Excellence in Electron Microscopy Awards –2017

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Project Title: Rock Art Pigment Characterization using SEM-EDS and FIB SEM

Project Description

Rock art sites, otherwise known as pictographs, are important archaeological locales, and their analysis can generate new insight into long-term histories of human-mineral interaction, resource use, and early artistic expression. The objective of this project was to develop and refine SEM methods for analyzing small fragments of rock art paintings to better understand the pigments used to create them. For this pilot study we analyzed a fragment of a pictograph panel from Lake Babine, British Columbia (Figure 1). While the exact date of the pictograph painting event is unknown, human occupation in the immediate vicinity dates as early as 6,000 years before present. To reconstruct ancient pigment preparation practices, we used a combination of SEM techniques, X-ray diffraction, SQUID magnetometry, μ-FTIR and μ-Raman to assess the chemical and mineralogical composition of the fragment layers. Rock art fragments are a complex strata of rock panel substrate (typically granite, quartz or limestone), mineral and/or biological accretionary deposits (weathering products, oxalate deposition), and the pigment itself (Fe-oxide matrix with accessory minerals, binders, and/or extenders). Using SEM techniques we were able to examine the phase structures of iron oxide pigment and accessory minerals, explore the condition of the pictograph, and gain some insight into the selective exploitation of Fe-oxide producing bacterial deposits for pigment production.

Results and Interpretation

Our results have revealed evidence pertaining to the source selection of the iron oxides used to paint the pictographs and potential evidence for pigment enhancement by pyrotechnology. Figure 2 is a cross-section EDS map showing the rock substrate, pigment particles, and surface accretionary deposit. The pictographs at Lake Babine were painted on an outcrop of argillaceous limestone covered in a kaolinitic weathering deposit. This natural canvas, and subsequent accretionary deposition, has aided in the long-term preservation of the rock art panel. The red pigment is composed of a homogenized mixture of ferrihydrite and hematite that was biogenically produced *ex situ*, most likely in a spring deposit, by aquatic Fe-oxide producing bacteria, including *Leptothrix ochracea* and *Gallionella* spp. The Fe-oxidizing bacteria are freshwater species that precipitate distinct microtubular sheaths of Fe-oxyhydroxide as a function of cellular reproduction. Figure 3 is a SE image mosaic the paint particle region of interest, showing the *L. ochracea* microfossil sheaths. The microfossils are fragmented and randomly oriented, which is a direct result of the pigment being homogenized by human hands. Figure 4 shows an area of *L. ochracea* microfossils alongside traces crystalline hematite (α–Fe_2O_3). The thin, sheet-like polymorph of hematite seen here is the result of crystallization of ferrihydrite to hematite either slowly by natural phase change, or rapidly as a result of low temperature thermal alteration. Low temperature thermal alteration (<400°C) will rapidly induce iron oxide phase change and enhance colour properties of the pigment. Preliminary results by high-sensitivity SQUID magnetometry support the interpretation that the pigment underwent low temperature thermal alteration. Our preliminary results demonstrate the potential of microanalytical applications in rock art studies, and have significant implications for pigment source selection, preparation practices, and decision-making in the placement of pictograph panels in British Columbia.

Acknowledgements

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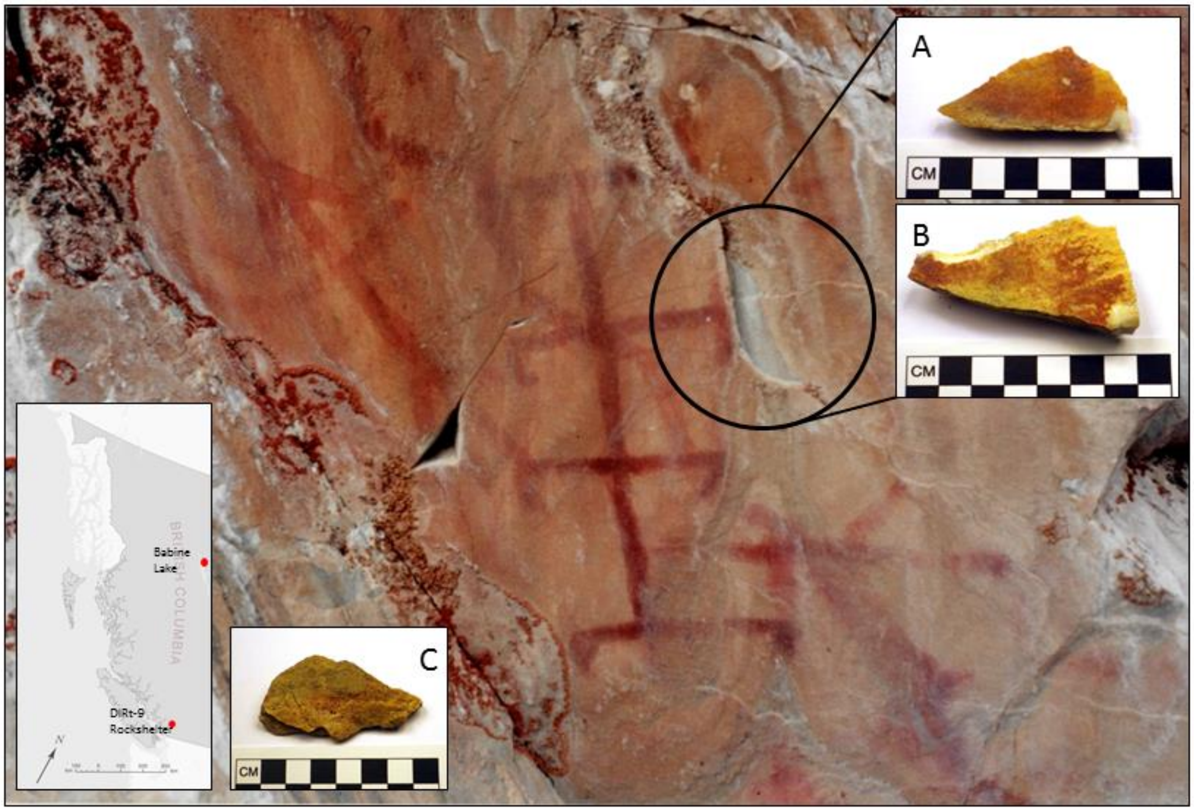

Figure 1: Composite image of Boling Point pictograph site on Lake Babine, British Columbia (Canada). A cross section of Sample A was the subject of analysis.

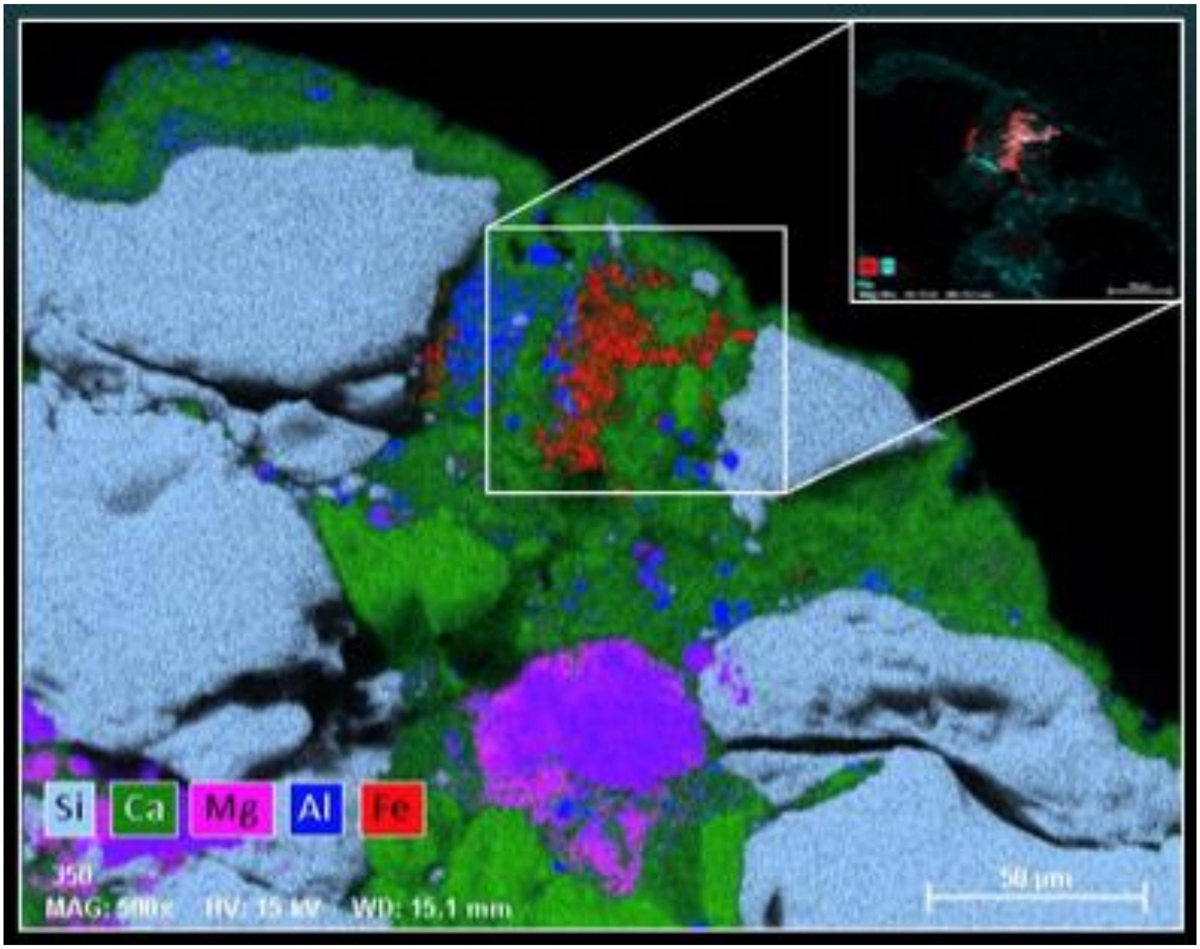

Figure 2: Composite EDS map focusing on an area with a red paint particle. Note the high Ca+Al surface encrustations (kaolinite), and particles of Mg+Fe (magnesioferrite). The rock substrate is an argillaceous limestone, while the red pigment particles are enriched with Fe. Inset: detail EDS map of paint particle area showing correlation of Fe and P, with P indicated in blue.

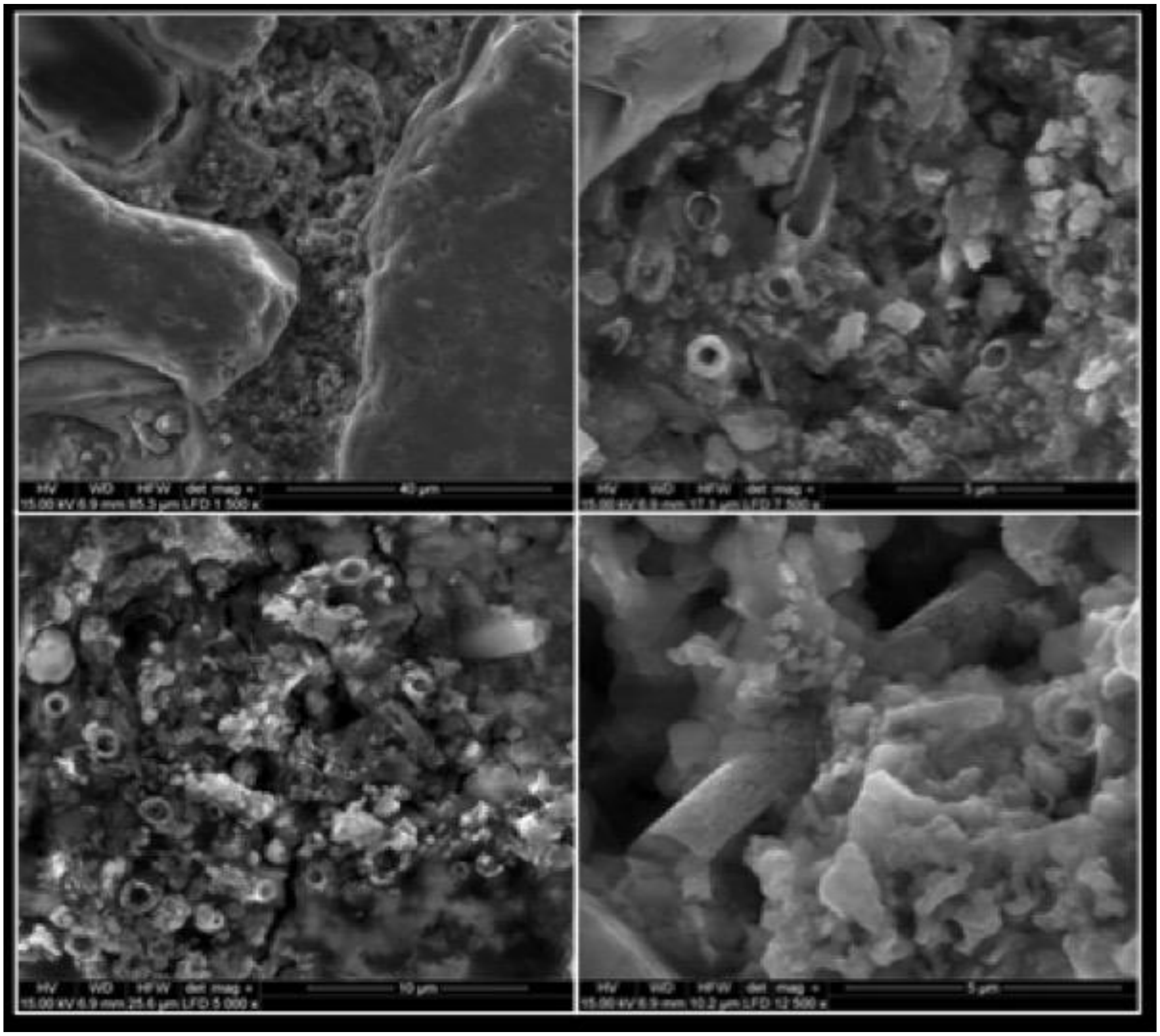

Figure 3: SE Image mosaic of paint particle regions of interest. Argillaceous limestone and paint matrix (upper left); details of L. ochracea microfossils showing fragmentation and variable directionality (upper right, lower left); detail of well-preserved L. ochracea sheath (lower right).

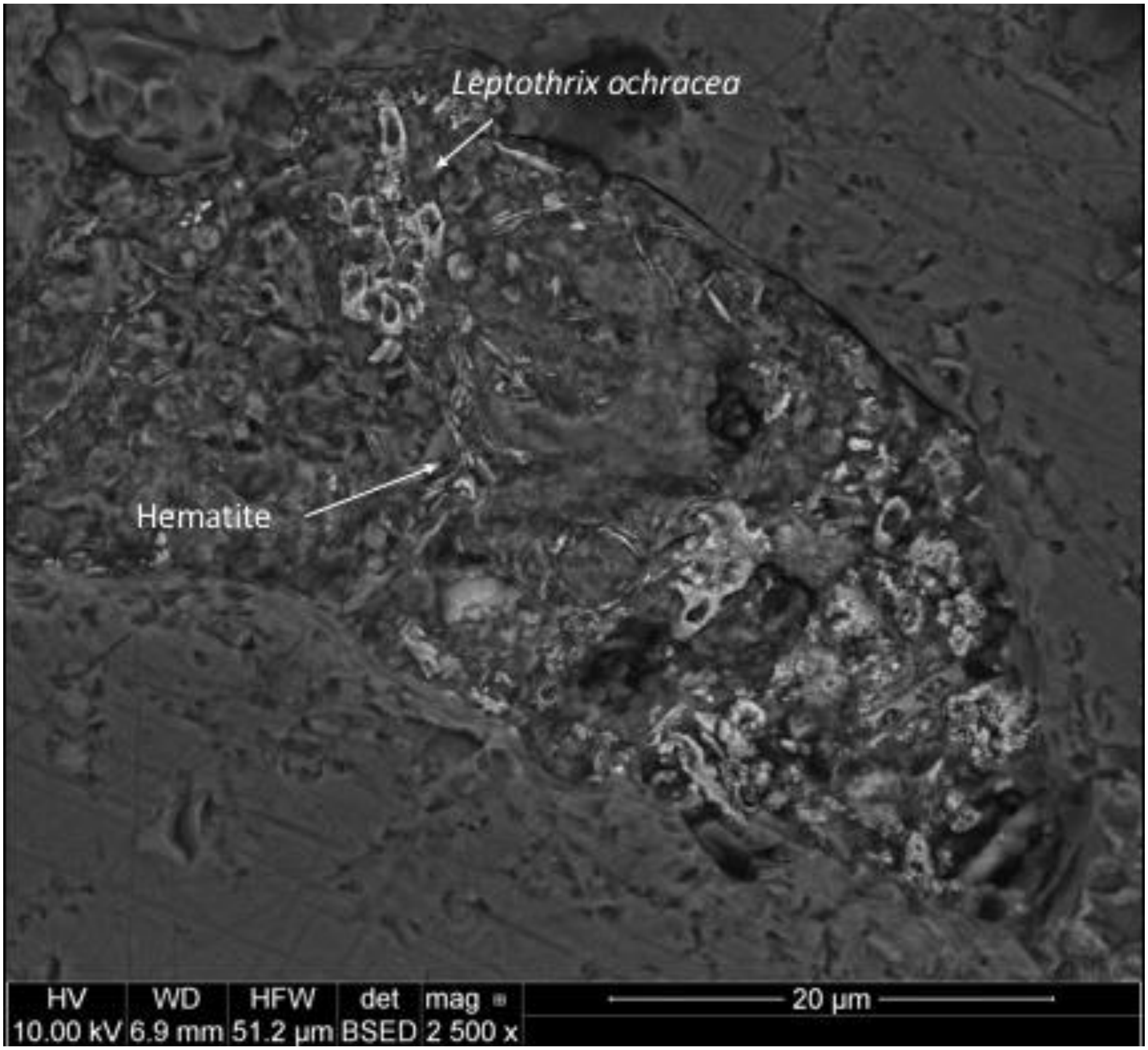

Figure 4: BSE image of paint particle area showing clusters of Leptothrix ochracea colonies. Thin, fibrous structures are a polymorph of hematite (α–Fe_2O_3).