



# UNIVERSITÀ DI PARMA

## ARCHIVIO DELLA RICERCA

University of Parma Research Repository

Raman spectroscopy of minerals and mineral pigments in archaeometry

This is the peer reviewed version of the following article:

*Original*

Raman spectroscopy of minerals and mineral pigments in archaeometry / Bersani, Danilo; Lottici, Pier Paolo. - In: JOURNAL OF RAMAN SPECTROSCOPY. - ISSN 0377-0486. - 47:(2016), pp. 499-530. [10.1002/jrs.4914]

*Availability:*

This version is available at: 11381/2805010 since: 2021-10-06T12:04:43Z

*Publisher:*

John Wiley and Sons Ltd

*Published*

DOI:10.1002/jrs.4914

*Terms of use:*

Anyone can freely access the full text of works made available as "Open Access". Works made available

*Publisher copyright*

note finali coverpage

(Article begins on next page)

02 May 2026



**Raman spectroscopy of minerals and mineral pigments in archaeometry**

Journal:	<i>Journal of Raman Spectroscopy</i>
Manuscript ID	JRS-15-0347.R1
Wiley - Manuscript type:	Review
Date Submitted by the Author:	n/a
Complete List of Authors:	Bersani, Danilo; University of Parma, Physics and Earth Sciences; Lottici, Pier Paolo; University, Physics;
Keywords:	Raman spectroscopy, minerals, archaeometry, pigments, ceramics

SCHOLARONE™  
Manuscripts

Review

# Raman spectroscopy of minerals and mineral pigments in archaeometry

D. Bersani and P.P. Lottici

Department of Physics and Earth Sciences, University of Parma, Parco Area delle Scienze 7/A,  
43124 Parma, Italy.

Keywords: Raman spectroscopy, minerals, archaeometry, pigments, ceramics, gems

## Abstract

Minerals, as raw structural materials or pigments, play a fundamental role in archaeometry, for the understanding of nature, structure and status of an artefact or object of interest for Cultural Heritage. A detailed knowledge of the mineral phases is crucial to solve archaeological problems: Raman spectroscopy is a powerful investigation technique and has been applied extensively in the last 30 years on mineral identification and on pigment degradation. Here we report an updated review, covering the last decade, of the applications of Raman techniques to issues in which raw minerals, including mineral pigments, are involved. Particular attention is devoted to cases where the Raman analysis of minerals is deeper than a simple identification of the phases present in an archaeological or artistic object.

## Introduction

The use of Raman spectroscopy for archaeometry applications has quickly grown in the last years, in both micro-Raman and mobile Raman versions of the technique, thanks to the main advantages as the small time required for the measurements, the possibility to study untreated raw material and, especially, the non-invasivity. This tendency is indicated by the increasing number of dedicated conferences, as the International Conference in Application of Raman Spectroscopy in Art and Archaeology (RAA), now arrived at the 8<sup>th</sup> edition: many examples of interesting applications are reported in the RAA conference special issues<sup>[1-3]</sup>. Some good review articles show the progression in the recent years of the state-of-the art of the use of Raman spectroscopy in different fields of archaeometry. We would like to cite only the most relevant for this work: Smith and Clark<sup>[4]</sup>, Smith<sup>[5]</sup>, Smith<sup>[6]</sup>, Fotakis et al.<sup>[7]</sup>, Vandenabeele et al.<sup>[8]</sup>, Bersani and Lottici<sup>[9]</sup>, Clark<sup>[10]</sup>, Colomban<sup>[11]</sup>, Capel Ferron et al.<sup>[12]</sup>, Vandenabeele et al.<sup>[13]</sup>, Madariaga<sup>[14]</sup>.

The possibility to study many different kind of materials, from crystalline to amorphous, organic and inorganic, even when largely heterogeneous, thanks to its micrometric space resolution, made Raman spectroscopy an unique tool for the study of archaeological materials. The complexity of the archaeological findings and the extremely wide range of substances they contain, make a complete analysis very difficult, especially when only non-destructive techniques can be used. For this reason, in many cases the identification of the different organic and inorganic phases is limited to a "raw" identification. In the case of

1  
2  
3 mineral phases, often the identification is at the level of the group (e.g. “feldspar” or “garnet”) or series  
4 (e.g. “nephrite”), because of the difficulty to obtain more detailed identification which is not seen as a  
5 priority. In this paper we would like to show the importance to have a detailed knowledge of the mineral  
6 phases encountered in some archaeological problems, how that knowledge is helpful for archaeometry and  
7 how it can be obtained by Raman spectroscopy.  
8

9 The development of Raman spectroscopy followed two main directions, both useful for applications in  
10 mineralogy and archaeometry: the increase in performance of the micro-Raman systems, especially in  
11 sensitivity, leading to fast Raman mapping machines, and the realization of affordable mobile  
12 spectrometers. Recently, Vandenabeele et al. <sup>[13]</sup> published a complete review about the mobile Raman  
13 instrumentation for applications in the field of archaeometry (and not only). From this overview, it appears  
14 that most mobile tools use as excitation the 785 nm line of a laser diode, considered one of the best  
15 compromises between efficiency and low fluorescence. Some of the instruments use instead the 532 nm  
16 line of a doubled Nd:YAG laser, allowing more efficiency and giving the possibility to explore the high  
17 wavenumber range of Raman spectrum (up to 4000 cm<sup>-1</sup>, including the OH stretching region). Only few  
18 models of mobile Raman spectrometers are up to now exploiting the new InGaAs detectors allowing using  
19 the 1064 nm line of the Nd:YAG laser as excitation. This solution allows to have an IR excitation and  
20 virtually no fluorescence, but with a very low scattering efficiency, due to the high wavelength. Works  
21 based on mobile or micro-Raman instrumentation are considered in this paper.  
22

23 This review, far from being a review of “Raman spectroscopy and pigments in Art and Archaeometry”, aims  
24 to provide a synopsis of recent Raman studies which escaped or which have appeared since the various last  
25 more general reviews carried out on the use of Raman spectroscopy for Art and Archaeometry. In addition,  
26 see the cumulative annual reviewing papers (I to VIII) appeared on Journal of Raman Spectroscopy or, in  
27 particular, the summaries of the works presented at the eight Raman in Art and Archaeometry (RAA)  
28 Congresses (or Conferences) up to that in 2013 in Ljubljana (see ref. [3] and references therein). Roughly,  
29 the last decade will be covered in this work, with some less recent but important or specific references.  
30

### 31 Ceramics and lapidary

32 Raman spectroscopy is largely used in the study of ceramics in their various components: body, paintings  
33 and decorations, ingobes and glazes <sup>[15–41]</sup>. The number of scientific papers about Raman spectroscopy and  
34 pottery is still increasing: a quick survey on Google Scholar shows that in the latest years nearly 300 papers  
35 per year on Raman spectroscopy and archaeological ceramics were published; this number was nearly one  
36 half seven years ago, and nearly one sixth fifteen years ago. In the very last years, some good review  
37 articles appeared, dedicated to the multi-technique characterization of the ceramics materials and more  
38 specifically to the Raman study of enamelled and glazed ceramics <sup>[42] [43]</sup>. Ancient pottery is a heterogeneous  
39 material from the mineralogical and chemical points of view. The minerals present in the body of pottery  
40 can be subdivided in primary phases, present in the raw material or added as tempers, new phases formed  
41 during the firing process, and secondary phases, formed later during the use of ceramics or their burial.  
42 While primary minerals are mostly used to identify the provenance of raw materials, new formed phases  
43 bring information on the firing technology. Finally, secondary minerals are related to the life of the object  
44 and the geological and chemical conditions during the burial. Due to the strong heterogeneity of the  
45 material, Raman spectroscopy is not the best technique to obtain the average composition of a ceramic,  
46 because it's mostly a “point” technique, analysing very small amount of material in each measurement and  
47 because of the large difference in scattering efficiency of the different minerals <sup>[16]</sup>. Nevertheless, especially  
48 when used in combination with different, more averaged, “volume” techniques, such as X-Ray diffraction  
49 (XRD) or neutron diffraction (ND) <sup>[24,25,31,35,40,41,44]</sup>, Raman spectroscopy can give interesting results,  
50 especially on the minor phases, hardly detected with other techniques, in a non-invasive way. For that  
51 reason, the coupling of Raman spectroscopy with optical or electron microscopy and a diffraction technique  
52 is the most typical combination in publications involving Raman study of ceramics. Very often, Fourier-  
53 transform infrared absorption (FTIR) <sup>[26,27,45–48]</sup> and elemental techniques such as scanning electron  
54 microscope coupled with energy dispersive X spectroscopy (SEM-EDXS) <sup>[40,41,49]</sup> or X-ray fluorescence  
55 (XRF) <sup>[24,50,51]</sup> are also present. Sometimes other techniques are present, as LIBS, PIXE, XAS, AAS and ICP-OES.  
56  
57  
58  
59  
60

We notice also the use of combined machines, with different techniques measuring the same spot, as in the case of the study of ceramics by a Raman/SEM-EDS apparatus<sup>[25]</sup>.

#### *Iron oxides*

Between the “minor” mineral phases present in ceramic bodies and decorations, iron oxides are probably the most studied, being responsible of most red-black colorations<sup>[41,52,53]</sup> and largely used to discriminate between annealing in oxidizing or reducing atmosphere. Iron oxides features appear often in pottery Raman spectra, thanks to their strong signal, in particular hematite. The main debated point is about the fact that the spectrum of hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) in archaeological samples is often accompanied by a band at  $\sim 670$  cm<sup>-1</sup>, not present in the Raman spectrum of pure hematite<sup>[54]</sup>. In various papers, this band was used as a marker of the presence of magnetite (Fe<sub>3</sub>O<sub>4</sub>), because it's very similar to magnetite main Raman band<sup>[17,55]</sup>. From a technological point of view, the correct identification of the iron oxide phase is very relevant: the red hematite means oxidizing environment while the black magnetite is obtained under reducing conditions. Different authors<sup>[53,56]</sup> showed that the band at  $\sim 670$  cm<sup>-1</sup> could be present in disordered or impure hematite. If the 670 cm<sup>-1</sup> band is always present together with other hematite bands and never alone, the presence of magnetite should be considered doubtful<sup>[35,57]</sup>. Only when it is found alone and at slightly lower wavenumbers ( $\sim 660$  cm<sup>-1</sup>) the attribution to magnetite can be considered as certain<sup>[41]</sup>. We have also to take into account that the presence in the magnetite structure of different metals (as chromium) usually leads to an increase of the wavenumber of its main band<sup>[58]</sup>. The constant presence of hematite in red ceramics and its strong Raman signal make it a good probe to investigate the thermal and mineralogical history of the ceramic bodies. The shifts, relative amplitudes and broadening of its Raman peaks were studied to differentiate natural hematite from that obtained by heating goethite ( $\alpha$ -FeOOH)<sup>[59]</sup>, to estimate the presence of Al in the hematite structure<sup>[40]</sup>, to evaluate purity, disorder and degree of crystallinity<sup>[26,36]</sup> or also finite-size effects in nano-crystalline hematite<sup>[17]</sup> and to relate them with raw materials provenance and firing conditions of ceramics. The main Raman band of hematite, at 287 cm<sup>-1</sup>, was used to obtain Raman maps in *terra sigillata*, to evidence the slip/body border<sup>[33]</sup>. Raman micro-maps were also obtained using the position and the width of the main Raman band of hematite, relating these parameters to hematite formation temperature. This made it possible to obtain the firing temperature of the different layers of Athenian pottery replicas<sup>[20]</sup>; the results indicated a very complex procedure in the manufacture of the red-black vessels, with two separate firings, each composed by two or three different steps. Different iron oxide phases were also identified in ceramic bodies. In particular, the detection of maghemite ( $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>), which could be seen as an iron-deficient form of magnetite, is helpful to understand the transformation hematite-magnetite in ceramics<sup>[36,40,57,60]</sup>. Rarely, even  $\epsilon$ -Fe<sub>2</sub>O<sub>3</sub> was detected<sup>[40]</sup>.

#### *Titanium oxides and thermometry*

Titanium oxides (anatase, rutile and brookite) are detected by Raman spectroscopy in a very large number of studies on archaeological pottery<sup>[24,26,31,48,55,61,62]</sup>, even when present in small amount, due to their huge Raman signal and their diffusion in many geological environments. This fact gave rise to some debated cases: the Raman spectra obtained on white decorations in many ceramics, coming from different areas and with very different ages<sup>[25,48,63,64]</sup> showed as main Raman feature the strong spectrum of anatase, like it was painted by “titanium white”, which was synthesized only at the beginning of 20<sup>th</sup> c. Elemental analyses revealed in all the cases that the white material was just a Ti-containing clay (Ti content usually lower than 2%). The Raman efficiency of anatase is so large to completely hide the Raman features of the clay minerals. A good review of these and other cases involving interesting white ceramic decorations are reported by Buzgar<sup>[15]</sup>. The couple anatase/rutile (the low-T and high-T polymorphs of TiO<sub>2</sub>, respectively) is often used as a thermometer to evaluate the firing temperature of the ceramics, because the anatase-to-rutile transition temperature is commonly considered to be nearly 650 °C<sup>[35,57]</sup>. Actually, this couple of minerals should be used very carefully as thermometers: some recent works<sup>[55] [65] [18] [66]</sup> have shown that the transformation temperature is largely influenced by many factors, such as chemical environment, association with different mineral phases, size and purity of the starting oxides. We report the case of synthetic undoped anatase which is not transformed into rutile after annealing over 950 °C<sup>[67]</sup>. The presence in potteries of an unusual large amount of brookite, the rarest TiO<sub>2</sub> polymorph, is sometimes seen

1  
2  
3 as an indication of incomplete anatase-to-rutile transformation<sup>[57] [68]</sup>, being considered an intermediate  
4 product. Actually, this cannot be taken as a rule: sometimes brookite is largely present in the raw material.  
5 In addition, the sequence of TiO<sub>2</sub> phases during thermal transformations depends on many different  
6 parameters, including crystal size. In particular, the presence of alkali ions as Na<sup>+</sup> and Ca<sup>2+</sup> stabilizes  
7 the brookite phase<sup>[69–71]</sup>. Raman analysis could however identify other minerals useful for thermometry<sup>[57]</sup>.  
8 Wollastonite, often detected by Raman spectroscopy and present as a new formed phase, can be used as  
9 thermometer<sup>[57]</sup>. Diopside-anorthite-quartz were also used<sup>[33]</sup>: the presence of the feldspar anorthite,  
10 formed starting from near 950 °C, of the pyroxene diopside, formed over 850 °C, and of  $\alpha$ -quartz, stable up  
11 to 1000 °C, defines a range of annealing temperature between 850 and 1000 °C in French sigillata wares. In  
12 a similar way, the couple quartz-crystalobalite is used to asses the temperatures in an higher range<sup>[22]</sup>.  
13 Calcite, easily detected by Raman spectroscopy, indicates a low firing temperature, as it starts to  
14 decompose into CaO and CO<sub>2</sub> around 650 °C and it disappears completely at about 900 °C<sup>[26] [31]</sup>. Many  
15 minerals, easily identified by Raman spectroscopy, including dolomite, diopside, wollastonite and titanium  
16 dioxides were used to define the firing temperature in Lancaster delftware<sup>[69]</sup>. In the same work, an  
17 extensive Raman study of the local rocks allowed to identify the provenance of the raw materials. Shoval et  
18 al.<sup>[72]</sup> applied second-derivative and curve-fitting techniques to distinguish between meta-smectite and  
19 meta-kaolinite in calcareous Iron-Age pottery, estimating the firing temperature. The best definition of the  
20 firing temperature was however obtained by a multi-technique approach, combining the phases detected  
21 by Raman spectroscopy with other phases revealed by complementary techniques<sup>[41]</sup>.  
22  
23

#### 24 *Feldspars*

25 A family of minerals largely present in ceramic bodies are feldspars. These tectosilicates are widespread in  
26 many rocks and geological environments<sup>[73]</sup> and are present in ceramics as part of the raw materials, or  
27 intentionally introduced as flux or also produced during the firing as neo-formation phases<sup>[74]</sup>. Despite the  
28 complexity of the feldspar family, where the members are distinguished not only by the composition but  
29 also by the order degree, different important Raman spectroscopy studies on feldspars are present in  
30 literature<sup>[75,76]</sup>. Many investigators used Raman spectroscopy to characterize feldspar in ceramics<sup>[25,69,77]</sup>  
31 because the correct identification of the right term could allow one to recognize the provenance of the raw  
32 materials or to better understand the firing conditions of the pottery. An important point to consider is that  
33 the correct phase identification (and, in turn, the possible geological origin) depends not only from the  
34 composition, but also from the structural order. This means that the width of the Raman bands is important  
35 as well as their positions<sup>[76]</sup>. The sub-micrometric heterogeneity and the usual strong fluorescence of  
36 archaeological ceramics often results in very noisy Raman spectra, not clean enough to have a precise  
37 identification of the feldspar species; frequently a generic mixed phase (as bitownite) is indicated. It is  
38 noteworthy that different results are obtained in the identification of feldspars when analysing the same  
39 ceramic with different techniques. This is due to an incomplete miscibility between the different members  
40 of the feldspar family, especially considering the most ordered (low-T) terms, leading to micrometric  
41 patterns of finely intergrown laminae with different compositions<sup>[73,78–80]</sup>. Because of this small-scale  
42 heterogeneity, techniques with different space resolution will give different results. In addition, the  
43 dependence on the composition of the position of the Raman peaks is not perfectly reproduced by the  
44 changes in the cell parameters. As an example, when analysing a K-rich albite with diffraction techniques  
45 (ND or XRD), cell parameters typical of plagioclases are obtained, and the feldspar is identified as albite or  
46 anorthite, while by Raman spectroscopy a signature very similar to K-feldspar is obtained, even at low  
47 potassium content (few percent)<sup>[25,75]</sup>. For this reason, for the identification of feldspar in ceramics, the use  
48 of multiple techniques is recommended; the Raman spectroscopy results should carefully compared with  
49 literature, avoiding the simple comparison with automated or generic databases.  
50  
51  
52

53 Lofrumento et al.<sup>[33]</sup> studied the distribution of feldspars in the body, and in particular around the body-  
54 coating boundary, by means of Raman imaging. Even if the spectral resolution was too low to discriminate  
55 between different feldspars, a strong decrease of feldspars content moving from body to coating was  
56 evidenced.  
57  
58  
59  
60

### Rare minerals in bodies

The ability of Raman, especially micro-Raman, spectroscopy to spot and identify minor and rare mineral phases during point-to-point measurements or mappings leads to a detailed knowledge, even if not quantitative, of mineralogy of ceramics. Up to 25 different crystalline phases were found by Raman spectroscopy on ancient ceramics from Macedonia<sup>[36]</sup> including titanite,  $\text{CaTiSiO}_5$ ; hornblende,  $\text{Ca}_2(\text{Mg,Fe,Al})_5(\text{Al,Si})_8\text{O}_{22}(\text{OH})_2$ ; phlogopite,  $(\text{Mg,Fe,Mn})_3\text{Si}_3\text{AlO}_{10}(\text{F,OH})_2$ ; epidote,  $\text{Ca}_2\text{Al}_2(\text{Fe}^{3+},\text{Al})(\text{SiO}_4)(\text{Si}_2\text{O}_7)\text{O}(\text{OH})$ ; barite,  $\text{BaSO}_4$ ; augite,  $(\text{Ca,Mg,Fe})\text{SiO}_3$ ; olivine,  $(\text{Mg,Fe})_2\text{SiO}_4$ ; fayalite,  $\text{Fe}_2\text{SiO}_4$ ; sphalerite,  $(\text{Zn,Fe})\text{S}$ ; spessartine,  $\text{Mn}_3\text{Al}_2(\text{SiO}_4)_3$ ; diopside,  $\text{MgCaSi}_2\text{O}_6$ ; siderite,  $\text{FeCO}_3$  and dolomite,  $\text{CaMg}(\text{CO}_3)_2$  (Fig.1).

### FIGURE 1

The local origin of raw materials was inferred by the 17 minerals found by Raman spectroscopy in bronze-age ceramics by Medeghini et al.<sup>[32]</sup>. In particular, the presence of mineral phases such as zircon and apatite suggests a contribution of granitic-metamorphic rocks while sulphate minerals, such as barite and gypsum, originate from evaporates and olivine from surrounding basic and ultrabasic rocks. The different kinds of porcelain (soft- and hard-paste ceramics) were identified by the peak intensity of the most characteristic minerals<sup>[29][81]</sup>: beta-wollastonite ( $\text{CaSiO}_3$ ) and/or tricalcium phosphate [ $\text{beta-Ca}_3(\text{PO}_4)_2$ ] have strong Raman signals in in soft pastes, whereas mullite ( $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ ) or mullite-like glassy-phase prevail in hard-paste porcelains.

### Pigments and decorations in ceramics

Decorations in ceramics revealed, under Raman investigation, a surprising rich mineralogy in terms of pigments, opacifiers and other crystalline compounds. Not all the crystalline phases found should be called "minerals" *sensu stricto*, due to the lack of the equivalent natural phase. As an example, the purple pigment  $\text{BaCuSi}_2\text{O}_6$ , a new silicate structure type with isolated four-ring tetrahedral and square-planar Cu, synthesized in 1988, was found in ceramics produced 1845 years ago<sup>[33]</sup>. Other unusual minerals detected by Raman as pigments were covellite ( $\text{CuS}$ ), used in decoration of lacquer wares in China during the West Han Dynasty (206 BC–8 AD)<sup>[82]</sup>, ilmenite<sup>[57]</sup> and lapis lazuli, historically used as pigment for paintings, jewels or decorative stones, but not considered as typical pigment for ceramics. Lapis lazuli was found underglaze on an ancient ewer (Iran, 13<sup>th</sup> c.) belonging to the Lajvardina blue glazed ceramics, confirming the ancient use of Lajvard (lapis lazuli) as reported in an old alchemist's treatise of 14<sup>th</sup> c.<sup>[83]</sup>. Lapis lazuli was also found in 13<sup>th</sup> - 14<sup>th</sup> c. ceramics from Apulia (Southern Italy)<sup>[49]</sup> and in 12<sup>th</sup>-13<sup>th</sup> c. enamels coming from Frederick II Castle in Melfi (Southern Italy)<sup>[84]</sup>. Caggiani et al.<sup>[85]</sup> investigated, by means of temperature-dependent Raman measurements and Raman mappings, the enamels from Melfi and natural lazurite and haüyne crystals, in order to evaluate the use as pigment of heated haüyne, a silicate of sodalite group as lazurite, easy to find in the volcanic rocks surrounding Melfi. The use of Raman micro-mapping was fundamental for the understanding of the distribution of S<sup>-</sup> blue chromophores in the crystals. The use of true lapis lazuli, composed of lazurite, and not of local haüyne was confirmed.

Among the white pigments used in ceramics, alumina  $\text{Al}_2\text{O}_3$  was one of the most common. In addition to the weak Raman bands of corundum, located at 379, 417, 644 and 750  $\text{cm}^{-1}$ <sup>[86]</sup>, alumina is often identified, when using the 632.8 nm excitation, by the strong doublet appearing at 1367 and 1397  $\text{cm}^{-1}$ <sup>[48,52]</sup>. It is important to note that this is not a real "Raman identification" because these are very strong photoluminescence bands of  $\text{Cr}^{3+}$  ions, always present in the alumina crystals. Another very common pigment, especially in non-glazed pottery, is carbon black: apart from the many attempts to differentiate the origin of carbon by the D and G carbon bands in the Raman spectra<sup>[87 - 89]</sup>, the presence of the phosphate Raman band (around 960  $\text{cm}^{-1}$ ) typical of apatite helps to distinguish between "bone black" and other kind of carbonaceous materials<sup>[48,90]</sup>. However, this method should be applied very carefully, because the strong and broad carbon bands could hide the peak of a minor phosphate phase. Caggiani and Colombari<sup>[91]</sup> reported a complete discussion on the identification of black ceramic pigments by Raman spectroscopy.

### Crystalline phases in glazes

The ceramic glaze is a silica glassy layer and was successfully characterized by Raman spectroscopy in terms of silica network using the deconvolution method proposed by Colombar's group<sup>[29,92–98]</sup> to obtain a polymerization index, an estimation of the fictive temperature and the amount of modifiers and to distinguish between different kinds of glasses. In addition, many crystalline phases are present in the glazes, as devitrification of recrystallization products, as residues of the raw materials, or migrating from the bulk. Many other crystalline phases were intentionally added in the glaze or underglaze as pigments or opacifiers. The use of minerals and rocks as pigments for glazes and their Raman detection was recently discussed<sup>[99]</sup>.

Raškowska et al.<sup>[36]</sup> found many different crystalline phases in Macedonian ceramic glazes, depending on their color: quartz, feldspars and anatase were found in the white parts while hematite, magnetite, maghemite, rutile, augite and  $\text{CrO}_4$ -based compounds in the brown parts. Colombar<sup>[99]</sup> found many chromophores in porcelain glazes, some of them very unusual: uvarovite, sphene,  $\text{PbUO}_4$ . The resonant Raman spectra obtained with suitable excitation wavelength was useful to detect chromophores present in very low amount.

Miao<sup>[100]</sup> found  $\text{Pb}$ ,  $\text{Sn}$  and  $\text{Sb}$  antimonates in porcelain glazes and enamels. Even if they could not be considered all as true minerals (lacking of a natural equivalent), the correct identification of these crystalline phases by their Raman spectra is fundamental to our understanding of the production technology and the chemical reactions involved. The lead antimonite "Naples Yellow" was found in 12<sup>th</sup>-13<sup>th</sup> c. Byzantine pottery glazes, together with many other compounds, by Kirmizi et al.<sup>[101]</sup>. Viera Ferreira<sup>[102]</sup><sup>[103]</sup> found many rare minerals in 16<sup>th</sup> c. portuguese ceramics glazes: e.g. kentrolite ( $\text{Pb}_2\text{Mn}^{3+}_2\text{O}_2(\text{Si}_2\text{O}_7)$ ), melanotekite ( $\text{Pb}_2\text{Fe}^{3+}_2\text{O}_2\text{Si}_2\text{O}_7$ ), malayaite ( $\text{CaSnO}(\text{SiO}_4)$ ), hausmannite ( $\text{Mn}^{2+}\text{Mn}^{3+}_2\text{O}_4$ ). Malayaite and rammelsbergite  $\text{NiAs}_2$ , were identified in the glazes of Lancaster delftware<sup>[69]</sup>.

#### Mobile Raman and data treatment

Pottery and ceramic fragments are easier to move than other archaeological findings or artworks, as paintings or statues; for this reason, mobile Raman equipments have up to now not been extensively used in studies on ceramics. However, their use is increasing and also in the ceramic field some works are appearing. In addition to the glass signal on the glazes, through portable systems Colombar et al.<sup>[61,62,92,93,104]</sup> were able to detect many minerals phases, useful to distinguish technology and provenance, in ceramic bodies and decorations: quartz, chromite spinels, hematite, calcium phosphate, mullite, dysthene and fluorite. As an example, in Chinese ceramics, the frequent presence in the Raman spectrum of a small peak at around  $322\text{ cm}^{-1}$ , confirmed that the fluorite use as opacifier dates back to the Tang dynasty. Mobile Raman was also used to differentiate between genuine artefacts and copies of Limoges enamels<sup>[105]</sup>.

Data treatment is an important part of the experimental procedures. In the analysis of Raman spectra, especially when dealing with identification of well-defined crystalline phases, the use of statistical methods, as principal component analysis, is not frequent. Rarely, multivariate analysis can be used to distinguish minerals in ceramics or to group and classify ceramics from the identified mineral phases<sup>[106]</sup>. In particular, to discriminate Raman signals of the different ceramic components in case of high fluorescence background, BTEM (Band-target entropy minimization), a self-modeling curve resolution technique, was proposed<sup>[107]</sup>. The resulting pure component spectra show an excellent signal-to-noise ratio.

#### Pietra Ollare

Common use dishes and pots were not only made of true ceramics, sometimes they were made of stones. Raman spectroscopy, coupled with other techniques, was used to characterize archaeological stone objects<sup>[108]</sup>. For wide historical periods, stoneware made of the so called *pietra ollare* (soapstone) was widely diffuse. Pietra ollare is a generic term referring to a metamorphic rock mostly composed of low-hardness silicates with high chemical, thermal and weathering resistance<sup>[109]</sup>. Pietra ollare can be classified in four main groups: chlorite-schists, talc-schists, serpentine-schists and ultrabasites. Provenance studies on pietra ollare pots and millstones<sup>[110,111]</sup> are usually based on standard petrological techniques as thin sections, XRD and SEM-EDS, so involving sampling and invasive techniques. Raman spectroscopy was proven to be effective in the identification of minerals phases (chlorite, chloritoid, talc, garnets, olivine, etc), useful to

1  
2  
3 assess the provenance of the raw materials and the consequent trade routes<sup>[112]</sup>. In the case of chlorite-  
4 schists, the study of the composition of included garnets, made using the Miragem software<sup>[113]</sup>, allowed to  
5 compare their zonation with that reported in literature for the historical quarry of St. Marcel (Aosta Valley,  
6 Italy), identified as provenance locality<sup>[114]</sup>. In the case of medieval talc-schists pot fragments, the  
7 combination between mobile Raman apparatus and laboratory micro-Raman allowed the direct  
8 comparison between the archaeological findings (studied in laboratory) and the stones present in the  
9 quarry identified as possible source (examined *in-situ* by mobile spectrometer)<sup>[112]</sup>. The Raman spectra  
10 showed the presence of the same minerals (mostly talc, chlorite, calcite, magnesite and iron oxides). In  
11 addition, it was possible to precisely identify the olivine phase as a prevalent forsterite in both cases,  
12 thanks to the Mg/Fe ratio obtained by the separation of the characteristic doublet present in the Raman  
13 spectrum<sup>[115]</sup>. This match between the olivine phases was a strong element supporting the provenance  
14 hypothesis of the archaeological fragments. The orientational texture of chlorite was also mapped by using  
15 the micro-Raman apparatus (Fig.2).

## 17 **FIGURE 2.**

### 18 **Gems and gemstones**

20 The use of Raman spectroscopy for the analysis of minerals, including gemstones, started with the origin of  
21 the technique. Raman spectrometers appeared in few gemological laboratories nearly 35 years ago,  
22 especially in France<sup>[116-119]</sup>. Only after the advent of compact micro-Raman instruments, and even more  
23 with the uptake of mobile Raman systems, the use of Raman spectroscopy became common in the analysis  
24 of gemologic material. In the last 15 years, few works tried to point out the main aspects of the applications  
25 of Raman spectroscopy to gemology<sup>[120]</sup>. In particular, some extensive review papers on Raman and  
26 gemology appeared few years ago<sup>[9,121]</sup> even related to forensic aspects<sup>[122]</sup>. A particular review, centered  
27 on mineralogical studies of archaeological gems by means of many techniques, including Raman  
28 spectroscopy, appeared few years ago<sup>[123]</sup>.

29 In this work we would like to update the last reviews, giving a quick overview of the most recent literature  
30 on Raman gem analysis, with particular attention to the works related to cultural heritage and archaeology.  
31 Despite the diffusion of the use of Raman spectroscopy both in mineralogy and in archaeometry, the  
32 number of papers dealing with Raman study of gems related with art or archaeological did not increase as  
33 much as in other fields (e.g. study of ceramics). Actually, most of the Raman analysis of gems is now carried  
34 out in laboratories for routine investigations, and only few of them are part of research projects.

#### 35 *Historical and archaeological gems*

36 Examples of the use of a particular setup of a micro-Raman instrument are given by Karampelas et al.  
37<sup>[124,125]</sup>, investigating the gems mounted in the important artworks (chalices and ciborium) present in the  
38 Benedictine Abbey of Einsiedeln, and by Jeršek and Kramar<sup>[126]</sup> analysing the huge amount of gems (465)  
39 embedded in a baroque chalice, including 24 diamonds, 93 rubies, 4 sapphires, 152 emeralds. UV-visible  
40 fluorescence was used to complement Raman spectroscopy for the identification of synthetic gems used to  
41 substitute original ones: the very strong red fluorescence characteristic of Verneuil type of synthetic rubies  
42<sup>[127]</sup> was detected in some red gems. The majority of recently published investigations on archaeological  
43 gems were performed using mobile equipment, thanks to the diffusion of powerful portable Raman  
44 systems, with sufficient spectral resolution and decreasing costs. This kind of *in-situ* investigation was very  
45 rare up to ten years ago<sup>[128]</sup>. To characterize not only the gems, but even the noble metals in the sceptre of  
46 the Faculty of Science of Charles University in Prague, Petrovà et al.<sup>[129]</sup> combined handheld Raman with  
47 handheld XRF instruments, obtaining a complete in-situ analysis. A large series of mounted gems was  
48 characterized, and in some cases re-attributed, by the sole use of mobile (handheld and portable) Raman  
49 apparatus in the regional museums of Messina<sup>[130]</sup> and Siracusa (Italy)<sup>[131]</sup> (Fig.3).

## 50 **FIGURE 3.**

51 The use of multiple laser lines allowed to evidence the higher number of identifications obtained by a laser  
52 diode at 785 nm, due to a lower fluorescence background, with respect to the other typical line used in  
53  
54  
55  
56  
57  
58  
59  
60

mobile Raman instruments, the 532 nm emission of the doubled Nd:YAG lasers. The latter is however useful when studying Cr<sup>3+</sup> containing gems, as corundum and beryls, in order to avoid the chromium photoluminescence<sup>[86,132]</sup>. The 785 nm line was however successfully used with a mobile spectrometer to clearly identify minerals of the group of beryls (aquamarine, goshenite and heliodor) during the characterization of gemstone beads of the Han Dynasties in Guangxi Province (China)<sup>[133]</sup>. The combined use of portable Raman and portable energy-dispersive X-ray fluorescence spectrometer (pXRF) allowed to obtain important information on provenance and trade of the gemstones, non-destructively and directly *in-situ*.

### *Silica gemstones*

Most of the ancient jewelry is not based on very precious gems, according to a modern point of view; most of the cameos, pendants and small objects were made on various silica-based materials, from siliceous stones (as jaspers), to the micro- and crypto-crystalline varieties of silica (chalcedony), to the chromatic varieties of quartz (amethyst, citrine, etc.). When investigated *in-situ*<sup>[131,134]</sup>, in a non-destructive way, the careful observation of texture and colours, possibly with the help of a microscope, should complement Raman analysis in the description of the material, because Raman spectrum will be very similar in most of the cases, showing mainly the features of quartz. In chalcedony (including agate and carnelian) the presence of minor moganite is expected. Moganite is the monoclinic silica polymorph approved as a new mineral by the IMA in 1999 and identified by its main band at 501 cm<sup>-1</sup><sup>[135–137]</sup>. In some rare case, objects carved in opal CT (cristobalite–tridymite) can be identified by the cristobalite band at 410 cm<sup>-1</sup><sup>[121,137]</sup>. The presence of hematite bands is also expected in some agates and carnelians. A rare use of hematite in gemology, as dyeing agent in the intermediate layer of a triplet simulating a red stone, was also signaled<sup>[138]</sup>. This simulant, as well as enhancement treatments performed on the gems in historic times, were detected by Raman and FTIR spectroscopies in the collections preserved in V&A museum in London. Provenance studies on silica gemstones, largely diffuse and lacking of characterizing elements, are very difficult. Raman spectroscopy was used by Gliozzo et al.<sup>[139]</sup> to complement synchrotron radiation X-ray diffraction (SR-XRD) and proton-induced X-ray emission spectroscopy (PIXE) to obtain a complete non-destructive characterization of the gemstones of the collection from Vigna Barberini (Rome, Italy), including 20 chalcedonies. Capel Ferrón et al.<sup>[140]</sup> published very recently a detailed combined Raman and Rietveld study on a set of prehistoric lithic tools from Spain. In particular they developed, from the Raman spectra of the archaeological objects, after a calibration procedure, a method to obtain the moganite to quartz ratio in a fast and non-destructive way.

### *Gemstones: nature, genesis and provenance*

The majority of the works that **have appeared recently**, especially on measurements obtained with laboratory micro-Raman instruments, are not strictly related to archaeological objects, but mostly devoted to the study of specific gemstones or family of gemstones: sapphires<sup>[86]</sup>, tourmalines<sup>[141]</sup>, emeralds<sup>[132,142–144]</sup>, aquamarine<sup>[145]</sup> and pezzottaite<sup>[146]</sup>, the new Cs-rich red gemstone related to beryls<sup>[147,148]</sup>.

In addition to the simple mineralogical identification of the gems, in jewellery the recognition of fakes (simulants or synthetic gems) and the identification of provenance are the most required information to the analysts<sup>[149]</sup>. Taking advantage of the confocality of the micro-Raman apparatus, it is possible to identify fluid or solid, organic and inorganic inclusions. This is one of the main tools for the study of provenance and to identify synthetic materials<sup>[9]</sup>. A study of organic inclusions in beautiful “watermelon” elbaite tourmalines from Nuristan was recently reported<sup>[141]</sup>. The diffuse presence of hydrogen sulphide (main band at 2610 cm<sup>-1</sup>), methane (2912 cm<sup>-1</sup>), ethane (2950 cm<sup>-1</sup>), propane (2895 cm<sup>-1</sup>) and carbonaceous matter (~1340 and ~1600 cm<sup>-1</sup>) was evidenced by the Raman spectra. This kind of inclusions is typical of natural materials and explained by a model of the graphitization process. The study of mineral inclusions by micro-Raman spectroscopy was recently extended to many different families of minerals used in gemmology. Important examples are yellow scapolites<sup>[150]</sup>, demantoid and topazolite garnets from Madagascar<sup>[151]</sup>, orange spinels<sup>[152]</sup>, tourmalines, peridot and garnets from Vietnam<sup>[153]</sup>, tanzanite<sup>[154]</sup> and chrysoprase from Turkey<sup>[155]</sup>: Raman spectroscopy has become a standard, routine technique for provenance studies. In addition, genetic information can be gathered from the Raman study of inclusions in

gemstones, as in the case of topaz from the miarolitic pegmatites from Ukraina, where the identified inclusions (including beryl, orthoclase, lepidolite, zinnwaldite and monazite) suggest a post-magmatic genesis<sup>[156]</sup>. Going in deeper detail, Noguchi et al.<sup>[157]</sup> used the well-known pressure dependence of Cr<sup>3+</sup> fluorescence in corundum to realize combined micro-Raman and photoluminescence micro-maps to visualize the internal stress fields in an Australian sapphire gemstone around a zircon inclusion. Crystallization pressure and temperature of the host sapphire can be deduced from the internal stress field, helping in the identification of the origin of the gemstone.

Organic gemmological material, as amber, can be fruitfully analysed by Raman spectroscopy, despite frequent fluorescence problems, thanks to the richness of the spectra<sup>[9]</sup>. Over 100 amber jewellery objects from Poland, dated to Iron Age, were studied by Raman spectroscopy complemented by positron annihilation spectroscopy (PAS)<sup>[158]</sup>. In addition to the classical estimation of the geological age from the polymerization degree, obtained by the intensity ratio between the peaks at 1645 and 1449 cm<sup>-1</sup><sup>[159–161]</sup>, the spectral region between 700 and 750 cm<sup>-1</sup> was used to distinguish between Baltic amber (succinite) from Moravian amber (valchovite). In addition, Rao et al.<sup>[162]</sup> from the presence of a Raman peak at 1589 cm<sup>-1</sup>, attributed to an unsaturated resin acid, differentiated colophony from amber and copal. Even the most poor (but very diffuse) gemmological material, as quartz, can be characterized in terms of naturalness and provenance by Raman spectroscopy: Zu et al.<sup>[163]</sup> proposed a method to discriminate between synthetic and natural quartz crystals, based on the linewidth of the main Raman band. Micro-Raman and optical microscopy were used to study mineral inclusions in prehistoric rock-crystal (quartz) artefacts from Lower Silesia (Poland)<sup>[164]</sup>. Anatase, kaolinite, chlorite, hematite and goethite were found allowing to recognize the provenance rocks of the quartz used as raw material.

When analyzing gems with a mobile equipment, the study of inclusions is usually impossible, with the only possible exception of TiO<sub>2</sub>: in a quartz or sapphire crystal full of rutile needles, the rutile main bands may appear even with a millimeter-sized laser spot. Due to the low space resolution of portable systems, it is often very difficult to gather information more than the simple gem identification from in situ measurements. One of the best possibilities to get deeper in the Raman study of the gems, even with mobile equipment, is offered by water. This requires, of course, a suitable wide spectral range, rarely obtained on portable systems, and only with the 532 nm line as excitation. In gems containing water or OH groups, the OH stretching region of the Raman spectra is usually very sensitive to the local environment of hydroxyls, i.e. the presence of different ions and impurities, order and geometry. The analysis of this region is very helpful to obtain information on the genesis of water containing minerals, as beryls, to identify synthetic ones and to made hypothesis on their provenance<sup>[132,142–144]</sup> (Fig.4).

#### FIGURE 4.

##### *Treatments*

The identification of enhancement treatments on the gems, in order to distinguish between “allowed” and “non-allowed” ones, is of great interest in gemmology, because the commercial value of a gem strongly depends on its “naturalness”<sup>[120]</sup><sup>[122]</sup><sup>[9]</sup>. From the beginning of its application to gemmology, Raman spectroscopy was required to help in the identification of gemstone treatments<sup>[165]</sup>. The fight between new treatments and their detection requires a continuous research and use of updated technique. In a recent overview<sup>[166]</sup>, the use of Raman spectroscopy is reported for the detection of treatments in heated black diamonds<sup>[167]</sup>, impregnated turquoise<sup>[168]</sup>, chalcedony simulating opals<sup>[169]</sup> and spinel. In fact, heat treatments in spinels can be detected by Raman spectroscopy, measuring the width of the band at 405 cm<sup>-1</sup><sup>[152]</sup>. The peak broadening, from 10 to 30 cm<sup>-1</sup> after the heating process, is related to the increase of inversion in the spinel structure<sup>[170]</sup>. Recently, the identification by FTIR and Raman spectroscopies of heat-treatments in aquamarine, affecting the 682, 1070 and 3604 cm<sup>-1</sup> bands of beryl, was proposed<sup>[145]</sup>.

##### *Raman Maps*

Raman systems able to perform micro-maps, with a large number of points in a very short time, are becoming largely available. The application in the field of gems, and generally in the mineralogical world,

1  
2  
3 can cover a variety of subjects of great interest<sup>[171]</sup>. However, in the last years the number of publications  
4 including Raman maps in gems was very limited, usually related to the study of residual stress, as in the  
5 previously cited work of Noguchi et al.<sup>[157]</sup> (Fig.5).  
6

#### 7 **FIGURE 5.**

8 Pink diamonds are among the rarest and most valuable gems, yet, the origin of the pink colour is still not  
9 fully understood. High spatial resolution Raman and FTIR mapping were used to study defects and  
10 remaining strain in the diamond structure. Raman spectroscopy allowed identifying and characterizing the  
11 defective zones, with many photo-luminescent defects, where the strain is mostly localized. These regions  
12 are related to the presence of inclusions, used by diamonds to accommodate a large amount of stress in  
13 mantle conditions<sup>[172]</sup>.  
14

#### 15 *Stones used in jewellery: jades*

16 The term jade refers to many different hard green translucent materials used in jewellery. Usually only  
17 jadeitic jades, made by the pyroxene jadeite, and nephritic jades, made by nephrite, a generic term of the  
18 amphibole series tremolite-actinolite, are considered “true” jades<sup>[173]</sup>. But, from commercial and  
19 archaeological point of view, many other rocks or minerals have been sometimes classified as “jades”.  
20 Wang et al.<sup>[174]</sup> performed an extended Raman study on ancient and modern Chinese jades of many  
21 different kinds, comparing classical amphibole jades with serpentine jades, turquoise jades and  
22 cryptocrystalline quartz jades. Great attention was put on the OH stretching region of the Raman spectra,  
23 between 3000 and 4000 cm<sup>-1</sup>, very sensitive to small compositional or structural variations, in all the  
24 investigated mineral families. In fact, even in the oldest works related to jades, the OH stretching was used  
25 to obtain detailed compositional information. In nephritic jades, the number and relative intensities of the  
26 OH stretching peaks, related to the Fe<sup>2+</sup>/(Fe<sup>2+</sup>+Mg) ratio, proved to be an effective method to identify the  
27 composition of a nephrite in the tremolite (Mg-rich term)-actinolite(Fe-rich term) series<sup>[175,176]</sup>. Even in the  
28 serpentine family the position of the OH bands allow to distinguish between the different polymorphs,  
29 obtaining their distribution on micrometric scale by means of Raman mapping of the different OH bands  
30<sup>[177]</sup>. Provenance of serpentine jades was non-destructively studied by the Raman identification of the  
31 inclusions<sup>[178]</sup>: actinolite, chlorite, quartz, magnetite and goethite, typical of metamorphism of ultramafic  
32 rocks, were found. In addition, jade quality was evaluated from the ratio of the Raman bands of serpentine  
33 (antigorite) and inclusions. A handheld Raman spectrometer was used, in a multi-technique campaign, to  
34 study in-situ jade (greenstone) objects in the Mayan site of Palenque, Mexico<sup>[179]</sup>. In addition to prevalent  
35 jadeite objects, many other green minerals were found: omphacite, amazonite, albite, muscovite and  
36 quartz.  
37  
38  
39

#### 40 **Mineral pigments**

41 Colour is extremely important when studying art and archaeological objects. Traces of pigments have been  
42 found in coloured prehistoric figures found in caves and rock shelters and in coloured objects in  
43 archaeological layers, dating at least in the Palaeolithic period. The colour palette used on art objects,  
44 paintings, tools and objects of daily life has been extended from natural (mainly mineral) pigments to  
45 synthetic colours. The identification of the nature of the pigments in archaeological artefacts (or  
46 “archaeomaterials”) allows to gain insight into the provenance, manufacture, use, exchange, alterations  
47 and to solve problems due the alteration of the colours over time, conservation and restoration. It is  
48 fundamental also to allow the reconstruction of ancient objects and paints as they would have appeared in  
49 their original state and can be useful to uncover forgeries.  
50  
51

52 Minerals have played a major role in the use of pigments. Most natural organic molecules cannot be used  
53 as colorants in artworks **because of weathering**: they fade with light, react with other chemicals (oil, resins,  
54 substrates, etc.) of the artwork itself or pollutants. Mineral pigments are usually more stable and are  
55 therefore preferred for artistic techniques, whether it is in mural paintings, oil paintings, or polychromatic  
56 pottery, etc. Natural coloured minerals are known from prehistoric times (red and yellow ochres, black  
57 manganese oxides). Carbon black may also be included when of fossil origin. The chronological use of most  
58  
59  
60

1  
2  
3 pigments has been assessed and certain pigments may be used as a dating criterion for coloured (painted)  
4 artworks.

5  
6 Inorganic (mainly mineral) pigments include hundreds of different types. Often the mineral pigments are  
7 embedded in a matrix. Each pigment is characterized by a particular composition, proportion of mineral  
8 phases and combination of different elements. Minor phases, inclusions, trace elements and specific  
9 graininess (particle morphology), allow in many cases a precise identification of the geographical  
10 provenance (sources) and give information on the manufacturing of particular pigments and on the  
11 pigment trading.

12  
13 Prehistoric painters used earth pigments, soot and charcoal. Ferric oxide monohydrate  $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$  or  $\text{FeOOH}$   
14 (goethite), mixed with silica and clay, is responsible for the yellow colour (yellow ochre). Red ochre may be  
15 produced by heating the yellow ochre to anhydrous ferric oxide  $\text{Fe}_2\text{O}_3$  (hematite) but occurs also naturally.  
16 Blues and greens were not available to prehistoric painters. Malachite and azurite mineral pigments, both  
17 copper carbonates, were used by Egyptians from the Fourth Dynasty. The Egyptians introduced also from  
18 about 4000 BC a synthetic calcium copper silicate, Egyptian blue, whose corresponding (rare) mineral is  
19 cuprorivaite ( $\text{CaCuSi}_4\text{O}_{10}$ ) and the Chinese made the barium based Chinese Blue ( $\text{BaCuSi}_2\text{O}_{10}$ ) and Purple  
20 ( $\text{BaCuSi}_2\text{O}_6$ ).

21  
22 Orpiment, yellow arsenic sulphide ( $\text{As}_2\text{S}_3$ ), was used for bright yellow or gold, and realgar, red arsenic  
23 sulphide ( $\text{As}_4\text{S}_4$ ), for bright reds. Their colours are not permanent and fade on exposure to light. Jarosite,  
24 potassium ferric sulphate hydroxide  $\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$ , was used to produce a pale yellow. The Chinese  
25 developed the red vermilion pigment 2000 years before the Romans by crushing, washing and heating the  
26 mineral cinnabar, or mercuric sulphide  $\text{HgS}$ . A synthetic route was also developed. Greeks created the  
27 white lead pigment (idrocussite  $(2\text{Pb}(\text{CO}_3)_2 \cdot \text{Pb}(\text{OH})_2)$ ) from metallic lead in vinegar. White lead and  
28 cerussite (lead carbonate  $\text{PbCO}_3$ ) remained the most used white pigments until the 19<sup>th</sup> c. Greeks used also  
29 red lead ( $\text{Pb}_3\text{O}_4$ ), found naturally as the mineral minium or synthesized by heating mineral litharge ( $\text{PbO}$ ) in  
30 air. The Romans made use of the pigments developed by the Egyptians and Greeks and of cinnabar mined  
31 in Spain. It was extensively used in wall decorations in the houses (as those found in Pompeii) and it was  
32 still being used in the 19<sup>th</sup> c. Maya Blue, a hybrid organic-inorganic pigment, was invented by pre-  
33 Columbian Mesoamericans.

34  
35 Other mineral pigments were used in medieval and renaissance periods as umbers (earth pigments  
36 containing iron oxides and manganese oxides) and green earths. In addition to azurite, the most important  
37 blue in the Middle Ages (but used from Aegyptian times) was ultramarine, made by grinding the semi-  
38 precious mineral lapis lazuli, a rock containing the mineral lazurite,  $\text{Na}_3\text{Ca}(\text{Al}_3\text{Si}_3\text{O}_{12})\text{S}$ , an aluminosilicate  
39 zeolite with the sodalite structure, imported mainly from Afghanistan. Ultramarine was an extremely  
40 expensive pigment until a synthetic ultramarine was invented in 1826 by Guimet. Malachite and verdigris  
41 (synthetic copper acetate) were used as greens, orpiment and ochres continued to be used for yellow,  
42 together with various forms of synthetic lead containing yellow pigments, known from the antiquity. Smalt,  
43 a blue pigment comprising ground glass containing cobalt, was discovered before the 16<sup>th</sup> c. and was made  
44 by heating quartz, potassium carbonate and cobalt chloride. It was replaced in the 19<sup>th</sup> c. by cobalt blue,  
45 developed in 1802 by Thenard. For much of recorded history, up to the 17-18<sup>th</sup> c., the pigments were  
46 mainly the minerals and the synthetic compounds described above <sup>[180]</sup> <sup>[181]</sup>. Then, large amounts of  
47 chemically synthesised pigments were introduced starting from 19<sup>th</sup> c. <sup>[182]</sup>.

48  
49 Raman spectroscopy technique is a most elegant method for pigment analysis of relevant artistic and  
50 archaeological materials. Pigment investigation is one of the most active research areas in cultural heritage  
51 (archaeometry and analysis of artefacts) using Raman spectroscopy. Many natural mineral pigments can be  
52 distinguished from their synthetic forms by their morphology or by the impurities. The original mineral  
53 components of the colour may be mixed with alteration products that have formed over time. In  
54 archaeometric investigations or on ancient artworks, pure minerals used as pigments, even for short  
55 periods, are continuously suggested: this work aims to review the micro-Raman spectroscopy  
56 contributions, mostly of the last years, both off and on-site, on the identification of mineral pigments,  
57 taking into account, when necessary, related aspects as photo-chemical degradations.  
58  
59  
60

1  
2  
3 This review is primarily targeted at pigments of mineral origin of interest for art, cultural heritage and  
4 archaeometry. In particular, it is devoted to how the micro-Raman spectroscopy studies have helped in  
5 understanding the use of mineral pigments in art history. Some mention has to be made to degradation  
6 products, which often provide other "natural pigments". From the review are almost totally excluded  
7 works done exclusively on pigments of certain synthetic origin, those on modern pigments or dyes of  
8 organic nature (unless involved with minerals in hybrids like indigo in Maya Blue) and those that  
9 characterize the colour in ceramics, glass and mosaics, coloured gems or minerals inside gems, which are  
10 the subject of the first part of this review. Therefore, SERS application are excluded.

11  
12 Always in the scheme of a review on Raman spectroscopy "and" mineral pigments, the emphasis is put on  
13 reported unusual or rare pigments and on the open issues relating to the difficult discrimination between  
14 intentionally used mineral pigments – intentionally used synthetic mineral pigments - mineral pigments of  
15 degradation origin. Some common mineral pigments will be excluded, in particular the white pigments and  
16 the well-known "anatase" issue.

17  
18 In the following, we list some recent applications of Raman spectroscopy to identify the pigments, when  
19 pigments of mineral origin are involved, even marginally, on different artworks. If any, the comments  
20 report particular results or issues.

### 21 *Prehistoric pigments*

22  
23 Palaeolithic rock art paintings are often found in excellent condition. Palaeolithic artists used mainly red,  
24 yellow, and black colours. The most common mineral pigments found in rock art are earths (red-yellow  
25 ochres) or manganese oxyhydroxides (black pigments). Ochre is coloured earth, composed of a mixture of  
26 clays, quartz, and iron oxides or oxy-hydroxides, such as hematite or goethite. Hematite is a widespread red  
27 pigment for rock paintings, in natural or synthetic form, when obtained from goethite by firing. Raman  
28 spectroscopy seems not effective in distinguishing between natural hematite and hematite produced by  
29 heating goethite.

30  
31 A large number (~30) of different mineralogical varieties of black manganese oxides/hydroxides exist and  
32 their identification through Raman spectroscopy is difficult and thermal laser induced transformations are  
33 possible.

34  
35 The prehistoric rock paintings have attracted a large amount of Raman investigations. Here we report only  
36 on some of the most recent works, starting from year 2008. The first Raman spectroscopic study of San  
37 rock art in the Ukhahlamba Drakensberg Park, South Africa, was reported by Prinsloo et al. [183]. According  
38 to a study by Hernanz et al. [184], hematite,  $\alpha\text{-Fe}_2\text{O}_3$ , with different granularities, was the pigment generally  
39 used in the pictographs from open-air rock shelters at the Sierra de las Cuerdas (Cuenca, Spain). Calcined  
40 bones and a mineral cement with alpha quartz, anatase, muscovite and illite have been found in the white  
41 pigment. Charcoal particles suggested a previous sketch of the pictograph. Similar conclusions were  
42 reported by Hernanz et al. [185] on Prehistoric rock paintings from the Hoz de Vicente, Minglanilla, Cuenca,  
43 Spain.

44  
45 Darchuk et al. [186] investigated on pigment samples from the Carriqueo rock shelter (Rio Negro Province,  
46 Argentina) by SEM-EDX, FTIR and Raman spectroscopy. The basic components were determined as yellow  
47 or red ochres. A green-grey pigment was recognized as celadonite, through FTIR and elemental SEM/EDS  
48 analysis. Gialanella et al. [187] explored red-ochre samples from the Palaeolithic site of Riparo Dalmeri, a  
49 rock-shelter in northeastern Italy, dated to 13 000 cal BP. According to the authors, a low level of chemical  
50 impurities can be inferred by the low intensity of the "disorder induced" hematite band at about  $660\text{ cm}^{-1}$   
51 [54]. The hematite pigment was probably obtained from the thermal treatment of goethite, available in the  
52 neighborhood of the site.

53  
54 In situ non-destructive analysis on prehistoric drawings with portable instruments was made on rock  
55 paintings in the Rouffignac-Saint-Cernin and Villars caves (Dordogne, France) by Lahlil et al. [188] and Beck et  
56 al. [189], confirming the use of mixtures of manganese oxides (romanachite and pyrolusite). De Faria et al.  
57 [190] experimented Raman spectroscopy on rock art paintings from Abrigo do Janelão (Minas Gerais, Brazil)  
58 and identified white pigment as calcite ( $\text{CaCO}_3$ ), charcoal as black and goethite ( $\alpha\text{-FeOOH}$ ) in yellow and  
59  
60

1  
2  
3 hematite ( $\alpha\text{-Fe}_2\text{O}_3$ ) in red ochres. Whewellite ( $\text{CaC}_2\text{O}_4\cdot\text{H}_2\text{O}$ ) and weddellite ( $\text{CaC}_2\text{O}_4\cdot 2\text{H}_2\text{O}$ ) were detected,  
4 common degradation products of microbiological activity.

5 Tournié et al. <sup>[191]</sup> reported new in situ results on San rock art in South Africa, whereas Lofrumento et al. <sup>[192]</sup>  
6 analysed Ethiopian prehistoric rock paintings, revealing celadonite as green pigment. Darchuk et al. <sup>[193]</sup>  
7 found red and yellow ochres in rock-painting pigments from Egypt (Gilf Kebia area) and claimed also the  
8 presence of rutile. Jezequel et al. <sup>[194]</sup> investigated by Raman, X-ray diffraction, ICP/MS and analytical TEM  
9 some paintings from the Magdalenian age in the Grottes de la Garenne (Saint-Marcel, Indre, France) and  
10 objects found on the floor, that could have been used as “crayons”. Hematite, clays, carbon matter and  
11 carbonates were found in the red pigments and in some crayons. Black pigment was obtained by  
12 cryptomelane, pyrolusite, clays, carbonates and carbon matter: an allochthonous origin is suggested.

13  
14 Erdogu and Ulubey <sup>[195]</sup> studied the red ochre (mainly hematite) and its symbolic use in Chalcolithic West  
15 Mound at Çatalhöyük (Turkey). Bonneau et al. <sup>[196]</sup> made a detailed investigation of the painting layers in a  
16 painted rock shelter in the Drakensberg Mountains of the Eastern Cape Province, South Africa, evidencing,  
17 on a complex substrate, carbon black and mixtures of red ochres with very fine texture. In a further work,  
18 Bonneau et al. <sup>[197]</sup> found gypsum, calcite and white clay for white paints in four rock art sites in the  
19 Phuthiatsana Valley in Lesotho. Martin-Sanchez et al. <sup>[198]</sup> attempted by SERS the study of black stains in  
20 Lascaux Cave, France, identifying their organic origin, while Hernanz et al. <sup>[199]</sup> <sup>[200]</sup> applied Raman  
21 spectroscopy to palaeolithic rock paintings from the Tito Bustillo and El Buxu Caves in Asturias, Spain, and  
22 in other sites, reporting the main contribution of hematite and revealing hydroxyapatite and wustite (by a  
23 Raman peak at  $643\text{ cm}^{-1}$ ) (Fig.6).

#### 24 **FIGURE 6.**

25  
26 Other research groups experimented Raman spectroscopy on the nature of the ochres and the presence of  
27 binders in the rock-shelter paintings at world-heritage site of Bhimbetka (India) <sup>[201]</sup>, in the Minateda rock  
28 shelters (Albacete) and other post-palaeolithic drawings of the Mediterranean Basin in Spain <sup>[202]</sup>, in the  
29 palaeolithic rock paintings in the La Pena cave in Asturias, Spain <sup>[203]</sup> and in the post-Palaeolithic blackish  
30 pictographs of Los Chaparros site (Albalate del Arzobispo, Teruel Province, Spain) <sup>[204]</sup>. A detailed analysis on  
31 the nature and production techniques of the red ochres was made by Gomes et al. <sup>[205]</sup> in a study of the  
32 Pego da Rainha and Lapa dos Coelhos rock-shelters in Portugal and in La Calderita in Badajoz and Frizo del  
33 Terror (Monfrague National Park) in Cáceres, Spain. Dayet et al. <sup>[206]</sup>, using also Raman data, performed an  
34 extensive study of ochre procurement, processing and use over a long sequence related to Middle Stone  
35 Age site of Diepkloof Rock Shelter (Western Cape Province, South Africa). The same group <sup>[207]</sup> carried out a  
36 detailed multi-technique analysis of pigment use and their provenance in three Châtelperronian sites Roc-  
37 de-Combe (Lot), Le Basté and Bidart (Pyrénées Atlantiques).

38  
39 Iriarte et al. <sup>[208]</sup> investigated pictographs, including an unusual bichrome figure, discovered in the Abrigo  
40 Remacha (Villaseca, Segovia, Spain). They found hematite as the most abundant component in the samples  
41 of red pigment and asserted that a bluish black pigment was made with amorphous carbon from charcoal  
42 or soot and paracoquimbite  $\text{Fe}_2(\text{SO}_4)_3\cdot 9\text{H}_2\text{O}$  (characterized by a very strong Raman band at  $1027\text{ cm}^{-1}$ ). This  
43 iron sulphate was also identified in fresco paintings on the walls of a Pompeian house <sup>[209]</sup>: a decaying  
44 process of hematite caused by atmospheric  $\text{SO}_2$  pollutant seems plausible (Fig.7).

#### 45 **FIGURE 7.**

46  
47 Gomes et al. <sup>[210]</sup> analysed painting materials from the Gode Roriso rock shelter, Ethiopia. They hypothesize  
48 white beeswax as white “pigment” and carbon black without phosphates. The spectra of a red pigment  
49 suggest a mixture of hematite and magnetite, through the debated Raman band at about  $660\text{ cm}^{-1}$  <sup>[54]</sup>. A  
50 thermal origin for hematite is claimed, contrary to Gialanella et al. <sup>[187]</sup> hypothesis.

51  
52 López-Montalvo et al. <sup>[211]</sup> identified carbon-based black pigments in the Cova Remigia shelters in the  
53 Valltorta-Gassulla area (Castellon, Spain), example of Spanish Levantine Rock Art, opening the possibility of  
54 radiocarbon dating, whereas Bonjean et al. <sup>[212]</sup> reported in Scladina Cave (Andenne, Belgium) for the first  
55 time a type of black pigment collected by Neandertals around 40.000-37.000 BP that is not a manganese  
56 oxide, but carbonaceous material.

1  
2  
3 Darchuk et al. <sup>[213]</sup> reported on prehistoric pigments from excavations and on coloured child bones from  
4 North Patagonia, Argentina. Excavated pigments show red or yellow ochres (containing minerals as  $\alpha$ - and  
5  $\gamma$ -FeOOH, hematite, erdite and haapalaite sulfosalts, and jarosite), probably used for burial ceremonies.  
6 Pigments covering human bones were identified as hematite and magnetite. Rogerio-Candelera et al. <sup>[214]</sup>  
7 investigated on red pigments spread over a single inhumation in a monumental Megalithic tomb  
8 surrounding Valencina de la Concepción, a Copper Age settlement. Cinnabar, mixed with small amounts of  
9 iron oxides was diffusely found: its provenance and use for funerary purposes are discussed.  
10

11 The ochre associated with the human burial of Magdalenian age in El Mirón Cave (Ramales de la Victoria,  
12 Cantabria, Spain) was analysed by Seva Román et al. <sup>[215]</sup> and found to be a special ochre with unique  
13 features (deep red colour, brightness and particle size distribution), identified as hematite with idiomorphic  
14 crystallinity.  
15

16 Perforated and pigment-stained marine shells from two sites of the Iberian Neandertal-associated Middle  
17 Palaeolithic, dated approximately 50.000 years ago, were analysed by Zilhão et al. <sup>[216]</sup>. Raman spectroscopy  
18 helped to identify the most important pigments as iron compounds (lepidocrocite  $\gamma$ -FeOOH, goethite,  
19 hematite and pyrite). On the other hand, Henshilwood et al. <sup>[217]</sup> investigated a liquefied ochre-rich mixture,  
20 stored in two *Haliotis midae* (abalone) shells dating back to 100.000 years ago, found during excavations at  
21 Blombos Cave, South Africa: they hypothesized a particular production process for this pigment.  
22

23 Villa et al. <sup>[218]</sup> recently reported on a case of a paint, preserved as a mineral and organic residue on the  
24 working edge of a stone flake from a Middle Stone Age (MSA) layer of Sibudu (South Africa), dated 49.000  
25 years ago. Gas chromatography/mass spectrometry (GC/MS), proteomic and SEM/EDS analyses indicate a  
26 mixture of ochre and casein from bovid milk. The powdered pigment mixed with milk is a paint medium  
27 that could have been applied to a surface or to human skin.  
28

29 Rousaki et al. <sup>[219]</sup> investigated 30 samples of different nature (rock art fragments, grinding tools, shells, raw  
30 pigment material, as well as painted ceramics and beads) from the archaeological excavation of two  
31 hunter-gatherer regions in Northern Patagonia (Traful Lake and Manso River areas). Micro-Raman analyses  
32 revealed mostly the use of red ochre (as always, not pure hematite ( $\text{Fe}_2\text{O}_3$ )). A comprehensive discussion on  
33 the origin of hematite (natural or by heating goethite) and on iron oxide phases is given: carbon black,  
34 anatase,  $\text{Mn}_3\text{O}_4$  is observed in some samples. Di Lernia et al. <sup>[220]</sup> analysed pigments and coloured residues  
35 from the Early-Middle Holocene site of Takarkori (SW Libya) and found jarosite and kaolinite, in addition to  
36 hematite and goethite. A recent work by Huntley et al. <sup>[221]</sup> on "mulberry rock art" reports at least two  
37 distinct mineral mulberry pigments, jarosite  $\text{KFe}_3(\text{OH})_6(\text{SO}_4)_2$  and hematite, on the basis of elemental  
38 analysis (SEM-EDXA and pXRF). No Raman analysis has yet been reported.  
39

#### 40 Manuscripts

41 The first application of the micro-Raman spectroscopy to cultural heritage material was on manuscripts <sup>[222]</sup>  
42 <sup>[223]</sup>. Extensive reviews on the application of Raman spectroscopy on pigments in manuscripts were  
43 published by Brown et al. <sup>[224]</sup> and Clarke <sup>[225]</sup>, on Anglo-Saxon illuminated manuscripts, and by Clark <sup>[226]</sup> and  
44 recently by Clarke <sup>[227]</sup>. Vandenabeele et al. <sup>[8]</sup> also detailed a review on the applications on manuscripts up  
45 to 2006. We give only the most important references, starting from 2005/2006, with some comments.  
46

47 A survey on the investigation on illuminated manuscripts appeared in 2012 by Pessanha et al. <sup>[228]</sup> and in  
48 2013 by Orna <sup>[229]</sup>. Chaplin et al. <sup>[230]</sup>, after the study on Gutenberg Bibles <sup>[231]</sup>, analysed astronomical and  
49 cartographic folios from an Islamic 13<sup>th</sup> c. book and found orpiment. A study of medieval illuminated  
50 manuscripts by means of portable Raman equipment was performed by Bersani et al. <sup>[232]</sup>; a 9<sup>th</sup> c. Italian  
51 manuscript containing the Homilies on the Gospels of Gregory the Great, now in Vercelli, was studied by  
52 Aceto et al. <sup>[233]</sup> and the Book of Kells by Bioletti et al. <sup>[234]</sup>. In all cases typical pigments were detected.  
53

54 Worth of mention are several other investigations using additional techniques <sup>[235-239]</sup>.  
55

56 Iron oxides in admixture with azurite were revealed on Medieval and Renaissance Italian Manuscript  
57 Cuttings by Burgio et al. <sup>[240]</sup>. Daniilia and Andrikopoulos <sup>[241]</sup> investigated two full-page Byzantine  
58 miniatures and found lapis lazuli, cinnabar, orpiment, yellow ochre, hematite, green earth, carbon black  
59  
60

and lead white. A deliberate use of pyrite and of black metallic bismuth as pigment is reported by Burgio et al.<sup>[242]</sup> in a study of Bourdichon miniatures.

Duran et al.<sup>[243]</sup> detected a forgery on an Arabic illuminated manuscript while Deneckere et al.<sup>[244]</sup> tried to identify the pigments in the 12<sup>th</sup> c. manuscript Liber Floridus or in three full-page miniatures from the Arnold of Egmond Breviary<sup>[245]</sup>. Two Byzantine 6<sup>th</sup> c. manuscripts known as Vienna Dioskurides and Vienna Genesis, held in the Austrian National Library at Vienna, were analysed by Aceto et al.<sup>[246]</sup>. The palettes are very rich: in addition to vergaut (indigo+orpiment), ultramarine blue is detected at least three centuries before its use in Western manuscripts.

Medieval Cistercian 12–13<sup>th</sup> c. manuscripts in Santa Maria de Alcobaça, Portugal, were explored by Muralha et al.<sup>[247]</sup>. The same group<sup>[248]</sup> identified the pigments on 16–17<sup>th</sup> c. Persian manuscripts: lazurite, red lead, vermilion, orpiment, a carbon-based black, lead white, malachite, hematite, indigo, carmine and pararealgar and mixtures of indigo and orpiment and indigo and vermilion.

Aceto et al.<sup>[249]</sup> proposed in 2012 an analytical protocol for miniature paintings. Rasmussen et al.<sup>[250]</sup> examined the constituents of the ink from a Qumran inkwell to get insight into the ink on the Dead Sea Scrolls and El Bakkali et al.<sup>[251]</sup> proposed a multi-technical non-invasive approach for the typology of inks, dyes and pigments in two 19<sup>th</sup> c. ancient Moroccan manuscripts. The Nastova's group in Macedonia investigated medieval old-Slavonic<sup>[252]</sup> <sup>[253]</sup>, Byzantine and post-Byzantine manuscripts<sup>[254]</sup> and Islamic illuminated manuscripts (16–18<sup>th</sup> c.)<sup>[255]</sup>, where a rich palette was identified: vermilion, red lead, lazurite, realgar/pararealgar, orpiment, malachite and its degradation products, atacamite and brochantite. In the illuminated mediaeval manuscript De Civitate Dei, Lauwers et al.<sup>[256]</sup> identified mosaic gold (i.e. tin(IV) sulphide SnS<sub>2</sub>): in mediaeval manuscripts the use of mosaic gold is rather rare.

Recently the list was increased by: an illuminated Manueline foral charter (LeGac et al.<sup>[257]</sup>), a 16<sup>th</sup> c. printed Book "Osorio" with colourful fore-edge Miniatures (Lukačević, et al.<sup>[258]</sup>), the Manueline foral charter of Sintra (Manso et al.<sup>[259]</sup>), a rare Old Slavic manuscript (Kostadinovska et al.<sup>[260]</sup>), a royal 15<sup>th</sup> c. illuminated parchment (Duran et al.<sup>[261]</sup>), a 15<sup>th</sup> c. manuscript (Zoleo et al.<sup>[262]</sup>), the Manuscript of The Gospel of Jesus's Wife (Yardley and Hagadorn<sup>[263]</sup>) and the pre-Hispanic Maya "Madrid Codex" (Buti et al.<sup>[264]</sup>).

### Paintings

As recalled before, different reviews, including the comments to the RAA Conferences up to 2013 (see Ref. [3] and references therein) describe the application of Raman spectroscopy to artworks. Paintings, icons, miniatures, polychromies, coffins, mummies etc. have been largely investigated.

Pigments from dynastic Egyptian funerary artefacts were considered by Edwards et al.<sup>[265]</sup>. A Raman spectroscopic study on a crucifix (15<sup>th</sup> c.) now in the National Museum in Gdansk, Poland, was performed by Kaminska et al.<sup>[266]</sup>; Correia et al.<sup>[267]</sup> <sup>[268]</sup> explored accurately 23 paintings by Henrique Pousao, a 19<sup>th</sup> c. Portuguese painter, belonging to the collection of Museo Nacional Soares dos Reis, Porto, Portugal. The Brécy Tondo, supposed an artwork by Raphael, was analysed by Edwards and Benoy<sup>[269]</sup> and a complete investigation on the technique of El Greco was reported by Daniilia et al.<sup>[270]</sup>.

Other artworks examined include a 16<sup>th</sup> c. painting Portrait of a Youth (Lau et al.<sup>[271]</sup>), a 13<sup>th</sup> c. panel painting (Van der Werf et al.<sup>[272]</sup>) and South-Asian Shaman paintings (Vandenabeele et al.<sup>[273]</sup>). The Raman analyses helped to identify bassanite and anhydrite as degradation products in 16<sup>th</sup> c. Portuguese oil paintings (Benquerenca et al.<sup>[274]</sup>) and Egyptian blue in a painting by Giovanni Battista Benvenuto from 1524 (Bredal-Jørgensen et al.<sup>[275]</sup>).

The pigments were identified in a 5<sup>th</sup> c. Chinese lacquer painting screen (Tao Li et al.<sup>[276]</sup>), in 16<sup>th</sup> c. Chinese folding screens (Pessanha et al.<sup>[277]</sup>), on a folding screen of the Momoyama period (Pessanha et al.<sup>[278]</sup>), in Murillo's paintings (Duran et al.<sup>[279]</sup>) and in 17<sup>th</sup> c. Indian miniatures by Ravindran et al.<sup>[280]</sup>. Odlyha et al.<sup>[281]</sup> described the alteration of selected pigments in paintings, Marchettini et al.<sup>[282]</sup> studied the pigments palette of 'Adorazione dei Magi', a wooden panel painted by Bartolo di Fredi of the second half of 14<sup>th</sup> c. Mancini et al.<sup>[283]</sup> analysed six French miniature portraits on ivory and paper and demonstrated that the pigments could be identified without removing the glass protection.

Raman was experimented also on a portrait and a paint box of a Turkish artist (Akyuz et al. [284]), on the ground layer of "St. Anthony from Padua" 19<sup>th</sup> c. oil painting (Vančo et al. [285]) and on 17<sup>th</sup> c. panel painting 'Servilius Appius' by Isaac van den Blocke (Pięta et al. [286]).

Gutiérrez-Neira et al. [287] made a careful investigation on Diego Velázquez paintings and found a reduced set of pigments. They supposed a laser induced transformation from hematite to magnetite (the debated well known Raman peak at ~660 cm<sup>-1</sup>) and distinguished between cerussite PbCO<sub>3</sub> and hydrocerussite PbCO<sub>3</sub>·Pb(OH)<sub>2</sub> by the hydrocerussite weak band at 828 cm<sup>-1</sup>.

Van de Voorde et al. [288] reported on a study of "Mad Meg" by Pieter Bruegel the Elder and evidenced an "economic" smalt pigment (SiO<sub>2</sub>+K<sub>2</sub>O+CoO+Al<sub>2</sub>O<sub>3</sub>) for the blue colour. A painting of the colonial art in the church of San Pedro Telmo in Buenos Aires was examined by Marte et al. [289].

Other recent investigations on paintings include: a 17<sup>th</sup> c. Japanese painting (Quattrini et al. [290]), altarpieces and painting workshops of 15<sup>th</sup> and 16<sup>th</sup> centuries from Viseu, Coimbra, Lisboa, and Évora (Antunes et al. [291]). Edwards et al. [292] found chrome yellow, synthesized in 1809, in limited zones of "The Malatesta" painting, most probably due to a 19<sup>th</sup> c. retouching.

17<sup>th</sup> c. gilded miniature portraits on copper were investigated by Veiga et al. [293]. Zmuda-Trzebiatowska et al. [294] reported a study of the yellow and ochre paints of J. Matejko. Two world-famous 17<sup>th</sup> c. panel paintings of the Gdansk School of Painting were examined by Pięta et al. [286] [295] and a characterization of a canvas painting by the Serbian artist Milo Milunović was presented by Damjanović et al. [296].

#### Icons

As concern the icons, several investigations appeared on Byzantine or post-Byzantine icons (Andrikopoulos et al. [297], Kouloumpi et al. [298]), coptic (Abdel-Ghani et al. [299], Abdel-Ghani et al. [300], Iordanidis et al. [301]), greek (Sotiropoulou and Daniilia [302], Karapanagiotis and Dimitrios [303]), Melkite (Lahlil and Martin [304]). Abdel-Ghani et al. [305] examined a Coptic-Byzantine icon dated to the 13<sup>th</sup> c. from St. Mercurius Church, Old Cairo: hydromagnesite Mg<sub>5</sub>(CO<sub>3</sub>)<sub>4</sub>(OH)<sub>2</sub>·4H<sub>2</sub>O was found and considered as an intentional white pigment. Abdel-Ghani [306] studied the pigment palette of an icon located in Saint Abanoub church in Samanoud, in Egyptian Delta. Two Serbian icons painted on canvas in the Museum of the Serbian Orthodox Church in Belgrade were investigated by Damjanović et al. [307].

Daveri et al. [308] examined gilding techniques of a 13<sup>th</sup> c. icon and evidenced mosaic gold SnS<sub>2</sub>. One of the first evidences of mosaic gold was given in 2000 by Edwards et al. [309] in a 13<sup>th</sup> c. polychrome statue. A review on gilding materials and techniques on ancient 'gilded' art-objects (9<sup>th</sup>–19<sup>th</sup> centuries) from the European cultural heritage was published by Sandu et al. [310].

#### Polychromies and various artefacts

The pigments of the polychrome limestone sculpture "Las tres generaciones" (Cathedral's Museum of Santiago de Compostela, Spain) were characterized by Prieto et al. [311]. Edwards et al. [312] reported a study on pigments on stone samples from an Augustinian friary. He et al. [313] performed a multi-analytical study of the polychromy in the Guangyuan Thousand-Buddha Grotto, "the museum of painted stone sculpture": the complex analysis suggests atacamite and malachite as true green pigments. The white colour was ascribed to anglesite and gypsum. Some arsenic-containing pigments were detected in the green samples.

Moolooite (copper oxalate, CuC<sub>2</sub>O<sub>4</sub>·nH<sub>2</sub>O), a very rare natural mineral, was found as degradation product on gypsum alabaster polychrome sculptures by Castro et al. [314]. The pigments after modern restorations on statues of Feixiange Cliff in China were identified by Jin et al. [315]. Wang et al. [316] reported on an accurate study of clay-based polychrome sculptures in Jizo Hall of Chongqing Temple, Shanxi Province of China. The mineral pigment used in a green layer was identified as atacamite (Cu<sub>2</sub>Cl(OH)<sub>3</sub>).

Baraldi et al. [317] carried out an analysis on a polychrome wood mask from Papua New Guinea and identified hematite, pyrolusite, magnetite, graphite, goethite and hausmannite together with carbon black. The black colour of the mask's background was obtained with pyrolusite and hausmannite.

1  
2  
3 A Hindu papier-mâché statue, Kali Walking on Siva, was examined by Edwards et al. [318]. Wooden  
4 sculptures were examined by Aliatis et al. [319], Franquelo et al. [320], Lo Monaco et al. [321] and Kuckova et al.  
5 [322].

6  
7 De Santis et al. [323] discussed on the laser induced degradation of the pigments on a 'Cembalo' model  
8 musical instrument (A.D. 1650). A micro-Raman spectroscopy study of a multi-coloured tile shard from the  
9 Citadel of Algiers was made by Kock and DeWaal [324]. Red pigments from seven Egyptian mummies of the  
10 Roman-period (red-shroud mummies) were identified by Walton and Trentelman [325] as red lead  $Pb_3O_4$   
11 with a minor lead tin oxide phase, due to high temperature treatment: the technology and trade between  
12 Spain and Aegypt is discussed. An Egyptian wood coffin was investigated by Bonizzoni et al. [326] using  
13 different techniques (EDXRF, micro FTIR, FT Raman, GC-MS, XRD and SEM-EDX. Only a few pigments  
14 (egyptian blue, cinnabar, probably orpiment) were identified.

15  
16 One should mention also the studies on pigments from different artworks of Southern Spain Cultural  
17 Heritage (Franquelo et al. [327]); on black powders contained in bronze vessels found in Pompeii houses  
18 (Canevali et al. [328]); on raw pigments and painted ceramics excavated at Szombathely-Oladi Plató, Hungary  
19 (Tóth et al. [329]); on painted pottery figurines from two tombs in Luoyang, China (Liu et al. 2013 [330]); on  
20 different artworks and from archaeological sites in Chile (Vallette Campos and Aguayo [331]); on funeral  
21 figurines, found in two Hellenistic and two Roman tombs in Thessaloniki, Greece (Fostiridou et al. [332]).

22  
23 Košařová et al. [333] performed a Raman investigation at different wavelengths of reference samples of  
24 natural clay pigments (white clay minerals, green earths and red earths) and samples from historical  
25 paintings, looking for the best conditions for the identification of the minerals in the earth pigments. Oujja  
26 et al. [334] examined the laser irradiation effects on vermilion, lead chromate and malachite pigments using  
27 different wavelengths and pulse duration. Navas et al. [335] applied PCA analysis on first-derivative Raman  
28 spectra to investigate historical tempera paint model samples. Using Raman data on the pigments, Siotto et  
29 al. [336] tried a virtual reconstruction of the ancient polychromy on a digital 3D model of the sarcophagus  
30 dedicated to Ulpia Domnina (National Roman Museum in Rome). Several examples of non-destructive  
31 analysis of painted layers on sculptures and plasters using micro-SORS (Spatially-Offset Raman  
32 Spectroscopy) have been presented by Conti et al. [337](Fig.8).

### 33 **FIGURE 8.**

#### 34 *Wall paintings*

35  
36 As concerns mineral pigments, ancient wall paintings are a major source of information. Here we report  
37 only recent works (roughly the past decade) with a few comments or significant references on mineral  
38 pigments.

39  
40 The list of investigations on mural paintings in which the Raman spectroscopy played a role in the last  
41 decade is indeed gigantic: samples of plasters and pictorial layers taken from a fresco of Acireale cathedral  
42 (Barilaro et al. [338]); mural paintings by the Italian miniaturist Napoleone Verga (Rosi et al. [339]); polychromy  
43 of the decoration of the façade of the Palace of King Pedro I, Seville, Spain (López-Cruz et al. [340]); Roman  
44 Plasters of the 'Domus Farini' in Modena (Baraldi et al. [341]); Korean wall paintings (Mazzeo et al. [342]);  
45 pigments in the Cemetery of Tutugi, Galera, Granada, Spain and in the Settlement Convento 2,  
46 Montemayor, Córdoba, Spain (Parras-Guijarro et al. [343]); pigments extracted from mural paintings in the  
47 Notre-Dame Cathedral of Tournai, Belgium (Lepot et al. [344]) or in a medieval monastery of Karaach-Teke,  
48 Varna, Bulgary (Zorba et al. [345]); roman wall paintings found in Verona (Mazzocchin et al. [346]); Byzantine  
49 wall painting complex in the Protaton Church on Mount Athos, Greece (Daniilia et al. [347]) and Roman  
50 plasters in Reggio Emilia (Baraldi et al. [348]).

51  
52 Pigments in painted mural decorations in a monastery temple from the 15<sup>th</sup> c. in Lo Manthang, Nepal, have  
53 been examined by Mazzeo et al. [349]. They found azurite for the blue colours, sometimes in combination  
54 with lazurite particles and malachite: brochantite, a copper sulfate hydrate,(see in the following) was found  
55 as alteration product of malachite. The fading of red lead pigment in wall paintings was investigated by Aze  
56 et al. [350]. Pérez-Alonso et al. [351] and [352] identified pigments and degradation processes and products  
57 (oxalates) in wall paintings in different regions in Spain. Anhydrite was considered an unexplained  
58  
59  
60

1  
2  
3 degradation product of gypsum. Mazzocchin et al. <sup>[353]</sup> analyzed different white pigments in Roman wall  
4 paintings of the VIII(a) Regio, Aemilia, and X(a) Regio, Venetia et Histria, identifying calcite, aragonite,  
5 dolomite, huntite.

6  
7 Specific pigments on wall paintings were identified by Raman spectroscopy in further works: samples from  
8 three buildings at the Maya site of Copan, Honduras (Goodall et al. <sup>[354]</sup>); Etruscan polychromes on  
9 architectural terracotta panels (Bordignon et al. <sup>[355]</sup>); St Stephen's wall paintings at Meteora, Greece  
10 (Daniilia et al. <sup>[356]</sup>); the fresco 'Trapasso della Vergine' in the Church of St. John the Baptist in Paterno  
11 Calabro, southern Italy (Castriota et al. <sup>[357]</sup>); frescoes of the Longobard temple in Cividale del Friuli, Italy,  
12 and of the 8<sup>th</sup> c. crypt of San Salvatore in Brescia, Italy (Zucchiatti <sup>[358]</sup>); 15<sup>th</sup> c. mural paintings and frescos of  
13 the Little Christopher chamber in the Main Town Hall of Gdan' sk, Poland (Sawczak et al. <sup>[359]</sup>); the wall  
14 paintings from two Romano-British urban centres of Colchester and Lincoln (Edwards et al. <sup>[360]</sup>).

15  
16 The first systematic Raman study of the pigments used in medieval wall painting in the churches of Republic  
17 of Macedonia has been reported by Minceva-Sukarova et al. <sup>[361]</sup>. Sodo et al. <sup>[362]</sup> investigated the mural  
18 painting, realized "a fresco", of the Tomba dell'Orco, in the Etruscan necropolis of Tarquinia, Italy. Red  
19 ochre ( $\alpha\text{-Fe}_2\text{O}_3$ ), cinnabar, orpiment, yellow ochre and egyptian blue were easily identified. The nature of a  
20 green pigment was not determined.

21  
22 Nevin et al. <sup>[363]</sup> performed an analysis of paint samples from a 16<sup>th</sup> c. wall painting in the church of Agios  
23 Sozomenos in Galata, Cyprus, and found hydrated copper oxalate, analogous to the naturally occurring  
24 blue-green mineral moolooite. The 16<sup>th</sup> c. external wall paintings (fresco technique) of St. Dumitru's Church  
25 in Suceava (Romania) were analysed by Hernanz et al. <sup>[364]</sup>, evidencing a degradation due to nitrogenous  
26 organic materials.

27  
28 Boselli et al. <sup>[365]</sup> reported, in La Verna Sanctuary frescoes, on a white pigment made by a complex mixture  
29 of zinc white, lithopone, a minor component of anatase and an unidentified organic material. The paintings  
30 in the tomb of Menna (TT69), Theban Necropolis, Egypt, were studied in situ by Vandenabeele et al. <sup>[366]</sup> but  
31 Raman spectroscopy was strongly hampered by fluorescence from paraloid B72 resin used in a previous  
32 conservation treatment. Wall painting fragments from Kaiping Diaolou (Qing Dynasty) were investigated by  
33 Zeng et al. <sup>[367]</sup>: lazurite and goethite were the main pigments. They found syngenite  $\text{K}_2\text{CaSO}_4\cdot\text{H}_2\text{O}$  of  
34 undetermined origin in the plaster.

35  
36 In 2010/2011 a lot of Raman studies dealing with mineral pigments were published: the complex gilt stucco  
37 surfaces of different monuments in Lombardia (Sansone et al. <sup>[368]</sup>); Pompeian wall paintings using EDS  
38 and HR-SRPD and micro Raman (Duran et al. <sup>[369]</sup>); pigments in 15<sup>th</sup> c. mediaeval and 16<sup>th</sup> c. renaissance  
39 vault paintings in the Our Lady's Cathedral in Antwerp, Belgium (Deneckere et al. <sup>[370]</sup>); mural paintings from  
40 the Pyrenean Church of Saint Eulàlia of Unha (Clark et al. <sup>[371]</sup>); the wall painting "Historia de Concepcion"  
41 by Gregorio De La Fuente in Concepcion, Chile (Aguayo et al. <sup>[372]</sup>); wall painting by Romans and Arabs  
42 (Garofano et al. <sup>[373]</sup>); fresco fragments at the Coriglia, Castel Viscardo, Orvieto, excavation site (Donais et  
43 al. <sup>[374]</sup>); wall paintings by Masolino da Panicale in the Baptistery of Castiglione Olona, Italy (Comelli et al.  
44 <sup>[375]</sup>); pigments from the Mortuary Temple Of Seti I, El - Qurna at Luxor, Egypt (Mahmoud <sup>[376]</sup>); Roman and  
45 Arabic wall paintings in the Patio de Banderas of Reales Alcazares' Palace (Duran et al. <sup>[377]</sup>); the ceiling of  
46 the Gilded Vault of the Domus Aurea in Rome (Clementi et al. <sup>[378]</sup>).

47  
48 Raman spectroscopy was used as a diagnostic tool in Marcus Lucretius House, Pompeii, to investigate the  
49 nature of deterioration on wall paintings exposed to different environments by Maguregui et al. <sup>[209]</sup>.  
50 Raman mapping allowed to identify oxalates, whewellite and weddellite, which are commonly observed on  
51 the surfaces of ancient monuments. They may result from the associated action of microorganisms and  
52 environmental conditions. A thermodynamic and spectroscopic investigation on the blackening of hematite  
53 into magnetite, attributed to  $\text{SO}_2$  attack, in Marcus Lucretius House was performed by Maguregui et al. <sup>[379]</sup>.

54  
55 Romero-Pastor et al. <sup>[380]</sup> explored the crystallinity and micro-textural characteristics of the pigments on  
56 paintings in the 14<sup>th</sup> c. Islamic University—Madrasah Yusufiyya— in Granada (Spain) – and discussed about  
57 the origin, manufacture and alteration processes of the pigments. Gil et al. <sup>[381]</sup> reported on an accurate  
58 study of the blue pigments from Portuguese 15<sup>th</sup> to 18<sup>th</sup> c. churches. Smalt and, in a minor extent, azurite  
59  
60

1  
2  
3 were found. Smalt pigment seems to be the most affected by conservation problems due to lixiviation.  
4 Azurite shows an extraordinary chemical and chromatic stability, probably due to its coarse grains.  
5 Iordanidis et al. <sup>[382]</sup> performed a characterization of Byzantine wall paintings from Kastoria, Northern  
6 Greece. Green colour is attributed to admixtures of Fe-rich minerals and lime and not to the commonly  
7 used green earths.

8  
9 The contribution of Raman spectroscopy in 2012/2013 to the pigment identification and on conservation  
10 issues has been equally significant: pigments and plasters from the Roman settlement of Thamusida (Rabat,  
11 Morocco) (Gliozzo et al. <sup>[383]</sup>); the tomb of Djehutyemhab (tt194), Elqurna necropolis, Upper Egypt  
12 (Mahmoud <sup>[384]</sup>); pigments from five Medieval Gotland churches in Sweden (Nord and Tronner <sup>[385]</sup>); the  
13 painted vaulted ceiling of the Sant Joan Del Mercat Church, Valencia, Spain (Doménech-Carbó et al. <sup>[386]</sup>);  
14 16<sup>th</sup> c. wall paintings in the Saint Andrew Church, Biañez, Biscay, and Saint John the Baptist Church, Axpe,  
15 Biscay (Irazola et al. <sup>[387]</sup>); Sala delle Maschere of the Domus Aurea in Rome (Paradisi et al. <sup>[388]</sup>); pigments  
16 from the 4<sup>th</sup> to the 3<sup>rd</sup> c. BC in the Iberian cemetery of Tutugi, Galera, Granada, Spain (Sánchez et al. <sup>[389]</sup>);  
17 Roman plasters applied over Pharaonic walls at Luxor temple, Upper Egypt (Mahmoud et al. <sup>[390]</sup>); chromatic  
18 alterations of Roman Heritage in Aosta (Conz et al. <sup>[391]</sup>); Roman mural paintings (Toschi et al. <sup>[392]</sup>); the  
19 fresco 'The Good and the Bad Judge' located at the medieval village of Monsaraz in southern Portugal (Gil  
20 et al. <sup>[393]</sup>); multi-pigmented surface from the wall decorations of the Theban tomb (TT277), Luxor, Egypt  
21 (Mahmoud <sup>[394]</sup>).

22  
23 Aceto et al. <sup>[395]</sup> on mural paintings in Ala di Stura hypothesized the use of pyrite mixed with smalt to  
24 reproduce a chromatic effect similar to lapis lazuli, where pyrite is a common accessory mineral. For  
25 example, Bersani et al. <sup>[396]</sup> identified pyrite in the 'Madonna col Bambino e S. Giovannino' by Botticelli. An  
26 intentional addition of pyrite to lapis lazuli cannot however be excluded.

27  
28 Maguregui et al. <sup>[397]</sup> studied the conservation state of walls and wall paintings in Pompeii, Italy. They  
29 confirmed that a severe decay is not observed when the rooms are covered by roofs. In Marcus Lucretius  
30 House, Pompeii, Maguregui et al. <sup>[398]</sup> investigated the nature and distribution of carotenoids in brown  
31 patinas from a deteriorated wall painting. Raman mapping also allowed to identify whewellite and  
32 weddellite. Oxalate film formation is a pathology that frequently occurs in mural paintings, because of the  
33 action of microorganisms and environmental conditions.

34  
35 Zoppi et al. <sup>[399]</sup> report a spectroscopic study on some fragments of wall paintings of the Minoan art of  
36 Phaistos (Crete) from the Archaeological National Museum in Florence: hematite, goethite, calcite, Egyptian  
37 blue, carbon and a green earth (celadonite) were identified.

38  
39 A rich palette of pigments, both natural/mineral and synthetic ones, was identified by micro-Raman  
40 spectroscopy by Cukovska et al. <sup>[400]</sup> in wall paintings of the 19<sup>th</sup> c. iconographer Dicho Zograph, in churches  
41 from Republic of Macedonia.

42  
43 De Benedetto et al. <sup>[401]</sup> claim that in the oldest pictorial cycle in the 12<sup>th</sup> c. monastery Santa Maria delle  
44 Cerrate there is the first known example of smalt and lapis lazuli in South Italy. Zhu et al. <sup>[402]</sup> analysed wall  
45 paintings from the Cizhong Catholic Church of Yunnan Province, China and described a peculiar degradation  
46 of emerald green (synthetic) into cornwallite (mineral).

47  
48 In the last period 2014/2015 we can cite further relevant studies on: wall paintings of two Greek Byzantine  
49 Churches from Kastoria, northern Greece (Iordanidis et al. <sup>[403]</sup>); pigments in the wall paintings at Jokhang  
50 Monastery in Lhasa, Tibet, China (Li et al. <sup>[404]</sup>); a wall painting attributed to Ambrogio Lorenzetti in the St.  
51 Augustine Church in Siena, Italy (Damiani et al. <sup>[405]</sup>); the pigments in dome wall paintings by Correggio in  
52 Parma cathedral (Bersani et al. <sup>[406]</sup>); 17<sup>th</sup> c. mural paintings, Dominican Convent of Nossa Senhora da  
53 Saudacao, Montemor, Portugal (Gil et al. <sup>[407]</sup>); medieval Nubia wall-paintings from Saras, Old Dongola and  
54 Banganarti archaeological sites (Syta et al. <sup>[408]</sup>); wall paintings in Pompeii (Madariaga et al. <sup>[409]</sup>); wall  
55 paintings from Qasr El-Ghuieta Temple, Kharga Oasis, Egypt (Mahmoud <sup>[410]</sup>); the wall paintings from the  
56 Baños de Doña Maria de Padilla in The Alcazar of Seville (Perez-Rodriguez et al. <sup>[411]</sup>); binder compositions in  
57 Pompeian wall paintings from Insula Occidentalis (Gelzo et al. <sup>[412]</sup>); gilded plasterwork in the Hall of the  
58 Kings in the Alhambra complex, Granada, Spain (de la Torre-López et al. <sup>[413]</sup>); wall paintings in the San  
59  
60

1  
2  
3 Francisco Church, Santiago, Chile (Araya et al. <sup>[414]</sup>); the wall paintings in the Churches of Panagia and  
4 Theotokos built in the settlements of Patsos and Meronas at Amari Rethymno, Crete (Cheilakou et al. <sup>[415]</sup>);  
5 wall painting fragments from Roman villas of the Sabina area, Rome (Paladini et al. <sup>[416]</sup>); the wall paintings  
6 from the Hellenistic hypogeum of Apaforte-Licata, Agrigento, Sicily (Aquila et al. <sup>[417]</sup>); wall paintings in the  
7 Villa of the Papyri in Herculaneum (Amadori et al. <sup>[418]</sup>); decorative fragments from the hypocaustum in the  
8 Roman villa of El Ruedo, Almedinilla, southern Spain (Mateos et al. <sup>[419]</sup>).

9  
10 Salvadó et al. <sup>[420]</sup> made a multi-technique microanalysis of the blue paints in different altarpieces in  
11 Catalonia and Crown of Aragon from the 15<sup>th</sup> c., identifying lapis lazuli, azurite and indigo. Veneranda et al.  
12 <sup>[421]</sup> <sup>[422]</sup> identified the compounds constituting a mural painting in the Assumption's church of Alaiza in  
13 Basque Country, Spain, and investigated the degradation induced by agricultural activities. Maguregui et al.  
14 <sup>[423]</sup> reported on accelerated weathering experiments on wall painting samples from Pompeii, confirming  
15 the reduction of hematite into magnetite and the formation of gypsum on calcite plaster. They assessed  
16 that high concentrations of SO<sub>2</sub> can cause the sulphation of hematite into paracoquimbite/coquimbite  
17 Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·9H<sub>2</sub>O.

18  
19 Kakoulli et al. <sup>[424]</sup> provided direct evidence for the earliest use of asbestiform fibres, in Byzantine wall  
20 paintings in Cyprus: chrysotile Mg<sub>3</sub>Si<sub>2</sub>O<sub>5</sub>(OH)<sub>4</sub> was found in CaCO<sub>3</sub>-rich finish coatings, just beneath the  
21 cinnabar paint layer, providing a very compact and smooth layer with mirror-like surface appearance.

22  
23 Piovesan et al. <sup>[425]</sup> described a polychrome sinopia, where cinnabar was also used, under the Lod Mosaic,  
24 Israel. Gill et al. <sup>[426]</sup> analysed the extraordinary palette of pigments on Buddhist wall paintings and  
25 sculptures, dating to the 12-13<sup>th</sup> c., in the interiors of the temple complex at Sumda Chun, Ladakh: azurite,  
26 orpiment, vermilion and minium were identified.

27  
28 Yong and Wang <sup>[427]</sup> in the wall paintings in Xialu Temple, Tibet Autonomous Region, China, found a large  
29 use of orpiment even mixed with cinnabar to produce a reddish orange and determined the sequence of  
30 interventions. Schmidt et al. <sup>[428]</sup> analysed a sample from a wall painting in a Buddhist cave along the  
31 northern Silk Road and reported atacamite between the mineral pigments. Gutman et al. <sup>[429]</sup> investigated  
32 mortar layers and pigments of wall paintings from the Roman town of Emona (Ljubljana, Slovenia) and  
33 found common earth pigments. Crupi et al. <sup>[430]</sup> studied the painted surface of plasters withdrawn from  
34 different areas of Villa dei Quintili (Rome, Italy) but, due to fluorescence problems, the in-situ Raman  
35 spectra, apart calcite, confirmed only the presence of cinnabar.

### 36 37 **Blue pigments**

38  
39 In the antiquity, the availability of natural coloured substances was a problem. Earth colours were readily  
40 available and were used in cave paintings (rock art) where no blue colour is found. In general, mineral  
41 sources for stable blue pigments are exceptionally rare. The first truly stable blue mineral pigment was  
42 most likely lapis lazuli. A blue pigment was also the more abundant mineral azurite, a basic copper  
43 carbonate. Then, blue-coloured glazes and glasses were prepared by the use of cobalt minerals or by lapis  
44 lazuli and methods to produce stable blue materials were developed: Egyptian Blue (CaCuSi<sub>4</sub>O<sub>10</sub>) and Maya  
45 Blue, a hybrid organic-inorganic. Synthetic blue pigments were developed in China: Chinese Blue and  
46 Chinese Purple, also known as Han Blue and Han Purple (BaCuSi<sub>4</sub>O<sub>10</sub> and BaCuSi<sub>2</sub>O<sub>6</sub>). Berke <sup>[431]</sup> published an  
47 excellent historical and scientific survey of the "Invention of blue and purple pigments in ancient times"  
48 including Maya Blue.

### 49 50 *Azurite*

51  
52 Azurite is one of the two basic copper(II) carbonate minerals, the other being green malachite. The first  
53 work on the application of micro Raman spectroscopy to cultural heritage was published in 1984 by  
54 Guineau <sup>[222]</sup> <sup>[223]</sup> on the identification of azurite and malachite in a 15<sup>th</sup> c. French manuscript. Then azurite  
55 was identified in a large amount of artworks. Unfortunately, this pigment suffers from chemical and/or  
56 thermal alterations: discoloration from blue to green due to the degradation of azurite into malachite or  
57 into basic copper chlorides (one of the supposed isomers like atacamite, paratacamite, clinoatacamite and  
58 botallackite). The conversion into black compounds as copper sulfide (covellite, CuS) or copper oxide  
59 (tenorite, CuO) occurs less frequently and is rarely investigated. Conversion of azurite into black tenorite

(CuO) can be due to two different causes: alkaline environment and heat. Mattei et al. <sup>[432]</sup> explored the conditions for the degradation of azurite into tenorite. They studied also laser-induced degradation of azurite as a function of the grain size. The degradation temperature decreases as the size increases. The conversion of azurite into moolooite has been recently reported by Daniel et al. <sup>[433]</sup> in a study of the paintings on the 'Royal Portal' of Bordeaux Cathedral. Azurite, being a secondary mineral that forms in the oxidised zones of copper deposits by the interaction of carbonated solutions with primary copper minerals, contains many different impurities. Aru et al. <sup>[434]</sup> analysed the mineral impurities in azurite pigments using several samples of azurite chosen from historical collections of minerals. They tried to get some hint to ascertain the provenance of an individual azurite-containing pigment.

### *Maya Blue*

Maya Blue, a synthetic pigment produced by the ancient Mayas in pre-Columbian America, is the combination of a fibrous clay (palygorskite-sepiolite) and an organic blue dye (indigo). Indigo was extracted from *Indigofera suffruticosa* plants. Palygorskite is a fibrous clay common in Yucatan. The indigo-palygorskite mixture acquires a considerable stability when a moderate thermal treatment is applied, constituting an artificial mineralization and the first example of a "hybrid" organic-inorganic pigment. The main features of the structure of Maya Blue are known: indigo seem to lie within the palygorskite channels partially substituting the zeolitic water (Chiari et al. <sup>[435]</sup>, Giustetto et al. <sup>[436]</sup>, Giustetto et al. <sup>[437]</sup>) but the structure of Maya Blue and the nature of its interactions with the clay framework are still investigated. The first Raman spectroscopic examination of a whole set of pigments from archaeological Maya wall painting fragments was made by Vandenabeele et al. <sup>[438]</sup>. Sánchez del Río et al. <sup>[439]</sup> performed a Raman study of different preparations of Maya blue and other mixtures of indigo with other inorganic materials. They report that the indigo vibrational spectrum does not change during the thermal treatment and with different clays like sepiolite or montmorillonite. Manciu et al. <sup>[440]</sup> carried out a Raman and IR study of synthetic Maya pigments as a function of heating time and dye concentration. Synthetic materials demonstrate chemical stability similar to that of the ancient Maya blue samples. The spectroscopic data show the disappearance of the indigo N–H bonding, as the organic molecules incorporate into palygorskite material.

Goodall et al. <sup>[354]</sup> reported on micro Raman analysis of stucco samples from the buildings of Maya Classic Copan. Wiedemann et al. <sup>[441]</sup> claimed that original Maya Blue was used to illuminate a fragment of the "Codex Huamantla", but the conclusion was questioned by del Río and Montes <sup>[442]</sup>. Moreno et al. <sup>[443]</sup> studied Maya blue–green pigments found in Calakmul, Mexico, whereas Manciu et al. <sup>[444]</sup> considered the chemical bonding occurring between thioindigo and inorganic palygorskite, synthesizing a pigment similar to Maya Blue. A review of the Raman results on Maya Blue is given by Doménech et al. <sup>[445]</sup>. They also considered Maya Blue samples and models obtained by the binding of indigo to phyllosilicate clays, such as palygorskite and sepiolite, using chemometric analysis. A detailed vibrational study of synthetic indigo-palygorskite Maya-Blue was reported by Tsiantos et al. <sup>[446]</sup>.

Indigo@silicalite hybrid pigments are currently investigated for stable pigment (Dejoie et al. <sup>[447]</sup>, Zhang et al. <sup>[448]</sup>).

### *Lapis lazuli*

Blue-hued minerals have played an important role in the cultural history of mankind. The oldest precious stone of this kind is lapis lazuli, which was already in use in the Sumerian civilisation about 5500 years ago. It was introduced in Europe from Afghanistan and was extensively used in the Middle Ages and during the Renaissance. Lapis lazuli (natural ultramarine blue) takes its colour to lazurite, which is a sodium aluminosilicate mineral,  $(\text{Na,Ca})_8(\text{Al}_6\text{Si}_6\text{O}_{24})(\text{SO}_4,\text{Cl},\text{S})_2$ . It took until 1806 for the first reliable analysis, suggesting that sulfur species were the colour centres. The earliest syntheses of blue ultramarines were performed in 1826 by J. B. Guimet and C. G. Gmelin, and in 1834 C. Leverkus founded the first plant manufacturing ultramarine in Germany. The colour of the ultramarine blue is due to polysulfur radical anions,  $\text{S}_3^-$  and  $\text{S}_2^-$ , chromophores embedded into sodalite cages. The ratio  $\text{S}_3^-/\text{S}_2^-$  determines the hue of the pigment. A tutorial review on the trisulfur radical anion  $\text{S}_3^-$  has recently appeared (Chivers and Elder <sup>[449]</sup>). The first evidence of the sulfur chromophore in lapis lazuli by Raman spectroscopy was given by Clark et al.

1  
2  
3 [450]. The Raman band observed at  $547\text{ cm}^{-1}$  is ascribed to the  $S_3^-$  symmetric stretching mode, whereas that  
4 at  $258\text{ cm}^{-1}$  corresponds to the bending vibration of the  $S_3^-$  ion: this molecular moiety is responsible for the  
5 blue colour. The  $S_2^-$  anion (responsible for yellow colour) gives rise to the green tones associated with some  
6 ultramarine pigments. Because of its very low concentration in the blue, the corresponding symmetric  
7 stretching  $S_2^-$  signal appears as a shoulder at about  $580\text{ cm}^{-1}$  with very weak intensity. Gobeltz et al. [451]  
8 found out that in blue ultramarine, different shades of blue pigments depend on the relative concentration  
9 of the two chromophores  $S_2^- S_3^-$ , as determined by Raman spectroscopy. Bicchieri et al. [452] characterized  
10 azurite and lazurite based pigments. Ostroumov et al. [453], observed also the presence of  $SO_4^-$  groups in the  
11 Raman spectra of lazurite from Pamir and Siberia. Gobeltz-Hautecoeur et al. [454] studied the occupancy of  
12 the sodalite cages, Desnica et al. [455] and Del Federico et al. [456] explored the application of Raman  
13 spectroscopy for the discrimination between different ultramarine pigments.  
14

15 Due to the strong electronic absorption at about 600 nm, resonance Raman effects are evident: Raman  
16 spectra show multiphonon processes as overtones and combination bands of the fundamental vibrational  
17 modes of  $S_3^-$  and  $S_2^-$  radical anions (Ballirano and Maras [457]). The 514 nm line excites into the broad  
18 absorption band of  $S_3^-$  but not into the absorption of  $S_2^-$  (at ca. 400 nm), thus resonance effects are  
19 observable only for the former species. Ali and Edwards [458] discussed on the discrimination between  
20 genuine and fake specimens of lapis lazuli using portable Raman spectrometers and different excitation  
21 lines, changing the resonance conditions for the dominant spectral feature arising from the S–S stretching  
22 mode of the  $S_3^-$  radical anion chromophore. High-pressure resonance Raman spectroscopic study of  
23 ultramarine blue pigment has been performed by Barsan et al. [459] indicating weak interactions of the  
24 chromophores with the sodalite lattice.  
25

26 Colomban [42] [99] gave a comprehensive review of the colours in glazed ceramic and enameled glasses with  
27 particular reference to the use of lapis lazuli in ceramics. A first evidence of the use of lapis lazuli as  
28 pigment in ceramics was given by Clark et al. [460] [461] on glazed pottery fragments from Castel Fiorentino  
29 Castle, Torremaggiore (Foggia, Southern Italy). Blue glazed plates containing lapis lazuli excavated from  
30 Siponto (Manfredonia, Apulia) were investigated by Catalano et al. [49]. A Raman and optical/electronic  
31 microscopy study of a 13<sup>th</sup> c. Lajvardina ewer confirmed the use of lapis lazuli grains as glaze pigment  
32 (Colomban [83] [462]). In the ewer, glaze cobalt was also detected, demonstrating the use of alternative  
33 technologies in the same artefact. Use of lapis lazuli was revealed in glazed Böttger porcelain, the earliest  
34 hard-paste "China" porcelain produced in Europe at the Meissen Saxon Court Factory at the beginning of  
35 18<sup>th</sup> c. (Colomban and Milande [93]).  
36

37 Greiff and Shuster [463] analysed four fragments of the famous Lübsow glass beaker, with enamelled  
38 decorations depicting mythological scenes, found in a 2<sup>nd</sup> c. tomb in the North of Poland, and the signal of  
39  $S_3^-$  chromophore was detected in the blue enamel. Calcite and diopside ( $CaMgSi_2O_6$ ) were also revealed,  
40 considered a signature of natural lapis lazuli rock, probably from Afghanistan.  
41

42 Blue faience artefacts found at Pompeii and assigned to the Ptolemaic–Roman Egyptian production (1st c.  
43 BC–1st c. AD) were found coloured by lapis lazuli by Mangone et al. [464]. New evidences on the lapis lazuli  
44 use were reported by the Colomban group in some trade blue beads found at Mapungubwe hill, the main  
45 archaeological site in South Africa (Tournié et al. [465] and Prinsloo et al. [466])(Fig.9).  
46

#### 47 **FIGURE 9.**

48 The resonance Raman spectrum of the vibrations associated to the lazurite chromophores  $S_3^-$  and  $S_2^-$  ions  
49 under green laser excitation demonstrated the presence of ultramarine in Mamluk enamelled precious  
50 objects (Colomban et al. [467]). According to Sendova et al. [468], the chromophores evidenced by Raman  
51 spectroscopy in some 'Della Robbia' blue glazes, arose from the thermal treatment of the used raw  
52 materials from Co-containing sulphide ores and not from lapis lazuli incorporation. The unicity of this  
53 finding has been questioned by Colomban [99].  
54

55 Derrick et al. [469] by a FTIR study, found a "typical" IR absorption band for lapis lazuli (natural ultramarine)  
56 from Afghanistan at about  $2340\text{ cm}^{-1}$ , tentatively assigned to  $S_6^+$  species and it was considered distinctive of  
57 natural Afghan lapis lazuli. Miliani et al. [470], investigating ultramarine blue pigments by FTIR, interpreted  
58  
59  
60

the absorption band at  $2340\text{ cm}^{-1}$  as due to the entrapment of carbon dioxide  $\text{CO}_2$  in the sodalite beta-cages of the natural pigment from Afghanistan. Bacci et al. <sup>[471]</sup> attributed, using also DFT calculations, the same absorption band at  $2340\text{ cm}^{-1}$  to the S-H stretching of  $\text{HS}_3^-$  species in Afghan lapis lazuli, claiming the absence of the band in other lapis lazuli and in the synthetic ultramarine pigments. The result could help in describing the geochemical origin of lapis lazuli. According to Favaro et al. <sup>[472]</sup> this absorption band, however, is not an indication of genuine Afghan lapis lazuli pigment as it occurs in the spectra of all natural pigments, despite being weaker, for example in the spectra of the Siberian and Chilean pigments. They suggested that it can only be used as a genuine discriminating marker for natural pigments as opposed to synthetic ones.

Osticioli et al. <sup>[473]</sup> <sup>[474]</sup> proposed an analytical protocol for the differentiation between natural lapis lazuli and artificial ultramarine blue pigments, as calcite inclusions seem present only in the samples of natural origin. According to Schmidt et al. <sup>[475]</sup>, who considered different natural and synthetic ultramarine samples, the Raman spectra of the natural samples contains non-lazurite features attributed to diopside that could help in provenance studies. These features may be indicative of natural lapis lazuli from Afghanistan. De Torres et al. <sup>[476]</sup> tried to quantify the Raman spectral differences up to about  $2000\text{ cm}^{-1}$  among the synthetic ultramarine blue and three lazurites corresponding to three lapis lazulis from different geographical sources (Chile, Afghanistan, Siberia).

Dominguez-Vidal et al. <sup>[477]</sup> studied the decorated plasterworks in the seven vaults of the Hall of the Kings of the Palace of the Lions in the Alhambra (Granada, Spain). They found lapis lazuli and a strong luminescence background together with several bands, the most intense located at  $1306$  and  $1508\text{ cm}^{-1}$ , which have been attributed to luminescence of diopside, a mineral commonly associated with lapis lazuli in nature.

#### *Covellite – Mineral pigment or degradation product ?*

Jin et al. <sup>[82]</sup> claimed that the faint blue covellite ( $\text{CuS}$ ), identified by micro-Raman spectroscopy by a characteristic peak at  $474.5\text{ cm}^{-1}$  on a Chinese funerary lacquer ware of West Han Dynasty, was used as an intentional pigment (Fig.10).

#### **FIGURE 10.**

According to Correia et al. <sup>[268]</sup> the covellite found in paintings by the Portuguese artist Henrique Pousao (1859–1884) originated from a degradation reaction between a copper-containing pigment and one with sulfur, in the same painted area. Veiga et al. <sup>[478]</sup>, investigating Portuguese portrait miniatures of 17<sup>th</sup> and 18<sup>th</sup> centuries, found bluish-black covellite, a pigment rarely found in oil paintings, and supported the hypothesis of an intentional use of the natural mineral species.

#### *Aerinite*

Aerinite is a blue fibrous aluminium and calcium hydrate silicate-carbonate with ideal formula  $(\text{Ca},\text{Na})_6(\text{Fe}^{3+},\text{Fe}^{2+},\text{Mg},\text{Al})_4(\text{Al},\text{Mg})_6[\text{Si}_{12}\text{O}_{36}(\text{OH})_{12}](\text{CO}_3)\cdot 12\text{H}_2\text{O}$ . This mineral was the blue pigment commonly used in most Catalan romanic paintings between the XI-XV centuries and in the Pyrenean region (Casas and Llopis <sup>[479]</sup>) and was extracted in the southern Pyrenees. Aerinite was identified by Raman spectroscopy by Clark et al. <sup>[371]</sup> in the wall paintings, dating from the Romanesque period to the 16<sup>th</sup> c., in the church of Santa Eulalia of Unha in the Val d'Aran. Aerinite was also identified in the south-west of France (Daniel et al. <sup>[480]</sup> <sup>[481]</sup>) in paintings of the vault of the old abbey home of Moissac (12<sup>th</sup> C., Tarn-et-Garonne), and in those of the church Saint-Nicolas of Nogaro (end 11<sup>th</sup> c., Gers). Aerinite was also reported in the Voronet Monastery (Romania) by Buzgar et al. <sup>[482]</sup>. An accurate micro-characterization of aerinite pigment is reported by Pérez-Arantegui et al. <sup>[483]</sup>.

#### *Veszelyite*

Garcia Moreno et al. <sup>[484]</sup> <sup>[443]</sup> investigated the blue-green chromatic palette in early Classic and Late Classic periods in Calakmul (300–850 A.D.), including Maya Blue and Maya Green. In addition to copper based pigments like malachite or pseudomalachite, they identified veszelyite as a green pigment in blue-green mosaic, polychrome masks and funerary offerings from the royal tombs. Veszelyite is a rare secondary Cu-Zn mineral (hydrated copper-zinc phosphate,  $(\text{Cu},\text{Zn})_2\text{ZnPO}_4(\text{OH})_3\cdot 2(\text{H}_2\text{O})$ ), and this poses serious questions

about its origin. It is found together with malachite, pseudomalachite and even chrysocolla and it could be a degradation product of malachite.

#### *Vivianite*

Vivianite, hydrated ferrous phosphate,  $\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ , has been rarely used as a blue pigment and in mixtures with yellow to produce greens (Scott and Eggert<sup>[485]</sup>). Mined in areas north of the Alps, vivianite has been identified in about 70 works of art of the European medieval times. It can discolor to yellowish brown, by oxidation to  $\text{Fe}^{3+}$  containing species. A comprehensive review and discussion on vivianite has been made by Čermáková et al.<sup>[486] [487]</sup>. Magnesian vivianite seems to have been identified in a Roman camp near Fort Vechten, Utrecht, The Netherlands, by Kloprogge et al.<sup>[488]</sup>.

#### *Glaucofane – riebeckite*

Riebeckite and/or glaucofane, a blue mineral (composed of sodium magnesium (or iron) aluminum hydrosilicate) was used by the Greeks as a blue pigment as early as the 17<sup>th</sup> c. BC. Riebeckite  $\text{Na}_2\text{Fe}^{2+}_3\text{Fe}^{3+}_2\text{Si}_8\text{O}_{22}(\text{OH})_2$  is a hydrous silicate mineral of the amphibole group and forms a solid solution with glaucofane  $\text{Na}_2\text{Mg}_3\text{Al}_2\text{Si}_8\text{O}_{22}(\text{OH})_2$ . The colour depends on the relative concentration of iron/magnesium. Riebeckite may occur as a fibrous asbestiform mineral (crocidolite or blue asbestos) and is no longer used, being one of the most hazardous asbestiform minerals. Riebeckite (or Mg-riebeckite) was first identified as a blue pigment in the context of studies on Bronze Age wall paintings by Filippakis et al.<sup>[489]</sup>. Riebeckite is suggested as a pigment in a fresco painted plaster of Bronze Age from Thebes, Greece, by Brysbaert<sup>[490]</sup>. Westlake et al.<sup>[491]</sup> carried out a very accurate investigation on 49 wall painting samples from Minoan, Roman and Early Byzantine periods to determine the evolution of the painting materials and reported the presence of blue riebeckite. A study on blue glaucofane-riebeckite pigment on the Akrotiri is reported by Vlachopoulos and Sotiropoulou<sup>[492]</sup> and by Sotiropoulou et al.<sup>[493]</sup>, but no Raman analysis was performed.

### **Green pigments**

#### *Malachite*

Roman artists had a wide knowledge of green pigments, including verdigris, malachite and green earths. Malachite, a copper carbonate hydroxide mineral  $\text{Cu}_2\text{CO}_3(\text{OH})_2$ , is identified in many of the previously cited works on paintings and manuscripts. A particular result was reported by Castro et al.<sup>[494]</sup>: the formation of a copper oxalate (moolooite) in the degradation processes of malachite. Useful for the Raman investigation of malachite and its degradation products is a study of Yu et al.<sup>[495]</sup> on the characteristics of the Raman spectra of archaeological malachites (not pigments) compared with natural malachites from different mines.

#### *Green Earths*

The minerals responsible for the colour of green earths are types of clay micas, glauconite and celadonite. Also smectite, chlorite, serpentines and pyroxenes can be responsible for this colour. The most famous deposits of green earths can be found near Verona, Italy, as well as in Tyrol, Bohemia, Saxony, Poland, Hungary, France, Cyprus and England. Verona earth is made by celadonite found in basaltic rocks. However, the presence of glauconite cannot be excluded from a green earth pigment because it can be found in sandstone levels as a result of mixing between extrusive tertiary products with Eocene sediments (Aliatis et al.<sup>[496]</sup>). Celadonite and glauconite are minerals with a complex chemical structure, with large variations in composition, crystalline order and morphology. In particular, celadonite  $\text{K}(\text{Al}, \text{Fe}^{3+})(\text{Fe}^{2+}, \text{Mg})(\text{AlSi}_3, \text{Si}_4)\text{O}_{10}(\text{OH})_2$  presents a crystalline structure with a blue nuance whereas glauconite  $(\text{K}, \text{Na})(\text{Fe}^{3+}, \text{Al}, \text{Mg})_2(\text{Si}, \text{Al})_4\text{O}_{10}(\text{OH})_2$  has a structure less crystalline than celadonite and its colour is characterised by a yellow component, according to the Fe oxidation state (see Moretto et al.<sup>[497]</sup>). The similarity in the structure and composition of glauconite and celadonite makes the analytical distinction difficult (Genestar and Pons<sup>[498]</sup>). Sodium is present just in glauconite, characteristic that could, in principle, be exploited for its identification.

1  
2  
3 In a detailed Raman study of Byzantine overpainted icons of the 16<sup>th</sup> c., Daniilia et al. <sup>[499]</sup> identified green  
4 earth but the actual mineral was not specified. Goodall et al. <sup>[500]</sup>, investigating the multiple layered wall  
5 paintings from the Rosalila temple, Copan, Honduras, identified the green pigment as a celadonite-based  
6 green earth. Ospitali et al. <sup>[501]</sup> compared the Raman spectra of green earths from commercial sources and  
7 from some fragments of Roman frescoes from two archaeological sites in central Italy at Suasa (Ancona)  
8 and Pisaurum (Pesaro-Urbino). They showed that the Raman peaks in the range 260–280 cm<sup>-1</sup> are helpful  
9 to discriminate between celadonite (272–279 cm<sup>-1</sup>) and glauconite (263–266 cm<sup>-1</sup>). Green coloured  
10 samples on wall paintings and green powder from a pigment pot found in Pompeii area were investigated  
11 by Aliatis et al. <sup>[496]</sup>: here the mineralogical identification of the green earths was attempted through the  
12 comparison of the vibrational features which, in the low wavenumber region, help in discriminating  
13 between the two species. The more ordered structure of celadonite gives sharper features than those of  
14 glauconite. The green earth found in the Pompeii wall paintings fragments shows Raman spectra  
15 compatible with celadonite, even if the presence of glauconite cannot be excluded.

16  
17 Cristini et al. <sup>[502]</sup> studied the alterations of green earths from wall paintings in three different European  
18 sites (France, Rome and Greece) of the Roman Empire, dated in the 1<sup>st</sup> and 2<sup>nd</sup> c. AD. Samples from mural  
19 paintings from archaeological sites from North-East of Italy were investigated by Moretto et al. <sup>[497]</sup> by a  
20 multitechnique approach, by comparison with celadonite and glauconite standards. Interpretative  
21 uncertainties, however, excluded FT-Raman technique as a source of reliable information when celadonite  
22 and glauconite are mixed. The green pigments in Roman mural paintings, from the Patio de Banderas  
23 excavation in Seville Alcazar, explored by Perez Rodriguez et al. <sup>[503]</sup>, showed a complex situation: celadonite  
24 and glauconite are found, mixed together and with Egyptian Blue and Egyptian green. Chlorite and  
25 chromium oxide could also be responsible for the green colour.

26  
27 Gebremariam et al. <sup>[504]</sup> analysed wall paintings from the Petros and Paulos Church in Ethiopia. Talc, a  
28 chlorite mineral and dolomite were identified as the main components of the preparatory layer. Green  
29 earth like glauconite or clinocllore were suggested for the green colours. Pelosi et al. <sup>[505]</sup>, in a study on the  
30 wall paintings on the rock-hewn Church of the Forty Martyrs at Şahinefendi in Cappadocia (Turkey),  
31 detected green earths showing a Raman spectrum similar to that of celadonite (Ospitali et al. <sup>[501]</sup>).

#### 32 *Copper based pigments or degradation products?*

33  
34 The copper secondary minerals sulphates, chlorides, arsenates, carbonates are ubiquitous in the Raman  
35 spectra taken on green painted artworks. These “pigments” could be alteration products of a copper  
36 mineral such as malachite, azurite or of Verdigris but also original pigments derived from a natural mineral  
37 or artificial products of corrosion of brass or another copper alloy in acid conditions. The Raman  
38 investigations on these green mineral pigments faces usually with (Scott <sup>[506]</sup>): copper trihydroxychlorides  
39 (found as atacamite, paratacamite, clinoatacamite, and botallackite polymorphs), copper sulphates  
40 (brochantite, posnjakite, antlerite), copper arsenates (conichalcite, cornwallite, olivenite), copper/zinc  
41 carbonates (aurichalcite, rosasite).

42  
43 Atacamite Cu<sub>2</sub>Cl(OH)<sub>3</sub> is a rare mineral that forms as alteration product of copper minerals in arid climates.  
44 This compound has been commonly identified as a degradation product of copper pigments or of metallic  
45 objects containing copper, but it is considered often as an intentional pigment. Atacamite as a pigment  
46 seems mentioned in old treatises such as the De Diversis Artibus from the monk Theophilus <sup>[507]</sup> but there is  
47 yet no agreement on the use of copper chlorides as raw materials. Gilbert et al. <sup>[508]</sup> performed a detailed  
48 Raman investigation of green copper pigments in illuminated manuscripts (15<sup>th</sup> and 16<sup>th</sup> centuries from  
49 north-Europe and Italy) identifying several similar phases and in particular posnjakite CuSO<sub>4</sub>·3Cu(OH)<sub>2</sub>·H<sub>2</sub>O  
50 as pigments. A careful investigation on mineral greens of a decorative wallpaper and the detection of  
51 antlerite is described by Castro et al. <sup>[509]</sup>. A discrimination between copper trihydroxychlorides is reported  
52 by Bertolotti et al. <sup>[510]</sup>. Eremin et al. <sup>[511]</sup> in the Japanese masterpiece The Tale of Genji, an album with 54  
53 illustrations, found the hydrated copper chlorides, atacamite and botallackite, maybe alteration products of  
54 original malachite and chrysocola, a natural copper silicate.

55  
56 Lepot et al. <sup>[344]</sup> in a study of mural paintings of the Tournai Cathedral (Belgium) identified atacamite and  
57 posnjakite as pigments (intentionally used and not due to degradation processes). Bidaud et al. <sup>[512]</sup>

1  
2  
3 identified clinoptacumite as a pigment by SEM-EDS and XRD in the 13<sup>th</sup> c. wall painting in the city castle in  
4 Krems, Lower Austria. Castro et al. <sup>[509]</sup> studied a bleu coloured map from the 17<sup>th</sup> c. and discussed about  
5 the presence of atacamite as pigment or as a degradation product: a molar relationship between copper  
6 and chlorine (1:1) suggested atacamite as a raw material.

7  
8 The use of atacamite as a green pigment seems not only limited to mural paintings. Through micro-Raman  
9 spectroscopy, Burgio et al. <sup>[513]</sup> and Muralha et al. <sup>[248]</sup> identified the pigments in Islamic religion manuscripts  
10 of the 16<sup>th</sup>-18<sup>th</sup> c., held at the Victoria and Albert Museum, and explicitly mentioned atacamite as an  
11 intentional pigment.

12 Campos-Sunol et al. <sup>[514]</sup>, on a polychromy on an exterior sculpted stone, identified a green pigment based  
13 on copper chlorides. Wei et al. <sup>[515]</sup> found atacamite in the wall paintings of a Ming Dynasty Dazhao Temple  
14 in Hohhot, Inner Mongolia of China. Tomasini et al. <sup>[516]</sup> recognized atacamite as a natural pigment in a  
15 South American colonial polychrome sculpture from the late 16<sup>th</sup> c. On mural paintings of Ala di Stura  
16 (Piedmont, Italy), Aceto et al. <sup>[395]</sup> evidenced the degradation of azurite to copper oxychlorides (atacamite  
17 or paratacamite) and reported green colours obtained by green earths (celadonite) and arsenic-containing  
18 green pigments (probably a mixture of olivenite  $\text{Cu}_2(\text{AsO}_4)(\text{OH})$ , cornwallite  $\text{Cu}_5(\text{AsO}_4)_2(\text{OH})_4$  or conichalcite  
19  $\text{CaCu}(\text{AsO}_4)(\text{OH})$  (Fig.11).

#### 20 21 **FIGURE 11.**

22  
23 Yong <sup>[517]</sup> proposed, by the analysis of pigments in the Forbidden City (Beijing) and some architectural  
24 pigments in Gansu, Northwest China, that the most popular green pigment for wall painting and  
25 architecture might be copper trihydroxychloride, rather than malachite, in the period from North Dynasty  
26 (386–581 CE) until late Qing Dynasty (1840–1911 CE). A mixed use of malachite and atacamite has been  
27 revealed in three green samples of a sculptural polychromy in the Zhongshan Grottoes, China, by Cauzzi et  
28 al. <sup>[518]</sup>: a synthetic origin of the copper compounds is proposed by their optical characteristics. Egel and  
29 Simon <sup>[519]</sup>, in an investigation of the painting materials in Zhongshan Grottoes (Shaanxi, China) identified in  
30 a green paint layer the mineral botallackite as an intentional pigments. A botallackite pigment was  
31 proposed also by Hu et al. <sup>[520]</sup>, studying the painting techniques and materials of the murals in the Five  
32 Northern Provinces Assembly Hall, Ziyang, China.

33  
34 Dominguez-Vidal et al. <sup>[521]</sup>, investigating the decorated plasterwork on the stalactite vaults of the Hall of  
35 the Kings in the Alhambra (Granada, Spain), evidenced azurite severely degraded to clinoptacumite.  
36 Švarcová et al. <sup>[522]</sup> attempted to differentiate copper pigments in paint layers of works of art by Raman  
37 spectroscopy in spite of the large fluorescence. Buzgar et al. <sup>[482]</sup> reported a series of copper compounds  
38 (pigments) in the wall paintings of the Voronet Monastery in Romania (16<sup>th</sup> c.), including atacamite,  
39 posnjakite and conichalcite ( $\text{CaCu}(\text{AsO}_4)(\text{OH})$ ).

40  
41 Valadas et al. <sup>[523]</sup> reported an intentional use of brochantite on 16<sup>th</sup> c. Portuguese-Flemish paintings  
42 attributed to the Master Frei Carlos workshop. Zhang et al. <sup>[524]</sup> identified atacamite as green pigment in the  
43 murals and sculptures in Mogao Grottoes. Wall paintings of Ottoman Fatih Mosque in Istanbul  
44 (reconstructed in 1770 and then restored) were studied by Akyuz et al. <sup>[525]</sup>. For the green colours they  
45 found a mixture of celadonite and glauconite, as both celadonite ( $277\text{ cm}^{-1}$ ) and glauconite ( $265\text{ cm}^{-1}$ ) peaks  
46 were identified in the Raman spectrum. They suggest also the intentional use of brochantite  $\{\text{CuSO}_4 \cdot$   
47  $3\text{Cu}(\text{OH})_2\}$  as pigment.

48  
49 Aliatis et al. <sup>[526]</sup> revealed the presence of copper arsenates in a green pigment found in a bowl during  
50 Pompei excavations, whereas Baraldi et al. <sup>[527]</sup> identified agardite, a group of hydrous hydrated arsenates  
51 of rare earth elements and copper, in fragments of a fresco painting from San Francesco Basilica, Assisi.  
52 Zeng et al. <sup>[528]</sup> identified as cornwallite  $\text{Cu}_5(\text{AsO}_4)_2(\text{OH})_4 \cdot (\text{H}_2\text{O})$ , and not as a synthetic green pigment, a  
53 copper arsenate on the shrine of Kaiping Diaolou (China, 20<sup>th</sup> c.).

54  
55 Aurichalcite  $(\text{Zn,Cu})_5(\text{CO}_3)_2(\text{OH})_6$  is reported as a green pigment by Klisińska-Kopacz <sup>[529]</sup> in a study on a 17<sup>th</sup>  
56 c. painted silk banner. Rosasite  $(\text{Cu,Zn})_2(\text{CO}_3)(\text{OH})_2$  has never been reported as pigment, but its discovery in  
57 the Darhib Mine, Egypt (Gatto Rotondo et al. <sup>[530]</sup>) is a good sign that soon it will appear in an artwork,  
58 perhaps Egyptian !  
59

## Yellow pigments

### Jarosite

Jarosite, an iron sulphate  $XFe_3(SO_4)_2(OH)_6$ , where X is usually a monovalent cation such as  $Na^+$  or  $K^+$ , is rarely found as a pigment. Jarosite was probably used in close association with natural iron ochre, but it was also possibly chosen due its distinctive hue. Jarosite has been identified in excavated prehistoric pigments by Dachuk et al. [213] and by Ambers [531] in ancient Egyptian paintings. Buzgar et al. [532] investigated fragments of a wall painting in Graeco-Roman contexts from the Beroe fortress, Romania (4<sup>th</sup>–6<sup>th</sup> c.) and identified a yellow-brown pigment as K-jarosite  $KFe^{3+}_3(OH)_6(SO_4)_2$  and/or Na-jarosite. Sepúlveda et al. [533] studied yellow blocks from the archaeological site Playa Miller 7 (PLM7), on the coast of Atacama Desert in northern Chile, and reported the use of K-jarosite and natrojarosite in prehispanic times (approx. 2500 year BP). Pelosi et al. [534], by micro-Raman analysis, revealed the presence of jarosite in wall paintings in Cappadocia (Turkey).

### Crocoite – Phoenicochroite - Hemihedrite

Chrome yellow,  $PbCrO_4$ , was made available commercially at the beginning of the 19<sup>th</sup> c. Lead chromate  $PbCrO_4$  occurs naturally as the reddish mineral crocoite but it is so rare that it is unlikely to find crocoite on an artwork (Edwards et al. [265]). Synthetic chrome orange,  $Pb_2CrO_5$  or  $PbCrO_4.PbO$ , has its equivalent in nature in the rare mineral phoenicochroite (Correia et al. [268] [267], Monico et al. [535]). Mugnaini et al. 2006 [536] [537] claim the use of crocoite ( $PbCrO_4$ ) as a natural pigment in the 13<sup>th</sup> c. wall paintings found under the Siena (Italy) Cathedral. They also report chrysocola, very unusual for European medieval paintings. Hradil et al. [538] identified natural crocoite by Raman micro-spectroscopy in wall paintings dated around 1300 in Kuřívody, Northern Bohemia, and claimed that it was used intentionally as yellow pigment. Abdel-Ghani and Mahmoud [539] reported a Raman study on the pigments on Sabil-Kuttab Umm 'Abbas ceiling, Mohammed Ali Era in Cairo, Egypt, and identified the chromate mineral hemihedrite ( $ZnPb_{10}(CrO_4)_6(SiO_4)_2F_2$ ) claiming that this unusual pigment was detected for the first time as an artistic pigment. This is a very rare mineral. The Raman spectrum reported corresponds however to the spectrum of phoenicochroite or more probably to the corresponding synthetic pigment chrome orange. A modern retouching could be less unusual. Edwards et al. [540] in a study of an important English oil painting of the 18<sup>th</sup> c. identified the hemihedrite mineral, but the reported Raman spectrum fits again well that of phoenicochroite or chrome orange, suggesting a more probable late retouching. Bellini et al. [541] reported accurate Raman spectra of crocoite, phoenicochroite and hemihedrite crystals, including the low-wavenumber region, usually not reported in literature (Fig.12). The Raman spectra of the three chromate crystals have characteristic features that allow a definite identification of the minerals species. This should avoid incorrect identification of exotic chromate species as hemihedrite for chrome orange. The spectrum of chrome orange is reported also by Zmuda-Trzebiatowska et al. [294] from artist palette of J. Matejko (1838–1893).

### FIGURE 12.

### Ochres (red-yellow)

Raman microscopy has been extensively used to identify the minerals in ochres, discussing the dependence of the Raman spectra on the laser power and wavelength and the particle size effects on the phase transformations. In particular, the identification of magnetite when hematite is present through the Raman peak at about  $660\text{ cm}^{-1}$  is still an open question, evoked in many papers on pigments. Ochres are generally divided in two large groups: red ochres (the main pigment is hematite, anhydrous iron oxide) and yellow ochres (characterized by goethite, a hydrous ferric oxide). Ochres always contain silicates. The colour of the ochre is not only determined by the hematite content, but also by other minerals. Grain (or crystal) size may also influence the colour. Specific Raman investigations on the red-yellow ochres include the following contributions: de Faria et al. [542], Bikiaris et al. [543], Bersani et al. [54], de Oliveira et al. [544], Hradil et al. [545], De Faria and Lopes [59], Chernyshova et al. [546], Legodi and de Waal [547], Hradil et al. [548], Palacios et al. [549]. Froment et al. [550] investigated about 50 natural or treated red to yellow ochre pigments and their secondary phases, discussing on possible provenance criteria. Montagner et al. [551] identified ochres

1  
2  
3 containing kaolinite matrix and/or sulfate matrix from ochres where only iron oxides and/or hydroxides  
4 were detected.

### 5 **Black pigments**

7 Appolonia <sup>[552]</sup> analysed Mural Paintings in the Aosta Valley (Italy) and found graphite as black pigment  
8 rather than wood or lamp carbon, related to the presence of graphite deposits in the region.

9  
10 Trentelman and Turner <sup>[553]</sup>, in a manuscript dating to the early 1480s of French artist Jean Bourdichon,  
11 found bismuth black (granular elemental bismuth) as a pigment (Fig.13). Metallic bismuth in Bourdichon  
12 miniatures was found also by Burgio et al. <sup>[242]</sup>. Trentelman <sup>[554]</sup> examined bismuth black pigments  
13 comparing the spectra of powdered metallic bismuth, Bi<sub>2</sub>S<sub>3</sub> and α-Bi<sub>2</sub>O<sub>3</sub> under different excitation  
14 wavelengths and laser powers.

### 15 **FIGURE 13.**

17 Centeno et al. <sup>[51]</sup> studied, by a multi-technique approach, the surface decorations in selected pottery wares  
18 from two Prehispanic archaeological sites in Northwestern (NW) Argentina, dating to the Inca period (AD  
19 900–1530): they found iron manganese spinel jacobite, (Mn<sup>2+</sup>,Fe<sup>2+</sup>, Mg)(Fe<sup>3+</sup>,Mn<sup>3+</sup>)<sub>2</sub>O<sub>4</sub>, as the main  
20 component of the fired black decorations. Buzgar et al. <sup>[555]</sup> <sup>[556]</sup> found mainly pyrolusite (MnO<sub>2</sub>) and  
21 jacobite in the black pigment in Cucuteni pottery painting (Neolithic Age, Romania). Jacobite could form  
22 by firing, under oxidizing conditions, manganese and iron-rich clay slips. Some suggestions are given about  
23 the provenance of the minerals.

25 Caggiani and Colombari <sup>[91]</sup> investigated the best experimental conditions for the identification of the black  
26 pigments in glazed ceramics (manganese oxides, cobalt oxides, hematite, magnetite and their mixtures).

27  
28 Tomasini et al. <sup>[87]</sup> <sup>[557]</sup> analysed commercial carbon-based black pigments and tried to find Raman spectral  
29 parameters discriminating between them. Tomasini et al. <sup>[558]</sup> identified, by Raman microscopy, black  
30 pigments in four 18<sup>th</sup> c. Jesuit wooden sculptures. It is very difficult to discriminate the source of carbon-  
31 based pigments from their very similar Raman spectra. According to the authors, the combined analysis of  
32 Raman spectral parameters (width, position and intensity of G and D bands) allows the identification of  
33 bistre, wood charcoal lampblack, and a humic earth pigment. Coccato et al. <sup>[89]</sup> discuss the carbon Raman  
34 signatures of many carbon based pigments, attempting to give some hints for their identification.

35  
36 Black earths are natural dark earth pigments of varying composition. There are varieties composed of coal,  
37 manganese black, stibnite, bismuth, galena and tin-rich bronze powder (Spring et al. <sup>[559]</sup>, Cavallo and  
38 Gianoli Barioni <sup>[560]</sup>). Despite of the historical evidences attesting the use of black earths as painting  
39 materials in both a fresco and a secco techniques, there is very little analytical proof of their use as painting  
40 material on architectural surfaces and no specific Raman investigation has been reported.

41  
42 Tomasini et al. <sup>[561]</sup> identified pyroxene minerals used as black pigments in painted human bones excavated  
43 in Northern Patagonia. On the skeleton of a male painted with parallel lines alternating red and black  
44 colours, excavated in a secondary burial context in the site of Cima de los Huesos, in the San Matías Gulf  
45 (Río Negro, Argentina), Raman and XDR show hematite in the red pigment and ferrosilite (FeSiO<sub>3</sub>) and  
46 enstatite (MgSiO<sub>3</sub>) pyroxenes along with kanoite (MnMgSi<sub>2</sub>O<sub>6</sub>) for the black colour.

47  
48 Ay et al. <sup>[562]</sup> reported on the black pigment material excavated at the cemetery in Müslümantepe, located  
49 in Upper Tigris, and dating to the Early Bronze Age. It was most likely used for cosmetic purposes: the major  
50 component was found to be pyrolusite, together with calcite and quartz.

51  
52 Iron oxide minerals and/or structurally disordered graphite consistent with a charred vegetable substance  
53 were found by Raman microscopy by van der Weerd <sup>[47]</sup> as black pigments on prehistoric Southwest  
54 American potsherds of the Ancestral Puebloan period.

### 55 **Darkening and photo-degradation**

56 *Cinnabar*

1  
2  
3 Colour degradation of paintworks induced by the action of light is an important issue and attracts the  
4 attention of spectroscopists. The light-induced darkening of vermilion (red mercury (II) sulfide  $\alpha$ -HgS,  
5 mineral cinnabar in nature) involves historical museum paintings and murals at archaeological sites  
6 worldwide (Noller et al. <sup>[563]</sup>). Chlorine plays a dominant role in the darkening process of  $\alpha$ -HgS, but the  
7 exact mechanism is not yet completely clear (Radeponet et al. <sup>[564]</sup>, Cotte et al. <sup>[565]</sup>). The occurrence of  
8 secondary compounds ( $\text{Hg}_3\text{S}_2\text{Cl}_2$  polymorphs,  $\text{Hg}_2\text{Cl}_2$  and  $\text{HgCl}_2$ ) during the transformation of vermilion is  
9 confirmed by X-ray spectroscopy (Hogan and da Pieve <sup>[566]</sup>).

#### 11 *Lead white and red lead*

12 The darkening of lead-containing pigments, namely red lead and lead white, is a widespread phenomenon  
13 in artworks: the degradation products are usually identified (or proposed) as plattnerite (lead (IV) oxide,  
14  $\text{PbO}_2$ ) or galena (lead (II) sulphide,  $\text{PbS}$ ). The "natural" degradation of white lead has been largely  
15 investigated by Raman (see for a review, Lussier and Smith <sup>[567]</sup>) attempting to discriminate between lead(II)  
16 sulfide (galena,  $\text{PbS}$ ), plattnerite ( $\text{PbO}_2$ ), or metallic lead ( $\text{Pb}^0$ ).

18 Burgio et al. <sup>[568]</sup> and Smith et al. <sup>[569]</sup> pointed out the problem of laser-induced degradation of lead pigments  
19 (lead white and red lead) in art conservation studies. Raman spectroscopy of black degradation products is  
20 difficult as dark materials absorb both incident and Raman-scattered light. This strong absorption can  
21 induce thermal or photo-oxidative transformation and in the past wrong identifications have been  
22 reported. The Raman spectrum from weathered and blackened lead white on the surface of a manuscript  
23 at low laser excitation was taken by Smith and Clark <sup>[570]</sup>. The direct identification by Raman microscopy of  
24  $\text{PbS}$  as a degradation product of lead white on manuscripts was erroneous as both the samples and the  
25 reference were photodegraded to a sulphate species (Clark and Gibbs <sup>[571]</sup> <sup>[572]</sup>, Burgio et al. <sup>[573]</sup>). Red lead  
26 transforms into plattnerite ( $\beta$ - $\text{PbO}_2$ ) and also in anglesite  $\text{PbSO}_4$ : the alteration process is controlled by  
27 environmental parameters.

29 The identification of plattnerite is not an easy task (Andalò <sup>[574]</sup>). Orthorhombic  $\text{PbO}$  (lead II oxide massicot)  
30 is easily photogenerated, presumably through the sequence plattnerite ( $\text{PbO}_2$ )  $\rightarrow$  minium ( $\text{Pb}_3\text{O}_4$ )  $\rightarrow$   
31 litharge (tetragonal  $\text{PbO}$ )  $\rightarrow$  massicot (orthorhombic  $\text{PbO}$ ) and  $\text{PbO}_2$  escapes observation (Smith et al. <sup>[569]</sup>,  
32 Burgio et al. <sup>[568]</sup>). Daniilia et al. <sup>[575]</sup> <sup>[576]</sup> in a study of wall paintings at the Cypriot Monastery of Christ  
33 Antiphonitis reported a detailed identification of pigments. The degradation of red lead from orange  $\text{Pb}_3\text{O}_4$   
34 to black plattnerite  $\text{PbO}_2$  is confirmed by its Raman spectrum. The chromatic alterations (blackening) of  
35 lead pigments (red lead and white lead) have extensively been investigated by Raman spectroscopy (Aze  
36 <sup>[577]</sup> and Aze et al. <sup>[350]</sup>, Rosado et al. <sup>[578]</sup>). De Santis et al. <sup>[323]</sup>, investigating fragments of the painted  
37 terracotta by Michele Todini, identified indirectly  $\text{PbO}_2$  as a black degradation of lead white through its  
38 laser degradation to  $\text{PbO}$ . The degradation of St. Euthymius byzantine wall paintings, in the Cathedral of  
39 Thessaloniki, was studied by Sotiropoulou et al. <sup>[579]</sup>: black tenorite  $\text{CuO}$  was found as a degradation product  
40 of azurite, evidenced by the darkening of the blue shades on the Virgin's mantlet. The alteration of orange  
41 minium ( $\text{Pb}_3\text{O}_4$ ) gives no plattnerite evidence in the Raman spectrum.

44 Kotulanová et al. <sup>[580]</sup> analysed in laboratory the interactions of lead-based pigments (lead white, massicot,  
45 red lead) with a number of inorganic salts, degradation agents of wall paintings, and identified  $\text{PbMg}(\text{CO}_3)_2$   
46 in the degradation products. The results should help in the understanding of the degradation of lead white  
47 (hydrocerussite) and red lead (minium). On 11<sup>th</sup> c. frescoes from the church of Saint George in Kostofány  
48 pod Tribečom, the oldest preserved wall paintings in Slovakia, they found plattnerite by XRD, confirming  
49 the red lead degradation.

51 On several samples from mural paintings of Ala di Stura (Piedmont, Italy), Aceto et al. <sup>[395]</sup> explored the  
52 chromatic alteration phenomena of lead pigments. The conversion of lead white  $\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$  to galena  
53 was not observed but they evidenced the conversion of red lead to plattnerite. The formation of  $\text{PbO}_2$  from  
54 white lead seems to be much more frequent than formation of lead sulfide. The possibility of lead white  
55 blackening through Bacteria capable of converting lead white into  $\text{PbO}_2$  has been proposed by Petushkova  
56 and Lyalikova <sup>[581]</sup>. Recently, a diffuse presence of plattnerite but not of sulphur bearing compounds was  
57 found by Costantini et al. <sup>[582]</sup>. The study was accomplished on degraded areas originally containing white  
58 lead, in a fresco of the castle chapel of St. Stephen in Morter, Italy, called the Sistine Chapel of Val Venosta.

The hypothesis of a lead white blackening through microbiological processes cannot in this case be discarded. The plattnerite spectrum is reported by Costantini et al.<sup>[582]</sup> up to low Raman wavenumbers. Gutman et al.<sup>[583]</sup> characterized the pigments in the newly discovered wall painting at the Dominican Monastery in Ptuj (Slovenia) and reported the darkening of the red lead areas into a black or brown plattnerite. The reported “characteristic” Raman band of plattnerite at  $521\text{ cm}^{-1}$ , is however too sharp (it is like a pure silicon spectrum !) and does not correspond to any published or reported plattnerite Raman spectrum (Burgio et al.<sup>[568]</sup>, Costantini et al.<sup>[582]</sup>). A peculiar result was found by Miguel et al.<sup>[584]</sup> studying the mechanisms of degradation in a medieval Portuguese codex, the Lorvao Apocalypse (1189), by Raman microscopy and micro-X-ray diffraction: the degradation of red lead was attributed to its reaction with orpiment, a lead arsenate compound being the main degradation product.

Inorganic pigments used in three 17<sup>th</sup> c. hand-coloured maps of Dutch manufacture, two of Portugal and one of the Iberian Peninsula, were studied by Mendes et al.<sup>[585]</sup>. A “mineral” was found in all the green areas: a copper oxalate, moolooite ( $\text{Cu}(\text{C}_2\text{O}_4)\cdot n\text{H}_2\text{O}$  ( $n < 1$ ), presumably a product of the degradation of Verdigris (Fig.14).

#### FIGURE 14.

##### *Realgar, pararealgar and orpiment*

Brightly coloured arsenic-sulphide minerals (realgar  $\text{As}_4\text{S}_4$ , pararealgar and orpiment  $\text{As}_2\text{S}_3$ ) ranging from red to orange or yellow have been largely used as pigments. They have been found, on Ancient Egyptian funerary papyri, medieval illuminated manuscripts and Greek icons. Orpiment and realgar are well known for their instability over time and their tendency to be altered by light. Realgar exposed to light degrades first to an orange product ( $\chi$ -realgar), then to deep yellow pararealgar. The product of complete photodegradation is arsenolite ( $\text{As}_2\text{O}_3$ ) which is also the product of the fading of orpiment: the final appearance of the fading of both pigments is colourless or white. The various phases/polymorphs of arsenic sulphides (orange-red natural realgar  $\alpha$ -AsS (or  $\alpha$ - $\text{As}_4\text{S}_4$ ), the high temperature form  $\beta$ -AsS, now found as mineral bonazziite, the intermediate  $\chi$ -phase, the yellow- orange light-induced polymorph pararealgar, the yellow orpiment  $\text{As}_2\text{S}_3$ ) and their complex photoinduced transformations have been studied by Raman spectroscopy over a period of more than 40 years (see for example, Bonazzi et al.<sup>[586]</sup> and Bindi et al.<sup>[587]</sup>). All phases, but  $\beta$ -AsS, have been identified in works of art using Raman spectroscopy (Trentelmann et al.<sup>[588]</sup>, Clark and Gibbs<sup>[571]</sup>, Vandenabeele et al.<sup>[589]</sup>, Edwards et al.<sup>[590]</sup>, David et al.<sup>[591]</sup>, Burgio et al.<sup>[592]</sup>, Vandenabeele and Moens<sup>[593]</sup>, Mazzeo et al.<sup>[349]</sup>, Daniels and Leach<sup>[594]</sup>, Burgio et al.<sup>[595]</sup>, Burgio et al.<sup>[513]</sup>, Murahla et al.<sup>[248]</sup>, Tanevska et al.<sup>[255]</sup>). It is possible that pararealgar was prepared and used as a pigment. The effect of different light sources on the realgar photo-degradation was investigated by Raman spectroscopy by Macchia et al.<sup>[596]</sup>. The complex light induced transformations of realgar are discussed in a recent paper by Pratesi and Zoppi<sup>[597]</sup>.

Orpiment, toxic yellow arsenic sulfide mineral, was revealed by Ogalde et al.<sup>[598]</sup> in an archaeological context from Chorrillos cemetery (Calama, Chile) dating 8<sup>th</sup>-2<sup>nd</sup> c. BC. The pigment sample was found in a mollusk shell that was part of the grave goods associated with a female individual. Orpiment was detected also in a 9<sup>th</sup> c. manuscript by Aceto et al.<sup>[233]</sup>, by Campos-Sunol<sup>[599]</sup> in the portal of a church of the 16<sup>th</sup> c., in a medieval manuscript by Miguel et al.<sup>[584]</sup>. El Bakkali<sup>[600]</sup>, in a study of coloring materials in ancient Moroccan Islamic manuscripts, found a mix of orpiment and indigo to produce shades of green (vergaut), a procedure employed in the Islamic world in the 14<sup>th</sup> c. Vergaut was also hypothesized by Bioletti et al.<sup>[234]</sup> in “The Book of Kells”, Trinity College Dublin MS 58, and by Aceto et al.<sup>[246]</sup> in Byzantine 6<sup>th</sup> c. manuscripts. Recently, Vermeulen et al.<sup>[601]</sup> identified an amorphous arsenic sulfide glass ( $\text{As}_x\text{S}_x$ ), synthesized from arsenic trioxide and sulfur, in the interior decorations of the Japanese tower in Laeken, Brussels, Belgium. Artificial arsenic sulphide pigments which were identified in artworks have been explored by Grundmann and Richter<sup>[602]</sup>, Grundmann et al.<sup>[603]</sup>, Grundmann and Richter<sup>[604]</sup>.

##### **Unusual mineral pigments**

Holakooei and Karimy<sup>[605]</sup> examined early Islamic pigments used at the Masjid-i Jame of Fahraj, central Iran. They identified a black paint mainly composed of black plattnerite mixed with mimetite  $\text{Pb}_5(\text{AsO}_4)_3\text{Cl}$ ,

hemimorphite  $Zn_4(OH)_2Si_2O_7 \cdot 7H_2O$  and galena and supposed that black plattnerite was most probably used as a pigment and not formed as a degradation product of lead-based pigments. A cave at about 35 km could have supplied the mineral. More investigations seem however necessary to confirm the intentional use of plattnerite as a pigment.

The white pigment (Melian-earth) of the famous painter Apelles was attributed to a  $TiO_2$  rich Kaolin by Katsaros et al. <sup>[606]</sup> even if, for a misprinting, the Raman spectrum they reported suggests rutile and not anatase.

Naturally irradiated violet fluorite, called antozonite, is a rare historic pigment. The irradiation is caused by uranium or thorium-rich minerals coexisting with fluorite in certain geological settings. Purple-violet fluorite has been identified on a small number of panel paintings, polychrome wooden sculptures, wall paintings and architectural polychromy of the 1450 to 1520 period in central Europe (Richter et al. <sup>[607]</sup>, Srein <sup>[608]</sup>, Chlumska et al. <sup>[609]</sup>). The fluorite was probably mined from the area of Wölsendorf in Bavaria. The first Raman spectroscopy identification of violet fluorite pigment was reported by Banerjee et al. <sup>[610]</sup> in the polychrome colour layers of a sculpture dated the end of the 15<sup>th</sup> c. Dáňová et al. <sup>[611]</sup>, in a Raman study of the late Gothic polychromy of the Nativity Relief from The Corona Sanctae Mariae Monastery in Třebořov, Moravia, reported the use of purple fluorite in the under-painting beneath the strong azurite layer on the reverse of the cloak of the Virgin Mary.

Two samples of purple fluorite from an altarpiece of the Triptych with St. James the Lesser and St. Philip (dated 1497) located in the chapel of St. Wenceslas and Ladislaus in Italian Court, Kutná Hora, Czech Republic, was compared with sixteen samples of mineral antozonite by Čermáková <sup>[612]</sup> using five different Raman excitation wavelengths (Fig.15).

#### FIGURE 15.

Aceto et al. <sup>[395]</sup> suggested the use of skutterudite  $(Co,Ni)_xAs_{3-x}$  as a mineral source for cobalt, to be used for the production of smalt, found in wall paintings in val di Stura, Piedmont, Italy. Skutterudite could have been excavated from Punta Corna mine, in the nearby valley of Viù.

The pigments used in pre-17<sup>th</sup> c. wall paintings of the Masjid-i Jame of Abarqu, central Iran, were identified by Holakooei and Karimy <sup>[613]</sup>: atacamite, red lead and smalt for green, red and blue, respectively, mixed with natural ultramarine blue and applied on a white substrate composed of huntite  $CaMg_3(CO_3)_4$ , reported for the first time in Persian mural paintings, but well known to the Egyptians. Raman spectra seem to indicate glushinskite, a magnesium oxalate  $(MgC_2O_4) \cdot 2H_2O$ , identified as a degradation product of the white huntite. In addition, they emphasized not only the use of atacamite as pigment but also claimed that the mineral woodhouseite  $(CaAl_3(PO_4,SO_4)_2(OH)_6)$  could be used as a pigment. Glushinskite was reported as a possible white pigment in the paintings of the Church of San Fiorenzo in Bastia Mondovì, Piedmont, Italy by Chiari and Scott <sup>[614]</sup>.

## CONCLUSIONS

This work aims to be a **review** of the most recent contributions of the Raman spectroscopy to the study of minerals and mineral pigments of relevance in Archaeometry and more generally for Cultural Heritage. About six hundred references, mainly in the last decade, demonstrate the large and increasing interest of the scientific community, especially from new geographical areas. In many fields as gemmology or pigments identification, Raman spectroscopy has become a standard technique. A routine use of the Raman technique, however, exacerbated by the spread of "portable" Raman equipments, must be accompanied by the use of the skills and knowledge of physics, chemistry and mineralogy. Works carried out only on the basis of automated Raman databases, without careful comparison with literature and without suitable knowledge of the materials, could lead to wrong identifications, especially when attempting to identify rare or strange phases. Actually, a surprising high number of rare crystalline phases are found in different kind of art and archaeological objects, even if in some cases their presence should be considered as accidental. Many recent works are pointing the attention on the large amount of data which is possible to harvest in a

1  
2  
3 short time when analysing museum objects with portable instruments. On the other hand, works carried  
4 out with high resolution laboratory spectrometer are showing how it is possible to deepen the knowledge  
5 of artistic and archaeological objects using Raman spectroscopy. The detailed study of the mineral phases is  
6 receiving a new impulse by the new generation of software based on DFT approach, allowing a very good  
7 simulation of the Raman spectra. The Raman data processing is starting to take advantage from  
8 chemiometry, even if multivariate analysis is not so diffuse as other analytical techniques and often limited  
9 to Raman map analysis.  
10  
11  
12  
13  
14  
15  
16  
17  
18  
19  
20  
21  
22  
23  
24  
25  
26  
27  
28  
29  
30  
31  
32  
33  
34  
35  
36  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60

For Peer Review

## REFERENCES

- [1] J.M. Madariaga, *J. Raman Spectrosc.* **2010**; *41*, 1389.
- [2] D. Bersani, J.M. Madariaga, *J. Raman Spectrosc.* **2012**; *43*, 1523.
- [3] P. Ropret, J.M. Madariaga, *J. Raman Spectrosc.* **2014**; *45*, 985.
- [4] G.D. Smith, R.J.. H. Clark, *J. Archaeol. Sci.* **2004**; *31*, 1137.
- [5] D.C. Smith, *Spectrochim. Acta - Part A Mol. Biomol. Spectrosc.* **2005**; *61*, 2299.
- [6] D.C. Smith, *Geol. Soc. London, Spec. Publ.* **2006**; *257*, 9.
- [7] C. Fotakis, D. Anglos, V. Zafiropulos, S. Georgiou, V. Tornari, *Lasers in the Preservation of Cultural Heritage: Principles and Applications*, CRC Press - Taylor & Francis, 2006.
- [8] P. Vandenabeele, H.G.M. Edwards, L. Moens, *Chem. Rev.* **2007**; *107*, 675.
- [9] D. Bersani, P.P. Lottici, *Anal. Bioanal. Chem.* **2010**; *397*, 2631.
- [10] R.J.H. Clark, *Chem. New Zeal.* **2011**; *75*, 13.
- [11] P. Colomban, *J. Raman Spectrosc.* **2012**; *43*, 1529.
- [12] C.C. Ferrón, S.E.J. Villar, F.M. Soto, J.L. Navarrete, V. Hernández, in *The Conservation of Subterranean Cultural Heritage*, Ed. by C. Saiz-Jimenez, CRC Press, Pages 281–292, Taylor and Francis Group, London, **2014**.
- [13] P. Vandenabeele, H.G.M. Edwards, J. Jehlička, *Chem. Soc. Rev.* **2014**; *43*, 2628.
- [14] J.M. Madariaga, *Anal. Methods* **2015**; *7*, 4848.
- [15] N. Buzgar, G. Bodi, A. Buzatu, A. Ionu, **2013**; *59*, 41.
- [16] B. Wopenka, R. Popelka, J.D. Pasteris, S. Rotroff, *Appl. Spectrosc.* **2002**; *56*, 1320.
- [17] J. Zuo, C. Xu, C. Wang, Z. Yushi, *J. Raman Spectrosc.* **1999**; *30*, 1053.
- [18] M. Sendova, V. Zhelyaskov, M. Scalera, M. Ramsey, *J. Raman Spectrosc.* **2005**; *36*, 829.
- [19] R. Alaimo, G. Bultrini, I. Eragalà, R. Giarrusso, I. Iliopoulos, G. Montana, *Appl. Phys. A Mater. Sci. Process.* **2004**; *79*, 221.
- [20] I. Cianchetta, J. Maish, D. Saunders, M. Walton, A. Mehta, B. Foran, K. Trentelman, *J. Raman Spectrosc.* **2015**; *46*, 996.
- [21] L. Medeghini, S. Mignardi, C. De Vito, D. Bersani, P.P. Lottici, M. Turetta, M. Sala, L. Nigro, *Anal. Methods* **2013**; *5*, 6622.

- 1  
2  
3 [22] G. Simsek, P. Colomban, S. Wong, B. Zhao, A. Rougeulle, N.Q. Liem, *J. Cult. Herit.* **2015**; *16*, 159.  
4  
5 [23] C. Ricci, I. Borgia, B.G. Brunetti, A. Sgamellotti, B. Fabbri, M.C. Burla, G. Polidori, *Archaeometry* **2005**;  
6 *47*, 557.  
7  
8 [24] M. A. Legodi, D. de Waal, *Spectrochim. Acta - Part A Mol. Biomol. Spectrosc.* **2007**; *66*, 135.  
9  
10 [25] D. Bersani, P.P. Lottici, S. Virgenti, A. Sodo, G. Malvestuto, A. Botti, E. Salvioli-Mariani, M.  
11 Tribaudino, F. Ospitali, M. Catarsi, *J. Raman Spectrosc.* **2010**; *41*, 1556.  
12  
13 [26] M.J. Ayora-Cañada, A. Domínguez-Arranz, A. Dominguez-Vidal, *J. Raman Spectrosc.* **2012**; *43*, 317.  
14  
15 [27] S. Akyuz, T. Akyuz, S. Basaran, C. Bolcal, A. Gulec, *Vib. Spectrosc.* **2008**; *48*, 276.  
16  
17 [28] P. Comodi, M. Bernardi, A. Bentivoglio, G.D. Gatta, P.F. Zanazzi, *Archaeometry* **2004**; *3*, 405.  
18  
19 [29] P. Colomban, G. Sagon, X. Faurel, *J. Raman Spectrosc.* **2001**; *32*, 351.  
20  
21 [30] D. Tenorio, M.G. Almazán-Torres, F. Monroy-Guzmán, N.L. Rodríguez-García, L.C. Longoria, *J.*  
22 *Radioanal. Nucl. Chem.* **2005**; *266*, 471.  
23  
24 [31] L. Medeghini, S. Mignardi, C. De Vito, D. Bersani, P.P. Lottici, M. Turetta, J. Costantini, E. Bacchini, M.  
25 Sala, L. Nigro, *Eur. J. Mineral.* **2013**; *25*, 881.  
26  
27 [32] L. Medeghini, P.P. Lottici, C. De Vito, S. Mignardi, D. Bersani, *J. Raman Spectrosc.* **2014**; *45*, 1244.  
28  
29 [33] C. Lofrumento, A. Zoppi, E.M. Castellucci, *J. Raman Spectrosc.* **2004**; *35*, 650.  
30  
31 [34] J. Striova, C. Lofrumento, A. Zoppi, E.M. Castellucci, *J. Raman Spectrosc.* **2006**; *37*, 1139.  
32  
33 [35] P. Ballirano, C. De Vito, L. Medeghini, S. Mignardi, V. Ferrini, P. Matthiae, D. Bersani, P.P. Lottici,  
34 *Ceram. Int.* **2014**; *40*, 16409.  
35  
36 [36] A. Raškovska, B. Minčeva-Šukarova, O. Grupče, P. Colomban, *J. Raman Spectrosc.* **2010**; *41*, 431.  
37  
38 [37] S. Kiruba, S. Ganesan, *Spectrochim. Acta - Part A Mol. Biomol. Spectrosc.* **2015**; *145*, 594.  
39  
40 [38] P. Ricciardi, P. Colomban, B. Fabbri, V. Milande, *E-Preservation Sci.* **2009**; *6*, 22.  
41  
42 [39] V. Tanevska, P. Colomban, B. Minčeva-Šukarova, O. Grupče, *J. Raman Spectrosc.* **2009**; *40*, 1240.  
43  
44 [40] E. Cantisani, M. Cavalieri, C. Lofrumento, E. Pecchioni, M. Ricci, *Archaeol. Anthropol. Sci.* **2012**; *4*, 29.  
45  
46 [41] C. De Vito, L. Medeghini, S. Mignardi, D. Orlandi, L. Nigro, F. Spagnoli, P.P. Lottici, D. Bersani, *Appl.*  
47 *Clay Sci.* **2014**; *88-89*, 202.  
48  
49 [42] P. Colomban, *Arts* **2013**; *2*, 77.  
50  
51 [43] P. Sciau, P. Goudeau, *Eur. Phys. J. B* **2015**; *88*, 132.  
52  
53 [44] A. Issi, A. Kara, A.O. Alp, *Ceram. Int.* **2011**; *37*, 2575.  
54  
55  
56  
57  
58  
59  
60

- 1  
2  
3 [45] S. Akyuz, T. Akyuz, S. Basaran, C. Bolcal, A. Gulec, *J. Mol. Struct.* **2007**; 834-836, 150.  
4  
5 [46] S. Cîntă Pînzaru, D. Pop, L. Nemeth, *Stud. Univ. Babeş-Bolyai, Geol.* **2008**; 53, 31.  
6  
7 [47] J. van der Weerd, G.D. Smith, S. Firth, R.J.H. Clark, *J. Archaeol. Sci.* **2004**; 31, 1429.  
8  
9 [48] A.S. Cavalheri, A. M.O.A. Balan, R. Künzli, C.J.L. Constantino, *Vib. Spectrosc.* **2010**; 54, 164.  
10  
11 [49] I.M. Catalano, A. Genga, C. Laganara, R. Laviano, a. Mangone, D. Marano, a. Traini, *J. Archaeol. Sci.*  
12 **2007**; 34, 503.  
13  
14 [50] F. Rosi, V. Manuali, C. Miliani, B.G. Brunetti, A. Sgamellotti, T. Grygar, D. Hradil, *J. Raman Spectrosc.*  
15 **2009**; 40, 107.  
16  
17 [51] S.A. Centeno, V.I. Williams, N.C. Little, R.J. Speakman, *Vib. Spectrosc.* **2012**; 58, 119.  
18  
19 [52] J.M. Pérez, R. Esteve-Tébar, *Archaeometry* **2004**; 46, 607.  
20  
21 [53] L. Wang, J. Zhu, Y. Yan, Y. Xie, C. Wang, *J. Raman Spectrosc.* **2009**; 40, 998.  
22  
23 [54] D. Bersani, P.P. Lottici, A. Montenero, *J. Raman Spectrosc.* **1999**; 30, 355.  
24  
25 [55] Y.S. Liou, Y. Chang Liu, H.Y. Huang, *J. Raman Spectrosc.* **2011**; 42, 1062.  
26  
27 [56] D. Bersani, P.P. Lottici, A. Montenero, *J. Mater. Sci.* **2000**; 35, 4301.  
28  
29 [57] M. Olivares, M.C. Zuluaga, L. A. Ortega, X. Murelaga, A. Alonso-Olazabal, M. Urteaga, L. Amundaray,  
30 I. Alonso-Martin, N. Etxebarria, *J. Raman Spectrosc.* **2010**; 41, 1543.  
31  
32 [58] K.F. McCarty, D.R. Boehme, *J. Solid State Chem.* **1989**; 79, 19.  
33  
34 [59] D.L.A. de Faria, F.N. Lopes, *Vib. Spectrosc.* **2007**; 45, 117.  
35  
36 [60] I. Chourpa, L. Douziech-Eyrolles, L. Ngaboni-Okassa, J.-F. Fouquenot, S. Cohen-Jonathan, M. Souce,  
37 H. Marchais, P. Dubois, *Analyst* **2005**; 130, 1395.  
38  
39 [61] P. Colomban, R. De Laveaucoupet, V. Milande, *J. Raman Spectrosc.* **2005**; 36, 857.  
40  
41 [62] G. Simsek, P. Colomban, V. Milande, *J. Raman Spectrosc.* **2010**; 41, 529.  
42  
43 [63] A.P. Middleton, H.G.M. Edwards, P.S. Middleton, J. Ambers, *J. Raman Spectrosc.* **2005**; 36, 984.  
44  
45 [64] R.J.H. Clark, Q. Wang, A. Correia, *J. Archaeol. Sci.* **2007**; 34, 1787.  
46  
47 [65] F.C. Gennari, D.M. Pasquevich, *J. Am. Ceram. Soc.* **1999**; 82, 1915.  
48  
49 [66] D. Bersani, G. Antonioli, P.P. Lottici, T. Lopez, *J. Non. Cryst. Solids* **1998**; 232-234, 175.  
50  
51 [67] I. Krivtsov, M. Ilkaeva, V. Avdin, Z. Amghouz, S.A. Khainakov, J.R. Garcia, E. Diaz, S. Ordonez, *RSC Adv.*  
52 **2015**; 5, 36634.  
53  
54  
55  
56  
57  
58  
59  
60

- 1  
2  
3 [68] L.C. Prinsloo, **2009**; available at: <http://repository.up.ac.za/handle/2263/24936>.
- 4  
5 [69] W.H. Jay, J.D. Cashion, B. Blenkinship, *J. Raman Spectrosc.* **2015**; doi: 10.1002/jrs.4750
- 6  
7 [70] E. Murad, *Clays Clay Miner.* **2003**; *51*, 689.
- 8  
9 [71] A. Di Paola, M. Bellardita, L. Palmisano, *Catalysts* **2013**; *3*, 36.
- 10  
11 [72] S. Shoval, E. Yadin, G. Panczer, *J. Therm. Anal. Calorim.* **2015**; *104*, 515.
- 12  
13 [73] J.Z. W. A. Deer, R. A. Howie, An Introduction to Rock-Forming Minerals, 2nd Ed., The Geological  
14 Society, Bath, 2001.
- 15  
16 [74] R.F. Geller, A.S. Creamer, *J. Am. Ceram. Soc.* **1931**; *14*, 30.
- 17  
18 [75] V. Bendel, B.C. Schmidt, *Eur. J. Mineral.* **2008**; *20*, 1055.
- 19  
20 [76] J.J. Freeman, A. Wang, K.E. Kuebler, B.L. Jolliff, L. A. Haskin, *Can. Mineral.* **2008**; *46*, 1477.
- 21  
22 [77] B. Minčeva-Šukarova, A. Issi, A. Raškowska, O. Grupče, V. Tanevska, M. Yaygingöl, A. Kara, P.  
23 Colomban, *J. Raman Spectrosc.* **2012**; *43*, 792.
- 24  
25 [78] J. V. Smith, Feldspar Minerals I, Springer-Verlag, Heidelberg, 1974.
- 26  
27 [79] P.H. Ribbe, Feldspar Mineral. (Reviews Mineral. 2), Mineralogical Society of America, Washington,  
28 1983.
- 29  
30 [80] J. V. Smith, W.L. Brown, Feldspar Minerals. 1. Crystal Structures, Physical, Chemical and  
31 Microtextural Properties, Springer-Verlag, Berlin, 1988.
- 32  
33 [81] P. Colomban, F. Treppoz, *J. Raman Spectrosc.* **2001**; *32*, 93.
- 34  
35 [82] P.J. Jin, Z.Q. Yao, M.L. Zhang, Y.H. Li, H.P. Xing, *J. Raman Spectrosc.* **2010**; *41*, 222.
- 36  
37 [83] P. Colomban, *J. Raman Spectrosc.* **2003**; *34*, 420.
- 38  
39 [84] M.C. Caggiani, N. Ditaranto, M.R. Guascito, P. Acquafredda, R. Laviano, L.C. Giannossa, S. Mutino, A.  
40 Mangone, *X-Ray Spectrom.* **2015**; *44*, 191.
- 41  
42 [85] M.C. Caggiani, P. Acquafredda, P. Colomban, A. Mangone, *J. Raman Spectrosc.* **2014**; *45*, 1251.
- 43  
44 [86] G. Barone, D. Bersani, V. Crupi, F. Longo, U. Longobardo, P.P. Lottici, I. Aliatis, D. Majolino, P.  
45 Mazzoleni, S. Raneri, V. Venuti, *J. Raman Spectrosc.* **2014**; *45*, 1309.
- 46  
47 [87] E.P. Tomasini, E.B. Halac, M. Reinoso, E.J. Di Liscia, M.S. Maier, *J. Raman Spectrosc.* **2012**; *43*, 1671.
- 48  
49 [88] T. Jawhari, A. Roid, J. Casado, *Carbon N. Y.* **1995**; *33*, 1561.
- 50  
51 [89] A. Coccato, J. Jehlicka, L. Moens, P. Vandenabeele, *J. Raman Spectrosc.* **2015**; *46*, 1003.
- 52  
53  
54  
55  
56  
57  
58  
59  
60

- 1  
2  
3 [90] D. Parras, P. Vandenabeele, A. Sanchez, M. Montejo, L. Moens, N. Ramos, *J. Raman Spectrosc.* **2010**;  
4 41, 68.  
5  
6 [91] M.C. Caggiani, P. Colomban, *J. Raman Spectrosc.* **2011**; 42, 839.  
7  
8 [92] P. Colomban, *J. Cult. Herit.* **2008**; 9, e55.  
9  
10 [93] P. Colomban, V. Milande, *J. Raman Spectrosc.* **2006**; 37, 606.  
11  
12 [94] P. Colomban, *Appl. Phys. A Mater. Sci. Process.* **2004**; 79, 167.  
13  
14 [95] P. Colomban, *J. Non. Cryst. Solids* **2003**; 323, 180.  
15  
16 [96] P. Colomban, M.P. Etcheverry, M. Asquier, M. Bounichou, A. Tournié, *J. Raman Spectrosc.* **2006**; 37,  
17 614.  
18  
19 [97] P. Colomban, A. Tournie, L. Bellot-Gurlet, *J. Raman Spectrosc.* **2006**; 37, 841.  
20  
21 [98] P. Colomban, O. Paulsen, *J. Am. Ceram. Soc.* **2005**; 88, 390.  
22  
23 [99] P. Colomban, *Eur. J. Mineral.* **2014**; 25, 863.  
24  
25 [100] J. Miao, B. Yang D. Mu, *Archaeometry* **2010**; 52, 146.  
26  
27 [101] B. Kirmizi, E.H. Göktürk, P. Colomban, *Archaeometry* **2015**; 57, 476.  
28  
29 [102] L.F. Vieira Ferreira, D.S. Conceição, D.P. Ferreira, L.F. Santos, T.M. Casimiro, I. Ferreira Machado, *J.*  
30 *Raman Spectrosc.* **2014**; 45, 838.  
31  
32 [103] L.F. Vieira Ferreira, D.P. Ferreira, D.S. Conceição, L.F. Santos, M.F.C. Pereira, T.M. Casimiro, I.  
33 Ferreira Machado, *Spectrochim. Acta - Part A Mol. Biomol. Spectrosc.* **2015**; 149, 285.  
34  
35 [104] P. Colomban, V. Milande, H. Lucas, *J. Raman Spectrosc.* **2004**; 35, 68.  
36  
37 [105] B. Kirmizi, P. Colomban, M. Blanc, *J. Raman Spectrosc.* **2010**; 41, 1240.  
38  
39 [106] E. Marengo, M. Aceto, E. Robotti, M.C. Liparota, M. Bobba, G. Pantò, *Anal. Chim. Acta* **2005**; 537,  
40 359.  
41  
42 [107] E. Widjaja, G.H. Lim, Q. Lim, A. Bin Mashadi, M. Garland, *J. Raman Spectrosc.* **2011**; 42, 377.  
43  
44 [108] G. Barone, V. Crupi, F. Longo, D. Majolino, P. Mazzoleni, S. Raneri, V. Venuti, *X-Ray Spectrom.* **2014**;  
45 43, 83.  
46  
47 [109] F. Antonelli, P. Santi, A. Renzulli, A. Bonazza, *Geol. Soc. London, Spec. Publ.* **2006**; 257, 229.  
48  
49 [110] P. Santi, F. Antonelli, A. Renzulli, *Archaeometry* **2005**; 47, 253.  
50  
51 [111] F. Antonelli, L. Lazzarini, *Archaeometry* **2012**; 54, 1.  
52  
53  
54  
55  
56  
57  
58  
59  
60

- 1  
2  
3 [112] C. Baita, P.P. Lottici, E. Salvioli-Mariani, P. Vandenabeele, M. Librenti, F. Antonelli, D. Bersani, J.  
4 *Raman Spectrosc.* **2014**; *45*, 114.  
5  
6 [113] D. Bersani, S. Andò, P. Vignola, G. Moltifiori, I.G. Marino, P.P. Lottici, V. Diella, *Spectrochim. Acta -*  
7 *Part A Mol. Biomol. Spectrosc.* **2009**; *73*, 484.  
8  
9 [114] T. Cerasoli, A. Coccato, D. Bersani, P.P. Lottici, R. Conversi, 6th International Congress on the  
10 Application of Raman Spectroscopy in Art and Archaeology (RAA 2011) 5-8 September 2011, Parma,  
11 Italy, Timeo ed. Bologna, p. 129-130 - ISBN: 9788897162209  
12  
13 [115] K.E. Kuebler, B.L. Jolliff, A. Wang, L. A. Haskin, *Geochim. Cosmochim. Acta* **2006**; *70*, 6201.  
14  
15 [116] H.J. Schubnel, M. Pinet, D.C. Smith, B. Lasnier, *La Microsonde Raman En Gemmologie*, Association  
16 française de gemmologie, Paris, 1992.  
17  
18 [117] M. L. Dele, P. Dhamelin court, J. P. Poirot, J. M. Dereppe, C. Moreaux, *J. Raman Spectrosc.* **1997**; *28*,  
19 673.  
20  
21 [118] M.-L. Delé Dubois, P. Dhamelin court, H.-J. Schubnel, *Rev. Fr. Gemmol.* **1980**; *63*, 11.  
22  
23 [119] M.-L. Delé Dubois, P. Dhamelin court, H.-J. Schubnel, *Rev. Fr. Gemmol.* **1980**; *64*, 13.  
24  
25 [120] L. Kiefert, J.P. Chalain, S. Haberli, in: H.G.M. Edwards, J.M. Chalmers (Eds.), *Raman Spectrosc.*  
26 *Archaeol. Art Hist.*, Royal society of chemistry, 2005.  
27  
28 [121] L. Kiefert, S. Karampelas, *Spectrochim. Acta - Part A Mol. Biomol. Spectrosc.* **2011**; *80*, 119.  
29  
30 [122] L. Kiefert, M. Epelboym, H.-P. Kan-Nyunt, S. Paralusz, in *Infrared Raman Spectroscopy in Forensic*  
31 *Science*, p.455, eds. J.M. Chalmers, H.G.M. Edwards, M.D. Hargreaves, Wiley, **2012**  
32  
33 [123] S. Domínguez-Bella, *Archaeomineralogy of Prehistoric Artifacts and Gemstones*, J.M. Herrero, M.  
34 Vendrell (Eds.), *Archaeometry and Cultural Heritage: the Contribution of Mineralogy. Seminarios*  
35 *SEM, Vol. 9 Sociedad Española de Mineralogía, Madrid (2012) 112 p. ISSN 1698-5478, pp. 5-28.*  
36  
37 [124] S. Karampelas, M. Wörle, K. Hunger, H. Lanz, *J. Raman Spectrosc.* **2012**; *43*, 1833.  
38  
39 [125] S. Karampelas, M. Wörle, K. Hunger, H. Lanz, D. Bersani, S. Gübelin, *Gems Gemol.* **2010**; *46*, 292.  
40  
41 [126] M. Jeršek, S. Kramar, *J. Raman Spectrosc.* **2014**; *45*, 1000.  
42  
43 [127] R.T. Liddicoat, *Handbook of Gem Identification*, Gemological Institute of America, Santa Monica,  
44 1993.  
45  
46 [128] L.L. Reiche I., Pages-Camagna S., *J. Raman Spectrosc.* **2004**; *35*, 719.  
47  
48 [129] Z. Petrová, J. Jehlička, T. Čapoun, R. Hanus, T. Trojek, V. Goliáš, *J. Raman Spectrosc.* **2012**; *43*, 1275.  
49  
50 [130] G. Barone, D. Bersani, J. Jehlička, P.P. Lottici, P. Mazzoleni, S. Raneri, P. Vandenabeele, C. Di  
51 Giacomo, G. Larinà, *J. Raman Spectrosc.* **2015**; *46*, 989.  
52  
53  
54  
55  
56  
57  
58  
59  
60

- 1  
2  
3 [131] G. Barone, P. Mazzoleni, S. Raneri, D. Bersani, J. Jehlička, P.P. Lottici, P. Vandenberghe, G. Lamagna,  
4 A.M. Manenti, *Applied Spectrosc* **2015**; *in press*.
- 5  
6 [132] D. Bersani, G. Azzi, E. Lambruschi, G. Barone, P. Mazzoleni, S. Raneri, U. Longobardo, P.P. Lottici, *J.*  
7 *Raman Spectrosc.* **2014**; 45, 1293.
- 8  
9 [133] J. Dong, Y. Han, J. Ye, Q. Li, S. Liu, D. Gu, *J. Raman Spectrosc.* **2014**; 45, 596.
- 10  
11 [134] P. Gołyźniak, L. Natkaniec-Nowak, M. Dumańska-Słowik, B. Naglik, *Archaeometry* **2015**; doi:  
12 10.1111/arcm.12174
- 13  
14 [135] J. Götze, L. Nasdala, R. Kleeberg, M. Wenzel, *Contrib. to Mineral. Petrol.* **1998**; 133, 96.
- 15  
16 [136] L. Paral, J. Garcia Guinea, R. Kibar, A. Cetin, N. Can, *J. Lumin.* **2011**; 131, 2317.
- 17  
18 [137] D. Pop, C. Constantina, D. Tătar, W. Kiefer, *Stud. UBB, Geol.* **2012**; 49, 41.
- 19  
20 [138] J. Whalley, *Studies Conservation* **2012**; 57, S313.
- 21  
22 [139] E. Gliozzo, N. Grassi, P. Bonanni, C. Meneghini, M.A. Tomei, *Archaeometry* **2011**; 53, 469.
- 23  
24 [140] C. Capel Ferrón, L. León Reina, S. Jorge-Villar, J.M. Compañía, M.A.G. Aranda, J.T. López Navarrete, V.  
25 Hernández, F.J. Medianero, J. Ramos, G.C. Weniger, S. Domínguez-Bella, J. Linstaedter, P. Cantalejo,  
26 M.Y. Espejo, J.J. Durán Valsero, *Archaeol. Anthropol. Sci.* **2015**; 235.
- 27  
28 [141] A. Weselucha-Birczyńska, L. Natkaniec-Nowak, *Vib. Spectrosc.* **2011**; 57, 248.
- 29  
30 [142] B. Kolesov, *Phys. Chem. Miner.* **2008**; 35, 271.
- 31  
32 [143] L.T.-T. Huong, W. Hofmeister, T. Häger, S. Karamelas, N.D.-T. Kien, *Gems Gemol.* **2014**; 50, 287.
- 33  
34 [144] L.T.-T. Huong, T. Hager, W. Hofmeister, *Gems Gemol.* **2010**; 46, 36.
- 35  
36 [145] Y. Ruzeng, Y. Song, *J. Gems Gemmol.* **2014**; 1, 9.
- 37  
38 [146] E. Lambruschi, G.D. Gatta, I. Adamo, D. Bersani, E. Salvioli-Mariani, P.P. Lottici, *J. Raman Spectrosc.*  
39 **2014**; 45, 993.
- 40  
41 [147] B.M. Laurs, W.B. Simmons, G.R. Rossman, E.P. Quinn, S.F. McClure, A. Peretti, T. Armbruster, F.C.  
42 Hawthorne, A.U. Falster, D. Günther, others, *Gems Gemol.* **2003**; 39, 284.
- 43  
44 [148] G.D. Gatta, I. Adamo, M. Meven, E. Lambruschi, *Phys. Chem. Miner.* **2012**; 39, 829.
- 45  
46 [149] M. Giarola, G. Mariotto, M. Barberio, D. Ajò, *J. Raman Spectrosc.* **2012**; 43, 1828.
- 47  
48 [150] M. Superchi, F. Pezzotta, E. Gambini, E. Castaman, *Gems Gemol.* **2010**; 46, 274.
- 49  
50 [151] F. Pezzotta, I. Adamo, V. Diella, *Gems Gemol.* **2011**; 47, 2.
- 51  
52 [152] A.-K. Malsy, S. Karamelas, D. Schwarz, L. Klemm, T. Armbruster, D.A. Tuan, *The Journal of*  
53 *Gemmology*, **2012**; 33, 19.
- 54  
55  
56  
57  
58  
59  
60

- 1  
2  
3 [153] L.T.-T. Huong, T. Häger, W. Hofmeister, C. Hauzenberger, D. Schwarz, P. Van Long, U. Wehmeister,  
4 N.N. Khoi, N.T. Nhung, *Gems Gemol.* **2012**; 48, 158.  
5  
6 [154] M. Giarola, G. Mariotto, D. Ajò, *J. Raman Spectrosc.* **2012**; 43, 556.  
7  
8 [155] M. Ayvackli, J. Garcia-Guinea, A. Jorge, I. Akaln, Z. Kotan, N. Can, *J. Lumin.* **2012**; 132, 1750.  
9  
10 [156] M. Dumańska-Słowik, A. Wesełucha-Birczyńska, L. Natkaniec-Nowak, *Spectrochim. Acta - Part A Mol.*  
11 *Biomol. Spectrosc.* **2013**; 109, 97.  
12  
13 [157] N. Noguchi, A. Abduriyim, I. Shimizu, N. Kamegata, S. Otake, H. Kagi, *J. Raman Spectrosc.* **2013**; 44,  
14 147.  
15  
16 [158] B.I. Łydzba-Kopczyńska, B. Gediga, J. Chojcan, M. Sachanbiński, *J. Raman Spectrosc.* **2012**; 43, 1839.  
17  
18 [159] R.H. Brody, H.G.M. Edwards, A. M. Pollard, *Spectrochim. Acta - Part A Mol. Biomol. Spectrosc.* **2001**;  
19 57, 1325.  
20  
21 [160] J. Jehlička, S.E. Jorge Villar, H.G.M. Edwards, *J. Raman Spectrosc.* **2004**; 35, 761.  
22  
23 [161] W. Winkler, M. Musso, E.C. Kirchner, *J. Raman Spectrosc.* **2003**; 34, 157.  
24  
25 [162] Z. Rao, K. Dong, X. Yang, J. Lin, X. Cui, R. Zhou, Q. Deng, *Sci. China Physics, Mech. Astron.* **2013**; 56,  
26 1598.  
27  
28 [163] E.D. Zu, S.Q. Li, Y. Zou, X.G. Zhao, Y.D. Sun, Y.F. Lin, H. Li, *Key Eng. Mater.* **2011**; 492, 341.  
29  
30 [164] M. Sachanbiński, R. Girulski, D. Bobak, B. Łydzba-Kopczyńska, *J. Raman Spectrosc.* **2008**; 39, 1012.  
31  
32 [165] L. Kiefert, H. a Hanni, J.P. Chalain, *Opt. Devices Diagnostics Mater. Sci.* **2000**; 4098, 241.  
33  
34 [166] S.F. McClure, R.E. Kane, N. Sturman, *Gems Gemol.* **2010**; 46, 218.  
35  
36 [167] M. Hall, T.M. Moses, *Gems Gemol.* **2001**; 37, 214.  
37  
38 [168] K.S. Moe, T.M. Moses, P. Johnson, *Gems Gemol.* **2007**; 43, 149.  
39  
40 [169] D. De Ghionno, P. Owens, *Gems Gemol.* **2003**; 39, 214.  
41  
42 [170] G.B. Andreozzi, F. Princivalle, H. Skogby, A. Della Giusta, *Am. Mineral.* **2000**; 85, 1164.  
43  
44 [171] L. Nasdala, O. Beyssac, J.W. Schopf, B. Bleisteiner, *Raman Imaging, Springer SDerives in Optical*  
45 *Sciences vol. 168, Springer, 2012, pp. 145–187.*  
46  
47 [172] E. Gaillou, J. E. Post, A. Steele, J. E. Butler, *AGU Fall Meeting Abstracts 2013*; A2350.  
48  
49 [173] Y. Tuncer Arslanlar, J. Garcia-Guinea, R. Kibar, A. Çetin, M. Ayvacikli, N. Can, *Appl. Radiat. Isot.* **2011**;  
50 69, 1299.  
51  
52 [174] R. Wang, W.S. Zhang, *J. Raman Spectrosc.* **2011**; 42, 1324.  
53  
54  
55  
56  
57  
58  
59  
60

- 1  
2  
3 [175] F. Casadio, J.G. Douglas, K.T. Faber, *Anal. Bioanal. Chem.* **2007**; 387, 791.  
4  
5 [176] D. Bersani, S. Andò, L. Scrocco, P. Gentile, E. Salvioli-Mariani, P.P. Lottici, in: 11th Int. GeoRaman  
6 Conf. St. Louis, Missouri, USA, Lunar and Planetary Institute, St. Louis, 2014.  
7  
8 [177] J.R. Petriglieri, E. Salvioli-Mariani, L. Mantovani, M. Tribaudino, P.P. Lottici, C. Laporte-Magoni, D.  
9 Bersani, *J. Raman Spectrosc.* **2015**; 46, 953.  
10  
11 [178] Y.Y. Wang, F.X. Gan, H.X. Zhao, *Vib. Spectrosc.* **2013**; 66, 19.  
12  
13 [179] A.A.D. Robles, J. Luis, R. Sil, P. Claes, M.D.M. Ortega, E.C. González, M. Ángel, M. Rojas, M.C. García,  
14 S.G. Castillo, *Herit. Sci.* **2015**; 1.  
15  
16 [180] J.R. Barnett, S. Miller, E. Pearce, *Opt. Laser Technol.* **2006**; 38, 445.  
17  
18 [181] D.A. Scott, *Stud. Conserv.* **2015**; doi: 10.1179/2047058414Y.0000000162.  
19  
20 [182] N. Eastaugh, V. Walsh, T. Chaplin, R. Siddall, *The Pigment Compendium: A Dictionary of Historical*  
21 *Pigments.*, Elsevier - Butterworth Heinemen, 2004.  
22  
23 [183] L.C. Prinsloo, W. Barnard, I. Meiklejohn, K. Hall, *J. Raman Spectrosc.* **2008**; 39, 646.  
24  
25 [184] A. Hernanz, J.M. Gavira-Vallejo, J.F. Ruiz-López, H.G.M. Edwards, *J. Raman Spectrosc.* **2008**; 39, 972.  
26  
27 [185] A. Hernanz, J.F. Ruiz-López, J.M. Gavira-Vallejo, S. Martin, E. Gavrilenko, *J. Raman Spectrosc.* **2010**;  
28 41, 1394.  
29  
30 [186] L. Darchuk, Z. Tsybrii, A. Worobiec, C. Vázquez, O.M. Palacios, E. A. Stefaniak, G. Gatto Rotondo, F.  
31 Sizov, R. Van Grieken, *Spectrochim. Acta - Part A Mol. Biomol. Spectrosc.* **2010**; 75, 1398.  
32  
33 [187] S. Gialanella, R. Belli, G. Dalmeri, I. Lonardelli, M. Mattarelli, M. Montagna, L. Toniutti, *Archaeometry*  
34 **2011**; 53, 950.  
35  
36 [188] S. Lahlil, M. Lebon, L. Beck, H. Rousselière, C. Vignaud, I. Reiche, M. Menu, P. Paillet, F. Plassard, *J.*  
37 *Raman Spectrosc.* **2012**; 43, 1637.  
38  
39 [189] L. Beck, D. Genty, S. Lahlil, M. Lebon, F. Tereygeol, C. Vignaud, I. Reiche, E. Lambert, H. Valladas, E.  
40 Kaltnecker, F. Plassard, M. Menu, P. Paillet, *Radiocarbon* **2013**; 55, 436.  
41  
42 [190] D.L. a De Faria, F.N. Lopes, L.A.C. Souza, H.D. De Oliveira Castello Branco, *Quim. Nova* **2011**; 34,  
43 1358.  
44  
45 [191] A. Tournié, L.C. Prinsloo, C. Paris, P. Colomban, B. Smith, *J. Raman Spectrosc.* **2011**; 42, 399.  
46  
47 [192] C. Lofrumento, M. Ricci, L. Bachechi, D. De Feo, E.M. Castellucci, *J. Raman Spectrosc.* **2012**; 43, 809.  
48  
49 [193] L. Darchuk, G.G. Rotondo, M. Swaenen, A. Worobiec, Z. Tsybrii, Y. Makarovska, R. Van Grieken,  
50 *Spectrochim. Acta - Part A Mol. Biomol. Spectrosc.* **2011**; 83, 34.  
51  
52 [194] P. Jezequel, G. Wille, C. Beny, F. Delorme, V. Jean-Prost, R. Cottier, J. Breton, F. Dure, J. Desprée, *J.*  
53 *Archaeol. Sci.* **2011**; 38, 1165.  
54  
55  
56  
57  
58  
59  
60

- 1  
2  
3 [195] B. Erdoğu, A. Ulubey, *Oxford J. Archaeol.* **2011**; 30, 1.  
4  
5 [196] A. Bonneau, D.G. Pearce, A. M. Pollard, *J. Archaeol. Sci.* **2012**; 39, 287.  
6  
7 [197] A. Bonneau, D.G. Pearce, P.J. Mitchell, C. Arthur, T. Higham, M. Lamothe, *Proc. 39th Int. Symp.*  
8 *Archaeom. Leuven* **2012**; 319.  
9  
10 [198] P.M. Martin-Sanchez, S. Sanchez-Cortes, E. Lopez-Tobar, V. Jurado, F. Bastian, C. Alabouvette, C.  
11 Saiz-Jimenez, *J. Raman Spectrosc.* **2012**; 43, 464.  
12  
13 [199] A. Hernanz, J.M. Gavira-Vallejo, J.F. Ruiz-López, S. Martín, Á. Maroto-Valiente, R. De Balbín-  
14 Behrmann, M. Menéndez, J.J. Alcolea-González, *J. Raman Spectrosc.* **2012**; 43, 1644.  
15  
16 [200] A. Hernanz, J.F. Ruiz-López, J.M. Madariaga, E. Gavrilenko, M. Maguregui, S. Fdez-Ortiz de Vallejuelo,  
17 I. Martínez-Arkarazo, R. Alloza-Izquierdo, V. Baldellou-Martínez, R. Viñas-Vallverdú, A. Rubio i Mora,  
18 À. Pitarch, A. Giakoumaki, *J. Raman Spectrosc.* **2014**; 45, 1236.  
19  
20 [201] T.R. Ravindran, A. K. Arora, M. Singh, S.B. Ota, *J. Raman Spectrosc.* **2013**; 44, 108.  
21  
22 [202] M. Mas, A. Jorge, B. Gavilán, M. Solís, E. Parra, P.P. Pérez, *J. Archaeol. Sci.* **2013**; 40, 4635.  
23  
24 [203] M. Olivares, K. Castro, M.S. Corchón, D. Gárate, X. Murelaga, A. Sarmiento, N. Etxebarria, *J.*  
25 *Archaeol. Sci.* **2013**; 40, 1354.  
26  
27 [204] À. Pitarch, J.F. Ruiz, S. Fdez-Ortiz de Vallejuelo, A. Hernanz, M. Maguregui, J.M. Madariaga, *Anal.*  
28 *Methods* **2014**; 6, 6641.  
29  
30 [205] H. Gomes, H. Collado, A. Martins, G.H. Nash, P. Rosina, C. Vaccaro, *Mediterr. Archaeol. Archaeom.*  
31 **2015**; 15, 163.  
32  
33 [206] L. Dayet, P.J. Texier, F. Daniel, G. Porraz, *J. Archaeol. Sci.* **2013**; 40, 3492.  
34  
35 [207] L. Dayet, F. d'Errico, R. Garcia-Moreno, *J. Archaeol. Sci.* **2014**; 44, 180.  
36  
37 [208] M. Iriarte, A. Hernanz, J.F. Ruiz-López, S. Martín, *J. Raman Spectrosc.* **2013**; 44, 1557.  
38  
39 [209] M. Maguregui, U. Knuutinen, K. Castro, J.M. Madariaga, *J. Raman Spectrosc.* **2010**; 41, 1400.  
40  
41 [210] H. Gomes, P. Rosina, P. Holakoei, T. Solomon, C. Vaccaro, *J. Archaeol. Sci.* **2013**; 40, 4073.  
42  
43 [211] E. López-Montalvo, V. Villaverde, C. Roldán, S. Murcia, E. Badal, *J. Archaeol. Sci.* **2014**; 52, 535.  
44  
45 [212] D. Bonjean, Y. Vanbrabant, G. Abrams, S. Pirson, C. Burlet, K. Di Modica, M. Otte, J. Vander Auwera,  
46 M. Golitko, R. McMillan, E. Goemaere, *J. Archaeol. Sci.* **2015**; 55, 253.  
47  
48 [213] L. Darchuk, E. a Stefaniak, C. Vázquez, O.M. Palacios, A. Worobiec, R. Van Grieken, *E-Preservation*  
49 *Sci.* **2009**; 6, 112.  
50  
51 [214] M.Á. Rogerio-Candelera, L.K. Herrera, A.Z. Miller, L. García Sanjuán, C. Mora Molina, D.W. Wheatley,  
52 Á. Justo, C. Saiz-Jimenez, *J. Archaeol. Sci.* **2013**; 40, 279.  
53  
54  
55  
56  
57  
58  
59  
60

- 1  
2  
3 [215] R.S. Román, C.B. Bañón, M.D. Landete Ruiz, *J. Archaeol. Sci.* **2015**; *60*, 84.  
4  
5 [216] J. Zilhão, D.E. Angelucci, E. Badal-García, F. d'Errico, F. Daniel, L. Dayet, K. Douka, T.F.G. Higham, M.J.  
6 Martínez-Sánchez, R. Montes-Bernárdez, S. Murcia-Mascarós, C. Pérez-Sirvent, C. Roldán-García, M.  
7 Vanhaeren, V. Villaverde, R. Wood, J. Zapata, J. Zilhao, D.E. Angelucci, E. Badal-García, F. d'Errico, F.  
8 Daniel, L. Dayet, K. Douka, T.F.G. Higham, M.J. Martinez-Sanchez, R. Montes-Bernardez, S. Murcia-  
9 Mascaros, C. Perez-Sirvent, C. Roldan-Garcia, M. Vanhaeren, V. Villaverde, R. Wood, J. Zapata, J.  
10 Zilhão, D.E. Angelucci, E. Badal-García, F. d'Errico, F. Daniel, L. Dayet, K. Douka, T.F.G. Higham, M.J.  
11 Martínez-Sánchez, R. Montes-Bernárdez, S. Murcia-Mascarós, C. Pérez-Sirvent, C. Roldán-García, M.  
12 Vanhaeren, V. Villaverde, R. Wood, J. Zapata, *Proc. Natl. Acad. Sci. U. S. A.* **2010**; *107*, 1023.  
13  
14 [217] C.S. Henshilwood, F. d'Errico, K.L. van Niekerk, Y. Coquinot, Z. Jacobs, S.-E. Lauritzen, M. Menu, R.  
15 Garcia-Moreno, *Science (80-. )*. **2011**; *334*, 219.  
16  
17 [218] P. Villa, L. Pollarolo, I. Degano, L. Birolo, M. Pasero, C. Biagioni, K. Douka, R. Vinciguerra, J.J. Lucejko,  
18 L. Wadley, *PLoS One* **2015**; *10*, e0131273.  
19  
20 [219] A. Rousaki, C. Bellelli, M. Carballido Calatayud, V. Aldazabal, G. Custo, L. Moens, P. Vandenberghe, C.  
21 Vázquez, *J. Raman Spectrosc.* **2015**; *46*, 1016.  
22  
23 [220] S. di Lernia, S. Bruni, I. Cislighi, M. Cremaschi, M. Gallinaro, V. Gugliemi, A.M. Mercuri, G. Poggi, A.  
24 Zerboni, *Archaeol. Anthropol. Sci.* **2015**; *486*, 2012.  
25  
26 [221] J. Huntley, M. Aubert, J. Ross, H.E. A. Brand, M.J. Morwood, *Archaeometry* **2015**; *57*, 77.  
27  
28 [222] B. Guineau, *Stud. Conserv.* **1984**; *29*, 35.  
29  
30 [223] B. Guineau, *J. Forensic Sci.* **1984**; *29*, 15.  
31  
32 [224] K. Brown, M. Brown, D. Jacobs, *Stud. Conserv.* **2002**; *47*, 4.  
33  
34 [225] M. Clarke, *Stud. Conserv.* **2004**; *49*, 231.  
35  
36 [226] R.J.H. Clark, *Comptes Rendus Chim.* **2002**; *5*, 7.  
37  
38 [227] M. Clarke, *Rev. Conserv.* **2013**; *2*, 3.  
39  
40 [228] S. Pessanha, M. Manso, M.L. Carvalho, *Spectrochim. Acta - Part B At. Spectrosc.* **2012**; *71-72*, 54.  
41  
42 [229] M.V. Orna, in: *Archaeol. Chem.* VIII, 2013, pp. 3–18.  
43  
44 [230] T.D. Chaplin, R.J.H. Clark, A. McKay, S. Pugh, *J. Raman Spectrosc.* **2006**; *37*, 865.  
45  
46 [231] T.D. Chaplin, R.J.H. Clark, D. Jacobs, K. Jensen, G.D. Smith, *Anal. Chem.* **2005**; *77*, 3611.  
47  
48 [232] D. Bersani, P.P. Lottici, F. Vignali, G. Zanichelli, *J. Raman Spectrosc.* **2006**; *37*, 1012.  
49  
50 [233] M. Aceto, A. Agostino, E. Boccaleri, F. Crivello, A.C. Garlanda, *J. Raman Spectrosc.* **2006**; *37*, 1160.  
51  
52 [234] S. Bioletti, R. Leahy, J. Fields, B. Meehan, W. Blau, *J. Raman Spectrosc.* **2009**; *40*, 1043.  
53  
54  
55  
56  
57  
58  
59  
60

- 1  
2  
3 [235] G. Van der Snickt, W. De Nolf, B. Vekemans, K. Janssens, *Appl. Phys. A* **2008**; 92, 59.  
4  
5 [236] P. Baraldi, G. Moscardi, P. Bensi, M. Aceto, L. Tassi, *E-Preservation Sci.* **2009**; 6, 163.  
6  
7 [237] T.D. Chaplin, R.J.H. Clark, M. Martínón-Torres, *J. Mol. Struct.* **2010**; 976, 350.  
8  
9 [238] M. Aceto, A. Agostino, E. Boccaleri, F. Crivello, A. Cerutti Garlanda, *J. Raman Spectrosc.* **2010**; 41,  
10 1434.  
11  
12 [239] P. Zannini, P. Baraldi, M. Aceto, A. Agostino, G. Fenoglio, D. Bersani, E. Canobbio, E. Schiavon, G.  
13 Zanichelli, A. De Pasquale, *J. Raman Spectrosc.* **2012**; 43, 1722.  
14  
15 [240] L. Burgio, R.J.H. Clark, R.R. Hark, *Proc. Natl. Acad. Sci. U. S. A.* **2010**; 107, 5726.  
16  
17 [241] S. Daniilia, K.S. Andrikopoulos, *J. Raman Spectrosc.* **2007**; 38, 332.  
18  
19 [242] L. Burgio, R.J.H. Clark, R.R. Hark, M.S. Rumsey, C. Zannini, *Appl. Spectrosc.* **2009**; 63, 611.  
20  
21 [243] A. Duran, M.L. Franquelo, M. A. Centeno, T. Espejo, J.L. Perez-Rodriguez, *J. Raman Spectrosc.* **2011**;  
22 42, 48.  
23  
24 [244] A. Deneckere, M. De Reu, M.P.J. Martens, K. De Coene, B. Vekemans, L. Vincze, P. De Maeyer, P.  
25 Vandenaabeele, L. Moens, *Spectrochim. Acta - Part A Mol. Biomol. Spectrosc.* **2011**; 80, 125.  
26  
27 [245] A. Deneckere, M. Leeflang, M. Bloem, C.A. A. Chavannes-Mazel, B. Vekemans, L. Vincze, P.  
28 Vandenaabeele, L. Moens, *Spectrochim. Acta - Part A Mol. Biomol. Spectrosc.* **2011**; 83, 194.  
29  
30 [246] M. Aceto, A. Agostino, G. Fenoglio, P. Baraldi, P. Zannini, C. Hofmann, E. Gamillscheg, *Spectrochim.*  
31 *Acta - Part A Mol. Biomol. Spectrosc.* **2012**; 95, 235.  
32  
33 [247] V.S.F. Muralha, C. Miguel, M.J. Melo, *J. Raman Spectrosc.* **2012**; 43, 1737.  
34  
35 [248] V.S.F. Muralha, L. Burgio, R.J.H. Clark, *Spectrochim. Acta - Part A Mol. Biomol. Spectrosc.* **2012**; 92,  
36 21.  
37  
38 [249] M. Aceto, A. Agostino, G. Fenoglio, M. Gulmini, V. Bianco, E. Pellizzi, *Spectrochim. Acta - Part A Mol.*  
39 *Biomol. Spectrosc.* **2012**; 91, 352.  
40  
41 [250] K.L. Rasmussen, A.L. Tenorio, I. Bonaduce, M.P. Colombini, L. Birolo, E. Galano, A. Amoresano, G.  
42 Doudna, A.D. Bond, V. Palleschi, G. Lorenzetti, S. Legnaioli, J. van der Plicht, J. Gunneweg, *J.*  
43 *Archaeol. Sci.* **2012**; 39, 2956.  
44  
45 [251] A. El Bakkali, T. Lamhasni, S. Ait Lyazidi, M. Haddad, F. Rosi, C. Miliiani, S. Sánchez-Cortés, M. El  
46 Rhaiti, *Vib. Spectrosc.* **2014**; 74, 47.  
47  
48 [252] I. Nastova, O. Grupče, B. Minčeva-Šukarova, S. Turan, M. Yaygingol, M. Ozcatal, V. Martinovska, Z.  
49 Jakovlevska-Spirovska, *J. Raman Spectrosc.* **2012**; 43, 1729.  
50  
51 [253] I. Nastova, O. Grupče, B. Minčeva-Šukarova, M. Kostadinovska, M. Ozcatal, *Vib. Spectrosc.* **2015**; 78,  
52 39.  
53  
54  
55  
56  
57  
58  
59  
60

- 1  
2  
3 [254] I. Nastova, O. Grupče, B. Minčeva-Šukarova, M. Ozcatal, L. Mojsoska, *Vib. Spectrosc.* **2013**; *68*, 11.  
4  
5 [255] V. Tanevska, I. Nastova, B. Minčeva-Šukarova, O. Grupče, M. Ozcatal, M. Kavčić, Z. Jakovlevska-  
6 Spirovska, *Vib. Spectrosc.* **2014**; *73*, 127.  
7  
8 [256] D. Lauwers, V. Cattersel, L. Vandamme, A. Van Eester, K. De Langhe, L. Moens, P. Vandenabeele, *J.*  
9 *Raman Spectrosc.* **2014**; *45*, 1266.  
10  
11 [257] A. Le Gac, S. Pessanha, S. Longelin, M. Guerra, J.C. Frade, F. Lourenço, M.C. Serrano, M. Manso, M.L.  
12 Carvalho, *Appl. Radiat. Isot.* **2013**; *82*, 242.  
13  
14 [258] I. Lukačević, I. Ergotić, M. Vinaj, *Museum* **2013**; *385*, 1.  
15  
16 [259] M. Manso, A. Le Gac, S. Longelin, S. Pessanha, J.C. Frade, M. Guerra, A.J. Candeias, M.L. Carvalho,  
17 *Spectrochim. Acta - Part A Mol. Biomol. Spectrosc.* **2013**; *105*, 288.  
18  
19 [260] M. Kostadinovska, Z. Jakovlevska-Spirovska, B. Minčeva-Šukarova, in: Adv. Res. Sci. Areas, EDIS -  
20 Publishing Institution of the University of Zilina, **2013**, pp. 311–316.  
21  
22 [261] A. Duran, A. López-Montes, J. Castaing, T. Espejo, *J. Archaeol. Sci.* **2014**; *45*, 52.  
23  
24 [262] A. Zoleo, L. Nodari, M. Rampazzo, F. Piccinelli, U. Russo, C. Federici, M. Brustolon, *Archaeometry*  
25 **2014**; *56*, 496.  
26  
27 [263] J.T.J. Yardley, A. Hagadorn, *Harv. Theol. Rev.* **2014**; *107*, 1.  
28  
29 [264] D. Buti, D. Domenici, C. Miliari, C. García Sáiz, T. Gómez Espinoza, F. Jiménez Villalba, A. Verde  
30 Casanova, A. Sabía de la Mata, A. Romani, F. Presciutti, B. Doherty, B.G. Brunetti, A. Sgamellotti, *J.*  
31 *Archaeol. Sci.* **2014**; *42*, 166.  
32  
33 [265] H.G.M. Edwards, S.E. Jorge Villar, K. A. Eremin, *J. Raman Spectrosc.* **2004**; *35*, 786.  
34  
35 [266] A. Kamińska, M. Sawczak, M. Oujja, C. Domingo, M. Castillejo, G. Śliwiński, *J. Raman Spectrosc.*  
36 **2006**; *37*, 1125.  
37  
38 [267] A.M. Correia, R.J.H. Clark, M.I.M. Ribeiro, M.L.T.S. Duarte, *J. Raman Spectrosc.* **2007**; *38*, 1390.  
39  
40 [268] A.M. Correia, M.J. V Oliveira, R.J.H. Clark, M.I. Ribeiro, M.L. Duarte, *Anal. Chem.* **2008**; *80*, 1482.  
41  
42 [269] H.G.M. Edwards, T.J. Benoy, *Anal. Bioanal. Chem.* **2007**; *387*, 837.  
43  
44 [270] S. Daniilia, K.S. Andrikopoulos, S. Sotiropoulou, I. Karapanagiotis, *Appl. Phys. A Mater. Sci. Process.*  
45 **2008**; *90*, 565.  
46  
47 [271] D. Lau, C. Willis, S. Furman, M. Livett, *Anal. Chim. Acta* **2008**; *610*, 15.  
48  
49 [272] I.D. van der Werf, R. Gnisci, D. Marano, G.E. De Benedetto, R. Laviano, D. Pellerano, F. Vona, F.  
50 Pellegrino, E. Andriani, I.M. Catalano, A.F. Pellerano, L. Sabbatini, *J. Cult. Herit.* **2008**; *9*, 162.  
51  
52 [273] P. Vandenabeele, M.C. Christensen, L. Moens, *J. Raman Spectrosc.* **2008**; *39*, 1030.  
53  
54  
55  
56  
57  
58  
59  
60

- 1  
2  
3 [274] M.-J. Benquerença, N.F.C. Mendes, E. Castellucci, V.M.F. Gaspar, F.P.S.C. Gil, *J. Raman Spectrosc.* **2009**; *40*, 2135.  
4  
5  
6 [275] J. Bredal-Jørgensen, J. Sanyova, V. Rask, M.L. Sargent, R.H. Therkildsen, *Anal. Bioanal. Chem.* **2011**;  
7 *401*, 1433.  
8  
9 [276] T. Li, Y.F. Xie, Y.M. Yang, C.S. Wang, X.Y. Fang, J.L. Shi, Q.J. He, *J. Raman Spectrosc.* **2009**; *40*, 1911.  
10  
11 [277] S. Pessanha, M.L. Carvalho, M.I. Cabaço, S. Valadas, J.L. Bruneel, M. Besnard, M.I. Ribeiro, *J. Raman*  
12 *Spectrosc.* **2010**; *41*, 1510.  
13  
14 [278] S. Pessanha, A. Le Gac, T.I. Madeira, J.L. Bruneel, S. Longelin, M.L. Carvalho, *J. Raman Spectrosc.*  
15 **2012**; *43*, 1699.  
16  
17 [279] A. Duran, M.B. Siguenza, M.L. Franquelo, M.C.J. De Haro, A. Justo, J.L. Perez-Rodriguez, *Anal. Chim.*  
18 *Acta* **2010**; *671*, 1.  
19  
20 [280] T.R. Ravindran, A. K. Arora, S. Ramya, R. V. Subba Rao, B. Raj, *J. Raman Spectrosc.* **2011**; *42*, 803.  
21  
22 [281] M. Odlyha, D. Thickett, L. Sheldon, *J. Therm. Anal. Calorim.* **2011**; *105*, 875.  
23  
24 [282] N. Marchettini, a Atrei, F. Benetti, N. Proietti, V. Di Tullio, M. Mascalchi, I. Osticioli, S. Siano, I.T.  
25 Memmi, *Surf. Eng.* **2012**; *29*, 153.  
26  
27 [283] D. Mancini, A. Tournié, M.C. Caggiani, P. Colomban, *J. Raman Spectrosc.* **2012**; *43*, 294.  
28  
29 [284] S. Akyuz, T. Akyuz, G. Emre, A. Gulec, S. Basaran, *Spectrochim. Acta - Part A Mol. Biomol. Spectrosc.*  
30 **2012**; *89*, 74.  
31  
32 [285] Ľ. Vančo, M. Kadlečíková, J. Breza, Ľ. Čaplovič, M. Gregor, *Appl. Surf. Sci.* **2013**; *264*, 692.  
33  
34 [286] E. Pięta, E. Proniewicz, B. Szmelter-Fausek, J. Olszewska-Świetlik, L.M. Proniewicz, *J. Raman*  
35 *Spectrosc.* **2014**; *45*, 1019.  
36  
37 [287] P.C. Gutiérrez-Neira, F. Agulló-Rueda, A. Climent-Font, C. Garrido, *Vib. Spectrosc.* **2013**; *69*, 13.  
38  
39 [288] L. Van De Voorde, J. Van Pevenage, K. De Langhe, R. De Wolf, B. Vekemans, L. Vincze, P.  
40 Vandenberghe, M.P.J. Martens, *Spectrochim. Acta - Part B At. Spectrosc.* **2014**; *97*, 1.  
41  
42 [289] F. Marte, V.P. Careaga, N. Mastrangelo, D.L. A. de Faria, M.S. Maier, *J. Raman Spectrosc.* **2014**; *45*,  
43 1046.  
44  
45 [290] M.V. Quattrini, M. Ioele, A. Sodo, G.F. Priori, D. Radeaglia, *Stud. Conserv.* **2014**; *59*, 328.  
46  
47 [291] V. Antunes, A. Candeias, M.J. Oliveira, S. Longelin, V. Serrão, A.I. Seruya, J. Coroado, L. Dias, J. Mirão,  
48 M.L. Carvalho, *J. Raman Spectrosc.* **2014**; *45*, 1026.  
49  
50 [292] H.G.M. Edwards, P. Vandenberghe, T.J. Benoy, *Spectrochim. Acta - Part A Mol. Biomol. Spectrosc.*  
51 **2015**; *137*, 45.  
52  
53  
54  
55  
56  
57  
58  
59  
60

- 1  
2  
3 [293] A. Veiga, D.M. Teixeira, A.J. Candeias, J. Mirão, A. Manhita, C. Miguel, P. Rodrigues, J.G. Teixeira,  
4 *Microchem. J.* **2015**; 123, 51.  
5  
6 [294] I. Żmuda-Trzebiatowska, M. Wachowiak, A. Klisińska-Kopacz, G. Trykowski, G. Śliwiński, *Spectrochim.*  
7 *Acta - Part A Mol. Biomol. Spectrosc.* **2015**; 136, 793.  
8  
9 [295] E. Pięta, E. Proniewicz, B. Szmelter-Fausek, J. Olszewska-Świetlik, L.M. Proniewicz, *Spectrochim. Acta*  
10 *- Part A Mol. Biomol. Spectrosc.* **2015**; 136, 594.  
11  
12 [296] L. Damjanović, M. Gajić-Kvaščev, J. Đurđević, V. Andrić, M. Marić-Stojanović, T. Lazić, S. Nikolić,  
13 *Radiat. Phys. Chem.* **2015**; 115, 135.  
14  
15 [297] K.S. Andrikopoulos, S. Daniilia, B. Roussel, K. Janssens, *J. Raman Spectrosc.* **2006**; 37, 1026.  
16  
17 [298] E. Kouloumpi, P. Vandenabeele, G. Lawson, V. Pavlidis, L. Moens, *Anal. Chim. Acta* **2007**; 598, 169.  
18  
19 [299] M. Abdel-Ghani, H.G.M. Edwards, R. Janaway, B. Stern, *Vib. Spectrosc.* **2008**; 48, 69.  
20  
21 [300] M. Abdel-Ghani, B. Stern, H.G.M. Edwards, R. Janaway, *Vib. Spectrosc.* **2012**; 62, 98.  
22  
23 [301] A. Iordanidis, J. Garcia-Guinea, A. Strati, A. Gkimourtzina, *Anal. Lett.* **2013**;  
24  
25 [302] S. Sotiropoulou, S. Daniilia, *Acc. Chem. Res.* **2010**; 43, 877.  
26  
27 [303] I. Karapanagiotis, D. Lampakis, A. Konstanta, H. Farmakalidis, *J. Archaeol. Sci.* **2013**; 40, 1471.  
28  
29 [304] S. Lahlil, E. Martin, *J. Cult. Herit.* **2012**; 13, 332.  
30  
31 [305] M. Abdel-Ghani, H.G.M. Edwards, B. Stern, R. Janaway, *Spectrochim. Acta - Part A Mol. Biomol.*  
32 *Spectrosc.* **2009**; 73, 566.  
33  
34 [306] M. Abdel-Ghani, *Mediterr. Archaeol. Archaeom.* **2015**; 15, xx.  
35  
36 [307] L. Damjanovic, O. Marjanovic, M. Maric-Stojanovic, V. Andric, U. Mioc, *J. Serbian Chem. Soc.* **2015**;  
37 80, 805.  
38  
39 [308] A. Daveri, B. Doherty, P. Moretti, C. Grazia, A. Romani, E. Fiorin, B.G. Brunetti, M. Vagnini,  
40 *Spectrochim. Acta - Part A Mol. Biomol. Spectrosc.* **2015**; 135, 398.  
41  
42 [309] H.G.M. Edwards, D.W. Farwell, E.M. Newton, F.R. Perez, S.J. Villar, *J. Raman Spectrosc.* **2000**; 31,  
43 407.  
44  
45 [310] I.C.A. Sandu, M.H. de Sá, M.C. Pereira, *Surf. Interface Anal.* **2011**; 43, 1134.  
46  
47 [311] A.C. Prieto, A. Guedes, A. Dória, F. Noronha, **2005**;  
48  
49 [312] H.G.M. Edwards, E.M. Newton, S. O' Connor, D. Evans, *Anal. Bioanal. Chem.* **2010**; 397, 2685.  
50  
51 [313] L. He, N. Wang, X. Zhao, T. Zhou, Y. Xia, J. Liang, B. Rong, *J. Archaeol. Sci.* **2012**; 39, 1809.  
52  
53  
54  
55  
56  
57  
58  
59  
60

- 1  
2  
3 [314] K. Castro, A. Sarmiento, M. Maguregui, I. Martínez-Arkarazo, N. Etxebarria, M. Angulo, M.U.  
4 Barrutia, J.M. González-Cembellín, J.M. Madariaga, *Anal. Bioanal. Chem.* **2008**; 392, 755.  
5  
6 [315] P.J. Jin, W. Huang, Jianhua-Wang, G. Zhao, X.L. Wang, *J. Mol. Struct.* **2010**; 983, 22.  
7  
8 [316] N. Wang, L. He, E. Egel, S. Simon, B. Rong, *Microchem. J.* **2014**; 114, 125.  
9  
10 [317] P. Baraldi, A. Lo Monaco, F. Ortenzi, C. Pelosi, F. Quarato, L. Rossi, *Archaeometry* **2014**; 56, 313.  
11  
12 [318] H.G.M. Edwards, E. Beale, N.C. Garrington, J. –M. Alia, *J. Raman Spectrosc.* **2007**; 38, 316.  
13  
14 [319] I. Aliatis, D. Bersani, P. Paolo, I. Gabriel, P.P. Lottici, I.G. Marino, *ArcheoSciences* **2012**; 36, 7.  
15  
16 [320] M.L. Franquelo, A. Duran, J. Castaing, D. Arquillo, J.L. Perez-Rodriguez, *Talanta* **2012**; 89, 462.  
17  
18 [321] A. Lo Monaco, E. Mattei, C. Pelosi, M. Santancini, *J. Cult. Herit.* **2013**; 14, 537.  
19  
20 [322] S. Kuckova, I.C.A. Sandu, M. Crhova, R. Hynek, I. Fogas, V.S. Muralha, A.V. Sandu, *Microchem. J.*  
21 **2013**; 110, 538.  
22  
23 [323] A. De Santis, E. Mattei, C. Pelosi, *J. Raman Spectrosc.* **2007**; 38, 1368.  
24  
25 [324] L.D. Kock, D. De Waal, *Spectrochim. Acta - Part A Mol. Biomol. Spectrosc.* **2008**; 71, 1348.  
26  
27 [325] M.S. Walton, K. TRENTELMAN, *Archaeometry* **2009**; 51, 845.  
28  
29 [326] L. Bonizzoni, S. Bruni, V. Guglielmi, M. Milazzo, O. Neri, *Archaeometry* **2011**; 53, 1212.  
30  
31 [327] M.L. Franquelo, A. Duran, L.K. Herrera, M.C. Jimenez de Haro, J.L. Perez-Rodriguez, *J. Mol. Struct.*  
32 **2009**; 924-926, 404.  
33  
34 [328] C. Canevali, P. Gentile, M. Orlandi, F. Modugno, J.J. Lucejko, M.P. Colombini, L. Brambilla, S.  
35 Goidanich, C. Riedo, O. Chiantore, P. Baraldi, C. Baraldi, M.C. Gamberini, *Anal. Bioanal. Chem.* **2011**;  
36 401, 1801.  
37  
38 [329] Z. Tóth, J. Mihály, A.J. Tóth, G. Ilon, *Archeometriai Műhely* **2013**; X, 103.  
39  
40 [330] Z. Liu, Y. Han, L. Han, Y. Cheng, Y. Ma, L. Fang, *Spectrochim. Acta - Part A Mol. Biomol. Spectrosc.*  
41 **2013**; 109, 42.  
42  
43 [331] M.M.V. Campos, T.A. Aguayo, *Herit. Sci.* **2015**; 3, 18.  
44  
45 [332] A. Fostiridou, I. Karapanagiotis, S. Vivdenko, D. Lampakis, D. Mantzouris, L. Achilara, P. Manoudis,  
46 *Archaeometry* **2015**; doi: 10.1111/arcm.12177n/a.  
47  
48 [333] V. Košářová, D. Hradil, I. Němec, P. Bezdička, V. Kanický, *J. Raman Spectrosc.* **2013**; 44, 1570.  
49  
50 [334] M. Oujja, M. Sanz, E. Rebollar, J.F. Marco, C. Domingo, P. Pouli, S. Kogou, C. Fotakis, M. Castillejo,  
51 *Spectrochim. Acta - Part A Mol. Biomol. Spectrosc.* **2013**; 102, 7.  
52  
53 [335] N. Navas, J. Romero-Pastor, E. Manzano, C. Cardell, *J. Raman Spectrosc.* **2010**; 41, 1486.  
54  
55  
56  
57  
58  
59  
60

- 1  
2  
3 [336] E. Siotto, M. Dellepiane, M. Callieri, R. Scopigno, C. Gratziu, A. Moscato, L. Burgio, S. Legnaioli, G.  
4 Lorenzetti, V. Palleschi, *J. Cult. Herit.* **2014**; *16*, 307.  
5  
6 [337] C. Conti, C. Colombo, M. Realini, P. Matousek, *J. Raman Spectrosc.* **2015**; *46*, 476.  
7  
8 [338] D. Barilaro, V. Crupi, D. Majolino, G. Barone, R. Ponterio, *J. Appl. Phys.* **2005**; *97*, 044907.  
9  
10 [339] F. Rosi, C. Miliani, I. Borgia, B. Brunetti, a Sgamellotti, *J. Raman Spectrosc.* **2004**; *35*, 610.  
11  
12 [340] O. López-Cruz, A. García-Bueno, V.J. Medina-Flórez, A. Sánchez-Navas, N. Velilla, *Mater.*  
13 *Construcción* **2015**; *65*, e054.  
14  
15 [341] P. Baraldi, A. Bonazzi, N. Giordani, F. Paccagnella, P. Zannini, *Archaeometry* **2006**; *48*, 481.  
16  
17 [342] R. Mazzeo, E. Joseph, V. Minguzzi, G. Grillini, P. Baraldi, D. Prandstraller, *J. Raman Spectrosc.* **2006**;  
18 *37*, 1086.  
19  
20 [343] D. Parras-Guijarro, M. Montejo-Gámez, N. Ramos-Martos, A. Sánchez, *Spectrochim. Acta - Part A*  
21 *Mol. Biomol. Spectrosc.* **2006**; *64*, 1133.  
22  
23 [344] L. Lepot, S. Denoël, B. Gilbert, *J. Raman Spectrosc.* **2006**; *37*, 1098.  
24  
25 [345] T. Zorba, K.S. Andrikopoulos, K.M. Paraskevopoulos, E. Pavlidou, K. Popkonstantinov, R. Kostova, V.  
26 Platnyov, S. Daniilia, *Ann. Chim.* **2007**; *97*, 491.  
27  
28 [346] G.A. Mazzocchin, D. Rudello, E. Murgia, *Ann. Chim.* **2007**; *97*, 807.  
29  
30 [347] S. Daniilia, S. Sotiropoulou, D. Bikiaris, C. Salpistis, G. Karagiannis, Y. Chryssoulakis, B. A. Price, J.H.  
31 Carlson, *J. Cult. Herit.* **2000**; *1*, 91.  
32  
33 [348] P. Baraldi, C. Baraldi, R. Curina, L. Tassi, P. Zannini, *Vib. Spectrosc.* **2007**; *43*, 420.  
34  
35 [349] R. Mazzeo, P. Baraldi, R. Luján, C. Fagnano, *J. Raman Spectrosc.* **2004**; *35*, 678.  
36  
37 [350] S. Aze, J.-M. Vallet, A. Baronnet, O. Grauby, *Eur. J. Mineral.* **2006**; *18*, 835.  
38  
39 [351] M. Pérez-Alonso, K. Castro, I. Martínez-Arkarazo, M. Angulo, M. A. Olazabal, J.M. Madariaga, *Anal.*  
40 *Bioanal. Chem.* **2004**; *379*, 42.  
41  
42 [352] M. Pérez-Alonso, K. Castro, M. Álvarez, J.M. Madariaga, *Anal. Chim. Acta* **2004**; *524*, 379.  
43  
44 [353] G.A. Mazzocchin, E.F. Orsega, P. Baraldi, P. Zannini, *Ann. Chim.* **2006**; *96*, 377.  
45  
46 [354] R. A. Goodall, J. Hall, H.G.M. Edwards, R.J. Sharer, R. Viel, P.M. Fredericks, *J. Archaeol. Sci.* **2007**; *34*,  
47 666.  
48  
49 [355] F. Bordignon, P. Postorino, A. Nucara, P. Dore, G. Trojsi, V. Bellelli, *J. Cult. Herit.* **2008**; *9*, 23.  
50  
51 [356] S. Daniilia, E. Minopoulou, K.S. Andrikopoulos, A. Tsakalof, K. Bairachtari, *J. Archaeol. Sci.* **2008**; *35*,  
52 2474.  
53  
54  
55  
56  
57  
58  
59  
60

- 1  
2  
3 [357] M. Castriota, E. Meduri, T. Barone, G. De Santo, E. Cazzanelli, *J. Raman Spectrosc.* **2008**; 39, 284.  
4  
5 [358] A. Zucchiatti, *Surf. Eng.* **2008**; 24, 162.  
6  
7 [359] M. Sawczak, A. Kamińska, G. Rabczuk, M. Ferretti, R. Jendrzewski, G. Śliwiński, *Appl. Surf. Sci.* **2009**;  
8 255, 5542.  
9  
10 [360] H.G.M. Edwards, P.S. Middleton, M.D. Hargreaves, *Spectrochim. Acta - Part A Mol. Biomol.*  
11 *Spectrosc.* **2009**; 73, 553.  
12  
13 [361] B. Minceva-Sukarova, O. Grupce, V. Tanevska, L. Robeva-Cukovska, S. Mamucevska-Miljkovic,  
14 *Maced. J. Chem. Chem. Eng.* **2007**; 26, 103.  
15  
16 [362] A. Sodo, D. Artioli, A. Botti, G. De Palma, A. Giovagnoli, M. Mariottini, A. Paradisi, C. Polidoro, M.A.  
17 Ricci, *J. Raman Spectrosc.* **2008**; 39, 1035.  
18  
19 [363] A. Nevin, J.L. Melia, I. Osticioli, G. Gautier, M.P. Colombini, *J. Cult. Herit.* **2008**; 9, 154.  
20  
21 [364] A. Hernanz, I. Bratu, O.F. Marutoiu, C. Marutoiu, J.M. Gavira-Vallejo, H.G.M. Edwards, *Anal. Bioanal.*  
22 *Chem.* **2008**; 392, 263.  
23  
24 [365] L. Boselli, S. Ciattini, M. Galeotti, M.R. Lanfranchi, C. Lofrumento, M. Picollo, A. Zoppi, *E-Preservation*  
25 *Sci.* **2009**; 6, 38.  
26  
27 [366] P. Vandenaabeele, R. Garcia-Moreno, F. Mathis, K. Leterme, E. Van Elslande, F.-P.P. Hocquet, S.  
28 Rakkaa, D. Laboury, L. Moens, D. Strivay, M. Hartwig, *Spectrochim. Acta - Part A Mol. Biomol.*  
29 *Spectrosc.* **2009**; 73, 546.  
30  
31 [367] Q.G. Zeng, G.X. Zhang, C.W. Leung, J. Zuo, *Microchem. J.* **2010**; 96, 330.  
32  
33 [368] A. Sansonetti, J. Striova, D. Biondelli, E.M. Castellucci, *Anal. Bioanal. Chem.* **2010**; 397, 2667.  
34  
35 [369] A. Duran, M.C. Jimenez De Haro, J.L. Perez-Rodriguez, M.L. Franquelo, L.K. Herrera, A. Justo,  
36 *Archaeometry* **2010**; 52, 286.  
37  
38 [370] A. Deneckere, W. Schudel, M. Van Bos, H. Wouters, A. Bergmans, P. Vandenaabeele, L. Moens,  
39 *Spectrochim. Acta - Part A Mol. Biomol. Spectrosc.* **2010**; 75, 511.  
40  
41 [371] R.J.H. Clark, R.R. Hark, N. Salvadó, S. Butí, T. Pradell, *J. Raman Spectrosc.* **2010**; 41, 1418.  
42  
43 [372] T. Aguayo, E. Clavijo, F. Eisner, C. Ossa-Izquierdo, M.M. Campos-Valette, *J. Raman Spectrosc.* **2011**;  
44 42, 2143.  
45  
46 [373] I. Garofano, A. Duran, J.L. Perez-Rodriguez, M.D. Robador, in: *Spectrosc. Lett.*, CSIC, Spain, Madrid,  
47 2011, pp. 560–565.  
48  
49 [374] M.K. Donais, D. George, B. Duncan, S.M. Wojtas, A. M. Daigle, *Anal. Methods* **2011**; 3, 1061.  
50  
51 [375] D. Comelli, A. Nevin, G. Valentini, I. Osticioli, E.M. Castellucci, L. Toniolo, D. Gulotta, R. Cubeddu, *J.*  
52 *Cult. Herit.* **2011**; 12, 11.  
53  
54  
55  
56  
57  
58  
59  
60

- 1  
2  
3 [376] H.H.M. Mahmoud, *Mediterr. Archaeol. Archaeom.* **2011**; *11*, 99.  
4  
5 [377] A. Duran, J.L. Perez-Rodriguez, M.C. Jimenez de Haro, M.L. Franquelo, M.D. Robador, *J. Archaeol. Sci.*  
6 **2011**; *38*, 2366.  
7  
8 [378] C. Clementi, V. Ciocan, M. Vagnini, B. Doherty, M.L. Tabasso, C. Conti, B.G. Brunetti, C. Miliani, *Anal.*  
9 *Bioanal. Chem.* **2011**; *401*, 1815.  
10  
11 [379] M. Maguregui, U. Knuutinen, I. Martínez-Arkarazo, K. Castro, J.M. Madariaga, *Anal. Chem.* **2011**; *83*,  
12 3319.  
13  
14 [380] J. Romero-Pastor, A. Duran, A.B. Rodríguez-Navarro, R. Van Grieken, C. Cardell, *Anal. Chem.* **2011**;  
15 *83*, 8420.  
16  
17 [381] M. Gil, M.L. Carvalho, S. Longelin, I. Ribeiro, S. Valadas, J. Mirão, A.E. Candeias, *Appl. Spectrosc.*  
18 **2011**; *65*, 782.  
19  
20 [382] A. Iordanidis, J. Garcia-Guinea, A. Strati, A. Gkimourtzina, A. Papoulidou, *Spectrochim. Acta - Part A*  
21 *Mol. Biomol. Spectrosc.* **2011**; *78*, 874.  
22  
23 [383] E. Gliozzo, F. Cavari, D. Damiani, I. Memmi, *Archaeometry* **2012**; *54*, 278.  
24  
25 [384] H.H.M. Mahmoud, *Archeometriai Műhely* **2012**; *3*, 205.  
26  
27 [385] G. Nord, K. Tronner, **2014**; *109*, 118.  
28  
29 [386] M.T. Doménech-Carbó, H.G.M. Edwards, A. Doménech-Carbó, J.M. Del Hoyo-Meléndez, J. De La  
30 Cruz-Canizares, *J. Raman Spectrosc.* **2012**; *43*, 1250.  
31  
32 [387] M. Irazola, M. Olivares, K. Castro, M. Maguregui, I. Martínez-Arkarazo, J.M. Madariaga, *J. Raman*  
33 *Spectrosc.* **2012**; *43*, 1676.  
34  
35 [388] A. Paradisi, A. Sodo, D. Artioli, A. Botti, D. Cavezzali, A. Giovagnoli, C. Polidoro, M. A. Ricci,  
36 *Archaeometry* **2012**; *54*, 1060.  
37  
38 [389] A. Sánchez, J. Tuñón, M. Montejo, D. Parras, *J. Raman Spectrosc.* **2012**; *43*, 1788.  
39  
40 [390] H.H.M. Mahmoud, N. Kantiranis, J. Stratis, *Mediterr. Archaeol. Archaeom.* **2012**; *12*, 81.  
41  
42 [391] E. Conz, L. Appolonia, P. Galinetto, M.P. Riccardi, S. Tarantino, M. Zema, *Procedia Chem.* **2013**; *8*, 78.  
43  
44 [392] F. Toschi, A. Paladini, F. Colosi, P. Cafarelli, V. Valentini, M. Falconieri, S. Gagliardi, P. Santoro, *Appl.*  
45 *Surf. Sci.* **2013**; *284*, 291.  
46  
47 [393] M. Gil, C. Araujo, M.L. Carvalho, S. Longelin, L. Dias, S. Valadas, C. Souto, J. Frade, I. Ribeiro, J. Mirão,  
48 A. Candeias, *X-Ray Spectrom.* **2013**; *42*, 242.  
49  
50 [394] H.H.M. Mahmoud, *Acta Phys. Pol. A* **2013**; *123*, 782.  
51  
52 [395] M. Aceto, G. Gatti, A. Agostino, G. Fenoglio, V. Giordano, M. Varetto, G. Castagneri, *J. Raman*  
53 *Spectrosc.* **2012**; *43*, 1754.  
54  
55  
56  
57  
58  
59  
60

- 1  
2  
3 [396] D. Bersani, P.P. Lottici, A. Casoli, M. Ferrari, S. Lottini, D. Cauzzi, *Lasers Conserv. Artworks Lacona VI*  
4 *Proceedings, Vienna, Austria, Sept. 21-25, 2005* **2007**; 383.  
5  
6 [397] M. Maguregui, U. Knuutinen, I. Martínez-Arkarazo, A. Giakoumaki, K. Castro, J.M. Madariaga, *J.*  
7 *Raman Spectrosc.* **2012**; *43*, 1747.  
8  
9 [398] M. Maguregui, U. Knuutinen, J. Trebolazabala, H. Morillas, K. Castro, I. Martinez-Arkarazo, J.M.  
10 Madariaga, *Anal. Bioanal. Chem.* **2012**; *402*, 1529.  
11  
12 [399] A. Zoppi, C. Lofrumento, M. Ricci, E. Cantisani, T. Fratini, E.M. Castellucci, *J. Raman Spectrosc.* **2012**;  
13 *43*, 1663.  
14  
15 [400] L.R. Čukovska, B. Minčeva - Šukarova, A. Lluveras-Tenorio, A. Andreotti, M.P. Colombini, I. Nastova,  
16 *J. Raman Spectrosc.* **2012**; *43*, 1685.  
17  
18 [401] G.E. De Benedetto, A. Savino, D. Fico, D. Rizzo, A. Pennetta, A. Cassiano, B. Minerva, *Open J.*  
19 *Archaeom.* **2013**; *1*, 12.  
20  
21 [402] T. Zhu, J. Chen, R. Hui, *Anal. Lett.* **2013**; *46*, 37.  
22  
23 [403] A. Iordanidis, J. Garcia-Guinea, A. Strati, A. Gkimourtzina, *Anal. Lett.* **2014**; *47*, 2708.  
24  
25 [404] Z. Li, L. Wang, Q. Ma, J. Mei, *Herit. Sci.* **2014**; *2*, 21.  
26  
27 [405] D. Damiani, E. Gliozzo, I. Memmi Turbanti, *Archaeol. Anthropol. Sci.* **2014**; *6*, 363.  
28  
29 [406] D. Bersani, M. Berzioli, S. Caglio, A. Casoli, P.P. Lottici, L. Medeghini, G. Poldi, P. Zannini, *Microchem.*  
30 *J.* **2014**; *114*, 80.  
31  
32 [407] M. Gil, V. Serrão, M.L. Carvalho, S. Longelin, L. Dias, A. Cardoso, A. T. Caldeira, T. Rosado, J. Mirão, A.  
33 E. Candeias, *Color Res. Appl.* **2014**; *39*, 288.  
34  
35 [408] O. Syta, K. Rozum, M. Choińska, D. Zielińska, G.Z. Żukowska, A. Kijowska, B. Wagner, *Spectrochim.*  
36 *Acta - Part B At. Spectrosc.* **2014**; *101*, 140.  
37  
38 [409] J.M. Madariaga, M. Maguregui, S.F.-O. De Vallejuelo, U. Knuutinen, K. Castro, I. Martinez-Arkarazo,  
39 A. Giakoumaki, A. Pitarch, *J. Raman Spectrosc.* **2014**; *45*, 1059.  
40  
41 [410] H.H.M. Mahmoud, *Herit. Sci.* **2014**; *2*, 18.  
42  
43 [411] J.L. Perez-Rodriguez, M.D. Robador, M.A. Centeno, B. Siguenza, A. Duran, *Spectrochim. Acta - Part A*  
44 *Mol. Biomol. Spectrosc.* **2014**; *120*, 602.  
45  
46 [412] M. Gelzo, M. Grimaldi, A. Vergara, V. Severino, A. Chambery, A. Dello Russo, C. Piccioli, G. Corso, P.  
47 Arcari, *Chem. Cent. J.* **2014**; *8*, 1.  
48  
49 [413] M.J. de la Torre-López, A. Dominguez-Vidal, M.J. Campos-Suñol, R. Rubio-Domene, U. Schade, M.J.  
50 Ayora-Cañada, *J. Raman Spectrosc.* **2014**; *45*, 1052.  
51  
52 [414] C. Araya, J. Jaque, N. Naranjo, M. Icaza, R.E. Clavijo, T. Aguayo, M.M. Campos-Vallette, *Spectrosc.*  
53 *Lett.* **2014**; *47*, 177.  
54  
55  
56  
57  
58  
59  
60

- 1  
2  
3 [415] E. Cheilakou, M. Troullinos, M. Kouli, *J. Archaeol. Sci.* **2014**; *41*, 541.  
4  
5 [416] A. Paladini, F. Toschi, F. Colosi, G. Rubino, P. Santoro, *Appl. Phys. A* **2014**; *118*, 131.  
6  
7 [417] E. Aquilia, A. Giuffrida, C. Ingoglia, P. Mazzoleni, S. Raneri, *Rend. Fis. Acc. Lincei* **2015**; *26*, 475.  
8  
9 [418] M.L. Amadori, S. Barcelli, G. Poldi, F. Ferrucci, A. Andreotti, P. Baraldi, M.P. Colombini, *Microchem. J.*  
10 **2015**; *118*, 183.  
11  
12 [419] L.D. Mateos, D. Cosano, M. Mora, I. Muñiz, R. Carmona, C. Jiménez-Sanchidrián, J.R. Ruiz,  
13 *Spectrochim. Acta - Part A Mol. Biomol. Spectrosc.* **2015**; *151*, 16.  
14  
15 [420] N. Salvadó, S. Butí, M. A. G. Aranda, T. Pradell, *Anal. Methods* **2014**; *6*, 3610.  
16  
17 [421] M. Veneranda, M. Irazola, A. Pitarch, M. Olivares, A. Iturregui, K. Castro, J.M. Madariaga, *J. Raman*  
18 *Spectrosc.* **2014**; *45*, 228.  
19  
20 [422] M. Veneranda, M. Irazola, M. Díez, A. Iturregui, J. Aramendia, K. Castro, J.M. Madariaga, *J. Raman*  
21 *Spectrosc.* **2014**; *45*, 1110.  
22  
23 [423] M. Maguregui, K. Castro, H. Morillas, J. Trebolazabala, U. Knuutinen, R. Wiesinger, M. Schreiner, J.M.  
24 Madariaga, *Anal. Methods* **2014**; *6*, 372.  
25  
26 [424] I. Kakoulli, S. V. Prikhodko, A. King, C. Fischer, *J. Archaeol. Sci.* **2014**; *44*, 148.  
27  
28 [425] R. Piovesan, L. Maritan, J. Neguer, *J. Archaeol. Sci.* **2014**; *46*, 68.  
29  
30 [426] M.S. Gill, C.P. Rendo, S. Menon, *Stud. Conserv.* **2014**; *59*, 300.  
31  
32 [427] L. Yong, W. Shiwei, *Stud. Conserv.* **2014**; *59*, 314.  
33  
34 [428] B.A. Schmidt, M.A. Ziemann, S. Pentzien, T. Gabsch, W. Koch, J. Krüger, *Stud. Conserv.* **2015**; doi:  
35 10.1179/2047058414Y.0000000152  
36  
37 [429] M. Gutman, B. Zupanek, M. Lesar Kikelj, S. Kramar, *Archaeometry* **2015**; doi: 10.1111/arcm.12167.  
38  
39 [430] V. Crupi, G. Galli, M.F. La Russa, F. Longo, G. Maisano, D. Majolino, M. Malagodi, A. Pezzino, M.  
40 Ricca, B. Rossi, S.A. Ruffolo, V. Venuti, *Appl. Surf. Sci.* **2015**; *349*, 924.  
41  
42 [431] H. Berke, *Chem. Soc. Rev.* **2007**; *36*, 15.  
43  
44 [432] E. Mattei, G. De Vivo, A. De Santis, C. Gaetani, C. Pelosi, U. Santamaria, *J. Raman Spectrosc.* **2008**;  
45 *39*, 302.  
46  
47 [433] F. Daniel, A. Mounier, J. Aramendia, L. Gómez, K. Castro, S. Fdez-Ortiz de Vallejuelo, M. Schlicht, *J.*  
48 *Raman Spectrosc.* **2015**; doi: 10.1002/jrs.4770  
49  
50 [434] M. Aru, L. Burgio, M.S. Rumsey, *J. Raman Spectrosc.* **2014**; *45*, 1013.  
51  
52 [435] G. Chiari, R. Giustetto, G. Ricchiardi, *Eur. J. Mineral.* **2003**; *15*, 21.  
53  
54  
55  
56  
57  
58  
59  
60

- 1  
2  
3 [436] R. Giustetto, F.X. Llabrés i Xamena, G. Ricchiardi, S. Bordiga, A. Damin, R. Gobetto, M.R. Chierotti, *J. Phys. Chem. B* **2005**; *109*, 19360.  
4  
5  
6 [437] R. Giustetto, K. Seenivasan, F. Bonino, G. Ricchiardi, S. Bordiga, M.R. Chierotti, R. Gobetto, *J. Phys. Chem. C* **2011**; *115*, 16764.  
7  
8  
9 [438] P. Vandenabeele, S. Bodé, A. Alonso, L. Moens, *Spectrochim. Acta - Part A Mol. Biomol. Spectrosc.* **2005**; *61*, 2349.  
10  
11  
12 [439] M. Sánchez Del Río, M. Picquart, E. Haro-Poniatowski, E. Van Elslande, V.H. Uc, *J. Raman Spectrosc.* **2006**; *37*, 1046.  
13  
14  
15 [440] F.S. Manciu, L. Reza, L. A. Polette, B. Torres, R.R. Chianelli, *J. Raman Spectrosc.* **2007**; *38*, 1193.  
16  
17 [441] H.G. Wiedemann, K.-W.W. Brzezinka, K. Witke, I. Lamprecht, *Thermochim. Acta* **2007**; *456*, 56.  
18  
19 [442] M.S. del Río, L. A. T. Montes, *Thermochim. Acta* **2007**; *466*, 75.  
20  
21 [443] G. Garcia Moreno, D. Strivay, B. Gilbert, *J. Raman Spectrosc.* **2008**; *39*, 1050.  
22  
23 [444] F.S. Manciu, A. Ramirez, W. Durrer, J. Govani, R.R. Chianelli, *J. Raman Spectrosc.* **2008**; *39*, 1257.  
24  
25 [445] A. Doménech, M.T. Doménech-Carbó, H.G.M. Edwards, *J. Raman Spectrosc.* **2011**; *42*, 86.  
26  
27 [446] C. Tsiantos, M. Tsampodimou, G.H. Kacandes, M. Sánchez del Río, V. Gionis, G.D. Chryssikos, *J. Mater. Sci.* **2012**; *47*, 3415.  
28  
29 [447] C. Dejoie, P. Martinetto, E. Dooryhée, P. Strobel, S. Blanc, P. Bordat, R. Brown, F. Porcher, M. Sanchez Del Rio, M. Anne, *ACS Appl. Mater. Interfaces* **2010**; *2*, 2308.  
30  
31 [448] Y. Zhang, L. Fan, H. Chen, J. Zhang, Y. Zhang, A. Wang, *Microporous Mesoporous Mater.* **2015**; *211*, 124.  
32  
33 [449] T. Chivers, P.J.W. Elder, *Chem. Soc. Rev.* **2013**; *42*, 5996.  
34  
35 [450] R.J.H. Clark, T.J. Dines, M. Kurnoo, *Inorg. Chem.* **1983**; *22*, 2766.  
36  
37 [451] N. Gobeltz, A. Demortier, J.P. Lelieur, C. Duhayon, *J. Chem. Soc. Faraday Trans.* **1998**; *94*, 677.  
38  
39 [452] M. Bicchieri, M. Nardone, P.A. Russo, A. Sodo, M. Corsi, G. Cristoforetti, V. Palleschi, A. Salvetti, E. Tognoni, *Spectrochim. Acta - Part B At. Spectrosc.* **2001**; *56*, 915.  
40  
41 [453] M. Ostroumov, E. Fritsch, E. Faulques, O. Cauvet, *Can. Mineral.* **2002**; *40*, 1.  
42  
43 [454] N. Gobeltz-Hautecoeur, A. Demortier, B. Lede, J.P. Lelieur, C. Duhayon, *Inorg. Chem.* **2002**; *41*, 2848.  
44  
45 [455] V. Desnica, K. Furic, M. Schreiner, *E-Preservation Sci.* **2004**; *1*, 15.  
46  
47 [456] E. Del Federico, W. Shöffberger, J. Schelvis, S. Kapetanaki, L. Tyne, A. Jerschow, *Inorg. Chem.* **2006**; *45*, 1270.  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60

- 1  
2  
3 [457] P. Ballirano, A. Maras, *Am. Mineral.* **2006**; 91, 997.  
4  
5 [458] E.M. a Ali, H.G.M. Edwards, *Spectrochim. Acta - Part A Mol. Biomol. Spectrosc.* **2014**; 121, 415.  
6  
7 [459] M.M. Barsan, I.S. Butler, D.F.R. Gilson, *Spectrochim. Acta - Part A Mol. Biomol. Spectrosc.* **2012**; 98,  
8 457.  
9  
10 [460] R. Clark, M. Curri, C. Laganara, *Spectrochim. Acta - Part A Mol. Biomol. Spectrosc.* **1997**; 53, 597.  
11  
12 [461] R. Clark, M. Curri, G. Henshaw, C. Laganara, *J. Raman Spectrosc.* **1997**; 28, 105.  
13  
14 [462] P. Colomban, *Revue Annuelle de la Société Française d'étude de la céramique Orientale* **2005**; 4, 145.  
15  
16 [463] S. Greiff, J. Schuster, *J. Cult. Herit.* **2008**; 9, e27.  
17  
18 [464] A. Mangone, G.E. De Benedetto, D. Fico, L.C. Giannossa, R. Laviano, L. Sabbatini, I.D. van der Werf,  
19 A. Traini, *New J. Chem.* **2011**; 35, 2860.  
20  
21 [465] A. Tournié, L.C. Prinsloo, P. Colomban, *J. Raman Spectrosc.* **2012**; 43, 532.  
22  
23 [466] L.C. Prinsloo, A. Tournié, P. Colomban, *J. Archaeol. Sci.* **2011**; 38, 3264.  
24  
25 [467] P. Colomban, A. Tournié, M.C. Caggiani, C. Paris, *J. Raman Spectrosc.* **2012**; 43, 1975.  
26  
27 [468] M. Sendova, B. Kaiser, M. Scalera, V. Zhelyaskov, *J. Raman Spectrosc.* **2010**; 41, 469.  
28  
29 [469] M. Derrick, D. Stulik, J. Landry, *Infrared Spectroscopy in Conservation Science*, The Getty , Los  
30 Angeles, **2000**.  
31  
32 [470] C. Miliani, A. Daveri, B.G. Brunetti, A. Sgamellotti, *Chem. Phys. Lett.* **2008**; 466, 148.  
33  
34 [471] M. Bacci, C. Cucci, E. Del Federico, A. Ienco, A. Jerschow, J.M. Newman, M. Picollo, *Vib. Spectrosc.*  
35 **2009**; 49, 80.  
36  
37 [472] M. Favaro, A. Guastoni, F. Marini, S. Bianchin, A. Gambirasi, *Anal. Bioanal. Chem.* **2012**; 402, 2195.  
38  
39 [473] I. Osticioli, N.F.C. Mendes, A. Nevin, F.P.S.C. Gil, M. Becucci, E. Castellucci, *Spectrochim. Acta - Part A*  
40 *Mol. Biomol. Spectrosc.* **2009**; 73, 525.  
41  
42 [474] I. Osticioli, N.F.C. Mendes, A. Nevin, A. Zoppi, C. Lofrumento, M. Becucci, E.M. Castellucci, *Rev. Sci.*  
43 *Instrum.* **2009**; 80, 78.  
44  
45 [475] C.M. Schmidt, M.S. Walton, K. Trentelman, *Anal. Chem.* **2009**; 81, 8513.  
46  
47 [476] A. R. De Torres, S. Ruiz-Moreno, A. López-Gil, P. Ferrer, M.C. Chillón, *J. Raman Spectrosc.* **2014**; 45,  
48 1279.  
49  
50 [477] A. Dominguez-Vidal, M. Jose de la Torre-Lopez, R. Rubio-Domene, M.J. Ayora-Cañada, *Analyst* **2012**;  
51 137, 5763.  
52  
53  
54  
55  
56  
57  
58  
59  
60

- 1  
2  
3 [478] A. Veiga, J. Mirão, A.J. Candeias, P. Simões Rodrigues, D. Martins Teixeira, V.S.F. Muralha, J. Ginja  
4 Teixeira, *J. Raman Spectrosc.* **2014**; *45*, 947.  
5  
6 [479] A. Palet Casas, J.D. Andrés Llopis, *Stud. Conserv.* **1992**; *37*, 132.  
7  
8 [480] F. Daniel, A. Mounier, B. Laborde, É. Coulon, in: Proceedings of V Congr. Naz. Di Archeometria,  
9 Syracuse, Italy, **2008**, pp 307-316  
10  
11 [481] F. Daniel, B. Laborde, A. Mounier, É. Coulon, *ArcheoSciences Rev. D'archéometrie* **2008**; *32*, 83.  
12  
13 [482] N. Buzgar, A. Buzatu, A.-I. Apopei, V. Cotiugă, *Vib. Spectrosc.* **2014**; *72*, 142.  
14  
15 [483] J. Pérez-Arantegui, C. Pardos, J.-L. Abad, J.-R. García, *Microsc. Microanal.* **2013**; *19*, 1645.  
16  
17 [484] R. Garcia Moreno, F. Mathis, V. Mazel, M. Dubus, T. Calligaro, D. Strivay, *Archaeometry* **2008**; *50*,  
18 658.  
19  
20 [485] D. A. Scott, G. Eggert, *Rev. Conserv.* **2007**; *52 Suppl.1*, 3.  
21  
22 [486] Z. Čermáková, J. Hradilová, J. Jehlička, K. Osterrothová, A. Massanek, P. Bezdička, D. Hradil,  
23 *Archaeometry* **2014**; *56*, 148.  
24  
25 [487] Z. Čermáková, S. Švarcová, J. Hradilová, P. Bezdička, A. Lančok, V. Vašutová, J. Blažek, D. Hradil,  
26 *Spectrochim. Acta - Part A Mol. Biomol. Spectrosc.* **2015**; *140*, 101.  
27  
28 [488] J.T. Kloprogge, D. Visser, W.N. Martens, L.V. Duong, R.L. Frost, *Netherlands J. Geosci. En Mijnbouw.*  
29 **2003**; *82*, 209.  
30  
31 [489] S.E. Filippakis, B. Perdikatsis, T. Paradellis, *Stud. Conserv.* **1976**; *21*, 143.  
32  
33 [490] A. Brysbaert, *J. Archaeol. Sci.* **2008**; *35*, 2761.  
34  
35 [491] P. Westlake, P. Siozos, A. Philippidis, C. Apostolaki, B. Derham, A. Terlix, V. Perdikatsis, R. Jones, D.  
36 Anglos, *Anal. Bioanal. Chem.* **2012**; *402*, 1413.  
37  
38 [492] A.G. Vlachopoulos, S. Sotiropoulou, *Talanta* **2012**; *44*, 245.  
39  
40 [493] S. Sotiropoulou, V. Perdikatsis, K. Birtacha, C. Apostolaki, A. Devetzi, *Archaeol. Anthropol. Sci.* **2012**;  
41 *4*, 263.  
42  
43 [494] K. Castro, A. Sarmiento, I. Martínez-Arkarazo, J.M. Madariaga, L.A. Fernández, I. Martínez-Arkarazo,  
44 J.M. Madariaga, L.A. Fernández, *Anal. Chem.* **2008**; *80*, 4103.  
45  
46 [495] B.S. Yu, J.N. Fang, E.P. Huang, *J. Raman Spectrosc.* **2013**; *44*, 630.  
47  
48 [496] I. Aliatis, D. Bersani, E. Campani, A. Casoli, P.P. Lottici, S. Mantovan, I.G. Marino, F. Ospitali,  
49 *Spectrochim. Acta - Part A Mol. Biomol. Spectrosc.* **2009**; *73*, 532.  
50  
51 [497] L.M. Moretto, E.F. Orsega, G.A. Mazzocchin, *J. Cult. Herit.* **2011**; *12*, 384.  
52  
53 [498] C. Genestar, C. Pons, *Anal. Bioanal. Chem.* **2005**; *382*, 269.  
54  
55  
56  
57  
58  
59  
60

- 1  
2  
3 [499] S. Daniilia, D. Bikiaris, L. Burgio, P. Gavala, R.J.H. Clark, Y. Chryssoulakis, *J. Raman Spectrosc.* **2002**;  
4 33, 807.  
5  
6 [500] R. A. Goodall, J. Hall, R. Viel, F.R. Agurcia, H.G.M. Edwards, P.M. Fredericks, *J. Raman Spectrosc.*  
7 **2006**; 37, 1072.  
8  
9 [501] F. Ospitali, D. Bersani, G. Di Lonardo, P.P. Lottici, *J. Raman Spectrosc.* **2008**; 39, 1066.  
10  
11 [502] O. Cristini, C. Kinowski, S. Turrell, *J. Raman Spectrosc.* **2010**; 41, 1410.  
12  
13 [503] J.L. Perez-Rodriguez, M.D.C.J. de Haro, B. Siguenza, J.M. Martinez-Blanes, *Appl. Clay Sci.* **2015**; 116-  
14 117, 211.  
15  
16 [504] K.F. Gebremariam, L. Kvittingen, F.-G. Banica, *Archaeometry* **2015**. doi: 10.1111/arcm.12163  
17  
18 [505] C. Pelosi, G. Agresti, M. Andaloro, P. Baraldi, P. Pogliani, U. Santamaria, M.F. La Russa, S. A. Ruffolo,  
19 N. Rovella, *Archaeometry* **2015**; doi: 10.1111/arcm.12184  
20  
21 [506] D. Scott, *Stud. Conserv.* **2000**; 45, 39.  
22  
23 [507] D.A. Scott, *Copper and Bronze in Art : Corrosion, Colorants, Conservation*, Getty Conservation  
24 Institute, **2002**.  
25  
26 [508] B. Gilbert, S. Denoël, G. Weber, D. Allart, *Analyst* **2003**; 128, 1213.  
27  
28 [509] K. Castro, S. Pessanha, N. Proietti, E. Princi, D. Capitani, M.L. Carvalho, J.M. Madariaga, *Anal.*  
29 *Bioanal. Chem.* **2008**; 391, 433.  
30  
31 [510] G. Bertolotti, D. Bersani, P.P. Lottici, M. Alesiani, T. Malcherek, J. Schlüter, *Anal. Bioanal. Chem.*  
32 **2012**; 402, 1451.  
33  
34 [511] K. Eremin, J. Stenger, M. Li Green, *J. Raman Spectrosc.* **2006**; 37, 1119.  
35  
36 [512] E. Bidaud, E. Halwax, E. Pantos, B. Sipek, *Stud. Conserv.* **2008**; 53, 81.  
37  
38 [513] L. Burgio, R.J.H. Clark, V.S.F. Muralha, T. Stanley, *J. Raman Spectrosc.* **2008**; 39, 1482.  
39  
40 [514] M.J. Campos-Suñol, M.J. De la torre-Lopez, M.J. Ayora-Cañada, A. Dominguez-Vidal, *J. Raman*  
41 *Spectrosc.* **2009**; 40, 2104.  
42  
43 [515] Q.M. S. Wei, M. Schreiner, H. Guo, *Int. J. Conserv. Sci.* **2010**; 1, 99.  
44  
45 [516] E.P. Tomasini, C.R. Landa, G. Siracusano, M.S. Maier, *J. Raman Spectrosc.* **2013**; 44, 637.  
46  
47 [517] L. Yong, *Stud. Conserv.* **2012**; 57, 106.  
48  
49 [518] D. Cauzzi, G. Chiavari, S. Montalbani, D. Melucci, D. Cam, H. Ling, *J. Cult. Herit.* **2013**; 14, 70.  
50  
51 [519] E. Egel, S. Simon, *Herit. Sci.* **2013**; 1, 29.  
52  
53 [520] K. Hu, *Herit. Sci.* **2013**; 1, 1.  
54  
55  
56  
57  
58  
59  
60

- 1  
2  
3 [521] A. Dominguez-Vidal, M.J. de la Torre-López, M.J. Campos-Suñol, R. Rubio-Domene, M.J. Ayora-  
4 Cañada, *J. Raman Spectrosc.* **2014**; *45*, 1006.  
5  
6 [522] S. Švarcová, Z. Čermáková, J. Hradilová, P. Bezdička, D. Hradil, *Spectrochim. Acta - Part A Mol.*  
7 *Biomol. Spectrosc.* **2014**; *132*, 514.  
8  
9 [523] S. Valadas, R. V. Freire, A. Cardoso, J. Mirão, C.B. Dias, P. Vandenabeele, A. Candeias, *Microsc.*  
10 *Microanal.* **2015**; *21*, 518.  
11  
12 [524] Y. Zhang, J. Wang, H. Liu, X. Wang, S. Zhang, *Anal. Lett.* **2015**; *48*, 2400.  
13  
14 [525] T. Akyuz, S. Akyuz, A. Gulec, *Spectrochim. Acta - Part A Mol. Biomol. Spectrosc.* **2015**; *149*, 744.  
15  
16 [526] I. Aliatis, D. Bersani, E. Campani, A. Casoli, P.P. Lottici, S. Mantovan, I.G. Marino, *J. Raman Spectrosc.*  
17 **2010**; *41*, 1537.  
18  
19 [527] P. Baraldi, P. Moioli, P. Santopadre, C. Seccaroni, *Boll. ICR* **2009**; *18-19*, 23.  
20  
21 [528] Q.G. Zeng, G.X. Zhang, J.H. Tan, C.W. Leung, J. Zuo, *J. Raman Spectrosc.* **2011**; *42*, 1311.  
22  
23 [529] A. Klisińska-Kopacz, *J. Raman Spectrosc.* **2015**; *46*, 317.  
24  
25 [530] G. Gatto Rotondo, L. Darchuk, M. Swaenen, R. Van Grieken *J. Anal. Sci. Methods Instrum.* **2012**; *2*,  
26 42.  
27  
28 [531] J. Ambers, *J. Raman Spectrosc.* **2004**; *35*, 768.  
29  
30 [532] N. Buzgar, A. Buzatu, A.I. Apopei, D. Aștefanei, F. Topoleanu, *Analele Stiint. Ale Univ. "Al. I. Cuza"*  
31 *Din Iasi, Geol.* **2011**; *57*, 15.  
32  
33 [533] M. Sepúlveda, S. Gutierrez, M. Campos-Vallette, E. Clavijo, P. Walter, J.J. Cárcamo, *J. Chil. Chem. Soc.*  
34 **2013**; *58*, 1836.  
35  
36 [534] C. Pelosi, G. Agresti, M. Andaloro, P. Baraldi, P. Pogliani, U. Santamaria, *E-Preservation Sci.* **2013**; *10*,  
37 99.  
38  
39 [535] L. Monico, K. Janssens, E. Hendriks, B.G. Brunetti, C. Miliani, *J. Raman Spectrosc.* **2014**; *45*, 1034.  
40  
41 [536] Mugnaini, S, A. Bagnoli, P. Bensi, F. Droghini, A. Scala, G. Guasparri, *J. Cult. Herit.* **2006**; *7*, 355.  
42  
43 [537] G. Guasparri, *J. Cult. Herit.* **2006**; *7*, 355.  
44  
45 [538] D. Hradil, J. Hradilová, P. Bezdička, S. Švarcová, Z. Čermáková, V. Košařová, I. Němec, *J. Raman*  
46 *Spectrosc.* **2014**; *45*, 848.  
47  
48 [539] M. Abdel-Ghani, H.H.M. Mahmoud, *J. Archaeol. Restor. Stud.* **2013**; *3*, 95.  
49  
50 [540] H.G.M. Edwards, P. Vandenabeele, J. Jehlicka, T.J. Benoy, *Spectrochim. Acta - Part A Mol. Biomol.*  
51 *Spectrosc.* **2014**; *118*, 598.  
52  
53  
54  
55  
56  
57  
58  
59  
60

- 1  
2  
3 [541] F. Bellini, D. Bersani, H.G.M. Edwards, J. Jehlicka, P. Vandenabeele, P. P. Lottici, 8th Congress on the  
4 Application of Raman Spectroscopy in Art and Archaeology - RAA 2015, Wroclaw, 1-5 September  
5 2015, M. Czarnecka and B. Lydzba-Kopczynska eds., Faculty of Chemistry, University of Wroclaw -  
6 ISBN:978-83-60043-27-1  
7
- 8 [542] D.L.A. de Faria, S.V. Silva, M.T. de Oliveira, *J. Raman Spectrosc.* **1997**; *28*, 873.  
9
- 10 [543] D. Bikiaris, S. Daniilia, S. Sotiropoulou, O. Katsimbiri, E. Pavlidou, A.P.P. Moutsatsou, Y. Chryssoulakis,  
11 *Spectrochim. Acta - Part A Mol. Biomol. Spectrosc.* **2000**; *56*, 3.  
12
- 13 [544] L.F.C. de Oliveira, H.G.M. Edwards, R.L. Frost, J.T. Klopogge, P.S. Middleton, *Analyst* **2002**; *127*, 536.  
14
- 15 [545] D. Hradil, T. Grygar, J. Hradilová, P. Bezdička, *Appl. Clay Sci.* **2003**; *22*, 223.  
16
- 17 [546] I. V Chernyshova, M.F. Hochella, a S. Madden, *Phys. Chem. Chem. Phys.* **2007**; *9*, 1736.  
18
- 19 [547] M. A. Legodi, D. de Waal, *Dye. Pigment.* **2006**; *74*, 161.  
20
- 21 [548] D. Hradil, J. Hradilová, P. Bezdička, in: D. Hradil, J. Hradilova (Eds.), Acta Artis Acad. 2010 Příběh  
22 Umení Proměn. Výtvarného Díla v Case Sborník 3. Mezioborové Konf. ALMA = Story Art Artwork  
23 Chang. Time Proc. 3rd Interdiscip. Conf. ALMA, Acad Mat Res Lab Painted Artworks, 2010, pp. 123–  
24 136.  
25
- 26 [549] P.R. Palacios, A. Bustamante, P. Romero-Gómez, J.C. González, *Hyperfine Interact.* **2011**; *203*, 113.  
27
- 28 [550] F. Froment, A. Tournié, P. Colomban, *J. Raman Spectrosc.* **2008**; *39*, 560.  
29
- 30 [551] C. Montagner, D. Sanches, J. Pedroso, M.J. Melo, M. Vilarigues, *Spectrochim. Acta - Part A Mol.*  
31 *Biomol. Spectrosc.* **2013**; *103*, 409.  
32
- 33 [552] L. Appolonia, D. Vaudan, V. Chatel, M. Aceto, P. Mirti, *Anal. Bioanal. Chem.* **2009**; *395*, 2005.  
34
- 35 [553] K. Trentelman, N. Turner, *J. Raman Spectrosc.* **2009**; *40*, 577.  
36
- 37 [554] K. Trentelman, *J. Raman Spectrosc.* **2009**; *40*, 585.  
38
- 39 [555] N. Buzgar, A.I. Apopei, A. Buzatu, *J. Archaeol. Sci.* **2013**; *40*, 2128.  
40
- 41 [556] N. Buzgar, G. Bodi, A. Buzatu, A.-I. Apopei, D. Aștefanei, *Analele Stiint. Ale Univ. "Al. I. Cuza" Din Iasi,*  
42 *Geol.* **2010**; *56*, 95.  
43
- 44 [557] E. P. Tomasini, G. Siracusano, M.S. Maier, *Microchem. J.* **2012**; *102*, 28.  
45
- 46 [558] E.P. Tomasini, B. Gómez, E.B. Halac, M. Reinoso, E.J. Di Liscia, G. Siracusano, M.S. Maier, *Herit. Sci.*  
47 **2015**; *3*, 19.  
48
- 49 [559] M. Spring, R. Grout, R. White, *Natl. Gall. Tech. Bull.* **2003**; *24*, 96.  
50
- 51 [560] G. Cavallo, K. Gianoli Barioni, *Herit. Sci.* **2015**; *3*, 5.  
52  
53  
54  
55  
56  
57  
58  
59  
60

- 1  
2  
3 [561] E.P. Tomasini, C.M. Favier Dubois, N.C. Little, S. A. Centeno, M.S. Maier, *Microchem. J.* **2015**; *121*,  
4 157.  
5  
6 [562] E. Ay, M. Kibaroglu, C. Berthold, *Archaeol. Anthropol. Sci.* **2014**; *6*, 125.  
7  
8 [563] R. Nöller, *Stud. Conserv.* **2015**; *60*, 79.  
9  
10 [564] M. Radepont, Y. Coquinot, K. Janssens, J.-J. Ezrati, W. de Nolf, M. Cotte, *J. Anal. At. Spectrom.* **2015**;  
11 *30*, 599.  
12  
13 [565] M. Cotte, J. Susini, N. Metrich, A. Moscato, C. Gratziu, A. Bertagnini, M. Pagano, *Anal. Chem.* **2006**;  
14 *78*, 7484.  
15  
16 [566] C. Hogan, F. Da Pieve, *J. Anal. At. Spectrom.* **2015**; *30*, 588.  
17  
18 [567] S.M. Lussier, G.D. Smith, *Rev. Conserv.* **2007**; *52*, 41.  
19  
20 [568] L. Burgio, R.J.H. Clark, S. Firth, *Analyst* **2001**; *126*, 222.  
21  
22 [569] G.D. Smith, L. Burgio, S. Firth, R.J.H. Clark, *Anal. Chim. Acta* **2001**; *440*, 185.  
23  
24 [570] G. D. Smith, R. J. H. Clark, *Journal of Cultural Heritage* **2002**; *3*, 101.  
25  
26 [571] R.J.H. Clark, P.J. Gibbs, *Chem. Commun.* **1997**; *11*, 1003.  
27  
28 [572] R.J.H. Clark, P.J. Gibbs, *Anal. Chem.* **1998**; *70*, 99A.  
29  
30 [573] L. Burgio, R. J. H. Clark, P. J. Gibbs, *J. Raman Spectrosc.* **1999**; *30*, 181.  
31  
32 [574] C. Andalò, M. Bicchieri, P. Bocchini, G. Casu, G.C. Galletti, P. a Mandò, M. Nardone, A. Sodo, M.  
33 {Plossi Zappala}, M. Zappalà, C. Andalo, P. a Mando, M. Plossi Zappala, *Anal. Chim. Acta* **2001**; *429*,  
34 279.  
35  
36 [575] S. Daniilia, E. Minopoulou, F.D. Demosthenous, G. Karagiannis, *J. Archaeol. Sci.* **2008**; *35*, 1695.  
37  
38 [576] S. Daniilia, E. Minopoulou, *Appl. Phys. A Mater. Sci. Process.* **2009**; *96*, 701.  
39  
40 [577] S. Aze, Alterations chromatiques des pigments au plomb dans les œuvres du patrimoine - Etude  
41 expérimentale des altérations observées sur les peintures murales. PhD Thesis, **2005**,  
42 <https://tel.archives-ouvertes.fr/tel-00079251>.  
43  
44 [578] M. G. T. Rosado, A. Candeias, A.T Caldeira, J. Mirao, in *Science, Technology and Cultural Heritage*, M.  
45 A. Rogerio-Candelera, Ed. (CRC Press, **2014**), pp. 217 - 222.  
46  
47 [579] S. Sotiropoulou, S. Daniilia, C. Miliani, F. Rosi, L. Cartechini, D. Papanikola-Bakirtzis, *Appl. Phys. A*  
48 **2008**; *92*, 143.  
49  
50 [580] E. Kotulanová, P. Bezdička, D. Hradil, J. Hradilová, S. Švarcová, T. Grygar, *J. Cult. Herit.* **2009**; *10*, 367.  
51  
52 [581] J.P. Petushkova, N.N. Lyalikova, *Stud. Conserv.* **2008**; *31*, 65.  
53  
54  
55  
56  
57  
58  
59  
60

- 1  
2  
3 [582] I. Costantini, A. Casoli, D. Pontiroli, D. Bersani, P.P. Lottici, in: P. Ropret, N. Ocepek (Eds.), 7th Int.  
4 Congr. Appl. Raman Spectrosc. Art Archaeol. RAA2013, ICPH of Slovenia, Ljubljana, 2013, pp. 6–7.  
5  
6 [583] M. Gutman, M. Lesar-Kikelj, A. Mladenovič, V. Čobal-Sedmak, A. Križnar, S. Kramar, *J. Raman*  
7 *Spectrosc.* **2014**; *45*, 1103.  
8  
9 [584] C. Miguel, A. Claro, A.P. Gonçalves, V.S.F. Muralha, M.J. Melo, *J. Raman Spectrosc.* **2009**; *40*, 1966.  
10  
11 [585] N. Mendes, C. Lofrumento, A. Migliori, E.M. Castellucci, *J. Raman Spectrosc.* **2008**; *39*, 289.  
12  
13 [586] P. Bonazzi, S. Menchetti, G. Pratesi, M. Muniz-Miranda, G. Sbrana, *Am. Mineral.* **1996**; *81*, 874.  
14  
15 [587] L. Bindi, G. Pratesi, M. Muniz-Miranda, M. Zoppi, L. Chelazzi, G.O. Lepore, S. Menchetti, *Mineral.*  
16 *Mag.* **2015**; *79*, 121.  
17  
18 [588] K. Trentelman, L. Stodulski, M. Pavlosky, *Anal. Chem.* **1996**; *68*, 1755.  
19  
20 [589] P. Vandenabeele, A. von Bohlen, L. Moens, R. Klockenkämper, F. Joukes, G. Dewispelaere, *Anal. Lett.*  
21 **2000**; *33*, 3315.  
22  
23 [590] H.G.M. Edwards, F. Rull, P. Vandenabeele, E.M. Newton, L. Moens, J. Medina, C. Garcia, *Appl.*  
24 *Spectrosc.* **2001**; *55*, 71.  
25  
26 [591] R. David, H.G.M. Edwards, D.W. Farwell, D.L. A. De Faria, *Archaeometry* **2001**; *43*, 461.  
27  
28 [592] L. Burgio, R.J.H. Clark, K. Theodoraki, *Spectrochim. Acta - Part A Mol. Biomol. Spectrosc.* **2003**; *59*,  
29 2371.  
30  
31 [593] P. Vandenabeele, L. Moens, in: K. Janssens, R. van Grieken (Eds.), *Compr. Anal. Chem.*, Elsevier,  
32 Amsterdam, **2004**, pp. 635–662.  
33  
34 [594] V. Daniels, B. Leach, *Stud. Conserv.* **2004**; *49*, 73.  
35  
36 [595] L. Burgio, R.J.H. Clark, M. Rosser-Owen, *J. Archaeol. Sci.* **2007**; *34*, 756.  
37  
38 [596] A. Macchia, S.N. Cesaro, L. Campanella, A. Maras, M. Rocchia, G. Roscioli, *J. Appl. Spectrosc.* **2013**;  
39 *80*, 1.  
40  
41 [597] G. Pratesi, M. Zoppi, *Am. Mineral.* **2015**; *100*, 1222.  
42  
43 [598] J.P. Ogalde, C.O. Salas, N. Lara, P. Leyton, C. Paipa, M. Campos-vallette, B. Arriaza, *J. Chil. Chem. Soc.*  
44 **2014**; *59*, 2571.  
45  
46 [599] M.J. Campos- Suñol, M.J. De la Torre-Lopez, M.J. Ayora- Cañada, A. Dominguez-Vidal, *J. Raman*  
47 *Spectrosc.* **2009**; *40*, 2104.  
48  
49 [600] A. El Bakkali, T. Lamhasni, M. Haddad, S. Ait Lyazidi, S. Sanchez-Cortes, E. Del Puerto Nevado, *J.*  
50 *Raman Spectrosc.* **2013**; *44*, 114.  
51  
52 [601] M. Vermeulen, J. Sanyova, K. Janssens, *Herit. Sci.* **2015**; *3*, 9.  
53  
54  
55  
56  
57  
58  
59  
60

- 1  
2  
3 [602] G. Grundmann, M. Richter, *Fatto D'archimia Los Pigment. Artif. En Las Técnicas Pictóricas* **2012**; 119.  
4  
5 [603] G. Grundmann, N. Ivleva, M. Richter, H. Stege, C. Haisch, *Stud. Old Master Paint. Technol. Pract.*  
6 *Natl. Gall. Tech. Bull. 30th Anniv. Conf. Postprints* **2011**; 269.  
7  
8 [604] G. Grundmann, M. Richter, *Chim. Int. J. Chem.* **2008**; 62, 903.  
9  
10 [605] P. Holakoei, A.-H. Karimy, *J. Archaeol. Sci.* **2015**; 54, 217.  
11  
12 [606] T. Katsaros, I. Liritzis, N. Laskaris, *Mediterr. Archaeol. Archaeom.* **2009**; 9, 29.  
13  
14 [607] M. Richter, O. Hahn, R. Fuchs, *Stud. Conserv.* **2014**; 46, 1.  
15  
16 [608] V. Šrein, B. Šreinová, J. Hradilová, in: D. Hradil, J. Hradilová (Eds.), *Acta Artis Acad. 2010 Příbeh*  
17 *Umení Promen. Výtvarného Díla v Case Sborník 3. Mezioborové Konf. ALMA = Story Art Artwork*  
18 *Chang. Time Proc. 3rd Interdiscip. Conf. ALMA, Acad Mat Res Lab Painted Artworks, 2010*, pp. 299–  
19 302.  
20  
21 [609] Š. Chlumská, D. Pechová, R. Šefcu, A. Treštíková, in: D. Hradil, J. Hradilová (Eds.), *Acta Artis Acad.*  
22 *2010 Příbeh Umení Promen. Výtvarného Díla v Case Sborník 3. Mezioborové Konf. ALMA = Story Art*  
23 *Artwork Chang. Time Proc. 3rd Interdiscip. Conf. ALMA, Acad Mat Res Lab Painted Artworks, 2010*,  
24 pp. 179–188.  
25  
26 [610] A. Banerjee, L. Nasdala, A. Wähning, *Arbeitsblätter Für Restaur.* **2000**; 32, 243.  
27  
28 [611] H. Dáňová, R. Šefců, A. Třeštíková, P. V., in: *Art'14. 11th Intern. Conf.*, Madrid, 2014, pp. 1–9.  
29  
30 [612] Z. Čermáková, P. Bezdička, I. Němec, J. Hradilová, V. Šrein, J. Blažek, D. Hradil, *J. Raman Spectrosc.*  
31 **2015**; 46, 236.  
32  
33 [613] P. Holakoei, A. Karimy, *Spectrochim. Acta - Part A Mol. Biomol. Spectrosc.* **2015**; 134, 419.  
34  
35 [614] G. Chiari, D. Scott, *Period. Mineral.* **2004**; 73, 227.  
36  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60

1  
2  
3  
4  
5  
6  
7  
8  
9  
10  
11  
12  
13  
14  
15  
16  
17  
18  
19  
20  
21  
22  
23  
24  
25  
26  
27  
28  
29  
30  
31  
32  
33  
34  
35  
36  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60**CAPTION FOR FIGURES**

Fig. 1 - Raman spectra of minerals identified in the ceramics body of glazed pottery finds from Skopsko Kale (Republic of Macedonia). (left) Main components: (a) hematite and magnetite; (b) maghemite; (c) quartz; (d) anatase; (e) rutile; (f) titanite; (g) albite; (h) microcline; (i) calcite; (j) carbon black; (k) graphite; (l) apatite. (right) Other minerals detected: (m) barite and sphalerite; (n) phlogopite; (o) epidote; (p) augite; (q) olivine; (r) fayalite; (s) hornblende; (t) diopside; (u) siderite; (v) dolomite; (w) spessartine (by Raškovska et al. <sup>[36]</sup>).

Fig. 2 - Raman micro-map of the orientation of the chlorite laminas in an archaeological sample of pietra ollare. A) 50x microscope image. B) Grey-scale map of the ratio between the areas of the bands at  $681\text{ cm}^{-1}$  and  $200\text{ cm}^{-1}$ . White = nearly horizontal laminas (laser polarization parallel to c axis). Black = nearly vertical laminas (by Baita et al. <sup>[112]</sup>).

Fig. 3 – Raman spectrum of a mounted gem on a Messinian goldsmith's artifact of XVIII c. (Messina Regional Museum, inv. A104). An indigo painted background was used to correct the hue of a diamond (reworked figure, by Barone et al. <sup>[130]</sup>).

Fig. 4 - Raman spectra, in the OH stretching region, of three gems with different origin. The band below  $3600\text{ cm}^{-1}$  is attributed to water type II (in presence of alkali ions), and the band over  $3600\text{ cm}^{-1}$  to water type I (reworked figure, by Bersani et al. <sup>[132]</sup>).

Fig. 5 - Maps of the shift of the six Raman bands –  $A_{1g}$  (a, b) and  $E_g$  (c–f) – around a zircon inclusion in a sapphire crystal. The maps show anisotropic patterns and vary with the Raman band. They include the regions of negative shifts, indicating contributions of nonhydrostatic stress components, induced by the zircon inclusion (by Noguchi et al. <sup>[157]</sup>).

1  
2  
3 Fig. 6 - Raman spectra of representative points of the specimens of red pigment from the Tito Bustillo and  
4 El Buxu caves (Spain): (a) wüstite (wü); (b) hematite (h); (c) hematite with a small amount of hydroxyapatite  
5 (ha) (by Hernanz et al. <sup>[199]</sup>).

6  
7 Fig. 7 - Raman spectra of a bluish black pigment from prehistoric paintings in the Abrigo Remacha rock  
8 shelter (Villaseca, Segovia, Spain): (a) representative spectrum of light violet microparticles and (b)  
9 representative spectrum of black microparticles. ac, amorphous carbon; ca, calcite; pq, paracoquimbite; w,  
10 whewellite; wd, weddellite (by Iriarte et al. <sup>[208]</sup>). In Fig. 7a a strong ripple is visible, maybe caused by  
11 etaloning. Some kind of spectral pre-processing could be useful in this case, but it's not always possible to  
12 obtain clean spectra without modifications of the Raman bands.  
13

14  
15  
16 Fig.8 - Micro-SORS spectra of a blue layered sample: (a) fragment image (the white square indicates the  
17 area analysed with micro-spatially offset Raman spectroscopy); (b) optical image and scheme of the  
18 stratigraphy; (c) the defocused spectra are shown for different distances from the 'imaged' plane indicated  
19 next to each spectrum (0 = 'imaged' position); (d) Raman intensity ratio (Prussian blue/lazurite) of the  
20 spectra acquired at different defocusing distances  $\Delta z$  (by Conti et al. <sup>[337]</sup>).

21  
22 Fig. 9 - Representative Raman signatures recorded on blue beads excavated at Mapungubwe hill (South  
23 Africa) (by Tournié et al. <sup>[465]</sup>).

24  
25 Fig. 10 - Raman spectrum of the faint blue layer on a Chinese funerary lacquer ware of West Han Dynasty,  
26 showing the band of CuS (by Jin et al. <sup>[82]</sup>).

27  
28 Fig. 11 - Raman spectrum of a copper arsenate from a green area in a mural painting of Ala di Stura  
29 (Piedmont, Italy) (by Aceto et al. <sup>[395]</sup>).

30  
31 Fig. 12 – The unpolarized Raman spectra of different lead chromates: crocoite, phoenicochroite,  
32 hemihedrite (by Bellini et al. <sup>[541]</sup>).

33  
34 Fig. 13 - Raman spectrum of bismuth black (powdered bismuth metal) from *The Annunciation to the*  
35 *Shepherds*, Katherine Hours, obtained by 1064 nm excitation. Inset: photomicrograph of a bismuth particle  
36 (by Trentelman and Turner <sup>[553]</sup>).

37  
38 Fig. 14 - The Raman spectrum of moolooite  $\text{Cu}(\text{C}_2\text{O}_4)_n\text{H}_2\text{O}$  ( $n < 1$ ) present in 17<sup>th</sup> c. coloured maps (by  
39 Mendes et al. <sup>[585]</sup>).

40  
41 Fig. 15 - Raman spectra of fragment of a crystal from naturally irradiated fluorite (photograph in the inset),  
42 indicating the increase of the bands below  $500 \text{ cm}^{-1}$  with increasing violet colour saturation (colourless—  
43 spectrum at the bottom, very deep violet—spectrum at the top): a) 532 nm laser, b) 780 nm laser. The  
44 bands above  $500 \text{ cm}^{-1}$  most probably relate to the different REE content in different positions (by  
45 Čermáková et al. <sup>[612]</sup>).

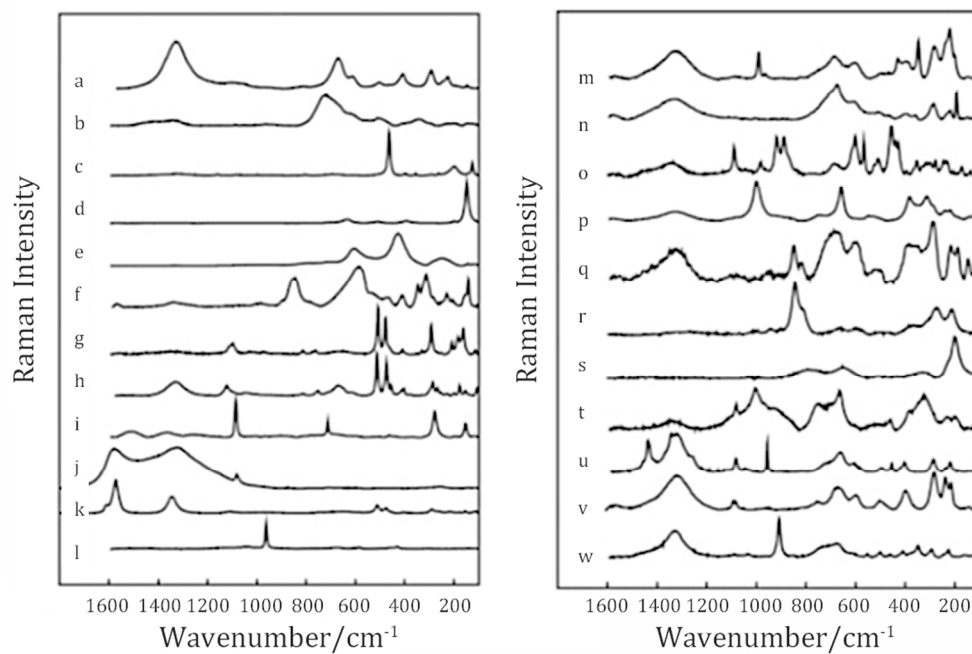


Fig. 1 - Raman spectra of minerals identified in the ceramics body of glazed pottery finds from Skopsko Kale (Republic of Macedonia). (left) Main components: (a) hematite and magnetite; (b) maghemite; (c) quartz; (d) anatase; (e) rutile; (f) titanite; (g) albite; (h) microcline; (i) calcite; (j) carbon black; (k) graphite; (l) apatite. (right) Other minerals detected: (m) barite and sphalerite; (n) phlogopite; (o) epidote; (p) augite; (q) olivine; (r) fayalite; (s) hornblende; (t) diopside; (u) siderite; (v) dolomite; (w) spessartine (by Raskovska et al. [36]).

427x280mm (72 x 72 DPI)

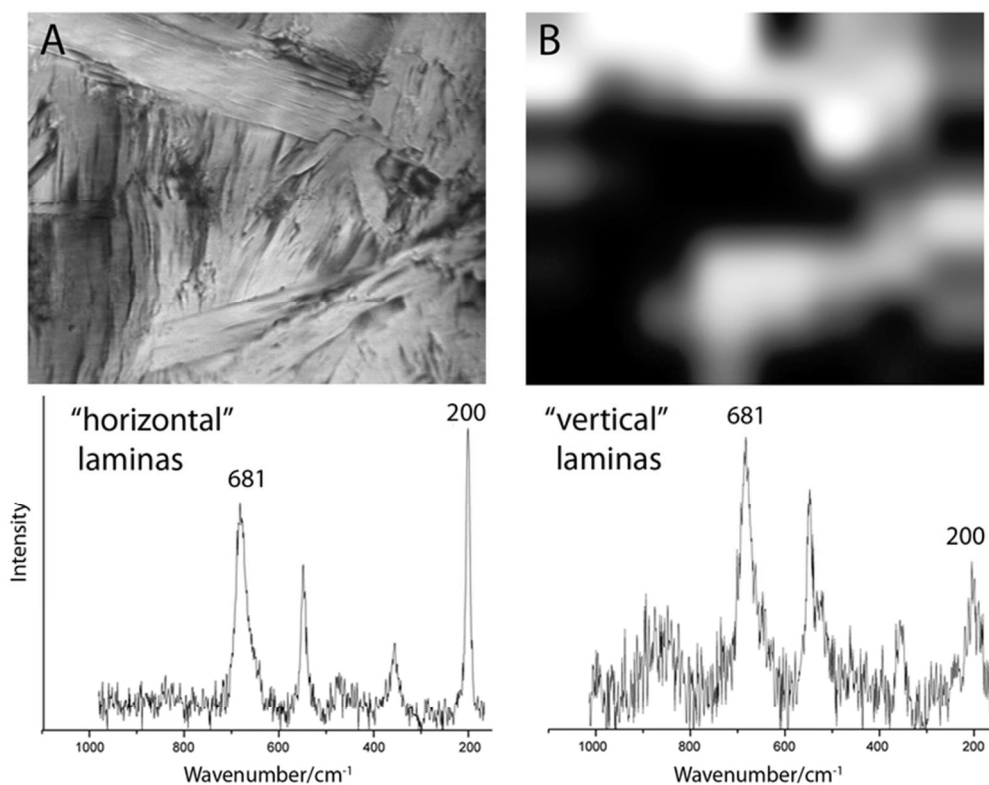


Fig. 2 - Raman micro-map of the orientation of the chlorite laminas in an archaeological sample of pietra ollare. A) 50x microscope image. B) Grey-scale map of the ratio between the areas of the bands at 681 cm<sup>-1</sup> and 200 cm<sup>-1</sup>. White = nearly horizontal laminae (laser polarization parallel to c axis). Black = nearly vertical laminae (by Baita et al. [112]).  
68x55mm (300 x 300 DPI)

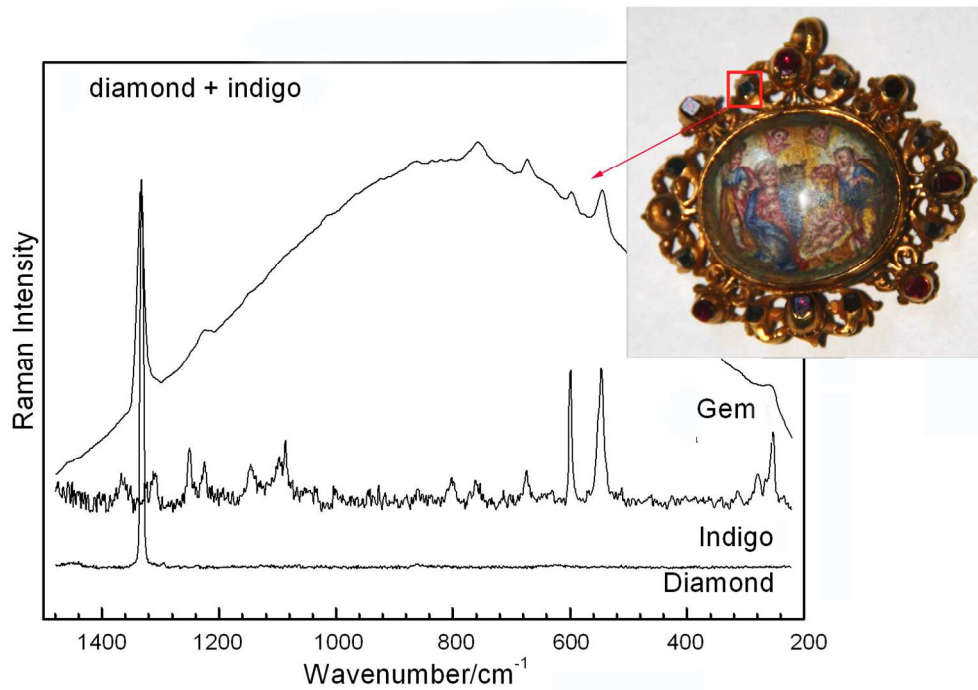


Fig. 3 – Raman spectrum of a mounted gem on a Messinian goldsmith's artifact of XVIII c. (Messina Regional Museum, inv. A104). An indigo painted background was used to correct the hue of a diamond (by Barone et al. [130]).  
135x104mm (299 x 299 DPI)

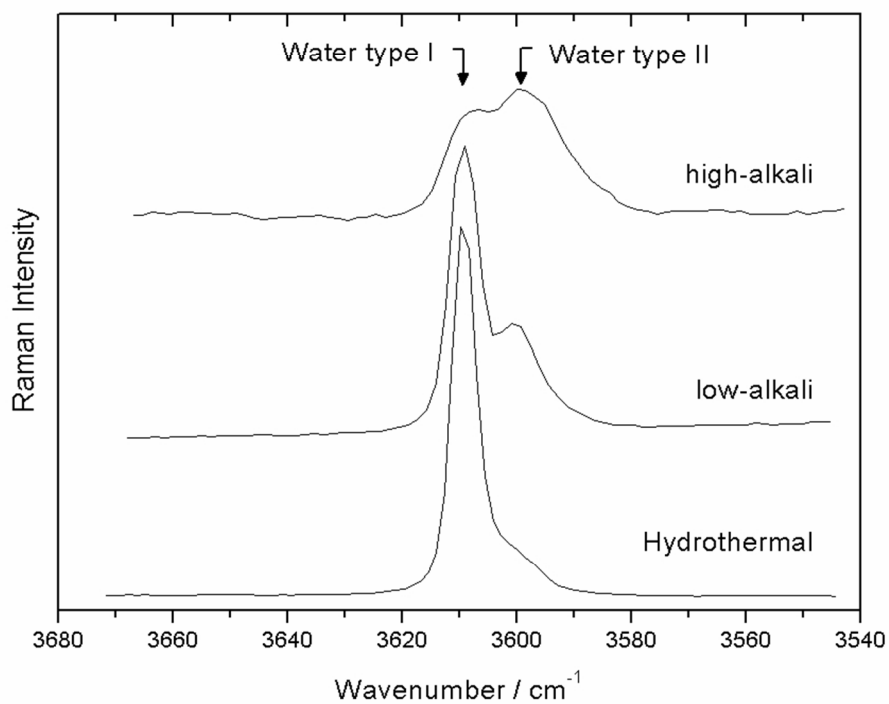


Fig. 4 - Raman spectra, in the OH stretching region, of three gems with different origin. The band below 3600 cm<sup>-1</sup> is attributed to water type II (in presence of alkali ions), and the band over 3600 cm<sup>-1</sup> to water type I (by Bersani et al. [132]).

79x64mm (300 x 300 DPI)

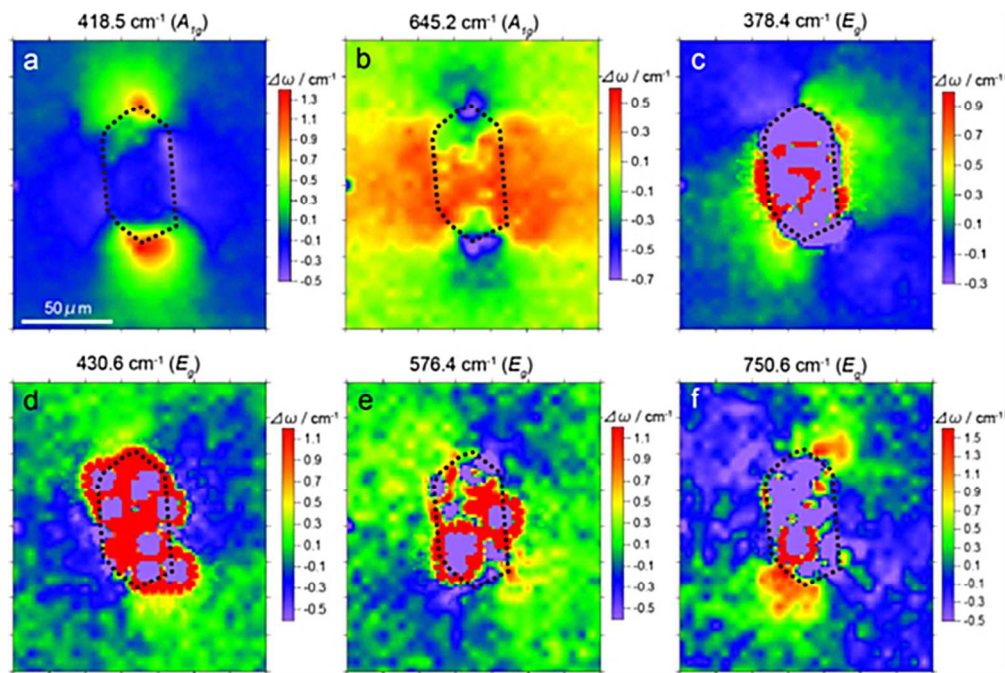


Fig. 5 - Maps of the shift of the six Raman bands –  $A_{1g}$  (a, b) and  $E_g$  (c–f) – around a zircon inclusion in a sapphire crystal. The maps show anisotropic patterns and vary with the Raman band. They include the regions of negative shifts, indicating contributions of nonhydrostatic stress components, induced by the zircon inclusion (by Noguchi et al. [157]).

453x302mm (72 x 72 DPI)

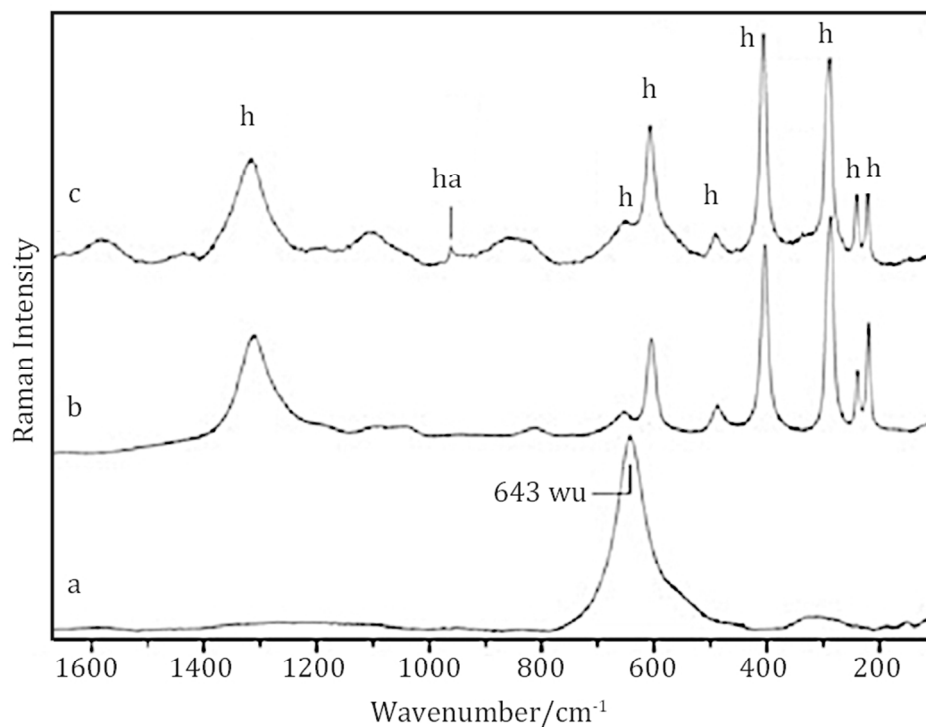


Fig. 6 - Raman spectra of representative points of the specimens of red pigment from the Tito Bustillo and El Buxu caves (Spain): (a) wüstite (wü); (b) hematite (h); (c) hematite with a small amount of hydroxyapatite (ha) (by Hernanz et al. [199]).  
360x280mm (72 x 72 DPI)

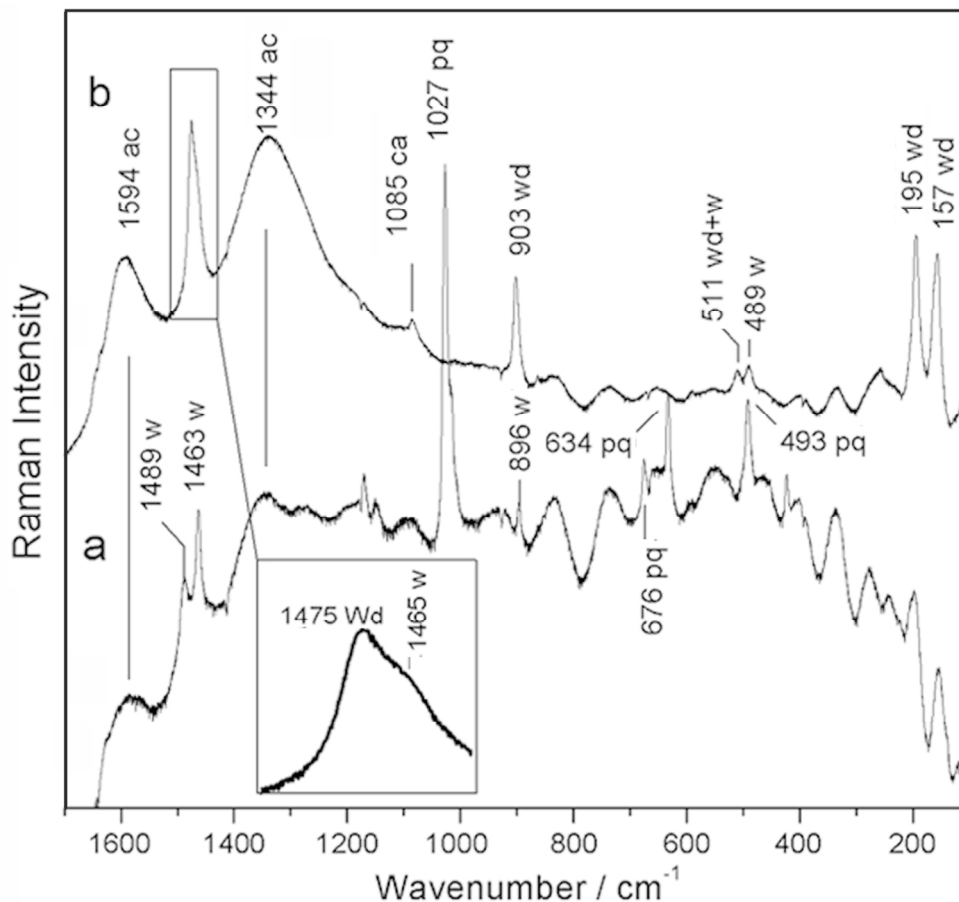


Fig. 7 - Raman spectra of a bluish black pigment from prehistoric paintings in the Abrigo Remacha rock shelter (Villaseca, Segovia, Spain): (a) representative spectrum of light violet microparticles and (b) representative spectrum of black microparticles. ac, amorphous carbon; ca, calcite; pq, paracoquimbite; w, whewellite; wd, weddellite (by Iriarte et al. [208]). In Fig. 7a a strong ripple is visible, maybe caused by etaloning. Some kind of spectral pre-processing could be useful in this case, but it's not always possible to obtain clean spectra without modifications of the Raman bands.

440x407mm (72 x 72 DPI)

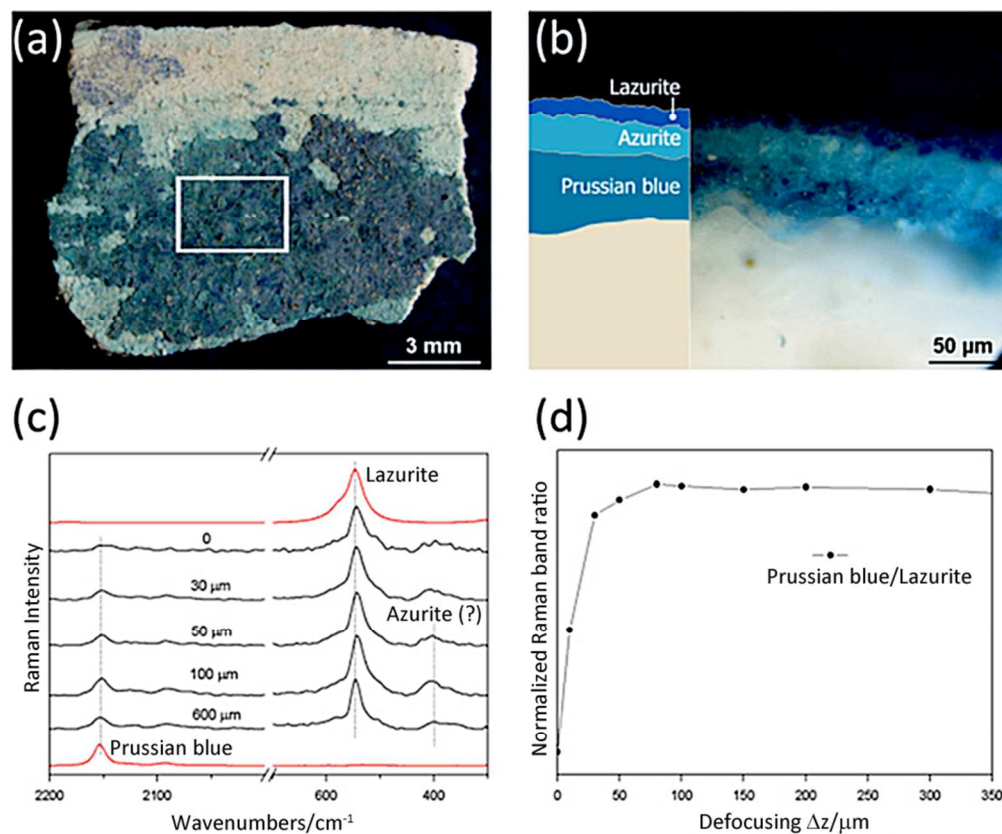


Fig.8 - Micro-SORS spectra of a blue layered sample: (a) fragment image (the white square indicates the area analysed with micro-spatially offset Raman spectroscopy); (b) optical image and scheme of the stratigraphy; (c) the defocused spectra are shown for different distances from the 'imaged' plane indicated next to each spectrum (0 = 'imaged' position); (d) Raman intensity ratio (Prussian blue/lazurite) of the spectra acquired at different defocusing distances  $\Delta z$  (by Conti et al. [337]).  
341x282mm (72 x 72 DPI)

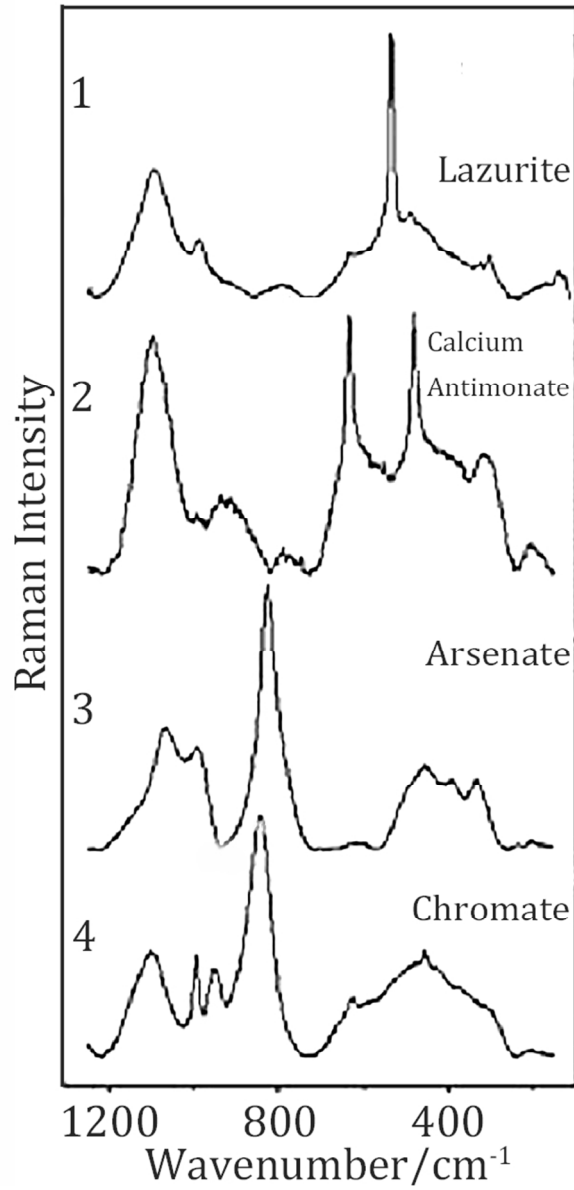


Fig. 9 - Representative Raman signatures recorded on blue beads excavated at Mapungubwe hill (South Africa) (by Tournié et al. [465]).  
280x446mm (72 x 72 DPI)

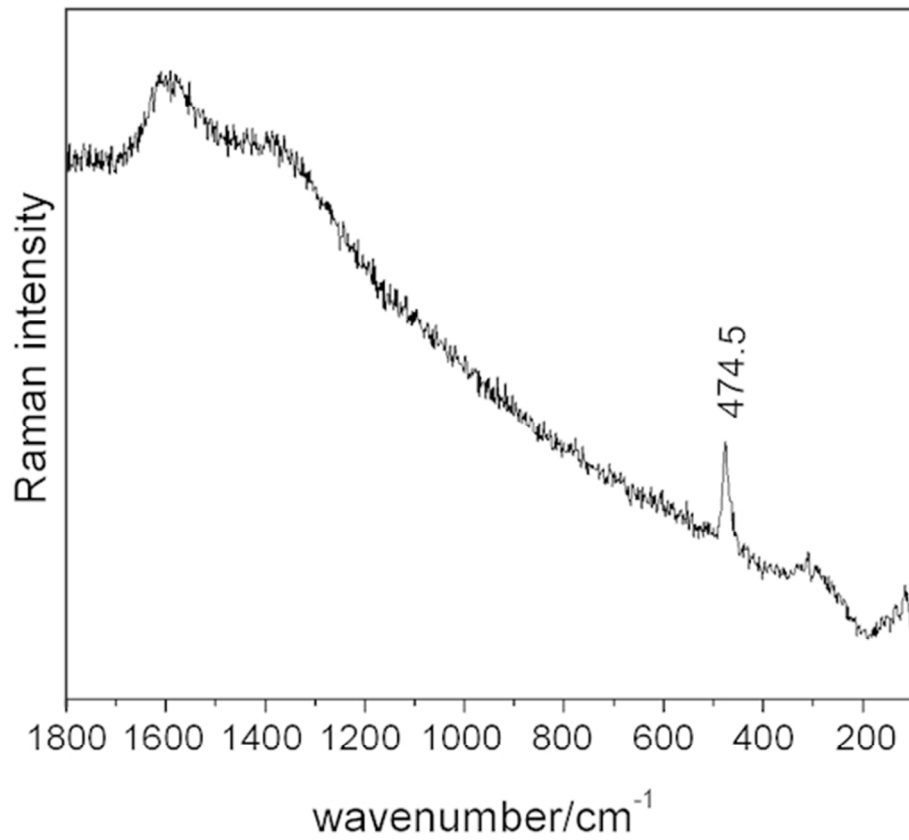


Fig. 10 - Raman spectrum of the faint blue layer on a Chinese funerary lacquer ware of West Han Dynasty, showing the band of CuS (by Jin et al. [82]).  
226x192mm (72 x 72 DPI)

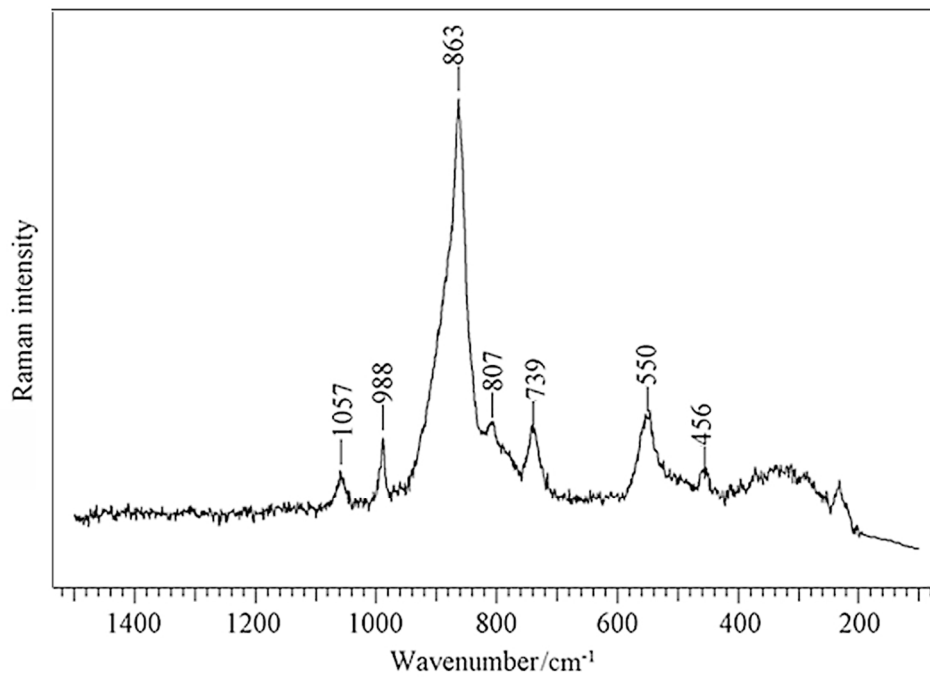


Fig. 11 - Raman spectrum of a copper arsenate from a green area in a mural painting of Ala di Stura (Piedmont, Italy) (by Aceto et al. [395]).  
412x301mm (72 x 72 DPI)

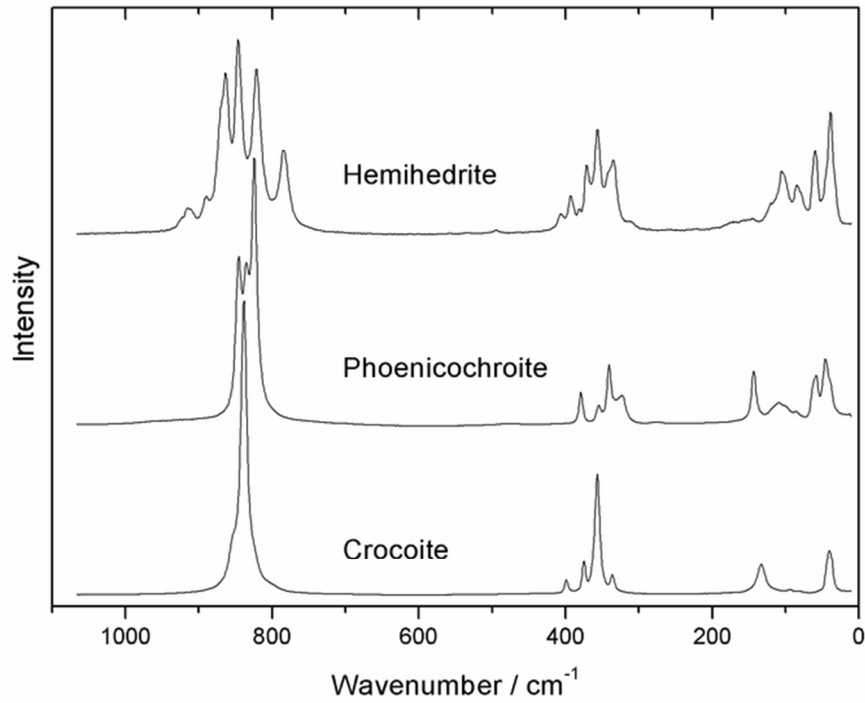


Fig. 12 – The unpolarized Raman spectra of different lead chromates: crocoite, phoenicochroite, hemihedrite (by Bellini et al. [541]).  
65x53mm (300 x 300 DPI)

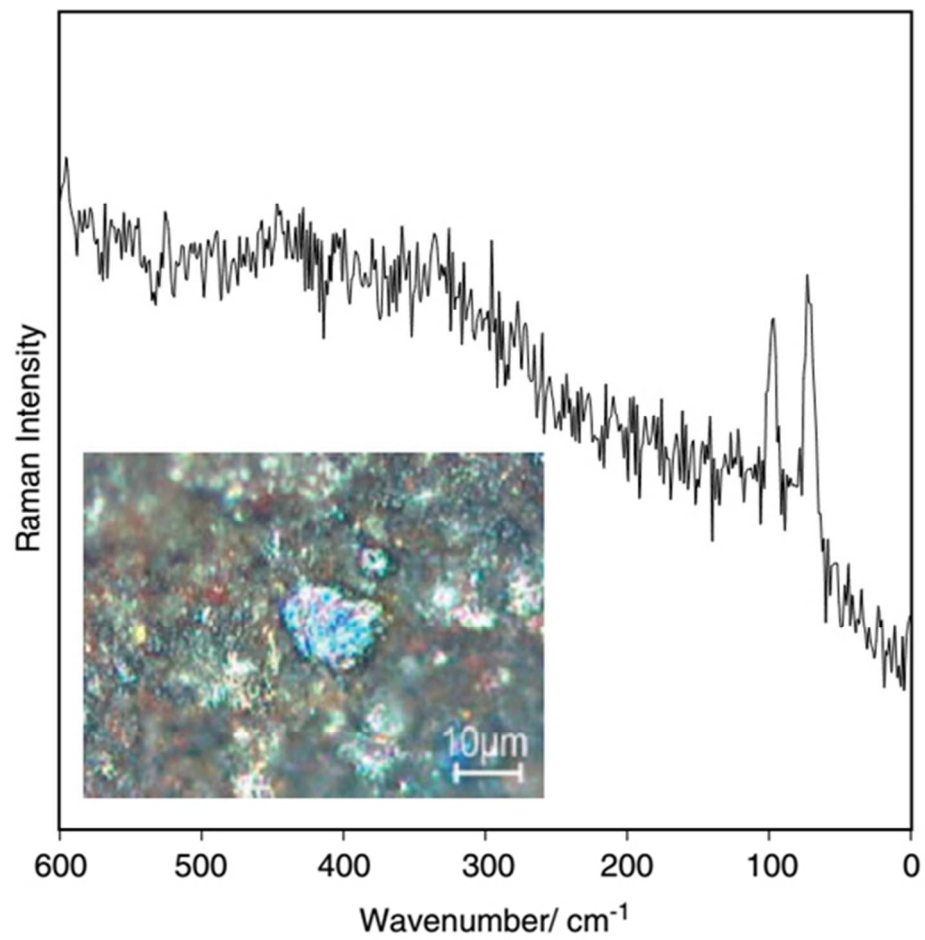


Fig. 13 - Raman spectrum of bismuth black (powdered bismuth metal) from The Annunciation to the Shepherds, Katherine Hours, obtained by 1064 nm excitation. Inset: photomicrograph of a bismuth particle (by Trentelman and Turner [553]).  
226x215mm (72 x 72 DPI)

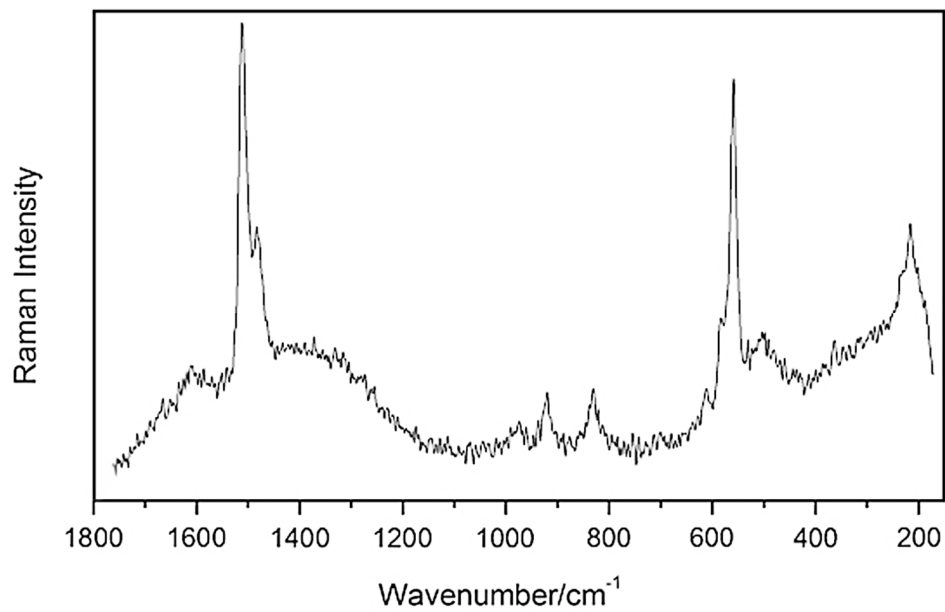


Fig. 14 - The Raman spectrum of moolooite  $\text{Cu}(\text{C}_2\text{O}_4)_n\text{H}_2\text{O}$  ( $n < 1$ ) present in 17<sup>th</sup> c. coloured maps (by Mendes et al. [585]).  
407x251mm (72 x 72 DPI)

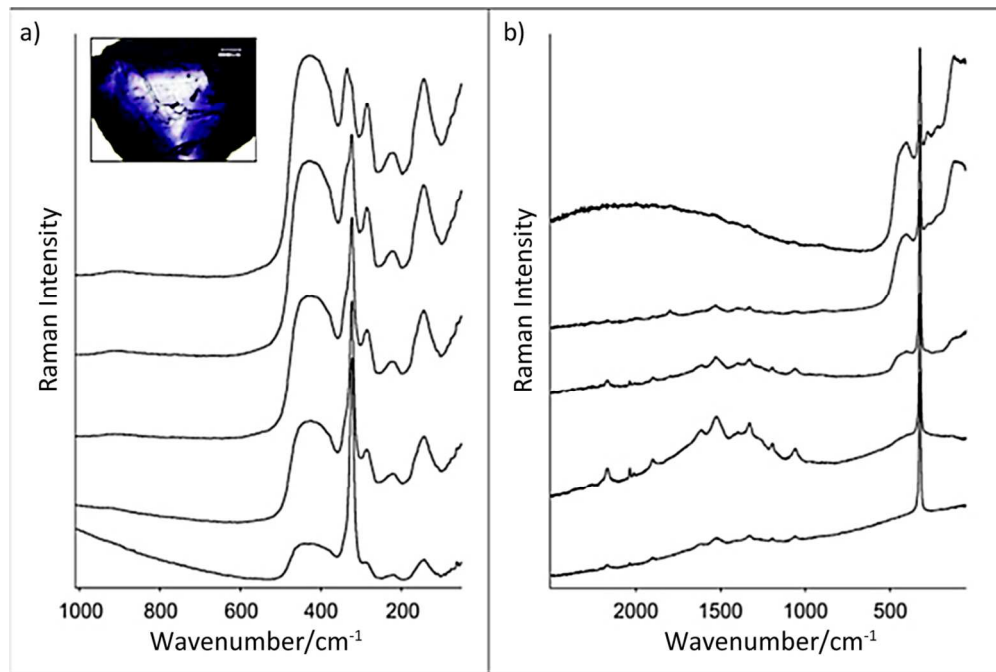
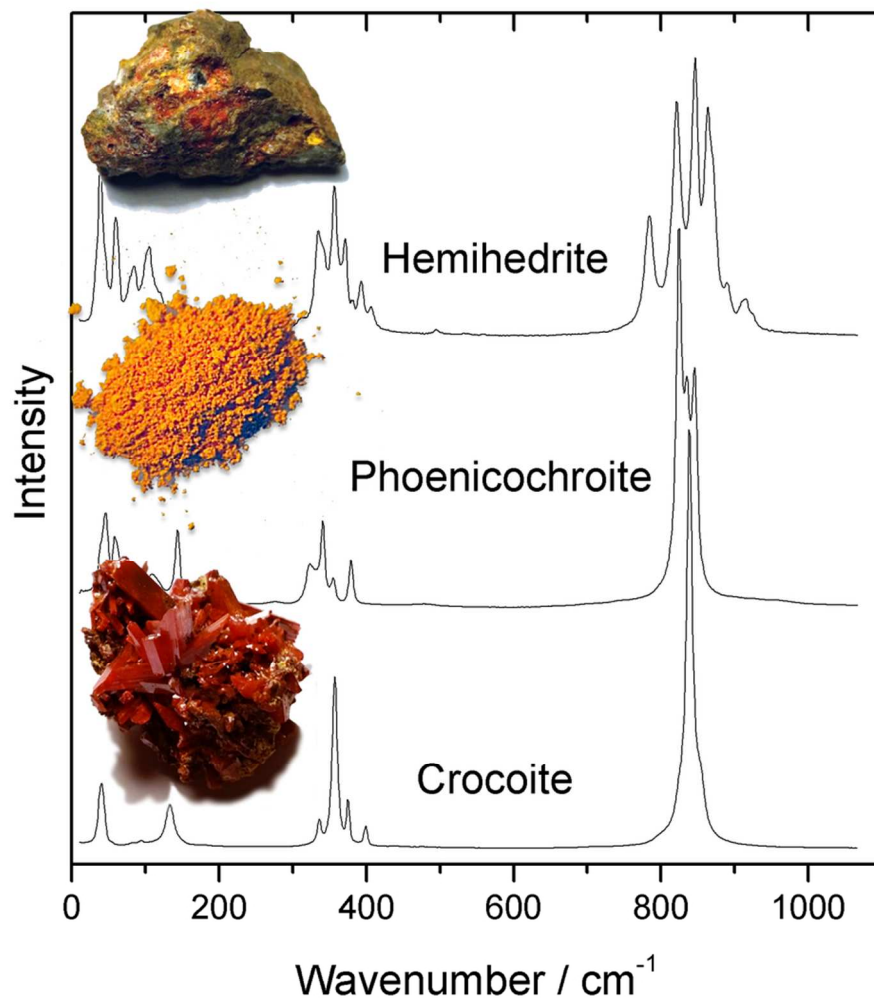


Fig. 15 - Raman spectra of fragment of a crystal from naturally irradiated fluorite (photograph in the inset), indicating the increase of the bands below  $500\text{ cm}^{-1}$  with increasing violet colour saturation (colourless—spectrum at the bottom, very deep violet—spectrum at the top): a) 532 nm laser, b) 780 nm laser. The bands above  $500\text{ cm}^{-1}$  most probably relate to the different REE content in different positions (by Čermáková et al. [612]).  
453x304mm (72 x 72 DPI)



89x99mm (300 x 300 DPI)

1  
2  
3  
4  
5  
6  
7  
8  
9  
10  
11  
12  
13  
14  
15  
16  
17  
18  
19  
20  
21  
22  
23  
24  
25  
26  
27  
28  
29  
30  
31  
32  
33  
34  
35  
36  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60