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Emilie Chalmin, B Schmitt, Claire Chanteraud, Aurélie Chassin de Kergommeaux, Fayçal Soufi, et al.. The contribution of diffuse reflectance spectroscopy to the knowledge of prehistoric red colouring matter. AIC Interim Meeting Natural Colors-Digital Colors, Nov 2020, Avignon, France. hal-03099173

HAL Id: hal-03099173

<https://hal.science/hal-03099173>

Submitted on 6 Jan 2021

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The contribution of diffuse reflectance spectroscopy to the knowledge of prehistoric red colouring matter

Emilie Chalmin^{a*}, Bernard Schmitt^b, Claire Chanteraud^a, Aurélie Chassin de Kergommeaux^a, Fayçal Soufi^a and Hélène Salomon^a

^a Univ. Savoie Mont Blanc, CNRS, EDYTEM (UMR 5204), Le Bourget du Lac, France

^b Univ. Grenoble Alpes, CNRS, IPAG (UMR 5274), Grenoble, France

* Corresponding author: emilie.chalmin-aljanabi@univ-smb.fr

Presenting author: Emilie Chalmin

ABSTRACT

Understanding archaeological colouring matter commonly found at prehistoric sites is not always easy, because powdering, mixing and weathering blur the characteristics of its provenance. However, studying colouring and coloured artefacts enables the questioning of the processing techniques used to exploit them.

Various studies are interested in recognizing these red colouring matter through their mineralogy, chemistry and petrography. Here, we seek to understand to what extent it is possible to isolate a spectral fingerprint of a ferruginous raw materials by radiospectrometry whatever their physical state (cohesive rock, powder, applied mixture on limestone). By using two spectro-gonio radiometers, we characterized the visible and near-infrared reflectance spectra of six geological references, selected for their singular mineralogical and chemical compositions as well as their hues. We identified single spectral signature for each reference. Furthermore, these signatures can be identified even in powders and mixtures due to mineral phase associations.

Keywords: red colouring materials, rock art, Prehistory, diffuse reflectance, visible-infrared spectra

INTRODUCTION:

The red colour is one of the most ancient one used to paint or draw on different kinds of surfaces (wall, rock, skin, wood, shell...). Even if this red colour could be obtained easily with ferruginous rocks during prehistoric times, several questions still remain to identify these materials and their origins and to understand their transformation. Indeed, numerous remains of colouring matter, often referred to as 'ochre', have been found in the archaeological sequences. They come in the form of cohesive blocks of rock, powder or material applied to various supports. Beyond their colouring properties, use-wear analysis suggests other characteristics were considered such as technical ones (e.g. hide processing, polishing) (Pradeau et al. 2014; Rifkin et al. 2015).

The interest of studying colouring matter used during Prehistory lies in the fact that this type of artefacts recorded stigmata related to practices and techniques performed by past societies. It is indeed possible to (i) identify the methods of preparation (scraping, grinding, crushing, abrasion...), (ii) recognize the type of the rocks exploited when they are still in the form of cohesive blocks or (iii) access their chemical composition which can be very informative in the presence of specific trace elements (e.g. Zipkin et al. 2017; Beck et al. 2012). However, characterizing archaeological colouring matter requires to perform a wide range of observations at different scales (macro, meso, micro-scopic) and different analyses which are for the majority invasive or even destructive. Typically, when colouring

materials were powdered and deposited on a substrate in the past, the characteristics of their provenance are blurred by eventual mixing and weathering.

Red colouring raw materials come from various types of ferruginous rock (sedimentary processes: e.g. Banded Iron Formation (BIF), Oolitic Iron Stones (OIS), iron-rich sandstone; mineralisations: e.g. veins, lode, metasomatism; weathering processes: e.g. ochre, laterite, bauxite; volcanic and metamorphic processes) which present various mechanical, physical, chemical and colouring properties (Salomon et al. submitted). Our reference collection of ferruginous rocks encompasses the diversity of these rock types (*Pigmentothonèque* project; Chassin de Kergommeaux et al. 2021). It documents the potential resources available during Prehistory (from Palaeolithic to Neolithic) and even more recent historic periods.

The samples of this collection are subjected to petrographic, mineralogical, geochemical and physical descriptions and analyses. They are conducted on various preparations (fresh cut, polished stud, powder sieved or not) based on a shared vocabulary (lexicon) documenting formation and evolution processes. Although it is quite obvious that red, orange and yellow colours are linked to the presence of iron oxides (red hematite $\alpha\text{-Fe}_2\text{O}_3$) or ox(hydrox)ides (yellow goethite $\alpha\text{-FeO(OH)}$), it is more complicated to compare colours of different materials and even to access their composition. Simple spectrophotometric measurements make it possible to classify materials by colour quantitatively. Even if the Munsell chart may help classifying qualitatively materials, the elaboration of a more objective and standardized method is required in order to give access not only to colour but also to the structure of the raw material and transformed matter. It is the reason why we used diffuse reflectance spectroscopy, which can scan over a wide spectral range from the visible to the mid-infrared, typically up to 0.3-5 μm (e.g. Bishop 2020), offering the possibility to objectively study the origin of the colour variability and the effects of texture. This method has also the advantage of being non-contact, non-invasive and can be used on any type of sample (powder, blocks, polished stud...) even on the field (Konik and Lafon-Pham, 2018).

The objective of this paper is therefore to present the feasibility, under controlled laboratory conditions, of using spectroradiometry to distinguish a selection of ferruginous rock types presenting a variety of textures and compositions. Based on a series of measurements made at the spectrogoniometer facility at IPAG (Institute of Planetology and Astrophysics of Grenoble, UGA/CNRS), we look for correlation between reflectance variations and spectral signatures of the samples due to their mineralogical compositions. To do so, we started by analysing the six geological standards used in the framework of the *Pigmentothonèque* project. As such, they have already been analysed thoroughly with several analytical tools, including some compatible with the constraints related to archaeological artefacts and can be used for quantitative comparison between analytical methods. These samples have been selected to be sufficiently different in terms of petrography, mineralogy and chemistry in order to embrace the diversity of ferruginous rocks.

MATERIALS AND METHODS

1. Geological samples selection

We present here the 6 rock samples selected for their clear-cut genetic and intrinsic characteristics to be used as standards in order to compare all the measurements made with different instruments on both geological and archaeological objects (see map on Fig. 1).

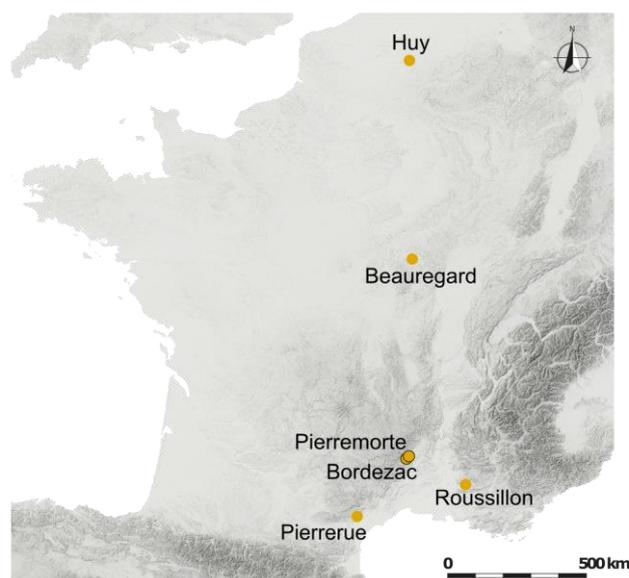


Figure 1: Location of the outcrops of the 6 reference samples (according to E. Camizulli)

Roussillon and **Pierrerue** samples are examples of weathering products displaying red colours. The sample from **Roussillon** (Vaucluse) is a ferricrete fragment from the top of the ochre profile which formed on top of a Cenomanian glauconite-rich sand/sandstone (Fig. 2e). The red irregular pisoids from **Pierrerue** (Béziers, Hérault) come from the ferricrete covering a Jurassic bauxitic weathering profile that has been silicified and ferruginised (Fig. 2b). It still contains kaolinite.

Bordezac (Gard) samples illustrate the case of a red hydrothermal hematite-rich vein (Fig. 2c). **Huy** (Belgium) samples are examples of a red iron-rich rock formed under sedimentary processes as they are Famennian Oolitic Iron Stones (OIS) from the Formation of Hodimont (Fig. 2a).

Two ferruginised limestones rich in crinoid fragments have been also selected because of their specific formation processes. The one of **Beauregard** (Thoste, Côte d'Or) is a Hettangian biogenic limestone rich in crinoid fragments whose carbonate phases (aragonite, calcite) were altered by hydrothermal fluids (natif iron, fluorite and barytine), the fossil structures have been preserved during ferruginisation (Fig. 2f). The Callovian limestone at **Pierremorte** (Courry, Gard) is rich in crinoids fragments that was ferruginised during pedogenesis and by secondary hydrothermal fluids along the Gagnière fault. In this case the original limestone is still present and the ferruginisation is heterogeneous (Fig. 2d).

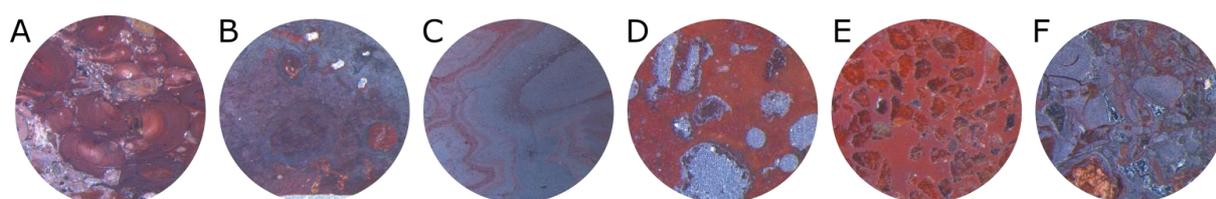


Figure 2: Polished cross section pictures: **A) Huy**: Clinton-type Oolitic Iron Stone (OIS): well sorted ferruginous flax seeds ooids with bioclastic, quartz (100 μm) or rare lithoclastic nuclei, ooids are embedded in dolomite and ferruginous clayey matrix and cement. **B) Pierrerue**: Ferruginous pisoliths. Iron duricrust in a bauxitic profile

containing mainly hematite. **C) Bordezac:** hydrothermal hematite: metallic vein composed of hematite and rare tabular micas (100 μm) and quartz inherited from the Triassic bedrock. **D) Pierremorte:** ferruginised limestone: partly ferruginised crinoid fragments in a ferruginised carbonated matrix. **E) Roussillon:** iron duricrust: corroded quartz grains (200-400 μm) in a kaolinitic and ferruginous matrix. **F) Beauregard:** limestone composed mainly of entirely ferruginised crinoid fragments (3 mm) in a ferruginised carbonated cement.

2. Preparation of samples

In addition to the raw blocks, sawn blocks and sieved powder below 160 μm (and in one case also > 160 μm) were prepared as well as paint layers applied on limestone blocks.

The powders are obtained by grinding rocks in an agate mortar followed by sieving below 160 μm . The density of the powder is accurately obtained from the measurement of its weight and volume in order to assess its porosity.

3. Petrographical observation

Macroscopic to microscopic observations (bare eye, binoculars, petrographic microscope, scanning electron microscope) are used to characterise all types of colouring matter. These observation tools are used in complementarity in order to link the different observation scales and to guide the bulk analysis (*sensu stricto*) or analysis on selected or isolated spots. Geological references are described according to the criteria of description and determination of rocks.

4. Spectro-gonio radiometers: set-up and acquisition parameters

The Cold Surface Spectroscopy facility of the IPAG laboratory holds two homemade spectro-gonio radiometers, SHINE (Brissaud et al. 2004) and SHADOWS (Potin et al. 2018) that allow records of reflectance spectra in the visible and infrared ranges (0.35 - 4.8 μm) over a wide range of illumination (0-80°) and observation angles (emergence: 0-80°, azimuth 0-180°). They have been used to characterize the reflectance of the selection of standard ferruginous rocks.

Measurements were taken in a 'standard' illumination/observation geometry (incidence 0°, emergence 30°) and over spectral ranges between 0.36 and 4.8 μm according to samples. The measurement campaigns were carried out with resolution between 4 and 15 nm and a spectral sampling between 4 and 8 nm. Samples of the different types are placed under the monochromatic illumination beam and their reflected light spectrum is acquired. The illumination spots are 5.2 mm (SHADOWS) and 7.5 mm (SHINE) in diameter. The measurements are calibrated in 'reflectance factor' using 2 reference targets (Spectralon® and Infragold®) characterized and calibrated in absolute at IPAG and measured during each campaign. The absolute photometric accuracy is better than 0.5%. Post processing is made in order to correct any residual spectral signature of atmospheric water.

RESULTS AND DISCUSSION

1. Reflectance spectra of red colouring matter

The Visible-infrared spectra (400-4200 nm) of the six standard materials as powders with grain size < 160 μm (Fig. 3) are available on-line in the PIG database of the SSHADE solid spectroscopy infrastructure (www.sshade.eu). A number of features can be recognized in these spectra, characteristic of the oxidation state of iron, the presence of OH groups, water in various states (in the structure, adsorbed, bulk, ...), and carbonate ions.

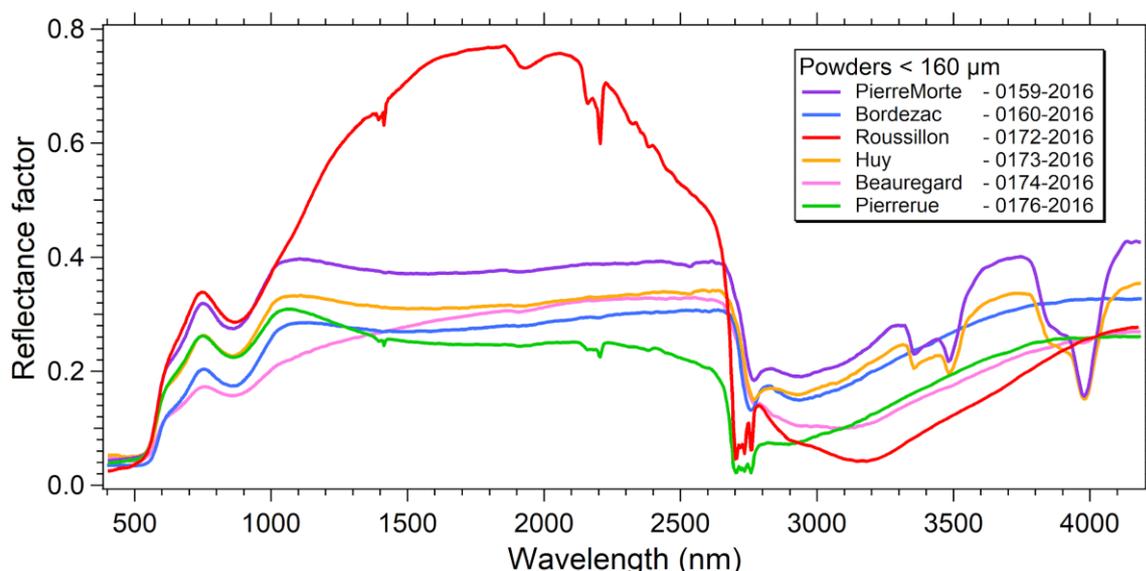


Figure 3: Vis-NIR reflectance spectra of the 6 standards: Pierremorte, Bordezac, Huy, Roussillon, Beauregard, Pierrerie (powders with grain size < 160 μm)

In the visible range (<1000 nm) there are 2 absorption edges and a band due to different electronic transitions of iron, the first edge being very strong around 580 nm and absorbs almost all light (reflectance 3-5% below 550 nm) for all materials. The second edge around 700 nm giving rise to a shoulder between 600 and 750 nm. The third band is slightly variable in position and is situated between 860 nm (Huy) and 870 nm (Roussillon), but displays only little difference in relative band depth between these materials.

The general shape between 1050 and 2600 nm is more variable and the origins of its variations are poorly known. Roussillon is the brightest sample in this range with a maximum reflectance around 1850 nm close to 80%, a strong 'red' slope (increasing reflectance with wavelength) below 1600 nm, but a marked 'blue' slope (decreasing reflectance with wavelength) above 2050 nm, while Pierremorte, Bordezac and Huy have a very similar nearly flat, but slightly curved, reflectance with medium level (0.3-0.4, slight blue slope below 1500 nm and slight red slope above 1900 nm). On the other hand, Beauregard displays a clear 'red' slope over almost the whole range, while Pierrerie has a 'blue slope' at both ends of this range (1050-1400 nm and 2200-2600 nm). Over this 'continuum infrared absorption' there are mostly 3 groups of bands around 1400 nm (hydroxyl OH stretch overtone, H₂O combinations), 1930 nm (H₂O stretch + bend combination) and 2200 nm (OH stretch + bend combination). The 1400 and 2200 nm features frequently have a double peak around 1395 and 1415 nm, and 2165 and 2205 nm, respectively. They are present only in Pierrerie and Roussillon, and quite strong in the latter. The 1930 nm H₂O band is wide and is clearly seen only in Roussillon, but is very weakly present (band depth < 0.004) in all other materials.

OH and H₂O also express with their very strong fundamental vibrations in the 2650-2800 nm range with several components depending on the cation with which they interact. Both Pierrerie and Roussillon have 4 narrow components while all other materials have only a wide band with a weak shoulder. The band around 2930 nm is relatively similar in almost all materials except Pierrerie which seems to have a stronger band and shifted toward lower wavelength (2890 nm). The 3150 nm band is particularly strong for Roussillon, strong for Beauregard but present only as a very wide shoulder for all other materials.

Finally, Pierremorte and Huy display a series of strong bands above 3300 nm (3355, 3482, shoulder

~3880, 3979 nm) characteristics of carbonates (fundamental vibrations of the CO_3^{2-} ion). A few weak combination bands of this ion are also barely seen at ~2340, ~2485 and 2534 nm in the spectra of these two materials that look very similar despite very different types of rocks and geologic histories.

2. The effect of the preparation

2.1 Effect of granulometry

In the case of Roussillon material, we measured two grain size ranges, below and above 160 μm with two different densities. The difference is mostly a decrease of about 12% of the overall reflectance when going from fine to larger grains, without any noticeable change in the occurrence or relative intensity of the various absorption bands and slopes (Fig. 4).

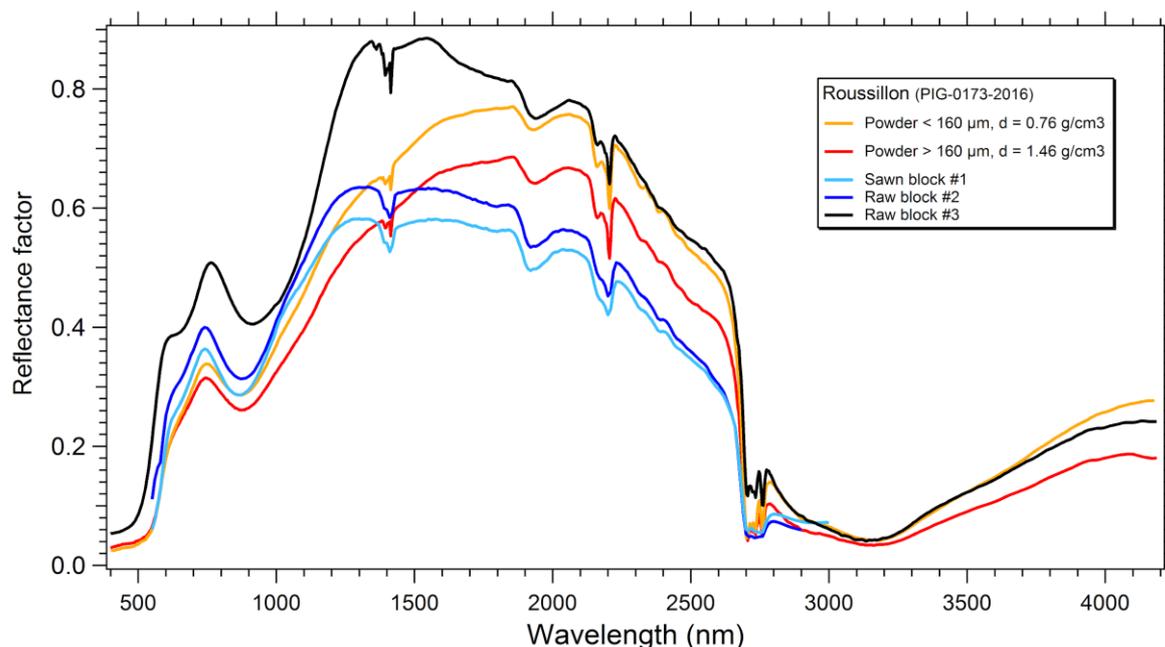


Figure 4: Vis-NIR reflectance spectra of Roussillon: powders (with grain size < 160 μm , $d=0.76 \text{ g/cm}^3$ and > 160 μm , $d=1.46 \text{ g/cm}^3$) and 3 different raw blocks

2.2 Raw block versus powder

When comparing the spectrum of a powder with that of a raw block of the original material one generally observes an overall decrease in reflectance (except in the 500 nm band which saturates at the 0.06-0.13 reflectance level for blocks instead of 0.03-0.055 for powders) with exactly the same continuum slopes and absorption bands, sometimes with similar intensities such as for Beauregard, Pierrerie and block #1 of Pierremorte, or with increased intensities of some bands, such as for the iron bands in the visible and the carbonate bands in the mid-infrared (above 2.3 μm) of block #2 of Pierremorte, along with a change of the infrared continuum slope (more 'red') (Fig. 5).

However, in some cases the composition probed by the spot on a raw block is relatively different from the global composition probed in well mixed grains of a powder. It should be noted that the depth of light penetration is typically of the order of the millimeter at 'bright wavelengths (reflectance > 0.7) but only a few tens of microns in the strong absorption bands, such as below 600 nm.

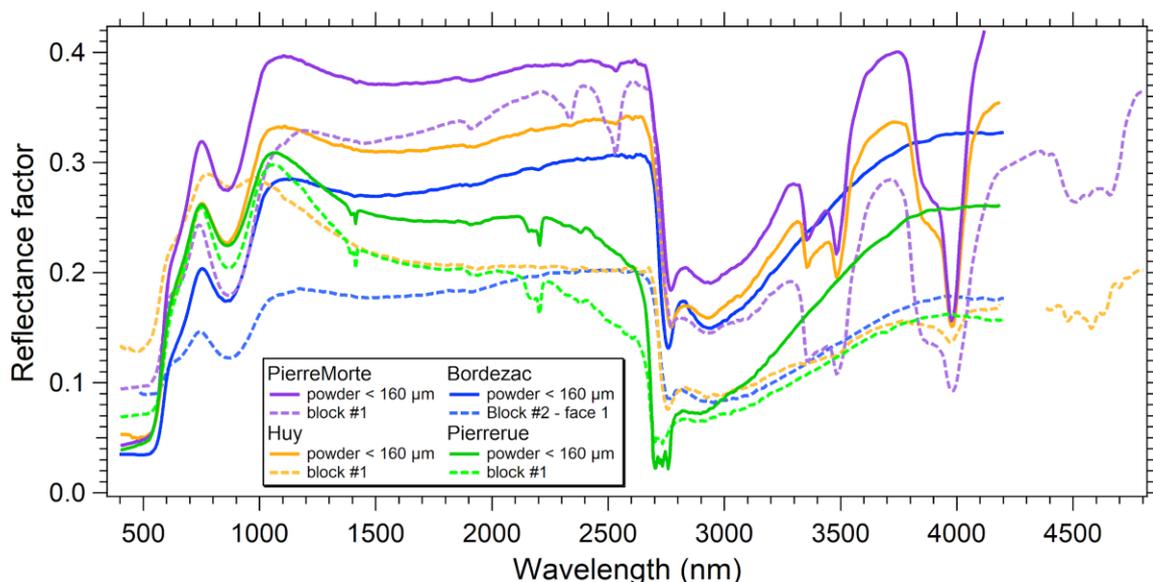


Figure 5: Vis-NIR reflectance spectra of the powder (grain size $< 160 \mu\text{m}$) and a raw block for Pierremorte, Bordezac, Huy, and Pierrerue.

CONCLUSION

With our geological surveys we systematically recorded and sampled ferruginous rocks with colouring properties and a wide range of mineralogical, chemical and petrographic characteristics. However, their simple colour is not sufficient to discriminate them, and the colour of the powder cannot inform on the origin of the rock, so the challenge was to find criteria linking powders and applied powders to corresponding cohesive rocks and therefore geological formation. Thus, the use of visible and near-infrared reflectance data revealed to be useful to categorize these different rocks even in powder. We were able to show on a first set of geological references that it is possible to provide exact colour spectra, to identify various iron oxides (hematite, goethite, maghemite ...) and additional minerals (carbonates, sulphates ...). Near-infrared reflectance spectra show the presence of structural H_2O and OH and the cations with which they interact. The direct comparison between raw blocks and powder show spectral signatures (bands and slopes) with little changes concerning band intensities and continuum level. However for some heterogeneous rocks the spectral signatures may be significantly different depending on the grain size and mineral distribution.

These first results open up the potential to compare painting matter with reference powders or block spectra to identify at least the type of ferruginous rock used to paint. However, the spectral signature of the substrate must be known as it strongly interferes at all wavelengths where the paint is mostly transparent (high reflectance). So spectroscopic field measurements appear to be interesting to easily get first information on painting matter without contact.

It emerges from this first study that using the position/width/intensity of all the bands, as well as the continuum slope and reflectance level in different wavelength ranges, it should be possible to classify all the spectra of the colouring matter within a defined set of classes or rock types with similar properties. These data will then be integrated into the *PIG @ SSHADE* database.

The detailed interpretation of the spectra of each class (bands and slopes), and its spectral variability, will then be necessary for a better understanding of the overall and specific spectral behaviours.

In particular, it has recently been shown that the morphology and size of hematite nanocrystallites, which depend on the geological formation conditions of the ferruginous rocks and Fe-minerals, have a significant effect on the shape and position of its bands in the visible spectrum, thus modulating its colour (Gerardin et al. 2020). Spectra of pure mineral components as well as cross-correlation with the petrographic, chemical and structural characteristics obtained from the same samples will be most useful for this aim. This classification may then be used for feasible, practical and non-contact field identification of the type of the painting matter.

ACKNOWLEDGEMENTS

This program takes advantage of the financial and scientific support of the Regional Archaeological Service of the Auvergne-Rhône-Alpes region and of the University of Savoie-Mont-Blanc (MASCARA and TRANSFERT projects). The SSHADE database infrastructure and the SHADOWS instrument have been developed in the frame of the Europlanet 2020 RI programme which received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 654208. We warmly thank all colleagues involved in the PCR Pigmentoθήque.

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