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Yellow and red ochre pigments from southern Portugal: Elemental composition and characterization by WDXRF and XRD

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Abstract

Three different yellow and red ochre pigments geological sources from Alentejo—*Terras rossas*, schist units and weathered iron ore deposits—were studied by elemental and phase analysis complemented with Munsell and CIELAB colour parameters. Central aims were to underline the mineralogical and chemical distinctiveness of natural pigment sources and establish a connection between local geology and use of specific colour pigments in traditional lime wash mural paintings.

According to the chemical composition the Fe abundance is 6 times higher than average crust values. The *Terras Rossas* are characterized by higher Ca contents. In yellow and red schists, phyllosilicates are major minerals, so pigments from these units are enriched in K and Rb. Besides Fe, the pigments from weathered ores are enriched in metals like Pb, As, Cu, and Zn, which can be used as fingerprints.

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Keywords: Portugal; Mural paintings; Ochre pigments; Chromophore; DRX; WDXRF; Munsell and CIELAB colour parameters

1. Introduction

Portugal is geologically rich in yellow and red ochre pigments, known also simply as ochres. These materials were widely used in the past by the local populations on lime washing exterior paintings (façades) and probably also, for centuries, by artists in interior decorative mural paintings (*fresco* and tempera techniques).

Natural colourant earths have been widely used as artistic pigments since prehistoric times not only because of their natural abundance, normal easy extraction and preparation or low commercial cost but also because of their colouring capacity and stability under varied weather conditions, light, oxidation and corrosion [1].

The study of these materials is an interdisciplinary task that intends to rule restoration and conservation activities and contribute to the knowledge of the ancient societies that promoted the artistic work. Especially important is to understand the economic activities or the relation between society and its natural environment like the availability of raw materials and the commerce routes from production to its final use.

With these pigments, a variety of colours can be obtained varying from olive yellow to dark red, due to the different minerals and proportions [2]. Therefore, the generally used yellow and red colours found in Alentejo have some variations that can be explained by differences in chemical and/or mineralogical composition. It is generally accepted

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that iron oxides are the phases responsible for ochre colour. Of them, hematite (α-Fe_2O_3) and goethite ($FeO(OH)$) configure iron as the main chromophore for red and yellow, respectively [2].

These minerals can be generated in different geological environments. This study intents to recognize a set of ochre characteristics to allow the establishment of a connection with its genesis.

2. Experimental

2.1. Samples

The 29 ochre pigments samples were collected from different sources covering the wide area of the Alentejo Region-Estremoz (E), Odemira (O), Moura (Mo), Barrancos (B), Serpa (Se), Alandroal (A), Portel (P), Mertola (M), Sousel (S), Fronteira (F), Redondo (R), Grandola (G) e Viana do Alentejo (V). Considering the geology of Southern Portugal (*in situ* observation of different tonalities—Obs.), the historic documental sources (BR) and the oral tradition (OT), three different origins for ochre were identified [3–5], namely: (i) carbonate rock weatherings (*Terras rossas*) (G.1), (ii) coloured areas in yellow and red schist units (G.2) and (iii) iron ore deposits weatherings (G.3). Central aims are to underline the mineralogical and chemical distinctiveness of natural pigment sources and establish a connection between local geology and use of specific pigments.

It must be highlighted that these materials are heterogeneous and can have contributions from different sources.

The samples were dried at 35 °C and sieved to obtain a fine fraction (<125 μm) for XRD (X-ray Diffraction), XRF (X-Ray Fluorescence) and colorimetric analyses (Table 1).

2.2. Analytical techniques

Quantitative elemental composition was obtained by WDXRF using a commercial Bruker S4 Explorer spectrometer equipped with an Rh X-ray tube without any chemical preparation of the samples. The X-ray generator was operated at 20 kV and 50 mA for lighter elements (Na, Mg, al, P and S) or 50 kV and 20 mA for the other elements. Quantitative calculations were made through the fundamental parameters method. The results of the analysis were expressed in *ppm* and *weight percentage* (wt%).

The mineralogical composition of earth pigments was determined by XRD, using a commercial Bruker AXS-D8 Advance diffractometer with Cu Kα radiation and step of 0.02°/s. The EVA code was used for the identification of the phases. Phase analysis and profile fitting were carried out using the program package PowderCell [6]. Semi-quantitative mineralogical composition of each pigment was obtained by successive iterations following the Le Bail Method [7].

The CIELAB a* co-ordinate was taken, in 1 cm^2 diameter plane sample surface, with Mercury–datacolour colorimeter, with illuminant D65/10°, specular ref.: 4.00%; internal ref.: 60.00%; fixed adj.: 100% and Eval type: Max absorption.

The Munsell colour parameters were taken with the Color Soil Chart 1992.

Table 1
Samples references (Ref.), selection criterion (S.C) and type of soil (G.)

Ref.	S.C.	G.	Colour	Ref.	S.C.	G.	Colour
A	Obs1	1	Dark red	F2b	Obs	2	Yellowish red–reddish yellow (intermediate hue)
E	Obs2	1	Dark reddish brown	O2	Obs	2	Yellow
S2	OT	1	Dark red	E1	BR/Obs1	2	Brownish yellow
V1	OT	1	Yellowish red–dark reddish brown (intermediate hue)	E3	BR/Obs1	3	Red
Mo2	OT	2	Strong brown–brown (intermediate hue)	E5	BR/Obs1	3	Red
Mo4	OT	2	Strong brown	E8	BR/Obs1	3	Yellowish brown
Mo5	OT	2	Yellowish red	E9	BR/Obs1	3	Olive yellow
B1	OT/BR	2	Yellowish red	A1	BR/Obs1	3	Dark reddish brown
B2	OT/BR	2	Reddish Yellow	A2	BR/Obs1	3	Yellowish red–reddish brown (intermediate hue)
B3	OT/BR	2	Yellowish–brownish yellow (intermediate hue)	M4	Obs	3	Olive yellow
Se2	OT/Obs1	2	Reddish yellow	M8	Obs	3	Red
Se3	OT/Obs1	2	Reddish yellow	P1	BR	3	Yellowish red
R5	Obs1	2	Red	P2	BR	3	Red
R7	Obs1	2	Reddish yellow	G1	Obs	3	Red
R10	Obs1	2	Reddish yellow				

Obs1—*in situ* observation near churches with mural paintings.

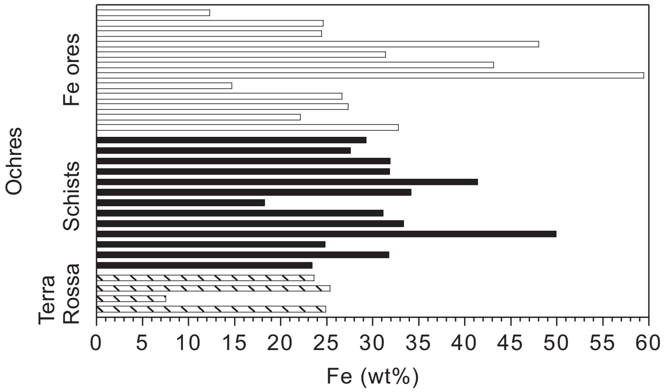

Fig. 1. Yellow and red ochres iron contents.

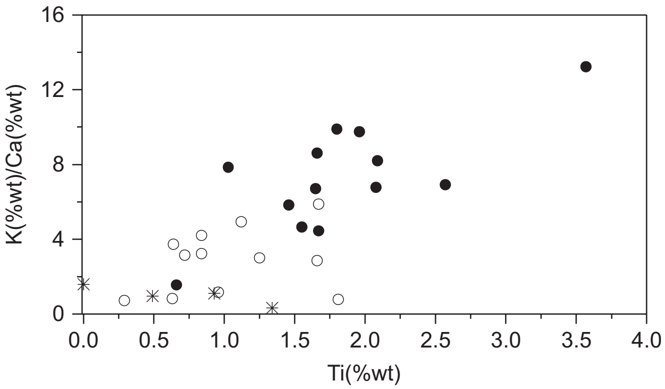

Fig. 2. Potassium to calcium ratio as a function of titanium content. •—*Schist ochre*, ○—*Iron ore ochre*, ✳—*Terra Rossa.*

3. Results and discussion

3.1. Chemical and mineralogical composition

As expected, the concentration of iron (the chromophore cation) is remarkably high (Fig. 1) and achieves 6 times the average crust values (∼4.5% [8]). Within the same group the iron content is highly variable, underling that iron concentration is not the only factor determining the colouring properties of ochres. The differences in iron content between the three different sources are not significant.

Calcium and potassium are common elements in superficial geological environments. But in the context of ochre admitted sources, their behaviour is distinct. Ca is expectably high on carbonate rocks while K is an important element of phyllosilicate like micas, illite or smectites which are essential minerals in shists. On the other hand, titanium is an element associated with the terrigenous component of the sediments, that could be more or less important in each ochre. So the plotting of the ratio K/Ca against Ti (Fig. 2) allows the visualization of the general compositions and trending of ochres with three different origins. The *Terras Rossas* are enriched in calcium because calcium carbonate is a fundamental component of the *mother rock* (carbonates).

The variability of Ti concentration is explained by variable terrigenous input. The ochres from schists show the higher K/Ca ratio as consequence of their mineralogical original composition and important concentration of Ti as indication of its terrigenous origin. The mineralogical composition of ores is poor on Ti, K, and K minerals. But the elemental composition of their ochres shows variable contents of this element as a function of the terrigenous input.

To strengthen the relationship between origin and composition of ochre, several minor elements are also analyzed. The group Cu + Zn + As + Pb are associated to sulphide ores (chalcophile elements), so the ochres from these rocks are enriched in this elements when compared with other ochres (Fig. 3). However, even though this sum can identify ochres from sulphide mother rock it cannot be used to identify ochres from oxide ores.

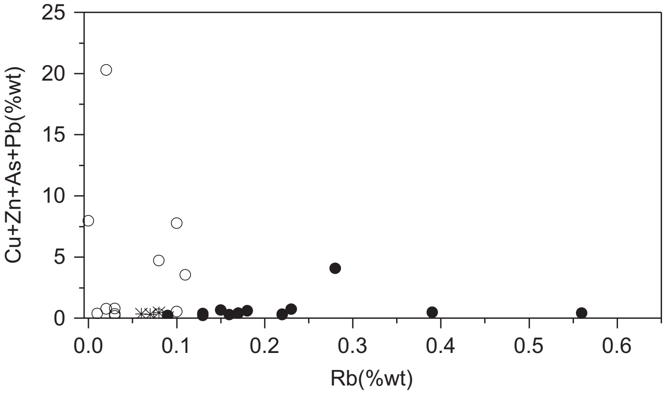

Fig. 3. Cu, Zn, As and Pb sum as a function of rubidium content. •—*Schist ochre* ○—*Iron ore ochre* ✳—*Terra Rossa.*

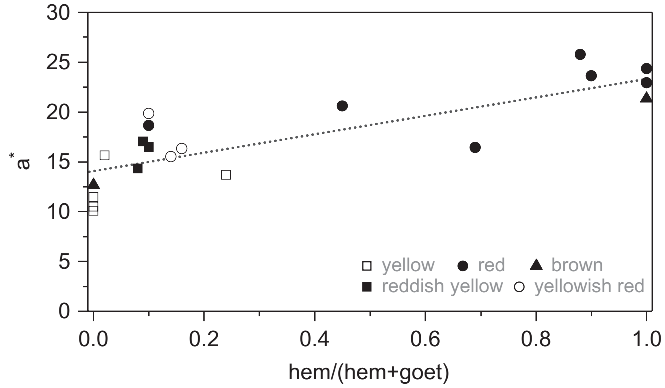

Fig. 4. a* coordinate as a function of volume ratio hematite/(hematite+goetite).

On the other hand, rubidium substitutes potassium in the clay and micas of shists. Consequently, the ochres from this kind of rocks show a Rb enrichment signature (Fig. 3).

The carbonate rocks are depleted in rubidium and chalcophile elements; consequently, the concentration of these elements is low in *Terras Rossas*.

Following the general trend of colour, *Terras Rossas* are enriched in hematite while in ochres from iron ores weathering and schists the ratio hematite/goethite is highly variable. Calcite is more important in *Terras Rossas* and the clay mineralogy seems be independent of the source of the ochre. The colour of these materials depends mainly on the electronic interactions of iron and oxygen. As expected, yellow ochres possess small values of a* and iron is present mainly in goethite (Fig. 4) while for red ochres (higher a*) is present in hematite [9].

Fig. 4 shows also that natural yellow ochres are only present in goethite domains while red ochres are present in more variable compostitions.

Another aspect to be considered is the presence of smectite clay minerals in some ochre samples. When smectites are present, ochres tend to brown colour due to their chromophore contribution. However, this effect is more pronounced when goethite is the major iron mineral.

4. Conclusions

Natural ochre pigments are complex materials which may have contributions from different sources. Nevertheless, it is possible to extract some indicators that can point to a specific source:

Terras Rossas have hematite as the main chromophore mineral and calcite is commonly identified. The original mineralogy imposes an enrichment in Ca relatively to K, variable input of terrigenous material imply variable concentrations of Ti.

Ochres from schists are enriched in K, Rb and Ti as a consequence of the importance of phyllosilicates in mother rocks and of its terrigenous origin. Their different colours can be explained by the relative abundance of hematite, goethite and smectite.

Ochres from iron ore weathering are mixes with schists materials and show variable concentration in K, Rb and Ti. Nevertheless, the sulphides ore impose enrichment in chalcophile elements.

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