Data Article

Characterization of mineral coatings associated with a Pleistocene-Holocene rock art style: The Northern Running Figures of the East Alligator River region, western Arnhem Land, Australia

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Abstract

This data article contains mineralogic and chemical data from mineral coatings associated with rock art from the East Alligator River region. The coatings were collected adjacent to a rock art style known as the “Northern Running Figures” for the purposes of radiocarbon dating (http://dx.doi.org/10.1016/j.jasrep.2016.11.016; (T. Jones, V. Levchenko, P.L. King, U. Troitzsch, D. Wesley, 2017) [1]). This contribution includes raw and processed powder X-ray Diffraction data, Scanning Electron Microscopy energy dispersive spectroscopy data, and Fourier Transform infrared spectral data.

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| Specifications Table |
|----------------------|
| **Subject area**    | Archeology |
| **More specific subject area** | Rock art |
| **Type of data** | Tables and Figures |
| **How data was acquired** | 1. Powder X-ray diffraction (XRD) analysis (PANalytical Empyrean powder X-ray diffractometer, Research School of Chemistry, Australian National University)  
2. Scanning Electron Microscope energy dispersive spectral (SEM-EDS) analysis (Hitachi 4300SE/N field emission scanning electron microscope equipped with an Oxford INCA Energy 350 EDS system at the Centre for Advanced Microscopy, Australian National University)  
3. Fourier Transform Infrared (FTIR) spectroscopic analysis – mid-infrared spectral range (Bruker Tensor 27, Research School of Earth Sciences, Australian National University) |
| **Data format** | Raw and analysed |
| **Experimental factors** | Characterization of mineralogy and chemistry of mineral coatings associated with rock art |
| **Experimental features** | Analysis of minerals, their quantities and their chemical composition |
| **Data source location** | Eastern Alligator River, western Arnhem Land, Australia |
| **Data accessibility** | The data is available with this article. |

**Value of the data**

- Data presented here will be useful to other researchers as a benchmark for Powder X-ray Diffraction and Fourier Transform Infrared spectra of natural oxalate-bearing mineral coatings.
- The raw XRD data may be reanalyzed with a different set of phosphate, sulfate and oxalate standards, which may help constrain the uncertainty in the Rietveld refinement values.
- The raw FTIR data may be deconvolved using other appropriate mineral databases and the results compared with the XRD Rietveld refinement values.

1. **Data**

1.1. **Data from X-ray diffraction with Rietveld refinement fits**

The oxalate mineral, whewellite, is found in all mineral crusts sampled (13–26.4 wt.%), except RLL3-1-1 where it is not detected (Table 1, Supplementary Figs. 1 and 2, Supplementary Table 1). Samples RLL32-B-S1 to RLL32-B-S4, RLL3-1-2 and RLL3-1-3 have the same mineral assemblage: whewellite and tinsleyite, with lesser taranakite, quartz and gypsum (Table 1). Sample RLL32-B-2011 is dominated by quartz and whewellite, with a little gypsum, a 10 Å-mica and a 7.1 Å-clay. Sr-crandallite or goyazite may be present at low levels (Table 1).

1.2. **Data from Scanning Electron Microscope analysis**

Backscattered electron (BSE) imaging data (Fig. 8a and 8d in [1]) indicates that the mineral crust contains at least four intimately mixed minerals (< 1 μm to ~3 μm). As shown in Table 2, SEM-EDS data from the mineral crust indicates whewellite, and Ca–Al–(Sr)–phosphate(s) –crandallite, Sr–crandallite, or crandallite mixed with apatite.
1.3. Data from Fourier Transform Infrared spectroscopy

Fourier Transform Infrared spectra provide constraints for the presence of oxalates, sulfates, phosphates and clay minerals in the crusts (Fig. 1a and b). Infrared bands associated with the calcium oxalate (whewellite) are evident in the spectra at 1315–1320 and 780 cm\(^{-1}\) (C\(_2\)O\(_4\)\(\cdot\)H\(_2\)O) and 3420 cm\(^{-1}\) (OH). Phosphate minerals (crandallite, Sr-crandallite/goyazite and apatite) have bands at 1383, 1110 and 890 cm\(^{-1}\) related to PO\(_4\) vibrations and 3486 cm\(^{-1}\) related to OH. Bands due to silicate minerals are found at 3246 cm\(^{-1}\) (Al\(_2\)-OH, clay) and 1020 cm\(^{-1}\) (SiO\(_4\)). The FTIR data does not rule out sulfate (Supplementary Table 2). Bands at 3344 and 3062 cm\(^{-1}\) are assigned to OH groups in minerals.

The six FTIR spectra obtained from the RLL032B-B site ([1], Fig. 1a) are consistent with one another with only slight differences observed in the topmost sample (RLL032-B-2011). The latter shows slightly less defined OH bands at 3490–3420 cm\(^{-1}\) and a doublet in the area near 670 cm\(^{-1}\). The FTIR data is consistent with the XRD that shows RLL032-B-2011 differs from the rest of the samples (Fig. 1a).

RLL3-1-2 and RLL3-1-3 both contain strong oxalate bands, phosphate bands and H–O molecular species (Fig. 1b). RLL3-1-1 does not show detectable oxalate, but instead contains bands between 1000–1100 cm\(^{-1}\) and 1800–2100 cm\(^{-1}\) (Fig. 1b) due to Al–O and Si–O vibrations (e.g, variscite and quartz; Table 1, Supplementary Table 2).

### Table 1
Quantitative data for minerals in the crusts based on Rietveld refinement fits of X-ray diffraction data.

| Sample          | RLL032-B-2011 | RLL032-B-S1 | RLL032-B-S2 | RLL032-B-S3 | RLL032-B-S4 | RLL3-1-1 | RLL3-1-2 | RLL3-1-3 |
|-----------------|---------------|-------------|-------------|-------------|-------------|----------|----------|----------|
| Scan No.        | A24950        | A25292      | A25302      | A25301      | A25290      | A24950   | A25292   | A25302   |
| Mineral- wt.% (sd) |               |             |             |             |             |          |          |          |
| Amorphous material | 70.5 (5.0)  | 53.8 (5.0)  | 52.3 (5.0)  | 65.9 (5.0)  | 69.5 (5.0)  | 28.3 (3.0)| 14.9 (3.0)| 40.6 (5.0)|
| Quartz SiO\(_2\) | 9.3 (0.7)    | 2.5 (0.1)   | 3.1 (0.1)   | 2.9 (0.2)   | 1.7 (0.2)   | 32.7 (0.6)| 5.6 (0.3) | 3.2 (0.2) |
| Gypsum CaSO\(_4\)2H\(_2\)O | 1.1 (0.2) | 3.7 (0.3) | 3.0 (0.3) | 0.8 (0.2) | 1.7 (0.2) | 1.8 (0.1) | 3.1 (0.2) | 2.0 (0.1) |
| Whewellite CaC\(_2\)O\(_4\)H\(_2\)O | 13.0 (0.9) | 20.3 (0.8) | 20.1 (0.7) | 17.4 (0.8) | 15.1 (0.9) | 26.4 (0.6) | 17.4 (0.6) |         |
| Tinsleyite K\(_2\)Al\(_2\)(PO\(_4\))\(_2\)OH\(_2\)H\(_2\)O | 17.7 (1.0) | 18.2 (0.8) | 12.9 (0.8) | 11.9 (0.9) | 21.5 (0.5) | 48.3 (0.8) | 35.2 (0.9) |         |
| Taranakite K\(_2\)Al\(_2\)(HPO\(_4\))\(_3\)(PO\(_4\))\(_2\)18H\(_2\)O | 2.1 (0.1) | 3.4 (0.3) | 0.1 (0.2) | 0.2 (0.2) | 0.3 (0.1) | 1.8 (0.2) | 1.6 (0.3) |         |
| Goyazite SrAl\(_2\)P\(_2\)O\(_7\)(OH)\(_7\) |               |             |             |             |             |          |          |          |
| 7.1 Å-clay\(^c\) | 0.8 (0.4)    |             |             |             |             |          |          |          |
| 10 Å-mica\(^c\) | 3.8 (0.6)    |             |             |             |             |          |          |          |
| Variscite AlPO\(_4\)2H\(_2\)O |               |             |             |             |             |          |          |          |
| Total           | 100           | 100          | 100          | 100          | 100          | 100      | 100      | 100      |

\(^a\) Goodness-of-fit indicator \(R_{wp}\) for the weighted profile: \(R_{wp} = \sqrt{[\sum w_i(y_o - y_{ic})^2/\sum w_i y^2_o]}^{1/2}\), where \(y_o\) is the observed intensity, \(y_{ic}\) the calculated intensity, and \(w_i\) the weight assigned to each observation based on counting statistics.

\(^b\) Refined variables included zero correction, scale factors, unit cell parameters of major phases and up to four peak shape parameters per mineral.

\(^c\) 7.1 Å-clay is likely kaolinite and 10 Å-mica is likely illite or muscovite.
2. Experimental design, materials and methods

2.1. Study area description

Mineral coatings were collected from rock walls adjacent to art described in detail by [1]. The locations are given in Table 3.

2.2. X-ray diffraction (XRD) methods

Samples were prepared as powders, mounted on a silicon low-background sample holder, and analyzed from 4 to 70° 2θ at a spacing of 0.02626° (Supplementary Table 1). Data was collected using Bragg Brentano geometry, fixed divergence slits with Cu Kα radiation and a PIXcel 1D detector (active length = 3.3473°, 255 channels, 542 s per step). Minerals were identified using the SIEMENS software package Diffracplus Eva 10 [2] (Supplementary Fig. 1) and quantified using Rietveld refinement [3,4] with the program Rietica [5] (Table 1, Supplementary Fig. 2). The background was fixed manually. The weight fraction of the amorphous material \( W_{AMORPH} \) was determined for each corundum-spiked

| Mineral                           | Whewellite | Crandallite | Sr crandallite | Crandallite |
|----------------------------------|------------|-------------|----------------|-------------|
| SEM analysis of                  | > 1 phase  | > 1 phase   | 1 phase        | > 1 phase   |
| Analysis #                       | #15        | #7          | #1             | #26         |
| wt% (norm C free)                |            |             |                |             |
| SiO₂                             | 6.5        | 5.22        | 0              | 0.2         |
| Al₂O₃                            | 5.15       | 7.09        | 42.83          | 37.73       |
| FeO                              | 1.29       | 1.08        | 0.27           |             |
| MgO                              | 0          | 0           | 0.01           | 0           |
| CaO                              | 79.36      | 68.48       | 9.87           | 11.23       |
| SrO                              |             |             |                | 43.65       |
| Na₂O                             | 0.74       | 1.13        | 0.57           | 0           |
| K₂O                              | 1.25       | 3.9         | 1.41           | 0.19        |
| P₂O₅                             | 5.37       | 11.06       | 37.56          | 29.64       |
| SO₃                              | 0          | 2.5         | 6.35           | 9.52        |
| Cl                               | 0.35       | 0.62        | 0.32           | 0.08        |
| Atomic formula unit, based on:   | 4 O + 2 C  | 4 O + 2 C   | 13 O           | 13 O        |
| Si                               | 0.21       | 0.17        | 0              | 0.02        |
| Al                               | 0.2        | 0.27        | 3.84           | 3.8         |
| Fe total                         | 0.04       | 0           | 0.07           | 0.02        |
| Mg                               | 0          | 0           | 0              | 0           |
| Ca                               | 1.40*      | 1.18*       | 0.8            | 1.03        |
| Sr                               |             |             | 0.55           |            |
| Na                               | 0.05       | 0.07        | 0.08           | 0           |
| K                                | 0.05       | 0.16        | 0.14           | 0.02        |
| P                                | 0.15       | 0.3         | 2.42           | 2.14        |
| Cl                               | 0.02       | 0.03        | 0.04           | 0.01        |
| TOTAL                            | 1.95       | 1.84        | 4.82           | 5.23        |
| Ideal Formula                    | CaC₂O₄.H₂O | CaAl₃(PO₄)₂ | (Ca,Sr)Al₃(PO₄)₂ | Ca₃Al(PO₄)₂ |
| Measured                         |            | (OH)₅H₂O    | (OH)₅H₂O       | (OH)₂H₂O    |
| Formula                          |            |             |                |             |
| Ca₅₀.9Al₃₅₄                 |            | (Ca,Sr)₁₅₈Al₃₈ |
| (PO₄)₄₂   |            | (PO₄)₁₄     |             |
| (OH)₅H₂O   |            | (OH)₅H₂O    |             |
Fig. 1. FTIR spectra of bulk samples from the mineral crusts. The positions of the bands identified in Supplementary Table 2 are indicated. (A) RLL032-B powders. (B) RLL3-1 powders. RLL3-1-1 does not contain detectable oxalate.

Table 3
Sample identification and location.

| Sample     | Latitude          | Longitude     |
|------------|-------------------|---------------|
| RLL032-B-2011 | 12°23'49.55"S     | 133° 0'26.81"E |
| RLL032-B-S1   | 12°23'49.55"S     | 133° 0'26.81"E |
| RLL032-B-S2   | 12°23'49.55"S     | 133° 0'26.81"E |
| RLL032-B-S3   | 12°23'49.55"S     | 133° 0'26.81"E |
| RLL032-B-S4   | 12°23'49.55"S     | 133° 0'26.81"E |
| RLL3-1-1      | 12°24'7.59"S      | 133° 0'5.51"E  |
| RLL3-1-2      | 12°24'7.59"S      | 133° 0'5.51"E  |
| RLL3-1-3      | 12°24'7.59"S      | 133° 0'5.51"E  |
sample according to equation $W_{AMORPH} = 1 - y/x$, where $y =\%$ corundum, and $x$ is the calculated % corundum given by the program Rietica [6]. Amorphous, poorly crystallized and/or very finely grained material is identified in all samples by elevated or undulating backgrounds.

2.3. Scanning electron microscopy – energy dispersive spectrometry (SEM-EDS) methods

Sample RLL032-B-2011 was mounted in epoxy perpendicular to the mineral crust surface and polished to a $1/4\mu$m diamond grit finish using kerosene, not water. SEM analysis was undertaken using a 15 kV accelerating voltage and 1 nA beam current with an approximately 2 $\mu$m beam diameter that overlapped multiple mineral phases.

2.4. Fourier Transform Infrared (FTIR) spectroscopy methods

Samples were ground, dried at $\sim$100°C, and mixed with KBr (sample:KBr = 0.6:1) and pressed into a 3 mm diameter disc held in a paper holder. Spectra were collected using a Bruker Tensor 27 with a Globar source, KBr beamsplitter and DTGS detector in transmission mode under a dry air purge from 400 to at least 4000 cm$^{-1}$, with 4 cm$^{-1}$ resolution and 100 scans. (Supplementary Table 3). FTIR bands were located using the OPUS software (v8.0) provided by Bruker and identified using data from the literature (Supplementary Table 2, [7–10]).

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Transparency document. Supporting information

Transparency data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.dib.2016.12.024.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.dib.2016.12.024.

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