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Chemistry of prehistoric rock art pigments from the Indonesian island of Sulawesi

Robi Kurniawan^{a,b}, Grandprix Thomryes Marth Kadja^{a§}, Pindi Setiawan^c, Basran Burhan^d,
Adhi Agus Oktaviana^e, Rustan^d, Budianto Hakim^f, Maxime Aubert^{g,h}, Adam Brumm^h and
Ismunandar^{a*}

^a Division of Inorganic and Physical Chemistry, Institut Teknologi Bandung, Jl. Ganesha no.
10, Bandung 40132, Indonesia

^b Department of Physics, Faculty of Mathematics and Natural Sciences, Universitas Negeri
Malang, Jl. Semarang no. 5, Malang 65145, Indonesia (permanent address)

^c Division of Visual Communication and Multimedia, Institut Teknologi Bandung, Jl.
Ganesha no. 10, Bandung 40132, Indonesia

^d Cultural Property Preservation Office of Heritage, Jl. Ujung Pandang no. 1, Makassar 9017,
Indonesia

^e The National Research Center of Archaeology, Jl. Condet Pejaten no. 4, Jakarta 12510,
Indonesia

^f Archaeology Research Office of Makassar, Jl. Pajjaiyyang no. 13, Makassar 90552,
Indonesia

^g Griffith Centre for Social and Cultural Research, Griffith University, Gold Coast,
Queensland 4222, Australia

^h Australian Research Centre for Human Evolution, Environmental Futures Research
Institute, Griffith University, Brisbane, Queensland 4111, Australia

E-mail: §kadja@chem.itb.ac.id, *ismu@chem.itb.ac.id

Abstract

Rock art comprises various forms of images and markings, including paintings, drawings, and engravings, created by prehistoric people on immobile surfaces of rocks. In Indonesia, the distribution of rock art sites has been relatively well studied and documented. Indeed, Uranium-series analysis of speleothem materials overlying negative hand stencils and naturalistic animal paintings from the limestone karsts of Maros in southern Sulawesi shows that the rock art in this region dates to at least 40,000 years ago, and is thus among the world's oldest. To our knowledge, the chemistry of the Sulawesi rock art, including that of the pigments used for making these images, and with particular regard to the topology and morphology of these materials, have not yet been systematically investigated. In this study, we report the results of our spectroscopic and microscopic analyses of two samples of pigment collected from rock art motifs at Leang Sumpang Bitu 2 in Pangkep, South Sulawesi. The first and second samples possess dark red and purple colours, respectively. Analysis shows that both samples contain iron oxide, which may explain their reddish colours. Nevertheless, microstructural differences are evident, including crystal morphology and size, and, in our view, are responsible for the discrepancy in the observed pigment colours. Our findings suggest that the sampled dark red and purple pigments are from the same raw material source (ochre), but differ in color because of mechanically-induced alteration, presumably the result of varying pigment-processing methods used by the prehistoric artists.

Keywords: Sulawesi rock art; mechanically-induced alteration; spectroscopic and microscopic studies

1. Introduction

The investigation of prehistoric cultural heritage, including rock art, is important for inferring the origins and spread of human cultures around the world. Indonesia harbours a particularly rich record of ancient human culture, including occupation by multiple hominin species and some of the earliest dated rock art anywhere. The presence of Late Pleistocene rock art in both Maros and Pangkep sites offers hints at the nature of early connections and migration routes between Indonesia, and Eurasia [1] and Australia [2]. Here, the oldest Indonesia Pleistocene rock art style was found in Leang Sumpang Bitu 2, Pangkep, South Sulawesi [3-5].

The imagery consists of several types, including negative human hand stencils, a negative human foot stencil, large naturalistic paintings of endemic Sulawesi land mammals, including Celebes warty pig (*Sus celebensis*) and dwarfed bovid anoa (*Anoa* sp.). A large painting of a canoe-like boat is also present. These paintings are dominated by red pigment, which is originated from haematite [6]. The site also contains rare paintings seemingly executed with purple-coloured pigment, which are generally uncommon in the region [7]. Usually, purple pigments used for rock art production do not occur naturally, with the most common hues naturally consisting of red (haematite), yellow (limonite), white (calcite), brown (manganite), and black (charcoal) [8, 9]. A previous study has reported similar colour use in Dalakngalarr 1 in central-western Arnhem Land, Australia [10]. The red and purple were obtained from haematite minerals, with purple pigment having a larger particle size than the red pigment. These findings suggest two approaches to the preparation technique used to create red and purple pigments: heating or mechanical processing [10, 11]. The use of these approaches for creating rock art pigment in the ancient human past is still little explored from an empirical perspective. We therefore proposed to study the relationship between the

techniques used in the preparation of red and purple rock art pigment at Leang Sumpang Bita 2, with the aim of collecting data that could be of use at other prehistoric rock art sites.

In this study, we performed the spectroscopic and microscopic analyses to investigate chemistry, topology, and morphology of red and purple rock art pigment samples from Leang Sumpang Bita 2. This study will provide a thorough understanding of the characteristics of each pigment and gives an overview of how the pigment is prepared.

2. Experimental Methods

Rock art specimens were collected from a prehistoric rock art site, Leang Sumpang Bita 2, a high level limestone cave in the Pangkep region of South Sulawesi. Two types of specimens, containing dark red and purple pigments, were collected. The dark red pigment sample was collected from dark red-hued human hand stencil, located around 3.2 m above the cave floor and the purple pigment sample was collected from purple-hued human hand stencil, located 1.1 m above the cave floor. The sample collection was conducted in an area affected by natural exfoliation of the rock art panel surface, as shown in Fig. 1.

Fig. 1. Human hand stencil with sampled dark red (above) and purple pigments (below) from Leang Sumpang Bita 2, Pangkep, South Sulawesi.

All characterisation and analyses were performed on the intact samples. The topology and material contents of the samples were characterised by X-ray fluorescence (XRF) using an Orbis EDAX, which is equipped with optical microscopy. The XRF spectra and topological images were obtained from measurement on spot area of $1.5 \times 1.5 \text{ mm}^2$ using $100\times$ magnification. Raman spectroscopy was used to investigate the chemical bonding of the samples. The Raman spectra were obtained by using a Bruker Senterra with a 785 nm excitation, the power output of 20 mW and spectral resolution of 4 cm^{-1} . The multiple Gaussian fitting was performed to determine the type of bonds and crystallinity of the samples. Furthermore, the morphology of the samples was investigated by scanning electron microscopy (SEM) with low ($100\times$) and high ($10,000\times$) magnifications, employing a Hitachi SU3500 with an acceleration voltage of 10 kV. Fourier transform infrared (FTIR) spectroscopy was also used to support the analysis of the chemical bonding of the samples. The FTIR spectroscopy was performed at room temperature using a Bruker Alpha FTIR spectrometer with a spectral resolution of 4 cm^{-1} by accumulating 128 scans. In addition, the multiple Gaussian fitting was performed to evaluate the characteristic of bonds of the samples.

3. Results

3.1. Optical microscopy

Fig. 2 presents the optical microscopy images of the rock art samples. There is a clear difference in the appearance of the dark red and purple pigments. For instance, the dark red pigment has a dull lustre, while the purple pigment is brighter than that of the dark red pigment, as shown in the circled area. The lustre is related to a characteristic of the material surface, which naturally reflects a light [12].

A plausible explanation for this observed difference in lustre is that the purple pigment sample has higher crystallinity than that of the dark red pigment sample. Samples with high crystallinity tend to show higher lustre due to the absence of the surface defects. In addition, the purple pigment sample has larger and denser particles than that of the dark red pigment sample. In another words, light passes easily through the sample with a porous texture and/or small particle size (dark red pigment sample), whereas with dense and/or large particle size (purple pigment sample) light tends to be reflected.

Fig. 2. Optical microscopy images of dark red (a) and purple pigments samples (b).

3.2. X-ray fluorescence

Fig. 3 represents a bar chart of the material content of the rock art samples (human hand stencils) with dark red and purple pigments. The XRF results suggest that the gross composition of the pigments is haematite. Here, the highest percentages of the material content of Fe_2O_3 are noted in both of the samples. Previous study confirmed that red and purple pigments originate from the high content of haematite mineral (Fe_2O_3) [10, 11]. The high concentration of SiO_2 and Al_2O_3 presumably comes from kaolinite, which is naturally

found in ochre [13, 14]. The small concentrations of other materials are also observed, consisting of MgO, CaO, and K₂O.

Fig. 3. Material content (in wt% ± error%) of the rock art samples with dark red and purple pigments.

3.3. Raman spectroscopy

Fig. 4 shows the characteristic of Raman modes of the dark red pigment, purple pigment, and rock substrate of samples. Rock substrate of samples contains gypsum (CaSO₄) indicated by peaks at ~180 cm⁻¹ and 400–1200 cm⁻¹, calcite (CaCO₃) indicated by a peak at ~275 cm⁻¹ [15], where both gypsum and calcite are minerals commonly formed on cave floors and walls [16]. Broad peaks in range 1200–1500 cm⁻¹ are presumably indicating organic minerals (whewellite) [17] or disordered aluminosilicates [18]. The organics are ascribed from the natural product of lichens. However, further investigation should be made to confirm if this is the case. Both dark red pigment and purple pigment samples show Raman characteristics of haematite [19, 20]. Haematite characteristic in dark red pigment samples is

shown by the presence of vibration mode of A_{1g} (1), E_g (1), E_g (2), E_g (3), A_{1g} (2), and E_g (4). In addition, a magnon mode is observed at 847.33 cm^{-1} [21, 22].

Other vibration modes of E_u (LO) and $2E_u$ (LO) are also observed at 664.98 cm^{-1} and 1300.6 cm^{-1} . The Raman characteristic of haematite is also observed in the purple pigment sample. However, the E_u (LO) and magnon modes do not exist and only $2E_u$ (LO) mode is observed at 1316.4 cm^{-1} . The existence of both E_u (LO) and $2E_u$ (LO) vibration modes in the sample are associated with crystal disorder [23]. The absence of the E_u (LO) and the small intensity of the $2E_u$ (LO) in the purple pigment sample confirm that the purple pigment sample has higher crystallinity than the dark red pigment sample.

Fig. 4. Raman spectra of the dark red pigment, purple pigment, and rock substrate of samples.**Table 1.** Raman shift and FWHM of Raman modes for rock art samples with dark red and purple pigments.

No	Raman modes	Dark red pigment		Purple pigment	
		Raman shift (cm^{-1})	FWHM (cm^{-1})	Raman shift (cm^{-1})	FWHM (cm^{-1})
0	A_{1g} (1)	190.91	4.7565	223.89	11.174
1	E_g (1)	224.51	51.661	243.87	11.805
2	E_g (2)	287.03	35.247	293.53	16.418
3	E_g (3)	402.28	38.991	409.96	17.002
4	A_{1g} (2)	489.15	34.459	494.62	19.057
5	E_g (4)	604.16	43.88	610.95	20.822
6	$E_u(\text{LO})$	664.98	30.747	673.32	10.379
7	Magnon	847.33	100.73	-	-
9	$2E_u(\text{LO})$	1300.6	92.328	1316.4	50.778

In order to confirm the crystallinity in both samples, multiple Gaussian fitting was performed. A list of Raman shift and full width at half maximum (FWHM) of dark red pigment sample is presented in Table 1. All vibration modes of purple pigment sample show higher Raman shift value than the dark red pigment sample. This condition is associated with a high crystallinity of the sample due to high binding energy. Furthermore, smaller FWHM values in purple pigment samples are associated with larger haematite particle sizes than the dark red pigment sample [24].

3.4. Scanning electron microscopy (SEM)

Fig. 5 shows the surface morphology of the rock art samples with dark red (left) and purple pigments (right). Figs. 5(a) and 5(b) show the dark red pigment sample exhibits a

small particle size and tends to be agglomerated, while the purple pigment sample has a rough surface. The investigation at higher magnification confirms that the surface of the purple pigment sample is denser than that of the dark red pigment sample, as presented in Figs. 5(c) and 5(d).

Fig. 5. Surface morphology of rock art samples with dark red (left) and purple pigments (right); low- (a)(b) and high-magnification (c)(d) SEM images and surface mapping (e)(f).

The surface density of both dark red and purple pigment samples was estimated by calculating 2D volume integration [25], with an obtained surface density of 39.5 % and 39.7 % for dark red and purple pigment samples, respectively. In addition, the surface distribution of the sample surface was characterised by surface mapping, with the sample thickness represented by a colour scale. Figs. 4(e) and 4(d) confirm the purple pigment sample has a more uniform colour scale than that of the dark red pigment sample. As noted, this is presumably due to the large particle size in the purple pigment sample.

3.5. FTIR spectroscopy

Figs. 6(a) and 6(b) present FTIR spectra of the dark red and purple pigments analysed by Gaussian fitting. Both samples are dominated by Si–O–Si and Si–O bonds in the wavenumber range of $\sim 781\text{--}1140\text{ cm}^{-1}$, which originated from kaolinite. The weak spectrum at 1322 cm^{-1} (dark red) and 1409 cm^{-1} (purple) are assigned to the mineral glushinskite (hydrated magnesium oxalate). In addition, O–H and water H–O–H bonds are observed in the wide range of $\sim 1470\text{--}3542\text{ cm}^{-1}$. The O–H stretching at 3542 cm^{-1} shows the crystalline hydroxyl, which indicates the kaolinite characteristic. Detail of infrared band of the samples is presented in Table 2.

Fig. 6. FTIR spectra of rock art samples with dark red (a), purple pigments (b) and comparison of Fe–O spectrum of both samples (c).

Table 2. List of infrared band of rock art samples with dark red and purple pigments.

Type of bond	Index number		Ref.
	Dark red pigment	Purple pigment	
Fe–O (haematite)	0, 1	0, 1	[26]
Si–O–Si stretching	2	2	[27]
Si–O in clay	3, 4	3, 4, 5	[27]
$\nu_s(\text{C–O}) + \delta(\text{OCO})$ (hydrated magnesium oxalate)	5	6	[28]
H–O–H bending	6, 7	7, 8	[10]
O–H bending	8	9	[10]
Mixture of O–H and water H–O–H stretching	9, 10, 11, 12	10, 11, 12	[29]
O–H stretching (crystalline hydroxyl)	13	13	[29]

As noted, the dark red and purple pigments may originate from the different particle sizes of haematite, with a purple pigment having a larger particle size than the dark red pigment [2]. The formation of the purple pigment was also associated with the increase of haematite crystallinity, which is indicated by the reduction of bonds in hydroxyl groups [10]. The presence of the haematite is indicated by the existence of Fe–O bond. Two Fe–O peaks are observed at the wavenumber of 670 and 602 cm^{-1} , as presented in Fig. 6(c). The higher absorbance of Fe–O bond in purple pigment indicates that purple pigment has a higher rate of haematite formation compared with dark red pigment. This result provides the evidence of lustre characteristic in previous optical microscopy characterisation. However, the result shows that the high intensity of Fe–O is not accompanied by the absence of hydroxyl groups in the purple pigment sample. Here, the purple pigment shows more intense hydroxyl groups than that of the dark red pigment.

4. Discussions

We studied the properties of dark red and purple pigments collected from rock art images at Leang Sumpang Bitu 2, a prehistoric site in the Maros karsts of Sulawesi. The dark red and purple pigments we sampled from the artworks comprise haematite, but both of the pigments show different chemistry, topology, and morphology. The purple pigment showed the higher lustre than that of the dark red pigment. We propose that crystallinity and differences in particle size are responsible for the appearance of dark red and purple pigments, in which the purple pigment comes from haematite with the higher crystallinity, denser and larger particle size than the dark red pigment. Furthermore, the crystallinity characteristics of the dark red and purple pigments samples have been explained by the Raman spectra analysis. The grinding mechanism used by prehistoric humans as part of the chain of technical steps required to produce pigment also provides a suitable explanation for

the low crystallinity characteristic of dark red pigment sample. A prolonged grinding process could promote a deformation (lattice expansion), subsequently leading to crystal disordering.

The mineral haematite is naturally contained in ochre, which is the most common raw material used in the preparation of prehistoric rock paintings. In this study, the use of ochre on the rock art was confirmed using Raman supported with FTIR spectroscopy results, with kaolinite and haematite dominating the content of all samples. Previously, the use of purple pigments has been reported for the rock art site of Dalakngalarr 1 in central-western Arnhem Land. It was proposed, in this particular instance, that dark red and purple pigments differ in characteristics because of the high-temperature heating process of goethite minerals (yellow pigment), such that the structural transformation into haematite, in which purple pigment is obtained from a higher heating process compared to dark red pigment. This result is evidenced by larger particle size and a higher crystallinity of purple pigment compared to the dark red pigment, which is shown by increased Fe–O bonds and decreased hydroxyl groups. This high-temperature heating presumably comes from Eucalyptus wood firing, which has a flame temperature above 1000 °C [10].

In this study, the presence of glushinskite is presumably due to the bacterial or lichen growth, which promotes colour fading in the rock art [8]. The existence of the glushinskite gives the possibility that the different colour of dark red and purple may happen naturally without human intervention. The presence of lichens may possible promotes biodeterioration processes and chemistry modification, from dark red to become purple. However, overall topology, morphology and chemistry characteristics of our sample gives evidence that the dark red and purple pigments in Leang Sumpang Bitu 2 site are not prepared through the heating and biodeterioration processes. Rather, we infer that the dark red and purple pigments reflect variation in mechanical processing used by prehistoric image-makers; for instance, differences in methods employing to reduce haematite into a powder that can be used to make

paint. The higher Fe–O bonds of purple pigment compared with dark red pigment are also observed in rock art from Leang Sumpang Bitu 2. Herein, the important result is noted that the hydroxyl groups existed in both dark red and purple pigments obtained from Leang Sumpang Bitu 2. We infer that variation in grinding time and force may result in the creation of powdered haematite pigment with varying particle sizes, and thus, distinct colour differences. The dark red pigment has the small and agglomerated particle size, which may reflect a prolonged grinding process [30]. Archaeological research may be useful for testing and refining our conclusions, including experimental reproductions and analysis of haematite-stained grinding stones and other known pigment processing tools [31-33].

5. Conclusions

The chemistry, topology, and morphology of dark red and purple pigments from rock art at Leang Sumpang Bitu 2, Pangkep, South Sulawesi, were studied by spectroscopic and microscopic analyses. Both samples were comprised of a high number of kaolinite and haematite minerals, with haematite playing the most important role in determining the colour pigment. The characteristics of haematite of the dark red and purple pigments were compared. The haematite of the purple pigment showed a higher lustre than that of the dark red pigment, and we conclude that this is due to higher crystallinity and larger particle size. Our spectroscopic and microscopic analyses suggest that, in the case of Leang Sumpang Bitu 2 samples, red and purple pigments may differ in colour because of mechanical differences in how prehistoric artists processed haematite into pigment used for rock art production, rather than due to heat processing or some other process. The existence of hydroxyl groups in purple pigment supports this conclusion. However, we should caution against drawing overly broad conclusions from these findings, as our field observations in Maros suggest that, at least in some instances, red pigments weather over time into darker purple or mulberry-like

hues. Clearly, more work is needed, including experimental ochre processing, to explore the issues raised by our study. At this stage, however, our findings provide the first insight into techniques used by prehistoric artists in South Sulawesi to create some of the world's oldest known surviving rock art, with implications for our understanding of ancient rock art traditions and associated cultural heritage sites in Indonesia and further afield.

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Highlights

- Both dark red and purple pigments have high content of haematite mineral.
- Purple pigment has higher crystallinity and larger particle than dark red pigment.
- Purple pigment has more intense hydroxyl groups than dark red pigment.