



Time takes its toll: Detection of organic binder media in ochre paints with visible near-infrared and short-wave infrared reflectance spectroscopy^{☆,☆☆}

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ABSTRACT

Organic binder media in ochre rock art have so far resisted in-situ spectroscopic analysis. In this study visible near-infrared and short-wave infrared (VNIR-SWIR) spectroscopy was investigated for its usefulness in characterising experimental paints made with ochre and local (Weld Range, Western Australia) organic materials. VNIR-SWIR spectroscopy is a proven technique for the detection of mineral molecular compounds. Historic art conservators have successfully detected organic binder materials in 500-year old Renaissance art with near-infrared (NIR) spectroscopy. In this study, the chemical morphological spectral features of organic materials in newly made ochre paints, and UV accelerated 100-year aged ochre paints, were investigated. The analysis revealed complexities that would affect the detection of organic materials as anthropogenic in rock art. The first of these concerned the nature of the organic materials. There were significant deteriorative spectral changes caused by reactions initially with hematite (red ochre), and additional changes caused by accelerated UV light, resulting in remnant features different from the raw materials. These would render current references and databases useless for identification. The spectroscopic identification of organic binders in old rock art may depend on such remnants. Secondly, the composition of naturally occurring red ochre included organic materials as natural constituents, confounding the potential to differentiate those added by humans. Finally, this study has challenged the assumption that all organic materials, in particular animal fats, might function as binders to chemically adhere pigment. This paper presents a novel approach to the characterisation and identification of the constituents of ochre and organic paints, using VNIR-SWIR spectroscopy.

1. Introduction

The characterisation or distinct nature of rock art paints has the potential to reveal cultural information about the paint makers. Conservation of rock art and the direct dating of paints in contrast, are contingent on the identification or the naming of constituent organic media (Aubert, 2012:575; Bednarik, 1996, 2002:1223; Watchman and Cole, 1993). Paints are mixtures that comprise media and pigments either in solution where the molecules are scattered, or in suspension where the pigment particles require amalgamation throughout the painting process (Duce et al., 2013:5975). Other types of mixtures occur that might present difficulties in the characterisation and identification of paint constituents. Paint coated over another paint might be difficult to separate one from another or from the substrate. Similarly for different paints applied closely together, or mixed together (Popelka-Filcoff et al., 2014:1314).

Compounds in mixtures at the molecular level are detectable by vibrational spectroscopic techniques (Clark, 1999:36). Mid-infrared (IR) detects C=O, C–O and C–F molecules, and Raman detects C–C, C=C, and S–S molecules (Metrohm, 2013:11). In the detection of the constituents of paints in heritage art works, laboratory-based spectroscopic techniques require paint sampling. Portable, non-destructive versions of these same techniques exhibit pigment interference and baseline fluorescence in the detection of organic materials, but detect minerals very well (Prinsloo et al., 2013:653; Roberts et al., 2000:35; Tournie et al., 2010:403). In contrast, portable visible near-infrared and short-wave infrared (VNIR-SWIR) spectroscopy detects the overtones and combination bands of C–H, O–H, N–H, and S–H molecules representative of compound identification bands in the IR spectrum (Cloutis et al., 2016:28; Metrohm, 2013:11; Pasquini, 2003:198; Ramanaidou et al., 2008:160; Ramanaidou et al., 2015:194; Workman, 2001:145). The VNIR-SWIR technique has a distinct advantage in the

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detection of organic materials in mixtures of iron oxide minerals such as red ochre or hematite ($\alpha\text{-Fe}_2\text{O}_3$) and yellow ochre or goethite ($\text{FeO}(\text{OH})$ or $\alpha\text{-FeOOH}$) common in rock art, and found in cultural objects (Popelka-Filcoff et al., 2014:1315). Hematite has a minimum identifying band around 860 nm and goethite around 910 nm and show little interference in the region of the spectrum above 1000 nm where features of organic materials occur (Cloutis et al., 2016:34, 43; Dooley et al., 2013:4839). While goethite is often found in composite with kaolinite, hematite is formed differently (Cloutis et al., 2016; Hradil et al., 2003:230; Montagner et al., 2013:229). Hematite, therefore may occur in pure or almost pure forms, but may also contain clays such as kaolin (Cloutis et al., 2016). Kaolin is identifiable above 1000 nm on the VNIR-SWIR spectroscopic wavelength (Clark, 1999:24; Cloutis et al., 2016:33; Frost et al., 2010; Madejova and Komadel, 2001:411; Zhang et al., 2011).

There are several complexities relevant to the identification of human added organic components in ochre rock art paints beyond the technical constraints of instrumentation. Ochre pigment in paints may naturally contain organic materials such as ‘lichens and bacteria’ (Bednarik, 2002:1224; Ridges et al., 2000) and microbial DNA has been identified in mine samples by Lenehan et al. (2017). A paint that contained such ochre would give misleading radiocarbon age determinations (Aubert, 2012:575; Bednarik, 2002:1224). Secondly, organic materials in paints degrade. Different chemical reactions occur between hematite in red ochre and vegetable and animal fat organic materials (Bernardino et al., 2014:76). Further deteriorative changes then occur over time, as the organic paint mixtures undergo non-linear and differential oxidative, UV and other reactions (Bernardino et al., 2014:77; Derrick et al., 1999:131; Dooley et al., 2013:4847; Duce et al., 2013:5975; Feller, 1994:133–170). These changes in ochre rock art are under researched and entirely relevant if remnants of organic materials that might be found in old rock art are to be understood.

Ochre paints are made with powdered pigments to which a liquid medium is added. The deterioration of organic materials used as media in rock art would limit the potential for their trade or long distance sourcing. This study focused on organic materials that were available in the Weld Range, mid-Western Australia, where rock art locations lie in the vicinity of the ancient Aboriginal red and yellow ochre mines of Little Wilgie and Wilgie Mia (Bates, 1909:44–45; Clarke, 1976; Davidson, 1952; Scadding et al., 2015:300; Winton et al., 2014). The Weld Range is situated 45 km northwest of Cue in an arid zone on the edge of the Western Desert (Fitzsimmons et al., 2013:80) (Fig. 1).

Historic painting techniques have a tradition of specific binders (Hawthorne and Smith, 1979). Oil painting uses drying oils such as walnut, poppy, or linseed. Tempera contains egg, animal glue, or milk. Watercolour paints contain polysaccharide gums such as tragacanth, acacia or cherry (Duce et al., 2013:5975; Vandenabeele et al., 2000:263). Identification of binder media has been achieved in pioneering studies of an early Renaissance painted panel by Cosimo Tura, an illuminated manuscript by Lorenzo Monaco, and cross sections of paints in a wooden panel and a wall painting with near-infrared and shortwave infrared (NIR-SWIR) spectroscopy (Dooley et al., 2013; Ricciardi et al., 2012; Sciotto et al., 2014). Egg yolk lipids, proteins of egg white and animal skin glue, and features of gum arabic (gum acacia) have been found after 500 years. The lasting quality of such paints has occurred because binders function to chemically cure paint, acting as dispersants of the particles of pigment and adhering those particles together, both in paint layers, and to the substrate (Duce et al., 2013:5975). The three C=C double bonds of linseed form a waterproof, protective or curing film over the surface of a painting through polymerisation of chains of fatty acids (Carlesi et al., 2016:866; Duce et al., 2013; Feller, 1994:30, 53, 113; Iseri-Caglar et al., 2014:81; Ploeger



Fig. 1. Location map of the Weld Range. (Google maps 2017).

et al., 2009:2036; Ravines, 1998:31; Vandenabeele et al., 2000:267). Curing occurs in proteinaceous binder media such as egg white through the polymerisation of the protein molecule (Vandenabeele et al., 2000:263). In saccharides such as gums, binding properties arise through hydrogen bond formation (Vandenabeele et al., 2000:266). Reeves et al. (2013) have analysed organic materials associated ethnographically with rock art. They have compared them with European binders using pyrolysis GC-MS, isolating lipid, proteinaceous, and saccharide classes of materials. However, the binding capability of these materials has not been tested.

Based on chemically binding organic materials in historic art, rock art binder materials might be found amongst those that are proteinaceous, contain polysaccharides, or are drying oils (Duce et al., 2013:5975; Vandenabeele et al., 2000:267). Drying oils include linseed oil that contains palmitic, stearic, linolenic (Omega 3), oleic and linoleic acids (Cloutis et al., 2016; Popa et al., 2012). These oils belong to the hydrocarbon (methyl, methylene or ethenyl) groups to which the lipids of waxes, fats, and other oils belong (Ricciardi et al., 2012:5608; Workman, 2001). Fat has been identified archaeologically (Bonneau et al., 2011:288; Henshilwood et al., 2011; Vazquez et al., 2008). Weld Range organic materials in this group might be rendered oils or fats of animals such as emus, kangaroos, or goannas, and eggs of reptiles and wild birds including the very large emu egg. Local oily plants might include sandalwood, *Santalum spicatum* (Byrne et al., 2013:99, 101, 104; Hettiarachichi et al., 2013; Markey and Dillon, 2008:160–161; Statham, 1990:26). It contains ximenynic oil, $\text{C}_{18}\text{H}_{30}\text{O}_2$, (Gunstone and Herslof, 2004:235) of which 50 to 60% is contained in the nuts (Hettiarachichi et al., 2013:285, 289). *Portulaca oleracea*, is a small, native, edible, succulent plant that contains alpha linolenic acid (Elliot and Jones, 1995:443–444; Liu et al., 2002:66). Proteinaceous or

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