Understanding the Durability of Iron Oxide Silica Bonds in Anishinaabe Cliff Face Paintings

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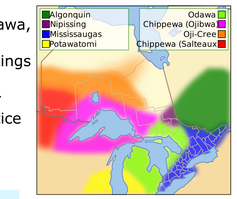
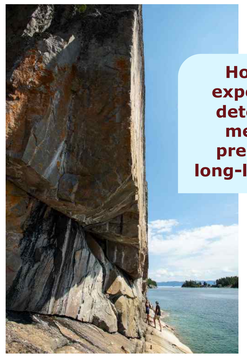
The Chemistry Behind Anishinaabe Art

The Anishinaabe Cultural Group

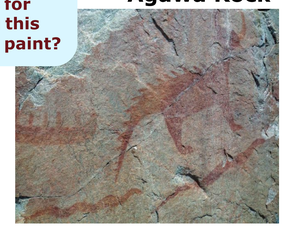
- Consists of the Ojibwe, Potawatomi, Odawa, Algonquin, Oji-Cree, Mississauga people
- Have created hematite (α-Fe_2O_3) rock paintings over the past 2,000 years
- Exposed year-round to rainfall and lake water
- Tradition of creating paints is now a lost practice



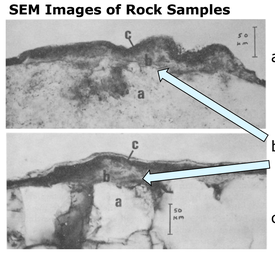


How can we experimentally determine the methods for preparing this long-lasting paint?

Agawa Rock



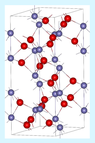
SEM Images of Rock Samples



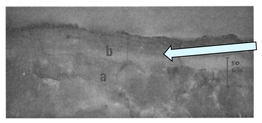
a) Rock base composed of many materials: quartz (silica), microcline, albite, biotite mica

b) White intermediate layer (contains high amounts of Si)

c) Pigment layer (hematite)



α-Fe_2O_3

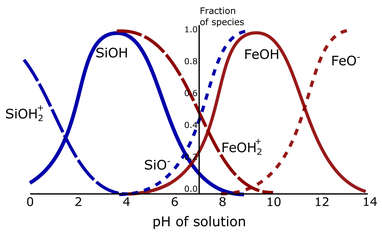


Even unpainted rock has white layer

Iron oxide is bonding to the silica in the white layer → **Goal: investigate the properties of these bonds**

pH and Surface Chemistry

Surface of pigment powder: **Fe-OH**
Surface of silica on cliff face: **Si-OH**



Goal: Study surface bonds between iron oxide and silica, determine when bonds are strongest

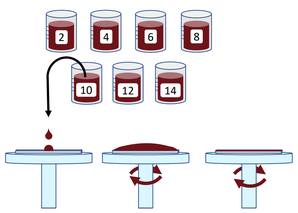
Point of Zero Charge:

- pH where surface density of cations and anions are equal
- Colloidal system is least stable

- Ion concentration & type of ion change depending on pH
- Fe-OH and Si-OH surfaces most likely to occur at point of zero charge (pzc)
- Hypothesis: **strongest bonds will be at pH 3.5-8.5**

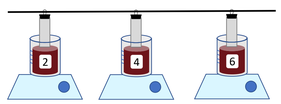
How to Prepare Hematite Paint

Spin Coating Setup



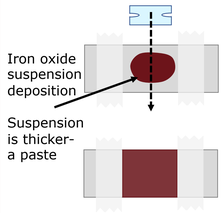
3 mL of iron oxide suspension is pipetted onto a microscope slide on the metal spin coater plate. The deposit mostly evaporates off (in about 45 mins) then spreads out while spinning for 30 seconds, leaving a thin film.

Dip Coating Setup



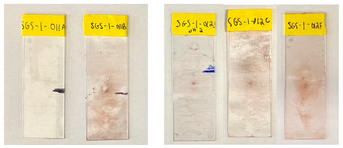
The slides are lowered into a stirring iron oxide suspension for about 12 hours.

Doctor Blading Setup



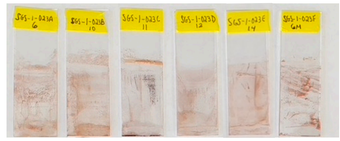
Iron oxide is painted on the slide, razor blade is slid across the surface; scotch tape allows for even coating.

Spin Coating Application Results



20 mg/100 mL Fe_2O_3 in DI water | 200 mg/100 mL Fe_2O_3 in DI water | pH 2 | pH 6 | pH 12

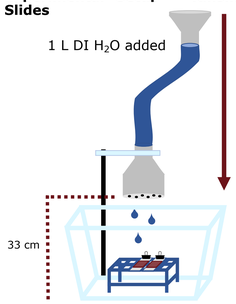
Dip Coating Application Results



Both spin coating and dip coating did not create evenly coated slides that could be easily analyzed once "rained on" → **doctor blading** was the most effective

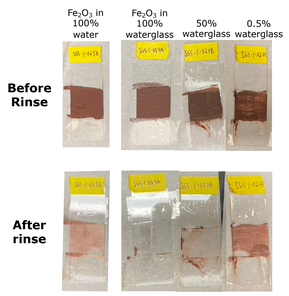
Comparing the Durability of Paint Using Rainfall

Experimental Setup – Rinsing Slides



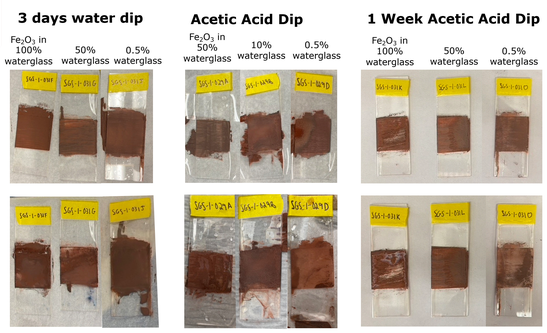
2 slides at a time rinsed with 1 L H_2O *via* Büchner funnel, left to dry & photographed

Paints Prepared using the Doctor Blading Method



The pigments were prepared by mixing iron oxide powder with varying concentrations of waterglass (sodium silicate), a highly basic solution. The paints were applied to microscope slides *via* doctor blading, then rinsed off.

How will changing the pH affect the adhesiveness? Dipping the slides in water and acid was a way to lower the pH after the paint was applied. It proved to be highly successful.



Pigment Making 101

Doctor blading was the most effective paint deposition method. It also most closely resembled traditional paint preparation in both the paint's consistency and its application.

Time plays a major role in the strength of the bonds: there is an aging process involved.
Much harder to remove pigment with Kimwipe; had to scrape at slide instead of wiping gently.

Dipping in acetic acid: changes pH of waterglass, hardens it into gel.
The pigment could still be removed with Kimwipe if applied and rinsed with Büchner funnel the same day.

Because it was concluded that the hematite pigment needed time for the bonds to be strengthened, it would have had to be painted on a day with **no rainfall and no high lake water levels** and given time to dry.

Future Directions

August
- SEM & profilometry, quantify with ImageJ
- More trials - standardized process

September
- Find better rainfall simulation
- Rinse more slides at once

October
- Substitute waterglass with natural bases: lye, horsetail

November
- Test with genuine rock sample
- Spinal fluid of a sturgeon

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Acknowledgements

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