spent nuclear fuel from the environment for ~ 1 million years.

(from Canadian Nuclear Safety Commision, 2020)

The Nuclear Waste Management Organization (NWMO) is proposing to construct one of these repositories ~500m below ground in Ontario where copper-coated (3mm) cannisters containing spent fuel rods and pellets are encased in bentonite clay (from weathered, 'greasy when wet', volcanic ash beds)
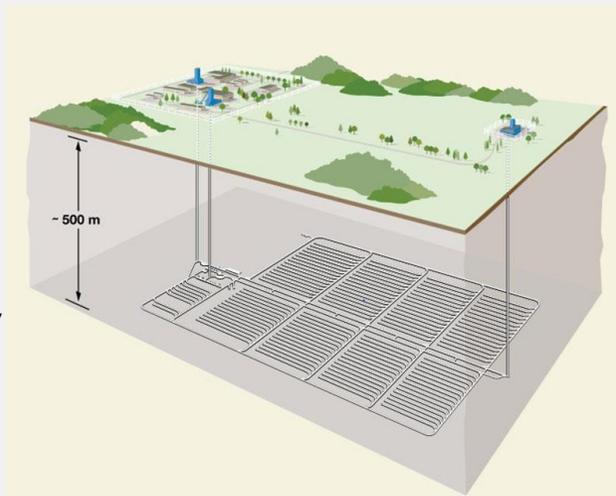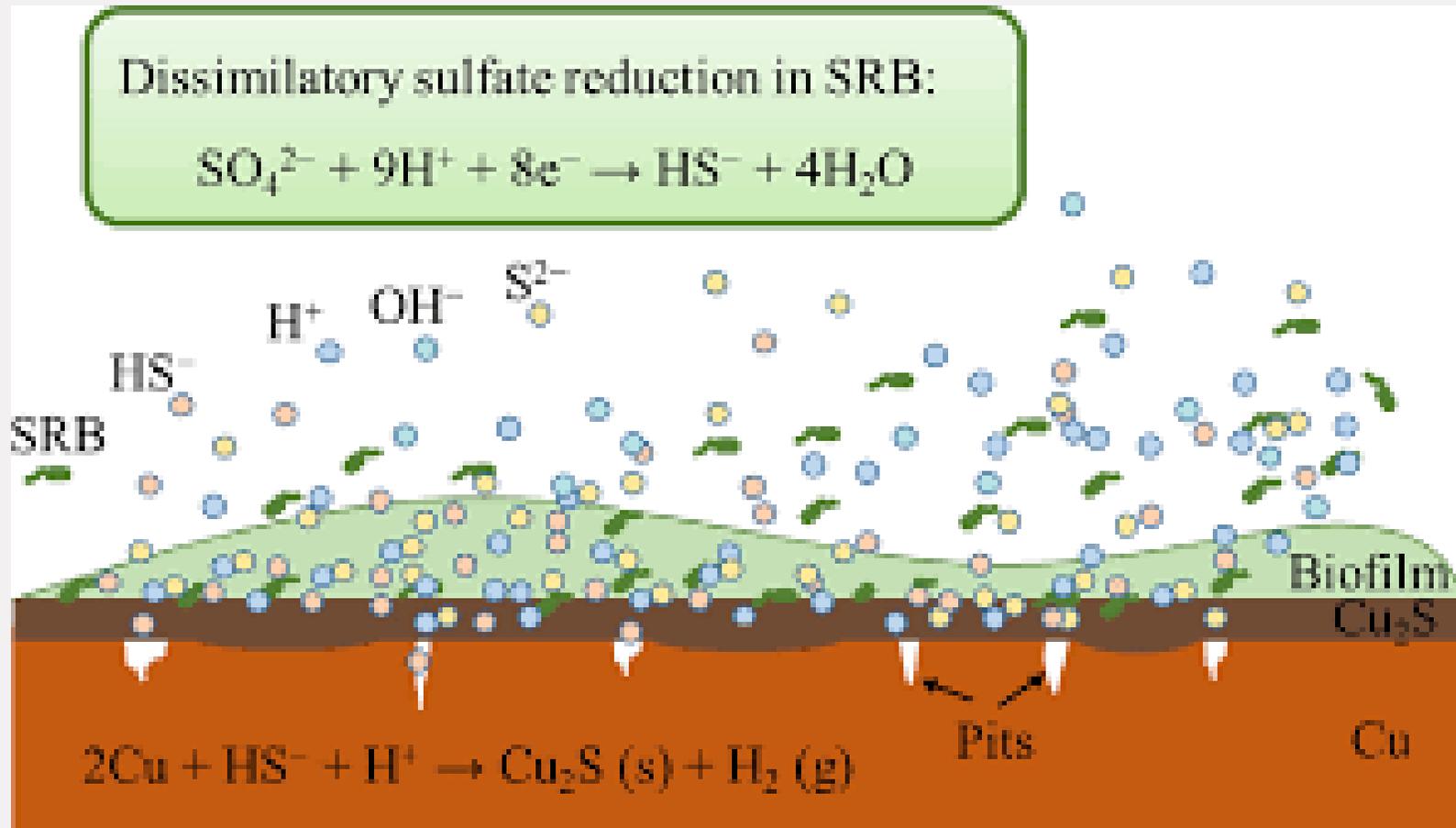
1. Background and Motivation

Copper was selected as a coating because it exhibits very slow rates of corrosion; but will it be slow enough? Experiments over a million years are not feasible BUT we can learn from ancient copper. A type of natural bacteria in DGR levels of the crust can speed up corrosion, did this happen in Ontario crust? Did bacteria affect ancient copper?

Sulphur Reducing Bacteria – how they work

Dissimilatory sulfate reduction in SRB:

$$SO_4^{2-} + 9H^+ + 8e^- \rightarrow HS^- + 4H_2O$$

$$2Cu + HS^- + H^+ \rightarrow Cu_2S\,(s) + H_2\,(g)$$

(from Dou et al., 2019)

Covellite as SRB biomarker

(from Tornos et al., 2018)

STUDIES SHOW EVIDENCE OF COVELLITE (CUS) EXCLUSIVELY IN POCKETS WERE MICROBES RESIDED, LEADING SCIENTISTS TO CONCLUDE THERE IS "CLOSE ASSOCIATION BETWEEN THE MICROBIAL AGGREGATES AND COVELLITE"
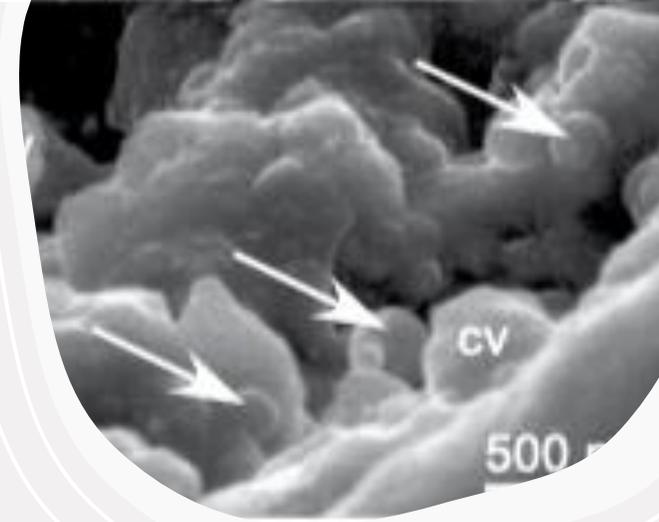
THEREFORE, COVEL LITE CAN BE TREATED AS A BIOMARKER FOR SULPHATE REDUCING BACTERIA

IN THIS STUDY, WE EXPLORED THE QUESTION: **CAN WE FIND EVIDENCE OF COVELLITE ON OUR NATIVE COPPER SAMPLES TO SEE IF THE SAMPLE HAD COME IN CONTACT WITH SULPHATE REDUCING BACTERIA?**

2. Materials

Lake Superior

Keweenaw Peninsula

Samples showing visible signs of secondary minerals/ alteration around copper (blue and green minerals) were selected for analysis for covellite (CuS); both samples came from the Keweenaw Peninsula

Covellite (Reference)

➢ Kennecott Mine, AK, USA

Sample K21-12A

➢ Osceola Mine, MI, USA
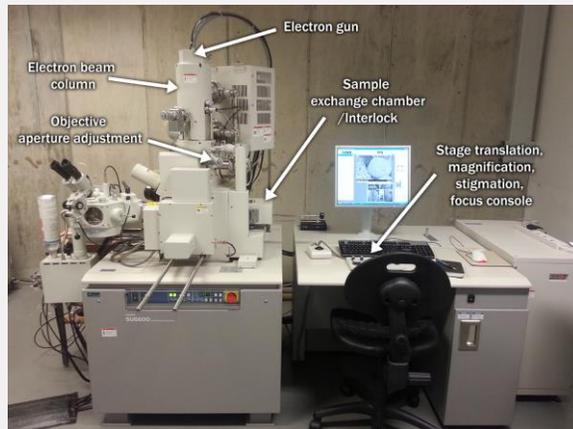

Sample K21-15

➢ Phoenix Mine, MI, USA

Methods



Sample Preparation

Samples were cut using a Buehler saw into a half-a-cm slab which was mounted onto epoxy; it was then polished, and carbon coated

EDS

The SEM was a Hitachi SU6600. First, we performed image registration using a Surface Map made at Surface Science Western; after that we set up an automated scan with the Aztec software from Oxford Instruments and took an SEM EDS map for the surface.

Following the completion of the scans, we ran the montage function to create a stitched image for EDS mapping and afterwards we used the autophase map function to find automatically selected phases the Aztec would fill out

EBSD

Samples were set onto a pre-tilted 70-degree holder, and loaded into the SEM; mapping was controlled by the Aztec software which was then exported for the post processing of the data

3. Methods

EDS = (X-ray) Energy Dispersive Spectroscopy; EBSD =Electron Backscatter Diffraction

Technique			
SEM-EDS	Y	Y	Y
SEM-EBSD	N	Y	Y

Covellite (Reference)

➢ Kennecott Mine, AK, USA

Sample K21-12A

➢ Osceola Mine, MI, USA

Sample K21-15

➢ Phoenix Mine, MI, USA

Covellite Reference Sample
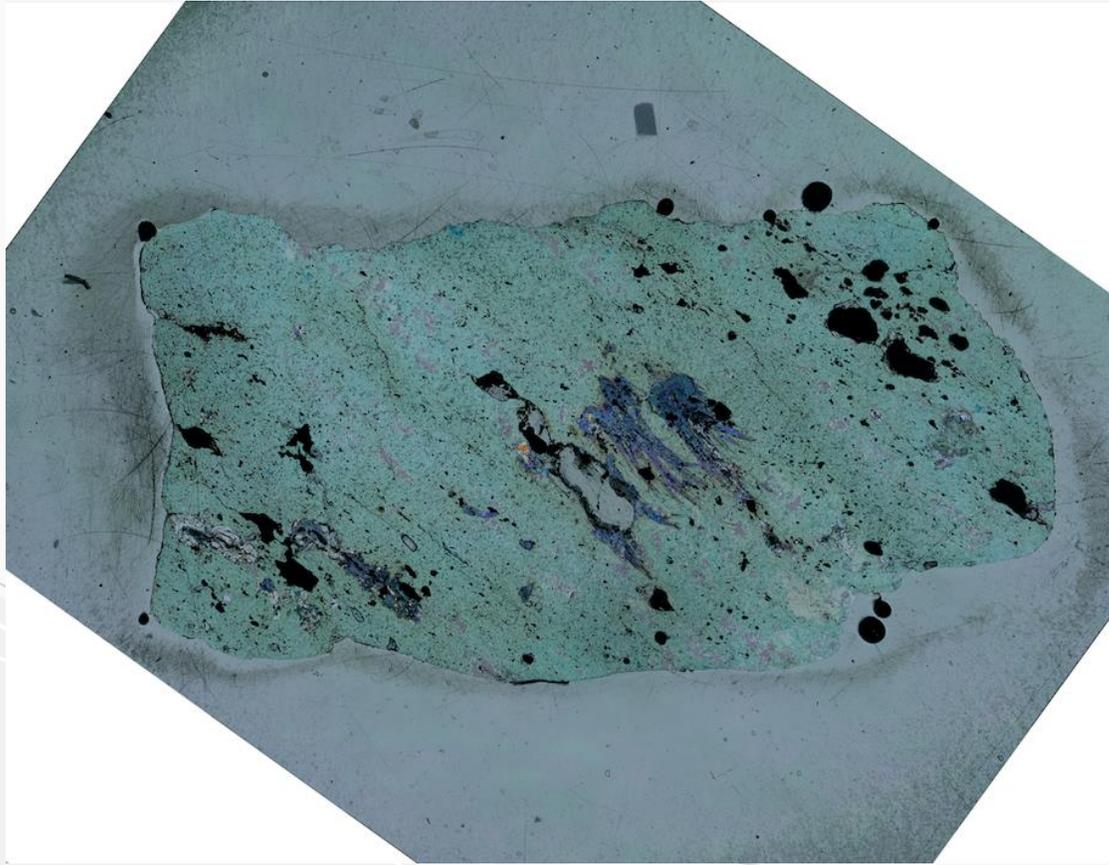
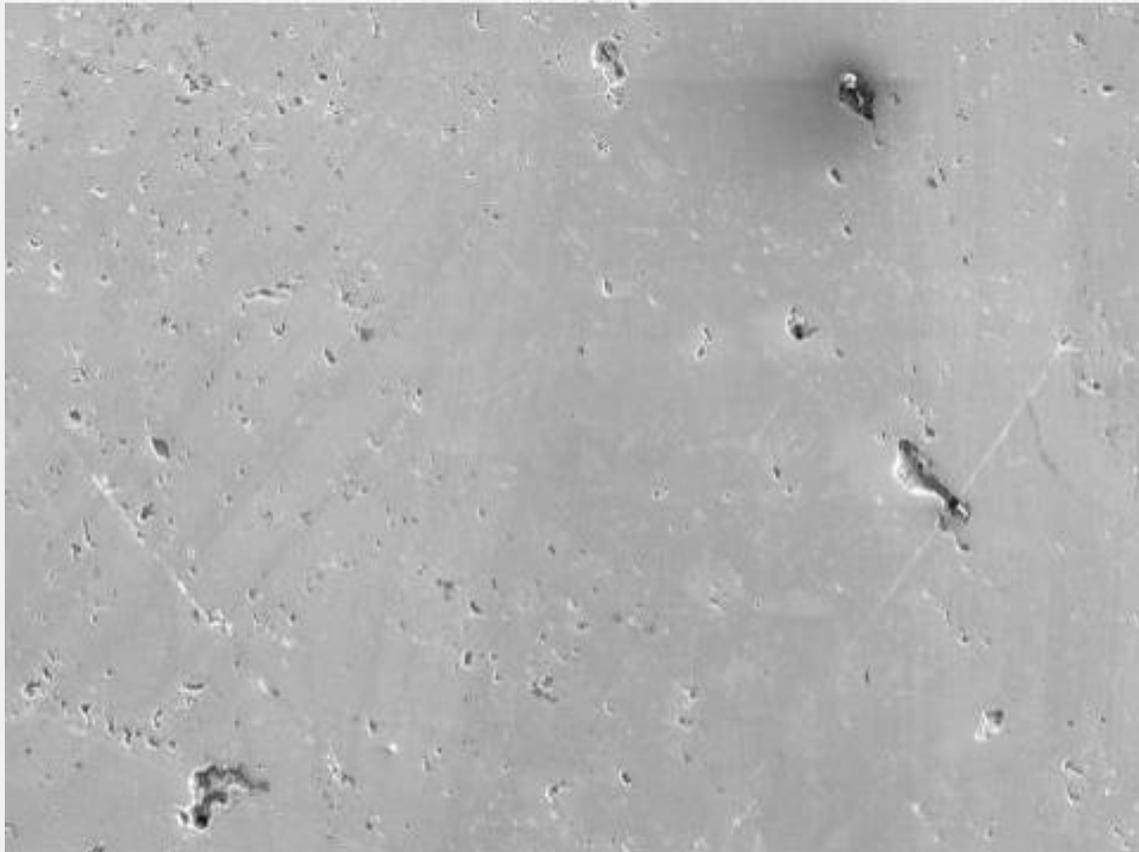Optical Scaled Image   5MM   EDS Image
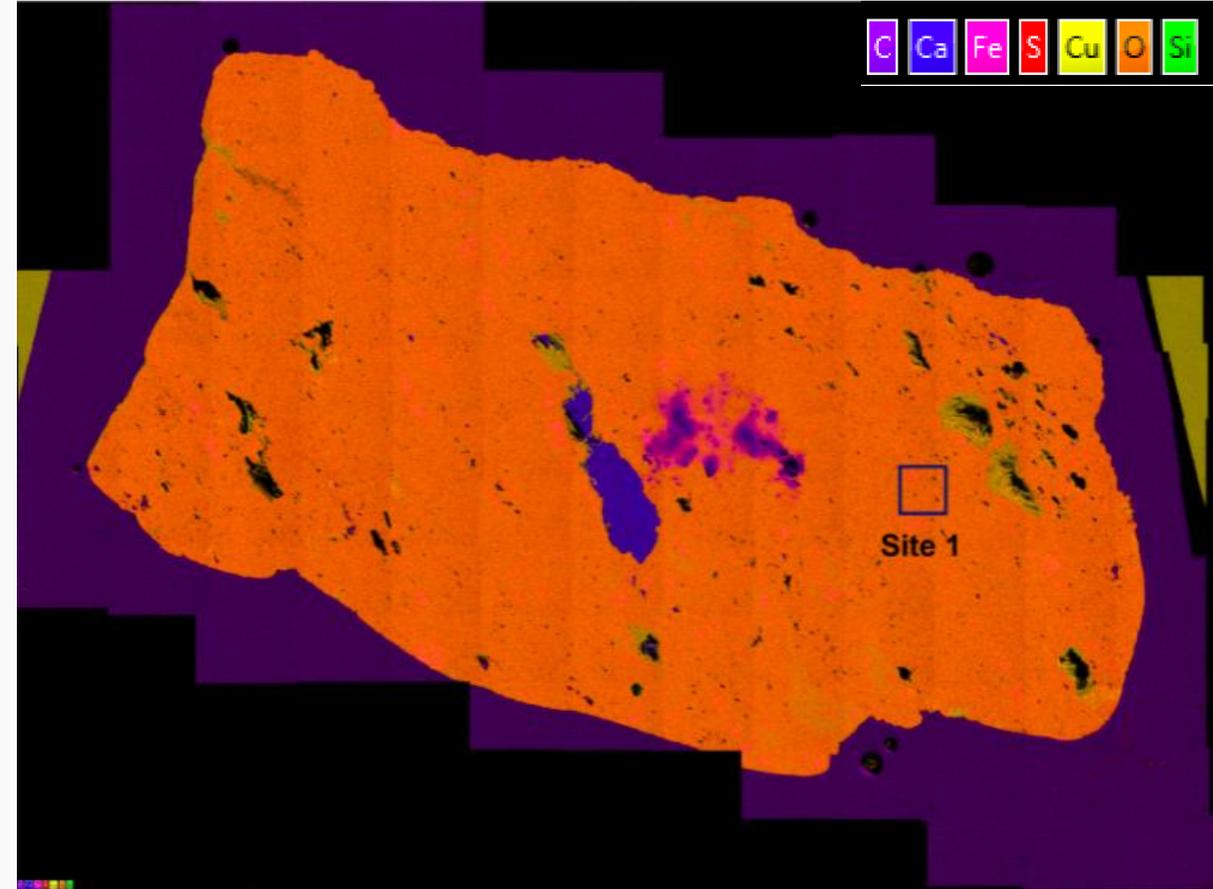
Covellite(CuS): Site 1

Secondary Electron Image

Fe S Cu O Si

500μm
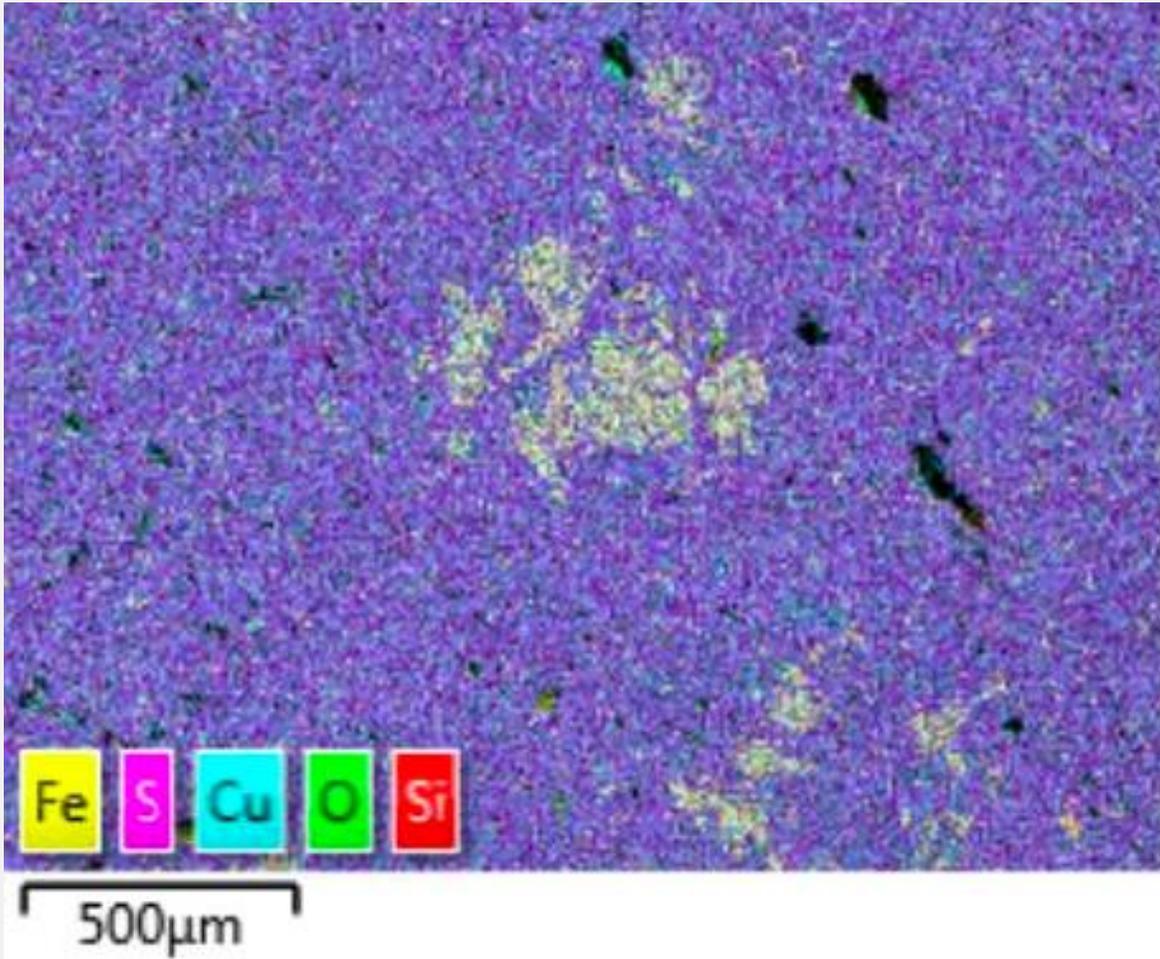
EDS mapping
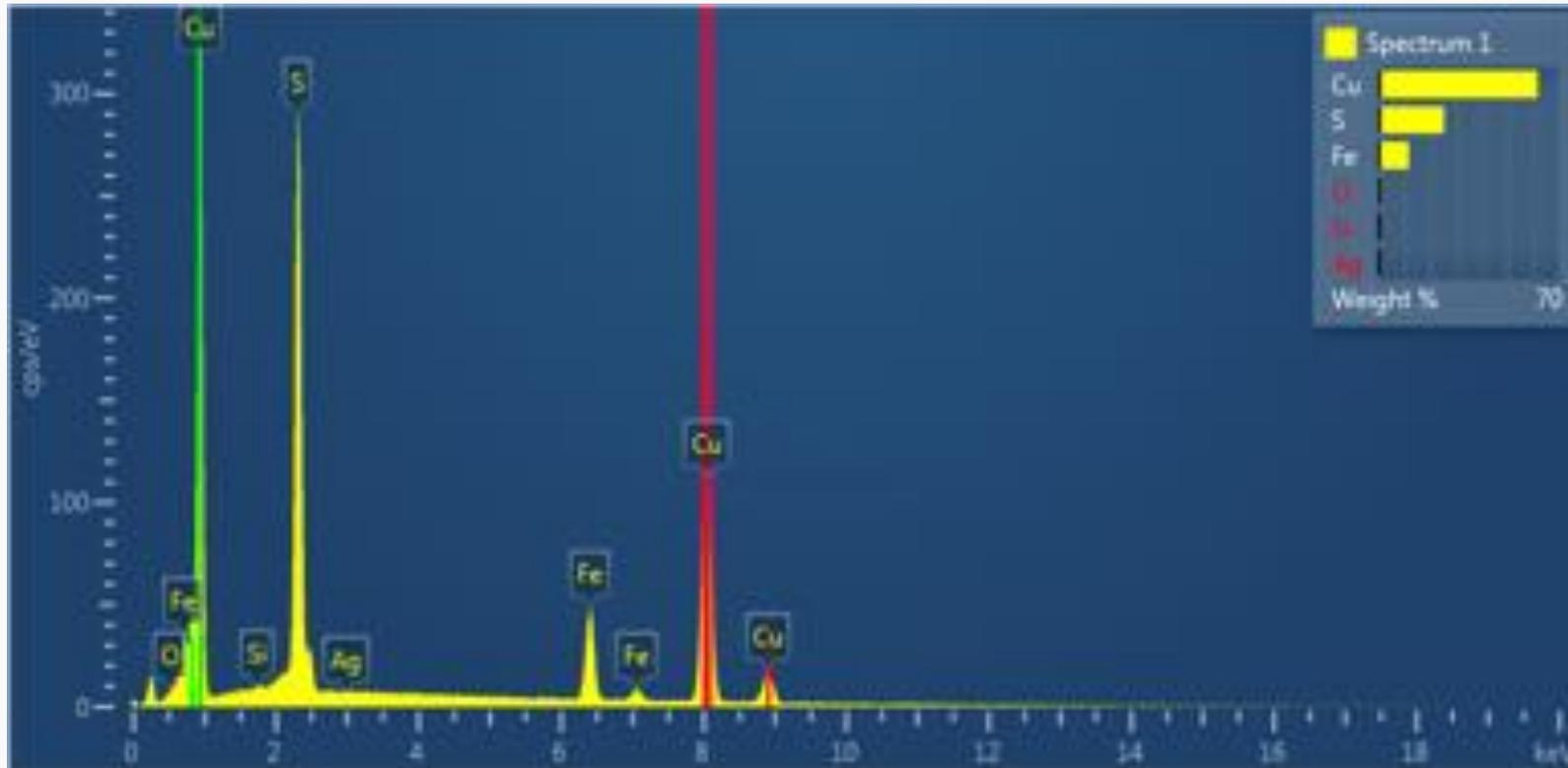
Covellite(CuS): Site 1 EDS Spectrum

Sample K-21-12A

Optical Stitched Image
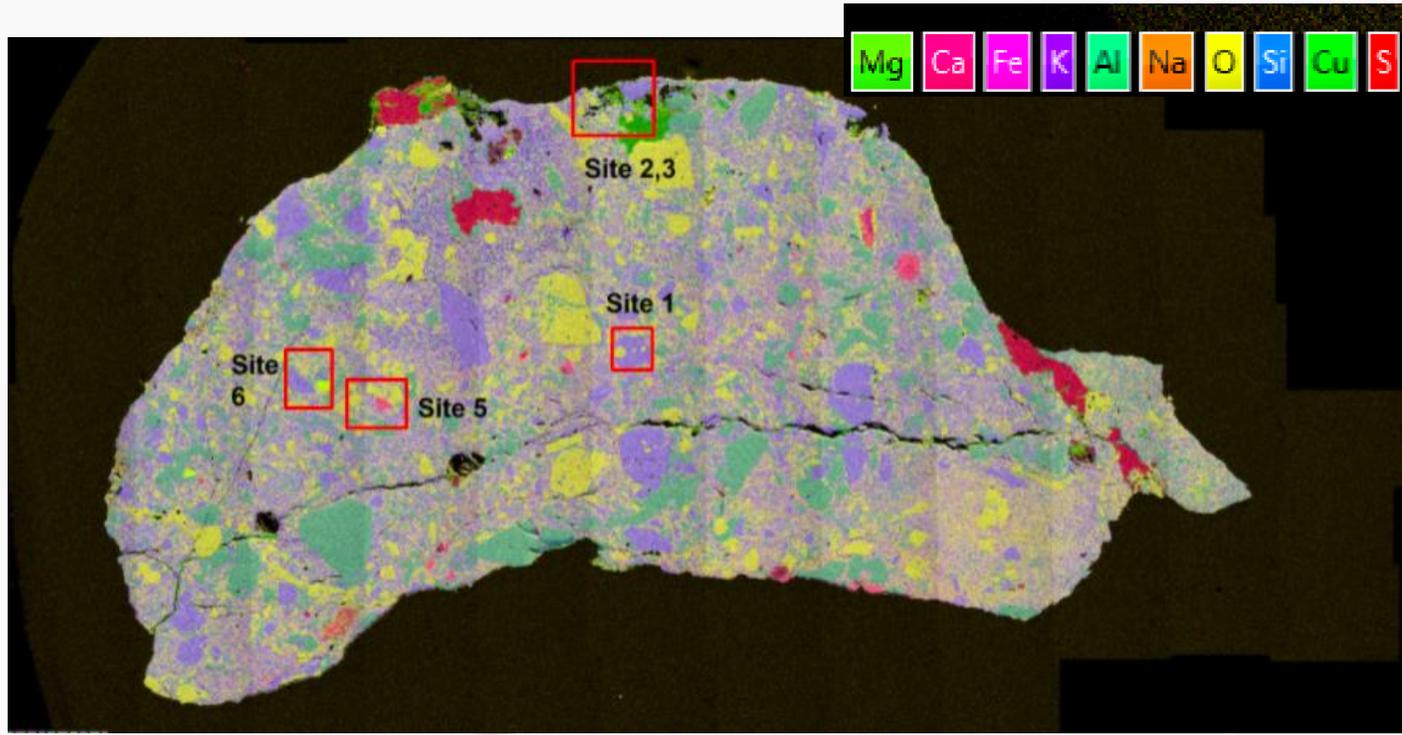
EDS Map showing analysis sites

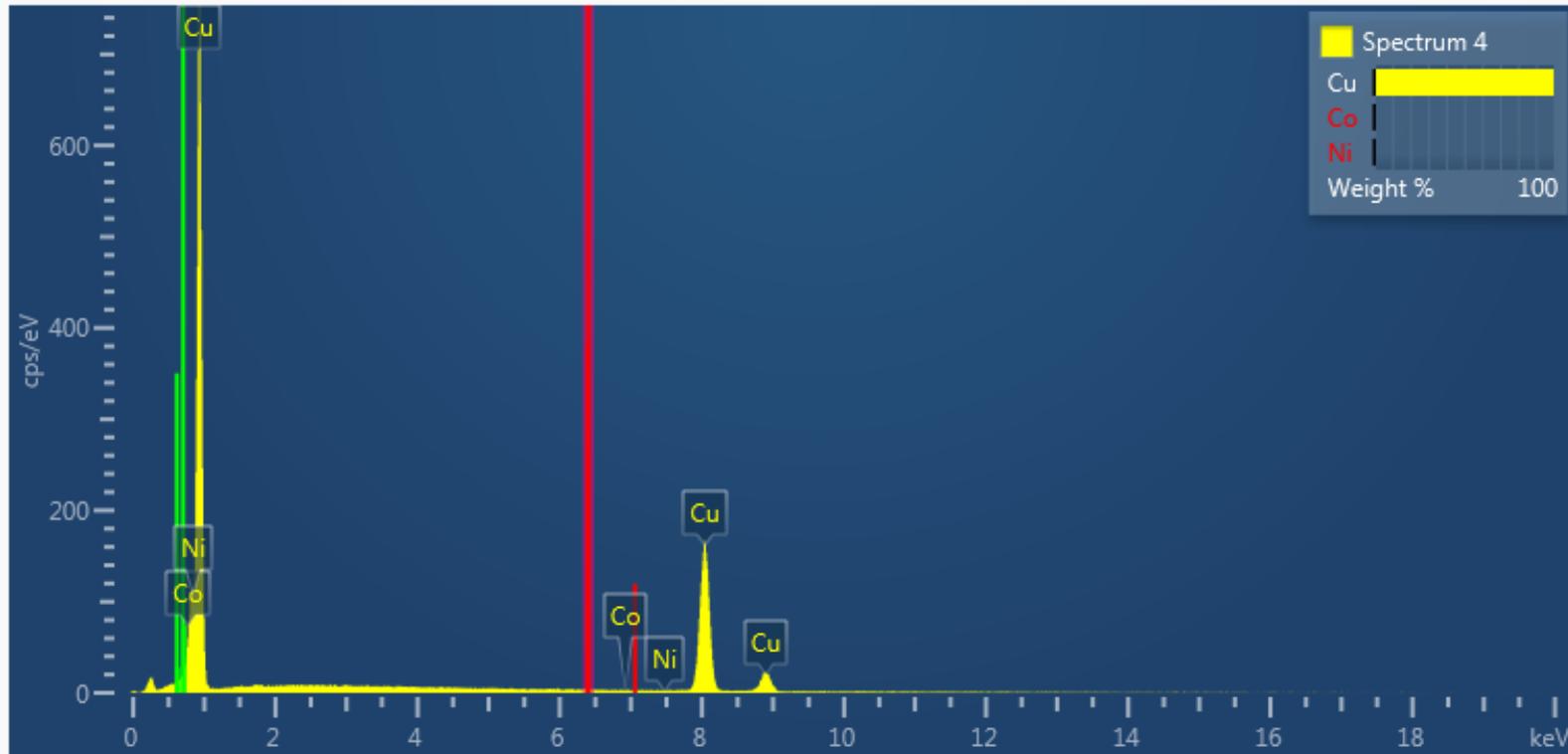# *Sample K-21-12A: Site 2*
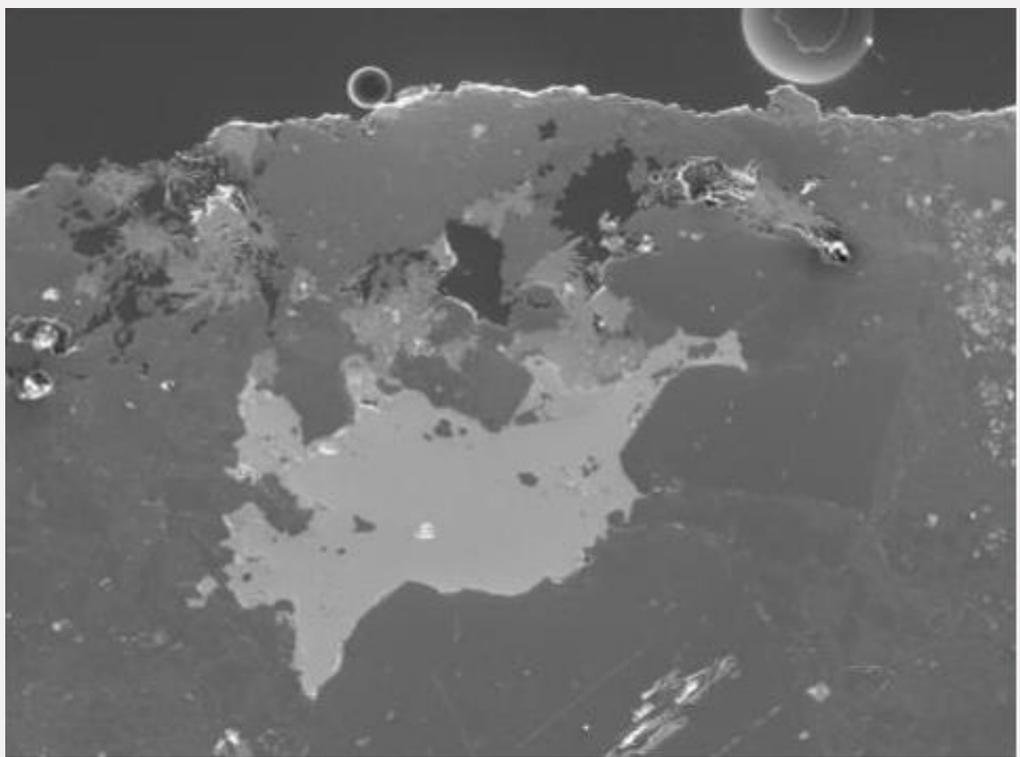
Electron Image of
Site 2 showing copper
(bright domain)
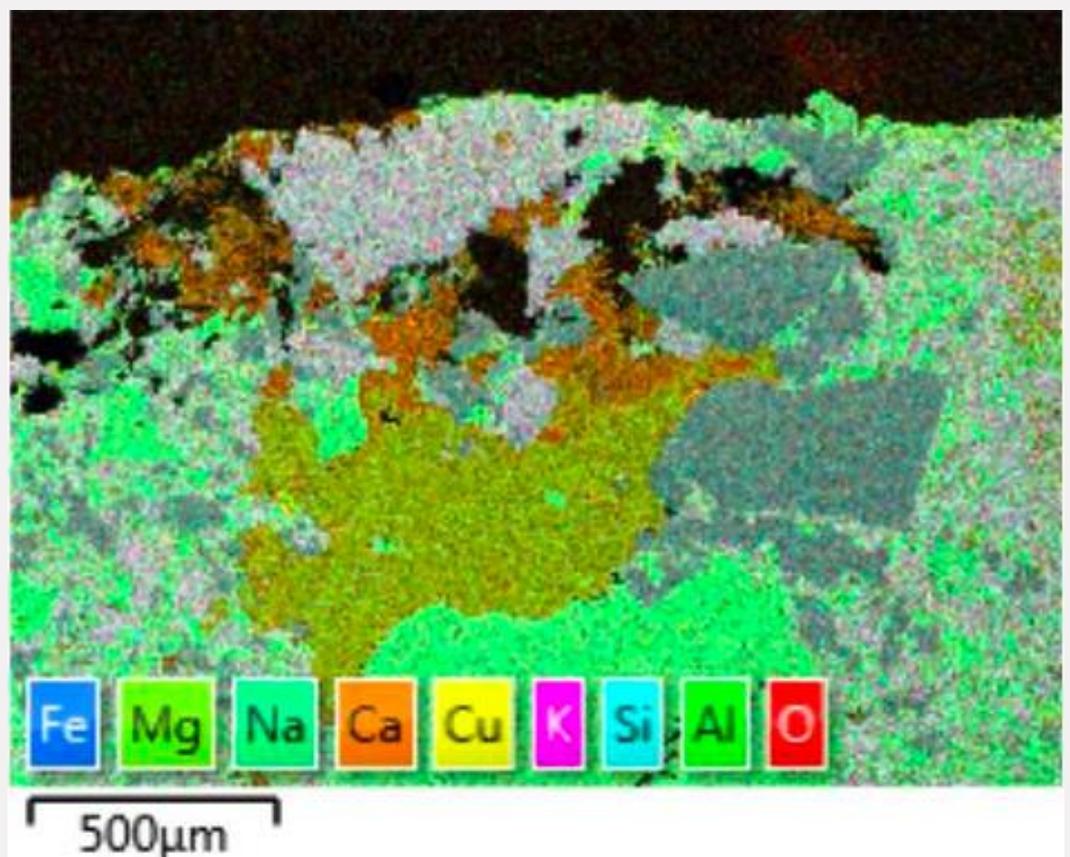
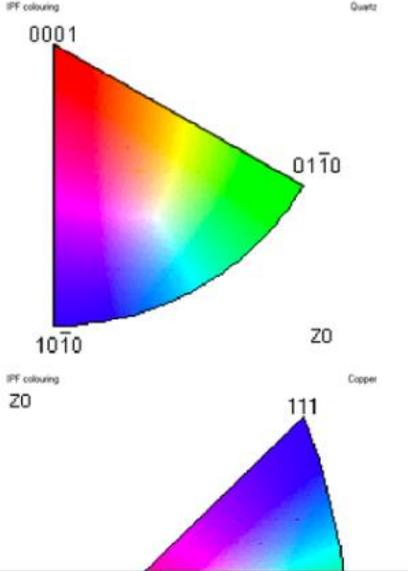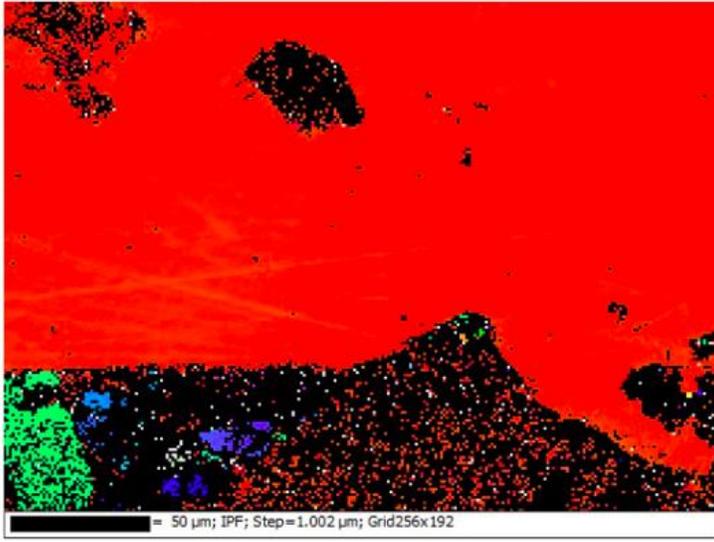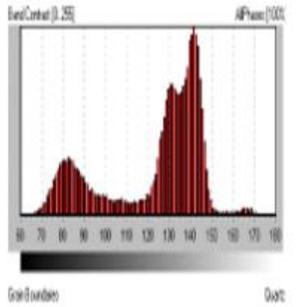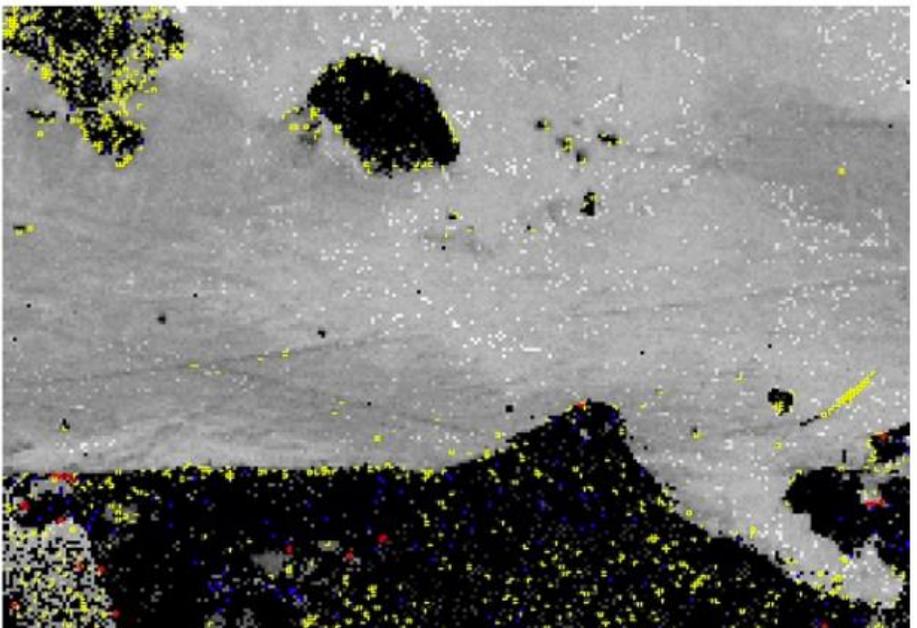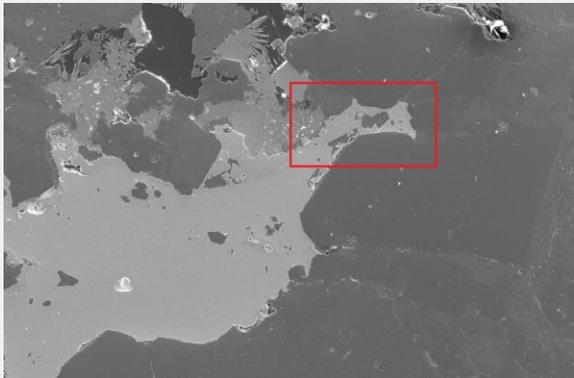EDS Map Data of Site 2; no
sulphur phases detected

Sample K-21-12A:
Site 2 EDS Spectrum

4. Results

EBSD Data for Site 2

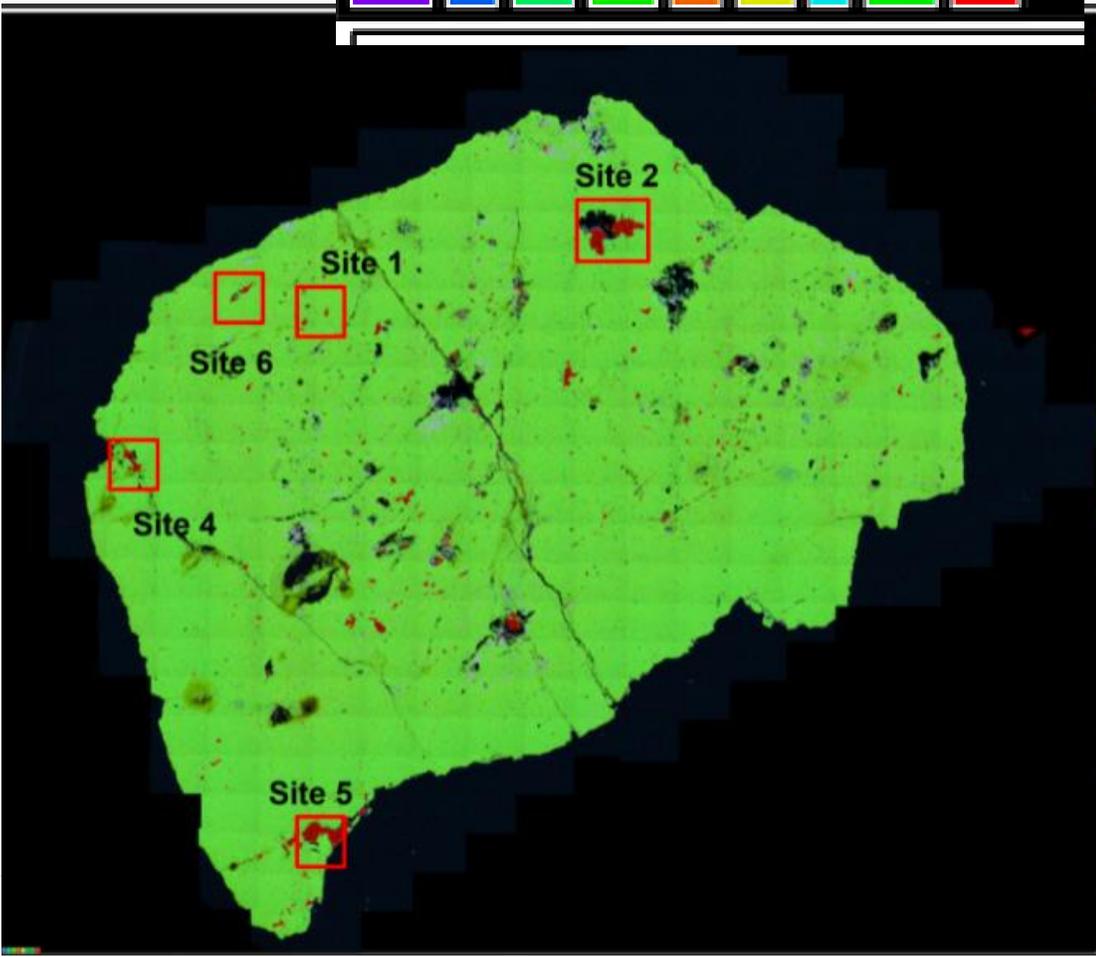EBSD band contrast map (greyscale) showing grain boundaries (yellow)

EBSD crystal orientation (IPF) map (red = c-axis normal to plane) showing Copper (red) and other minerals (colours). Note absence of sulphide at contact.
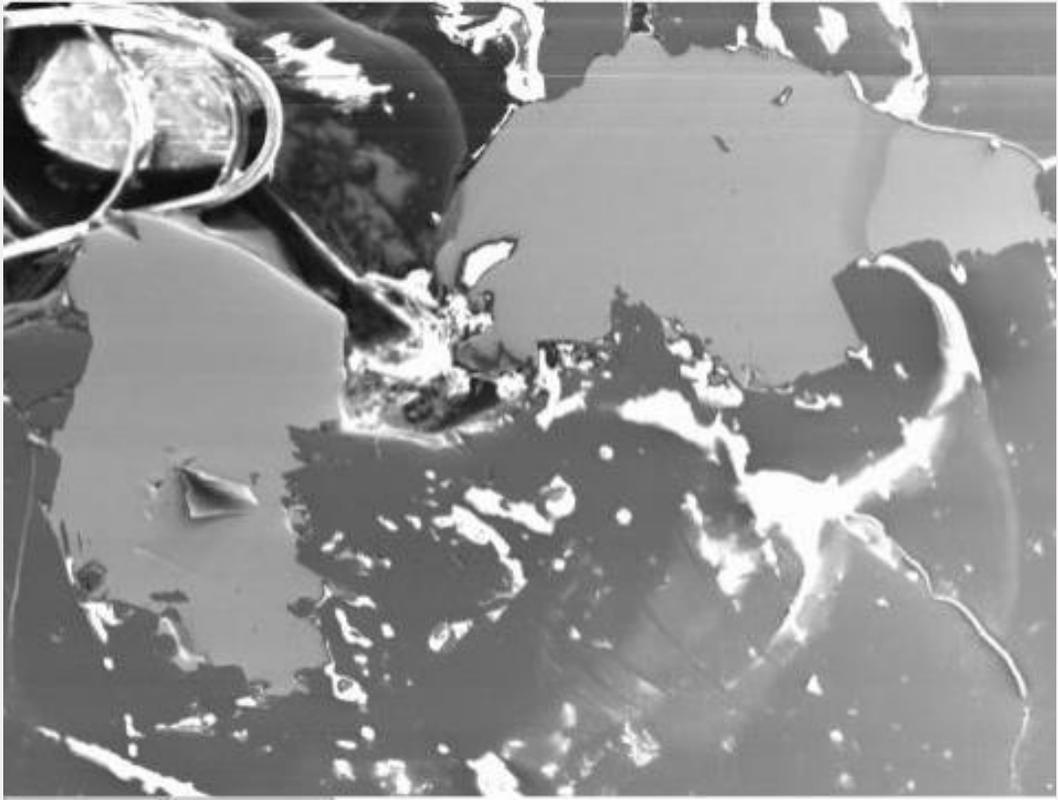
Sample K-21-15

Optical Scaled Image
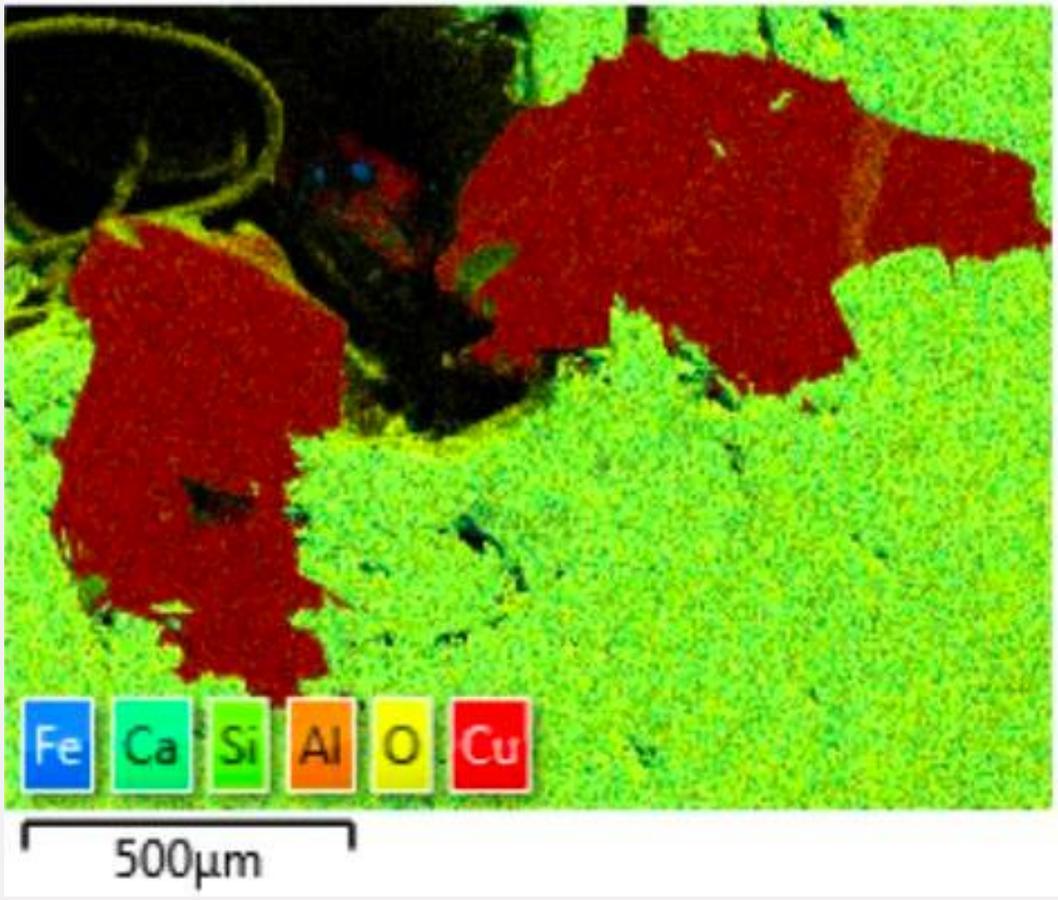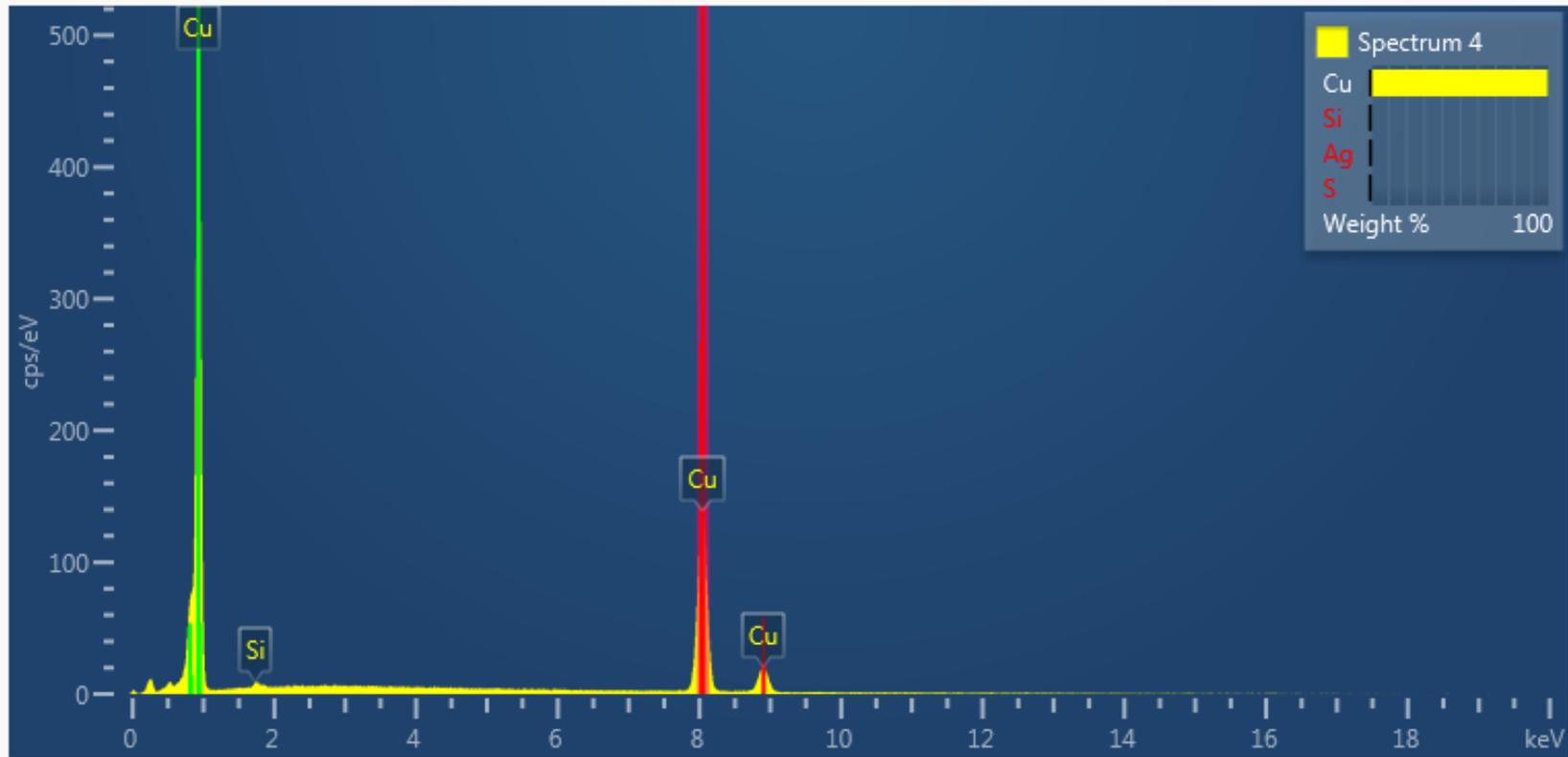
EDS Image

4. Results

Sample K-21-15: Site 2

Secondary Electron
Image of Site 2

EDS Map Data of
Site 2

Sample K-21-15:
Site 2 EDS Spectrum

5. Discussion and Next Steps

- Covellite (CuS) reference sample obtained and analyzed with SEM-EDS

- Two altered samples bearing 1 billion-year-old copper from L. Superior region analyzed for covellite ... no Sulphur bearing minerals were detected in contact with copper, no Sulfide (ex-Covellite) detected at copper contacts

- No evidence (so far) of ancient Sulphur Reducing Bacterial corrosion but number of samples too small to make confident test of SRB past activity in region

- No similar work has been carried out an ancient copper sample to the best of our knowledge. This is a first step in a large-scale study testing whether SRB corrosion is detectable and whether SRB's are likely to affect copper coatings on used nuclear fuel containers in a Deep Geological Repository

6. References

COMPLETE REFERENCE LIST

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Tornos, F., Oggerin, M., Ríos, A. de, Rodriguez, N., Amils, R., Sanz, J. L., Rojas, P., Velasco, F., Escobar, J. M., Gómez, C., & Slack, J. F. (2018). Do microbes control the formation of giant copper deposits? *Geology*, *47*(2), 143–146. https://doi.org/10.1130/g45573.1

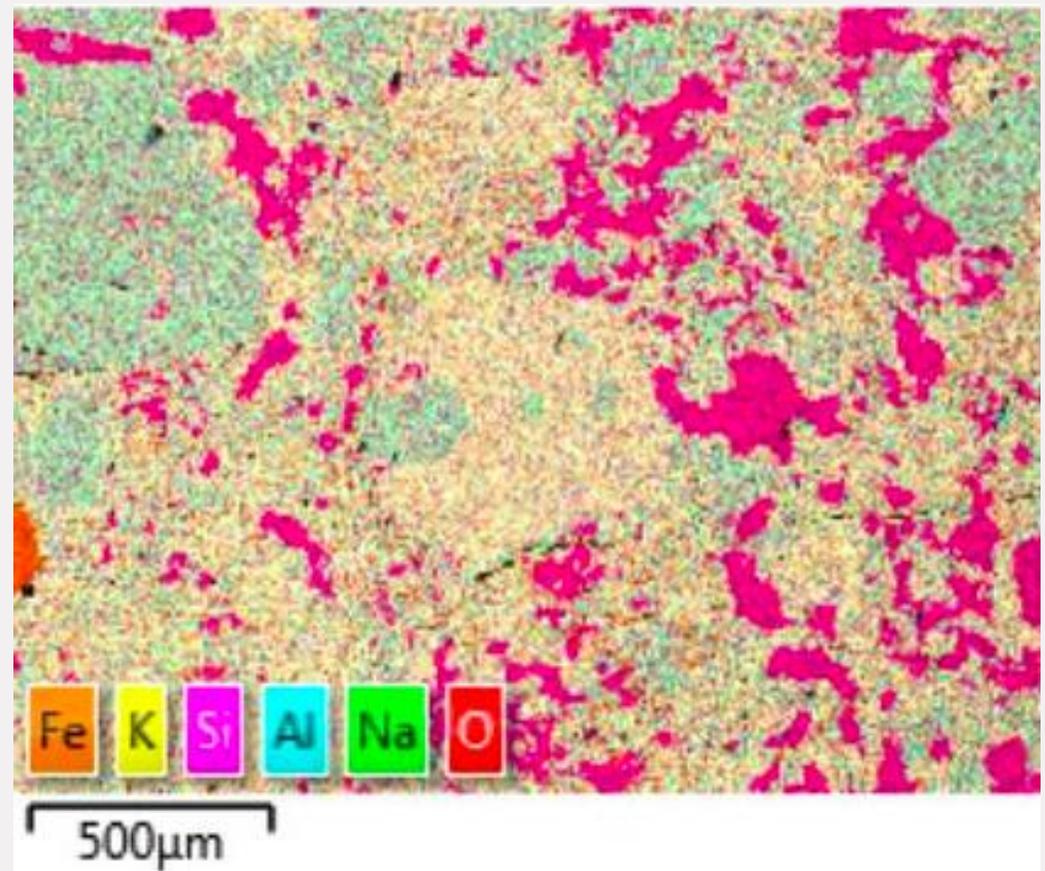White, C., & Gadd, G. M. (2000). Copper accumulation by sulfate-reducing bacterial biofilms. *FEMS Microbiology Letters*, *183*(2), 313–318. https://doi.org/10.1111/j.1574-6968.2000.tb08977.x
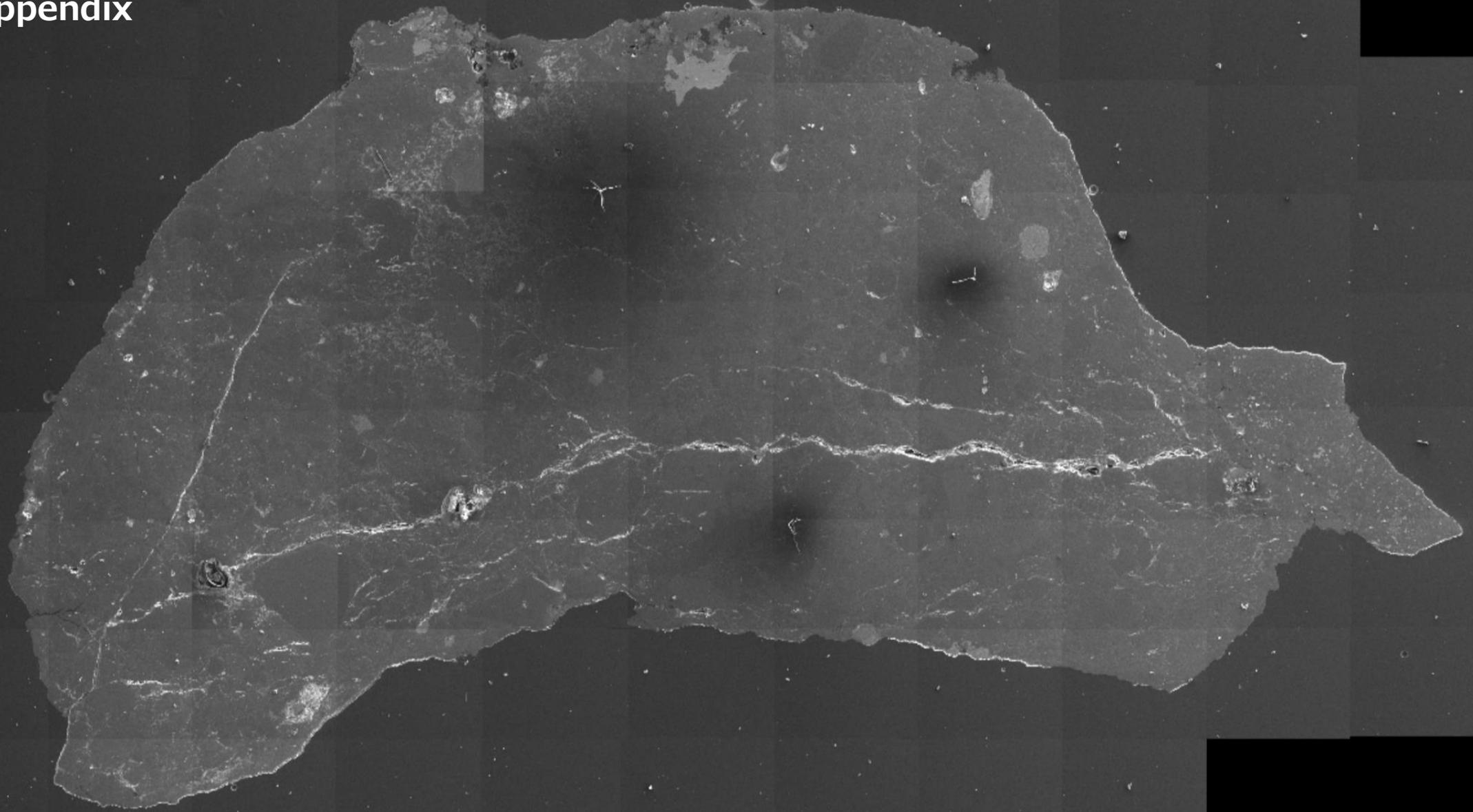
Backscattered Electron Map of Sample K-21-12a

Sample K-21-12A: Site 1
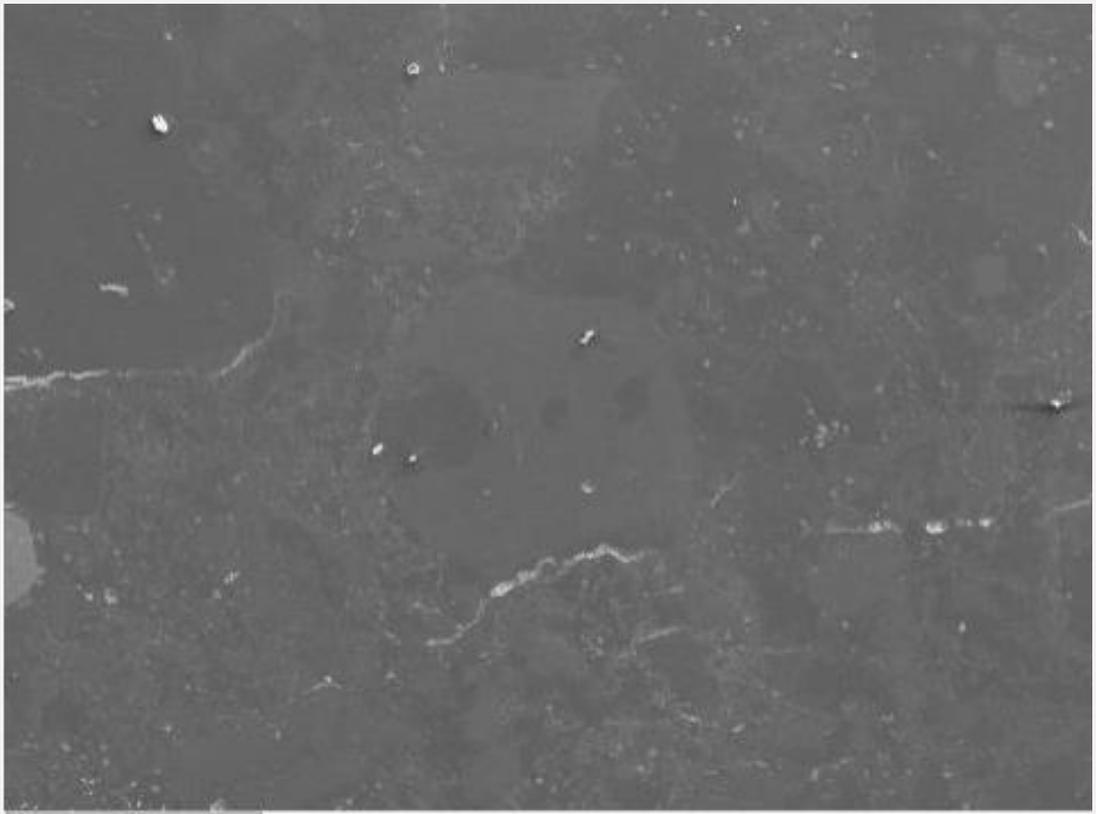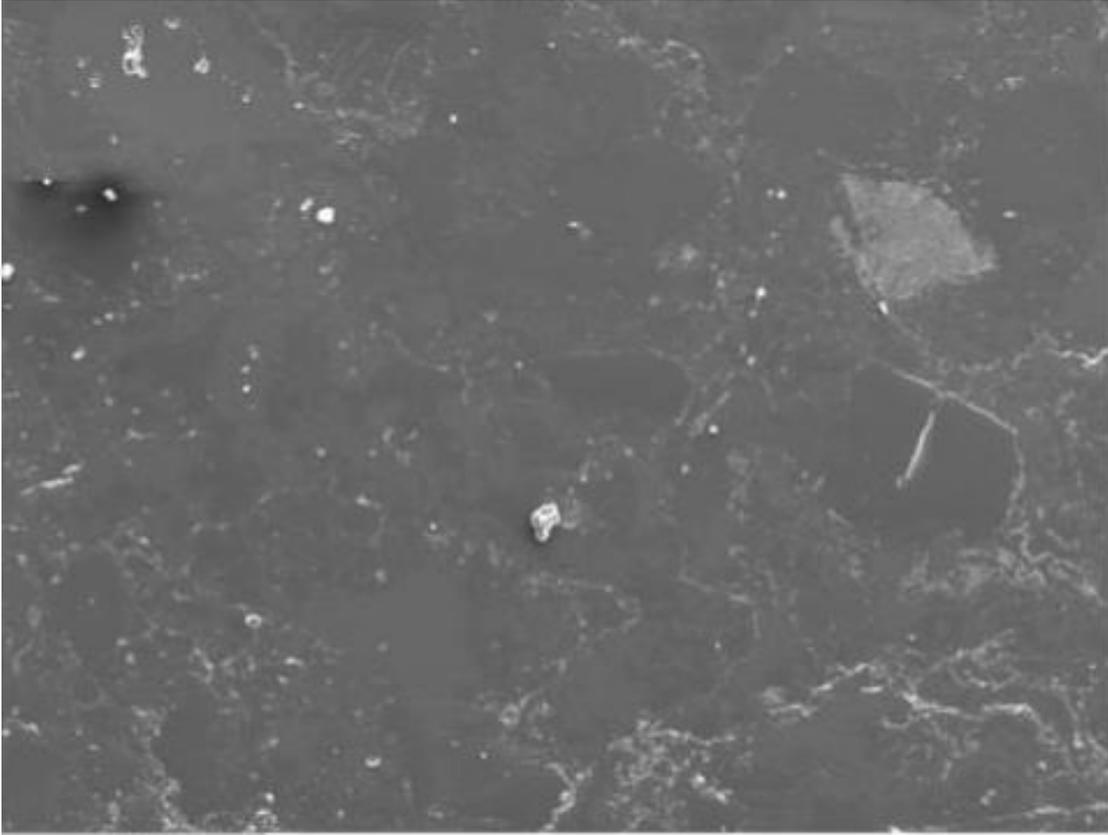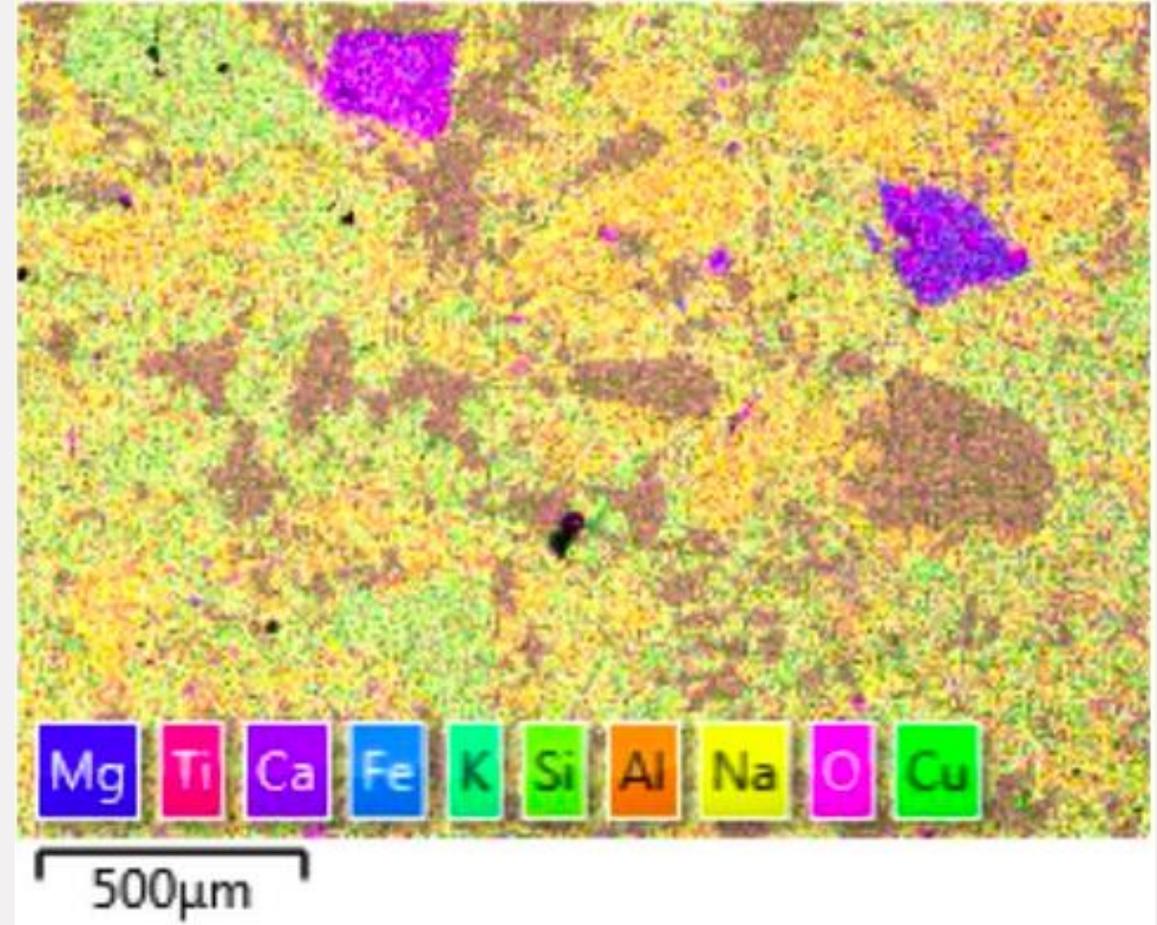

Secondary Electron image
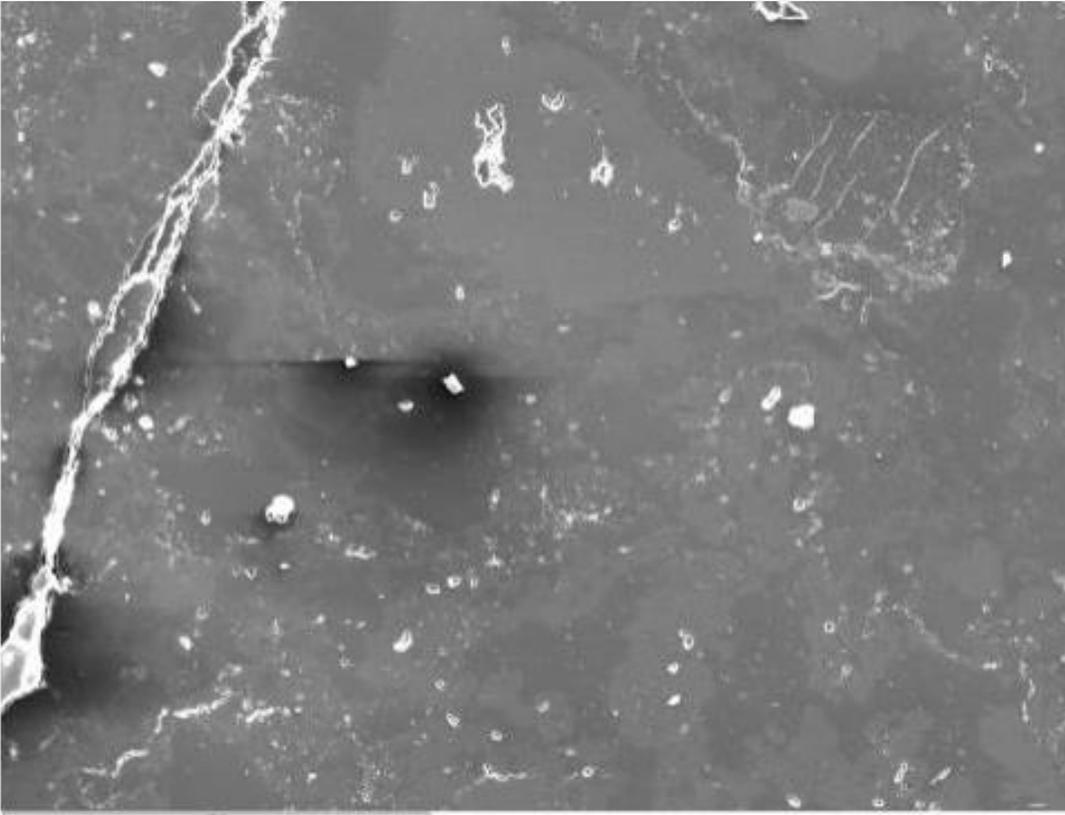

EDS Map Data of Site 1

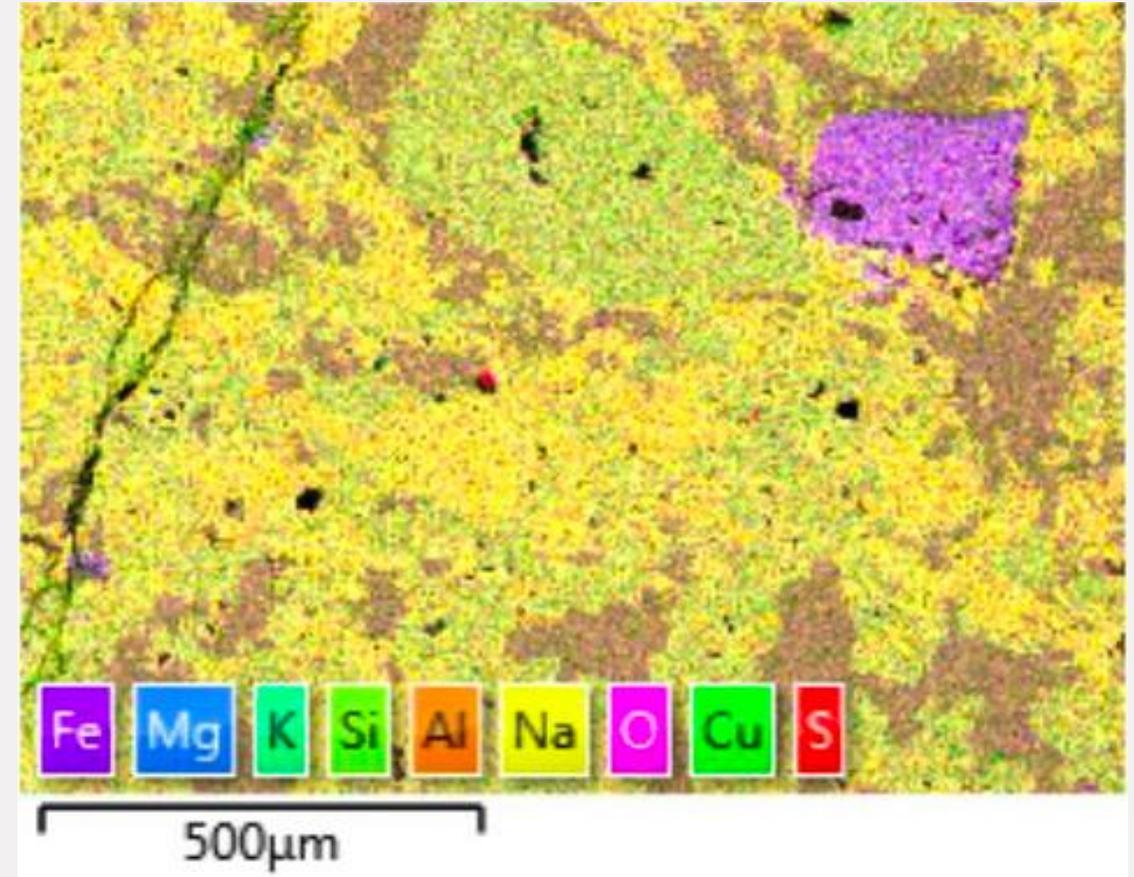# *Sample K-21-12A: Site 5*

Secondary Electron
Image of Site 5

EDS Map Data of
Site 5
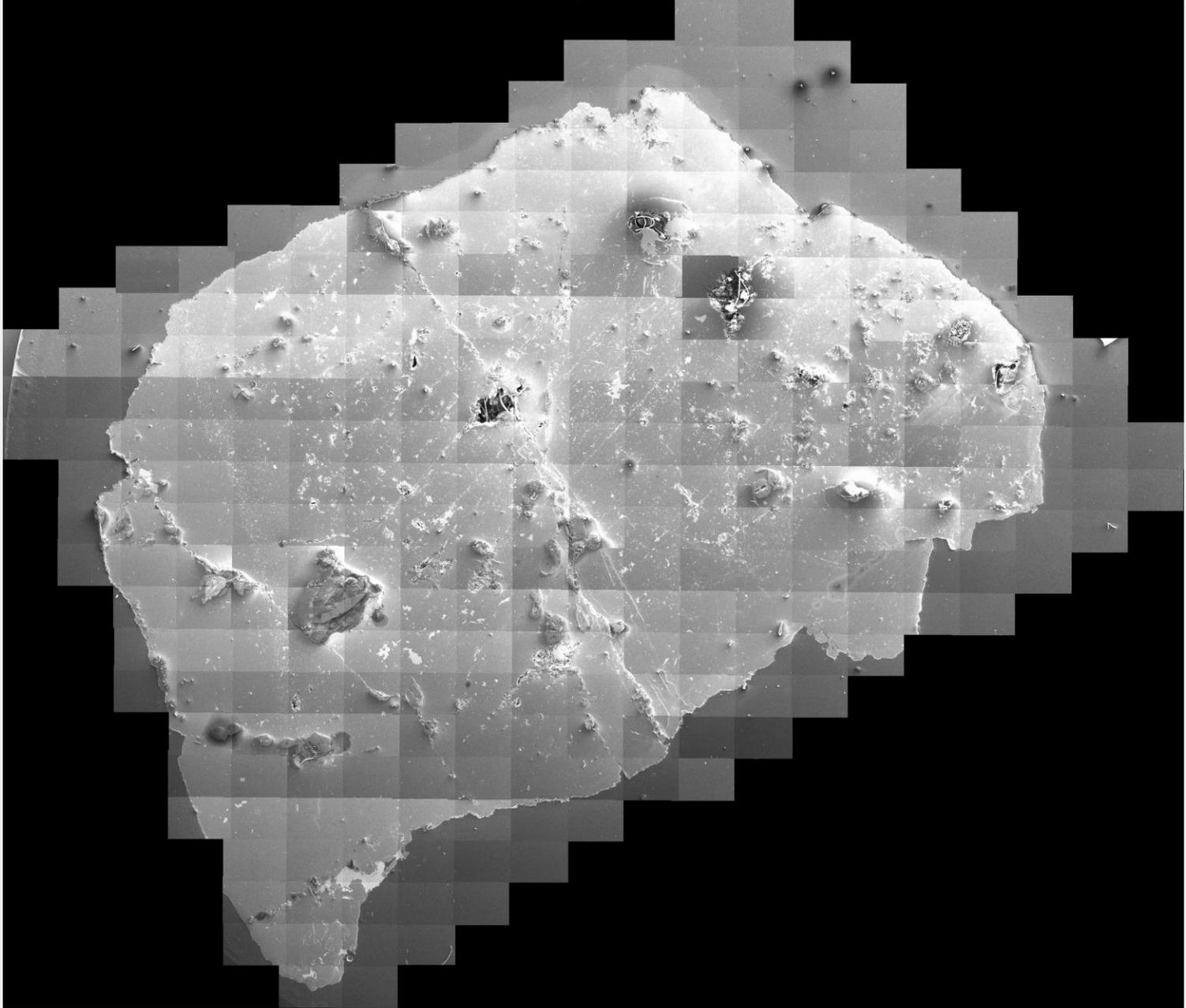
Sample K-21-12A: Site 6
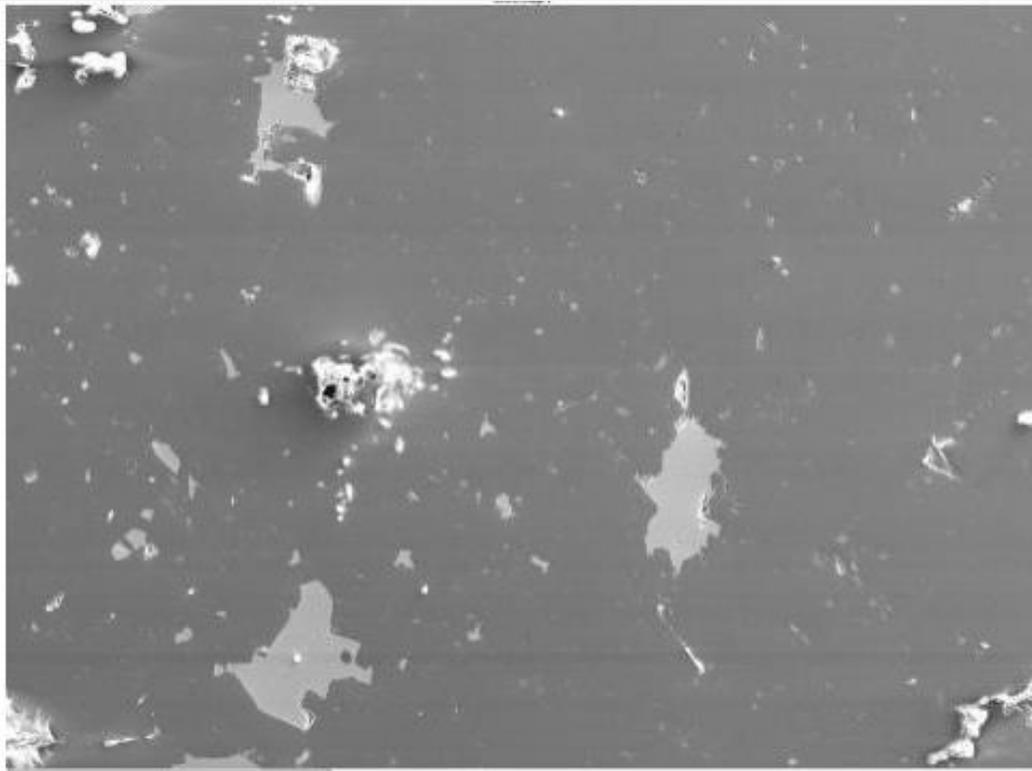

Secondary Electron
Image of Site 6

EDS Map Data of
Site 6

7. Appendix

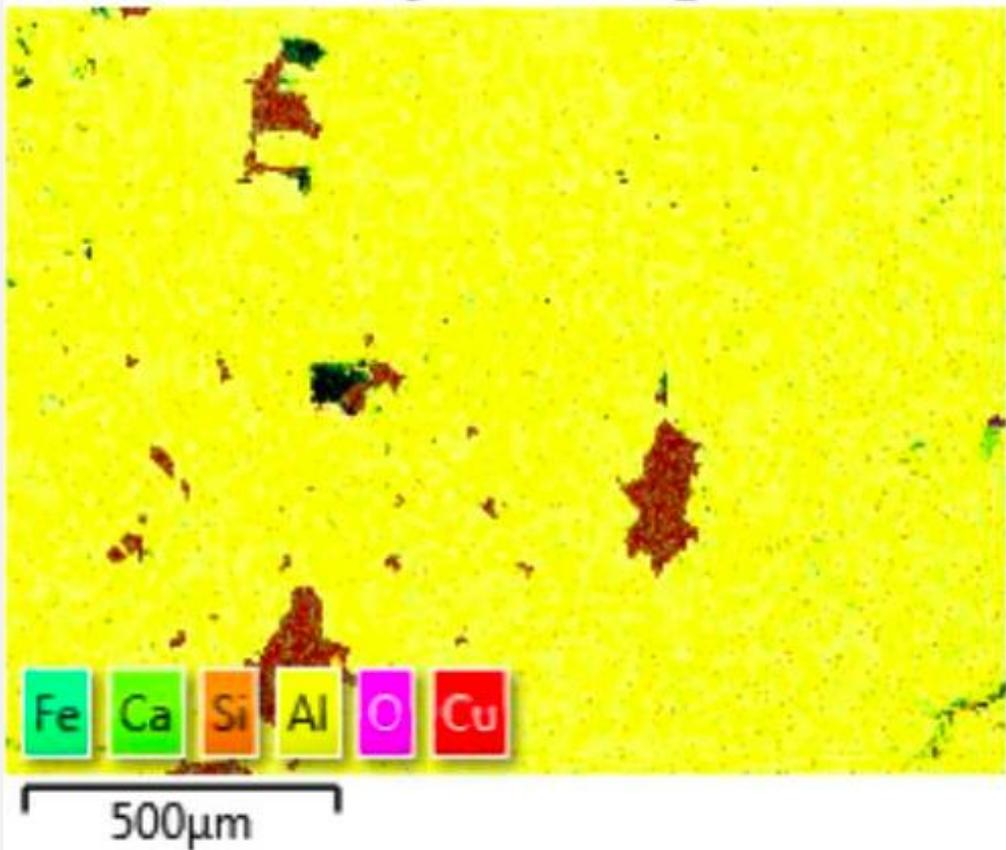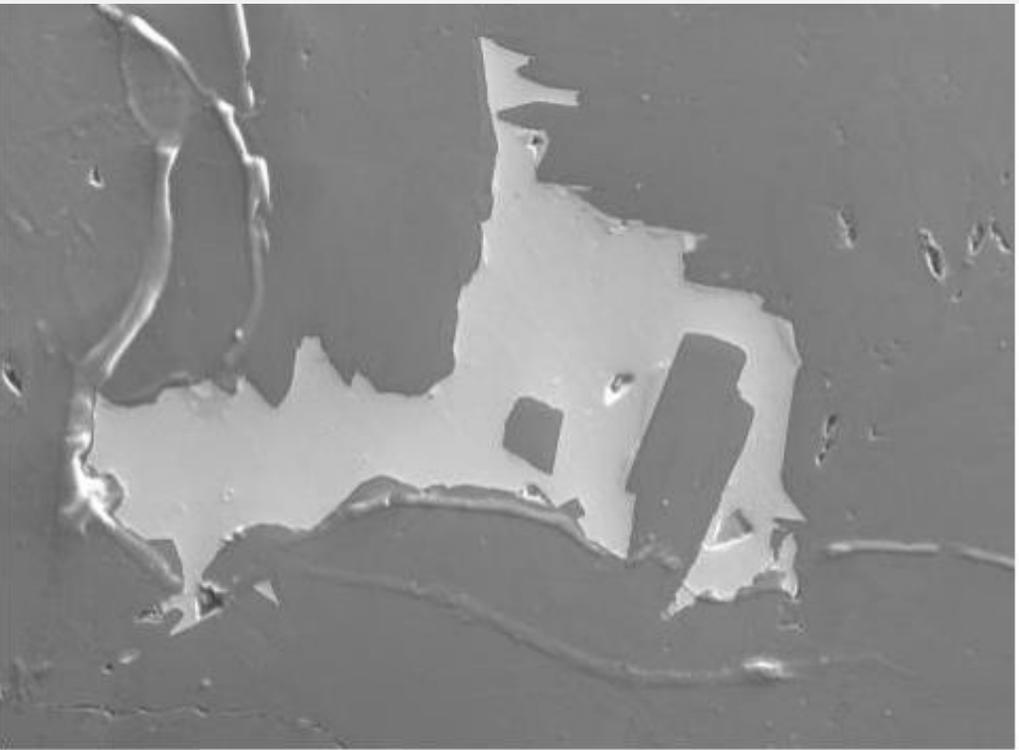**EDS Backscattered Image of Sample K-21-15**

Sample K-21-15: Site 1
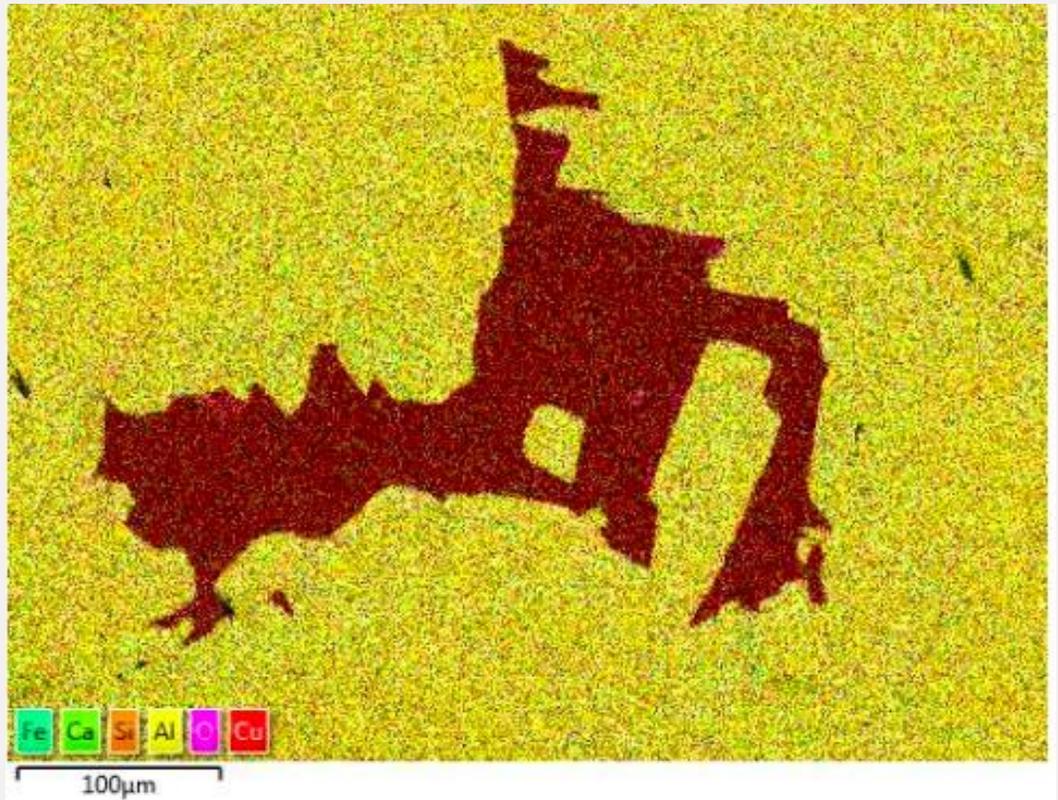

Secondary Electron
Image of Site 1

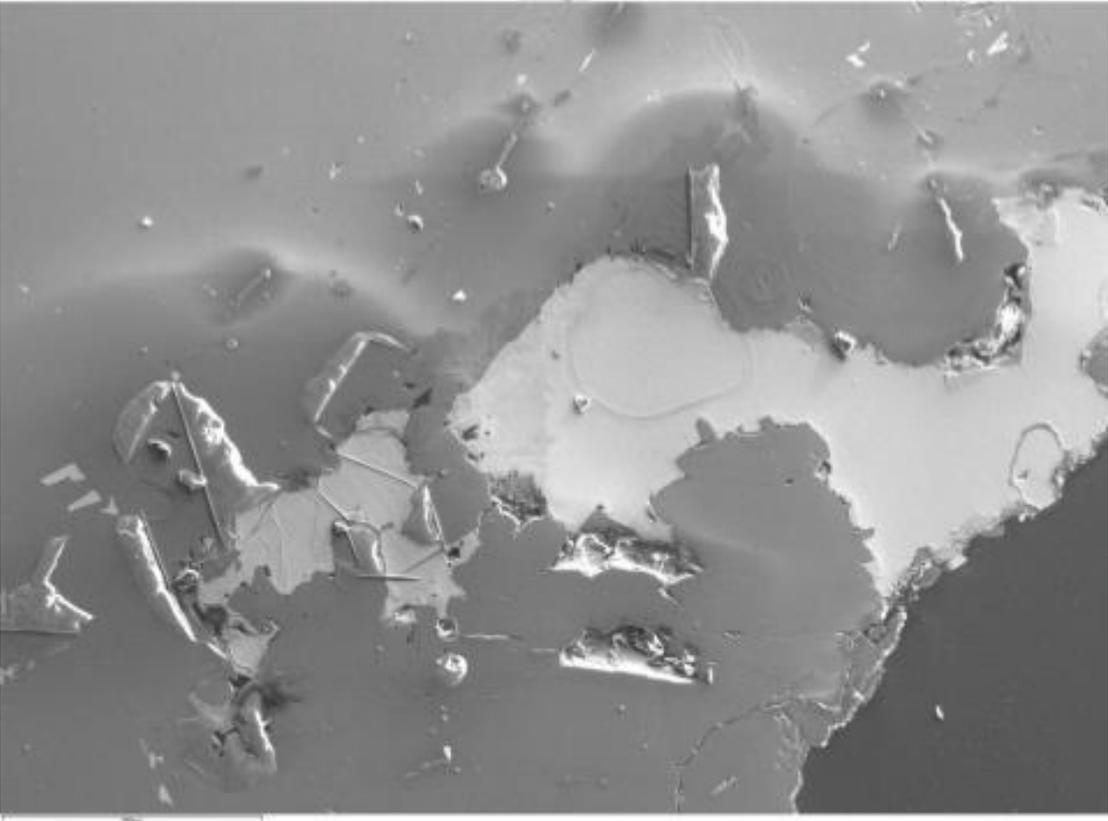EDS Map Data of
Site 1

Sample K-21-15: Site 4
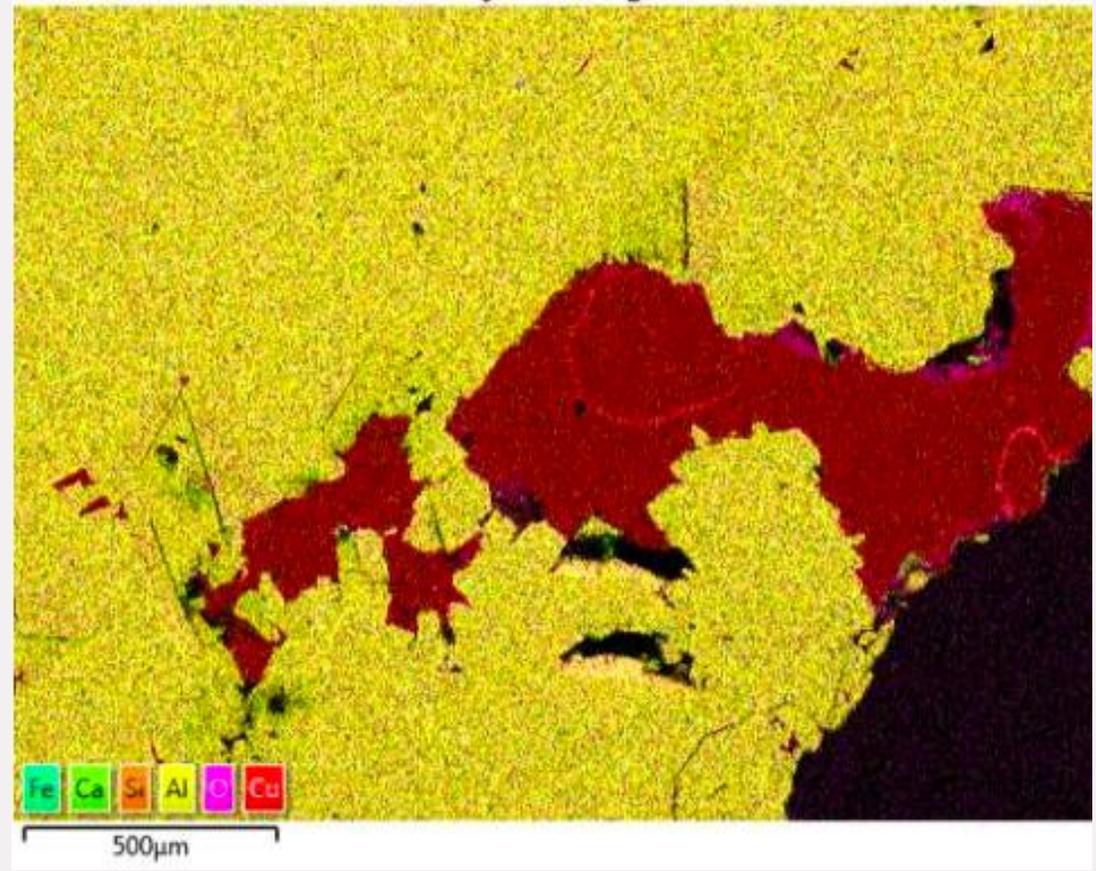

Secondary Electron
Image of Site 4

EDS Map Data of
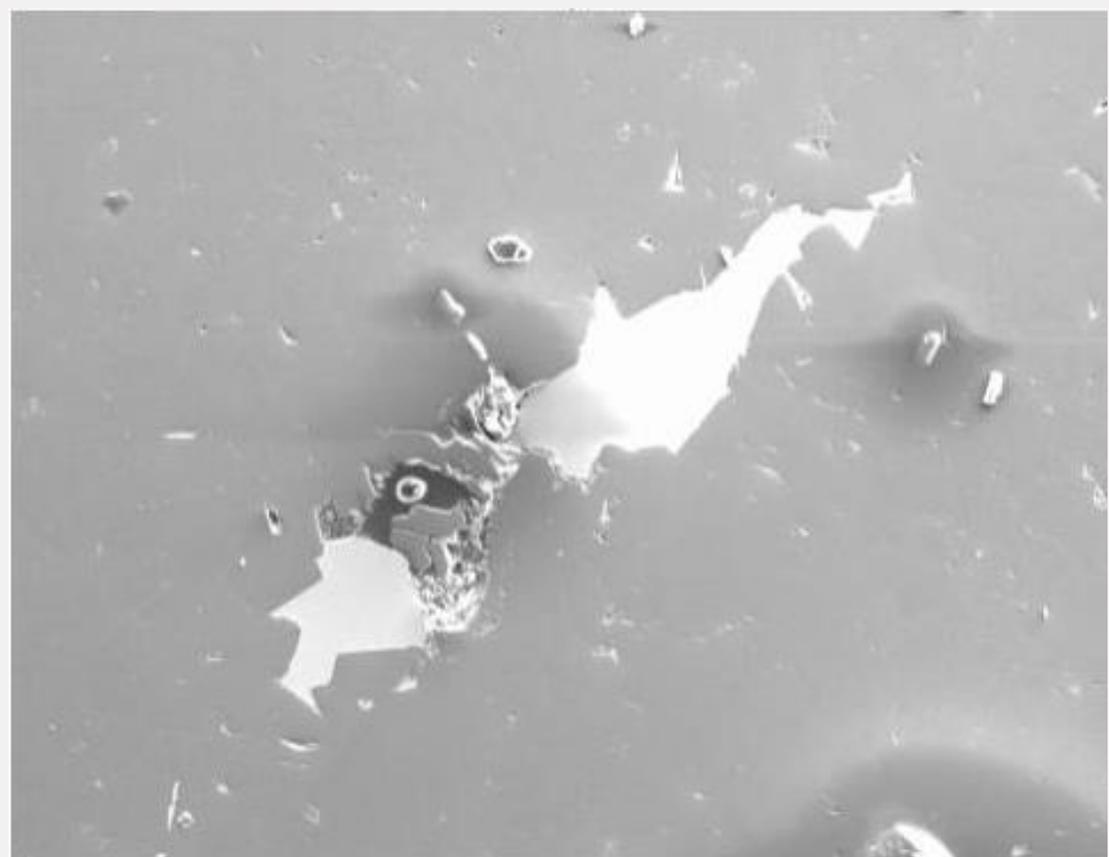Site 4

Sample K-21-15: Site 5
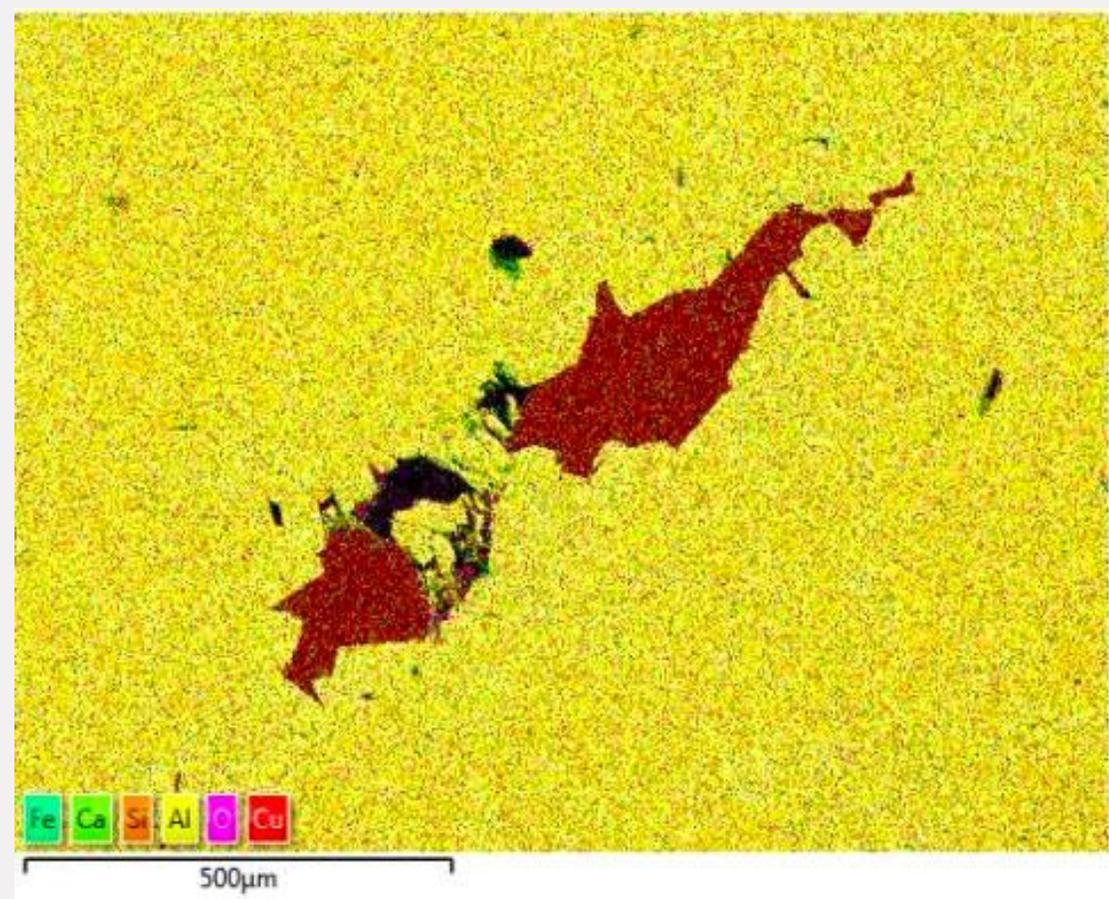

Secondary Electron
Image of Site 5

EDS Map Data of
Site 5

Sample K-21-15: Site 6

Secondary Electron
Image of Site 6

EDS Map Data of
Site 6