Er:YAG APPLICATION TO TEMPERA PAINTS: INFLUENCE OF PIGMENT AND BINDER NATURE

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INTRODUCTION

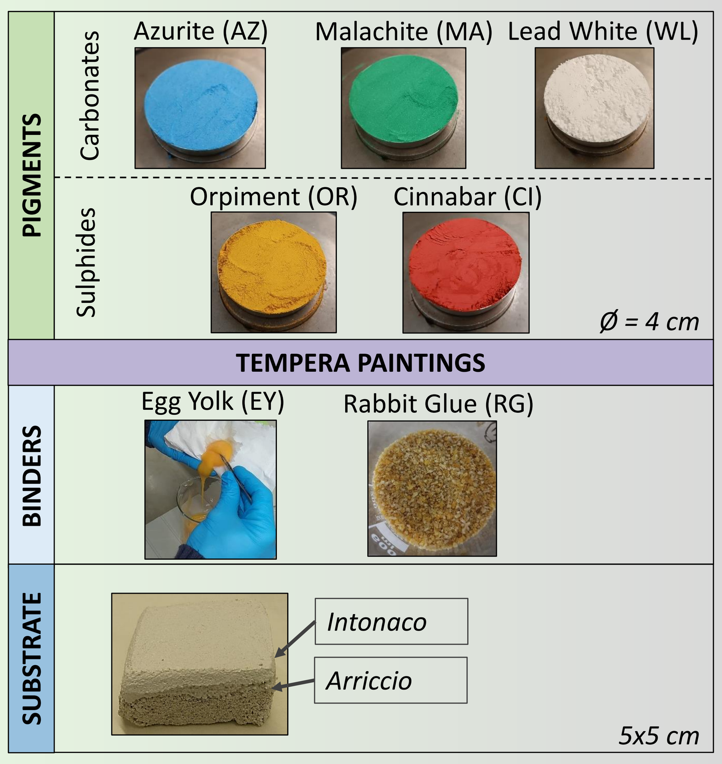
Er:YAG lasers have shown consolidated results in the cleaning of organic crusts and patinas. The OH groups are the main absorbers at the laser wavelength of 2940 nm (infra-red region), leading an explosive vaporisation of the OH-containing molecules of the crusts. This explains the efficacy of the treatment [1]. When cleaning a wall painting, conservators need to be aware of any possible laser-induced effects on the paints under the organic crusts. So, it remains crucial to deeply evaluate these effects on the paint components and the whole painting from the physical-chemical and mineralogical point of view.

OBJECTIVES

To investigate the effects of Er:YAG irradiation on pigment-binder interaction and tempera paints. The two specific objectives are: 1) determination of damage thresholds for each pigment and rabbit glue- or egg yolk-based paintings and 2) characterization of chemical and micromorphological changes under the highest fluences.

MATERIALS AND METHODS

Raw materials



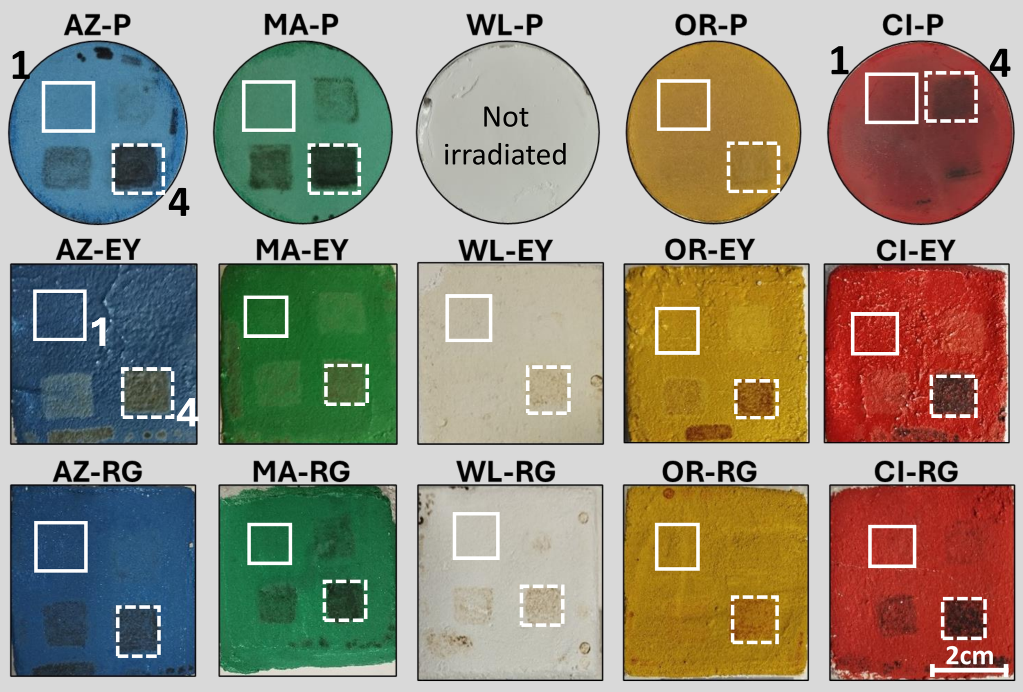
Laser application on pigment pellets (P) and mock-ups (EY or RG)

Parameters

- Er:YAG
- Wavelength (λ): 2940 nm
- Pulse duration: 150 µs
- Frequency: 7, 10, 15 Hz
- Max. energy/pulse: 100 mJ
- Spot diameter: 0.8 mm

Methodology

Four irradiated areas were performed increasing the fluence.



Multi-analytical approach

Study of irradiated areas: 1 (damage threshold) and 4 (the highest fluence).

- Stereomicroscopy
- Spectrophotometry
- IR sensor

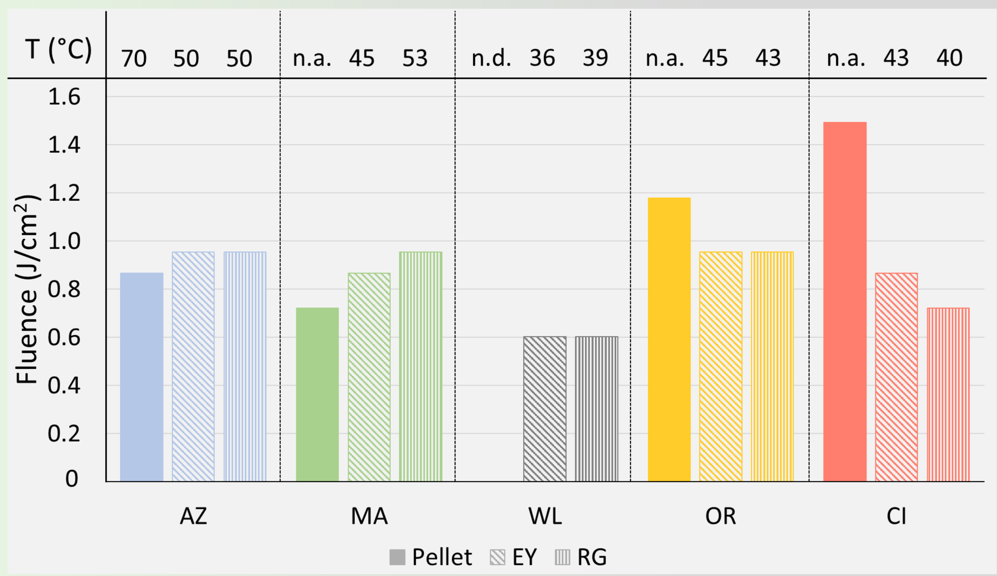
Physical evaluation

- FTIR (Fourier-Transform Infrared Spectroscopy)*
- Py-GC-MS (Pyrolysis-Gas Chromatography-Mass Spectrometry)*
- SEM-EDX (Scanning Electron Microscopy)

Chemical evaluation
*After scalpel sampling of a few mg

RESULTS

1 Determination of damage threshold

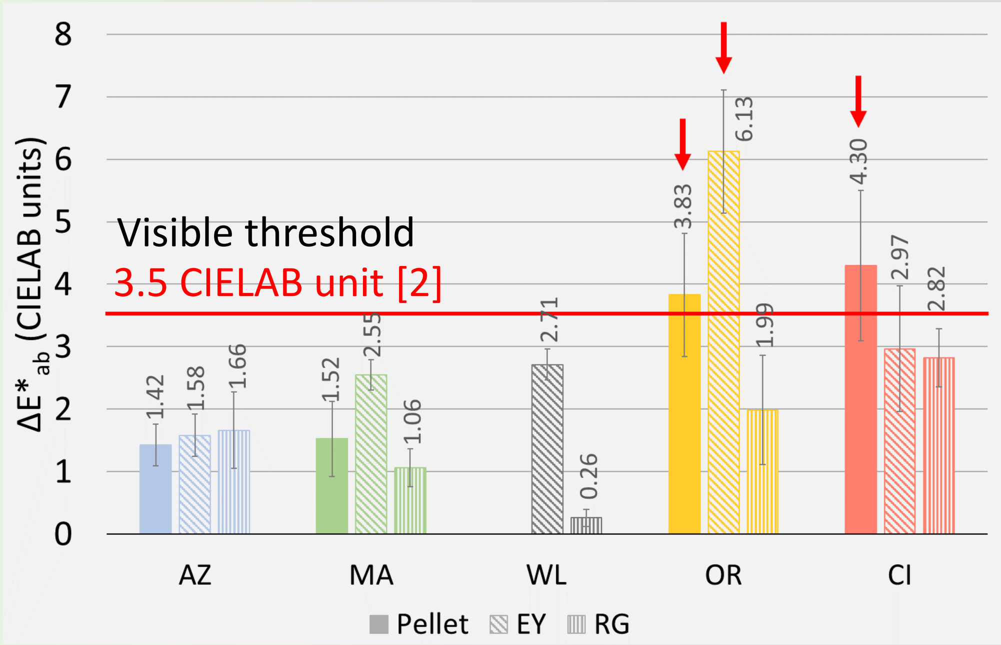


Regarding pigments:

- **Sulphide** pigments were less sensitive to Er:YAG radiation (higher fluences) than **carbonates**.

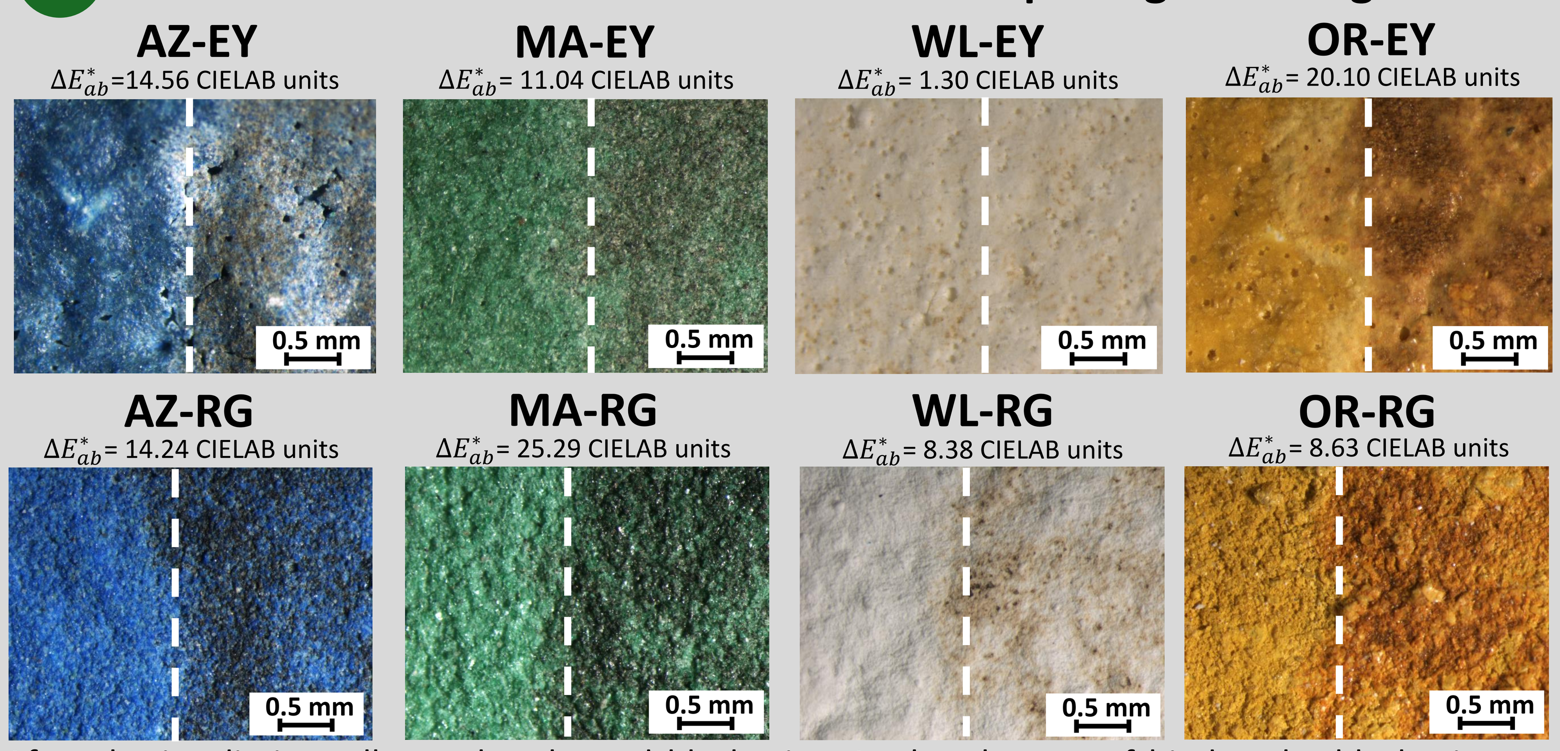
Regarding temperas (EY and RG):

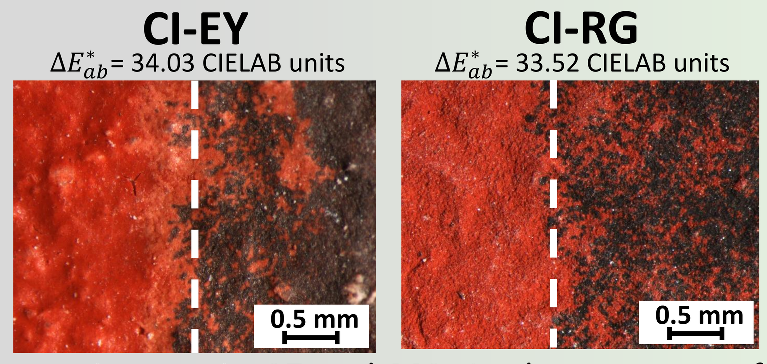
- In **AZ** and **MA**: higher damage threshold fluences than in pigments alone – protective effect of binder.
- In **WL**, **OR** and **CI**: lower damage threshold fluences than pigments alone – binder does not exert any protective effect.

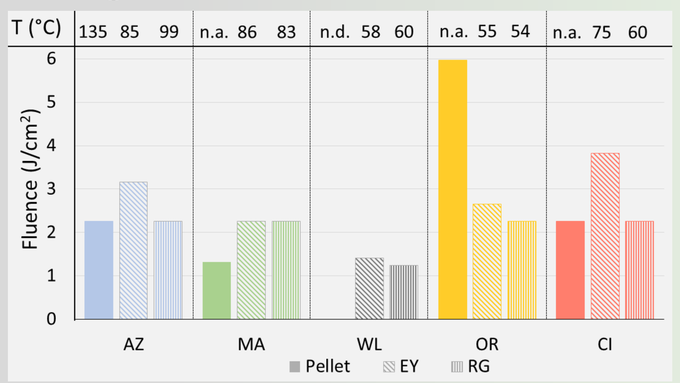


Only **OR-P**, **OR-EY** and **CI-P** suffered ΔE^*_{ab}> 3.5 CIELAB units. However, these changes were not visible at the naked eye.

2 Characterisation of chemical and micromorphological changes under the highest fluences



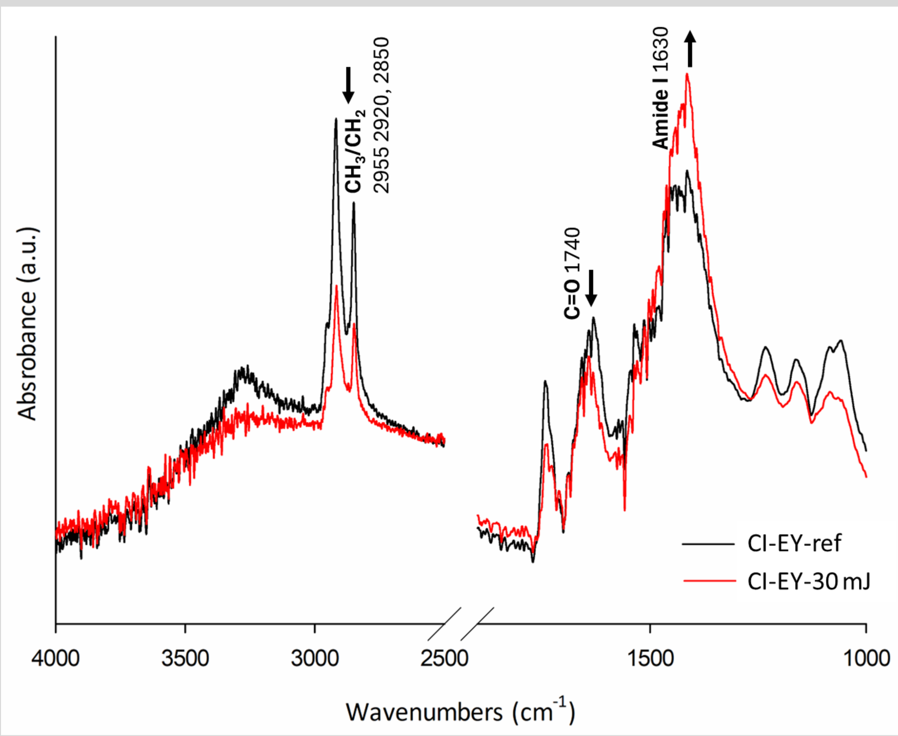


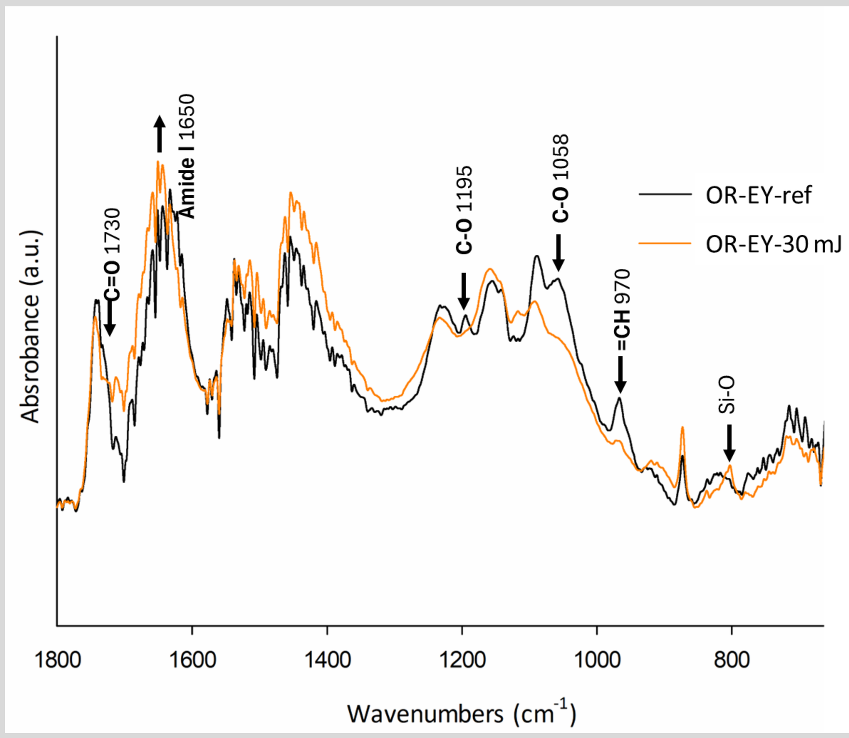


At compared fluences, carbonates achieved a T (°C) greater than sulphides do.

After the irradiation, all samples showed blackening. In the absence of binder, the blackening was more intense in **AZ** and **MA**. In the presence of binder (tempera), the blackening was greater in **CI with EY and RG**. The colour changes suffered at **WL paints** were reversed within ~2 months after radiation.

FTIR-ATR





Regarding pigments:

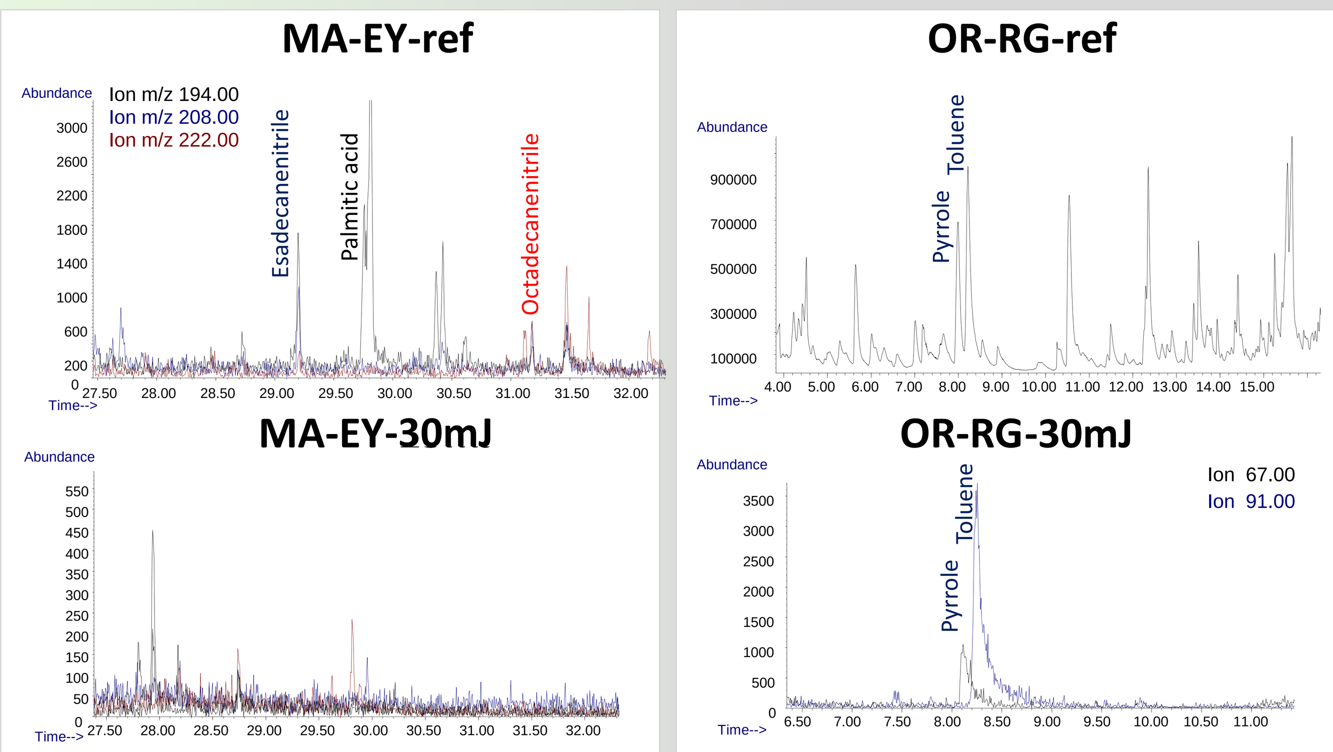
- No changes.

Regarding tempera:

- Modifications (disappearance or reduction in intensity) of bands (1740, 1195, 1058, 970 cm^{-1}) assigned to the C=O (esters), C-O or C-H and appearance of a band at 1217 cm^{-1} assigned to C-O ester - oxidation processes of lipids and proteins.
- Modification of the relationship of intensities in the doublet at 1650-1630 cm^{-1} from amide I – modification of the secondary structure of the protein.

The changes were much more intense in EY tempera.

Py-GC-MS



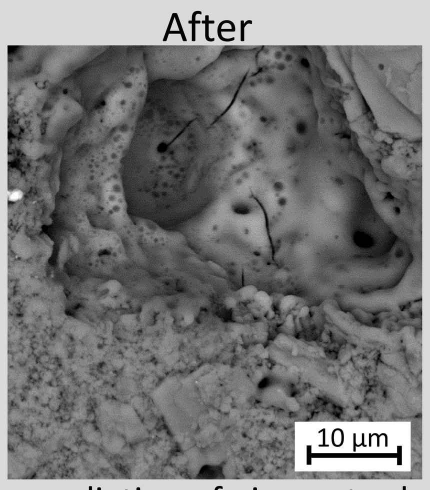
Regarding egg tempera:

- The characteristic markers of egg binder (esadecanenitrile and octadecanenitrile) were not detected after laser irradiation with 30 mJ.

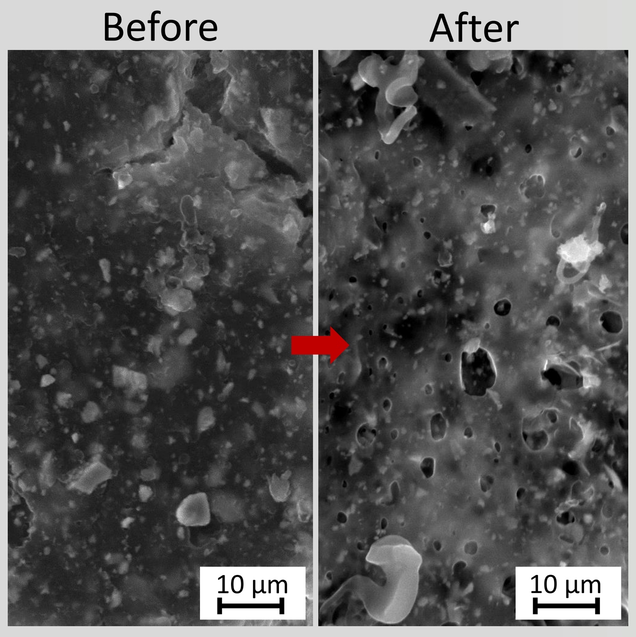
Regarding rabbit glue:

- The amount of the characteristic marker (pyrrole) drastically decreased after laser irradiation.

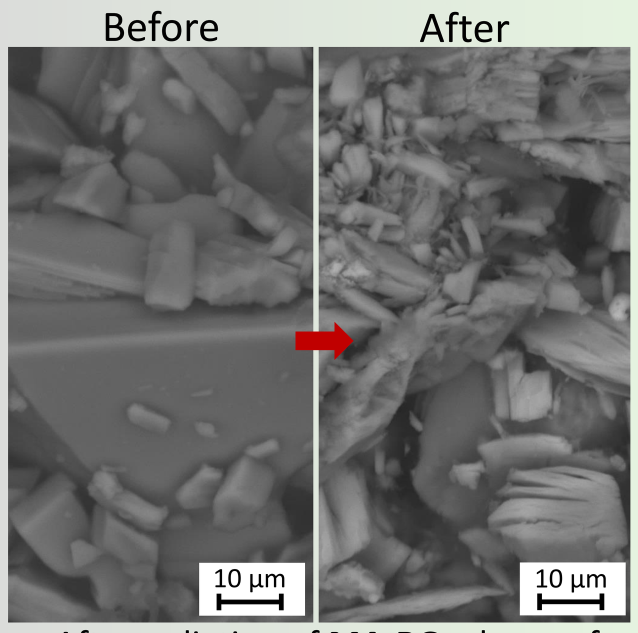
SEM-EDX



After radiation of pigments alone: changes were only found in **OR-P** (melting of the pigment particles).



After radiation of **CI-EY**: pores on EY and no melting signals.



After radiation of **MA-RG**: planes of pigment opening, mineral breakage and no melting signals.

CONCLUSIONS

Regarding damage threshold:

- Sulphide pigments were more resistant than carbonates. WL was the least susceptible (no damage even at high fluences).
- Binder showed two behaviours: **protection** (AZ, MA) and **no protection** (WL, OR and CI). ΔE^*_{ab} of the irradiated areas usually were lower than the visible threshold (3.5 CIELAB u.).

Regarding damages:

- About pigments: the analytical techniques applied were unable to identify the causes of blackening.
- About tempera: blackening was produced in all tempera paints regardless of the binder. This colour change could be related to the deterioration of the binders, which has been confirmed by the chemical analytical approach.

[1] L. Pereira-Pardo and C. Korenberg, "The use of erbium lasers for the conservation of cultural heritage. A review," Journal of Cultural Heritage, vol. 31, pp. 236–247, May 2018, doi: 10.1016/j.culher.2017.10.007.
[2] R. F. Witzel, R. W. Burnham, and J. W. Onley, "Threshold and suprathreshold perceptual color differences," J. Opt. Soc. Am., vol. 63, no. 5, p. 615, May 1973, doi: 10.1364/JOSA.63.000615.

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