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A multi-technique characterization and provenance study of the pigments used in San rock art, South Africa

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ABSTRACT

During the course of a conservation project at the rock shelter known as RSA TYN2 (Eastern Cape, South Africa), a sample of 33 painted fragments that had become detached from the wall were collected. They have been studied using a multi-technique approach (optical microscopy, SEM-EDS, Raman spectroscopy and FTIR), with the aim of achieving a better understanding of their paint stratigraphy, composition, and provenance. The paintings are on a Clarens Formation sandstone and are embedded in calcium sulphates and oxalates. The red pigments show two different 'hues', corresponding to two different compositions. The light red is a red ochre, possibly pure, which is probably a degradation product of the Clarens Formation sandstone. The dark red contains more iron oxides and may be a mixture between the red ochre and pure haematite. Because of the presence of crystals which may be identified as augite we suggest this haematite came from the basaltic upper part of the Drakensberg, at least 4 km away from the rock shelter. The black pigments have been identified as carbon black, that is to say, incomplete combustion products of organic compounds, and are radiocarbon dated to between 2120 and 1890 cal BP, making these samples the oldest directly dated South African rock art.

1. Introduction

The San rock art of southern Africa is one of the best understood traditions of rock art in the world; detailed interpretations explain much of the imagery (e.g., Lewis-Williams and Pearce, 2004). It occurs over much of southern Africa south of the Zambezi and is particularly prolific in the Drakensberg mountain range. Although a great deal is known about the meaning of the art, much less is known about the composition of paint and the techniques used to make it. Studies to determine the composition of San paint have been undertaken since the 1980s using a variety of techniques such as scanning electron microscopy coupled with energy dispersive X-ray spectrometry (SEM-EDS), X-ray fluorescence (XRF), X-ray diffraction (XRD), particle induced X-ray emission (PIXE) (Van Rijssen, 1990; Wilson et al., 1990; Peisach et al., 1991; Mazel and Watchman, 1997; Hughes and Solomon, 2000; Arocena et al., 2008; Hall et al., 2007; Hœrlé et al., 2008) and more recently Raman and Fourier transform infrared (FTIR) spectroscopy (Prinsloo et al., 2008; Tournié et al., 2011). All these studies show that the red paint is made with red ochre or haematite, the yellow with yellow ochre or goethite, the white with calcite, gypsum or white clay, and the black with amorphous carbon or manganese oxides, and that the pigments sometimes contain anatases, feldspars, quartz and calcium oxalates.

Almost all of these previous studies have used only a single analytical technique and have worked on one or a very few samples. In contrast, our study applies complementary techniques to the problem of characterizing the inorganic components of rock paint (organic characterization is ongoing). Our intention is to address issues of provenance as well as of pigment identification.

2. Site description

RSA TYN2 is a painted rock shelter in the Drakensberg mountains of the Eastern Cape Province, South Africa (Fig. 1). The shelter is about 25 m long, 3 m high and 6 m deep. It is painted through most of its length, although the majority of the paintings are located towards the centre of the shelter. One section (approximately 2 × 3 m) of the painted wall on the right-hand side of the shelter is spalling severely. A conservation project in 2008 and 2009 collected 154 painted flakes from the shelter floor (Pearce, 2010).

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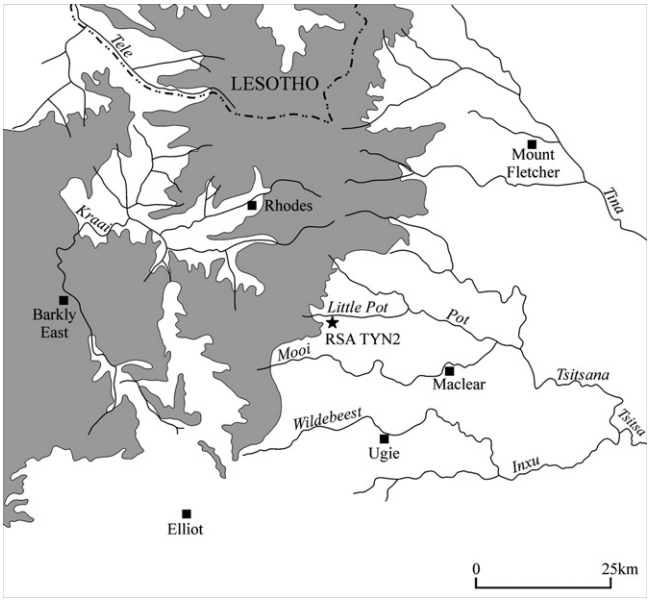

Fig. 1. Location of the RSA TYN2 site. Shaded areas indicate the extent of overlying basalt. Other areas are sandstone.

Because they were surface collected, there is no stratigraphic information about the likely timing or sequence of spalling, other than to observe that they are most likely to have fallen relatively recently since they have not become buried. The painting on the flakes is in very good condition but some show the presence of a grey layer on top of the painting as discussed below. The rock shelter is very dry and there is no evidence of transportation of the flakes once detached from the wall. Thirty three of these, with the highest densities of paint, were selected for analysis. The advantage of using these flakes is that relatively large samples of paint were available for analysis without the need to further damage the intact wall paintings, but the disadvantage is that the pieces were small and could not be re-fitted, or matched to remaining paintings on the wall (Pearce, 2010), so it was not possible to identify the subject of the paintings.

There are very few radiocarbon dates for San rock paintings – the existing dating evidence has recently been reviewed by Mazel (2009a,b). Following our identification of the black pigment on the flakes from RSA TYN2 as carbon black (see below), we developed a protocol to remove calcium oxalates and AMS dated the remaining residues. Three results were obtained (2072 ± 28 BP, 2100 ± 40 BP and 2083 ± 32 BP), which constitute the oldest results so far obtained for direct dates on South African rock art. The most likely calibrated date range from these three results at RSA TYN2 is between 2120 and 1890 cal BP (Bonneau et al., 2011).

3. Method

The studied fragments measured between 2 and 12 cm in length, 1 and 6 cm in breadth, and from a few millimetres to more than 1 cm thick. The first observations showed the presence of four colours: black, dark red, light red and pinkish-red, the last colour found on just one sample. The thickness of the pigment layer varied between samples, and thus might contribute to the observed variation in colour. Analysis of their cross-section showed that the paint layer is between 20 and 100 μm thick.

Samples were analysed directly onto the surface and in cross-section: only fragments which seemed to have the thickest layers of paint were prepared in cross-section. Polishing of the sections was attempted, but it damaged the pigment layer. Instead, a very fine saw was used to prepare the sections. All the fragment surfaces were analysed with SEM-EDS, FTIR and Raman spectroscopy, and the cross-sections were studied using SEM-EDS and Raman spectroscopy.

SEM-EDS analyses were carried out with a Jeol JSM-840A SEM with an Oxford Instruments Isis 300 EDS, in high vacuum mode. This EDS detector can analyse elements starting from boron ($Z = 5$). The accelerating voltage was 20 kV for EDS analyses. Samples and cross-sections, apart from those with black paint, were coated with carbon prior to electron microscopy. FTIR analyses were carried out with a Bruker Vertex FTIR equipped with a diamond ATR system. The spectra were acquired with 32 scans on a range from 400 to 4000 cm^{-1}. The spectral resolution was 4 cm^{-1}. The Raman apparatus used on the red and blacks pigments was a Bruker Senterra Raman system, equipped with a microscope having three lenses (×10, ×20, ×50). The spectral resolution was 3 cm^{-1}. For all the samples, the laser used was a near infrared laser, 785 nm, with a power of 10 mW. Additional Raman spectroscopy on the black pigments was carried out using a Horiba Infinity spectrometer with a green (531 nm) laser. For the Horiba instrument, the spot size used was around 3 μm (approximately the size of the crystals occurring in the pigment samples) with a maximum power of 4.5 mW at the sample. For FTIR and Raman, the identification of the peaks was done using the IRUG and RRUFF databases (available online at www.irug.org and http://rruff.info/). In other cases, the reference spectra used are noted in the appropriate discussion.

4. Results and discussion

Prior to the analysis of pigments and deposits, observations with light microscopy, SEM and FTIR analyses were made of the underlying rock. They confirmed the composition of Clarens Formation sandstone: quartz and feldspars connected by a calcium and/or chlorine base matrix (Tournié et al. 2011). It is possible to refine this composition using FTIR analyses (Fig. 2). The rock is composed of quartz (peaks at 1001, 796 and 777 cm^{-1}), large quantities of anorthoclases (alkali feldspar (Na,K) $AlSi_3O_8$) and orthoclases (potassium feldspar $KAlSi_3O_8$) (peaks at 1162, 1001, 648, 462 and 420 cm^{-1}), interconnected by a calcite base matrix (peaks at 1410, 873 and 711 cm^{-1}). Moreover, zircon ($ZrSiO_4$), ilmenite ($FeTiO_3$) and anatase (TiO_2) crystals are present in small quantities. SEM-EDS analysis revealed a low presence (≤1%: see Table 1) of iron and magnesium, the former probably from ilmenite and from the degradation of feldspars by sericitisation, and the latter from the rock formation which has a volcanic episode (Du Toit, 1926) and whose lava contains magnesium. These analyses correspond to a sandstone of the Clarens Formation. This analysis of the background rock is necessary to allow a distinction to be made between readings on paint and rock.

Underneath the pigment layers (and a white deposit, described below), the rock surface has a highly crystalline layer 0.5 mm–1.5 mm thick which proved to be composed only of quartz and feldspar, as shown in cross-sections analyzed by SEM-EDS and Raman spectrometry. The calcium carbonates contained in the matrix of the rock surface seem to have disappeared. This layer appears to be due to either weathering or human activity. On areas where there are no pigments or white deposit, there is no crystallized layer. It therefore seems to be related, in some way, to the positioning of the paintings. Unfortunately, it is not possible to say more about its nature from our samples. Several hypotheses may explain this: