X-ray Raman scattering as a novel probe to discriminate carbon-based compounds in ancient, art and fossil materials

Rafaella Georgiou[a,b*], Pierre Gueriau[a], Jean-Pascal Rueff[b,c], Uwe Bergmann[d], Nathan Daly[e], and Loïc Bertand[a,b]

a. IPANEMA, CNRS, Ministère de la Culture, UVSQ, Université Paris-Saclay, BP 48 Saint-Aubin, 91192 Gif-sur-Yvette, France

b. Synchrotron SOLEIL, BP 48 Saint-Aubin, 91192 Gif-sur-Yvette, France
c. Sorbonne Universités, UPMC Université Paris 06, CNRS, UMR 7614, Laboratoire de Chimie Physique-Matiere et Rayonnement, F-75005 Paris, France
d. Stanford PULSE Institute, SLAC National Accelerator Laboratory, Menlo Park, California 94025, United States
e. Getty Conservation Institute, 1200 Getty Center Drive, Los Angeles, CA 90049, United States

* rafaella.georgiou@synchrotron-soleil.fr

Deciphering the chemical nature of carbon-based compounds in ancient materials although challenging is an essential source of information in many archaeological and paleontological studies [1,2]. Carbon is ubiquitous and occurs in a diversity of chemical forms. However, difficulties in the characterization and identification of organic carbon compounds are common both due to specificities of the material (e.g., alteration during time, fine scale association with inorganic phases, turbostraticity) and to experimental constraints (high absorbance across the electromagnetic spectrum). X-ray Raman scattering (XRS) recently proved very promising to probe carbon speciation in complex heterogeneous solid ancient samples [3]. In this hard X-ray inelastic scattering technique, a small fraction of the X-ray energy is transferred to the electrons by inelastic scattering, allowing to collect speciation signal for light elements in a nondestructive manner, in air, with bulk sensitivity, to provide information not compromised by surface contamination, thus overcoming important constraints in the characterization of ancient materials [3].

The potential of XRS will be demonstrated through the analysis of carbon-based artists' pigments, which are until today poorly understood due to their complex chemistry [4]. We determined the carbon speciation of a consistent set of modern and historical samples used in the arts. As an example, the sensitivity of XRS is high enough to distinguish carbon black pigments obtained by the burning or pyrolysis of gas or oil from fine charcoal. We also collected XRS-based carbon K-edge XANES on fossil samples that allow discussing their fossilization. By providing information on the degree of aromaticity, the signatures of oxidized COO groups, the presence of carbon bound with heteroatoms and turbostraticity, XRS appears as a novel powerful and convenient probe to discriminate carbon-based compounds in complex, heterogeneous samples, and could be further applied to a wide range of ancient and historic materials.

[1] R. P. Evershed, Archaeometry 50.6 (2008): 895-924.
[2] D. Marguerie, Dominique, and J-Y. Hunot., Journal of archaeological science 34.9 (2007): 1417-1433.
[3] P. Gueriau, J-P. Rueff, S. Bernard, J.A. Kaddissy, S Goler, C. J. Sahle, D. Sokaras, R. A. Wogelius, P. L. Manning, U. Bergmann, L. Bertrand, Analytical chemistry, 89(20) (2017).: 10819-10826.
[4] J. Winter, and E. W. FitzHugh, Artists' pigments, 4 (2007): 1-37.