

## Advances in Raman Spectroscopy for the non-destructive subsurface analysis of artworks: micro-SORS

C. Conti<sup>a\*</sup>, A. Botteon<sup>a\*</sup>, C. Colombo<sup>a</sup>, D. Pinna<sup>b</sup>, M. Realini<sup>a</sup>, P. Matousek<sup>c</sup>

<sup>a</sup> *Consiglio Nazionale delle Ricerche, Istituto per la Conservazione e la Valorizzazione dei Beni Culturali (ICVBC), Via Cozzi 53, 20125, Milano, Italy.*

<sup>b</sup> *University of Bologna, Ravenna Campus, via Guaccimanni 42, 48121, Ravenna, Italy.*

<sup>c</sup> *Central Laser Facility, Research Complex at Harwell, STFC Rutherford Appleton Laboratory, Harwell Oxford, OX11 0QX, United Kingdom.*

\* Corresponding authors:

[c.conti@icvbc.cnr.it](mailto:c.conti@icvbc.cnr.it)

[botteon@icvbc.cnr.it](mailto:botteon@icvbc.cnr.it)

Key words: Spatially offset Raman spectroscopy, subsurface, non-destructive, non-invasive, Cultural Heritage, polychromy on stone sculptures.

### Abstract

A new imaging modality in Raman microscopy, Micro-Spatially Offset Raman Spectroscopy (micro-SORS) to explore the subsurface of materials in non-destructive and non-invasive way has been developed recently. Micro-SORS facilitates the investigation of the chemical composition of subsurface, micrometer-scale-thick diffusely scattering layers at depths more than an order of magnitude larger than those accessible with the depth resolving power of conventional confocal Raman microscopy, avoiding need to resort to cross sectional analysis. This article provides an overall view of the research carried out at CNR-ICVBC in the last five years concerning the development, optimization and application of micro-SORS to Cultural Heritage materials. Moreover, two illustrative micro-samples obtained from medieval polychrome sculptures of the Parma baptistery and Ferrara cathedral have been non-destructively investigated with micro-SORS, supporting its potential in Cultural Heritage field.

## Introduction

One of the aims of conservation science is the identification of materials used in Cultural Heritage objects and monuments, as well as the investigation of their decay. These materials often exhibit a multi-layered, micro-metre scale structure as in the case of painted stratigraphies, over a thicker substrate (millimetres or more).

The retrieving of the complete compositional information, from their surface to the inner portions, is crucial since it allows acquiring indispensable knowledge for reconstructing artwork's and artist's histories, the decay processes affecting the most internal areas and the presence and diffusion of conservation products within the substrates. However, for several decades the analysis of sample cross sections, which is an invasive and destructive approach, had been the only way for the selective investigation of subsurface materials.

Search for non-invasive and non-destructive methods able to characterize what is beneath the surface of artworks is one of the key endeavours of the current research in conservation science. Recently, a number of techniques have been proposed in Cultural Heritage field for this purpose, such as multispectral and hyperspectral imaging [1-2], Terahertz imaging [3], X-ray radiography (XRR) and infrared reflectography (IRR) [4], scanning macro X-Ray fluorescence (MA-XRF) [5], macroscopic X-ray powder diffraction mapping (MA-XRPD) [6], confocal X-Ray fluorescence (confocal XRF) [7] and optical coherence tomography (OCT) [8].

Each of these techniques provides its own specific and valuable contribution to the knowledge of subsurface analysis by non-invasive means; however, the direct retrieval of molecular composition, which is extremely important for the unequivocal identification of the present compounds, is not fully accomplished by these techniques.

In the last few years, a non-invasive Raman spectroscopy method for the investigation of the molecular composition of subsurface layers (Micro Spatially Offset Raman Spectroscopy – micro-SORS) has been proposed and demonstrated [9-10] by a collaboration between the CNR Institute for the Conservation and Valorisation of Cultural Heritage (ICVBC) and the Rutherford Appleton Laboratory (RAL - UK). This method is related to (macro)-SORS, Spatially Offset Raman Spectroscopy [11-12], a technique developed at RAL more than ten years ago; a specific feature of macro- and micro-SORS is their capability to resolve the molecular composition of compounds located under turbid, highly diffusely scattering surfaces, as encountered with paint, stones and in many situations related to the art field as well as in polymer, biomedical, pharmaceutical, forensic and security areas. Macro and micro-SORS rely on photon migration processes in which Raman photons generated deeper within the sample are more likely to migrate laterally from the illumination zone more before being emitted from the sample surface than photons generated in shallower layers. In fact, due to a large number of scattering events, in turbid matrices the photons direction is completely randomised resulting in sideways areas yielding deeper photons. Macro-SORS is applicable to relatively thick layers (on the order of millimetre or higher), whereas micro-SORS to micrometre thick layers; in artworks the concealed substances are often on the order of micro-metres, thus micro-SORS is the most suited method for their non-invasive detection. With such sample conventional confocal Raman spectroscopy is typically severely limited much shallower depths due to its inability to form direct optical images of inner components in turbid matrices.

A wide micro-SORS literature has been produced in the last few years reporting several possible micro-SORS variants, from the most basic set-up (defocusing micro-SORS) [9] to more sophisticated and effective modalities including the separation of laser illumination and collection areas (full micro-SORS) by using an

external laser probe [13] or fiber optics [14], by moving a laser spot across the focal plane with “beam-steer” mirrors [15-16], by a CCD spatially resolved read out [17], by moving the tip of the Raman detection fiber from the confocal position [18], by using a digital micro-mirror device in the detection optical path [19] or by combining hyperspectral SORS and defocusing micro-SORS [20]. Up to date, heritage sciences [21-23] and biomedical field [15-18, 20] constitute the main micro-SORS application areas, even though their analytical capability has also been demonstrated with stratified polymers and papers and with samples coming from biology field [24].

The main micro-SORS achievements in Cultural Heritage field till now concern the non-destructive investigation of pigments used in painted stratigraphies of terracotta polychrome sculptures [21] and in street art paintings [23], performing measurements on the intact fragments taken from the artworks without any sample preparation. Moreover, micro-SORS allowed the non-invasive identification of a preparation layer under a porcelain card decoration, placing the card directly under the microscope objective of the spectrometer [22]. These outcomes have paved the way for establishing micro-SORS as one of the emerging Raman techniques in Cultural Heritage [25-26].

More complex situations, often encountered in Cultural Heritage have also been explored with micro-SORS using mock-up samples, mimicking real situations of painted stratigraphies with highly heterogeneous composition [27], hidden paintings or drawings covered by superimposed painted layers or whitewash [28], layers covered by intensely fluorescing turbid over-layers [29]. Moreover, the determination of the thickness of investigated overlayer was also attempted, with promising results, in case of calibrated systems [30].

One of major challenges is a provision of portable micro-SORS. Such device would unlock the possibility of *in-situ* measurements, in museum collections, conservation and archaeological sites; to date, two prototypes have been proposed and demonstrated based around a modified conventional portable Raman spectrometer to deliver both defocusing [31] and full micro-SORS [32]. Even though promising results have been obtained, further system optimizations are needed for developing a more effective and more compact device capable of obtaining accurate and consistent results even under suboptimal measurement conditions.

About five years of micro-SORS development, optimization and experiments have provided appropriate time for the evaluation of its potentiality but also of its limitations, since it is apparent that micro-SORS is not applicable to all multilayer problems; the most important limits comes from excessive fluorescence originating from a target layer, the presence of a strong Raman scattering cross section compound in the top position combined with a weak one below surface, high absorption of the laser or Raman photons in the sample and the presence of extremely thin layers (less than 10  $\mu\text{m}$ ). To overcome some of these limitations the research has also focussed on combining micro-SORS with other emerging non-destructive techniques as confocal X-Ray fluorescence [33], grazing incidence X-Ray diffraction [34] or Frequency offset Raman spectroscopy, already coupled with SORS [35]. The complementarities of the results achieved by these methods open prospects for the provision of a more comprehensive non-destructive and non-invasive analysis tool for Cultural Heritage.

### **Research aim**

Here, we provide a demonstration of micro-SORS capability to elucidate the composition of hidden compounds through the non-destructive analysis of micro-samples taken from medieval painted stone sculptures of the Parma baptistery and Ferrara Cathedral. Two illustrative examples are reported where the

pigment stratigraphy and the decay products are identified without resorting to cross sectional analysis allowing the use of the intact micro-samples subsequently in other, destructive analyses, such as GC-MS or ATR-FTIR. It is worth to highlight the importance of collecting data on polychrome stone sculptures; in fact, scientific studies on decorated stones items are scarce in the literature [36] mainly because the original polychromies applied in the past have largely been lost for stylistic changes and decay reasons. Conservation scientists should analyse these precious traces in non-invasive way or, at least, in non-destructive way, with the attempt to extract as much information as possible.

## Materials

Sample 1 (S1) was obtained from a painted sculpture of the Ferrara cathedral portal during the last restoration work dating back to 1970s. The sculpture is located in the loggia, the upper part of the porch, and was sculptured in around 1230-40 by an unknown master [37] and decorated with a depiction of the Last Judgement.

Sample 2 (S2) was acquired from a painted sculpture of the baptistery of Parma, one of the most important Medieval monuments in Europe, during the last restoration work dating back to 1980s. Its construction began in 1196 and was unlikely completed in its architectural entirety until ca. 1281 [38], the baptistery was designed by Benedetto Antelami, an Italian architect and sculptor of the Romanesque school. Largely surviving polichromy is present on the west, north and south portals. S2 originates from the south portal dedicated to the legend of Barlaam and Josaphat. The stone used for both the sculptures is Pietra di Verona, a carbonatic lithotype.

## Methods

The experiments were carried out using a dispersive Raman microscope (Senterra, Bruker Optik GmbH) equipped with a Peltier cooled charge-coupled (CCD) detector ( $1,024 \times 256$  pixels). The laser excitation wavelength was 785 nm and the spectra were acquired using a  $50 \times 1000 \mu\text{m}$  slit, a  $20\times$  microscope objective, a laser power of 10 mW and acquisition times of 100 s. In the present study, micro-SORS experiments were carried out using the most basic variant of micro-SORS (defocusing) in which Raman spectra are collected at imaged (in focus) position and, afterwards, at several defocused positions by simply moving the microscope objective away from the sample. Three defocusing series for each sample were collected to average out their heterogeneity. The spectra were cut, baseline corrected and normalized to a Raman band of each compound to highlight the relative signal intensities changes among substances located at different depths. Moreover, the integration of a main Raman band for each compound was carried out in order to calculate the changes of the intensity ratios as a function of defocusing distances. All spectral manipulations were carried out using OPUS software.

## Results

The spectra acquired from sample S1 at imaged position, which corresponds to conventional backscattering confocal Raman microscopy, exhibit the most characteristic signatures of cinnabar (HgS), minium ( $2\text{PbO}\cdot\text{PbO}_2$ ) and white lead  $[(\text{PbCO}_3)_2\cdot\text{Pb}(\text{OH})_2]$ . Gypsum ( $\text{CaSO}_4\cdot 2\text{H}_2\text{O}$ ) and anglesite ( $\text{PbSO}_4$ ) are

occasionally present, demonstrating that these are randomly distributed. The spectra acquired at different  $\Delta z$  distances show a change in the relative intensities of the Raman bands, suggesting a different distribution of these compounds with depth (Figure 1).

First, the averaged spectra for each  $\Delta z$  distances of the three series were extracted (Figure 1); then, the intensity ratios were calculated relatively to one band for each compound, at 549, 626, 977, 1008 and 1052  $\text{cm}^{-1}$  for minium, cinnabar, anglesite, gypsum and white lead, respectively (Figure 2). These ratios suggest the presence of distinct trends in particular when minium, cinnabar and white lead are considered. In fact, they allow to unequivocally ascertain that white lead is mainly located below cinnabar, and minium below white lead. As for gypsum and anglesite, despite their signals being rather random, a general distribution could be hypothesized looking at the intensity ratios: they are predominantly below cinnabar and over minium and white lead, even though their relation with white lead is not linear and fully understandable. This behaviour could be connected with decay processes, rather than a constituency of the stratigraphy, as also confirmed by the random distribution on the sample surface. Anglesite is commonly found in painted stratigraphies due to sulphation processes of white lead and gypsum is most likely due to the decay of the stone substrate mainly made of calcite.

These findings lead to a suggestion that the stratigraphy is mainly composed of cinnabar at the external position, white lead in the middle position and minium in the most internal layer. However, the presence of coarse grains of white lead, often encountered in painted stratigraphy, in mixture with cinnabar or minium could also justify the increase of white lead signal with depth. Gypsum and anglesite are randomly distributed within the first two layers, whereas they are scarce or even absent in the minium layer. It is important to be aware of the fact that micro-SORS provides information on the most abundant constituents of a specific layer, and the detection of some species does not exclude the presence of other pigments in mixture with it. For instance, it is likely that white lead is also present with cinnabar at the top position and with minium at the bottom layer, even if at a minor extent; however, the micro-SORS result indicate that a higher amount of this pigment is present between cinnabar and minium.

For the sake of clarity it is worth noting that the suggested stratigraphy could be incomplete, since other layers could be present below minium that are not detectable due to the limited spatial resolution of the method.

Sample 2 shows a highly heterogeneous surface, where most of the areas are covered by a black layer of dust and carbonaceous particles, related to pollution. From these areas no Raman signal could have been collected due to severe photon absorption. In the areas not covered by the black deposits, micro-SORS sequences was acquired successfully from the present blue crystals.

The imaged position spectra are dominated by the presence of the most characteristic bands of azurite [ $\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$ ] and calcite ( $\text{CaCO}_3$ ). Gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) and weddellite [ $\text{Ca}(\text{C}_2\text{O}_4) \cdot 2(\text{H}_2\text{O})$ ] are occasionally present, indicating their random distribution on the surface (Figure 3).

The overall trend of the relative intensity change of the compounds has been evaluated by averaging the micro-SORS spectra (Figure 3) and relative intensity ratios calculated (Figure 4).

First notable point is that the micro-SORS spectra show an increasing contribution of the calcite signal ascribable to the substrate for increasing defocusing. This suggests that the sample is characterized largely by the entire stratigraphy, from the external layer to the stone mostly made of calcite.

Assuming the heterogeneities have been well averaged, it is also unequivocal that azurite is on top of all the other layers represented by the other detected compounds. Weddellite is related to decay processes, indicating the presence of calcium oxalate films, observed on the surface of several monuments; the origin of these films is still controversial and, nowadays, the extensive lichen colonization of stone surfaces, the oxidative degradation of organic compounds applied to the stone surface during past conservation works and the reaction of oxalic acid of the atmosphere due fuel combustion processes are the main hypotheses [39-40]. As for S1, gypsum could be originated from the sulphation processes of calcite from the substrate. Considering the individual series, it is apparent that there is a complex distribution of gypsum and weddellite with depth; however, the average spectra show that they are mainly located below azurite and over calcite; as already mentioned, a minor contribution of these compounds in the surface layer with azurite cannot be excluded.

The analysis of the single micro-SORS series provides additional information about this heterogeneous sample. A sequence (Figure 5) shows the presence of the more stable calcium oxalate phase, whewellite [ $\text{Ca}(\text{C}_2\text{O}_4) \cdot (\text{H}_2\text{O})$ ]. Previous studies [41] have been carried out to find a mutual relation between the position of whewellite and weddellite within calcium oxalate films formed on stone substrates of historical monuments, which could provide important information on the controversial origin of these films. To date, in literature the analyses have been carried out by Raman microscopy only on sample cross sections; here for the first time, the information on the location and the composition of the two phases is obtained in a non-destructive way, showing, in this specific area, the predominant presence of whewellite on top of weddellite.

## Conclusions

An overall view of the recently developed micro-SORS technique was presented here, including a number of available variants, its analytical capability and its potential in Cultural Heritage outlined. Furthermore, a case study applying micro-SORS to non-destructively reconstruct the stratigraphy and degradation processes of two painted stone samples was presented. The study demonstrates the applicability of micro-SORS to this type of samples extending the depth applicability of Raman spectroscopy and with its inherently high chemical specificity expanding the portfolio of existing non-destructive analytical tools in Cultural Heritage. Limitations of the method are also presented, highlighting the need of a non-destructive/non-invasive multi-analytical approach for a comprehensive investigation of materials subsurface layers.

## References

- [1] C. Cucci, J. K. Delaney, M. Picollo, Reflectance Hyperspectral Imaging for Investigation of Works of Art: Old Master Paintings and Illuminated Manuscripts, *Acc. Chem. Res.* 49 (10) (2016) 2070-2079.
- [2] P. Ricciardi, J. K. Delaney, *The Encyclopedia of Archaeological Sciences*, DOI: 10.1002/9781119188230.saseas0394.
- [3] A. Doria, G. P. Gallerano, E. Giovenale, A. Casini, C. Cucci, M. Picollo, M. Poggesi, L. Stefani, K. Fukunaga, M. Tamassia, Vis-NIR Hyperspectral and Terahertz Imaging Investigations on a Fresco Painting on “Tavella” by Alessandro Gherardini, *J. Infrared, Millimeter, Terahertz Waves* 38 (4) (2017) 390–402.
- [4] M. Alfeld, J.A.C. Broekaert, Mobile depth profiling and sub-surface imaging techniques for historical paintings—A review, *Spectrochim Acta B* 88 (2013) 211-230.
- [5] M. Alfeld, L. de Viguerie, Recent developments in spectroscopic imaging techniques for historical paintings - A review, *Spectrochim Acta B* 136 (2017) 81-105.
- [6] F. Vanmeert, W. De Nolf, J. Dik, K. Janssens, Macroscopic X-ray Powder Diffraction Scanning: Possibilities for Quantitative and Depth-Selective Parchment Analysis, *Anal. Chem.* 90 (11) (2018) 6445-6452.
- [7] R. Prokeš, V. Antušková, R. Šefců, T. Trojek, Š. Chlumská, T. Čecháka, Investigation of color layers of Bohemian panel paintings by confocal micro-XRF analysis, *Radiation Physics and Chemistry* 151 (2018) 59-64.
- [8] C. L. Koch Dandolo, M. Lopez, K. Fukunaga, Y. Ueno, R. Pillay, D. Giovannacci, Y. Le Du, X. Bai, M. Menu, V. Detalle, Toward a multimodal fusion of layered cultural object images: complementarity of optical coherence tomography and terahertz time-domain imaging in the heritage field, *Applied Optics* 58 (5) (2019) 1281-1290.
- [9] C. Conti, C. Colombo, M. Realini, G. Zerbi, P. Matousek, Subsurface Raman Analysis of Thin Painted Layers, *Appl. Spectrosc.* 68 (6) (2014) 686-691.
- [10] P. Matousek, C. Conti, M. Realini, C. Colombo, Micro-scale spatially offset Raman spectroscopy for non-invasive subsurface analysis of turbid materials, *Analyst*, 141 (2016) 731-739.
- [11] P. Matousek, I. P. Clark, E. R. C. Draper, M. D. Morris, A. E. Goodship, N. Everall, M. Towrie, W. F. Finney and A. W. Parker, Numerical Simulations of Subsurface Probing in Diffusely Scattering Media Using Spatially Offset Raman Spectroscopy, *Appl. Spectrosc.*, 59 (12) (2005) 393–400.
- [12] K. Buckley and P. Matousek, Non-invasive analysis of turbid samples using deep Raman spectroscopy, *Analyst* 136 (15) (2011) 3039–3050.
- [13] C. Conti, M. Realini, C. Colombo, P. Matousek, Comparison of key modalities of micro-scale spatially offset Raman spectroscopy, *Analyst*, 140 (24) (2015) 8127-8133.
- [14] P. Vandenabeele, C. Conti, A. Rousaki, L. Moens, M. Realini, P. Matousek, Development of a Fiber-Optics Microspatially Offset Raman Spectroscopy Sensor for Probing Layered Materials, *Anal. Chem.* 89 (17) (2017) 9218-9223.

- [15] K. Buckley, C. G. Atkins, D. Chen, H. G. Schulze, D. V. Devine, M. W. Blades, R. F. B. Turner, Non-invasive spectroscopy of transfusable red blood cells stored inside sealed plastic blood-bags, *Analyst* 141 (2016) 1678-1685.
- [16] R. Gautam, Joo-Y. Oh, R. P. Patel, R. A. Dluhy, Non-invasive analysis of stored red blood cells using diffuse resonance Raman spectroscopy, *Analyst*, 143 (2018) 5950-5958.
- [17] Z. Di, B. H. Hokr, H. Cai, K.Wang, V. V. Yakovlev, A. V. Sokolov, M. O. Scully, Spatially offset Raman microspectroscopy of highly scattering tissue: theory and experiment, *Journal of Modern Optics* 62 (2) (2015) 97-101.
- [18] K. M. Khan, N. Ghosh, S. K. Majumder, Off-confocal Raman spectroscopy (OCRS) for subsurface measurements in layered turbid samples, *J. Opt.* 18 (2016) 095301 (9pp).
- [19] Z. Liao, F. Sinjab, G. Gibson, M. Padgett, I. Notinger, DMD-based software-configurable spatially-offset Raman spectroscopy for spectral depth-profiling of optically turbid samples, *Optic Express* 24 (12) (2016) DOI:10.1364/OE.24.012701.
- [20] M. Matthiae, A. Kristensen, Hyperspectral spatially offset Raman spectroscopy in a microfluidic channel, *Optic Express* 27 (3) (2019) 3782-3790.
- [21] C. Conti, C. Colombo, M. Realini, P. Matousek, Subsurface analysis of painted sculptures and plasters using micrometre-scale spatially offset Raman spectroscopy (micro-SORS), *J. Raman Spectrosc* 46 (5) (2015) 476-482.
- [22] A. Rousaki, A. Botteon, C. Colombo, C. Conti, P. Matousek, L. Moens, Development of defocusing micro-SORS mapping: a study of a 19th century porcelain card, *Anal Methods*, 9 (45) (2017) 6435-6442.
- [23] A. Botteon, C. Colombo, M. Realini, S. Bracci, D. Magrini, P. Matousek, Exploring street art paintings by microspatially offset Raman spectroscopy, *J Raman Spectrosc* 49 (10) (2018) 1652-1659.
- [24] C Conti, M Realini, C Colombo, K Sowoidnich, NK Afseth, M Bertasa, A. Botteon, P. Matousek, Noninvasive Analysis of Thin Turbid Layers Using Microscale Spatially Offset Raman Spectroscopy, *Anal.Chem.* 87 (11) (2015) 5810-5815.
- [25] D. Bersani, C. Conti, P. Matousek, F. Pozzi, P. Vandenabeele, Methodological evolutions of Raman spectroscopy in art and archaeology, *Anal. Methods*, 8 (48) (2016) 8395-8409.
- [26] F. Casadio, C. Daher, L. Bellot-Gurlet, 2017, Raman Spectroscopy of cultural heritage Materials: Overview of Applications and New Frontiers in Instrumentation, Sampling Modalities, and Data Processing. In: Mazzeo R. (eds) *Analytical Chemistry for Cultural Heritage*. Topics in Current Chemistry Collections. Springer, Cham.
- [27] C. Conti, A. Botteon, C. Colombo, M. Realini, P. Matousek, Investigation of Heterogeneous Painted Systems by Micro-Spatially Offset Raman Spectroscopy, *Anal Chem*, 89 (21) (2017) 11476-11483.
- [28] A. Botteon, C. Conti, M. Realini, C. Colombo, P. Matousek, Discovering Hidden Painted Images: Subsurface Imaging Using Microscale Spatially Offset Raman Spectroscopy, *Anal Chem.* 89 (1) (2017) 2017792-798.



- [29] C. Conti, A. Botteon, C. Colombo, M. Realini, P. Matousek, Fluorescence suppression using micro-scale spatially offset Raman spectroscopy, *Analyst* 141 (18) (2016) 5374-5381.
- [30] C. Conti, M. Realini, C. Colombo, A. Botteon, M. Bertasa, J. Striova, M. Barucci, P. Matousek, Determination of thickness of thin turbid painted over-layers using micro-scale spatially offset Raman spectroscopy, *Philosophical Transactions of the Royal Society A*, 374 (2082) (2016) 20160049.
- [31] M. Realini, A. Botteon, C. Conti, C. Colombo, P. Matousek, Development of portable defocusing micro-scale spatially offset Raman spectroscopy, *Analyst*, 141 (10) (2016) 3012-3019.
- [32] M. Realini, C. Conti, A. Botteon, C. Colombo, P. Matousek, Development of a full micro-scale spatially offset Raman spectroscopy prototype as a portable analytical tool, *Analyst* 142 (2) (2017) 351-355.
- [33] C. Conti, A. Botteon, C. Colombo, M. Realini, P. Matousek, P. Vandenabeele, B. Laforce, B. Vekemans, L. Vincze, Contrasting confocal XRF with micro-SORS: a deep view within micrometric painted stratigraphy, *Analytical Methods* 10 (31) (2018) 3837-3844.
- [34] E. Possenti, C. Colombo, C. Conti, L. Gigli, M. Merlini, J.R. Plaisier, M. Realini, G. D. Gatta, What's underneath? A non-destructive depth profile of painted stratigraphies by synchrotron grazing incidence X-ray diffraction, *Analyst*, 143 (18) (2018) 4290-4297.
- [35] S. K. V. Sekar, S. Mosca, A. Farina, F. Martelli, P. Taroni, G. Valentini, R. Cubeddu, A. Pifferi, Frequency offset Raman spectroscopy (FORS) for depth probing of diffusive media, *Optics Express* 25 (5) (2017) 4585-4597.
- [36] P. Arjonilla, A. Domínguez-Vidal, M. J. de la Torre Lopez, R. Rubio-Domene, M. J. Ayora-Canada, In situ Raman spectroscopic study of marble capitals in the Alhambra monumental ensemble, *Appl. Physics A* 122 (1014) (2016) DOI 10.1007/s00339-016-0537-2.
- [37] R. Rossi Manaresi. The polychromy of the 13th century stone sculptures in the façade of Ferrara cathedral. Proc. of the 6th Triennial Meeting, ICOM Committee for Conservation (1981) Ottawa 81/5/3-1, 81/5/3-13.
- [38] D.F. Glass. "The Sculpture of the Baptistery at Parma: Context and Meaning," *Mitteilungen des Kunsthistorischen Institutes in Florenz* 57/3 (2015) 255, 91.
- [39] F. Cariati, L. Rampazzi, L. Toniolo, A. Pozzi, Calcium oxalate films on stone surfaces: experimental assessment of the chemical formation, *Studies in Conservation* 45 (3) (2000) 180-188.
- [40] L. Rampazzi, Calcium oxalate films on works of art: A review, *J. Cult. Herit* (2019) doi.org/10.1016/j.culher.2019.03.002.
- [41] C. Conti, I. Aliatis, C. Colombo, M. Greco, E. Possenti, M. Realini, C. Castiglioni, G. Zerbi,  $\mu$ -Raman mapping to study calcium oxalate historical films, *J. Raman Spectrosc.* 43 (11) (2012) 1604-1611.

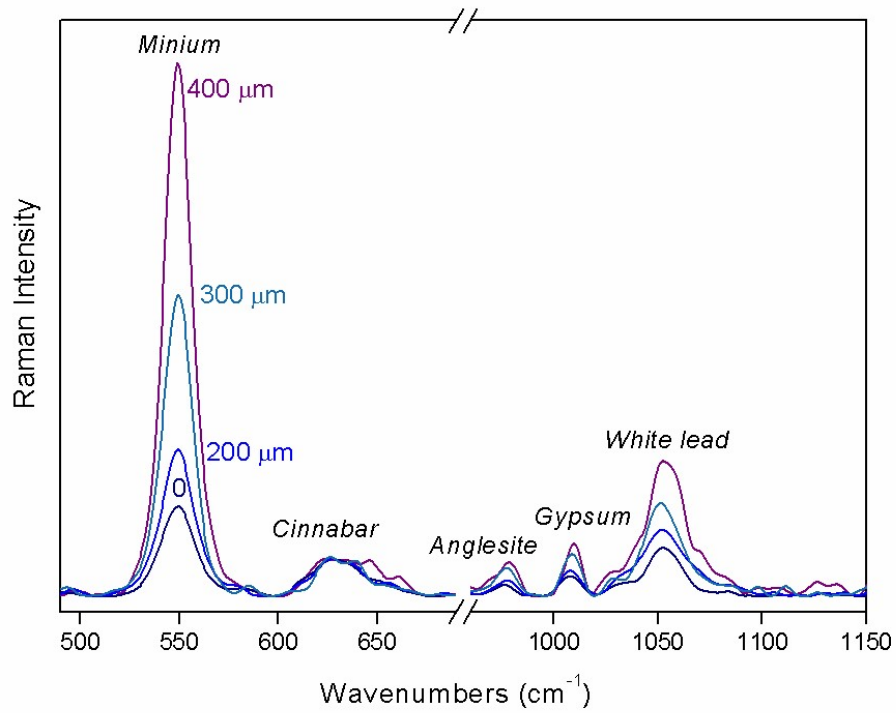


Figure 1: S1 – micro-SORS average sequence normalized to cinnabar. The values in the graph indicate the defocusing steps.

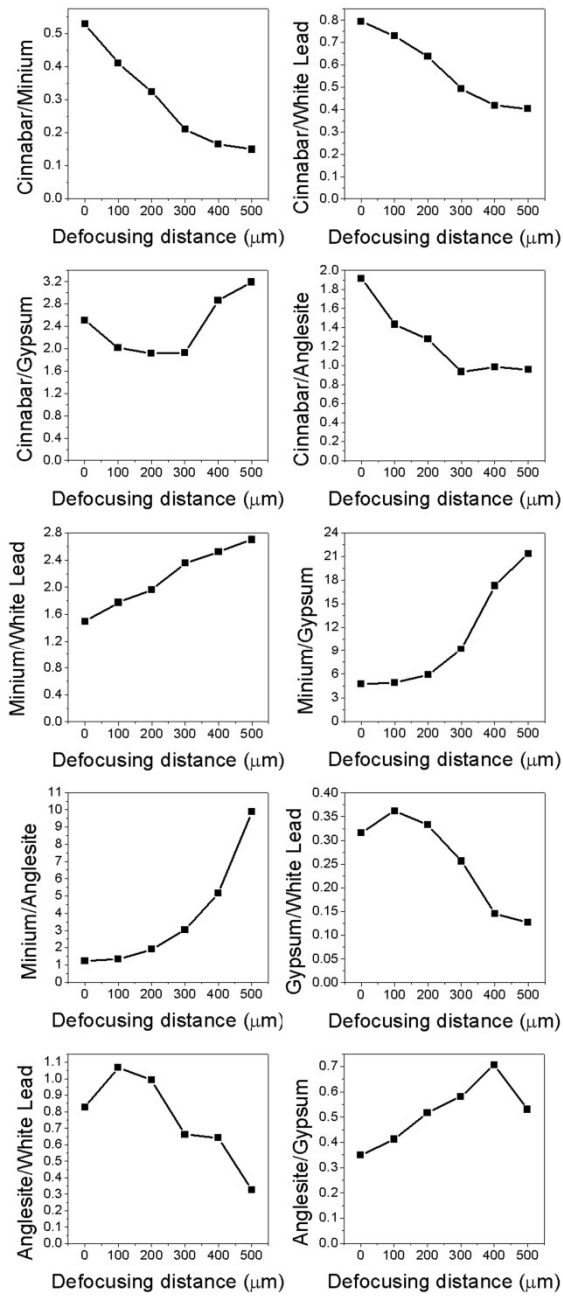


Figure 2: S1 – relative intensity ratios calculated for the main detected phases as a function of the defocusing steps.

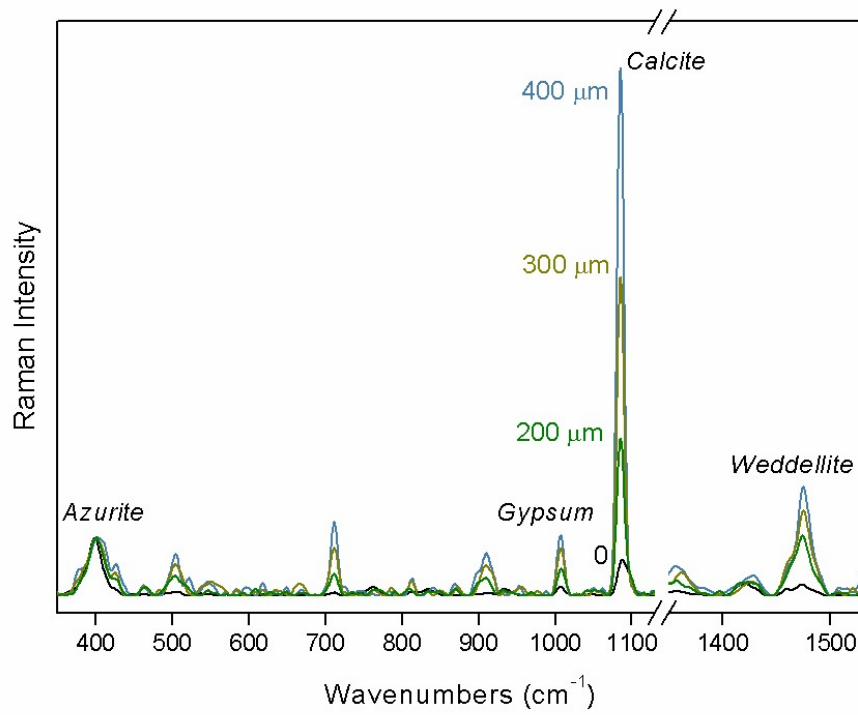


Figure 3: S2 – micro-SORS average sequence normalized to azurite. The values in the graph indicate the defocusing steps.

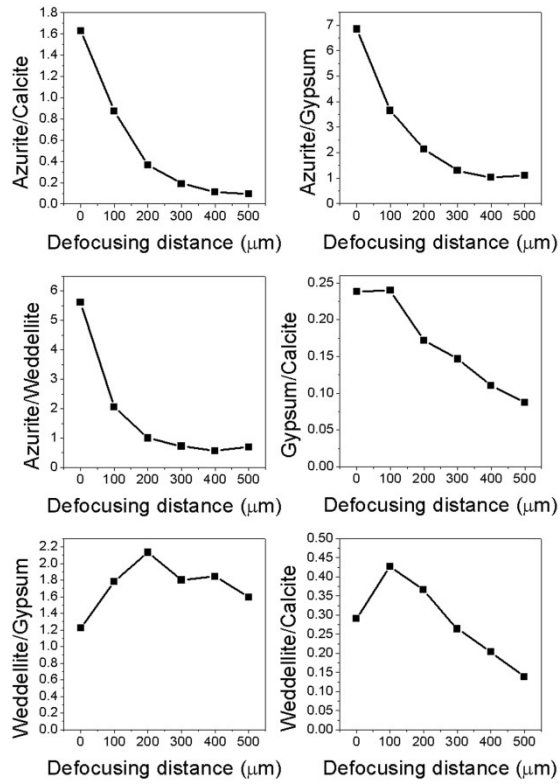


Figure 4: S2 – relative intensity ratios calculated for the main detected bands as a function of the defocusing steps.

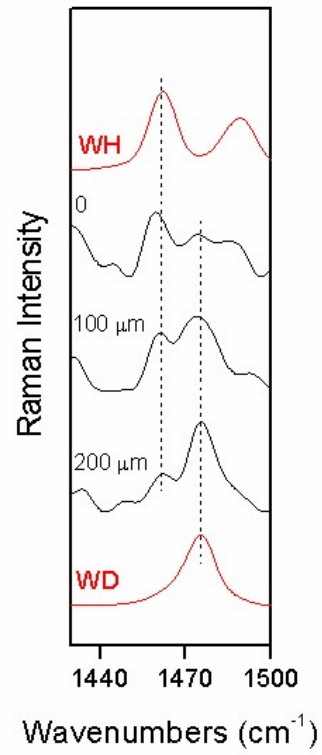


Figure 5: S2 – micro-SORS sequence in the range of the main bands of whewellite (WH) weddellite (WD) phases (reference spectra in red). The values in the graph indicate the defocusing steps.