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Raman study of the brownish-yellow pigment from a Roman Basilica (Dobrogea, Romania – 4th–6th century A.D.)

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Abstract

11 fragments of wall painting from the Beroe fortress, Romania (4^{th} –6^{th} century) were analysed through Raman spectroscopy. The yellow-brown pigment on the fragments is jarosite and/or Na-jarosite. Other than at 445 cm^{-1}, the Raman lines of all the spectra are identical. This Raman line is slightly shifted in different spectra, and this fact proves the presence of both jarosite and Na-jarosite.

Keywords: jarosite, natrojarosite, brownish-yellow pigment, Dobrogea, Beroe, Roman, wall painting, Raman spectroscopy.

Introduction

Jarosite is an ancient and exotic pigment used seldom in the painting of Egyptian and Roman artwork. It is a member of the alunite group, having the formula $\boldsymbol{X}Fe_3(SO_4)_2(OH)_6$. The X is usually a large monovalent cation, such as Na^+ and K^+, but Pb^+, Ag^+, NH_4^+ and H_3O^+ may also be observed. Jarosite is either a weathering product of oxidized iron sulphides under acidic conditions, or a *desert varnish* (Berry, 1999; Kakoulli and Michaelides, 2000). The Raman spectra of jarosite compounds are characterized by five to seven Raman lines assigned to the (SO_4^{2-}) vibrational modes, and four or five Raman bands assigned to the external modes of the Fe–O bonding (Sasaki et al., 1998; Downs, 2006). The fundamental modes of (SO_4^{2-}) appear in the 1168–1091 cm^{-1} (ν_3), 1002–1015 cm^{-1} (ν_1), 623–625 cm^{-1} (ν_4) and 449–455 cm^{-1} (ν_2) wavenumber regions. The Raman lines in the 200–445 cm^{-1} wavenumber region are assigned to the vibrational modes of the Fe–O bonding (Sasaki et al., 1998). One of the Raman bands of the

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Fe–O vibrational modes (the one at cca 440–445 cm^{-1}) is assigned by Frost et al. (2006) to the vibrational modes of $\nu_2(SO_4^{2-})$. The Raman bands of the (ν_3) and (ν_1) vibrational modes are shifted based on the type of the ***X***-position cation (Sasaki et al., 1998).

Jarosite has previously been identified as an ancient Egyptian pigment (Noll, 1978; Colinart, 2001; Middleton and Humphrey, 2001). Schiegl et al. (1992) suggested that the jarosite found in Egyptian contexts was never used as a pigment in its own right, but is rather a degradation product of an iron-rich glass applied as a pigment. Greco–Roman artists used goethite (yellow ochre) as a yellow pigment, and, rarely, jarosite as a yellow or yellow-brown pigment (Kakoulli and Michaelides, 2000; Berry, 1999; Buzgar et al., 2010).

The Beroe archaeological site is located on the bank of the Danube River, 3 km south of the Ostrov village (Dobrogea region, Romania). The first historical reference related to the fortress dates back to the 2nd century A.D., the fortress being inhabited by Romans until the early 7th century.

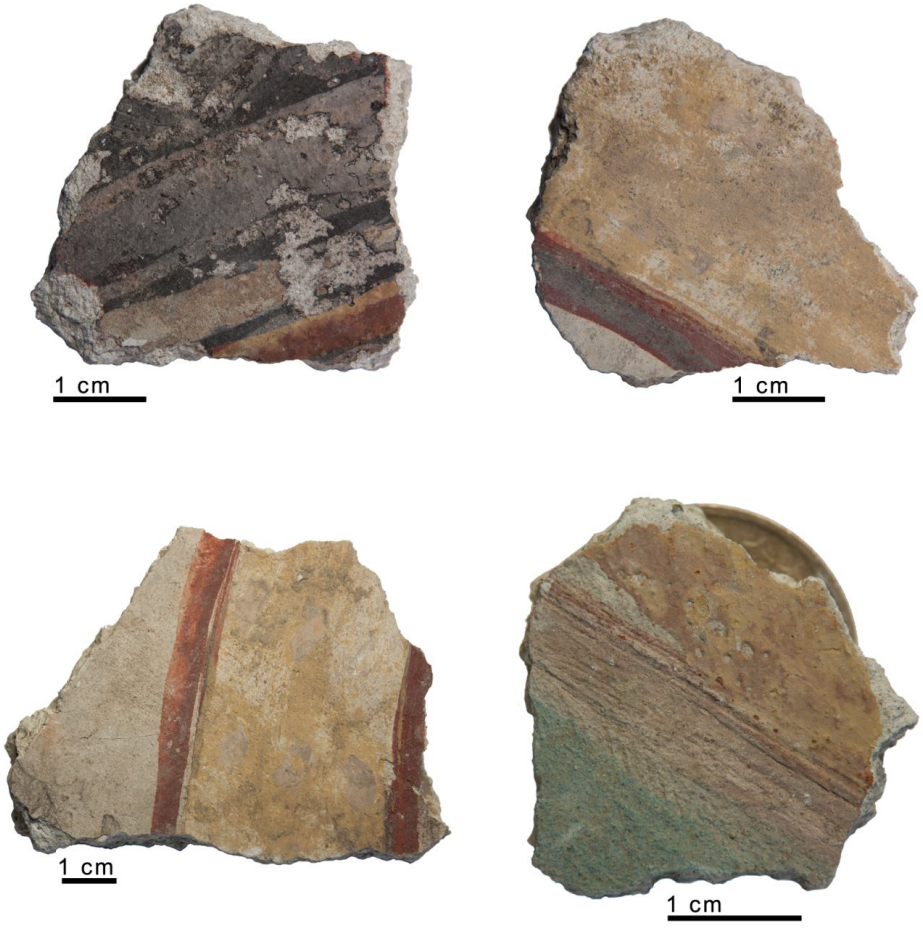

Fig. 1 Four wall painting fragments from a Roman Basilica (Dobrogea, Romania – 4th–6th century A.D.)

The aim of the present paper is to analyse the yellow-brown pigment found on fragments of wall painting, by means of Raman spectroscopy.

Materials and methods

Raman measurements were performed on 11 fragments of wall painting belonging to a Roman basilica (4^{th}–6^{th} century A.D.) discovered at Beroe. Four wall painting fragments are shown in Figure 1. More photos are available on the website of the project *http://rdrs.uaic.ro*.

The Raman spectra were acquired using a Horiba Jobin–Yvon RPA–HE 532 Raman Spectrograph with a multichannel air cooled (–70°C) CCD detector, using a frequency doubled NdYag laser at 532 nm and a nominal power of 100 mW. The spectral range was 200–3400 cm^{-1}, and the spectral resolution – 3 cm^{-1}. The Raman system includes a "Superhead" fibre optic Raman probe for non-contact measurements, with a 50X LWD Olympus visible objective, NA = 0.50, WD = 10.6 mm. Sulphur and cyclohexane bands were used for the calibration of the frequencies of the Raman spectra. The data were acquired through 30–100 acquisitions at a laser magnification of 50–70%, and an exposure of 2–5 seconds. The Raman spectra were processed using the LabSpec 5.25 software (removing background noise, smoothing, values of peaks).

Results and discussions

The Raman spectra of the yellow-brown pigment are illustrated in Figure 2. Corresponding Raman lines appear in all the spectra and present almost matching wavenumbers. The Raman lines were assigned to jarosite compounds, in agreement with Downs (2006). In the 1100–1200 cm^{-1} wavenumber region, two Raman bands appear at 1107 and 1155 cm^{-1}. They are assigned to the vibrational modes of $\nu_3(SO_4^{2-})$. The Raman line at 1010 cm^{-1} is assigned to the vibrational mode of $\nu_1(SO_4^{2-})$. The bending vibrational modes of (SO_4^{2-}) – ν_4 and ν_2 appear at 662 cm^{-1}, and cca 445 cm^{-1}, respectively. In some spectra, the very weak Raman line at 569 cm^{-1} was assigned to the vibration mode of γ(OH), in agreement with the data from the literature (Frost et al., 2006; Downs, 2006; Sasaki et al., 1998).

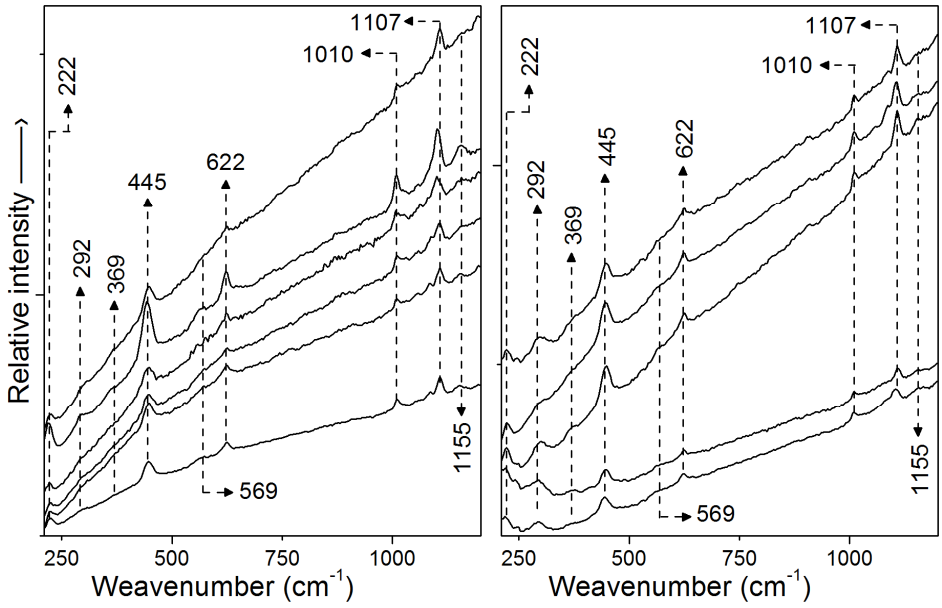

Fig. 2 The Raman spectra of the yellow-brown pigment from 11 wall painting fragments (4^{th}–6^{th} century, Beroe fortress).

The Raman lines in the low wavenumber region were attributed to the vibrational modes of the Fe–O bonding. They appear at 369 and 292 cm^{-1}, but not in all the spectra.

The Raman line at 445 cm^{-1} (ν_4 vibrational mode) is slightly shifted (±5 cm^{-1}), which indicates the different chemical composition of the yellow-brown pigment. Some of the samples are jarosite, while others are Na-jarosite, in good agreement with Downs (2006) and Sasaki et al. (1998).

Conclusions

The yellow-brown pigment used by Roman artists in the painting of the artwork from the Beroe fortress consisted of jarosite compounds. The slight shifting of the Raman line at cca 445 cm^{-1} proves the presence of both jarosite and Na-jarosite. This expensive pigment might have been brought either from Laurion (Greece) or the Sahara desert.

Acknowledgments

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References

Berry, M., 1999. A study of pigments from a Roman Egyptian shrine. AICCM Bulletin, 1–9.

Buzgar, N., Buzatu, A., Apopei, A.I., Cotiuga, V., Topoleanu, F., 2010. Mineral pigments of greco-roman and byzantine ages from Dobrogea. An. Șt. Univ. „Al. I. Cuza" Iași, Geologie, Sp. Iss., GEO IASI – 2010, 13.

Colinart, S., 2001. Analysis of inorganic yellow colour in ancient Egyptian painting. In: Davies, W.V. (Ed.), (2001). Colour and Painting in Ancient Egypt. British Museum Press, London, 1–5.

Downs, R.T., 2006. The RRUFF Project: an integrated study of the chemistry, crystallography, Raman and infrared spectroscopy of minerals. Program and Abstracts of the 19th General Meeting of the International Mineralogical Association in Kobe, Japan.

Frost, R.L., Wills, R-A., Weier, M.L., Martens, W., 2006. A Raman spectroscopic study of selected natural jarosites. Spectrochimica Acta, **63**, 1–8.

Kakoulli, I., Michaelides, D., 2000. Technological Investigation of Monumental Graeco-Roman Tomb Paintings in Cyprus. Proceedings of the 32nd International Symposium of Archaeometry, Mexico City, 15–19.

Middleton, A., Humphrey, S., 2001. Pigments on some Middle Kingdom coffins. In: Davies, W.V. (Ed.), (2001). Colour and Painting in Ancient Egypt. British Museum Press, London, 10–16.

Noll, W., 1978. Mineralogy and technique of ancient Egypt painted ceramics. Neues Jahrbuch, Mineralogie-Abhandlung, **133**, 3, 227–290. (In German).

Sasaki, K., Tanaike, O., Konno, H., 1998. Distinction of jarosite-group compounds by Raman spectroscopy. Canadian Mineralogist, **36**, 1225–1235.

Schiegl, S., Weiner, K.L., El Goresy, A., 1992. The diversity of newly discovered deterioration patterns in ancient Egyptian pigments: consequences to entirely new restoration strategies and to the Egyptological colour symbolism. Proceedings of the Materials Research Society Symposium, **267**, 831–858.

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