



Materials science insights into Indigenous rock art painters and ochre pigment materiality at Babine Lake, Canada

Brandi L. MacDonald^{1,2} · Alexa Kuo¹ · Farid Rahemtulla³ · Kwun Whess^{3,4} · David Stalla⁵

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Abstract

Pictographs, and the landscape formations they are featured upon, are culturally significant places among Indigenous communities. Here, we present the results of a field survey and compositional analysis of pictographs and the mineral pigments used to produce them at Babine Lake (British Columbia), in the traditional territory claimed by the Lake Babine Nation, the Tl'azt'en Nation, and the Yekooche Nation. The monochrome motifs are produced with iron oxide mineral pigments (red ochre), and are all painted on prominent, open-air rock faces overlooking deep water. This study also includes collection and analysis of red ochre pigment sources within the area for comparison to the pictographs. Using a series of microanalytical methods applied to the local raw materials and rock art paints, we offer insights into characteristics of pigment materiality, such as artistic selection of minerals with different physicochemical properties and the *chaîne opératoire* of paint preparation. Our results show that rock art painters active at Babine Lake chose a diversity of iron oxide types to produce different pigment mixtures with distinctive properties, including the harvesting and thermal enhancement of iron-rich biominerals from colonies of aquatic, iron-oxide-producing bacteria.

Keywords Rock art · Ochre pigment materiality · *chaîne opératoire* · Microanalysis · SEM-EDS · Raman spectroscopy

Introduction

Documenting, analyzing, and preserving rock art heritage is a high priority for Indigenous communities, archaeologists, and rock art researchers worldwide. For several decades, rock art research in British Columbia (Canada) has had a predominant focus on interpreting motifs and exploring how pictographs are connected to landscapes and descendant Indigenous communities (Arnett and Morin 2018, York et al. 1993, Mitchell 2015, Lundy 1974, Williams 2001). Recently,

studies have begun to integrate field-portable instrumentation and lab-based analyses to document and analyze rock art and the material characteristics of the pigments used to produce them (MacDonald et al. 2019a, 2019b, Skala 2015, Velliky and Reimer 2013). Earlier research using materials-based approaches was led by Wainwright and colleagues in the 1970s and 1980s (Wainwright 1985, 1990), with an emphasis on studying the age and deterioration of rock paintings in efforts to develop strategies for their conservation. Our study uses a materials-based approach, applying methods in materials sciences to explore the concept of the rock art *chaîne opératoire*, which includes various aspects of mineral selection, pigment materiality, and the production of paints with specific physiochemical properties.

This study is centered on rock art pigments used at Babine Lake, located in the northern interior of British Columbia (Fig. 1), in addition to a small assemblage of artifacts from an occupational site at Babine Lake, and locally-available source deposits of iron-rich raw materials. This research takes place under the aegis of the Babine Archaeology Project (Rahemtulla 2019, 2020), developed with and for the Lake Babine Nation (LBN). The project is a 10+ years long collaboration, integrating

✉ Brandi L. MacDonald
MacDonaldB@Missouri.edu

¹ Archaeometry Laboratory, University of Missouri Research Reactor, Columbia, MO, USA

² Materials Science and Engineering Institute, University of Missouri, Columbia, MO, USA

³ Department of Anthropology, University of Northern British Columbia, Prince George, BC, Canada

⁴ Lake Babine Nation, Burns Lake, BC, Canada

⁵ Electron Microscopy Core, University of Missouri, Columbia, MO, USA

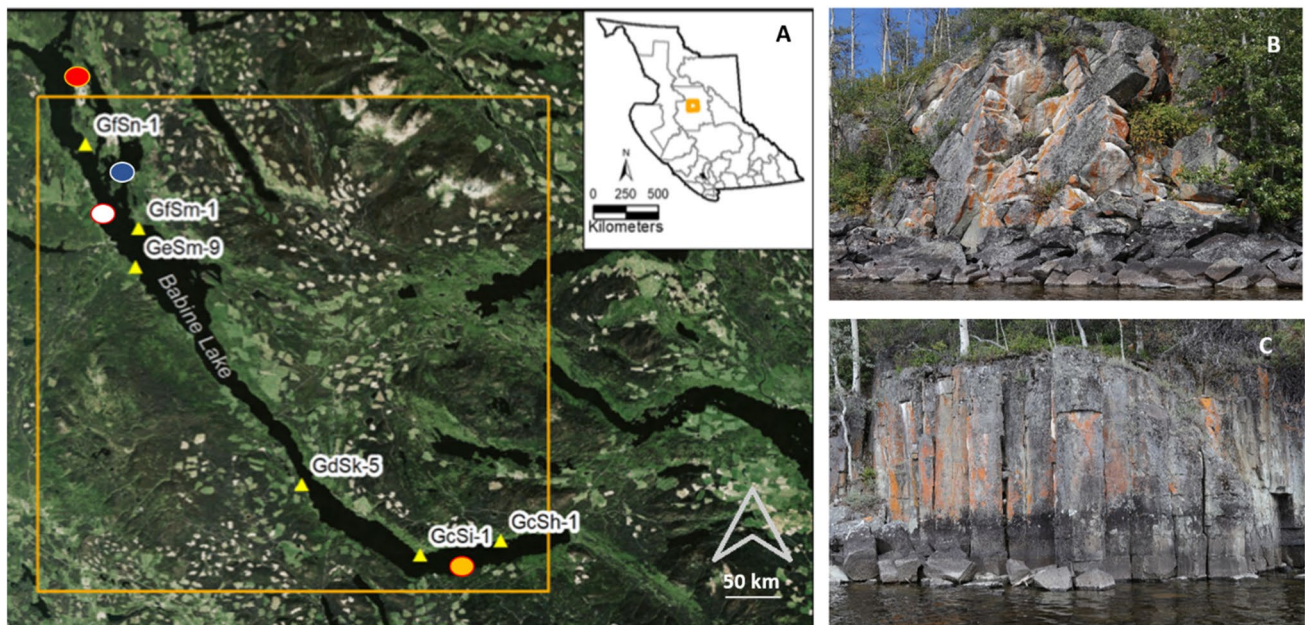


Fig. 1 Study area and typical rock art settings. **A** Babine Lake, British Columbia. Rock art sites are labelled. Ochre sources key: ● Granisle Mine ● Bell Mine ○ Red Bluff Provincial Park ● Silver Island.

a community-engaged archaeological field school and outreach program with LBN (Rahemtulla 2020).

Archaeological context

Human occupation and archaeology at Babine Lake

Babine Lake is situated between the Skeena and Fraser Rivers, two major waterways that run through northern interior British Columbia. Prior to European incursion, the communities that occupied this area were highly mobile, their movement around the landscape tied largely to seasonally-based social gatherings and subsistence procurement through fishing, hunting, trapping, and root and berry gathering. The Babine Lake area was important for regional-scale socio-economic interaction, by both land and water, connecting the Interior Dakelh-Carrier groups to the Heiltsuk, Nuxalk, and Tsimshian-speaking groups on the outer Pacific coast to the west, and to other Interior Plateau and Fraser Valley communities to the east and south. Archaeological research and ethnohistorical documentation have shown that the Babine Lake area was an active setting for Coast-Interior socioeconomic exchange networks along what are known as the *grease trails*, where eulachon oil, obsidian, nephrite, copper, ochre pigments, and textiles and foodstuffs were traded (Mitchell and Donald 1988; Bishop 1987; Morice 1906, Reimer 2012). Seasonal intercommunity gatherings

Silver Island could not be accessed during fieldwork. **B** Granodiorite outcrop bearing Gullwing pictograph (GcSh-1); **C** Section of massive columnar basalt at Newman Peninsula (GfSm-1)

were crucial events through which social and economic relationships were mediated, both within the region and beyond.

The history of Indigenous settlement on Babine Lake is under investigation as part of the Babine Archaeology Project. Preliminary results have corroborated oral histories and written historic accounts on subsistence economic practices. Ethnohistoric records (Morice 1906) indicate that Babine Peoples (traditionally known as the peoples from the pre-contact villages of Wit'at and Nedoats) harvested Skeena River salmon with the use of wooden fish weirs, but the antiquity of this practice was unknown. Recent excavations have revealed a large fishing village dating to at least 1,300 years before present (Rahemtulla 2012), and preserved fish weir elements dating to 1,000 years ago (Rahemtulla 2019). The lake harbors spawning grounds for the vast majority of Skeena River Sockeye salmon and other fish, which provided a significant economic resource for several centuries, if not longer. Ongoing work suggests that sophisticated land and resource management practices were applied to sustain economic and cultural systems (Rahemtulla 2020).

Rock art at Babine Lake

The shorelines around Babine Lake are rocky, steeply sloped, and thick with deciduous tree cover. Various points along the ~ 150 km of shoreline are punctuated by prominent, vertical rock faces striking upward from the water

below. There are six panels of rock art painted on these open-air rock faces, ranging in scale from a single pictograph (Gullwing Point, GcSh-1) to a concentration of over forty motifs (Newman Point, GfSn-1), for an estimation of over 150 individual glyphs across the lake. Although archaeological evidence for human occupation in the area dates to at least 5,000 years before present (Ames 1979), the timing of rock art production at Babine Lake remains largely undetermined. The possibility for direct or indirect dating of the pictographs in this area is limited due to a combination of factors. The open-air nature of Babine Lake rock art is generally not conducive to rapid buildup of thick calcite or silicate mineral accretions that could be conducive for radiometric dating (Bonneau et al. 2017; Aubert et al. 2004), as is more typical in rock shelter and cave settings. The climate and exposure are also unfavorable to the preservation of datable organic components that may have been added to the paint mixtures. At minimum, we can indirectly attribute many of the paintings to pre-date the time of European settlement in the area because written accounts from 1876 (Cole and Lockner 1989) and through the 1880s (Morice 1906) indicate that the rock art was already present at that time, that some already

exhibited signs of aging (visibility loss, obscuration through overlying mineral deposition, lichen overgrowth), and that Indigenous Elders alive at that time attributed the rock art painters as people from multiple generations before (Morice 1906, Cole and Lockner 1989, Mitchell 2015).

Figure 1 illustrates the study area and typical rock art settings. Nearly all of the paintings that remain visible today are monochrome red, with shades ranging from red–orange, pale red–pink, to violet–red. Table 1 is a summary of the characteristic motifs. Figure 2 shows examples of glyph styles. The motifs are either figurative and depict humans, anthropomorphic animals (caribou, snake, fish, beaver, bird, toad, otter, bear) or objects (canoe, sticks, fish weirs, various tools), or non-figurative geometric forms (circles, straight, curved or zig-zagged lines, dots, crosses, chevrons, diamonds, tally marks). The predominant artistic and symbolic themes communicate information about food resources and territoriality, such as depictions of good hunting and fishing areas and demarcations of clan territories (Morice 1906). Thus, as highly-mobile groups moved around this landscape by boat on a seasonal basis, many of the paintings were intended to function as prominent signposts, signaling key information

Table 1 Babine Lake rock art sites and their characteristic features. All sites are accessible only by boat. Glyph descriptions are current as of 2022 fieldwork

Site & samples	Characteristics
Newman Peninsula—Pillar Point (GfSn-1) <i>n</i> = 3 samples	Setting: pictographs are painted along an outcrop of tall-standing, columnar basalt. Off-boat access is narrow but possible if lake water levels are low. Several of the basalt columns are cleaving from the rock formation and will topple into the water resulting in permanent loss. Fading and lichen coverage are prominent Glyphs: 40+ individual glyphs. Non-figurative forms include vertical, horizontal, forked, waved, and zig-zagged lines, circles, dots, curved forms, chevrons, and tally marks. Figurative forms include a snake, two bear claws, fish, a frog, two human figures, and a fishing net (see Figs. 2a, 5c, e, f)
Nose Bay (GfSm-1) <i>n</i> = 3 samples	Setting: paintings spanning a granite outcrop at water level with some at higher elevation (> 2 m). Some image loss is evident from rock wall spallation and collapse. Extensive coverage by black and orange lichen Glyphs: 40+ glyphs. Non-figurative forms include: curved and straight lines, circles, dots, chevrons. Identifiable figurative forms include a bear, bear claw, human forms, a canoe with four passengers, a wide-eyed, winged figure (possible owl), a beaver, and a mountain (see Fig. 2b, f, g)
Tachek Island (GeSm-9) <i>n</i> = 1 sample	Setting: glyphs are painted at water level on a steep granite batholith. Many glyphs are obscured by extensive black lichen. Most are highly faded Glyphs: 8 glyphs including a curved line, circles, radiating waves, two sun depictions, a bear claw, and a horizontal wavy line indicating water (Fig. 2h)
White Cross Pictographs (GdSk-5) <i>n</i> = 3 samples	Setting: pictographs are painted on a granite outcrop. Moderate coverage by orange and black lichen. Notable image loss due to rock wall spallation. A narrow stone platform enables access by foot to a portion of the panel Glyphs: 28+ glyphs. Non-figurative forms include forked and vertical lines, crosses, chevrons, tally marks, diamonds, dots. Figurative forms include a caribou, bear claw, snake, human figures, fish, beaver, large horned animal (mountain goat?), and several unidentifiable animals (see Figs. 2d, 4d)
Boling Point Pictographs (GcSi-1) <i>n</i> = 3 samples	Setting: paintings are on a long outcrop of silicified limestone. Several appear faded due to thick accretions of calcite deposited overtop. Loss of panel sections due to rock wall collapse is evident. Moderate lichen coverage Glyphs: 35+ glyphs. Figurative forms include: beavers, bear claw, avifauna, a deer, a moon, human figures with missing limbs, a waterline or trapline. Non-figurative forms include circles, straight and stemmed lines, dots, forked vertical lines, crosses, curved lines, chevrons (see Figs. 2e, 4c, 5d, 7d)
Gullwing Pictograph (GcSh-1) <i>n</i> = 2 samples	Setting: single glyph painted high on an outcrop of granodiorite, overtop a thick white, matte, mineral accretion. Rock collapse enables foot access Glyphs: Single glyph depicting anthropomorphized, bird-like, winged figure with two legs (see Fig. 2c)



Fig. 2 Examples of glyph styles at Babine Lake. **A** GfSn-1. A complex panel depicting a large animal figure, a fish, a series of dots and tally marks, zig-zagged lines, circles with dots inside. Scale=5 cm. **B** GfSm-1. Animal face with wings or feathers, or antlers (owl, crane?). Scale=3 cm. **C** GcSh-1. Standing bird figure. Scale=5 cm. **D** GdSk-

5. Four vertical lines and cross-lined elements. Scale=3 cm. **E** GcSi-1. Bird figure. Note the rock wall losses to the bottom and lower left of the glyph. Scale=3 cm. **F** GfSm-1. Panel of lines and circles. Scale=3 cm. **G** GfSm-1. Bear claw. Scale=3 cm. **H** GeSm-9. Inverted bear claw. Scale=3 cm

between social groups about shared identity, subsistence practices, and relationships to the land.

In early twentieth century ethnohistorical writing, Morice (1906) sketched and described the rock art from Babine Lake as short communications between mobile hunting parties drawing attention to ideal camping sites or hunting or fishing areas, the distances between campsites, potential hazards along travel routes, the injury or death of an individual, or to the presence of other parties passing through the area. He wrote that, in some instances, these communications were ephemeral, drawn using charcoal and not intended to maintain a long-term presence on the landscape. Decades later, efforts to document the pictographs at Babine Lake were completed by Corner (1968), and Mohs and Mohs (Mohs and Mohs 1976a, 1976b). In *Pictographs in the Interior of British Columbia*, Corner provided sketches of selected glyphs at Babine Lake (Corner 1968), but with minimal

description. Later, Mohs and Mohs (Mohs and Mohs 1976a, 1976b) undertook surveys of the region's archaeological sites, which included general descriptions and hand-drawn sketches of the motifs at the six sites included in our study.

Those previous surveys of Babine Lake lacked details on the setting and condition of the rock art. Since those recordings it is clear that physical damages have occurred, such as vandalism, rock wall collapse, and lichen overgrowth, stressing a need to document and develop monitoring strategies for those that remain intact. There are few oral histories or written records available to us that detail any aspects of pigment selection or preparation in the Babine Lake area, although there are sources of information available on the traditions of neighboring communities that we can draw analogies from, such as the communities around Stuart Lake, Takla Lake, and Burns Lake. For instance, Morice's (1906) records made reference to ochre pigment use for

other applications, noting that the Dakelh-speaking people around Burns Lake used it for face paint, for “daubing half of each [beaver] trap... for good luck” (1906:117), coating snowshoes in red ochre, using ochre to infill geometric designs incised into caribou horn worn as personal ornamentation, and smearing house posts in carp roe oil and painting over with red ochre. Contemporary interviews by Mitchell offer insight into traditional knowledge from Elders who described details of ochre mineral selection; that “*a special type of rock*” was sought out and that “*not any type of rock will do*”, and that the ochre-bearing rocks were “ground to a fine powder and boiled” (Mitchell 2015:177). Another interview described the ochre preparation process as “*mak[ing] it just like powder. They pound and pound until it get [sic] just like powder and they put grease on it and that’s what they paint it with*” (Mitchell 2015:177). In other regions of British Columbia, organic components such as blood, saliva, tree pitch/sap, fish eggs, and bear grease have been noted as binding agents, although the in situ identification of these in archaeological research is a rarity (Corner 1968, York et al. 1993, Leechman 1932, Teit 1900).

While those ethnographic and historical accounts have inherent value, they only begin to scratch the surface of how mineral pigments were collected and prepared for making rock art. Informally, some scholars question the accuracy of many of those early ethnohistoric accounts, claiming that they should be interpreted with caution. Our study seeks to deepen our understanding of these processes using scientific methods, to better interpret decision-making and the *chaîne opératoire* of Indigenous rock art production in the Babine Lake area.

Ochre pigments and their study

In most literature on rock art in British Columbia, “ochre” is used as a catchall term to describe iron-enriched, red-dish-hued, inorganic pigment. Perhaps more accurately, it is a red, orange, brown, purple, or yellow iron-rich, pigmentaceous material that can include organically-derived biominerals (MacDonald et al. 2019a). This includes a variety of rocks and minerals that bear iron oxides/oxyhydroxides (henceforth, Fe-oxides) that can produce a streak or stain, including hematite (Fe_2O_3), goethite (FeOOH), pyrite (FeS_2), and magnetite (Fe_3O_4), among over a dozen more Fe-oxide-enriched chemical compounds. Furthermore, the term ochre is often conflated with the complex paint mixtures that Indigenous painters used to produce rock art; mixtures which can include non-ferrous inorganic and organic components, including binding and wetting agents (plant exudates, fats, avifauna or marine fauna egg), or raw materials added for sociocultural reasons, such as spiritual potency (blood, animal products), and the transformative properties of certain materials by anthropogenic means (e.g. roasted iron

oxides or vivianite, see Ancheta 2019, or Popelka-Filcoff and Zipkin 2022).

Therefore, while the term ochre is useful for informal discourse, it is crucial to bear in mind that not all red-hued, iron-enriched paints are necessarily made from the same raw material. Red mineral pigments that visually appear similar in color and texture can, and often do, have distinctive mineralogical and physical properties (Chalmin and Huntley 2019; Salomon et al. 2021), which are further infused with complexity and meaning through the anthropogenic processes involved in their selection, preparation, and use contexts. To understand such properties, pigment research draws on concepts from geology (geogenic origins), art history (pigment selection and paint preparation), and materials science (structural and performative properties). This approach necessitates the use of methods from analytical chemistry and physics. For example, elemental analysis (X-ray fluorescence, XRF, or mass spectrometry, ICP-MS) is used to determine the composition and purity of a pigment, and holds the potential to determine its geologic origins through trace element provenance (Salomon et al. 2021). To characterize inorganic phases, organic components (e.g. binders, resins), or their physiochemical or structural properties (thermal or physical alterations) materials can be characterized using methods such as XRD (X-ray Diffraction), Raman spectroscopy (RS), or scanning electron microscopy (coupled with energy dispersive spectrometry, SEM-EDS). Multi-proxy approaches are often mutually informative, but also rely heavily on the context and condition of the materials available for study. Here, we used a range of techniques in our analytical toolkit to enhance the scientific understanding of the selection processes and technical choices used by Indigenous painters at Babine Lake.

Methods and materials

Fieldwork and sample collection

Our field surveys to document the Babine Lake rock art and collect source materials took place in 2019 and 2022. We (MacDonald, Rahemtulla, Whess) travelled by boat to the six rock art sites and conducted digital macrophotography (DSLR), portable microscopy (Dino-Lite™, coupled to a field laptop), and in situ analysis of the pigments, mineral accretions, and rock substrates using pXRF and portable Raman spectroscopy. The latter two methods were used for initial screening purposes. In combination with field observations, we used those results to inform our selection of 15 sampling points to extract fragments of the pictographs for microanalysis. Non-painted rock control samples were also collected wherever possible. The criteria that were used for deciding where to sample was also influenced by the

condition and integrity of the pictographs (visibility loss, lichen coverage, vandalism), the potential for future compromise or loss (i.e. rock wall collapse, spallation, foliation), where visual impact would be minimized, and whether a fragment could be readily removed from areas where damage or flaking already existed. The sampling procedure involved carefully removing a small fragment ($< 5 \text{ mm} \times 5 \text{ mm}$) using a miniaturized, diamond-bladed rotary tool attachment, although some specimens that were heavily spalled could be easily removed using tweezers. Photographs were taken before and after to document the impacts of sample removal.

Ochre sources and artifacts in the Babine Lake vicinity

We are aware of four locales in the area of Babine Lake that bear high-concentration Fe-oxide deposits: Bell Mine, Granisle Mine, Red Bluffs, and Silver Island. To date have been

able to survey all but the source on Silver Island (Figs. 1 and 3).

Bell Mine and Granisle Mine are located near the northern tip of Babine Lake on the eastern mainland and on Sterett Island, respectively. They are both outcrops belonging to the same horseshoe-shaped porphyry belt deposit, and their exposures are roughly 2–4 km in diameter and ~8–10 km apart. They were commercially mined in the 1980–90's for their Cu-Pb-Zn ore and Ag-Au potential. Bordering the perimeter of the porphyry deposit is a halo of Fe-enriched hydrothermal ores that include iron-rich breccias, hematite, magnetite, siderite (FeCO_3), and pyrite (FeS_2) (Singer et al. 2005). It is now impossible to find field evidence for precisely where and how the Fe-enriched iron deposits would have been accessed and collected prior to modern mining activities, however we located secondary deposits around the perimeter of the mining areas at both sites. These deposits are now disturbed, but it is clear that the Fe-enriched zones

Fig. 3 Iron-enriched source deposits on the north arm of Babine Lake. **A, B:** secondary deposits at Granisle Mine, including hematite and goethite. Scale = ~10 cm **C, D:** mining back piles of iron-rich material, including pyrite and hematite at Bell Mine. Scale = ~5 cm **E:** collecting *L. ochracea* from Red Bluff. **(F)** Aliquots of *L. ochracea* prepared for experimental heat treatment



were potentially substantial. Although the Bell and Granisle Mine localities are part of the same ore body, their mineralogical profiles differ between exposures. The Fe-oxides at Bell Mine are predominantly hematite, magnetite, and pyrite, whereas those at the Granisle exposure are hematite, magnetite, goethite, and siderite (McArthur 1986).

The Red Bluff Provincial Park locality was where we first identified a thriving colony of the aquatic, iron-oxidizing bacterium *Leptothrix ochracea* (MacDonald et al. 2019b). This species of bacterium flourishes in iron-enriched, slow-moving freshwater marshes and streams, and natively, it resembles a floating, orange-red mass. *L. ochracea* bacteria gain metabolic energy through chemosynthesis, scavenging Fe^{III} from iron-saturated water to grow iron-silicate-phosphorus biomineral sheaths that protect cellular growth as the colony expands (Fleming et al. 2018; Chan et al. 2016). The *L. ochracea* colonies can be collected by scooping the floating mass from the water surface and dehydrating the H₂O to attain an orange-red sediment. This particular colony of iron-oxidizing bacteria (FeOB) was found in a marshy habitat located downslope of a massive, iron-enriched granodiorite-monzonite volcanic intrusive formation at Red Bluff. The weathered iron from that formation is transported downslope by meteoric water to the marshy area, providing a continuous source of energy and creating an optimal habitat for FeOB growth. The marshy area at Red Bluff would have been a seasonally-available source of biogenically-derived materials used to make paint. We collected control samples of this material and included it in our experimental analysis, described further below.

We surveyed for ochre deposits in the vicinity of Specularite Lake, located approximately 10 km inland of the eastern shore of Babine Lake's north arm. The surface deposits in this area are dominated by a thick layer of glacial till, interspersed with diabasic and gabbroic rounded intrusive formations up to 1,000 m elevation. The Lake's namesake, Specularite, refers to a variety of hematite which has a characteristic sparkling metallic luster. This mineral form of iron oxide is unique in its transformative properties. What begins as a dark, sparkling metallic rock turns to a shimmering, blood red powder once it is mechanically pulverized. Although we could not locate a primary outcrop of specularite, we did find secondary deposits of iron-rich nodules transported downstream from the Specularite Lake creek bed.

Silver Island, located on the south arm of Babine Lake, is a small island roughly 500 m × 200 m, and could not be accessed by us during fieldwork. It is located < 5 km from two of the rock art sites on the lake (GcSi-1, GcSh-1). Mining survey reports indicate the Ag-Cu-Zn-Pb deposits exposed there host chalcopyrite, galena, silver, and minor iron-rich veins that include siderite, pyrite, and magnetite (Marko 2013). Although it remains unstudied, it is a

potential source for pigmentaceous materials in the Babine Lake vicinity.

In addition to the rock art paint samples and source materials, six ochre artifacts recovered from excavations at Smokehouse Island (GiSp-1) were included for a comparative analysis. Images of the artifacts are included in Supplementary Text 1. Ochre artifacts are commonly recovered from archaeological sites in the interior of British Columbia (MacDonald et al. 2011, MacDonald 2016), although are few in number. The artifacts are small, lumpy nodules of iron oxide (< 5 cm) that were recovered from stratigraphic layers dating to 890 BP (uncalibrated ¹⁴C AMS). For more background on the excavations at Smokehouse Island, see Rahemtulla 2019.

Methods for sample characterization

Contemporary rock art research uses a diverse toolkit of methods, ranging from macro-to-micro-scales of analysis: various imaging modalities, remote sensing and digital reconstructions (3D modelling, multi-spectral imaging, D-stretch image enhancement) (Jalandoni 2021; Horn et al. 2022; Kowlessar et al. 2021; Skala 2015), in situ characterizations using portable devices, and laboratory-based microanalyses of tiny fragments collected from pictographs and rock substrates (Huntley et al. 2020; Chalmin and Huntley 2019; Chanteraud et al. 2021; Sepúlveda 2021; Bonneau et al. 2021; Sepúlveda et al. 2012; Dayet et al. 2019). Data derived from this combination of imaging, geospatial, and geochemical methods are synthesized to infer different aspects of pigment composition and materiality, rock art condition, and the surrounding microenvironment. Following this tradition, we used a multi-proxy approach to characterize our rock art, source material, and artifact samples. Table 2 summarizes the methods, sample preparation, and experimental conditions. A full description of the experimental conditions for each method are provided in Supplementary Text 1.

Framework for evaluating ochre mineral pigments

Our framework for characterizing pigment materiality draws in part upon attributes used in research on paint properties and quality (Guo and Barnard 2013; Sayed and Polshettiwar 2015; Nikraves et al. 2011; Dhoke and Khanna 2009; Cornell and Schwertmann 2003; Shen et al. 2013; Ryan et al. 2017; Legodi and de Waal 2007; Touazi et al. 2020; Marshall et al. 2005). In those assessments of pigment characteristics and paint performance, the data collected includes the size, shape, homogeneity, orientation, and atomic arrangement of the paint mixtures because those characteristics directly impact their structural and pigmentaceous properties. For instance, Fe-oxide

Table 2 Summary of methods of analysis used in this study, including sample preparation and experimental conditions where relevant. Portable Raman spectroscopy and pXRF were used in the field to screen for specific minerals and aid in the identification and selection of samples for microanalysis. Those data are not presented in detail here, although are the basis of a forthcoming contribution on evaluating the performance and utility of field-portable instrumentation

Method and data produced	Sample preparation	Instrumentation and experimental conditions
Field portable XRF and Raman spectroscopy for in situ qualitative elemental and mineralogical characterization	Visual assessment of rock surfaces, selection of areas with high opacity paint and least visible surface contamination	Brüker Tracer 5i pXRF: Points on rock art and substrates were screened to determine major components. Assays taken for 30 s at 50 kV, 35 μA, no filter Brüker BRAVO portable Raman was operated in dual laser mode (785 and 852 nm) for 10–200 coadds (1–3 min measurements)
Optical microscopy for low magnification imaging and textural analysis	Rock art fragments: trimmed in half to retain archive sample, embedded in cross-section in epoxy resin, polished to 6 μm grit using diamond paste slurry Artifacts and source samples: trimmed to produce an optically-flat section, mounted on standard petrographic slides	Leica S8 APO stereo microscope with Flexacam C3 camera, up to 80$\times$ magnification resolution
Benchtop Raman spectroscopy for mineralogical characterization		Renishaw inVia equipped with a 633 nm laser source. Spectral analysis was done using a 50 $\times$ objective lens at a spot size of 1 μ m over a spectral range of 100–2,000 cm^{-1} . Multiple measurements were taken at low laser outputs (0.1%–5%) for 10 and 30 s each
Scanning electron microscopy coupled with energy dispersive spectroscopy (SEM-EDS) for high-magnification textural analysis and semi-quantitative elemental mapping	Source materials from Red Bluff: sub-samples of aquatic <i>L. ochracea</i> were heated under oxidizing conditions in a muffle furnace at 200 $^{\circ}$C intervals to a maximum of 1,000 $^{\circ}$C and held for 3 h each Control samples: fragments of rock substrate and overlying mineralization layers were collected at each rock art location	FEI Quanta 600F environmental SEM equipped with a Bruker Quantax 200 silicon drift detector for EDS. Operated in low vacuum mode at variable pressure. Hyperspectral EDS data were collected at 15–20 kV
Inductively coupled plasma-mass spectrometry (ICP-MS) coupled with a nanosecond laser for high-sensitivity elemental analysis		PerkinElmer SCIEX NexION 300 quadrupole ICP-MS coupled with a Teledyne Analyte Excite HelEx 193 nm excimer laser system. Ablations were set at 10 μ m spot size, using a laser scanning rate of 5 μ m/s and laser bursts at 10/s at 65% of the max output. The carrier gas was helium

particles can develop in one of several nanostructural crystalline or non-crystalline forms, including rods, spheres, platelets, rosettes, disordered cubes, and acicular forms. Each of these forms directly influence aspects of hue, tone, shade, intensity, lightfastness, light reflectance, tinting strength, coverage, resistance to corrosion, and dispersion rate in a liquid medium. The presence of impurities (whether anthropogenic or naturally occurring), the use of thermal interventions, and the additive use of wetting or binding agents can further enhance or diminish those properties. The decisions made through the sequence of steps that resulted in the final paint mixture will impact its performance properties such as viability, durability, visibility, and longevity. Figure 4 illustrates the relationships between some of these interrelated variables and the criteria used in our evaluation.

Results

This study includes the analysis of 42 rock art paint samples, source materials, and archaeological artifacts. Among those 42 samples we have classified them into four primary types of Fe-oxide pigments based on their morphological and compositional characteristics. Table 3 is an inventory of all samples included in this study and their respective paint types. For each type we have identified aspects of pigment collection practices, preparation methods (including the use of heat treatment), the performance properties of each paint mixture, and the distribution of

where they were used by Indigenous painters to produce rock art across Babine Lake. Supplementary Text 1 lists the results from Raman spectroscopy and Supplementary Data File 1 provides LA-ICP-MS element concentration data for all samples.

Paint Type A—Biogenic (FeOB – iron-oxidizing bacteria) iron oxide

This paint mixture is biogenic in origin, comprised of the iron-silicon-phosphate biominerals produced by colonies of aquatic iron-oxidizing bacterium *L. ochracea*. Under high-magnification SEM, these forms are distinctive (Fig. 5), and this type has been identified in three instances at Babine Lake rock art (two motifs at GdSk-5 and one motif at GcSi-1). Natively, the intact biomineral particles consist of elongated, filament-shaped forms, 1–2 μm in diameter and up to 10 μm long that grow uniformly into a dendritic structural mass. Because the *L. ochracea* colonies float in freshwater streams as a buoyant microbial mat, the raw sediment must be collected from the water surface before dehydrating the residual H_2O , resulting in coarse-grained, orange-reddish-brown sediment. The next step in the preparation process involves pulverizing the dried sediment to a fine, homogeneous powder, which causes the FeOB biomineral particles to shatter into smaller fragments that appear disaggregated and randomly oriented. Under high magnification, the FeOB particles in the Babine Lake samples appear loosely packed and interspersed with air voids, and the pigment layers often show a moderate proportion of sediment impurities such as grains of crushed freshwater diatoms, angular quartz, or

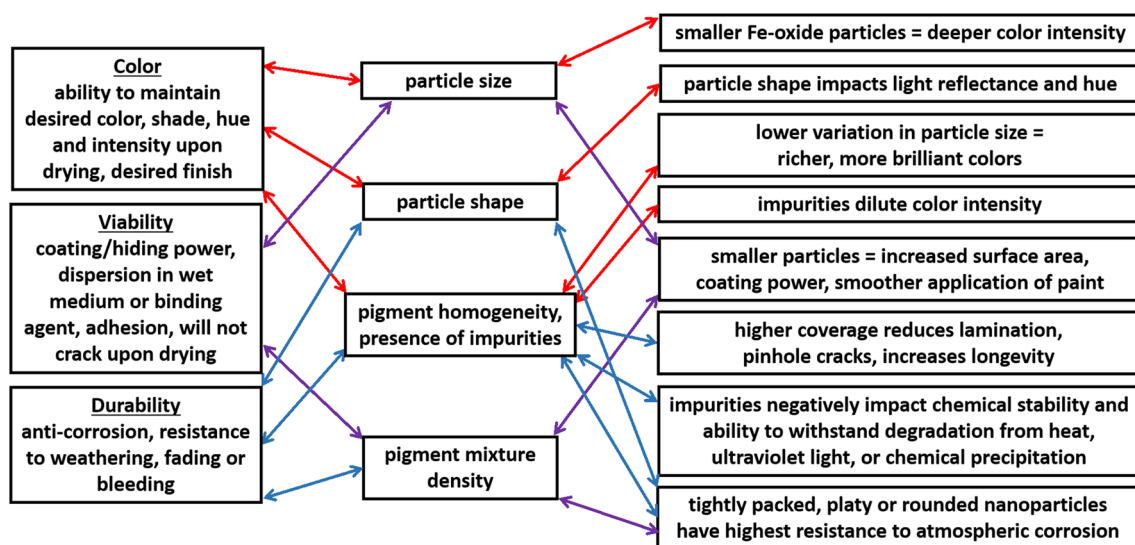


Fig. 4 Inter-relationships between selected variables for evaluating pigment and paint quality and performance. Colored arrows represent the multi-directional connections between the desired properties

(color, viability, durability) the observable physical characteristics (size, shape, homogeneity, density), and the impact those characteristics have on the desired properties

Table 3 Inventory of samples analyzed in this study. Those fully analyzed by all methods are provided a Paint Type. All samples only analyzed macroscopically and by LA-ICP-MS are indicated

ANID	Site	Sample Description	Type A	Type B	Type C	Type D
BAB001	GdSk-5	Lower right “X” cross (see Fig. 5d)	X			
BAB002	GdSk-5	Bottom lip of far-right vertical line (Fig. 5d)	X			
BAB003	GdSk-5	Top edge of figurative shape			X	
BAB004	GeSm-9	Left edge of wave-shape			X	
BAB007	GfSm-1	Bottom right circle (see Fig. 7d)			X	
BAB008	GfSm-1	Top lip of bear motif (see Fig. 7c)			X	
BAB009	GfSm-1	Bottom left edge of vertical line, lower left (see Fig. 8c)				X
BAB010	GfSn-1	Bottom edge of lower curved line (see Fig. 6f)		X		
BAB011	GcSi-1	Circle with dot in middle. (see Fig. 6d)		X		
BAB012	GcSi-1	“X” cross, piece of pictograph was cleaving from rock face, was removed with minimal pressure (see Fig. 8d)				X
BAB014	GfSn-1	Abstract, gridded lines (fishing net?). Sample taken from edge (see Fig. 6c)		X		
BAB015	GcSh-1	Anthropomorphic figure, two flaked samples taken from same figure (see Fig. 7a and 7e)			X	
BAB016	GcSh-1				X	

calcite (Fig. 5a, b). An example of this paint type at GcSi-1 was first reported in MacDonald et al. (2019b), where high-temperature roasting was identified as a key step in the preparation of the paint.

Characterization of the Type A paints showed a composition of ~ 70% Fe-oxide, with ~ 20% silicon, and minor calcium (< 5%). Previous research has shown that, in its unheated form, this sediment contains non-crystalline iron oxide, specifically ferrihydrite (Cudenec and Leclerc 2006, Emerson et al 2010, Hanesch et al 2006), with few other Raman active phases. The process of thermal treatment at temperatures above 600 °C induces the formation of crystalline magnetite and hematite, among other intermediate Fe-oxide phases (goethite, lepidocrocite). The two other instances of this paint type at GdSk-5 also showed mineralogical (hematite and magnetite formation) and morphological evidence (warping, melting) consistent with the same

processes of heat treatment evident at GcSi-1. While roasting may have been a part of the dehydration process, it also succeeded in intensifying the pigments’ red color and enhanced colorfastness and thermostability (Fiuza et al. 2018; Hashimoto et al. 2012).

Paint Type B – Nano-spherical/nano-ovoid

This paint type appears as dense, tightly packed clusters of spherical, ovoid, or peanut-shaped crystalline forms under high magnification. This paint type was identified in four instances of rock art at GcSi-1 and GfSn-1, respectively. The individual Fe-oxide particles range in size from 5–10 nm, and silicate or feldspathic mineral impurities are rarely observed. The edges of the spherical/ovoid particles are clearly defined in backscattered electron micrographs. Micrographs showing examples of Type B and the associated pictographs are shown in Fig. 6. Results from Raman

Table 3 (continued)

BAB017	GfSn-1	Complex motif, sample taken from central horizontal line (see Figs 3a and 6e)		X		
BAB018a-BAB018f	Red Bluff source	Pigment source near Red Bluffs. Marshy habitat with <i>L. ochracea</i> colonies. Six subsamples were experimentally heated.	X (n=6)			
BAB019	GcSi-1	Crossed lines (see Fig. 5c)	X			
BAP029	GiSp-1	Red ochre nodule artifact (1 of 4)	LA-ICP-MS, optical microscopy			
BAP030	GiSp-1	Red ochre nodule artifact (2 of 4)	LA-ICP-MS, optical microscopy			
BAP031	GiSp-1	Red ochre nodule artifact (3 of 4)	LA-ICP-MS, optical microscopy			
BAP032	GiSp-1	Red ochre nodule artifact (4 of 4)	LA-ICP-MS, optical microscopy			
BAP033	GiSp-1	Red ochre nodule artifact (1 of 2)	LA-ICP-MS, optical microscopy			
BAP034	GiSp-1	Red ochre nodule artifact (2 of 2)			X	
BAP035	Granisle	Flat tabular, fine-grained iron oxide	LA-ICP-MS, optical microscopy			
BAP036	Granisle	Yellow-orange chunk of iron oxide			X	
BAP037	Granisle	Red, rounded nodule.	LA-ICP-MS, optical microscopy			
BAP038	Granisle	Dark red nodule, grinds to red-brown powder	LA-ICP-MS, optical microscopy			
BAP039	Granisle	Flat tabular, fine-grained iron oxide			X	
BAP040	Granisle	Vibrant yellow, clumpy, creates fine powder				X
BAP041	Bell Mine	Vibrant yellow, chunky material	LA-ICP-MS, optical microscopy			
BAP042	Bell Mine	Brown-yellow rounded cobble, grinds to yellow powder			X	
BAP043	Bell Mine	Crystalline pyrite			X	
BAP044	Bell Mine	Pink-red stone assoc. with crystalline pyrite	LA-ICP-MS, optical microscopy			
BAP045	Bell Mine	Red-violet sparkling mineral seam in red rock (high pyrite inclusions)			X	
BAP046	Specularite	Violet-red specularite nodule	LA-ICP-MS, optical microscopy			
BAP047	Specularite	Red-orange nodule, visible vugs	LA-ICP-MS, optical microscopy			
BAP048	Specularite	Violet-red rounded specularite nodule				X
BAP049	Specularite	Violet-red cobble (1 of 6)				X
BAP050	Specularite	Violet-red cobble (2 of 6)	LA-ICP-MS, optical microscopy			
BAP051	Specularite	Violet-red cobble (3 of 6)	LA-ICP-MS, optical microscopy			
BAP052	Specularite	Violet-red cobble (4 of 6)	LA-ICP-MS, optical microscopy			
BAP053	Specularite	Violet-red cobble (5 of 6)	LA-ICP-MS, optical microscopy			
BAP054	Specularite	Violet-red cobble (6 of 6), creek bed	LA-ICP-MS, optical microscopy			
Totals			9	4	12	5

spectroscopy and SEM-EDS indicate predominant phases of hematite, magnetite, with some trace goethite, as well as the consistent presence of flecks of ground charcoal embedded within the paint mixture. This is a strong indicator that either heat treatment was used to enhance the color intensity of this type, or that finely-ground charcoal was deliberately mixed into the paint. Raman results do not show evidence for residual phosphate (PO_3^{4-}) that is

typically observed in measurements of bone black (roasted bone), suggesting instead that plant charcoal was used here.

Paint Type C – Nano-needle/nano-platelet

This type is dominant in Babine Lake vicinity. It is observed at all rock art sites except GfSn-1, in a total of six motifs,

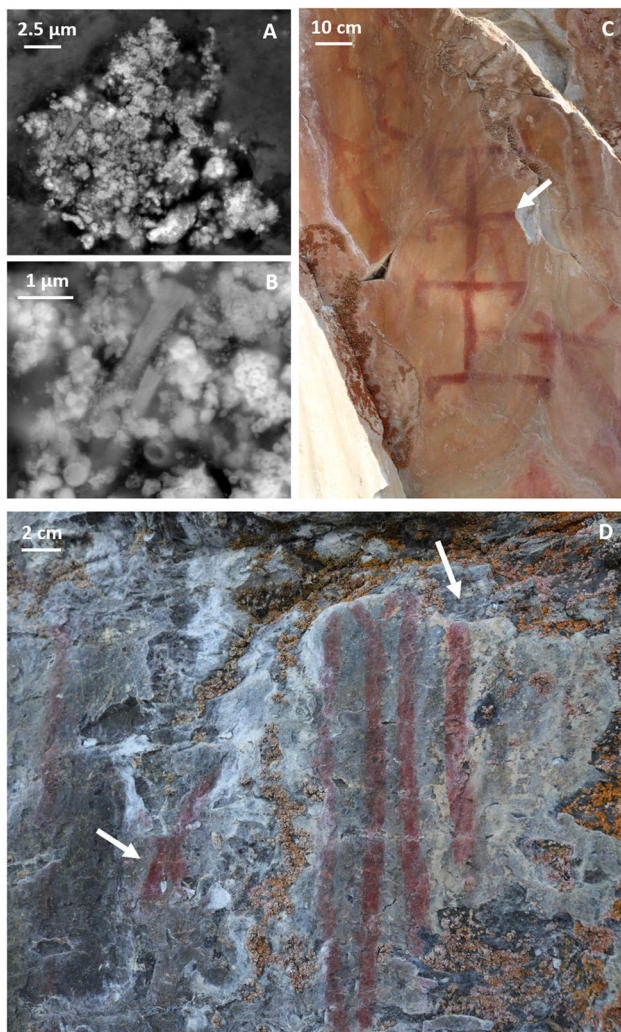


Fig. 5 Paint Type A. **A, B** Backscattered electron micrographs from GdSk-5 samples (BAB001, BAB002) The FeOB mineral forms show lumpy, bubbled, and warped textures which is consistent with previous findings that such features indicate high temperature thermal alteration. **C** Sampling area from GcSi-1, archival sample taken by Mohs and Mohs 1976a. **D** Two sampling spots at GdSk-5

as well as one of the ochre nodule artifacts from GiSp-1, and most of the source materials collected from the Bell and Granisle Mine localities. Under high magnification the pigment particle forms are flat, elongate, tabular, or acicular (needle-shaped). Some tabular forms appear platy and stacked, resembling a micaceous or phyllosilicate mineral habit. The individual crystals are thin and range from 10–500 nm in length. The Fe-oxide particles are laminated, tightly clustered, and oriented in a preferred direction (see Fig. 7b). Raman results on the rock art samples indicate the predominant presence of hematite and magnetite, while the analysis of the source materials showed the additional presence of pyrite and siderite.

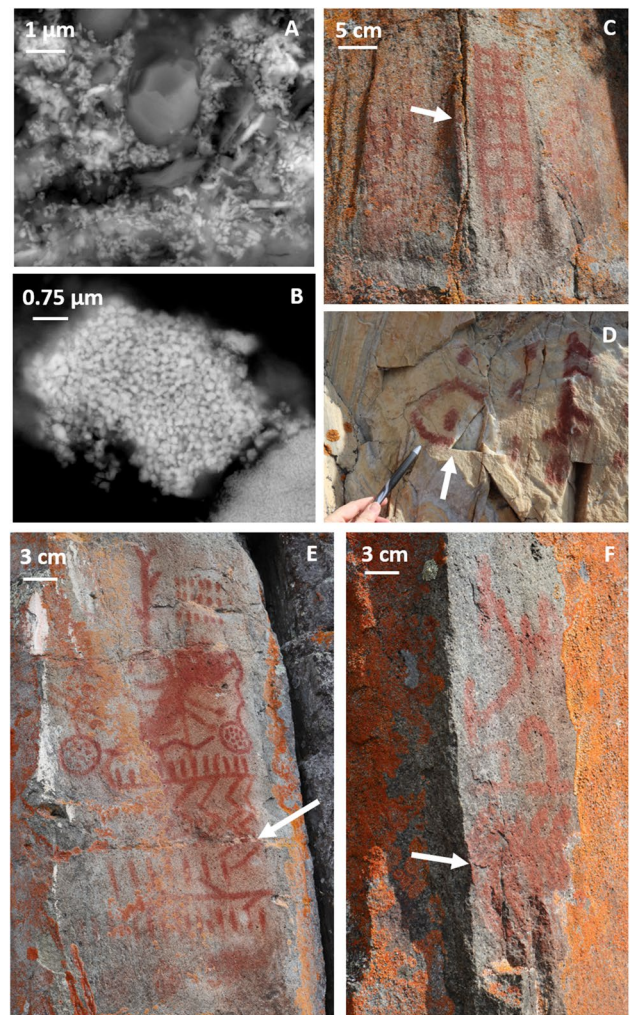


Fig. 6 Paint Type B. **A, B** Backscattered electron micrographs of samples from GfSn-1 and GcSi-1 (BAB010, BAB011) **C** Sampling location at GfSn-1 (BAB014); **D** Sampling location at GcSi-1, archival sample taken by Mohs and Mohs 1976a (BAB019); **E, F** Sampling locations at GfSn-1 (BAB017, BAB010)

Paint Type D – Flaked/amorphous type

This type was identified in two instances of rock art, at GcSi-1 and GeSm-1, respectively. The Fe-oxide particles resemble loosely packed clumps or layers of “flaked corn”, with torn edges. The crystal form is poorly defined, and particles are inhomogeneous and range in size from 10–200 nm. This type is predominantly composed of goethite, with minor amounts of hematite and magnetite. One deposit of vibrant yellow, clumpy ochre from the Granisle Mine showed high proportions of goethite. Two instances of violet-red ochre nodules from Specularite Lake were morphologically consistent with

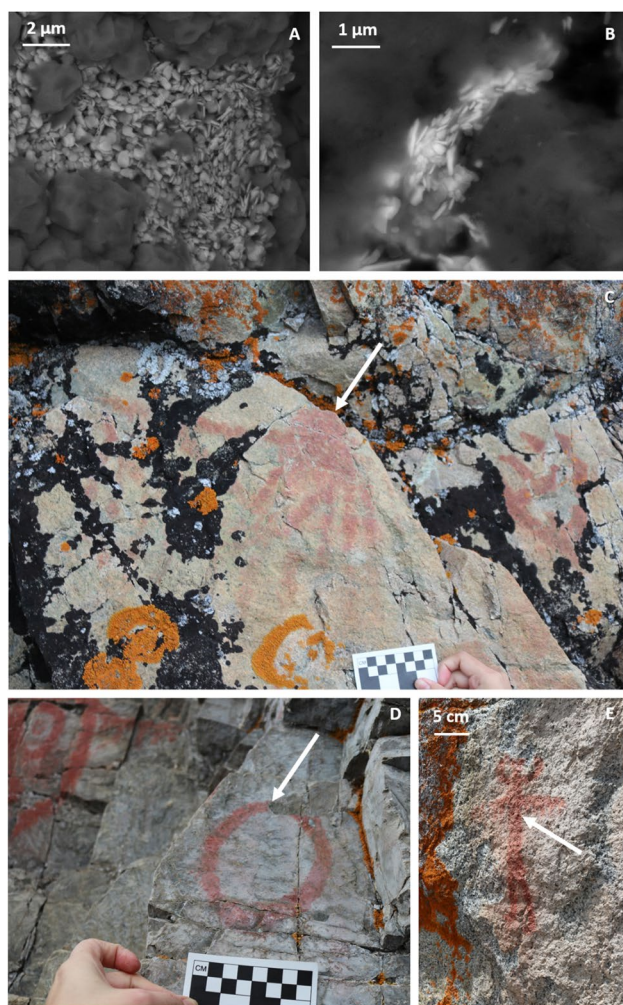


Fig. 7 Pigment Type C. **A, B** Backscattered electron micrographs of GcSh-1 and GfSn-1 (BAB015, BAB007); **C, D** Sampling locations at GfSm-1 (BAB008, BAB007); **E** Sampling location at GcSh-1 (BAB015)

goethite, although the color and compositional chemistry were highly distinct. Examples of Type D are shown in Fig. 8a, b. LA-ICP-MS analysis indicated that this paint is average ~65% Fe-oxide, with ~17% silicon and ~2.0% aluminum.

Results from Raman spectroscopy

Raman spectroscopic analysis of rock art fragments provided an opportunity to examine not only the paint components, but also the characteristics of the depositional environment and taphonomic impacts on the motifs. The Raman results are detailed in Supplementary Text 1, Supplementary Table 1, and summarized briefly here.



Fig. 8 Pigment Type D. **A, B** Backscattered electron micrographs of samples from GfSm-1 and GcSi-1 (BAB009, BAB012); **C** Sampling location at GfSm-1 (BAB009); **D** Sampling location at GcSi-1 (BAB012)

Iron oxide components

All samples have hematite as their predominant ferrous component with characteristic Fe-O bending and stretching bands at 215, 280, 400, and 610 cm^{-1} , and 2nd order phonon scattering at ~1320 cm^{-1} . A marker at 117–121 cm^{-1} frequently appears in samples that have high aluminum content (>0.5%), which has been previously identified as hematite with aluminum substitution (RUFF R040024.2). Several measurements have additional band markers typically attributed to magnetite (650 cm^{-1}) and goethite (385, 485–495, 554 cm^{-1})

as minor or co-occurring phases. The exception to this is Type D paint, which is goethite-rich and lacking, or absent entirely, in hematite or magnetite. Maghemite ($\gamma\text{-Fe}_2\text{O}_3$), a phase often associated with heating (Pomies et al. 1999), was present in Type A experimentally heated FeOB samples and in one instance of Type C paint (BAB004). Lepidocrocite, an intermediate iron phase often observed in hydrothermal ore deposits, is seen in some Type A and Type C (Bell Mine) examples. Pyrite is evident along with goethite in the yellow pigment at the Bell Mine locality. Pyrite is also abundant at the red and violet ochre deposits at the Bell Mine locality.

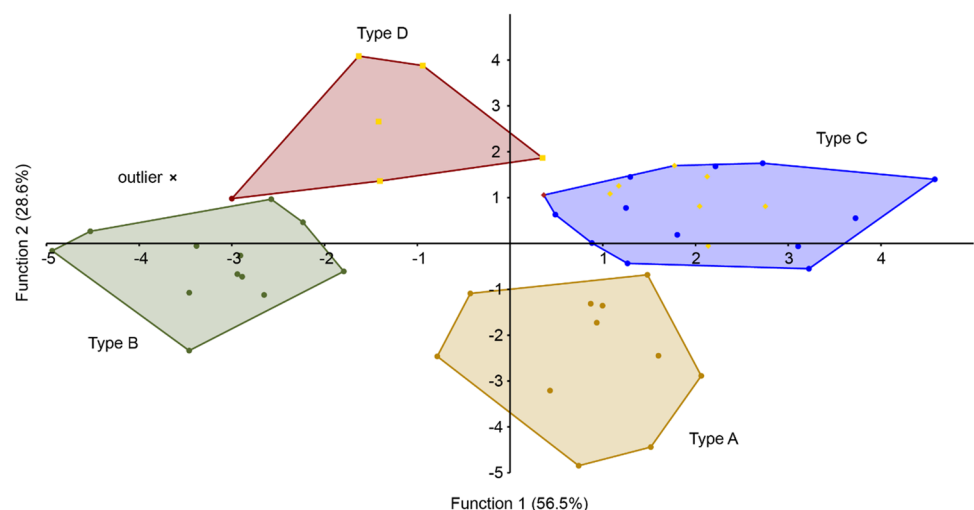
In order to explore and graphically represent the similarities and differences between the paint types, we used chemometric approach to the Raman spectroscopic data. All Raman measurements were taken at consistent durations and laser powers, the resulting data underwent baseline corrections and a vector normalization standardization procedure. To avoid unwanted bias by the presence of taphonomic impurities (calcite, charcoal, etc.), we followed the example by Lafrumento et al. (2011) for our multivariate analysis of Raman spectra. We selected only the variables associated with ferrous components and calculated the values of the normalized maximum signal intensity for band markers for hematite, magnetite, goethite and lepidocrocite (see Supplementary Text 1). The signal intensity data were calculated at the vector-normalized apex of each band, regardless of minor shifts in wavenumber cm^{-1} . Those values were used as variables for linear discriminant analysis (LDA) and Mahalanobis distance calculations to determine the similarities between paint types, ochre artifacts, and source materials. Figure 9 is a scatterplot showing the results of LDA of Raman chemometric data. Supplementary File 1 contains tables shows the loading scores and group classifications of the LDA. As seen in Fig. 9, the results show that each

paint type has quantitatively distinct mineralogical properties based on Raman spectroscopic data. One outlier measurement, BAP016 (spot 2), is individually marked. Note that in this representation, nearly all source materials from Bell and Granisle Mines align with Type C and Type D pigments. Type A or Type B pigments do not align with any of the source materials.

Non-ferrous components

Calcium oxalates (weddelite, $\text{CaC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$) are present to some extent at all sites. This is to be expected in consideration of the ubiquitous coverage of orange Starburst Lichen (*Xanthoria parietina*) and black lichen (spp. unknown) on many rock face exposures on Babine Lake. Biomarkers for lichen activity are present in several measurements, including possible β -carotene bands ($1151, 1528 \text{ cm}^{-1}$), chlorophyll (1290 cm^{-1}), and calcium oxalates ($910, 1465, 1490, 1600 \text{ cm}^{-1}$) (Villar et al. 2005; Edwards et al. 1998). Band markers potentially suggestive of monohydrocalcite ($\text{CaCO}_3 \cdot \text{H}_2\text{O}$) were found at two motifs at GdSk-5, which were situated under a bird nest and clearly contaminated by white droppings. This is the potential source of the monohydrocalcite, although it also forms through the decomposition of oxalates (Swainson 2008), therefore its origin could be a combination of factors. Regardless, it is clear that the presence of this is an environmental signature. Raman band markers for what could be a combination of one or more of calcite (CaCO_3), PO_4^{3-} , or tricalcium phosphate ($\beta\text{-Ca}_3(\text{PO}_4)_2$) are observed, although spectral interferences have created some ambiguities on their discrete interpretation. For instance, the assignment of tricalcium phosphate could be a combination of calcium and residual phosphorous as an environmental signature, therefore we present these Raman assignments with caution. These instances are present at sites GeSm-9, GdSk-5, and GfSn-1, and are all

Fig. 9 Scatterplot showing Function 1 (56.5%) versus Function 2 (28.6%) of the results of Linear Discriminant Analysis (LDA) of Raman chemometric data. Paint types are labelled. Outlier sample = BAB016a



considered to be alteration products forming on the surfaces of the rock substrates and are unlikely to be deliberately added components to the paint mixtures. It is also worth noting that one site, GcSi-1, consists of a long outcrop of silicified limestone, and calcite is abundant in all substrate measurements.

Other minor instances of non-ferrous components are present either as mixtures in the paint, accessory minerals associated with the Fe-oxide source, or environmental components. As mentioned above, charcoal was identified both visually and spectroscopically in Type B pigments. The feldspathic mineral microcline was identified exclusively in Type C paints (those from GcSm-9 and GfSm-1), and the raw materials from the Bell Mine. Quartz is most common in Type C paints, although it does also occur as a component in paints from GcSi-1 (silicified limestone rock wall), and in the Specularite Lake raw materials. Generic Raman markers for clay minerals (AlOH) are observed at GcSi-1, although this was previously identified as a weathering product from the silicified limestone (MacDonald et al. 2019b). This marker also occurs in the secondary deposit materials from Specularite Lake, which is likely due to contamination from glacial till. Anatase is present in source materials from Specularite Lake, which is to be expected with their high TiO₂ concentration (up to 2.5%). The Specularite Lake samples also show enrichment in feldspathic minerals, clay, and Na, Mg, and K.

Results from LA-ICP-MS

Elemental analysis by LA-ICP-MS provided data on the potential source(s) of the paint raw materials and to corroborate the interpretation of Raman data. The tabulated data are provided in Supplementary File 1 and their key characteristics are summarized briefly here. The majority of rock art data points are highly enriched in iron, which

are consistent with all other analytical observations. Some rock art measurements are enriched in Ca and Si, which can be attributed to impurities imparted by the rock substrates or environmental contamination from animal droppings and calcium oxalates produced by lichens and algae. Isolated measurements of the rock substrate and overlying mineral accretions (where evident) were tested (see Supplementary Text 1), and show primarily silicon and calcium-enriched phases. Source materials from Granisle and Bell Mine localities are relatively high in Fe-oxide purity, and enriched in trace elements that would be associated with a porphyry-type deposit: Cu, Zn, and Pb. Samples from the Bell Mine locality are among the highest in sulfur (pyrite). The source materials from Specularite Lake have high concentrations of Na₂O (1.0–6.7%), TiO₂ (0.7–2.4%), K₂O (2.0–7.6%), AlO₂ (up to 11.6%), and quartz (up to 52%), which is consistent with Raman results showing higher amounts of feldspathic and clay mineral impurities.

The element concentration data underwent standard explorations, such as Pearson correlation tests, and treatments for multivariate statistical analysis, including Fe-normalization and logarithmic transformation (Mauran et al. 2021; MacDonald et al. 2018). Fifteen elements correlate positively with Fe: Al, V, Co, Cu, Zn, Ge, Rb, Y, Nb, Mo, Sn, Sb, W, and Bi. The dataset was then tested by Principal Component Analysis (PCA) to determine which elements explained the greatest variation within the set. Of the 58 elements measured, 25 of them contributed the greatest variation: Li, Na, Mg, Al, S, K, Ti, Mn, Co, Cu, Zn, Ge, As, Rb, Y, Zr, Nb, Mo, In, Sn, Sb, Ba, W, Pb, and Bi. That subset of elements was used as variables to test the multivariate relationships between paint types, artifacts, and sources. Figure 10 is a scatterplot that shows the results of LDA for all groups, and Fig. 11 is a reanalysis of a subset showing only the rock art paint type data points. The Specularite

Fig. 10 Scatterplot showing Function 1 (58.1%) versus Function 2 (19.5%) of the results of Linear Discriminant Analysis (LDA) of LA-ICP-MS data. Paint types, source materials, and artifacts are labelled

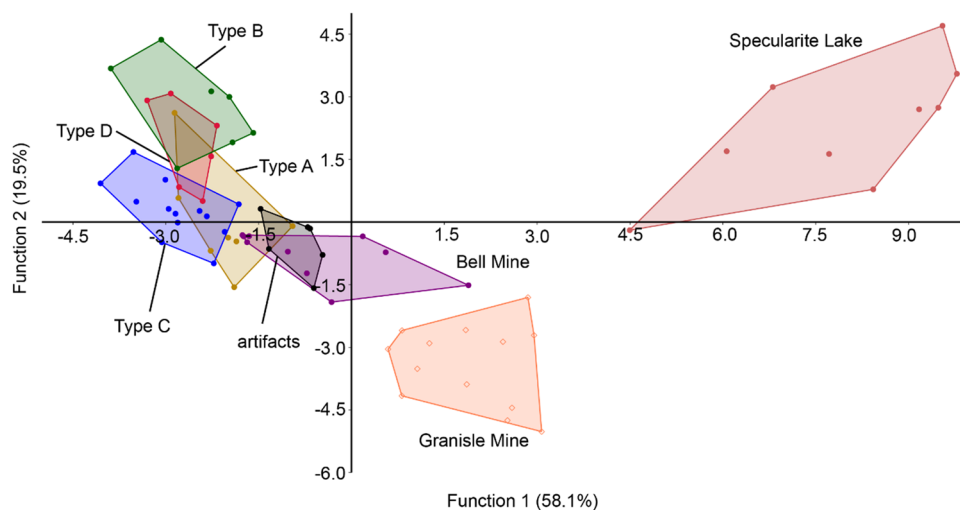
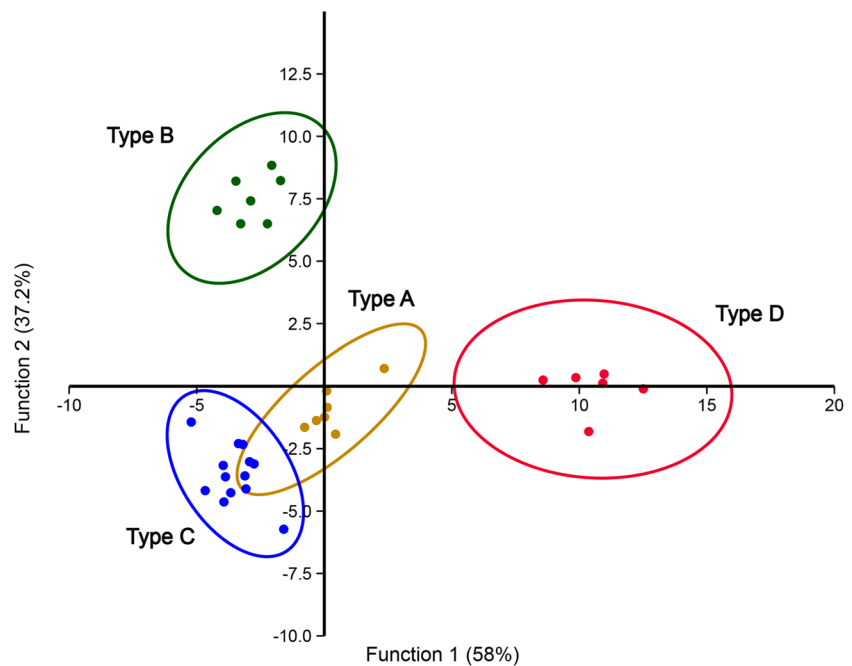


Fig. 11 Scatterplot showing Function 1 (58.0%) versus Function 2 (37.2%) of the results of Linear Discriminant Analysis (LDA) of LA-ICP-MS data, using rock art paint data only. Ellipses are drawn at 90% confidence



Lake source materials are consistently distinct from other groups. Paint Types A, B, C, and D can be differentiated from each other. The artifact samples from GiSp-1 show a tendency to cluster with the Bell Mine source material. Overall, the results from the elemental analysis appear to refine the groupings evidence in the Raman chemometric analysis by showing a stronger overlap between the artifacts, pigment Types A and C, and raw materials from the Bell Mine locality.

Discussion

Our research has shown that, even though all are monochrome red, not all ochres that the Indigenous painters used at Babine Lake are identical. Of the 42 samples we examined, four distinctive pigment types were classified based on their morphological properties and chemical compositions. Overall, there is no strong pattern that correlates pigment type with motifs styles, rock wall substrates, or site locations, which could be expected given our relatively small sample size. In light of the patterns observed from the chemometric and compositional analyses, it appears that the Bell Mine locality was the most probable local source used. This does not preclude the use of materials from the Granisle Mine locality, especially considering that Bell and Granisle are outcrops of the same deposit within < 10 km. One interesting consideration is the presence of pyrite in the Bell Mine source materials and the GiSp-1 ochre nodule artifact, yet absent from all rock art measurements. Although experimentation would be needed to confirm this, the absence of

pyrite could be a result of processing steps taken during the preparation of pigment, particularly where heating could be involved as one of the main components of pyrite, sulfur, will thermally decompose at relatively low firing temperatures (~540 °C) (Hu et al. 2006). If true, this would impact the resulting chemistry and mineralogy to the degree to which a false negative interpretation could be made about the use of Bell or Granisle Mine materials. It is also possible that pyrite may have undergone natural processes of oxidation, either during grinding during pigment preparation, or environmental exposure, that resulted in its transformation over time. It also is clear that raw materials from Specularite Lake were unlikely to be used as paint components at Babine Lake.

Raw material selection and paint properties

Paint Type A, the biogenic type, is found at two sites: GcSi-1 and GdSk-5, and may have been locally procured at Red Bluff or around the Bell or Granisle Mine outcrops. It is worth noting that while *L. ochracea* are known for their chemolithotrophic affinity to iron, they can also metabolize other waterborne heavy metals with similar chemical properties, such as As, Sb, Cu, Pb, and Zn. Therefore, it is unsurprising to find through multivariate statistics, that the Type A paints contain similar trace element profiles as the source materials from Bell Mine, which themselves are enriched in the same trace elements. It is possible that the *L. ochracea* colonies that were harvested may have thrived in the runoff streams in the immediate vicinity of the Bell Mine deposit. As previously mentioned, the topography of

the area has been irreparably modified by modern mining activity, so we will never know exactly where this could have occurred, but we can say that it was a likely possibility that the bacteria were seasonally collected in the vicinity of either the Bell or Granisle Mines, or Red Bluff marsh on the opposite shoreline of Babine Lake.

With regard to paint preparation, our previous research found that one example of the biogenic pigment from GcSi-1 was heated to high temperatures ($> 600\text{ }^{\circ}\text{C}$) as part of the pigment *chaîne opératoire* (MacDonald et al. 2019b). This interpretation was supported by evidence from Raman spectroscopy, SEM-EDS, TEM, magnetometry, and thermal experimental studies of FeOB. The two examples at GdSk-5 exhibit the same characteristics indicative of thermal exposure, consistent with those observed at GcSi-1 (bubbling, warping), suggesting the potential of the use of the same prepared pigment by one or more painters, or shared traditional knowledge on the use of thermal enhancement in the preparation of that paint type. In terms of pigment quality, the biogenic paint would have required a thermal intervention to produce a notably vivid and intensified hue, and in doing so would have been significantly enhanced in its thermostability and durability (Hashimoto et al. 2012). Interestingly, modern materials science research in ceramic and aerospace engineering study the same species of bacteria, touting them as one of the most highly sought after, renewable, non-toxic, thermostable, and colorfast pigments that can withstand high-temperature and extreme environments (Hashimoto et al. 2012, Safarik et al. 2017). Yet, the large, angular grain sizes and high proportion of mineral impurities in these raw materials suggests this paint would have had low smoothness and poor coverage of rock surfaces, and would have required additional buildup of paint layers to attain the desired opacity.

Paint Type B, the nano-spherical/ovoid type, is among the highest quality paints by contemporary standards of pigment performance. The paint matrix consists of small, densely-packed, rounded nanoparticles with almost no impurities to dilute the intensity of the red colorant. This particular combination of crystal morphology and density is the form that is most resistant to weathering, corrosion, and cracking, thus increasing the longevity potential of the paint. This type was only identified in four samples from two sites, GfSn-1 and GcSi-1, and was used for figurative and non-figurative forms. Notably, all three of the samples collected from one site, GfSn-1, are exclusively made from Type B paint.

Paint Type C, the nano-needle/platelet type, is the most common, occurring in six of the fifteen samples and at four of the six rock art sites (GcSh-1, GdSk-5, GfSm-1, GeSm-9). This type was used for both figurative and non-figurative motifs. Based on what we would consider to be optimal pigment properties, this type would be among the best quality

relative to the others. It is high in Fe-oxide purity, consisting of very small, densely packed particles, resulting in high color intensity and tinting strength. Compared to the other pigment types, the laminar and platy particle matrix would have had the smoothest application and densest coverage, and would be the most resistant to cracking and lamination, resulting in high durability under prolonged environmental exposure. This type is the only mixture where minor feldspathic mineral impurities are found, in addition to quartz, suggesting the possibility of its association with clay-bearing deposits.

Paint Type D, the flat, flaky type, is the least common, with only two instances found (GfSm-1, GcSi-1). Both are found on the largest and most complex rock art panels where other pigment types co-occur for different motifs. The Fe-oxide morphology, heterogeneity, and high presence of diluting impurities would have resulted in an irregular, unsmooth surface, reduced color intensity, and increased susceptibility to visibility loss. Based on qualitative criteria, this may have been the poorest quality pigment and therefore more susceptible to environmental and taphonomic impacts. This could be one contributing factor as to why it is the least commonly identified – it is possible that it was at one time a commonly used paint, but its low survivability has reduced our capacity to identify it today.

It is clear that the Indigenous painters in the Babine Lake vicinity selected and prepared a diversity of raw materials to make paints, ranging from high to low quality ingredients. The most abundant mixtures, Type B and Type C, also have the best physicochemical properties for durability and longevity. Although we have identified the Bell Mine as the probable source area for ochre artifacts and paint-making ingredients, there are still other potential sources to explore (e.g. Silver Island). It is important to note here that the classifications we use to describe the paints are based on known mineralogical and structural properties based on materials sciences, and at this time do not account for cultural values ascribed to mineral pigments that may have influenced their selection or use. Indeed, specific hues or consistencies may have been preferred by the Indigenous painters regardless of their mechanical properties. Perhaps the technical gestures and skills that were associated with pigment preparation, such as transformations through pyrotechnology or knowing the correct proportions of binding agents or organic components (Mitchell 2015: 177), were more important cultural norms that bore influence on the selection of Fe-oxide minerals. Equally possible is the cultural value that may have been ascribed to the pigment sources themselves, their stories and locations within traditional Indigenous lands taking precedence over the Western characterizations of their mineral compositions that we described here. It also stands to reason that some of the ochres may have been acquired

through social interactions, such as the gifting or exchange networks along the grease trails (Mitchell and Donald 1988; Bishop 1987), as a way of mediating important relations within and between neighboring communities. These gifting or exchange contexts also have the potential to imbue the ochre pigments with social meaning. Although archaeology will never unequivocally determine all of the culturally significant aspects of pigment collection and rock art, our work continues to corroborate Indigenous knowledge that people in this region were active stewards of their landscapes and resources, with diverse cultural practices that were developed and sustained over millennia (Lyons and Ritchie 2017; Lepofsky and Armstrong 2018, Gottesfeld 1994).

Concluding remarks

In this paper we have shown that at least four different paint types were being used to produce rock art at Babine Lake. Our research has revealed a diversity of mineral pigment selection and use within a relatively restricted geographic area, hinting at a complex body of decision-making and knowledge of paint preparation. Each of the four pigment types hold distinctive mineralogical and compositional properties that convey variations in quality, performance, longevity, technological process, and landscape origin. We emphasize here the potential scientific value of minimally-invasive, multi-method investigations of rock art pigments. All of these new insights were obtained from tiny fragments of rock art, each not much larger than a fingernail clipping. We have also not yet even begun to delve into the possibility of preservation of organic binders, or determining the ages and sequence of rock art production to assess change over time; both efforts will require significantly more experimentation. Our forthcoming work will also aim to integrate more Indigenous perspectives from the Lake Babine Nation, efforts of which have unfortunately been constrained by more pressing local concerns, including wildfires, travel restrictions, and community health and housing needs. Not least of all, we advocate here that rock art research should integrate local Indigenous knowledge with informed consent and due credit wherever possible.

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Data availability All data supporting the results presented in the paper are published as supplementary online data with this article.

Declarations

Competing interests The authors declare no competing interests.

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