KEYWORDS: ***ATR-FTIR – Pigment – Binder – Database – Rock art – Pre-Historic***

IN SEARCH OF THE ATR-FTIR SIGNATURES OF EXPERIMENTALLY MIXED INGREDIENTS PRESUMABLY USED IN PRE-HISTORIC ROCK ART

Sara Garcês, Hugo Gomes, Lydia Haddab, Pedro Cura and Pierluigi Rosina

Abstract. In this study, a collection of 29 samples of possible pigments, binders and carrying agents were selected based on artistic considerations and analysed with ATR Fourier-transform infrared spectroscopy in order to determine usable marker bands for each ingredient. It was decided to establish a preliminary and specific database for ATR-FTIR applied to pre-Historic rock art that can be compared with other existing databases and then applied and compared with data on field research.

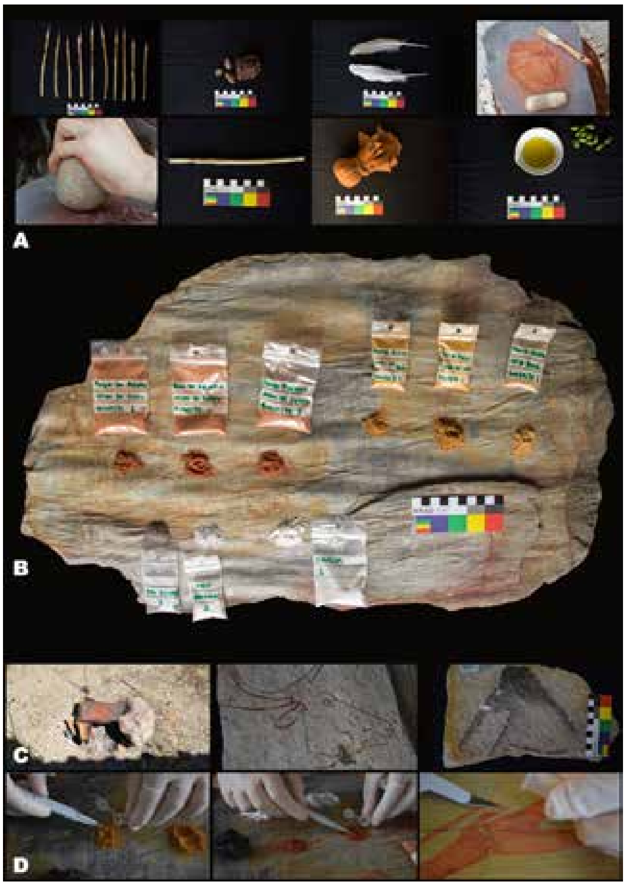

Figure 1. *Set of the experimentation process: (A) Set of figures of tools used in the experimentation; (B) Several pigments used (red ochre; yellow ochre; Clay [kaolinite-type] for white and phyllite and charcoal for black; (C) heating pigment process and painted images from experimentation; (D) sampling of pigments.*

Introduction

Attenuated total reflection Fourier-transform infrared (ATR-FTIR) spectroscopy is considered a reliable analytical technique to study both organic and inorganic materials in pre-Historic pigments (Vázquez et al. 2008; Darchuk et al. 2010; Cavalcante et al. 2011, 2018; Lofrumento et al. 2012). However, the detection of organic binders, diluents and extenders has been scarce and difficult to interpret.

In this study, a collection of 29 samples of possible pigments (red ochre, yellow ochre, clay [kaolinite-type] and charcoal), binders (animal fat, egg, blood) and carrying agents (saliva etc.) were selected based on artistic considerations and analysed with ATR-FTIR spectroscopy in order to determine usable marker bands for each ingredient. Based on the research work of one of the authors (Haddab 2017) it was decided to carry out a preliminary and specific database for ATR-FTIR applied to pre-Historic rock art that can be compared with other existing databases (*http://lisa.chem.ut.ee/IR_spectra/*) and then applied and compared with data on field research. Although other similar studies have been made using different methods of analyses (Prinsloo et al. 2013), this study is meant to be a useful tool for researchers in the fields of rock art research, conservation and materials science. In this paper, ATR-FTIR is used mainly because of the need for the identification of the organic components of experimentation pigments.

Current knowledge implies that the rock artists mixed both organic and inorganic substances together in order to achieve desired pigment colours. Different shades can be the result of the use of different pigments, the treatment the pigments have been subjected to and

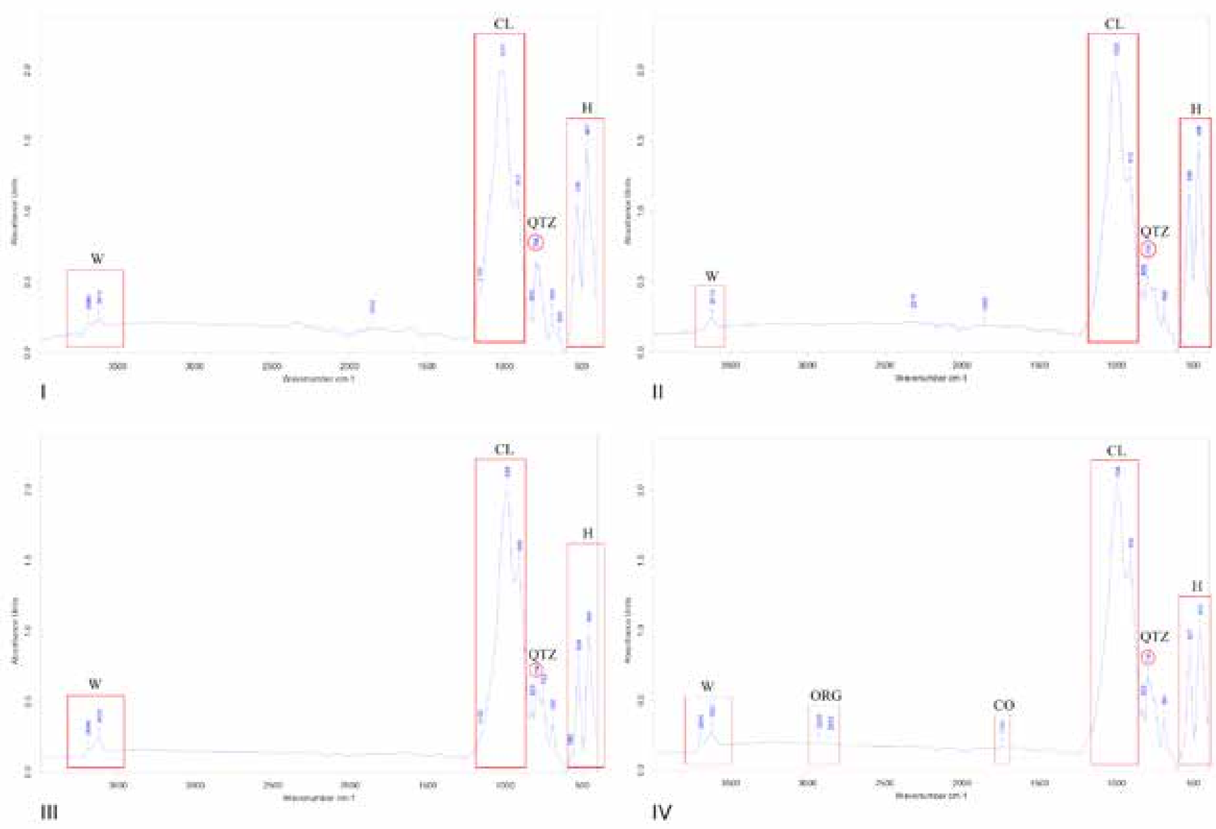

Figure 2. ATR-FTIR spectra of I: red ochre; II: heated red ochre; III: red ochre and human saliva; IV: red ochre and vegetable oil.

different particles size (Bikiaris et al. 1999; Marshall et al. 2005).

Within a pre-Historic context, red and yellow colours were a popular choice among artists (Hradil et al. 2003; Elias et al. 2006; Barnett et al. 2006). The use of red (and of various shades of red) is found on rock panels across most the world. These variations of colour can be linked to the nature of the colouring materials, but also to their position on the wall, as a consequence of the application methods and sometimes also of later removals through taphonomic processes such as water runoff (Bednarik 1994; Konik et al. 2018).

Material and methods

For the reproduction of the figures, red ochre has been used for the red, yellow ochre for the yellow, clay (kaolinite-type) for white and phyllite and charcoal for black. These materials have been pulverised employing a quartz hammer, except the charcoal which was used as a crayon. One part of the powdered iron oxide has been exposed to fire over a stone for four hours at a temperature between 500°C and 700°C.

Twenty-nine samples in total were selected (individual masses not exceeding few milligrams) (Fig. 2) from the experimentation pigments and analysed by ATR-FTIR. The following were used as possible binder material: human blood, burnt cow bone, olive oil, animal fat, egg yolk, egg white, human saliva and *Rubia tinctorium* sap. The choice of these materials was made based on the literature assumption that these materials are supposed to have been used as binders in pre-Historic rock art (Clottes 1993; Lorblanchet et al. 1990a, 1990b) though there is still poor evidence that binders were used. However, there are some examples of plant cells (Cole and Watchman 1992; Watchman and Cole 1993; López-Montalvo et al. 2017) and fatty acids were reported in pigment 'recipes' (Boschín et al. 2002; Gomes et al. 2013; Rosina et al. 2018; Brook et al. 2018). Regarding the use of plants, it was decided to use three different types of plants: a tree species (pine tree), a herbaceous perennial plant species (*Rubia tinctorium*) and a member of the plant family Cactaceae (*Opuntia ficus*). For application tools, we have used a cow-hair brush, goose feathers and fingers.

Each sample was obtained using a sterilised tungsten scalpel and inserted in a 0.5 ml microcentrifuge tube. ATR-FTIR spectra of samples were collected using a Bruker Alpha FT-IR, Opus 7.5 software, spectrometer employing an ATR (Attenuated Total Reflection) sampling device. The ATR-FTIR spectrometer was equipped with a global source, a KBr beam splitter and a Deuterated Lanthanum α Alanine doped triglycine sulphate detector at room temperature. The ATR sampling device worked with a diamond internal reflection element (IRE) in a single-reflection configuration. Spectra were recorded over the spectral range of 400–4000 cm^{-1} at a 4 cm^{-1} resolution, 24 scans.

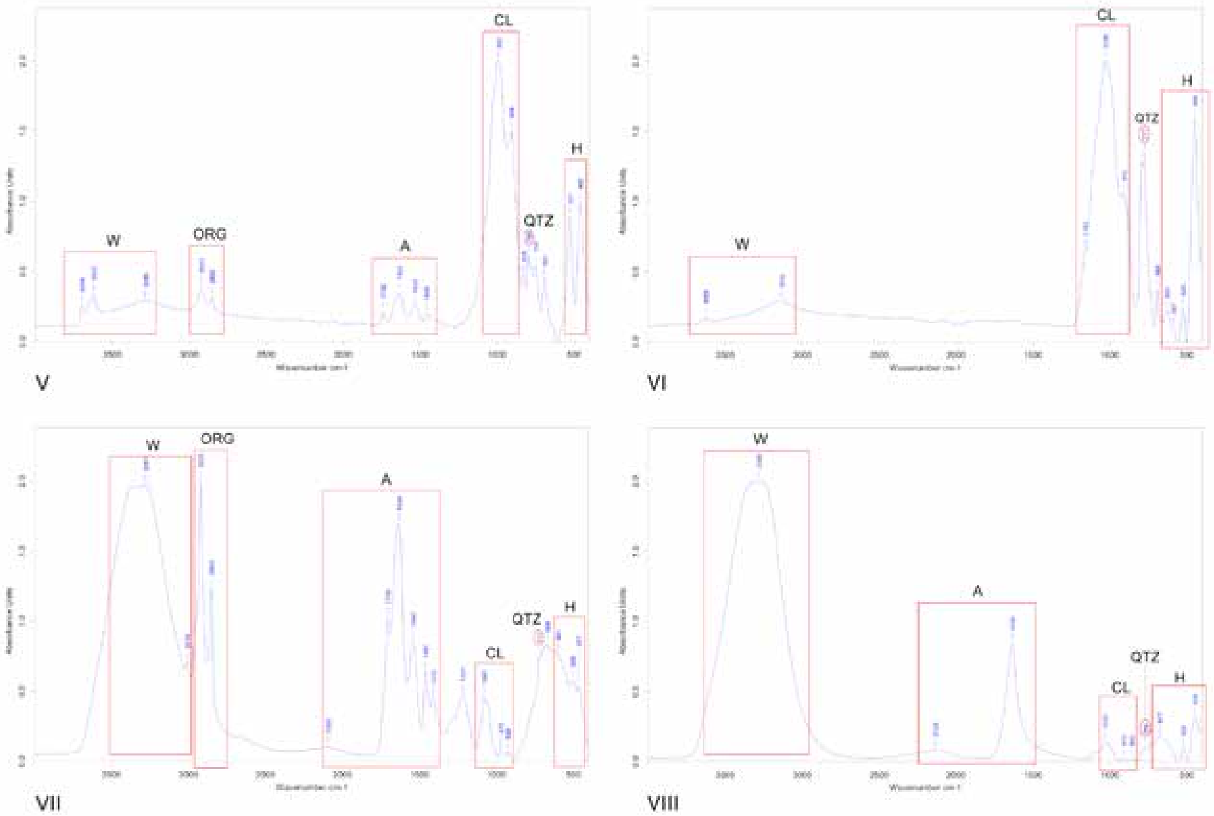

Figure 3. *ATR-FTIR spectra of V: red ochre and egg yolk; VI: yellow ochre; VII: yellow ochre and egg yolk; VIII: yellow ochre and* Rubia tinctorium *sap.*

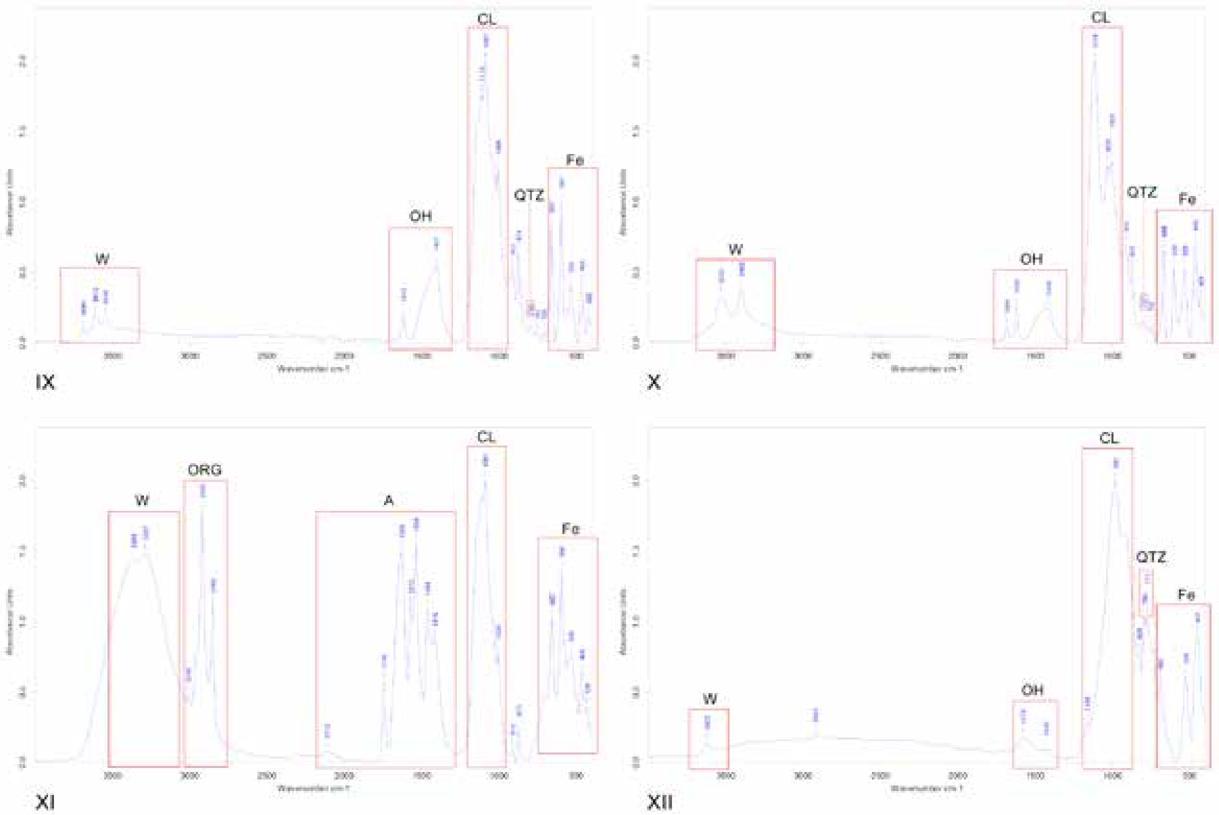

Figure 4. *ATR-FTIR spectra of IX: clay (kaolinite-type); X: clay (kaolinite-type) and water; XI: clay (kaolinite-type) and egg yolk; XII: phyllite.*

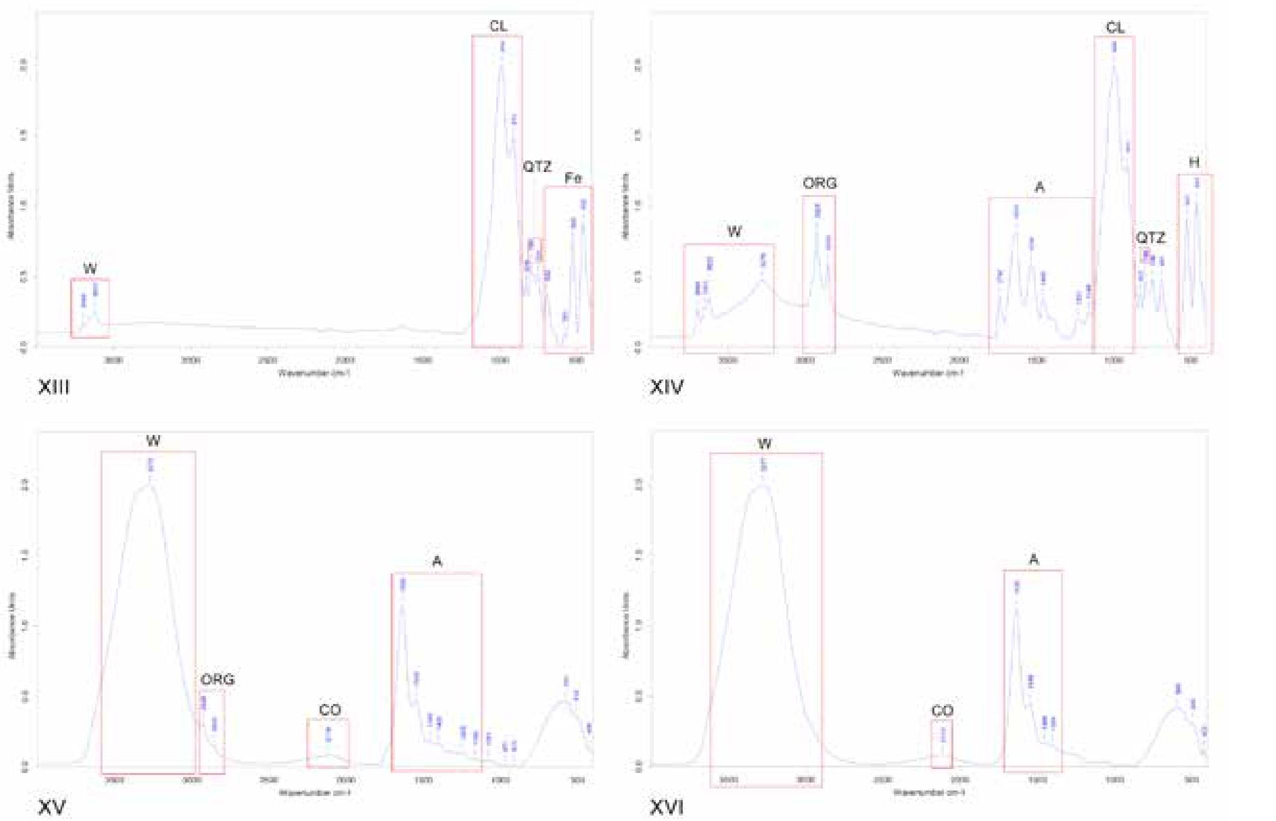

Figure 5. *ATR-FTIR spectra of XIII: phyllite and water; XIV: phyllite and egg yolk; XV: egg white and egg yolk; XVI: egg white.*

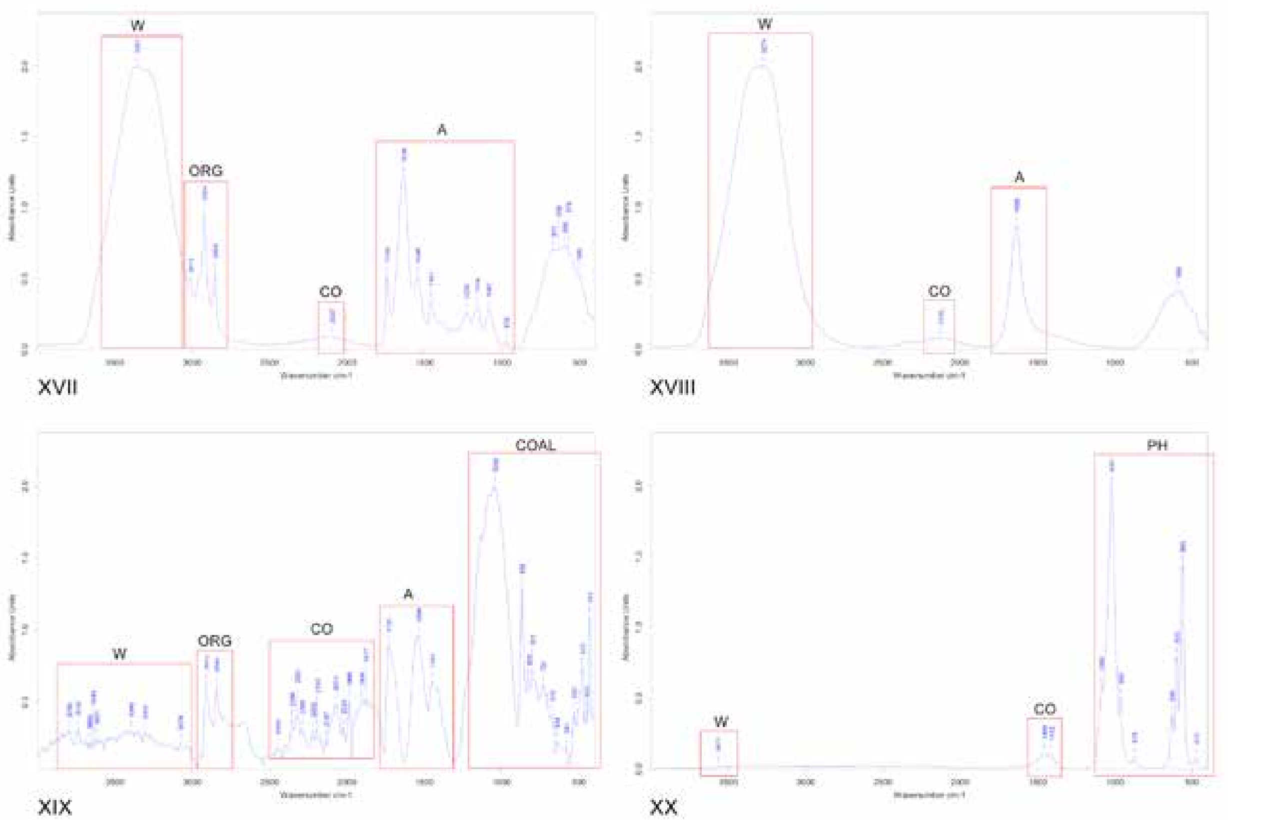

Figure 6. *Spectra of XVII: egg yolk; XVIII:* Opuntia ficus *sap; XIX:* Pinus *charcoal; XX: burned cow bone.*

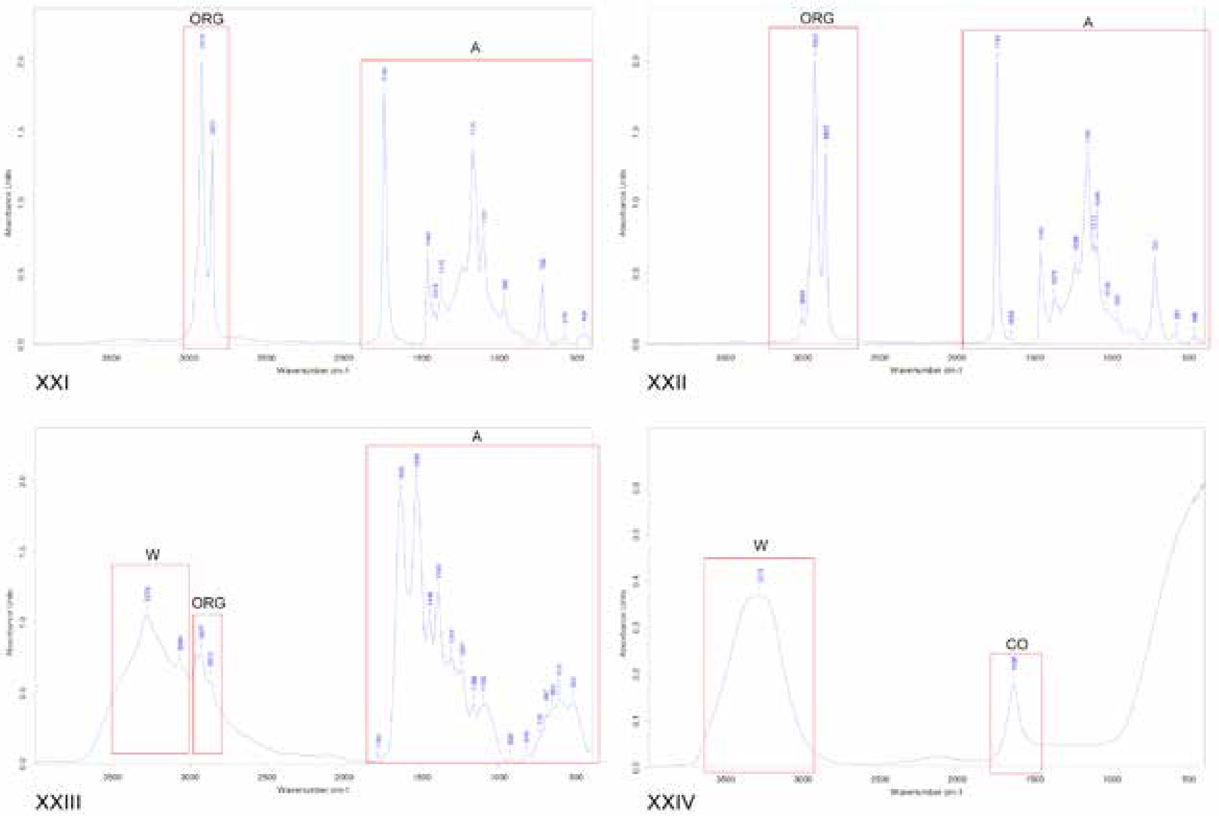

Figure 7. *ATR-FTIR spectra of XXI: cow fat; XXII: olive oil; XXIII: human blood; XIV:* Rubia tinctorium *sap; W: water; ORG: organic; A: starch; CL: clay (kaolinite-type); H: haematite; QTZ: quartz; CO: carbonyl; ORG: organics; Fe: iron; OH: hydroxyl; COAL: black coal; PH: phyllites.*

Results

During the experiment, we noticed that some binders did not associate easily with certain types of rocks and that some pigments mixed better with some binders than with others. The mixture red ochre/vegetable oil, which is a perfectly homogeneous mixture, showed a satisfactory result on the sandstone, contrary to that obtained on the granite. In the same way, the mixture red ochre/water lacked homogeneity but was better controlled and more accepted on the granite than on the sandstone. This allows us to deduce that it is possible that the nature of the rock has influenced the choice of adopted technique.

We noticed the appearance of an outline result of a concentration of the pigments deposited by the two parallel edges of the brush which creates other parallels of a darker red than the median surface, i.e. the inner part of the brush. Hypothesis: the traits resulting from a concentration of pigments on both edges are more time resistant than the pigments of the inner surface which is more vulnerable and fades faster; this can give the illusion of a double outline.

This experiment allowed us to question if different shades of red may be the result of the use of different binders with which they were mixed.

Different shades in pigment rock art can be obtained in many situations, including through preparation and treatment of the pigments (Zuo et al. 1999; Froment et al. 2008). An example is an umber. Raw umber is a light-brown colour; heating raw umber removes water from the mineral, yielding a warmer, darker brown of burnt umber (Barnett et al. 2006; Li et al. 2012). On granite, mixing red ochre with water presented a lighter red than mixing with vegetable oil. When red ochre was heated for four hours at between 500 degrees and 700 degrees, a change of colour was observed from a bright-red to a red-brown due to its oxidation.

Conclusion

The sampled substances analysed by ATR-FTIR contained different red ochres and yellow ochres (heated or not), charcoal, phyllite, clay (kaolinite-type), olive oil, animal fat, cactus sap, egg white and egg yolk, human blood, saliva and other materials.

Through archaeometric study, applying an experimentation approach, it was possible to evaluate the behaviour of organic substances used in the possible production of pre-Historic pigments. The samples of inorganic and organic paint recipes were used to create several ATR-FTIR spectra that will assist in the determination of the various constituents that were used in pre-Historic rock paintings.

Acknowledgements

Sara Garcês benefits from a research fellowship in the Scientific Area of Holocene Archaeology and Rock Art of

Tagus Valley in the scope of the Tomar Polytechnic Institute through the FCT - Foundation for Science and Technology - Funding at the Geosciences Centre of the University of Coimbra (Project UID/Multi/00073/2013). This research was undertaken as part of the strategic program of the Instituto Terra e Memória and the Geosciences Centre of Coimbra University, Portugal, having benefitted from the financial support of FCT-MEC through national funds and, when applicable, co-financed by FEDER in the ambit of the partnership PT2020, through the research project UID/Multi/00073/2013 of the Geosciences Centre. The authors thank Dr Vitor Gaspar from the Laboratory of Physics and Chemistry and X-Ray (Tomar Polytechnic Institute). We are particularly grateful to the three anonymous *RAR* reviewers of our paper for their valuable feedback, which has helped us to re-focus our work.

Dr Sara Garcês
Quaternary and Prehistory Group of Geosciences Centre (u. ID73 – FCT) (CGEO (u. ID73 – FCT)); Earth and Memory Institute, (ITM); Polytechnic Institute of Tomar (Portugal)
saragarces.rockart@gmail.com

Dr Hugo Gomes
Quaternary and Prehistory Group of Geosciences Centre (u. ID73 – FCT) (CGEO [u. ID73 – FCT])

Lydia Haddab
Muséeum National d'Histoire Naturelle (MNHN) – Museum National d'Histoire Naturelle (France)

Pedro Cura
Prehistoric Rock Art Museum and the Sacred Tagus Valley, Mação (Portugal)

Dr Pierluigi Rosina
Polytechnic Institute of Tomar (Portugal); Quaternary and Prehistory Group of Geosciences Centre (u. ID73 – FCT) (CGEO [u. ID73 – FCT])

REFERENCES

Barnett, J. R., S. Miller and E. Pearce 2006. Colour and art: a brief history of pigments. In *Optics and Laser Technology*. *https://doi.org/10.1016/j.optlastec.2005.06.005*.

Bednarik, R. G. 1994. A taphonomy of palaeoart. *Antiquity* 68(258): 68–74.

Bikiaris, D., S. Daniilia, S. Sotiropoulou, O. Katsimbiri, E. Pavlidou, A. P. Moutsatsou and Y. Chryssoulakis 1999. Ochre-differentiation through micro-Raman and micro-FTIR spectroscopies: application on wall paintings at Meteora and Mount Athos, Greece. *Spectrochimica Acta - Part A: Molecular and Biomolecular Spectroscopy* 56(1): 3–18.

Boschín, M. T., A. M. Seldes, M. Maier, R. M. Casamiquela, R. E. Ledesma and G. E. Abad 2002. Análisis de las fracciones inorgánica y orgánica de pinturas rupestres y pastas de sitios arqueológicos de la Patagonia Septentrional Argentina. *Zephyrvs* 55: 183–198.

Brook, G. A., N. V. Franco, A. Cherkinsky, A. Acevedo, D. Fiore, T. R. Pope, R. D. Weimar, N. Gregory, E. A. Hayden and T. T. Salguero 2018. Pigments, binders, and ages of rock art at Viuda Quenzana, Santa Cruz, Patagonia (Argentina). *Journal of Archaeological Science: Reports* 21(January): 47–63.

Cavalcante, L. C. D., M. de F. da Luz, N. Guidon, J. D. Fabris and J. D. Ardisson 2011. Ochres from rituals of prehistoric human funerals at the Toca do Enoque site, Piauí, Brazil. *Hyperfine Interactions* 203(1–3): 39–45.

Cavalcante, L. C. D., J. D. Fabris and M. C. S. M. Lage 2018. Archaeometric analysis of prehistoric rupestrian paintings from the Toca do Estevo III site, Piauí, Brazil. *Journal of Archaeological Science: Reports* 18: 798–803.

Clottes, J. 1993. Paint analyses from several Magdalenian caves in the Ariège region of France. *Journal of Archaeological Science*; *https://doi.org/10.1006/jasc.1993.1015.*

Cole, N. and A. Watchman 1992. Painting with plants. Investigating fibres in Aboriginal rock paintings at Laura north Queensland. *Rock Art Research* 9(1): 27–36.

Darchuk, L., Z. Tsybrii, A. Worobiec, C. Vázquez, O. M. Palacios, E. A. Stefaniak, G. Gatto Rotondo, F. Sizov and R. Van Grieken 2010. Argentinean prehistoric pigments' study by combined SEM/EDX and molecular spectroscopy. *Spectrochimica Acta - Part A: Molecular and Biomolecular Spectroscopy* 75: 1298–1402.

Elias, M., C. Chartier, G. Prévot, H. Garay and C. Vignaud 2006. The colour of ochres explained by their composition. *Materials Science and Engineering: B* 127(1): 70–80.

Froment, F., A. Tournié and P. Colomban 2008. Raman identification of natural red to yellow pigments: ochre and iron-containing ores. *Journal of Raman Spectroscopy* 39(April): 560–568.

Gomes, H., P. Rosina, P. Holakooei, T. Solomon and C. Vaccaro 2013. Identification of pigments used in rock art paintings in Gode Roriso-Ethiopia using micro-Raman spectroscopy. *Journal of Archaeological Science* 40(11): 4073–4082.

Haddab, L. 2017. Contribution à la compréhension des caractéristiques techniques de réalisation des peintures bovidiennes par l'expérimentation. Abris Abaniora et Tahilahi (Tadjlahine -Tassili N'Ajjer- Algérie) et Abris Wan Tissemt et Tan Tifeltassin (Téfedest -Hoggar- Algérie). Unpubl. MA thesis, Muséum National d'Histoire Naturelle.

Hradil, D., T. Grygar, J. Hradilová and P. Bezdička 2003. Clay and iron oxide pigments in the history of painting. *Applied Clay Science* 22(5): 223–236.

Konik, S. and D. Lafon-Pham 2018. Apports de la colorimétrie et de la spectroradiométrie à la caractérisation in situ des peintures paléolithiques de la grotte Chauvet (Ardèche, France). *Comptes Rendus Physique* 19(7): 612–624.

Li R., S. Baker, C. Selvius DeRoo and R. A. Armitage 2012. Characterization of the binders and pigments in the rock paintings of Cueva la Conga, Nicaragua. In *ACS Symposium Series*, Vol. 1103, pp. 75–89; *https://doi.org/10.1021/bk-2012-1103.ch004*.

Lofrumento, C., M. Ricci, L. Bachechi, D. De Feo and E. M. Castellucci 2012. The first spectroscopic analysis of Ethiopian prehistoric rock painting. *Journal of Raman Spectroscopy* 43(6): 809–816.

Lorblanchet, M., M. Labeau, J. L. Vernet, P. Fitte, H. Valladas, H. Cachier et al. 1990a. Etude des pigments des grottes ornees paleolithiques du Quercy. *Bulletin Société Études du Lot* 2: 93–143.

Lorblanchet, M., M. Labeau, J. L. Vernet, P. Fitte, H. Valladas, H. Cachier and M. Arnold 1990b. Palaeolithic pigments in the Quercy, France. *Rock Art Research* 7(1): 4–20.

López-Montalvo, E., C. Roldán, E. Badal, S. Murcia-Mascarós and V. Villaverde 2017. Identification of plant cells in black pigments of prehistoric Spanish Levantine rock art by means of a multi-analytical approach. A new method for social identity materialization using chaîne opératoire. *PLoS ONE* 12(2): 1–27.

Marshall, L. J. R., J. R. Williams, M. J. Almond, S. D. M. Atkinson, S. R. Cook, W. Matthews and J. L. Mortimore 2005. Analysis of ochres from Clearwell Caves: the role of particle size in determining colour. *Spectrochimica Acta - Part A: Molecular and Biomolecular Spectroscopy*; *https://doi.org/10.1016/j.saa.2004.03.041*.

Prinsloo, L. C., A. Tournié, P. Colomban, C. Paris and S. T. Bassett 2013. In search of the optimum Raman/IR signatures of potential ingredients used in San/Bushman rock art paint. *Journal of Archaeological Science*; *https://doi.org/10.1016/j.jas.2013.02.010*.

Rosina, P., H. Gomes, H. Collado, M. Nicoli, L. Volpe and C. Vaccaro 2018. Micro-Raman spectroscopy for the characterization of rock-art pigments from Abrigo del Águila (Badajoz – Spain). *Optics and Laser Technology* 102: 274–281.

Vázquez, C., M. S. Maier, S. D. Parera, H. Yacobaccio and P. Solá 2008. Combining TXRF, FT-IR and GC-MS information for identification of inorganic and organic components in black pigments of rock art from Alero Hornillos 2 (Jujuy, Argentina). *Analytical and Bioanalytical Chemistry* 391: 1381–1387.

Watchman, A. and N. Cole 1993. Accelerator radiocarbon dating of plant-fibre binders in rock paintings from north-eastern Australia. *Antiquity* 67: 355–358.

Zuo J., Xu C., Wang C. and Yushi Z. 1999. Identification of the pigment in painted pottery from the Xishan site by Raman microscopy. *Journal of Raman Spectroscopy*. *https://doi.org/10.1002/(SICI)1097-4555(199912)30:12<1053::AID-JRS473>3.0.CO;2-F*.

RAR 36-1296

Call for papers
for a Special Issue of *Emerging Science Journal* on the subject of
ORIGINS OF HUMAN MODERNITY
Editor: Prof. Robert G. Bednarik

The principal concern of 'emerging science' is to review and chronicle major developments in science that are likely to affect its future course. In the particular field of hominin evolution, we are currently witnessing — as a result of developments in human genetics and correlated changes in archaeological understanding — the demise of an old paradigm and the ascent of a new one. This has significant implications in various fields of enquiry because it reverberates in how we perceive the narratives of who we are and how we became what we are as a species: it is fundamental to understanding ourselves. The new perceptions currently being secured by the contributors of this Special Issue may seem audacious to some in the conservative mainstream, but that has historically always applied to new paradigms and it is what constitutes 'emerging science'.

The purpose of this Special Issue is to bring together the scholars that have contributed — or wish to do so — to the demise of the 'replacement hypothesis' by exposing its flaws, or who have promoted an alternative explanation of 'modern human' origins. This collection of articles is intended to provide guidance to developing a new paradigm in the discipline and to encourage open debate of an issue that has significant effects on how our species perceives itself.

Emerging Science Journal is a non-commercial, well-reviewed Open Access journal with exceptionally low author fees of 40 euros. Please visit the journal's homepage at *https://ijournalse.org/index.php/ESJ*.

Submissions can be sent to *robertbednarik@hotmail.com*
Closing date for papers, max. 8000 words: 31 March 2020
Publication date: 30 September 2020