Laser yellowing effect: study of the nanophases created by laser irradiation of natural and model gypsum crusts using transmission electron microscopy (TEM) and electron paramagnetic resonance (EPR) spectroscopy

Marie Godet[1,2,3*], Véronique Vergès-Belmin[1], Christine Andraud[2], Mandana Saheb[4], Judith Monnier[5], Eric Leroy[5], Julie Bourgon[5], Laurent Binet[6]

[1]*Laboratoire de Recherche des Monuments Historiques (LRMH-CRC, USR3224), 29 rue de Paris 77420 Champs-sur-Marne, France*
[2]*Centre de Recherche et Conservation des Collections (CRCC-CRC, USR3224, MNHN), 36 rue Geoffroy-Saint-Hilaire – CP 21, 75005 Paris, France*
[3]*SILLTEC, 4 rue René Razel, 91400 Saclay, France*
[4]*Laboratoire Interdisciplinaire des Systèmes Atmosphériques (LISA), 61 Avenue du Général de Gaulle, 94010 Créteil Cedex, France*
[5]*Institut de Chimie et des Matériaux Paris-Est (ICMPE), 2/8 rue Henri Dunant, 94320 Thiais, France*
[6]*Institut de Recherche de Chimie Paris (IRCP), 11 rue Pierre et Marie Curie, 75005 Paris, France*
*Marie.godet@culture.gouv.fr

Nd-YAG Q-switched laser devices operating at 1064 nm have been considered in the 1990s as the most promising tools for cleaning stone sculptures, and more particularly for the elimination of indurated black gypsum crusts. However, the spreading of the laser technology has been undermined because of the yellow hue it occasionally conveys to the cleaned surfaces. Especially in France, this yellow effect is considered as a major esthetical issue by the conservators. At the present time this discoloration is still only partly explained: a currently admitted hypothesis states that the iron oxides present in the black crusts would transform, on laser irradiation, into yellow iron-rich nanophase(s) that would re-deposit on the cleaned substrate. To verify this hypothesis, two types of samples were prepared: i) natural black crust fragments collected at the Saint-Denis Basilica in Saint-Denis, France and ii) simplified model crusts composed of a mixture of red hematite α-Fe_2O_3 and gypsum $CaSO_4 \cdot 2H_2O$ applied like a coating on a plaster platelet. Natural black crusts and model red crusts were then irradiated using a Nd-YAG QS laser: as a result an instantaneous shift of their colour to yellow was observed. In order to identify the phases created by irradiation, a multi-scale analytical methodology was developed, as the size of the irradiation products vary from some nanometres to some hundreds of micrometres. Optical microscopy and scanning electron microscopy (SEM) have permitted to study the micro-morphology of the products of irradiation whereas transmission electron microscopy (TEM) has enabled observations of the nano-sized products which are very probably responsible of the yellowing. (See figure below: a yellow gypsum platelet covered by iron containing nanoparticles)

The elementary chemical composition of the nanophases was determined by energy dispersive X-ray spectrometry (EDS) and electron energy loss spectroscopy (EELS) coupled with scanning transmission electron microscopy (STEM). In addition, electron paramagnetic resonance (EPR) spectroscopy has been used to ascertain the presence of ferrimagnetic and super-paramagnetic materials in the same samples to aid in the identification of the neo-formed yellow phase(s).