

# Using silicon levels to rediscover lost rock art painting techniques

Deborah Oke<sup>1</sup>, Blake Catlett<sup>2</sup>, Antony Peng<sup>2</sup>, Emma Endres<sup>2</sup>, Janet Macdonald<sup>2, 3</sup>

<sup>1</sup>Northeastern University, Department of Chemistry & Chemical Biology, Boston, MA, 02115

<sup>2</sup>Vanderbilt University, Department of Chemistry, Nashville, TN, 37235

<sup>3</sup>Vanderbilt Institute of Nanoscale Science and Engineering, Nashville, TN, 37235

## Introduction

### Background

- The Anishinaabe people in the Great Lakes region consist of several indigenous tribes
- Their rock art has evaded erosion for centuries
- Graffiti only survives 1-2 years
- Paint's pigment is made of hematite ( $\alpha\text{-Fe}_2\text{O}_3$ )

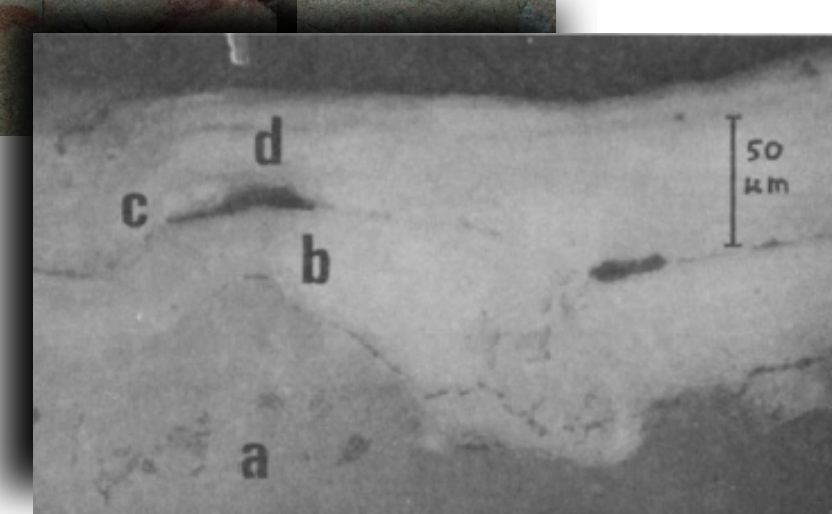


### Focus

- Methods to make the paint have been lost
- Silica layer mixed with and surrounding hematite



Agawa Rock

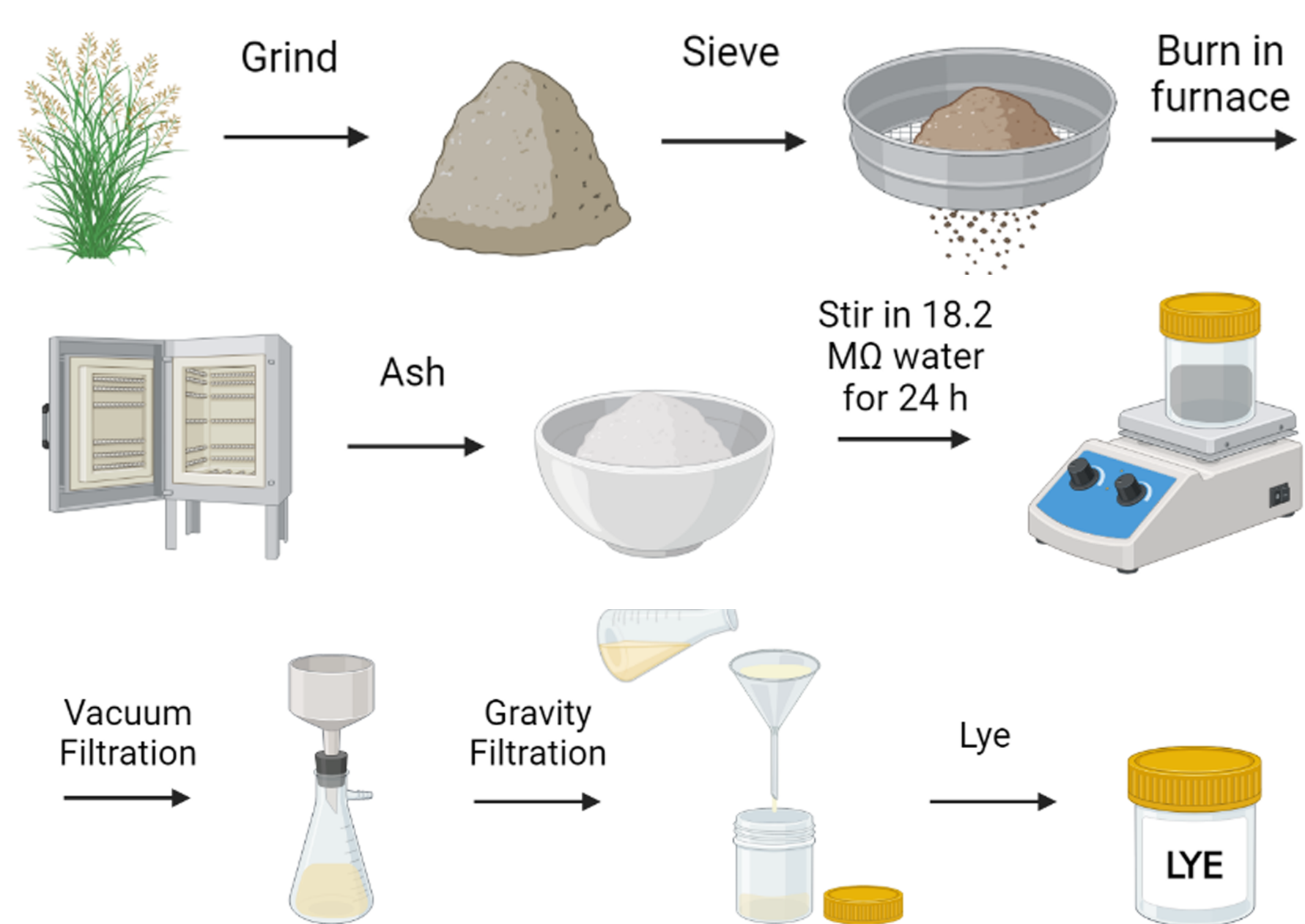


SEM of Rock Sample  
a) Rock base  
b) Majority silica white layer  
c) Paint made of hematite  
d) Silica layer on surface

### Objective

Can the painting techniques be reverse-engineered using lye as natural sources of silica?

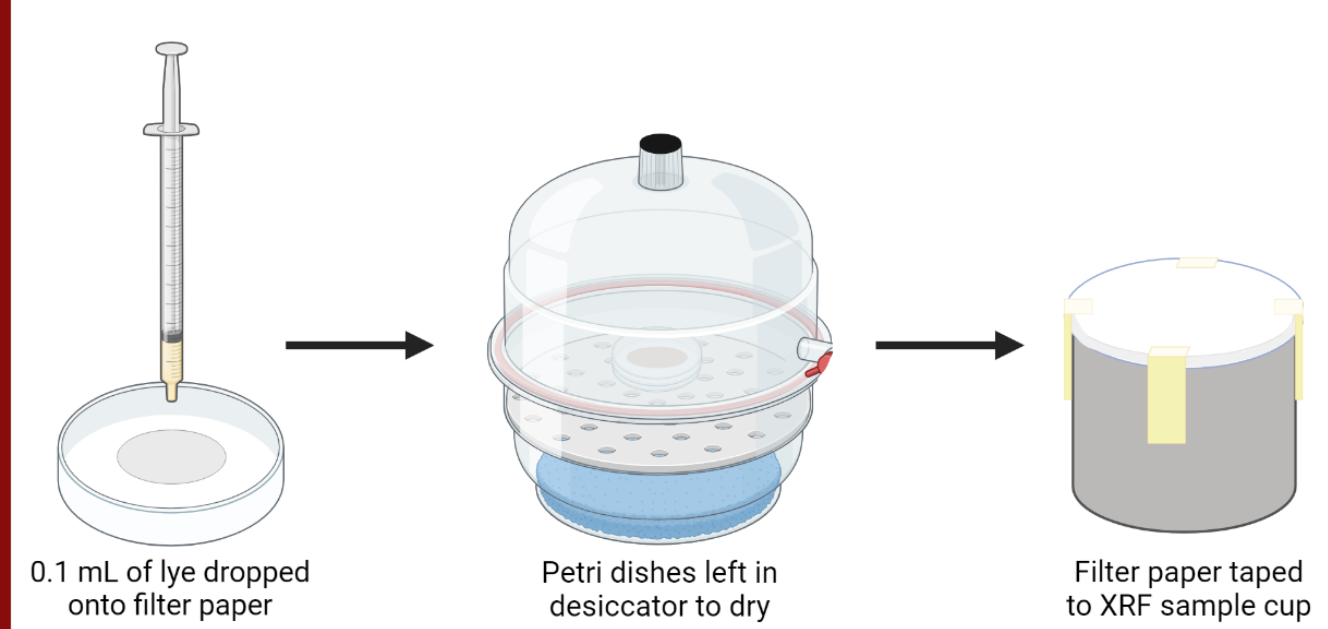
## Lye Formation



Sweetgrass, horsetail, cedar bark, red osier dogwood, and tamarack bark were used to make lyes

## Determining Silicon Contents

### Preparing Samples for X-ray Fluorescence

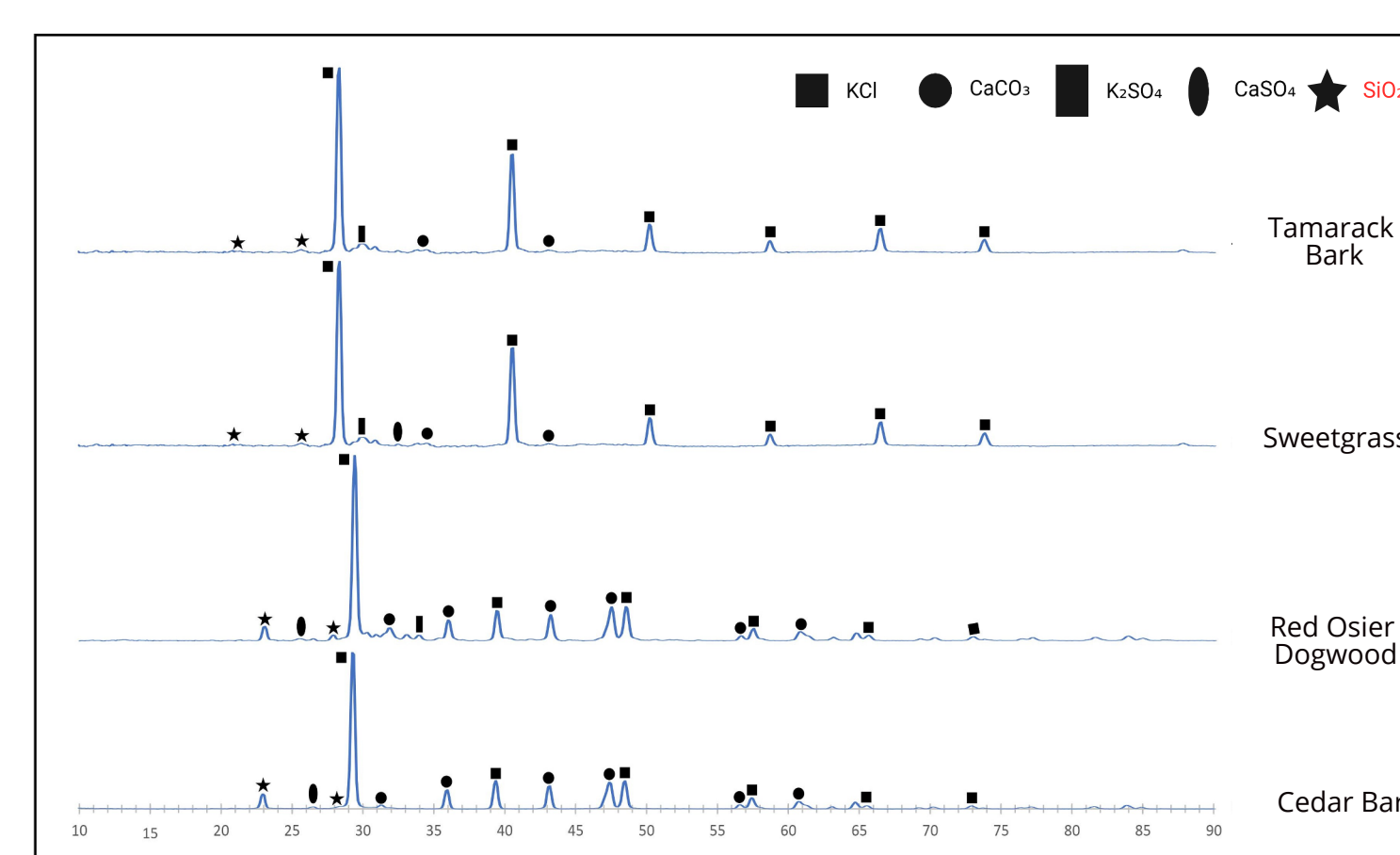


### Average Changes in pH of Lyes

Given that the lye made from 2h combusted ash had the smallest average difference in pH, those lyes were used for later experiments

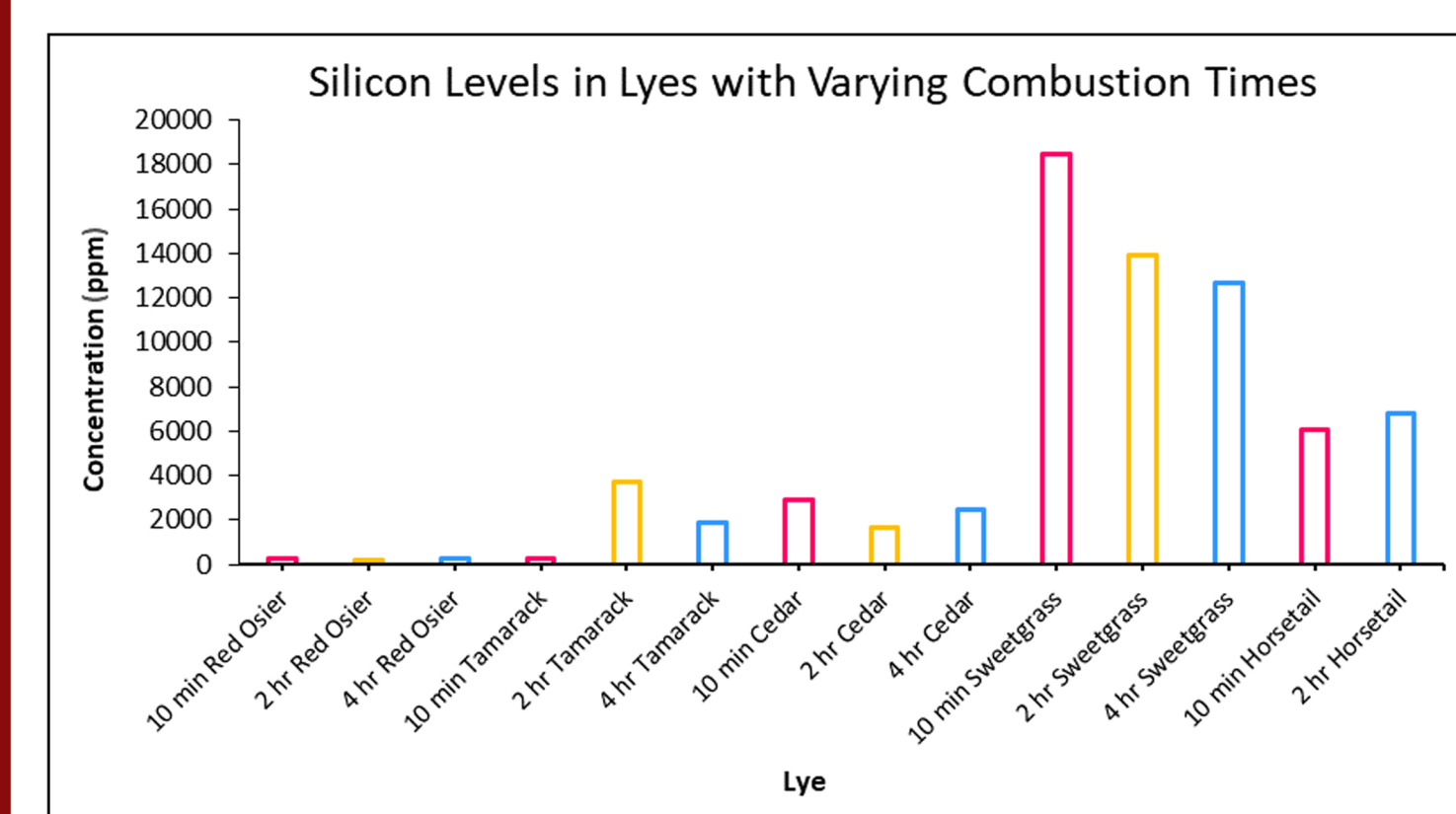
Combustion Time	Average Change in pH
10 minutes	0.738
2 hours	0.330
4 hours	0.497

### X-ray Diffraction Results



XRD determined that there was not a significant amount of crystalline silicon in the combusted ashes, indicating that most of the silicon contents detected were due to **amorphous silicon**

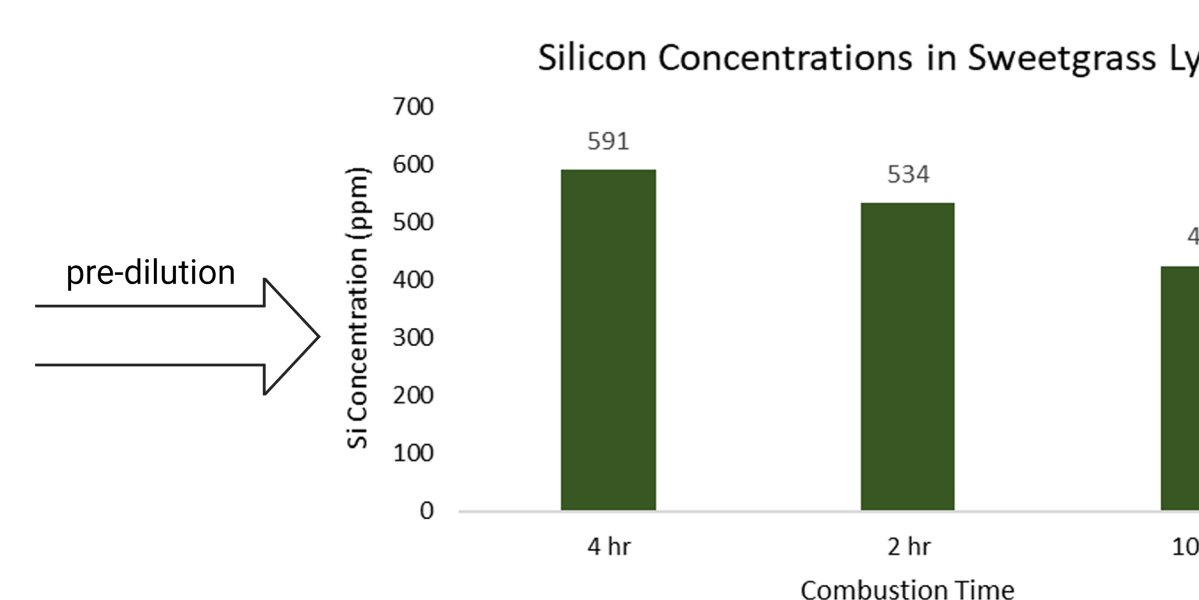
### X-ray Fluorescence Results



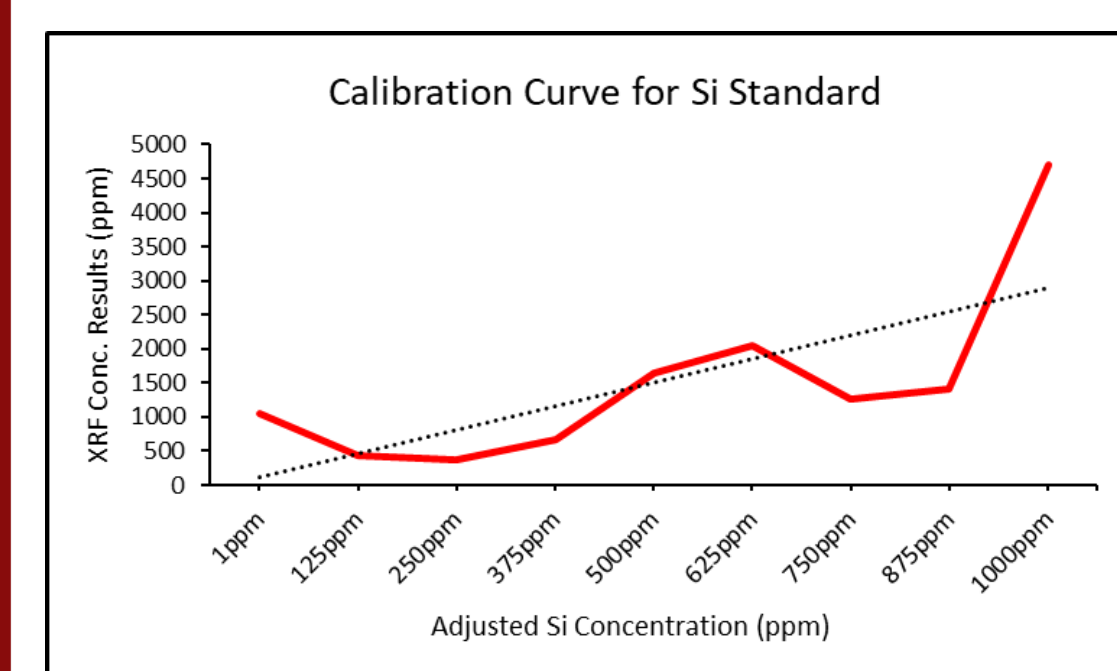
### Inductively Coupled Plasma Optical Emission Spectroscopy Results

Sweetgrass samples were diluted to less than 1 ppm and ran through ICPOES

10 min - 0.327 ppm  
2 hr - 0.411 ppm  
4 hr - 0.455 ppm



ICPOES data gave opposite silicon conc. results than XRF



Though XRF was unable to provide accurate silicon concentrations, the results indicated **relative silicon concentrations** in the lyes made

## Painting

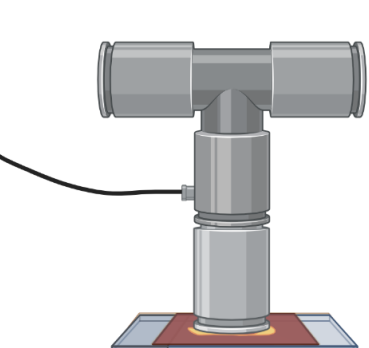
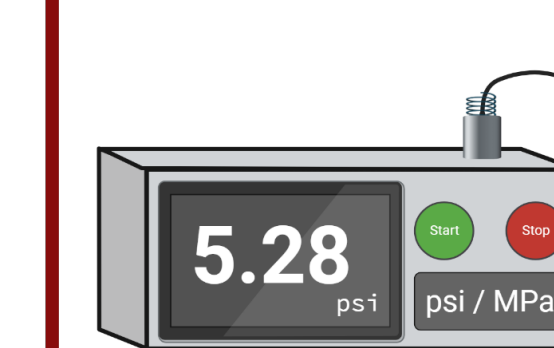


All slides were rinsed with 1L of deionized water after the paint had dried

Nearly all painted slides had most of paint removed after rinsing, with the exception of water glass (Si conc. of 6000 ppm)

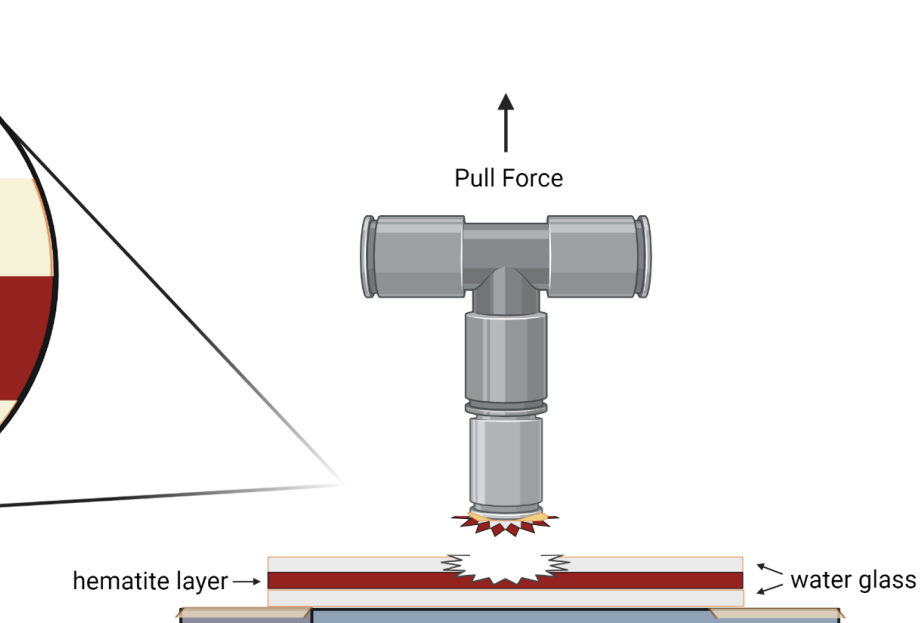
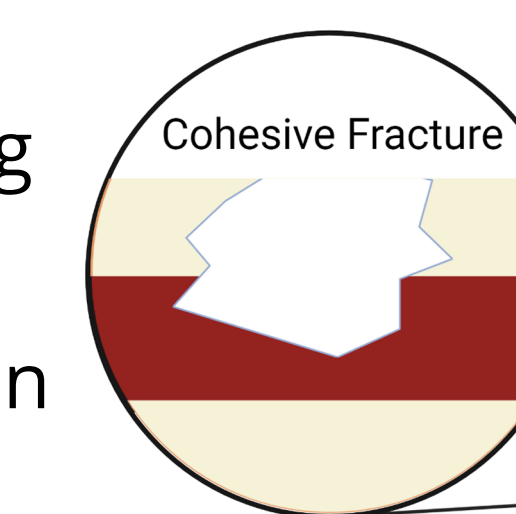
All slides retained the majority of their paint, with few areas completely rinsed off

## Future Directions

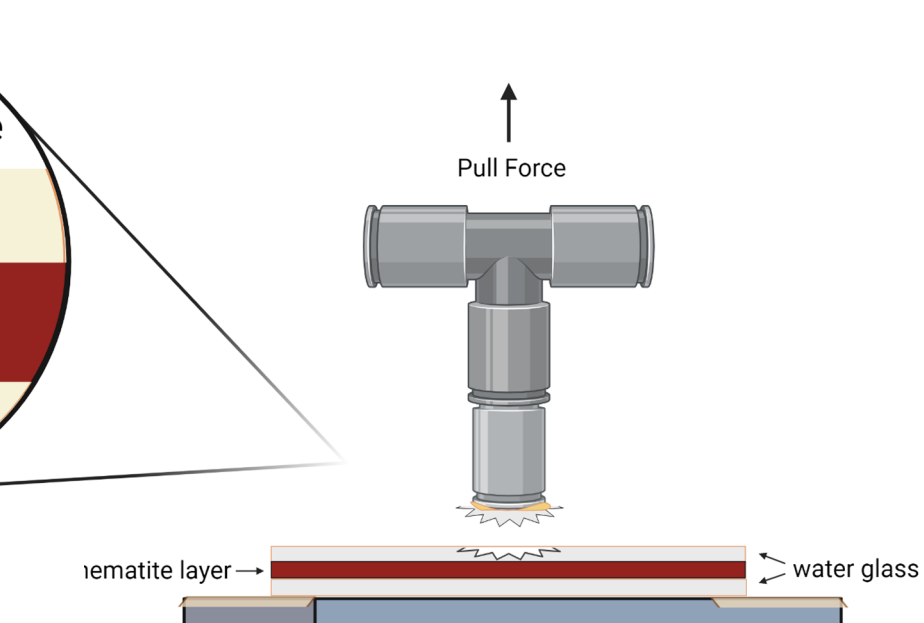
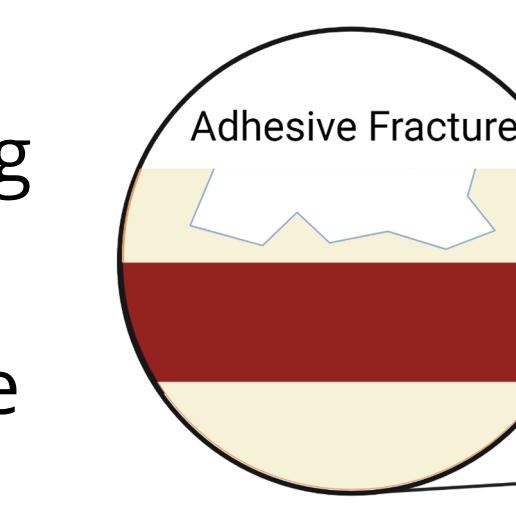


Have a pull-off test (ASTM D4541) conducted on samples to determine force needed to remove paint

Cohesive fractures occur when coating is removed within layers, which may indicate adsorption of silicon to the paint

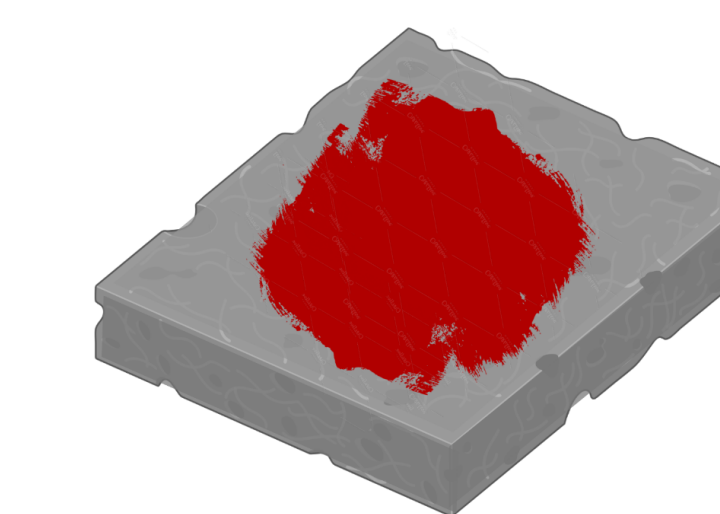


Adhesive fractures occur when coating is removed between layers, which may indicate a lack of silicon adsorption



Create lye with additional plants such as spirit wood, bullrush, kinnikinnick, etc., and determine silicon concentrations of each

Paint directly onto rock and test for the effect of surface roughness on durability



## References

- [1] C. Martin. Kayaking among Pictographs, Islands (24 Photos). SooToday.Com, 25 Aug. 2022,
- [2] J. M. Taylor, R. M. Myers, and I. N. M. Wainwright, JSTOR., 1974, 14 (2), 28-43
- [3] J. R. Dodson (2011). Wheat straw ash and its use as a silica source [Doctoral dissertation, University of York]
- [4] T. Moriyama, A. Morikawa, Rigaku Journal, 2017, 33 (1), 24-29
- [5] Test Methods for Coating Adhesions, DeFelsko Inspection Instruments, DeFelsko.com

## Acknowledgements

Funding for this research was provided by the National Science Foundation (Grant: NSF-DMR 1852157)

Thank you to VINSE, the Morgan Lab, and the Macdonald Lab, largely to Dr. Janet Macdonald, Blake Catlett, Antony Peng, and Emma Endres

Graphics created with biorender.com

