A photograph of a long, single-story brick building with a metal roof, identified as the Starkville Research and Development Center. The building has several windows and a large glass entrance on the left. In the foreground, there is a large green lawn. To the right of the main building, there is a stone sign that reads "STARKVILLE RESEARCH AND DEVELOPMENT CENTER".

# Mapping of copper in wood treated with a copper-based preservative and exposed to the copper-tolerant brown rot fungus *Fibroporia radiculosa*

Benoit Duchemin, Normandie University, Le Havre, France

Yoshiharu Nishiyama, University Grenoble Alpes, Grenoble, France

Solenn Reguer, Synchrotron Soleil, Saint-Aubin, France

**Juliet D. Tang, USDA FS, Forest Products Laboratory, Starkville, MS**

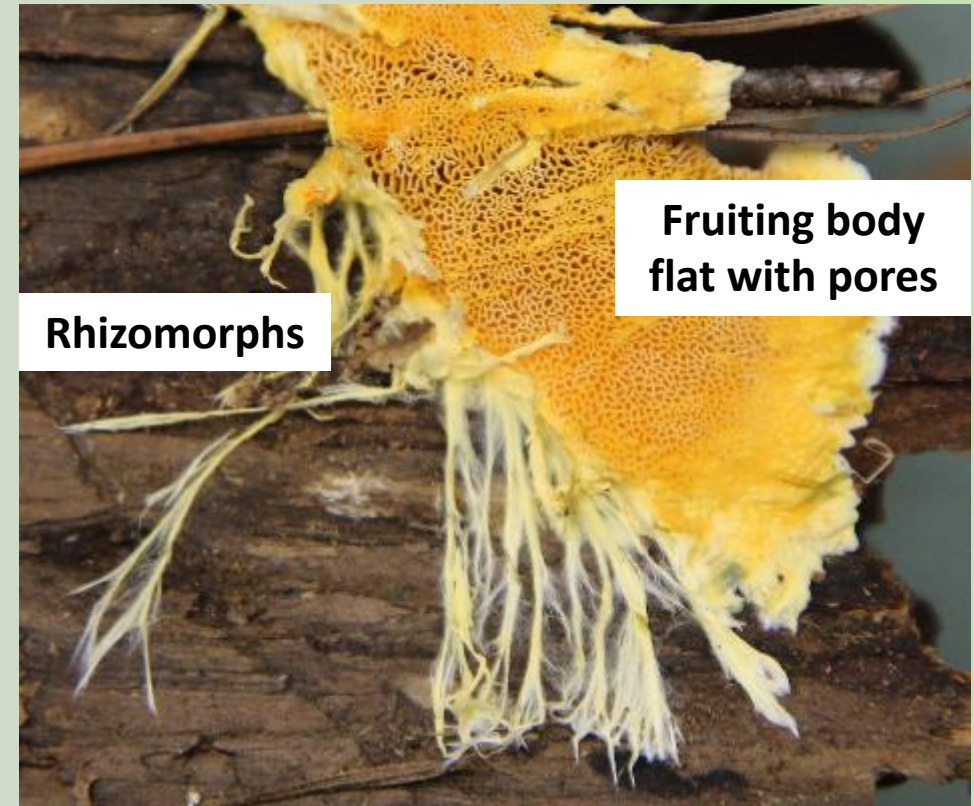
Yu Ogawa, University Grenoble Alpes, Grenoble, France

Daniel Chateigner, University de Caen Normandie, Caen, France

Darrel D. Nicholas, Sustainable Bioproducts, Mississippi State University, MS



# Study Organism – *Fibroporia radiculosa*



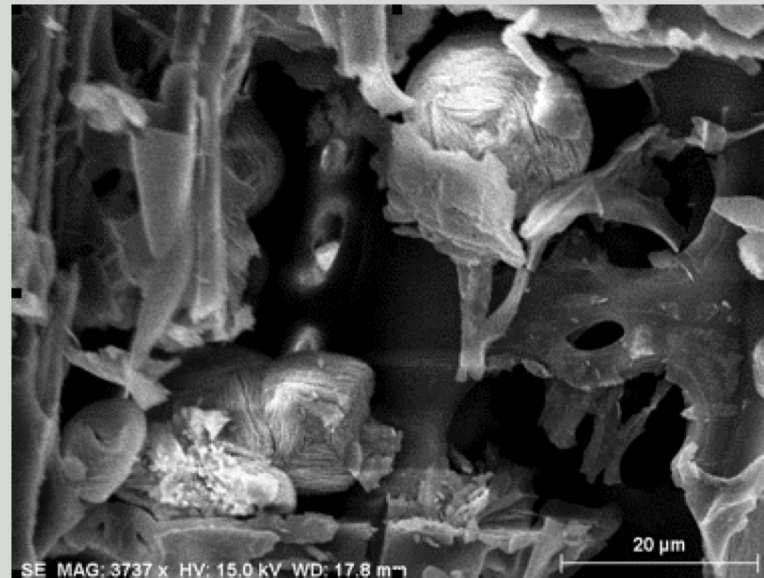
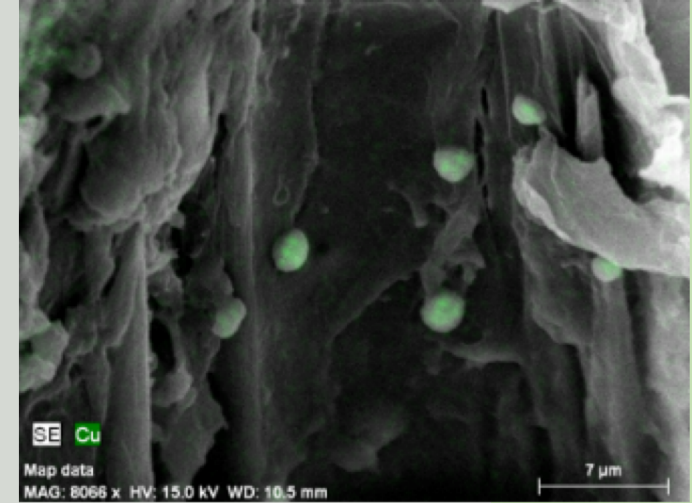
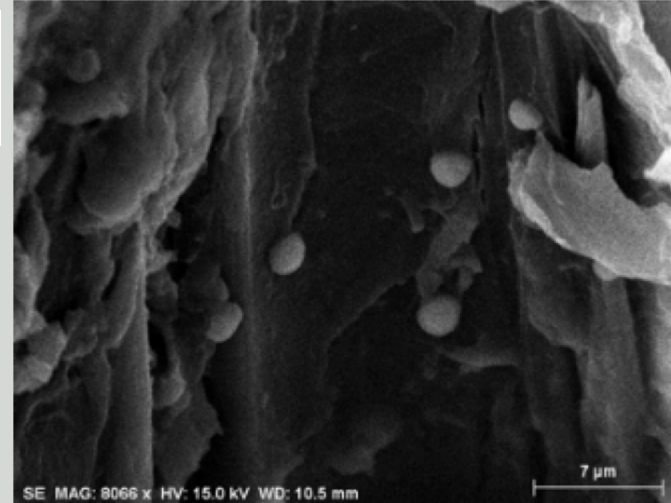
- Brown rot fungus
- Cosmopolitan

- Aggressive decomposer
- Copper tolerant

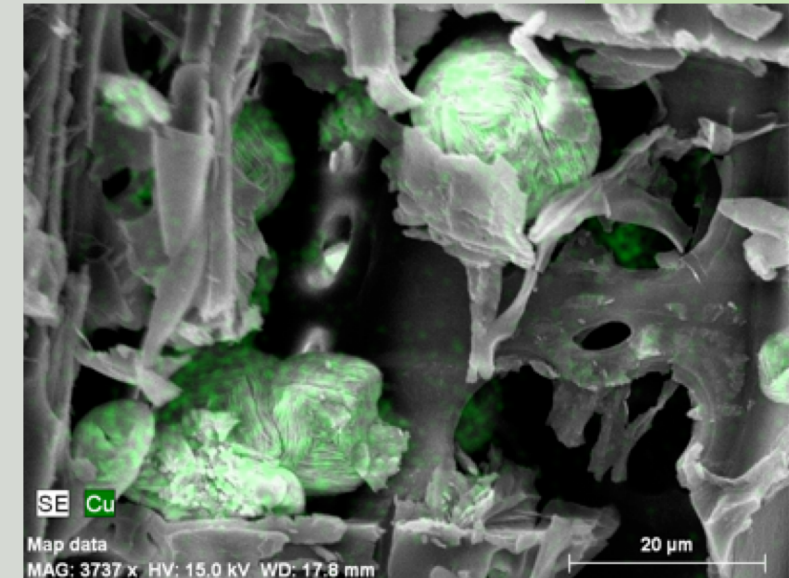
# Mechanism of Copper Tolerance

- Pressure-treated wood for residential use
  - ACQ CA MCA
  - all copper-based
- Transforms copper to copper oxalate crystal
  - SEM-EDX images confirms transformation
  - Cu is non-toxic because crystal is insoluble
- Spatial and temporal details?

$\text{CuCO}_3$   
unexposed



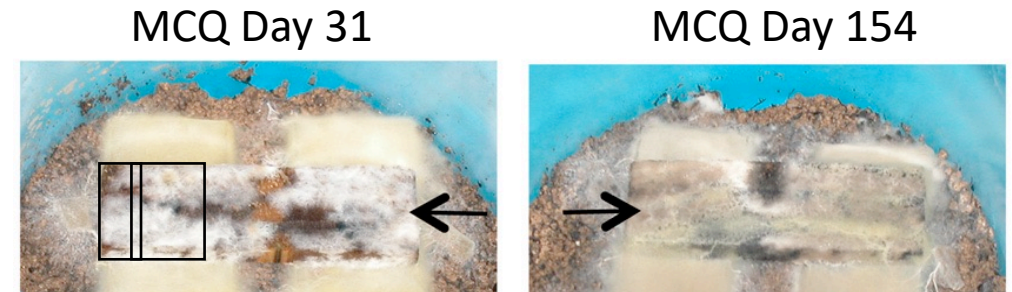
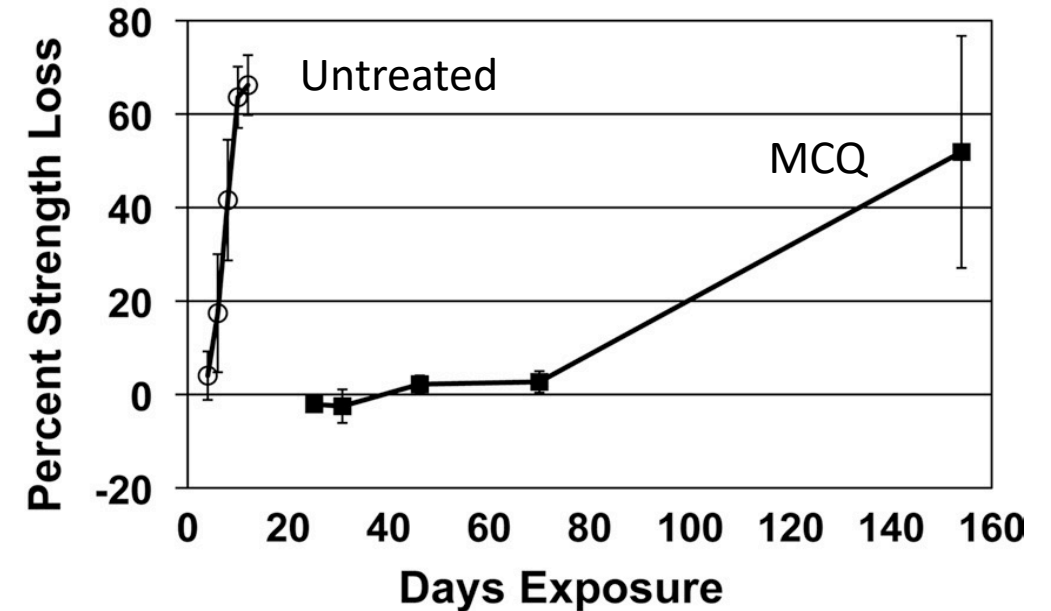
$\text{CuC}_2\text{O}_4$   
exposed day 154





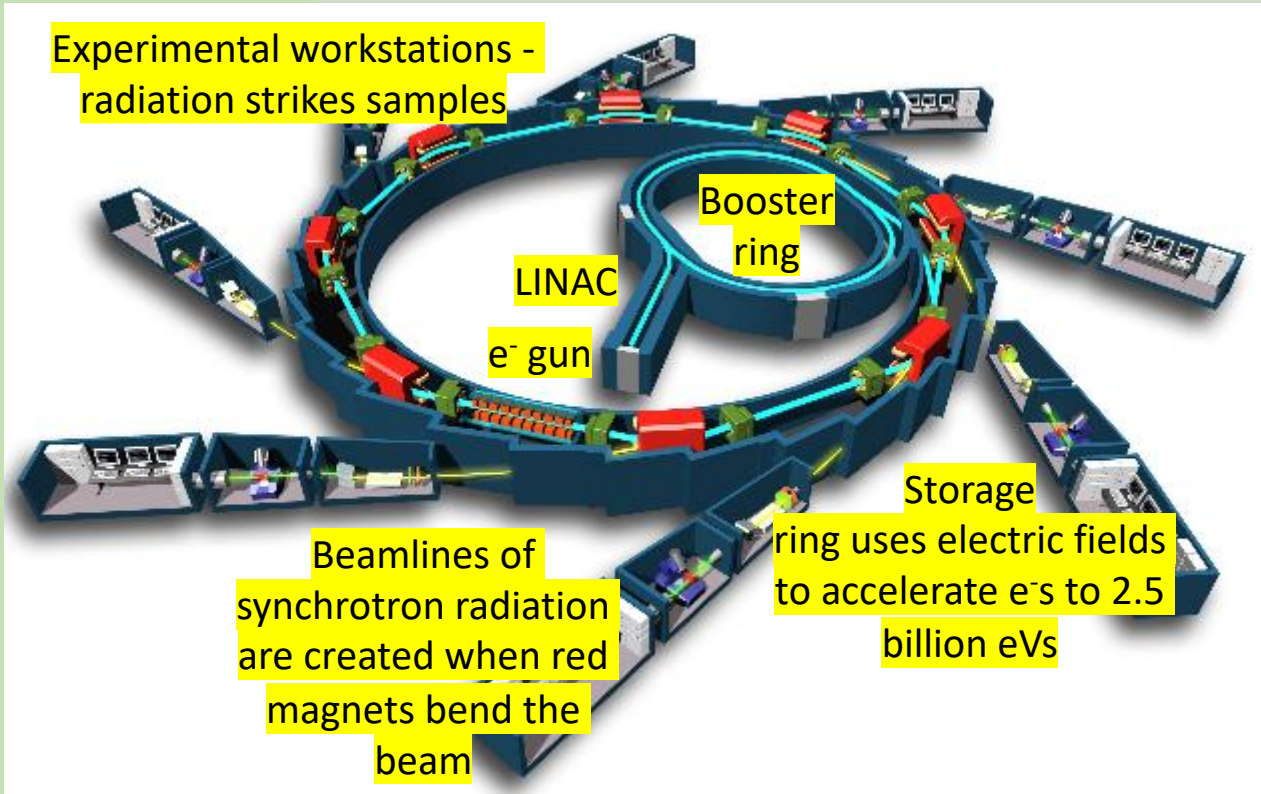
# Specimen Treatment and Fungus Exposure

- SYP sapwood wafers
  - 54 x 18 x 5 mm (tang x radial x long)
- Full cell treatment 0.34 pcf MCQ
  - Vacuum -28 in Hg for 10 min
  - Pressure 140 psi for 10 min
- Expose to *Fra* in soil block test to get maximum % compression loss
- Cut section for compression test
  - 18 x 18 x 5 mm
- Cut 1 mm section for XRF and XRD analysis
  - 1 x 18 x 5 mm





# Synchrotron Radiation for XRD and XRF Analysis



Synchrotron Soleil (copyright EPSIM 3D/JF Santarelli)

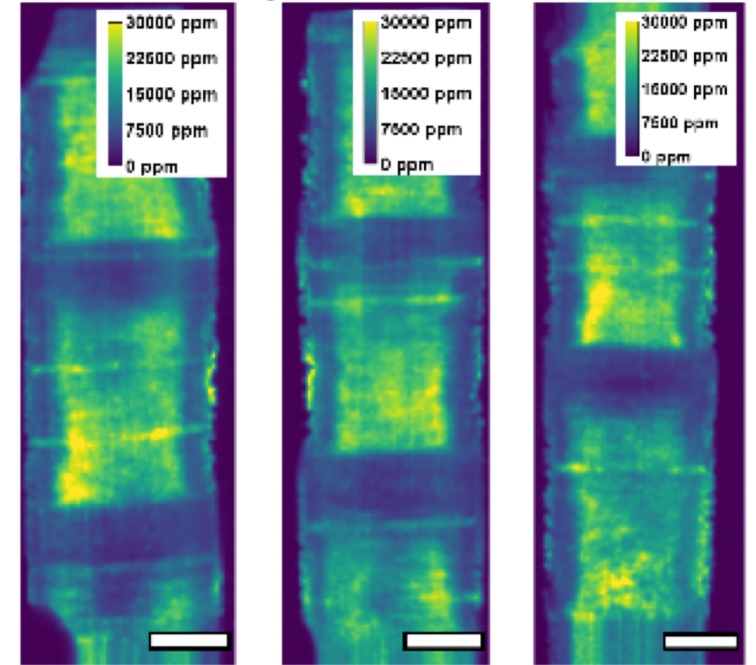
- DiffAbs Workstation



# XRF Mapping of Cu

- Shoot beamline at pellets made with a known amount of  $\text{CuCO}_3$  for ppm calibration curve
- Unexposed MCQ wood
  - More Cu in earlywood (> 22K ppm) than latewood (7500 ppm)
    - smaller pores of latewood pickup less preservative
  - Fairly uniform distribution in both earlywood and latewood
    - Some regions of high concentration and an occasional area of low concentration
  - X-sectional faces generally have lower Cu (7500 ppm)
    - wafers dabbed on paper towels to remove excess

## Unexposed MCQ



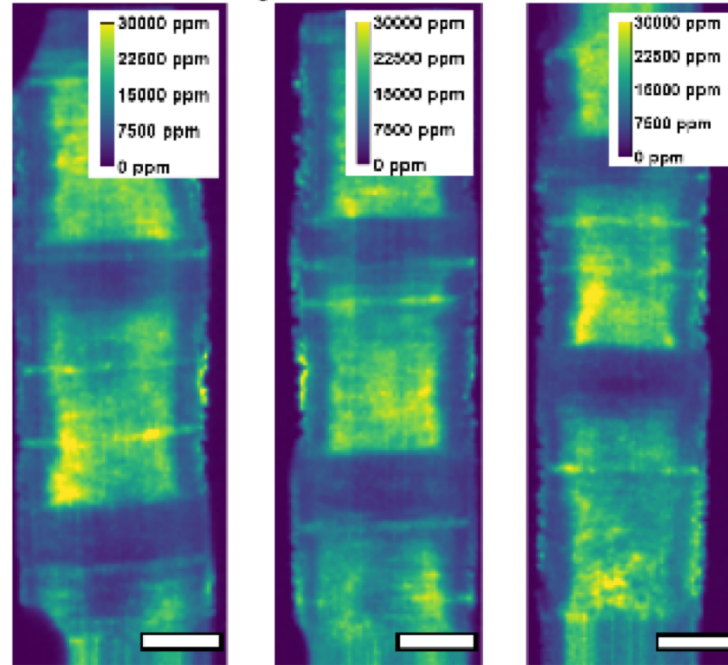
Unexposed  
untreated 0 ppm Cu



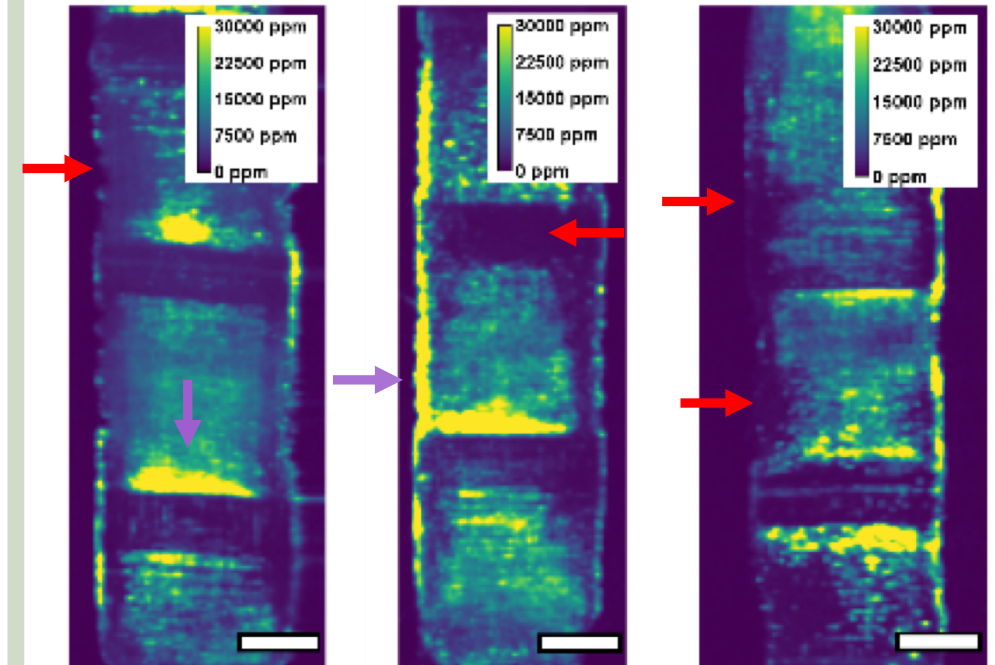
# XRF Mapping of Cu in MCQ Wood

- Day 25
- 0% strength loss
- Cu distribution more patchy
- Uniform glow less apparent
- High Cu (→) 30K ppm
- Low Cu (→) <7500 ppm

## Unexposed



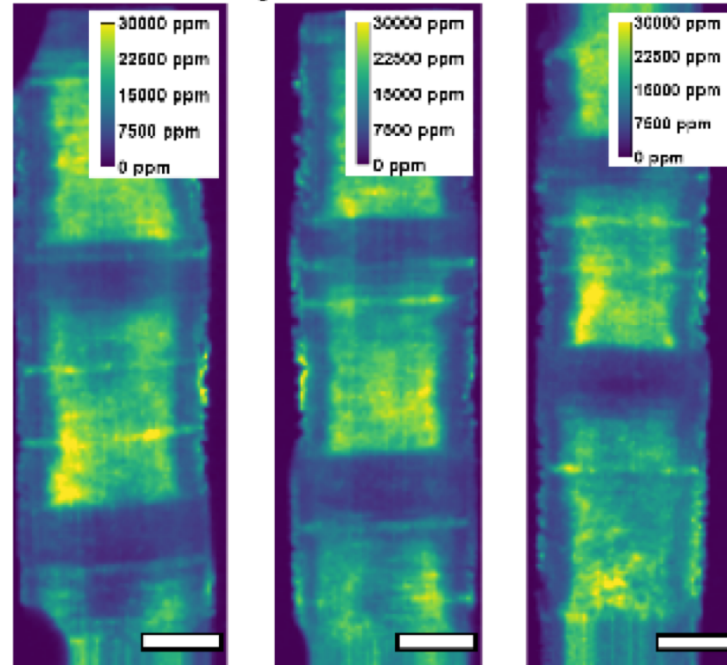
## Exposed 25 Days



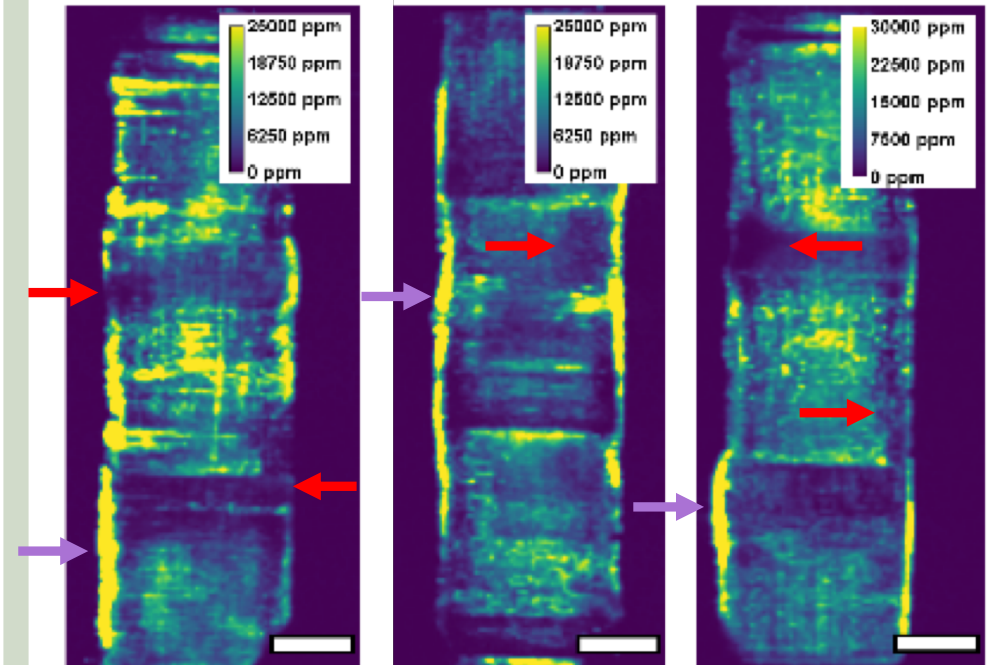
# XRF Mapping of Cu in MCQ Wood

- Day 70
- < 5% strength loss
- Patchiness more obvious in both earlywood and latewood
- More areas with high Cu (→) (25K – 30K ppm)
- More areas with low Cu (→) (<7500 ppm)

## Unexposed



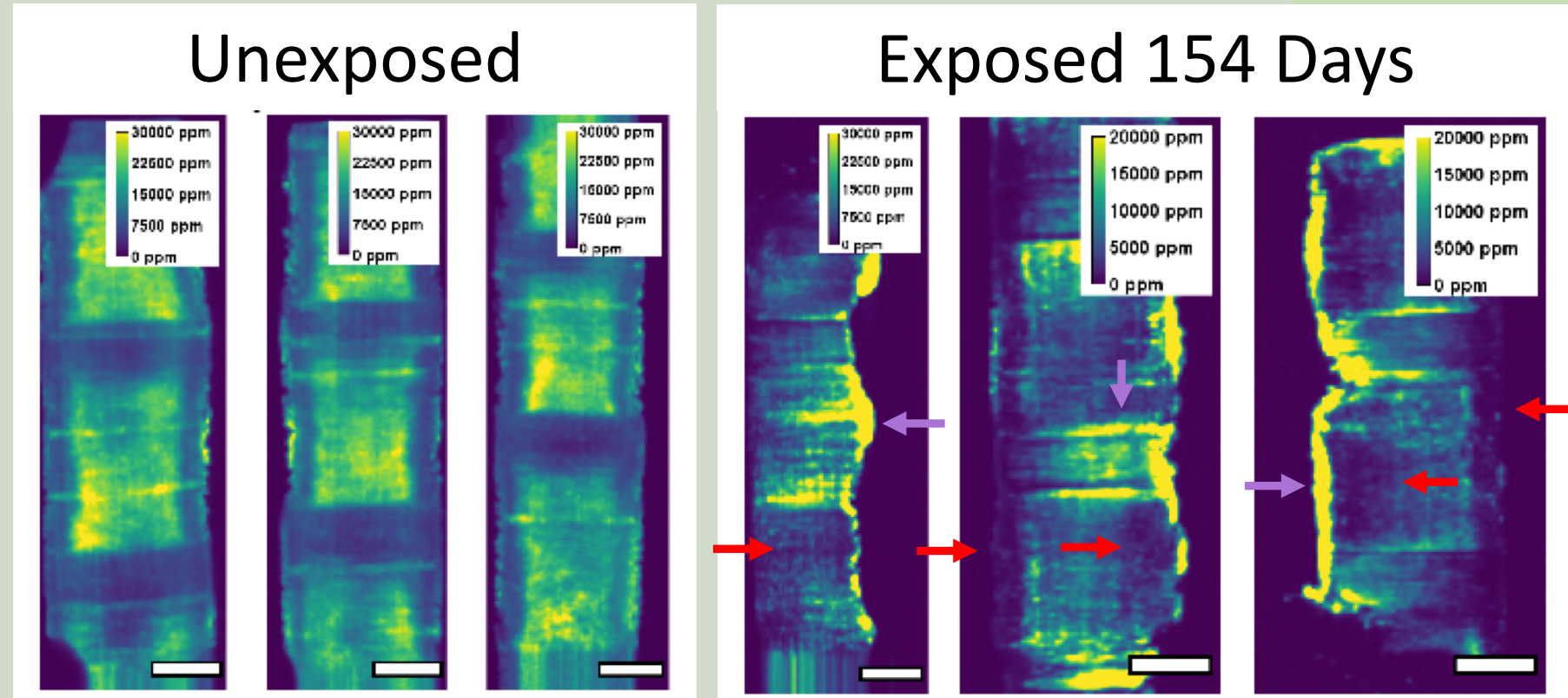
## Exposed 70 Days





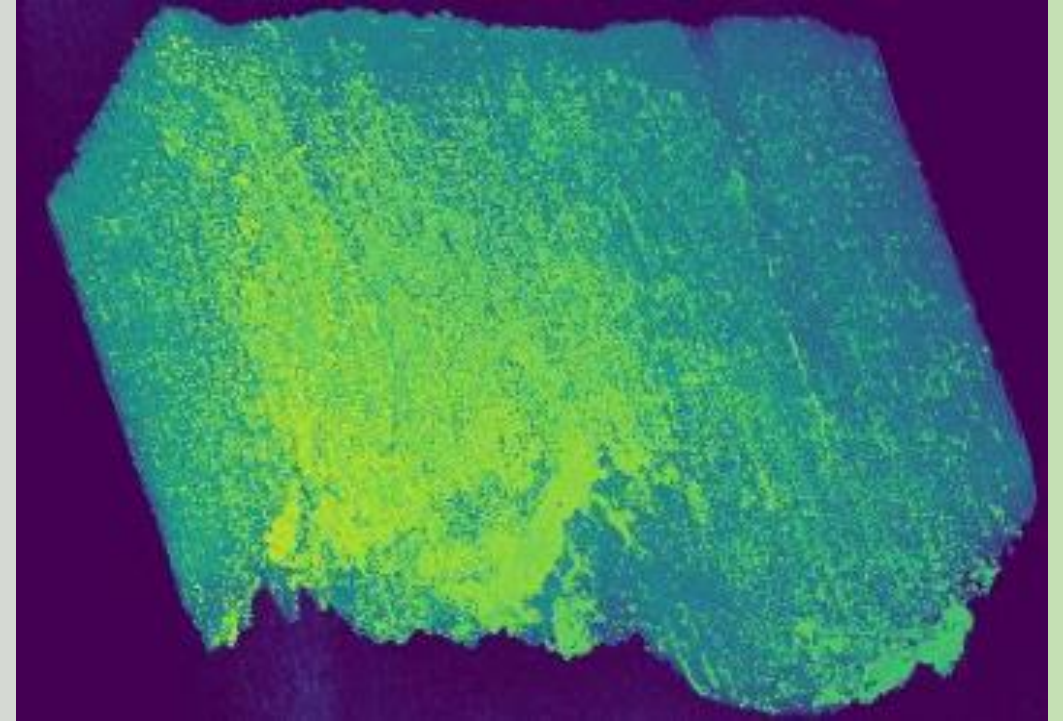
# XRF Mapping of Cu in MCQ Wood

- Day 154
- > 50% strength loss
- Shrinkage along X-cut face in contact with fungus on feeder strip
- High Cu along shrunken edges and at boundary of earlywood and latewood (→)
- Low Cu elsewhere within wafer and on X-cut face that was not in contact with fungus (→)



# XRD 3D Crystal Map of MCQ Wood Day 154

- Distribution and loading of copper oxalate crystal
  - CuOx crystal distribution is not uniform but extremely patchy
- Consistent with XRF Cu mapping results

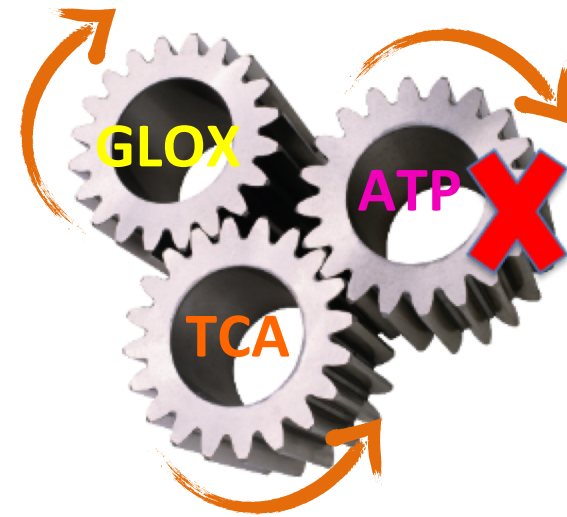




# Summary & Conclusions

- Fungus action on treated wood
  - Spatial - uniform to patchy Cu distribution
  - Temporal – starts before wood shows strength loss and appears to continue as wood is decayed
  - Chemical - transformation of Cu from carbonate to oxalate forms
- Implications
  - Activities require high amounts of energy or ATP

Adds support to hypothesis that disabling ATP production will defeat Cu tolerance



# Acknowledgments

- Funding and instrumentation provided by Soleil Synchrotron
- Funding provided by USDA Forest Service
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- Micronized CuCO<sub>3</sub> provided by Koppers, Griffin, GA