

Original Study

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Emigdiano Blues: The California Indigenous Pigment Palette and an *In Situ* Analysis of an Exotic Colour

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Abstract: The Native inhabitants of South Central California produced rock art containing red, orange, black, white, green and blue colours using a range of mineral and organic materials. Many of these same colours were used on material culture and body painting. This paper focuses on a sub-group of the Chumash, called the Emigdiano, who produced an enigmatic blue colour used in the creation of rock art. Here, we focus on the blue pigment at the rock shelter site of Three Springs in the Wind Wolves Preserve in South Central California. The composition of blue pigments has previously been the focus of discussion with suggestions that they were produced either using European pigments taken from Spanish missions, or that azurite from a local quarry was the source. Previous experimental work had demonstrated that it was possible for the blue to be produced from locally available azurite. Here we present the *in situ* analyses of these enigmatic blue pigments using handheld X-ray Fluorescence (pXRF). Results from pXRF analysis of rock art, quarried azurite samples and experimental rock art reconstructions showed that the Emigdiano Blue at Three Springs were not azurite based and was composed of optical blue (a mixture of black and white or grey materials which mimic the appearance of blue). This paper discusses the surprising implications of the use, given the availability of a ‘true’ blue pigment, and the wider ontological importance of combining multiple colours to produce the effect of blue in a rock art panel.

Keywords: Pigment analysis, Chumash, azurite, optical blue, XRF

1 Introduction

This paper focuses on a sub-group of the Chumash, native inhabitants of southern central and coastal California (see figure 2). This sub-group is called the Emigdiano, who occupied inland sites and produced an enigmatic blue colour used in the creation of rock art. Here, we focus on the blue pigment at the rock shelter site of Three Springs in the Wind Wolves Preserve in South Central California. Three Springs (CA-KER-3388) is one of seven rock art sites in the Wind Wolves Preserve associated with occupation sites at which excavations have taken place (Robinson & Sturt, 2008a, 2008b; Robinson et al., 2009, 2010).

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For Native Californians, pigments enacted tangible connections between people and place. Some pigments could be quite simple such as a found piece of ochre directly applied; others far more complex compositional combinations of plant oils, animal fats or bloods, plus ranges of minerals. From the journey of acquisition to source materials from the landscape, to the return transport, possible exchange or trade, processing and mixture of pigments with binding agents, the use of a painting implement such as badger tail brush, to the selection of painted surface (skin, material culture, rock surface) each stage of this chaîne opératoire was imbricated within social relations. Pigment helped create the identity of a person at a particular time: face paint turning a dancer into Coyote; body paint helping a women during menstruation; paint marks on a stone vessel enhancing its value; finger painting on a rock marking a puberty ritual; a compositional painting at a rock-art site giving the artist the power to influence the extended environment and social world; pigment on the corpse heralding its final journey to šimalaqša (Land of the Dead) beyond the western Pacific horizon. Pigments could reference the power of place of extraction, and be used to activate supernatural power such as atəšwən of the Chumash or ‘tripne of the Yokuts. Thus, pigment is relational, substances deeply enmeshed in ontological notions of causality and essence (Robinson, 2004, 2013a, 2013b). This paper outlines the native Californian palette, its uses and importance, while focusing in on the most obscure and enigmatic of paints: the case of the exotic blueish Emigdiano Blue, a pigment that has confused interpretation, defied experimentation, while showcasing a remarkable indigenous artistic eye for contrast, mix, and perception of colour. Discussion of this Emigdiano Blue focuses on the rock art site of Three Springs and a local quarry site both located within the Wind Wolves Preserve in South Central California. The study area is shown in figure 1.

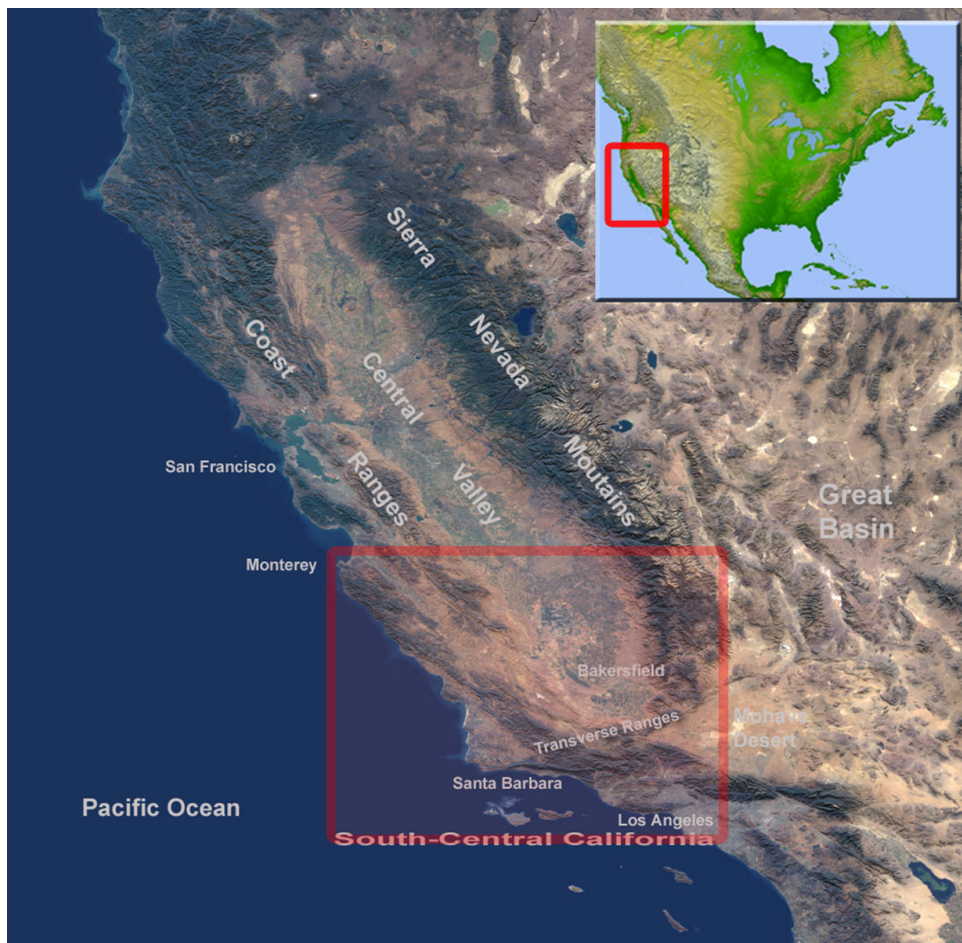


Figure 1. Map showing South Central California and study area for Emigdiano Blue.

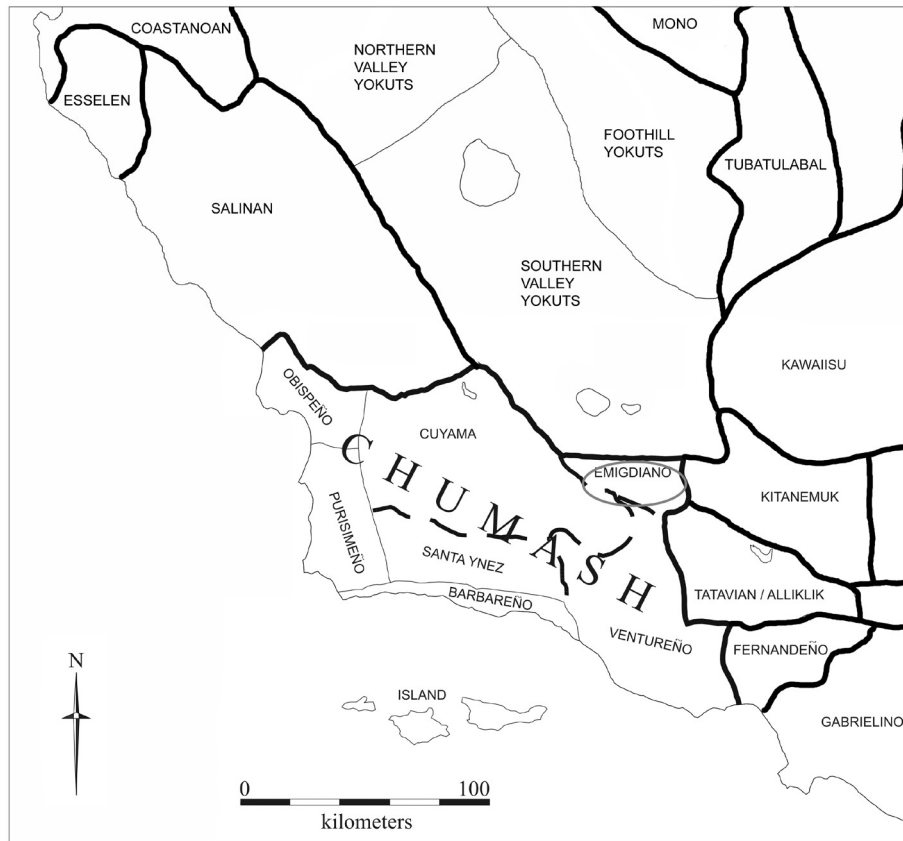


Figure 2. Linguistic divisions and their approximate boundaries of the Emigdiano and surrounding groups (graphic by Ian Forbes after Beeler and Klar, 1977). The study area of this paper is marked by a grey ellipse. To the north of this map are the Wintu, Pomo and Miwok. To the north east are the Owens Valley Paiute and Panamint Shoshone. The Cocopa are south east of the area covered by this map.

2 The Californian Palette

In California, mineral or ‘earth’ pigments were widely used for both body and rock painting. A wide range of colours including red, black, yellow, white and green were produced from such earth materials, a range of colour which are displayed in the experimental reconstruction in figure 3. Examples of such available pigments found within the Wind Wolves Preserve are shown in figure 4. However, California also provides a wealth of organic sources for pigments, and for binding materials for making paints. The various potential sources and methods by which they would be used are described below.



Figure 3. Experimental reconstruction of Chumash paintings, by Dan Reeves (Plate 3 from Reeves *et al.*, 2009).

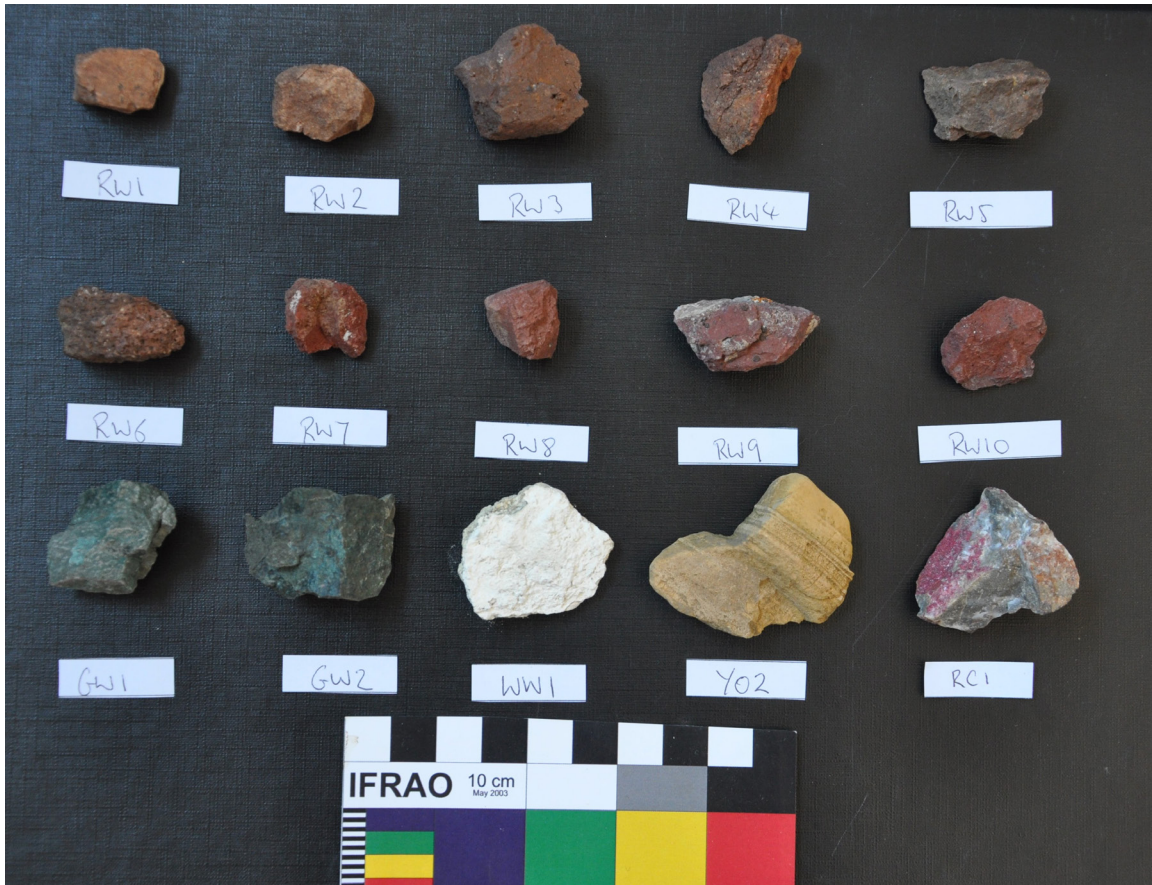


Figure 4. Sample pigment materials collected from the Wind Wolves Preserve for experimental processing and comparison with rock art pigments.

2.1 Red Pigments

Mineral sources such as red ochre and cinnabar were used as red pigments (Heizer & Elasser, 1980). Red ochre is iron oxide based and is by far the most common source of red pigment used by native Californians (Grant, 1965, p. 85). It is usually in the form of haematite and sometimes a lump of haematite would be used like to chalk to directly apply pigment to a rock surface (Grant, 1965). The Paiute and Cocopa tribes are recorded as having roasted red ochre to make its colour more vibrant (Campbell, 2007, p. 39; Heizer & Treganza, 1972, p. 296). This roasting was often achieved by putting haematite in a hole and building a fire over it. The Cocopa are described digging a hole into a haematite quarry and building a fire in the hole to provide heat which would make the colour brighter (Heizer & Treganza, 1972, p. 296). Some accounts explain that ochre was obtained by trade, often from the Mojave or Eastern Mono (Campbell, 2007; Gayton, 1948b, p. 162; Heizer & Treganza, 1972, p. 308).

Cinnabar is a naturally occurring mercuric sulphide which is also red in colour. It is less abundant than ochre (Campbell, 2007, p. 76) but is known to have been used as a pigment to produce vermilion paint by the Owens Valley Mono who quarried it and mixed it with grease (Steward, 1933, p. 276). The type of grease was not specified but it is known that deer grease was used by other tribes such as the Modoc (Campbell, 2007, p. 88). Highly valued, cinnabar became a traded import for the Panamint who purchased vermilion from Chinese immigrants (Coville, 1892, p. 361). Among the Costanoan people, whose territory included what became New Almaden Mine, New Almaden cinnabar was a valued trade commodity traded across the state and Western seaboard. This great value resulted in in-fighting among the various bands of Costanoans as well as battles with neighbouring tribes over access to cinnabar mining (Bancroft, 1886, p. 370; Taylor, 1860; Swan 1857, pp. 313–314; Harrington, 1942, p. 17). The Chumash are also known to have used cinnabar

in face paint, as well as employing it as a medicine (Travis & Hudson, 1986b, p. 182; Campbell, 2007, p. 76). As a medicine cinnabar is described as ‘a physic to rid the stomach of its contents’ (Campbell, 2007, p. 76).

In addition to these mineral sources, a range of organic materials have been documented as sources of red pigment. These include red tuna cactus fruit, octopus or seahare used by the Chumash (Hudson & Blackburn, 1986a, p. 181; Campbell, 2007, p. 70), fir tree fungus used by the Maidu and Yokuts (Sherwin, 1963, p. 84; Latta, 1977, p. 624), scorched mescal syrup used by the Ipai (Waterman, 1910, p. 212), iron rich water from bacterial growth used by the Eastern Mono and Luiseño (Campbell, 2007, p. 76; DuBois, 1908, p. 141), haws of wild rose used by the Valley Maidu, elderberry juice used by the Southern Maidu, alder sap and flowerets of yellow or white pine used by the Wintu (Voegelin, 1942, p. 197), and the roots of the rusty popcorn flower used by the Tubatulabal (Voegelin, 1938, p. 24).

2.2 Yellow and Orange Pigments

Yellow and orange pigments were also produced from iron oxide minerals, commonly called ochres. Minerals used as yellow pigment include limonite (Grant, 1965, p. 85) and goethite (Rifkin, 2016, p. 175). In addition to these, oranges and yellows were produced from organic sources such as the sulphur pea flower used to create yellows by the Yana (Campbell, 2007, p. 70). The Shasta made yellow paint from hazel pollen, the eastern Shasta from oak pollen and the Cocopa used tule pollen (Campbell, 2007, p. 43). In addition, there are other accounts of the use of pine, alder or hazel pollen, the inner bark of oak, and a fungus occurring on wild rose (Dixon, 1907, p. 480; Voegelin, 1942, p. 84; Sherwin, 1963, p. 85; Kelly, 1932, p. 116). The Maidu used orange fistulae on spruce burls (Campbell, 2007). During the historic period, a yellow paint of European manufacture came to be used by the Mohave, Paiute, and potentially Yokuts. The paint was described as brighter than ochre yellow but its composition is not described (Taylor & Wallace, 1947, p. 8).

2.3 White Pigments

Native Californians are known to have used a range of materials to produce white pigments. These include kaolin (aluminium silicate), magnesite (magnesium silicate), chalk (calcium carbonate), gypsum (calcium sulphate), shell, bone and diatomaceous earth (Campbell, 2007; Grant, 1965; Latta, 1977).

The Chumash and Yokuts burnt and pulverized shells, and the Cocopa burnt and pulverized fish bones; the Chumash may have used gypsum which was locally available (Campbell, 2007, p. 65; Gayton, 1948a, pp. 21, 69). Chalk was the usual source of white pigment in Northeast California, used by the Klamath, Modoc, Shasta, Wintu, Atsugewi, Nisenan, Maidu and known to be used further south among the Yokuts (Voegelin, 1942, p. 184; Sherwin, 1963; Latta, 1977, p. 301).

The Yokod Yokuts mined and traded magnesite (magnesium carbonate), and both the Yokuts and Chumash used silicon dioxide rich diatomaceous earth to produce white pigments (Grant, 1965, p. 85; Latta, 1977, p. 301). White clays or kaolin, formed by the weathering of silicates such as feldspar (Rapp & Hill, 1998, p. 126), were used by the Chumash, Yokuts, Kitanemuk, Serrano, Costanoan, Salinan, as well as many other tribes across the state (Harrington, 1942, p. 18; Gayton, 1948b, p. 162; Sherwin, 1963, p. 88; Campbell, 2007, p. 67).

Heizer and Treganza (1972, p. 295) describe the soft brown-tan chalk rock used by the Paiute. This rock was soaked to leach out the brown colour leaving a white powder used to make face paint. Along with accounts of red and yellow ochres being heated to alter their colour (Campbell, 2007, p. 39; Heizer & Treganza, 1972, p. 296), this demonstrates that pigment sources may not always resemble the pigment they produce. It is important to bear this in mind when searching for sources of rock art pigment materials.

2.4 Black Pigments

The majority of black pigments were charcoal based but mineral blacks were also used by native Californians. The Chumash, Costanoan, Salinan, Kitanemuk and Gabrielino (see figure 2) used ash tree and oak bark (Harrington, 1942, p. 18), the Nisenan burnt acorns and the Modoc would use any wood but favoured the

nut of the wild plum. The Luiseno charred wild cucumber seeds and mashed them into a black mass for body painting. Soot provides a finer black powder than charcoal and this was collected from the ceiling of a hut by the Hupa and Luiseno, or by special apparatus as built by the Kitanemuk (Campbell, 2007, p. 72; Sherwin, 1963).

Other materials such as manganese dioxide, graphite (Campbell, 2007, p. 73; Grant, 1965, p. 85; Latta, 1977, p. 599) and lead based galena occur in natural deposits and were used widely. Manganese dioxide was used by the Luiseno, Gabrielino and Cocopa and was pulverized to produce paint (Campbell, 2007, p. 73; Sherwin, 1963; Harrington, 1942, p. 18). The Cocopa would heat it first to break it up (Heizer & Treganza, 1972, p. 296). Similarly, graphite employed as a black pigment by the Wukchumne Yokuts and Ipai was heated in a hole covered in hot coals to break it into powder (Campbell, 2007, p. 73). The Choinumni Yokuts would grind down black pigment of unknown origin and mix it with grease to make paint (Gayton, 1948b, p. 147).

Black pigments may consist of various types of charcoal (Lopez-Montalvo, 2014) and pyroxenes which may consist of iron or manganese based compounds (Tomasini et al., 2015; Roldan et al., 2010). Different forms of charcoal include vegetable charcoal, ivory or bone charcoal, or lamp black. The Chumash were also known to burn a black mineral stone containing lead to produce black pigment (Hudson & Blackburn, 1986a).



Figure 5. Example of Willow charcoal produced in the UK.

2.5 Blue and Green Pigments

A small number of rock art sites in California contain blue and green pigments. Copper carbonate provides a source of both blue and green in the form of azurite (figure 6) and malachite respectively and these are found widely across the deserts of eastern California (Campbell, 2007, p. 43), but blue clays, green volcanic ash and sediment mixtures (Campbell, 2007, pp. 43–44; Sherwin, 1963; Hudson & Blackburn, 1986a, p. 185), and iron based celadonite or ‘green earth’ (Scott et al., 2002) also provide mineral based pigments (Campbell, 2007, p. 61).

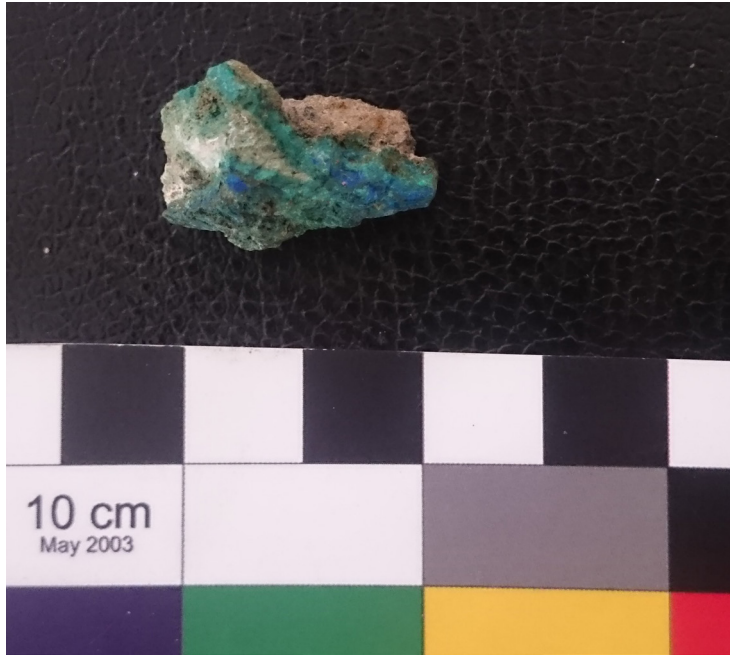


Figure 6. Sample of azurite from the quarry site in the Wind Wolves Preserve.

Fuchsite, a variation on muscovite in which some of the aluminium has been replaced by chromium is another potential green pigment. It was found at an old Luiseno rock art site, and processed fuschite was found at a late pre-historic Chumash graves at Medea Creek (Campbell, 2007, p. 49; King, 1969, p. 37).

Grant suggests that serpentine may have been used by the Chumash to produce green and blue pigments, though Lee was not able to replicate the pigment (Grant, 1965; Lee, 1979, p. 302). Heizer and Treganza (1972, p. 301) mention that turquoise was mined in San Bernardino County, presenting another potential source of blue. A mineral blue referred to as *kʷalyan* paint is described as being available in the San Emigdio mountain area (Reeves et al. 2009).

In addition, blue and green pigments have traditionally been produced from plant sources such as green moss and green colour from an onion like plant used by the Yana. Blue is available from the flowers of the larkspur pounded in a mortar with a salmon glue binder and barberries, and from a ‘potato like plant’ as described by a Yana source (Campbell, 2007, p. 70).

An alternative source of blue colour is that of ‘optical blue’ also known as ‘perceptual blue’. This is a grey material, often grey clay or a mixture of calcite or gypsum with charcoal. When placed next to yellow or red hues this grey appears blue to the human eye (Campbell, 2007).

2.6 Pigment Processing and Application

To produce paints many pigments were ground into a fine powder and then mixed with a binding material. Some pigments, such as red clay and soot naturally occur as fine powders and need less preparation. The Mohave placed white pigments in water to separate fine and coarse pigment particles. The fine particles would float in the water which was then poured off and evaporated to extract the powder (Taylor & Wallace, 1947, pp. 7–8; Campbell, 2007, p. 77). This technique can also be applied to clay and ochre. Once the fine powder was obtained, it would be dampened and shaped into a cake for transportation or trade. These cakes could be crushed to produce fine powder to mix with a binder such as animal or vegetable fat, plant gum or water. Alternatively, they could be used like a stick of chalk to directly apply pigment to a surface (Campbell, 2007, p. 81; Grant, 1965).

Various substances were used as binders for pigments to produce paint. The first is water, which is the most effective for fixing pigment to humid rock surfaces according to Claude Couraud’s experiments (Campbell, 2007, p. 87). Saliva was also used, by the Klamath, Modoc, Shasta and Pomo. The Shasta chewed

charcoal with marrow, combining pigment and fat with saliva to produce paint (Sherwin, 1963; Campbell, 2007, p. 88). Animal oils were also widely used, commonly deer fat, but also squirrel and snake oil (Sherwin, 1963; Gayton, 1948b; Campbell, 2007, p. 88). The Yurok and Karuk used animal glues from fish (Campbell, 2007, p. 93) and Scott et al. (1996) identified blood, specifically a mixture of human and antelope blood as a binder in a black pigment cake from Santa Barbara. Oils obtained from plant sources feature prominently in pigment recipes. Oil from wild cucumber seeds was used by the Chumash, Yokuts, Gabrielino and Luiseno (Campbell, 2007, pp. 89–92). Pine pitch has the advantage of avoiding the darkening effect of oil binders and was used by the Achomawi, Wintu, Cocopa and Chumash. It was particularly effective with charcoal and manganese based pigments.

The Cocopa mixed pitch with the juice of arrow weed bark. Milkweed juice was mixed with crushed wild cucumber seeds by the Foothills Yokuts, and soap root, mesquite gum and baked mescal soaked in water were also used as binders (Campbell, 2007, pp. 92–93). Gypsum added to pigments with water makes them smooth and easier to brush, and when mixed with oil binders dries to produce a hard surface (Campbell, 2007, p. 65). When mixed with white pigments such as chalk, oils tend to alter the colour and turn the white to a yellow-brown paste. The Modoc used deer grease with most pigments but mixed white pigments with water or saliva which do not affect the colour (Campbell, 2007, p. 88).

Pigments were applied either directly, by rubbing a lump of raw pigment onto a surface, or as a paint using a finger or a type of brush (Campbell, 2007, p. 95). Brushes were made from both plant and animal materials. Wooden sticks with a pointed, flattened or chewed end were used by the Yurok, Cocopa, Cupeno, Karok and Hupa. In particular, arrow weed twigs were favoured by the Cocopa, with wild grape or chamise twigs also being effective (Sherwin, 1963, p. 92; Campbell, 2007, pp. 98–101). Plant fibres, such as frayed yucca (Grant, 1965), husks of soap root bulbs, willow bark or cordage were also used as fibres for brushes (Campbell, 2007, p. 101). The Kumeyay used agave fibre cordage and the Yuma willow cord for fine work. The Wintu used a feather tip for fine work, and both Ishi and Chumash painters utilised animal hair, the Ishi with foxtail and the Chumash with badger, tree squirrel, duck and coon tail (Campbell, 2007, p. 101; Harrington, 1942, p. 18; Sherwin, 1963).

3 Emigdiano Rock Art: The Case of Emigdiano Blue

Within South-Central California, the Chumash are world renowned for their beguiling polychromatic rock painting tradition. The Chumash are well known in anthropological literature for developing complex hunter-gatherer ‘chiefdom societies’ with far reaching alliances created and maintained with marriage relationships which cross linguistic boundaries (Gamble, 2008). Among the Chumash are multiple linguistic groups as shown in figure 2. Along the interior boundary, perhaps the least understood linguistic group was the Emigdiano Chumash. The rock-art of the Emigdiano region is amongst the most complex in North America. This opinion is held largely because of its most famous site: Pleito Creek (CA-KER-77). This site contains arguably the widest colour palette of any site known of on the continent, with many hundreds of individual paintings tightly spaced in complex superimposed panels, particularly in the Main Cave of the site. Currently, we are working on a major project to ‘unravel’ the painting sequences and the painting recipes which constitute the art by integrating imaging techniques and portable analytical instrumentation (Robinson et al., 2015; Bedford et al., 2016; Kotoula et al., 2018). However, within this remarkable site can be found a particular kind of blueish pigment that has drawn attention from scholars for many decades. The blue colour has a distinct greyish hint to it. In combination with the rare use of highly opaque greens, the Chumash rock art expert Georgia Lee (1979) hypothesized that the pigments at Pleito were actually of Spanish or Mexican in origin, brought to the region by fleeing Natives from the oppressive Mission system in the late 1700s to early 1800s AD. Scott et al. (2002) recovered exfoliated fragments from this site, and their analysis was a surprise: the blue that they examined was not of European origin, nor was it even actually blue. It was an ‘optical blue’, which was created by mixing or overpainting a black substance (likely charcoal) and a gypsum based white powder. Still, there are a number of bluish hued paintings at Pleito which were not analysed by Scott and his team. The question of the origin of all the blue pigments remained open.

The discovery of a quarry site with blue and green minerals within the Wind Wolves Preserve called into question again Lee's suggestion that the pigments used at Pleito came from a mission. Reeves et al. (2009) found references in unpublished ethnographic notes stating that a "blue-black variant called *kʔalyan* was said to be an "earth" obtained north-east of 'San Emigdio Potrero Mountain' and was thought to be accessible up 'San Emigdio Creek.' It was used as a face-paint for women, was said to be applied by Yokuts dancer and shaman Bob Batista on the body, and was used medicinally" (Reeves et al., 2009). More accounts were detailed and it became clear the region was well known by Native people from around the region for its blue pigment. To further test this connection, Reeves et al. (2009) took samples from the quarry and painted them on sandstone similar to Pleito. They were able to replicate all the greens and blues evident at Pleito, as they currently appear. The age of the rock art at Pleito is not currently known, and therefore the effect of taphonomy on the appearance of these colours is unclear. However, based on the reproducibility of these colours as they currently appear, the suggestion was that the colours found at Pleito were nearby and readily available. Indeed, survey and excavations at the quarry site have produced a bird-bone bead and a biface, ephemeral but clear signs of prehistoric activity at the mineral seam.

However, if mineral blues were available, why did Scott and his team discover an 'optical blue'? With the advent of portable instruments such as handheld XRF, it is now possible to examine the blue paintings in situ. However, the many over painting events at Pleito complicate that procedure: matrix effects resulting from the superimposition of blue over other pigments complicate interpretation of the spectra. But there is another, lesser-known painted site in the Emigdiano territory that incorporates blue paint which is not in a stratified relationship with other pigments. This site is called Three Springs (CA-KER-3388), a rock shelter approximately 7km from the quarry site, which contains two panels of predominantly red and black motifs, as well as prominent bluish-grey transomorphic figure known as Blueboy (Bedford et al., 2014; Robinson, 2013a). There does not appear to be any earlier motif under the blue hued belly of this painting. Therefore, we decided to hone in on this famous figure to investigate if it contained the elemental signatures from the nearby quarry, or might be another example of an optical blue.

4 Chemical Analysis of Pigments

Developments in analytical instrumentation over the last century has greatly increased the speed and efficiency with which archaeological materials can be characterised and reduced the destructiveness of such analysis (Shugar & Mass, 2012, p. 17). The earliest studies of pigment composition used traditional chemistry techniques and were necessarily destructive, but identified the elemental composition of pigment minerals as well as some organic compounds present in pigments. These methods included examination of reactions when substances were burnt, or precipitates produced when samples were dissolved in acid. Examples of such analyses include work by John Haslam in AD1800 who examined vermilion, red ochre, red lead, lead white, verdigris and ultramarine in samples from wall paintings in St Stephen's Chapel in Westminster (Rees-Jones, 1990), and Sir Humphry Davy in AD1814 who identified ochre as iron oxide, and identified copper oxide blue in apartment wall paints, cobalt blue in glass, copper oxide in the form of malachite, as well as carbon black, two earth browns and a manganese dioxide brown pigment from Rome (Rees-Jones, 1990). Over the 20th century advances in methods in analytical chemistry methods and instrumentation have led to increasingly reliable analysis of pigment materials requiring much smaller sample sizes (Armitage et al., 2001). In addition to this, the advent of hand held instrumentation has made it possible to perform chemical analyses of pigments in situ without requiring the removal of any samples. The portable X-Ray fluorescence (pXRF) spectrometer is an example of such handheld instrumentation.

4.1 Portable X-Ray Fluorescence

The use of portable XRF in pigment analysis is becoming increasingly widespread in the analysis of archaeological materials including lithics, ceramics, glass, metallurgy and pigments obsidian (Barker et al., 2015; Craig et al., 2007; Jia et al., 2010; Nazarooff et al., 2010), lithics (Williams-Thorpe et al., 1999; Jones, G.

T. et al., 1997; Bedford et al., submitted for publication), ceramics (Terenzi et al., 2010; Papachristodoulou et al., 2010), glass (Kato et al., 2009), bronze (Dungworth, D., 1997), iron (Mentovich et al., 2010) as well as pigment materials (Nuevo et al., 2011; Olivares et al., 2012; Roldan et al., 2010). These analyses include raw pigment materials and pigments which have been applied to objects, rock faces, frescoes and murals as detailed below. A range of other analytical techniques including Raman, Fourier transform infrared spectrometry (FTIR), X-Ray diffraction (XRD), neutron activation analysis (INAA) and inductively coupled plasma mass spectrometry (ICP-MS) have often been used alongside pXRF as their results complement the pXRF data. These techniques complement the elemental data acquired using pXRF by providing additional structural information. This includes the identification of specific compounds and organic functional groups. Complementary techniques such as FTIR and Raman are particularly useful when examining materials containing lighter elements such as hydrogen, oxygen, nitrogen and carbon which are indicative of organic materials but which portable XRF does not detect.

4.2 Examination of Ochres

Numerous studies have demonstrated the applicability of pXRF to rock pigments, and the scope of this analytical technique for identification of the major elements in pigments which can be used to characterise mineral ingredients and differentiate between pigments. For example, studies by Nuevo et al. (2011), Roldan et al. (2010) and Olivares et al. (2012) show that portable XRF can be extremely valuable in the study of in situ rock art. They agree that red pigments tend to be iron oxides and black pigments are likely to be either charcoal or manganese (Nuevo et al., 2011, p. 4; Olivares et al., 2012). Usefully, Nuevo et al. (2011) suggest the potential for differentiation between pigments on the basis of different iron levels at from the 'Abrigo dos Gaivões' and 'Igreja dos Mouros' caves in Portugal, and Roldan et al. (2010) discuss the possibility that the presence or absence of manganese in ochre may indicate different sources and preparation techniques used in rock art production (Roldan et al., 2010, p. 243).

Roldan et al. (2010) studied in situ pigments in rock art, in 3 of 9 rock shelters at the Saltadora site in Spain. These pigments were red and black (Roldan et al., 2010, p. 243). Here it was concluded that the black pigments may be made from mineral pigments such as romanechite, hollandite, cryptomelane or todokorite rather than organic materials such as carbon black, based on the presence of manganese and barium in the elemental signature detecting using portable EDXRF. The red pigments here were identified as iron oxides with trace elements including sulphur, potassium, calcium, titanium, arsenic, strontium and barium (Roldan et al., 2010, p. 247). According to Roldan et al. (2010) these trace elements are typical of prehistoric red pigments such as ochres, and that manganese occurs an impurity of iron oxides in ochre. Therefore, Roldan et al. (2010) suggest that fluctuating levels of manganese within red pigments therefore could indicate different preparation techniques, whereas the absence of manganese in one pigment could indicate a different ochre source (Roldan et al., 2010, p. 248).

Jercher et al. (1998, p. 383) examined Australian Aboriginal ochres using XRF and XRD to try to establish sources for red and yellow ochre materials. Jercher et al. (1998) characterised the yellow ochre as goethite or jarosite based and the red ochres as haematite based. Goethite and haematite are difficult to separate using XRF analysis, as XRF will only detect the iron content without differentiating the iron compound. However, the jarosite pigments contain sulphur which is detectable by portable XRF (Huntley et al., 2015).

4.3 Sourcing Ochres

Data from pXRF analysis, often combined with other techniques, has proved extremely useful in comparisons between artefacts and geological sources. The approach is well established in sourcing internally consistent materials such as obsidian (Barker et al., 2015) but has also been successfully applied to differentiate between ochres in situ and between ochre fragments (Jercher et al., 1998; Huntley et al., 2015; Samson et al., 2017). The internal variation of many mineral pigments combined with matrix effects within applied pigments and the impact of weathering on rock art present significant challenges when analysing and comparing pigments in situ (Huntley et al., 2015; Huntley & Galamban, 2016). As such, quantitative

techniques requiring some physical sampling such as SEM-EDX (Huntley *et al.*, 2015; Samson *et al.*, 2017) and analysis using destructive techniques such as X-Ray diffraction or scanning electron microscopy with energy dispersive XRF are often used as complementary methods to identify likely sources (Huntley *et al.*, 2015; Syta *et al.*, 2014).

Aquila *et al.* (2012) used handheld EDXRF to perform initial chemical characterisation of pigments on Hellenistic painted plasters from Licata in Sicily. This was then quantified using SEM-EDX. Desnica and Schreiner (2006) similarly used portable XRF for preliminary characterisation of pigments on a wooden inventory in the Trski Vrh Church in Croatia. Other techniques requiring sampling were only used if the XRF results were unsuitable. The only limitations in this case seemed to be that carbon and other lighter elements indicative of organic materials cannot be identified using portable XRF, and identification of ultramarine (Desnica & Schreiner, 2006).

Gil *et al.* (2007) examined red and yellow ochres in geological sources. The intention was to examine the chemical and mineralogical distinctiveness of natural pigment sources (Gil *et al.*, 2007, p. 728). This study identified chemical elements which could be used to provide a chemical fingerprint for pigments, including lead, arsenic, copper and zinc. Gil *et al.* argued these elements could be diagnostic but were limited by the resolution of the techniques (Gil *et al.*, 2007, p. 728).

5 Examination of Blue Pigments Using pXRF

XRF has also been used to analyse pigments such as blacks, greens and blues, indicating that it could be used to examine complex polychrome rock art and address the question of the Emigdiano Blues. As with red and yellow pigment studies, pXRF has been used to identify major elements within pigment materials which are useful in characterising blue and green pigments. For example, Uda *et al.* (2005, p. 77) used a portable XRD device with XRF capability to simultaneously perform both analyses non-destructively on a bronze mirror. The pXRF results identified that an underlying layer was painted with emerald green, thus demonstrating its potential usefulness in identifying the composition of layers of material.

Uda (2004) also used a portable XRD and XRF device to identify materials used in the plaster and red, yellow and blue pigments in Amenhotep III's tomb (Uda, 2004, p. 758). The blue colour was identified as copper rich Egyptian blue based on its high copper and low iron content (Uda, 2004, p. 760).

Yoshinari Abe *et al.* (2009) used portable XRF and XRD to identify materials used in blue, red and black pigments from Saqqara in Egypt. Some of the blue pigments were identified as cobalt blue, based on the detection of elevated aluminium, manganese, iron, cobalt, nickel and zinc in the pXRF spectra.

Aliatis *et al.* (2009) used micro-Raman, FT-IR and SEM-EDX to look at green pigments from Pompeii, and was able to identify green earths, malachite, Egyptian blue and yellow ochre which were all contributing to the green colour. In this case Raman spectroscopy was used to identify the specific green pigments (Aliatis *et al.*, 2009).

Portable XRF provides important information about relative abundance of elements which can be used to characterise different materials and to differentiate between them. Despite its limitations in detecting organic materials, it is a quick and non-destructive method which has been shown to be effective for in situ pigment analysis (Roldan *et al.*, 2010; Nuevo *et al.*, 2011; Olivares *et al.*, 2012).

5.1 Investigating Blueboy

Three Springs has red, black, white, grey and blue areas of pigment, with a combination of red, blue, black and grey forming a set piece that is referred to here as 'Blueboy' (see figures 7 and 8). Set pieces are specific combinations of rock art motifs which are widely distributed amongst other Chumash rock art sites, and sometimes those of their neighbours (Robinson, 2013, p. 381). The red pigments from this site are discussed and compared in detail in a previous paper (Bedford *et al.*, 2014), but we are particularly interested here with seeing if we can distinguish between mineral blue and optical blue using the pXRF. To do this, we examined the Quarry Site itself, taking in situ readings from the blue and green mineral seams directly

as well as from one loose fragment collected from the seam; then we took readings from the experimental paintings made in 2009 in order to see if the elemental signatures could be detected after application on rock; and finally, readings were taking of Three Springs and 'Blueboy' in particular.



Figure 7. Overview of rock art in rock shelter at Three Springs with XRF assay points marked.



Figure 8. Quarry site during excavation. A thin azurite band is visible to the left of the image.

5.2 Methodology

This work was undertaken using a Bruker Tracer III-V handheld X-Ray fluorescence spectrometer with a rhodium target and Si-Pin detector with a typical resolution of 195eV. S1PXRF software was used to accumulate the spectra and the device was set at 40kV and 3.4uA and was run for 60 analytic seconds for each assay. ARTAX software was used to calculate the net area under each elemental peak and the peak volumes were exported into Microsoft Excel. This analysis examines the relative proportions of counts of each element to identify the relative abundance of major chemical elements present. These relative abundances were compared to determine the most likely type of material used to produce the blue colour.

5.3 The Quarry Site

As mentioned above, a quarry within Emigdiano territory provides material which could be used to produce bright blue or green pigments. The quarry is approximately 7km from Three Springs and 14km from Pleito. Figure 6 shows an example of the blue green material available and figure 8 and 9 show it as it naturally occurs.



Figure 9. Overview of quarry site showing areas from which assays were taken (see supplementary material¹ for full data).

A total of 33 pXRF readings were accumulated from this quarry site, including nine from 3 different areas of blue or blue-green materials, as well as from white, yellow and red areas. The blue-green mineral appears to be azurite ($\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$) and presents a high proportion of copper counts as shown by the spectrum in figure 10 and table 1.

¹ The online version of this article offers supplementary material (Table 2. Table of net area counts from XRF spectra processed using ARTAX).

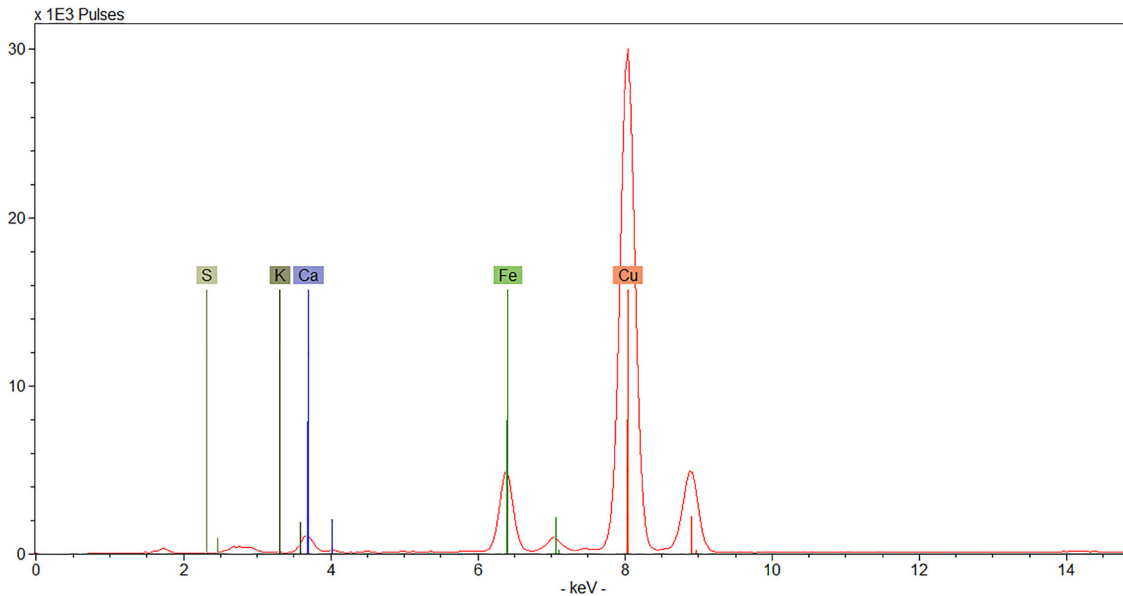


Figure 10. Example of XRF spectrum from assay of blue mineral at quarry site displayed using ARTAX software.

Table 1. pXRF results from the quarry site, panel reconstruction and Three Springs calculated as a percentage of the total counts after processing in ARTAX.

% of total counts	Al K12	Ca K12	Cr K12	Cu K12	Fe K12	K K12	Mn K12	S K12	Si K12
<i>dan bg 1</i>	0.71	5.98	0.00	4.99	52.51	6.32	9.44	0.24	5.38
<i>reconstruction blue 2</i>	0.22	1.86	0.15	56.51	28.73	1.59	2.73	0.00	2.21
<i>reconstruction blue</i>	0.31	2.29	0.00	49.68	32.63	2.75	3.96	0.05	2.05
<i>quarry sample blue</i>	0.06	0.11	0.02	87.19	7.03	0.02	0.24	0.00	0.08
<i>quarry blue left 1</i>	2.34	20.05	0.21	20.37	27.40	0.01	1.72	0.01	1.88
<i>quarry blue left 2</i>	0.14	1.74	0.02	77.80	16.15	0.03	0.23	0.00	0.83
<i>quarry blue left 3</i>	0.18	2.14	0.13	58.94	34.48	0.35	0.25	0.08	0.81
<i>quarry blue 4</i>	0.14	2.50	0.04	81.13	12.66	0.04	0.12	0.03	0.56
<i>quarry blue 5</i>	0.10	3.31	0.18	68.86	24.49	0.00	0.31	0.05	0.35
<i>quarry blue 6</i>	0.07	1.78	0.00	84.49	10.07	0.00	0.06	0.21	0.14
<i>quarry blue green stone1</i>	0.62	20.70	0.34	0.44	69.43	0.41	1.07	0.00	2.55
<i>quarry blue green stone2</i>	0.51	18.98	0.21	0.52	70.28	1.06	1.49	0.00	2.55
<i>quarry blue green stone3</i>	0.58	17.88	0.27	0.65	66.06	3.60	1.76	0.00	3.33
<i>blueboy bg 3</i>	0.21	48.94	0.00	0.55	26.46	5.98	0.14	4.36	2.77
<i>blueboy bg 4</i>	0.52	47.35	0.15	0.64	28.23	4.46	0.18	3.50	2.55
<i>blueboy bg1</i>	0.29	46.59	0.19	0.77	26.05	5.82	0.49	4.17	2.48
<i>blueboy bg2</i>	0.52	40.15	0.00	0.66	32.81	6.63	0.24	3.06	3.47
<i>blueboy blue 2</i>	0.39	72.10	0.07	0.58	13.57	2.28	0.14	0.48	0.90
<i>blueboy blue top</i>	0.27	68.99	0.12	0.43	16.47	2.67	0.28	0.32	1.13
<i>blue boy blue 1</i>	0.32	63.74	0.00	0.67	19.92	2.77	0.26	0.25	0.75
<i>blue boy limb1</i>	0.23	45.80	0.03	0.40	30.55	5.18	0.28	3.92	2.66
<i>blueboy dk grey 1</i>	0.45	47.37	0.18	0.73	26.97	4.75	0.21	2.13	2.34
<i>blueboy dk grey 2</i>	0.15	61.81	0.05	0.46	18.31	2.90	0.19	3.68	1.32
<i>blueboy dk grey 3</i>	0.54	47.97	0.27	0.96	26.77	3.72	0.33	3.49	2.01

5.4 The Reconstructed Panel

As described in Reeves *et al.* (2009), mineral from the quarry was painted onto sandstone in figures mimicking that of Emigdiano rock-art at the site of Pleito which is approximately 6km south-east of Three Springs (the original rock art panel is shown in figure 11). As at Three Springs, the blue pigment forms part of a complex combination of colours, as part of a set piece (Robinson, 2013a, p. 381). The range of colours at Pleito is discussed in detail in Robinson *et al.* (2015) and Bedford *et al.* (2016).



Figure 11. Panel A at Pleito which was reconstructed by Dan Reeves.

When taking readings of *in situ* material, the elemental composition of the rock surface will also be included in the spectrum. Therefore, readings were taken from the bare rock at both Three Springs and the reconstructed panel and *in situ* pigment readings are compared with these. Any discussion of pigment material here is based on elements showing greater abundance in the pigment than in the bare rock surface.

The results of two background, and three pigment readings from the reconstructed panel showed a distinctly high copper peak in applied pigment readings relative to the readings from the rock surface (see figure 12). When compared with readings from azurite samples from the quarry a strong similarity can be seen between these quarry samples and the applied pigment, with some variation in potassium (K) and manganese (Mn) levels also seen in the rock surface. Such variation may also be caused by attenuation of X-Rays in air pockets in the rock surface. This demonstrates that the presence of azurite based pigment applied to rock surface should be easily detectable using pXRF.

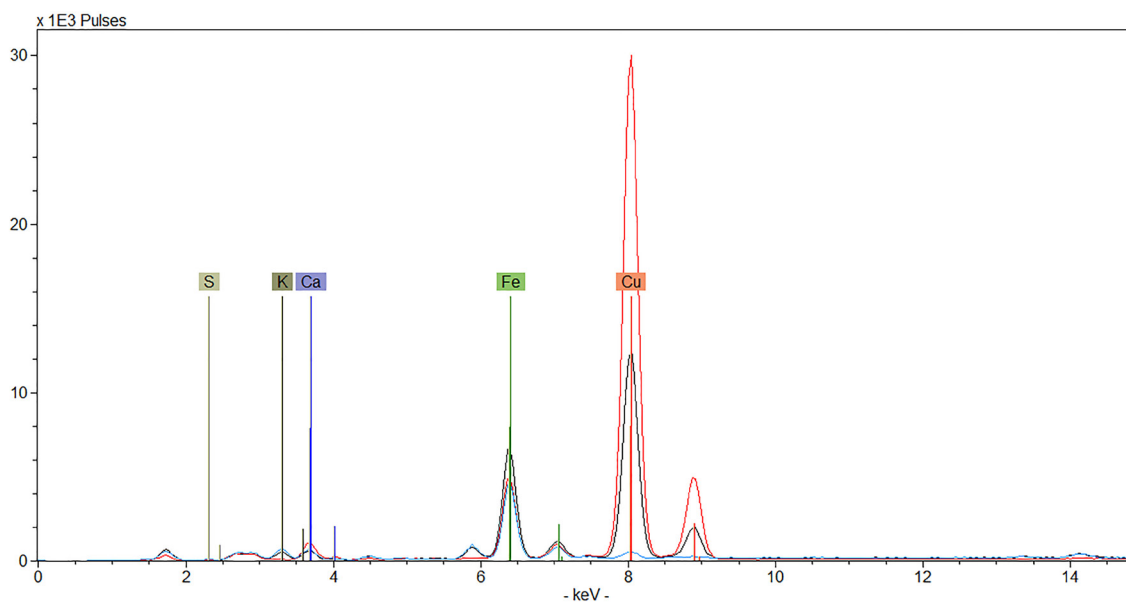


Figure 12. XRF spectra from applied azurite based pigment made by Daniel Reeves (black line) and rock surface (blue line) and assay at the quarry site (red line) overlaid using ARTAX.



Figure 13. Image of 'Blueboy' element at Three Springs with assay points marked with white dots.

5.5 Three Springs

Following rock-art documentation conventions (see Bury et al., 2003), painting groups were classified as panels, each of which were comprised of one or more individual motifs. Just as with the Reconstruction site, readings were then compared to check that pigments significantly contrasted with the rock to which they were applied.

A total of 70 spectra were accumulated from Three Springs, with six on the bluish pigment in Blueboy. The red pigments at Three Springs are iron rich and mostly likely ochre. The black pigments appear to be consistent across the site and are most likely a type of vegetable based charcoal as there are no elevated manganese or phosphorus levels, which could indicate charcoal made from bone or ivory. The grey pigments are likely to be either calcite or gypsum based on the higher proportion of calcium in the grey compared with the bare rock. The presence of sulphur can indicate that gypsum is present, but it is also possible the sulphur present is the result of sulphur salt precipitation on the rock surface rather than the use of gypsum as pigment (see Scott *et al.*, 2002). This is likely at Three Springs given similarity between the proportion of sulphur counts in the bare rock (bg) and the grey readings (see table 1).

6 Discussion

When compared with azurite from the quarry a clear contrast can be seen. The blue pigment in ‘Blueboy’ at Three Springs displays a very low proportion of copper counts which is no higher than the bare rock, whereas copper counts are very high in the quarry azurite readings. However, the blue at Three Springs shows higher calcium levels than both the azurite and the bare rock surface assays taken close to the blue motif (see figure 14 and table 1). Optical blue is produced by mixing black and white (often calcium rich pigments such as calcite, gypsum or chalk) to produce a pale grey which creates the illusion of blue when placed next to red or yellow (Campbell, 2007). The presence of high calcium levels in the blue at Three Springs when compared with readings from the bare rock (see figure 14 and table 1) is therefore consistent with the use of optical blue. It appears that ‘Blueboy’ was not produced using a copper rich blue or green pigment such as that found at the quarry site.

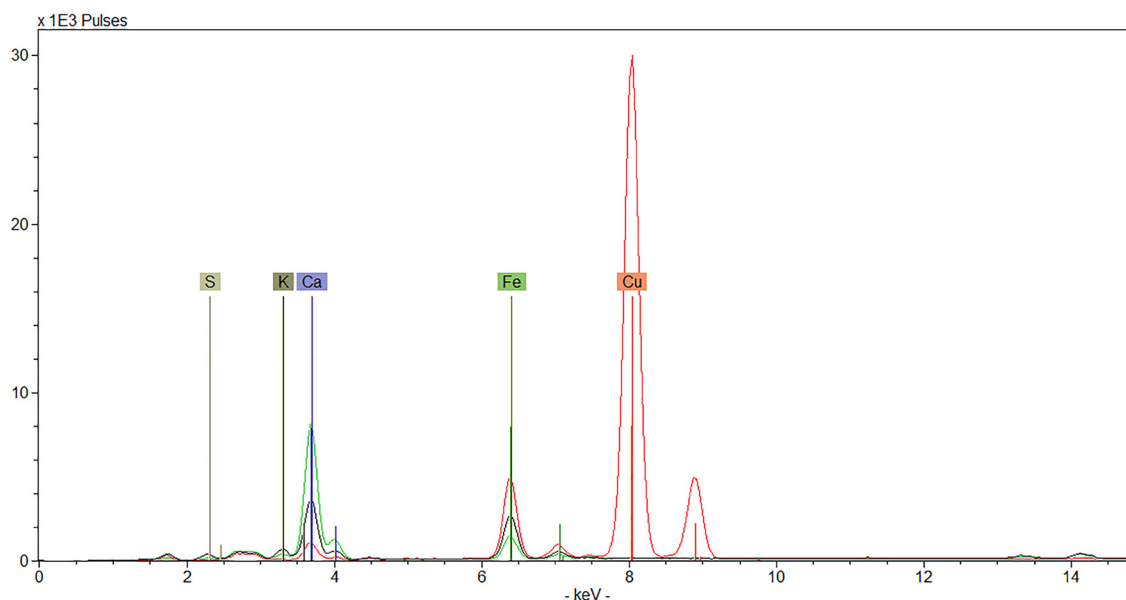


Figure 14. XRF spectra from azurite from the quarry (red line), blue area at Three Springs (green) and rock substrate (black) overlaid using ARTAX.

The composition of the blue pigment at Three Springs raises questions regarding the selection of blue pigment materials by the Emigdiano Chumash. Although a readily available source of copper rich blue minerals with evidence of prehistoric use is present, and we know it could be used to produce the very paintings we witness, we have yet to find any evidence of its use in the manufacture of pigment at Three Springs, just as Scott *et al.* (2002) did not observe the presence of copper rich pigments in fragments analysed at Pleito. To date, despite excavations at seven Emigdiano rock-art sites including Three Springs

and Pleito, no fragments of azurite have been found. This is all the more confusing considering the renown of the area for its kʔalyan paint and bluish pigments.

When specified, almost every reference to blue pigment refers to it as medicinal with references to “face paint”. Furthermore, when the availability of kʔalyan is contrasted by its absence at Emigdiano rock art sites, the cultural usage—as inferred from the presence of kʔalyan in the ethnographic record—suggests socially prescribed rules and considerations, potentially limiting its application in rock art. In other workds, such socially prescribed rules may have restricted the use of substance such as kʔalyan to body painting. This implies that there may have categorical differences between sources and uses, with pigments used in rock-art not necessarily transferable to other uses, and vice-versa.

And what of ‘optical blue’? Scott et al. (2002) in their analysis of exfoliated pieces from Pleito noted that extra processing was required by the artists to produce the small particle sizes of the pigments which they saw in the pigment samples; they also noted that a high level of skill was needed to produce the optical blue. Campbell (2007) eventually was able to replicate optical blue, but only after quite a difficult process. The making of optical blue appears to have been a highly specialized practice, very much focussed upon in select elements of Pleito and Three Springs. As suggested by Robinson (2004) in his study of coastal Chumash rock-art sites, the source material for pigment in Native California “were bound within a nexus of interrelationships involving the body, concepts of power (i.e. *atəšwən*), mythological understandings and experiences of places.” The use of optical blue shows that creators of rock art were artists: careful attention to the admixture had to be balanced against the visual perception it played against the colour of the sandstone rock surface. The effect of this optical blue is influenced by the red and yellow pigments around it. Perhaps the components of set pieces containing blue were placed to produce a carefully combined effect involving each pigment in specific balance. Too much or too little of white or black, applied in the wrong manner would ruin the perceptual effect. So, if rock-art was, at least in part, meant to be employed to be affectual works, then the care and attention of the elements produced with optical blue may be indicative of the power that was meant to be employed in their making. Were the charcoals and whites used in the paintings making reference to some special place in the landscape, something other than the azurite quarry? Were the artists (or artist?) viewed by others as having a special status? Though we have gained new insights into the creation and considerations of rock art, new questions arise.

7 Conclusion

It appears that the blue pigments at Three Springs are most likely optical blue based on the presence of elevated calcium counts relative to the bare rock and the absence of elevated copper counts which would indicate the use of an azurite type pigment. This is similar to the conclusions of Scott et al. (2002) at Pleito about exfoliated blue paint on rock fragments, also identified as optical blue. This is intriguing, given the proximity of an available ‘true blue’ copper rich mineral seam. This prompts questions regarding the reasons behind the selection of raw materials and technique used to create such blue paints for rock art. Following the study at Three Springs, we will be performing more experimental work alongside the use of pXRF, portable Raman and FTIR in attempts to clarify the constituents of the optical blues found at Pleito, and perhaps other blues are yet to be identified during that process. Perhaps our work there will reveal the missing azurite, or will the Emigdiano Blues continue to play on?

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