



# **New wavelength-dependent femtosecond pulsed LASER cleaning: A case study with stones of different provenance locality, Portugal**

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**Abstract:** Laser cleaning techniques have been considered amongst the most impactful contributions of Physics towards the restoration of stonework. Contamination and deterioration products in stones eliminated by laser-assisted techniques is a new and promising development that may highlight the use of laser cleaning methodology in this sector. This research work reports on studies aimed to evaluate the use of ultrafast femtosecond (fs) pulsed lasers for the removal of contaminants on significant stone surfaces with different locality from Portugal. A series of studies have been carried out to assess the controlled laser cleaning parameters using two different laser systems: a 238 fs pulsed UV laser with emission at 343 nm and a 228 fs pulsed n-IR laser with emission at 1030 nm. In both cases, line scan pulse mode was employed to explore contaminant removal efficiency while, at the time, assessing the degree of damage produced to the underlying original substrate surface. Adequate repetition-rate generation, wavelength-dependent absorption and materials thermal properties are amongst the parameters considered, and the main results obtained will be presented and discussed in an effort to evaluate the potential that these new types of lasers offer towards an increased cleaning efficiency of stones with deteriorated surfaces.

**Keywords:** femtosecond laser; short pulse; stone; cleaning; restoration;

## LIGHT FOR ART

New wavelength-dependent femtosecond pulsed LASER cleaning:  
A case study with stones of different provenance locality, Portugal



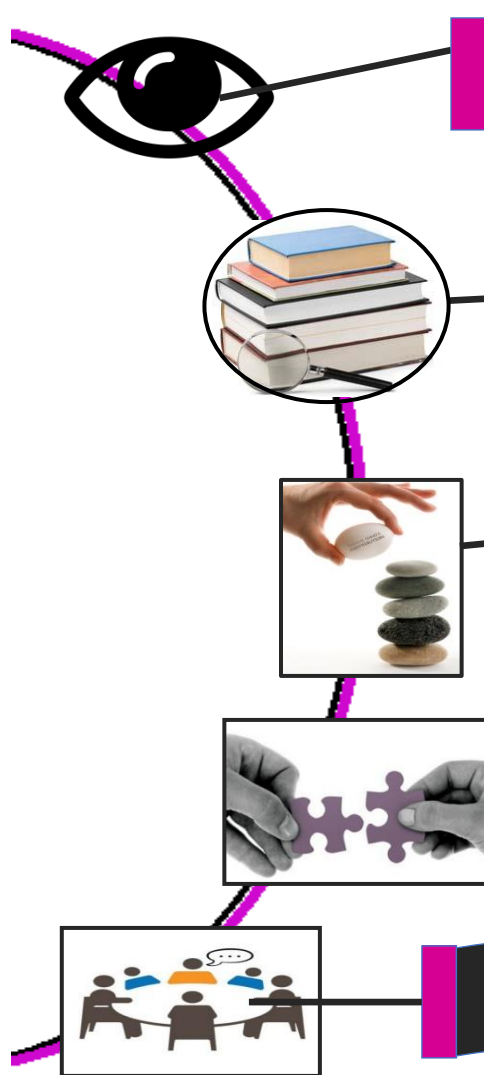
**SUPERVISOR:**

**PROF. DR. LUÍS LOPES**

DEPARTMENT OF GEOSCIENCES, SCHOOL OF  
SCIENCE AND TECHNOLOGY

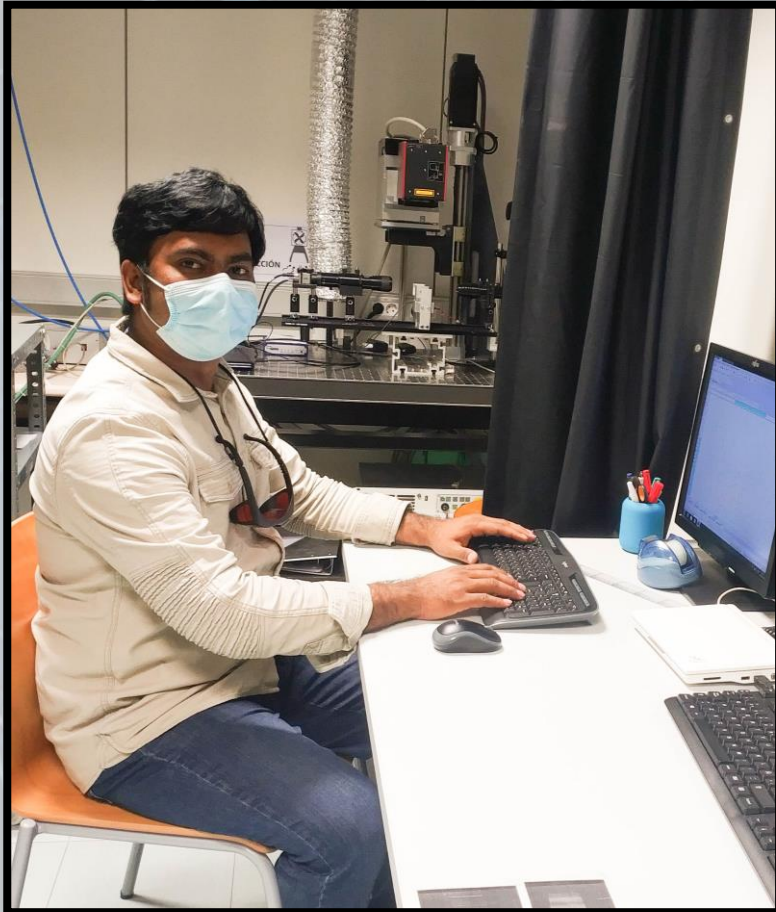
INSTITUTE OF EARTH SCIENCES (ICT)

UNIVERSIDADE DE ÉVORA (PORTUGAL)



- Introduction
- Research Objectives
- Materials and Methods
- Results – Laser based intervention
- Discussions and Q.A.





Places I call/ed home..



# Md Ashiqur Rahman

Predocctoral Investigator  
Spanish National Research Council (CSIC: INMA)

## Academic Endeavors



Marie Sklodowska Curie PhD : H2020-MSCA- ITN- **ED-ARCHMAT**  
Spanish National Research Council - Institute for Nanoscience and Materials of Aragón (CSIC-INMA), University of Burgos (Spain) & University of Evora (Portugal)



Marie Sklodowska Curie PhD: H2020-MSCA-COFUND **T4C**  
University of Torino (Italy)



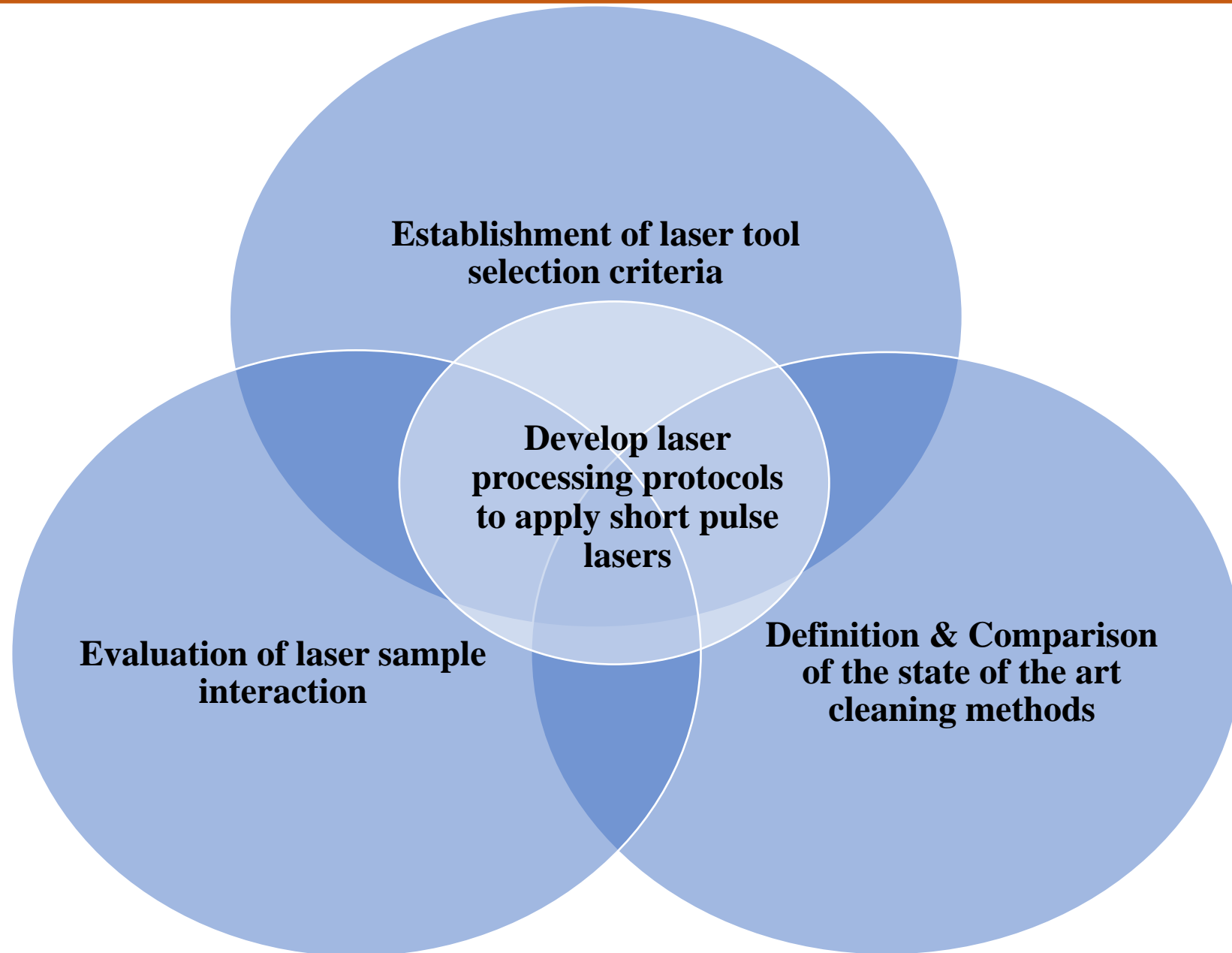
Erasmus Mundus European Master in **ARCHMAT**  
University of Evora (Portugal), University of Rome La Sapienza (Italy) & Aristotle University of Thessaloniki (Greece)



M.S. Engg. & B.Sc. Engg  
Dept. of Applied Physics, Electronics & Communication Engineering  
University of Chittagong (Bangladesh)

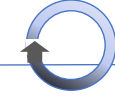
Places I belong to...



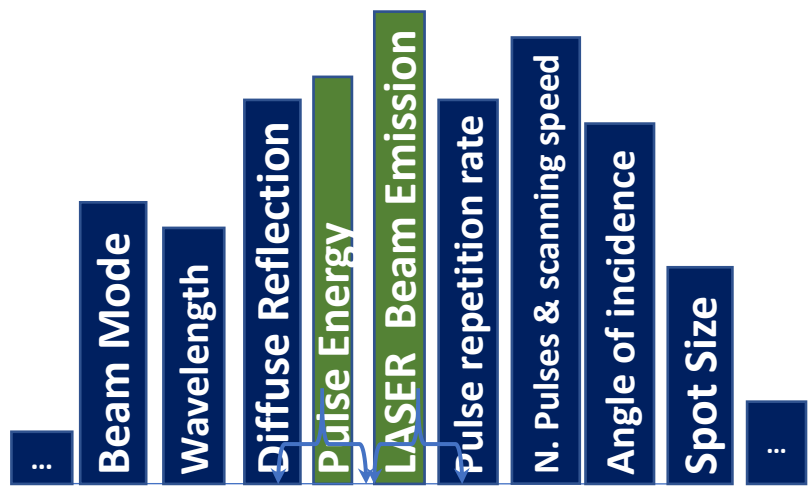




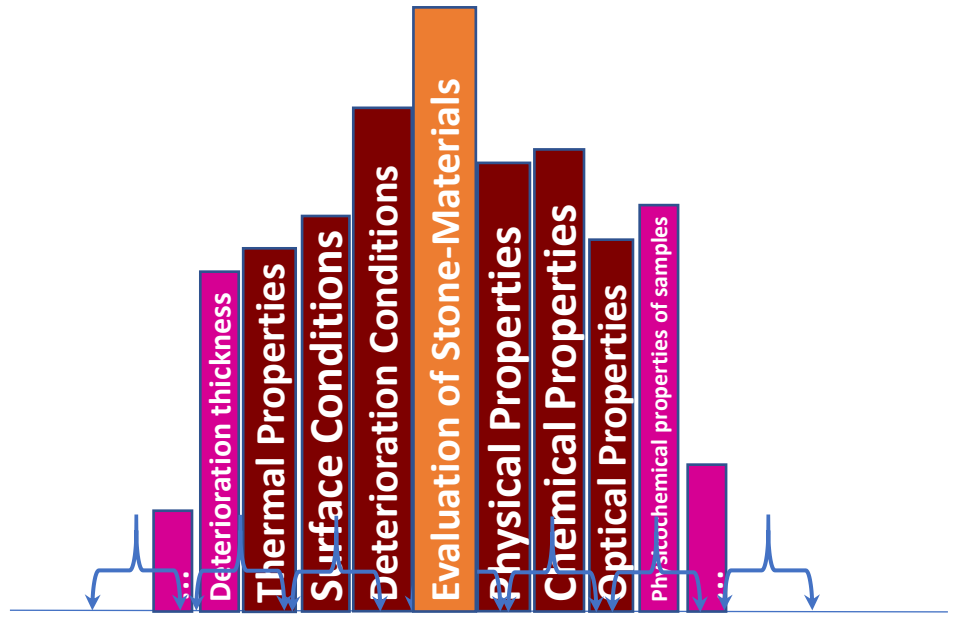
## Controlled LASER methodology design



## Evaluation of Stones and artifacts



Analyze the possibilities that the new short pulse lasers open in CH conservation.



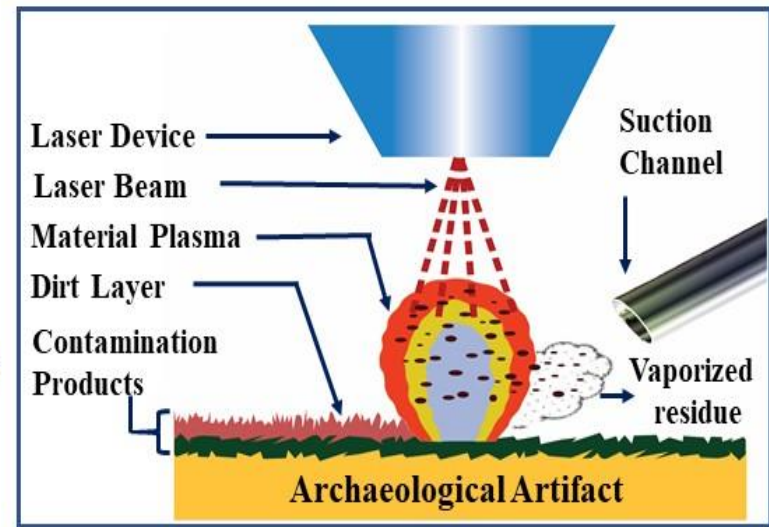
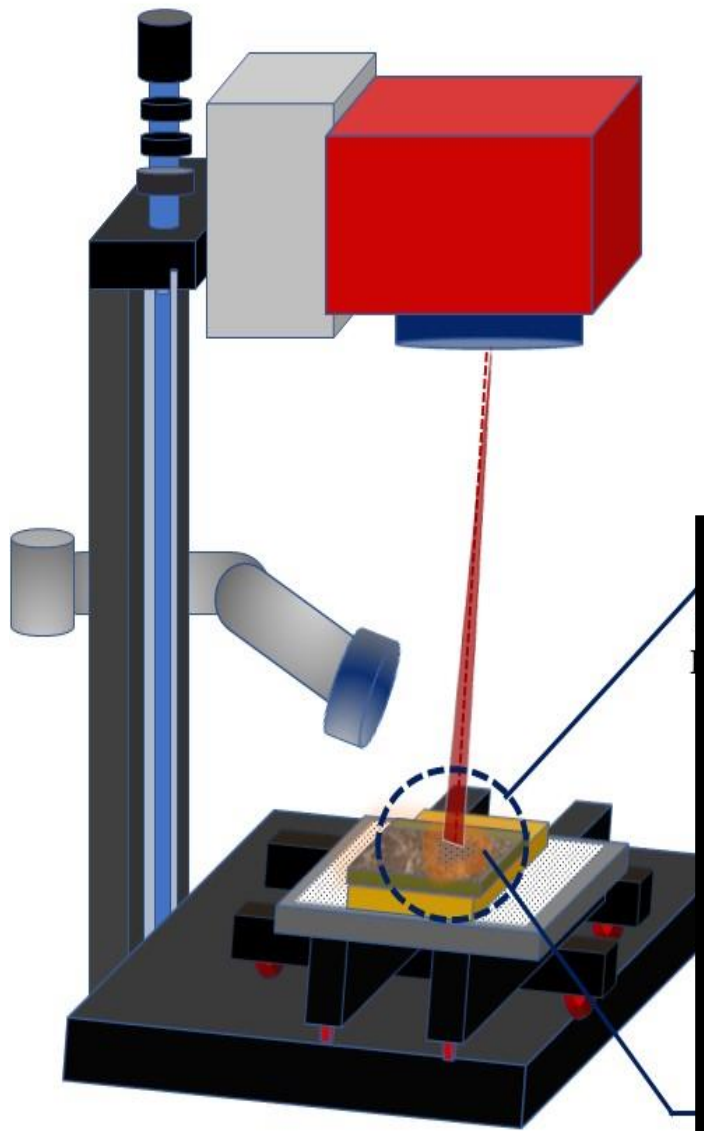
If newly controlled LASER methodology works perfectly, then will go for large scale research

Evaluation of laser sample interaction (laser emission parameters and the material physicochemical properties)



## Evaluation of Laser- Sample Interaction









"Moca Crème" Limestone. Provenance locality: Santarém, Alcanede



Grey Granite Provenance locality: Portalegre, Santa Eulália



"Vidraço" Limestone. Provenance locality: Leiria, Alcobaça



White Estremoz Marble with pink veins, slab surface oblique to foliation. Provenance locality: Vila Viçosa, Lagoa



White Estremoz Marble with well-defined foliation parallel to the slab surface. Provenance locality: Estremoz



# Samples Description



White Estremoz Marble, slab surface oblique to foliation. Provenance locality: Estremoz



White Estremoz Marble with blueish aleatory veins, "Pele de Tigre" variety (Tiger Skin variety). Provenance locality: Vila Viçosa, Lagoa



White Estremoz Marble with pink veins, slab surface oblique to foliation. Provenance locality: Vila Viçosa, Lagoa



Cream Estremoz Marble, slab surface oblique to foliation. Provenance locality: Vila Viçosa, Lagoa





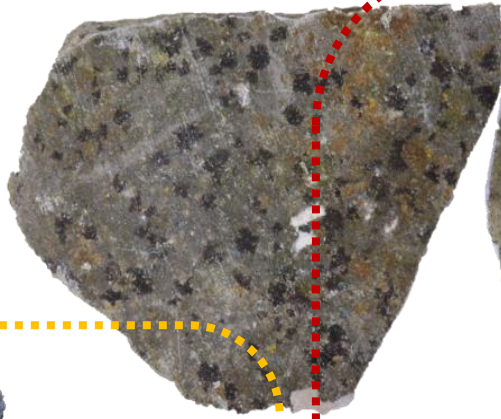
# Samples Description



“Moca Crème” Limestone. Provenance locality: Santarém, Alcanede



Grey Granite Provenance locality: Portalegre, Santa Eulália



“Vidraço” Limestone. Provenance locality: Leiria, Alcobaça



White Estremoz Marble with pink veins, slab surface oblique to foliation. Provenance locality: Vila Viçosa, Lagoa

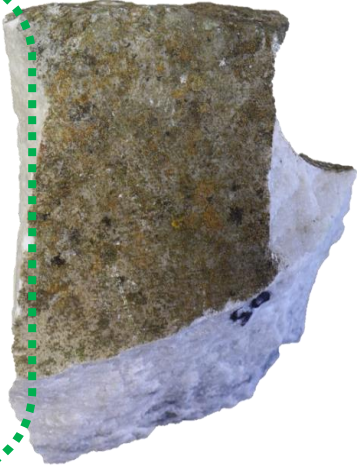


White Estremoz Marble with well-defined foliation parallel to the slab surface. Provenance locality: Estremoz

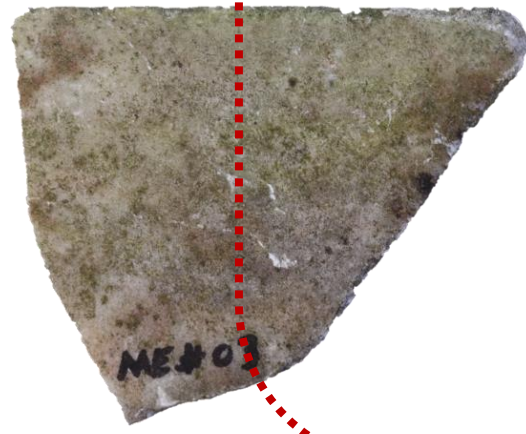
White Estremoz Marble, slab surface oblique to foliation. Provenance locality: Estremoz



White Estremoz Marble with blueish aleatory veins, “Pele de Tigre” variety (Tiger Skin variety). Provenance locality: Vila Viçosa, Lagoa



White Estremoz Marble with pink veins, slab surface oblique to foliation. Provenance locality: Vila Viçosa, Lagoa



Cream Estremoz Marble, slab surface oblique to foliation. Provenance locality: Vila Viçosa, Lagoa



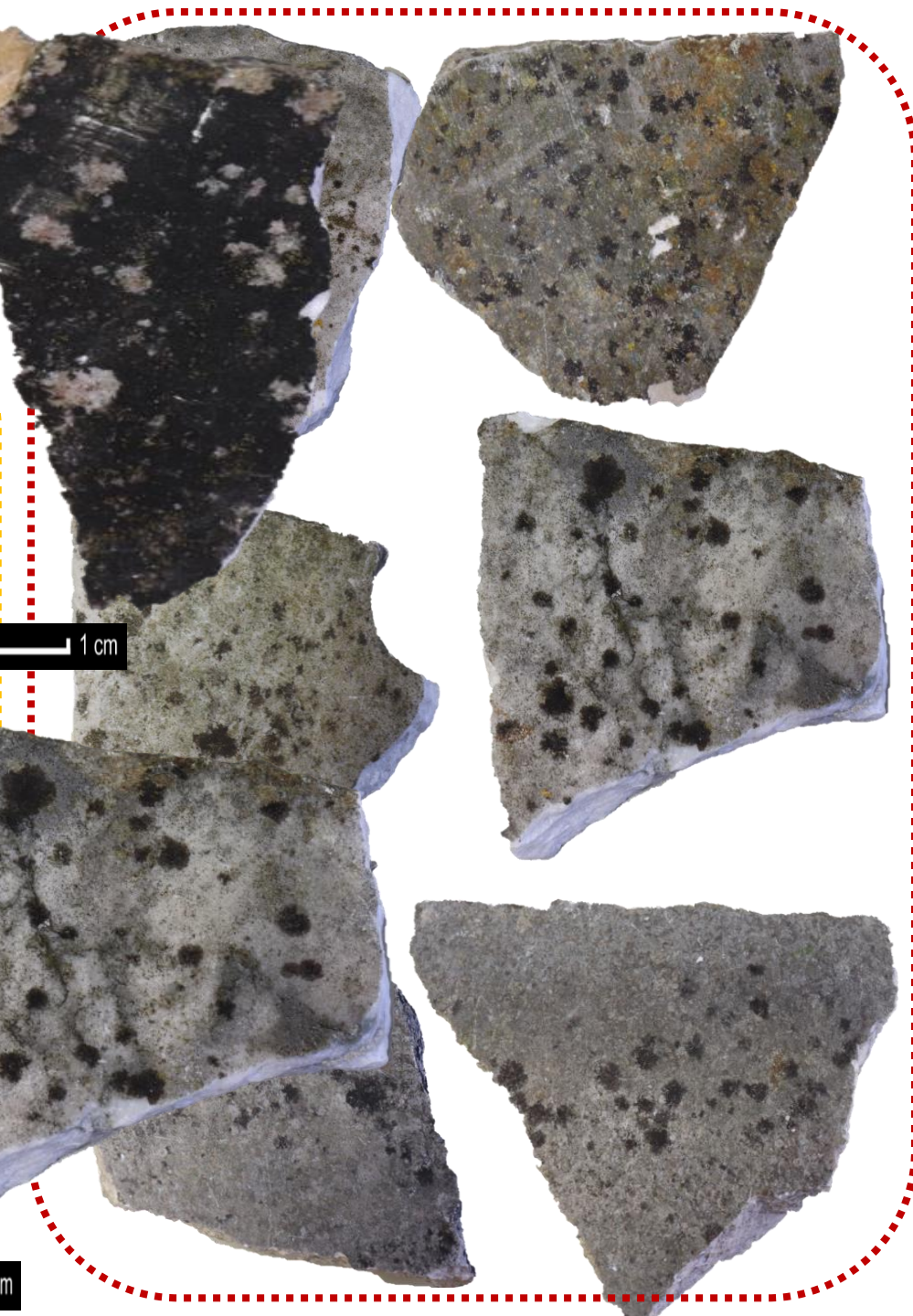




Sample



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EVORA



ME#03

1 cm

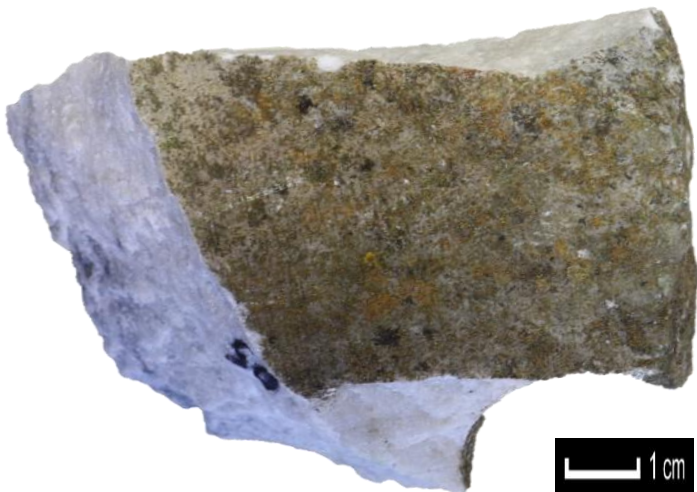




Material: Marble  
 Code: **White Estremoz Marble**  
 Provenance locality: Vila Viçosa, Lagoa  
 Problems: with pink veins, slab surface oblique to foliation.  
**OBJECTIVE:** Remove bio-colonization and clean the surface stains without altering the surface.



Material: Marble  
 Code: **Cream Estremoz Marble**  
 Provenance locality: Vila Viçosa, Lagoa  
 Problems: Slab surface oblique to foliation.  
**OBJECTIVE:** Remove bio-colonization and clean the surface stains without altering the surface.



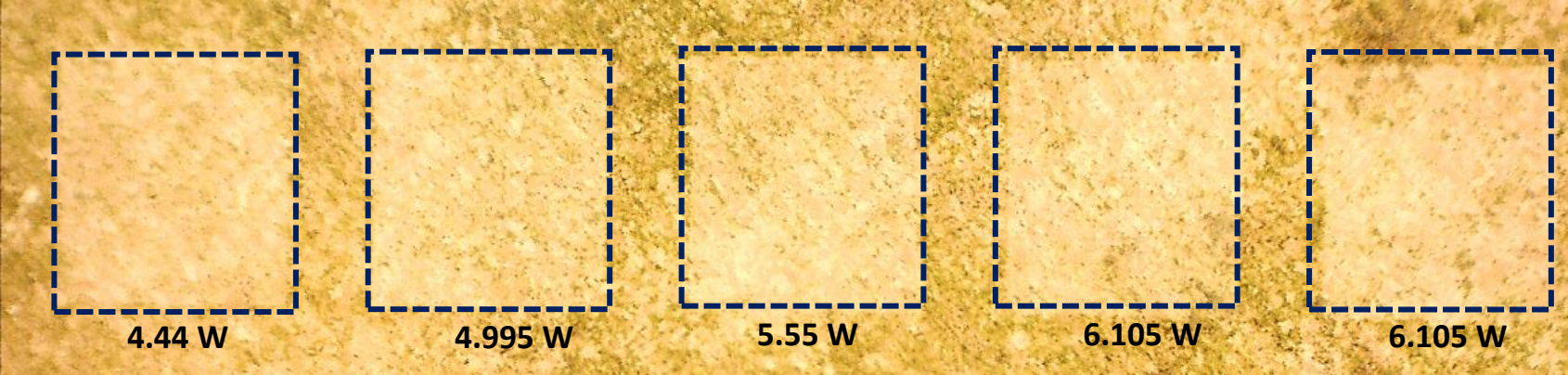
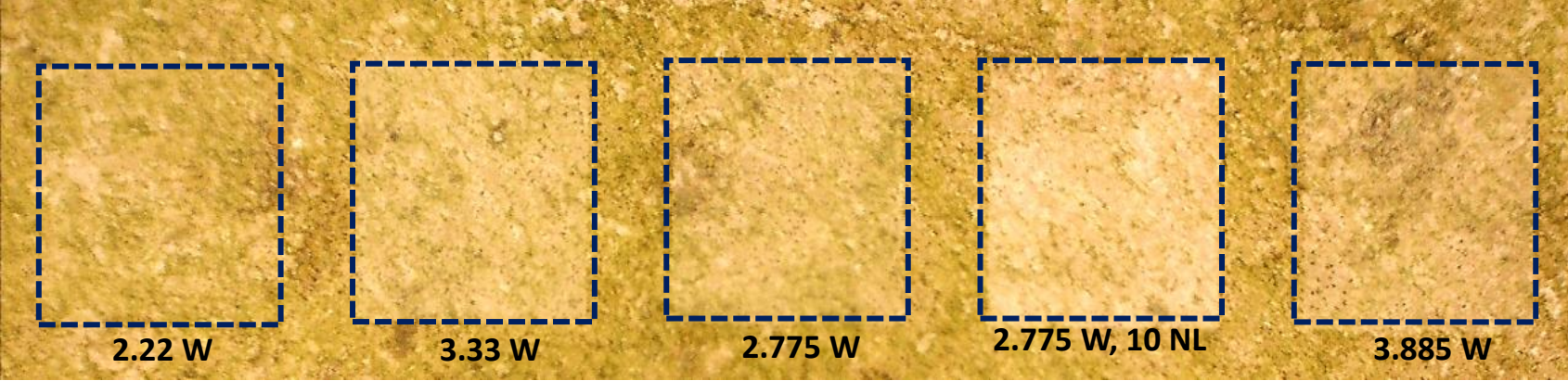
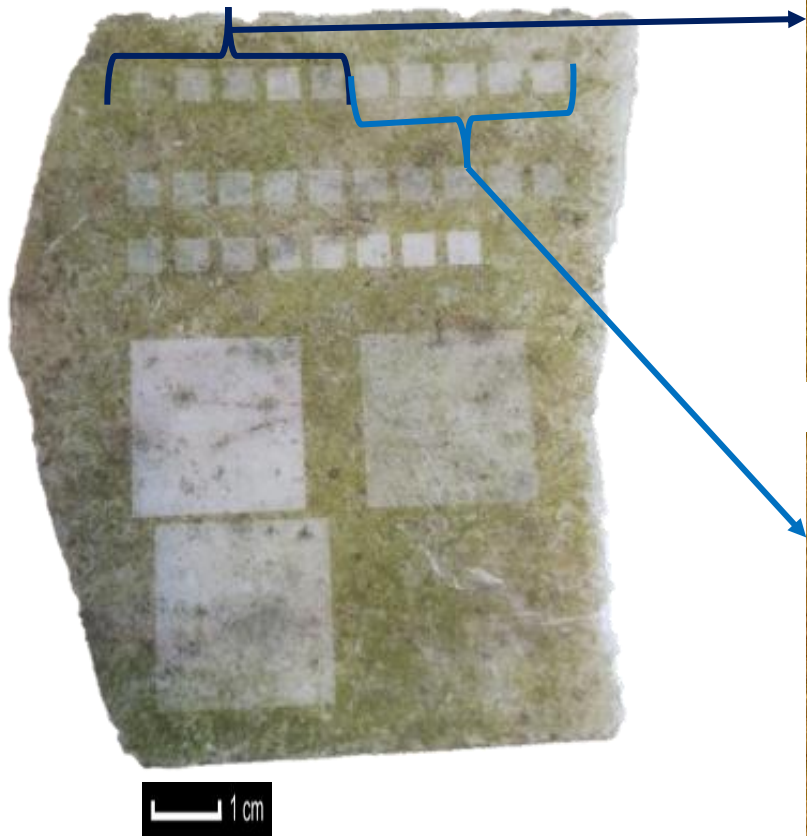
Material: Marble  
 Code: **White Estremoz Marble with blueish aleatory veins, "Pele de Tigre" variety (Tiger Skin variety).**  
 Provenance locality: Vila Viçosa, Lagoa  
 Problems: Slab surface oblique to foliation.  
**OBJECTIVE:** Remove bio-colonization and clean the surface stains without altering the surface.



Material: Marble  
 Code: **White Estremoz Marble**  
 Provenance locality: Estremoz  
 Problems: Slab surface oblique to foliation.  
**OBJECTIVE:** Remove bio-colonization and clean the surface stains without altering the surface.



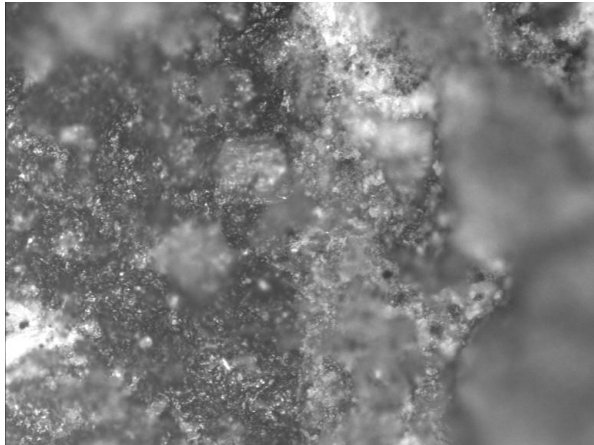
Laser type	$P_{max}$ (W)	$\lambda$ (nm)	$t_p$ (fs)	$f_p$ (kHz)	$D_b$ ( $\mu\text{m}$ )	Mark speed (mm/s)	Spacing between lines ( $\mu\text{m}$ )
fs UV	11.1	343	238	200	30	150	15



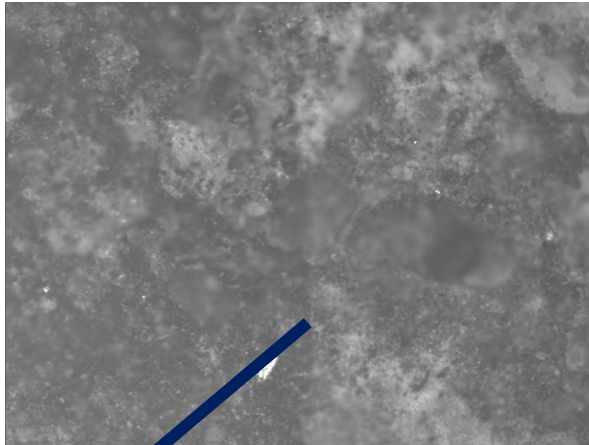
200KHz (/20ppd), 15 $\mu\text{m}$ , 150mm/s, NL:1



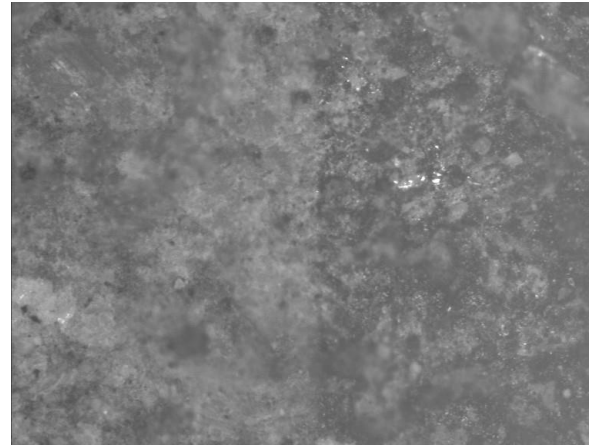
2.22 W



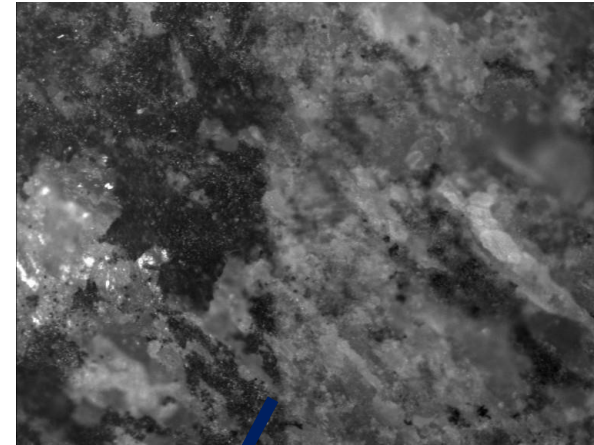
2.775 W



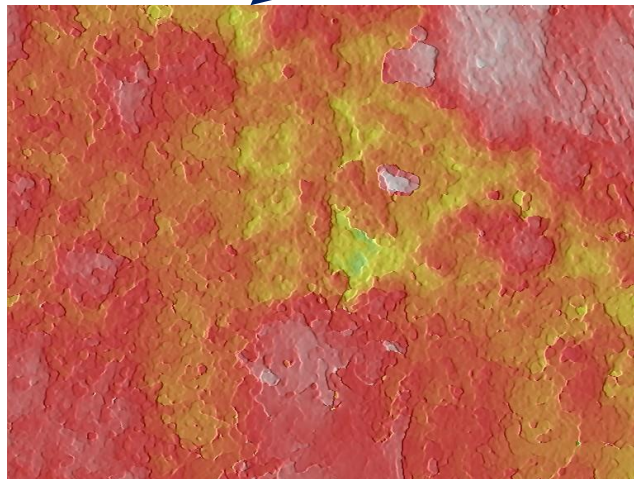
3.33 W



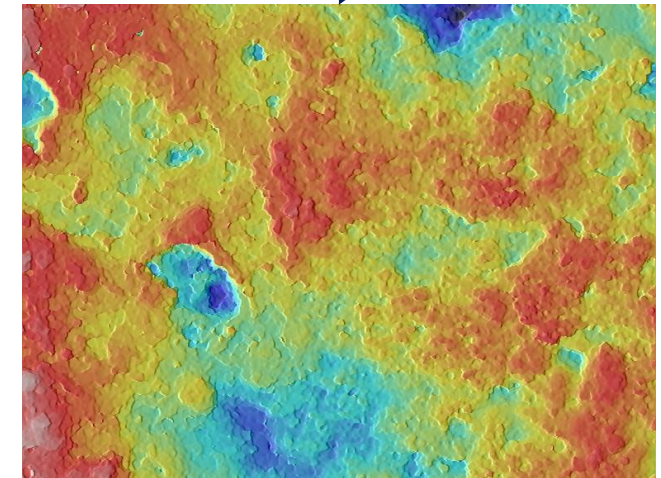
5.55 W



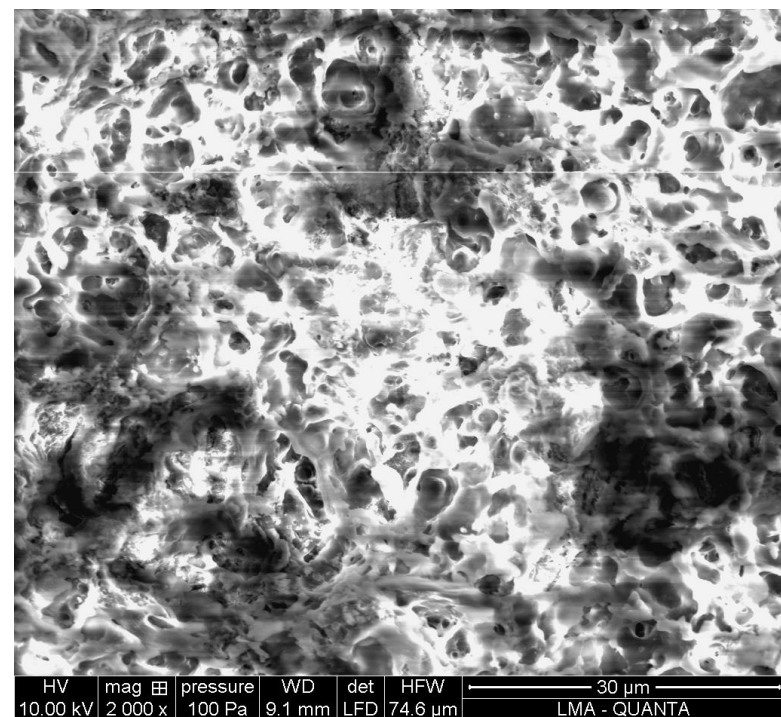
Confocal microscopy images correspond with the original laser treated and uncleaned area



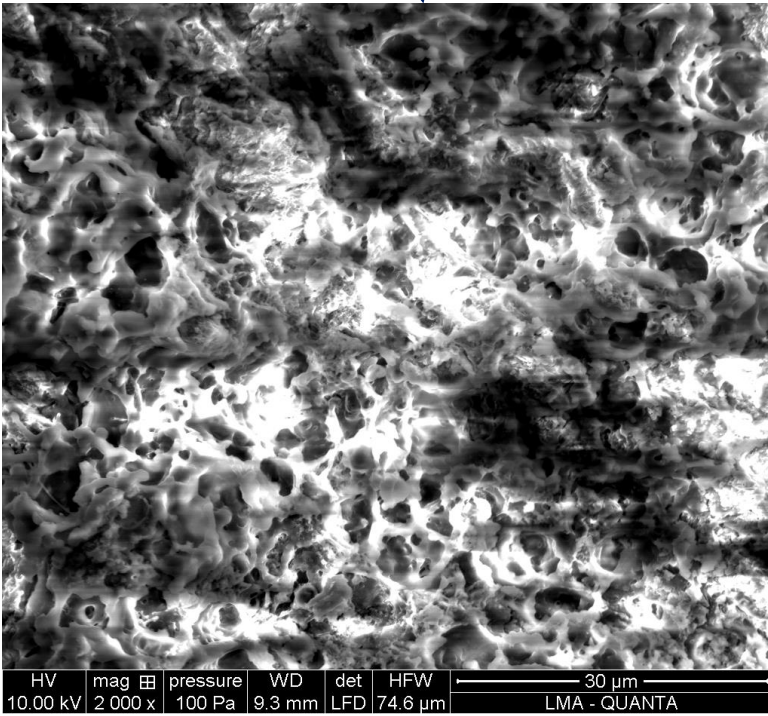
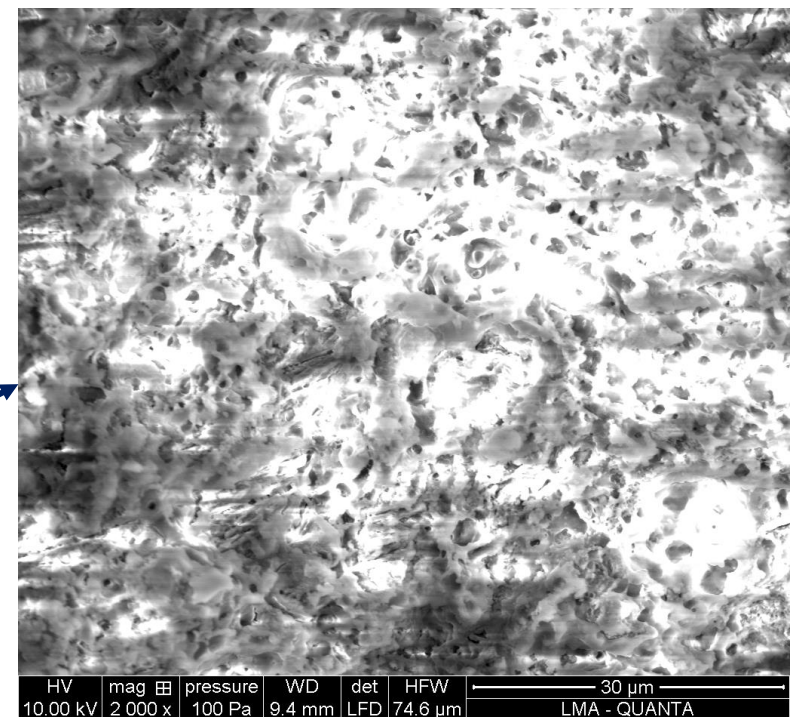
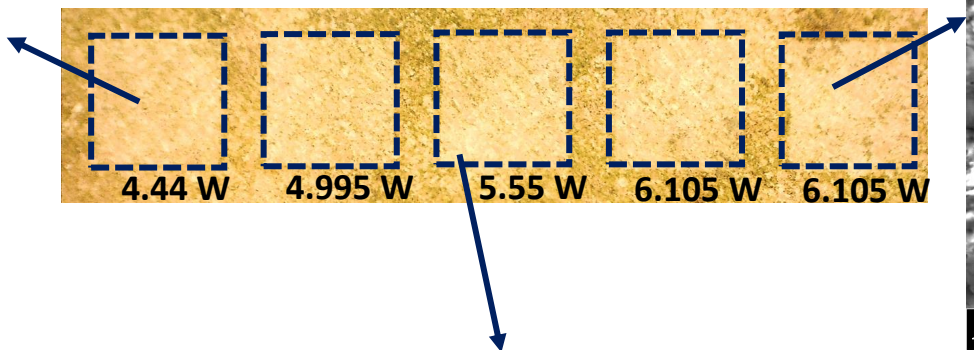
Tomography images from Confocal Microscopy correspond with the original laser treated and uncleaned area







200KHz (/20ppd), 15μm, 150mm/s, NL:1

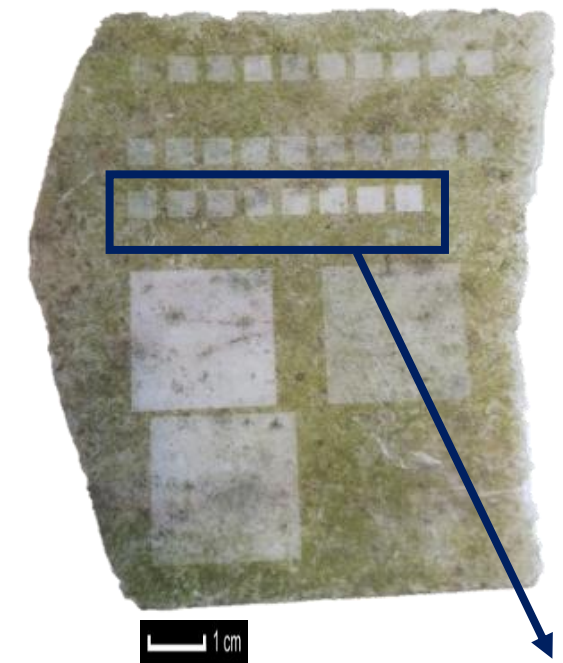


SEM images correspond with the original laser treated area





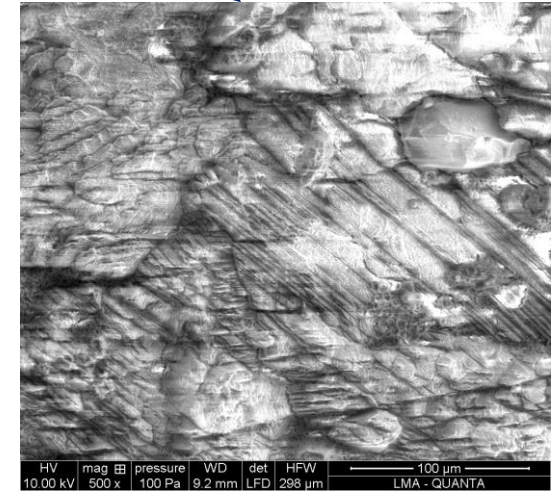
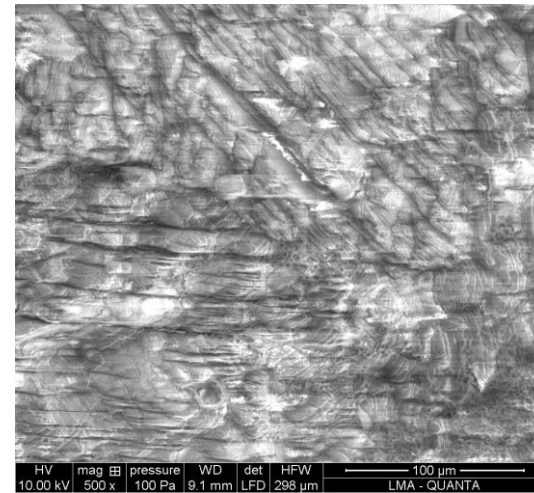
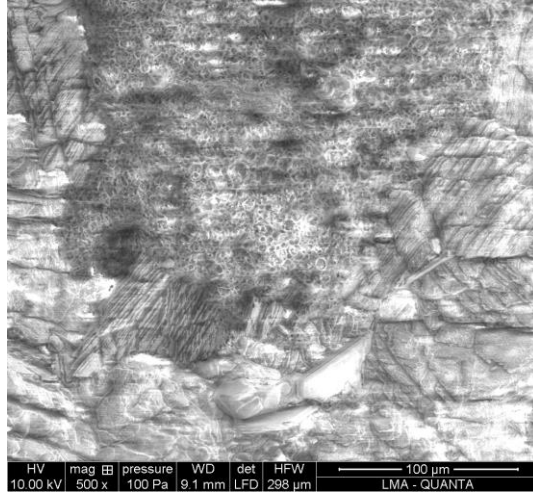
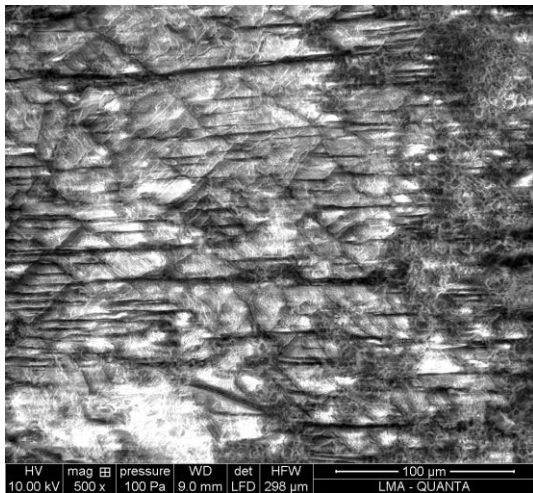
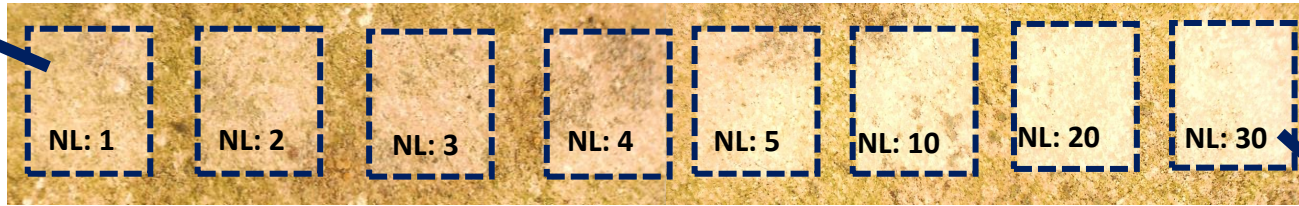
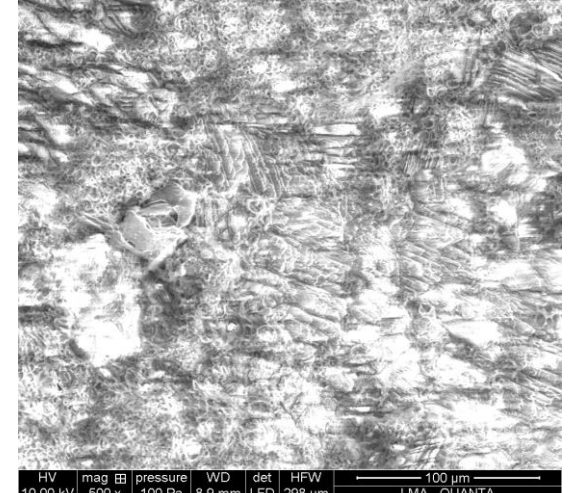
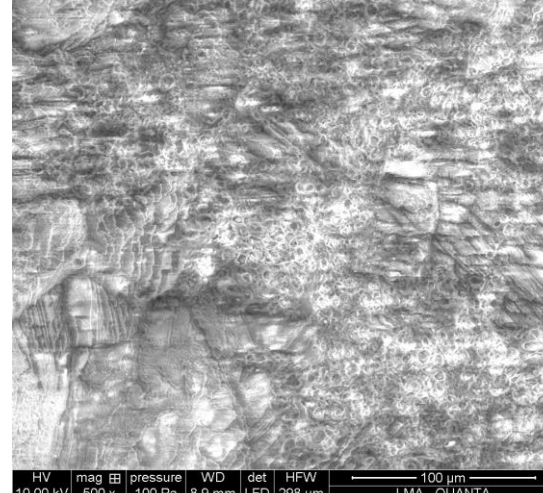
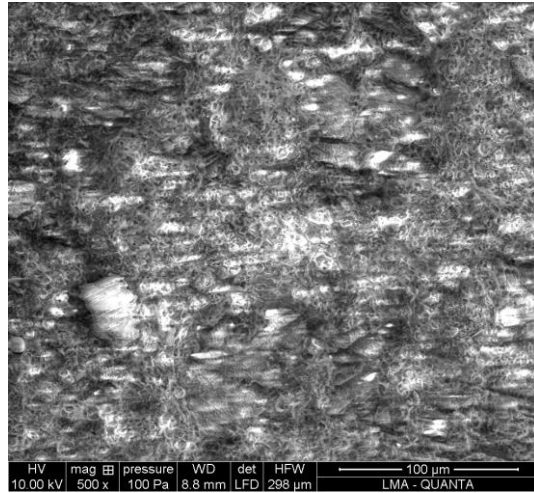
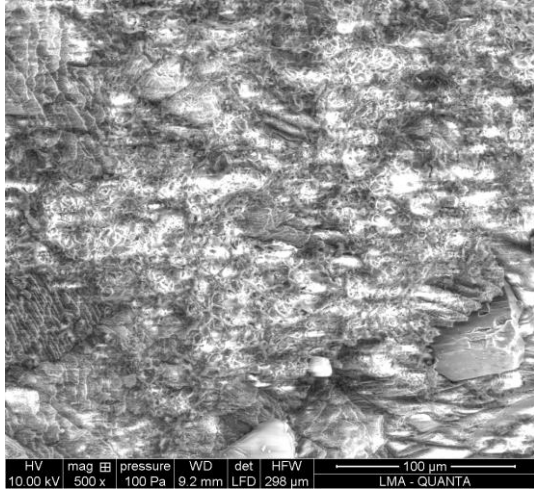
Laser type	$P_{max}$ (W)	$I$ (nm)	$t_p$ (fs)	$f_p$ (kHz)	$D_b$ ( $\mu\text{m}$ )	Mark speed (mm/s)	Spacing between lines ( $\mu\text{m}$ )
fs UV	11.1	343	238	200	30	150	15



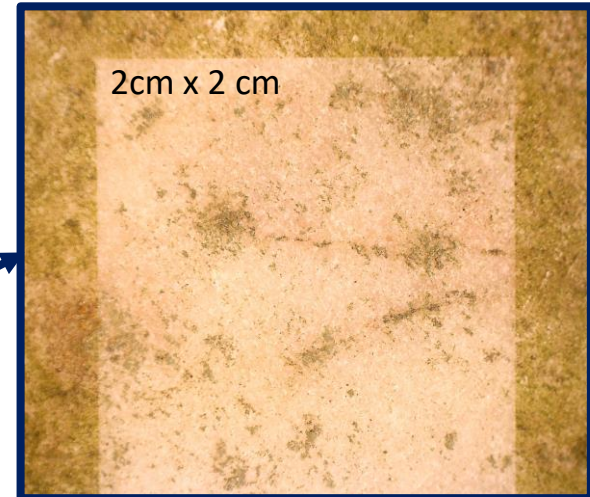
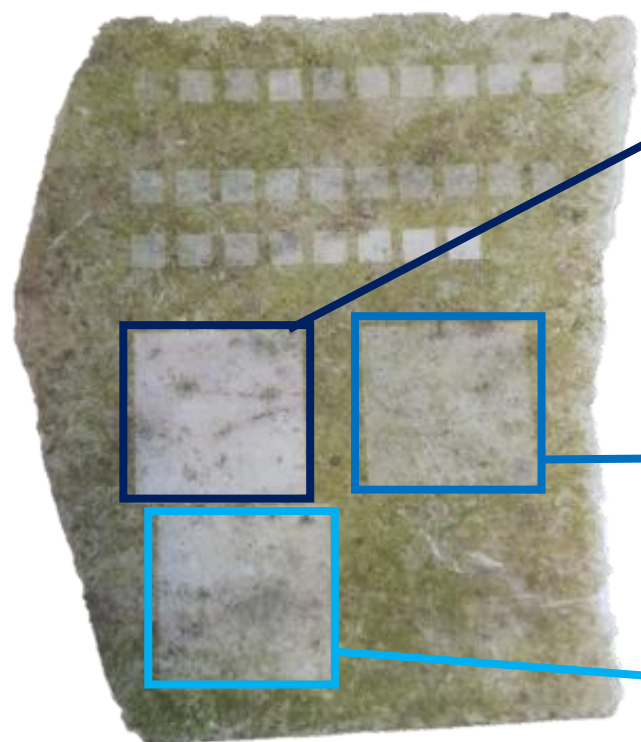
2.775W, 200KHz (/20ppd), 15 $\mu\text{m}$ , 150mm/s





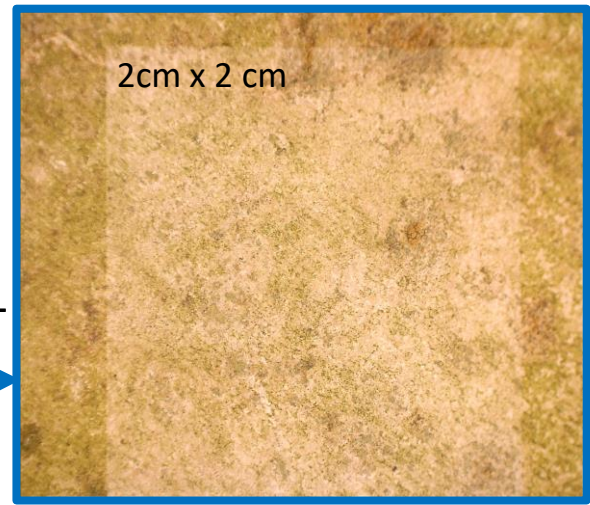






Fluence: 1.96 J/cm<sup>2</sup>  
Irradiance: 8247.525 GW/cm<sup>2</sup>

2.775W, 200KHz(/20ppd), 15μm, 150mm/s, 10 nL



Fluence: 1.96 J/cm<sup>2</sup>  
Irradiance: 8247.525 GW/cm<sup>2</sup>

2.775W, 200KHz(/10ppd), 30μm, 600mm/s, 10 nL

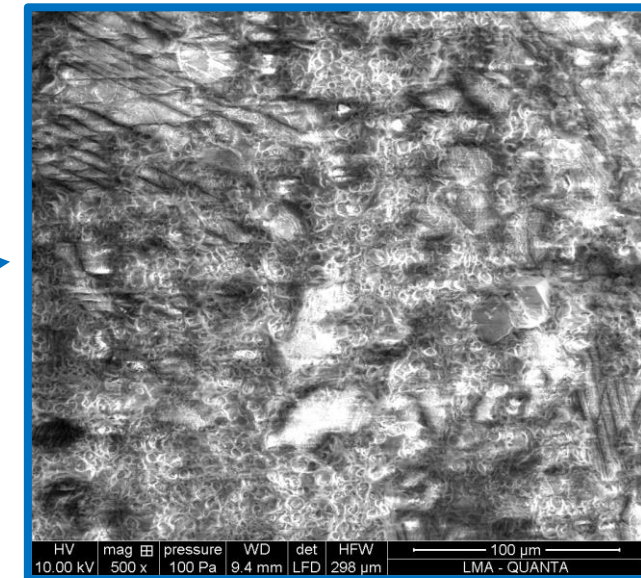
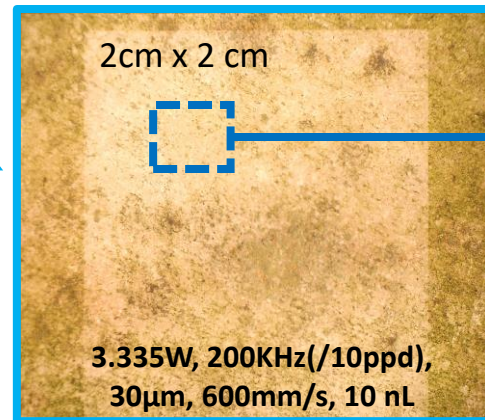
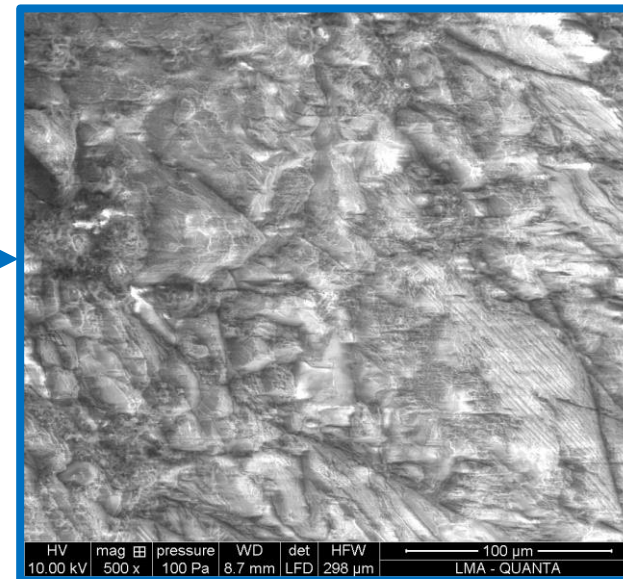
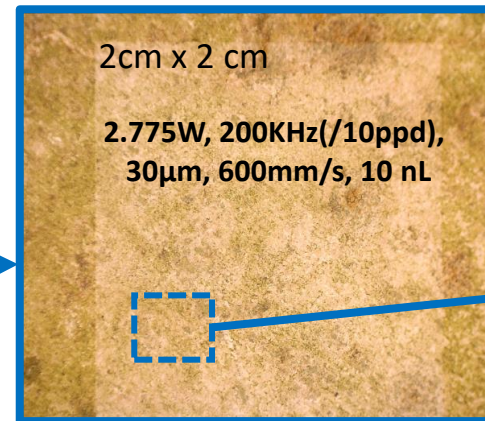
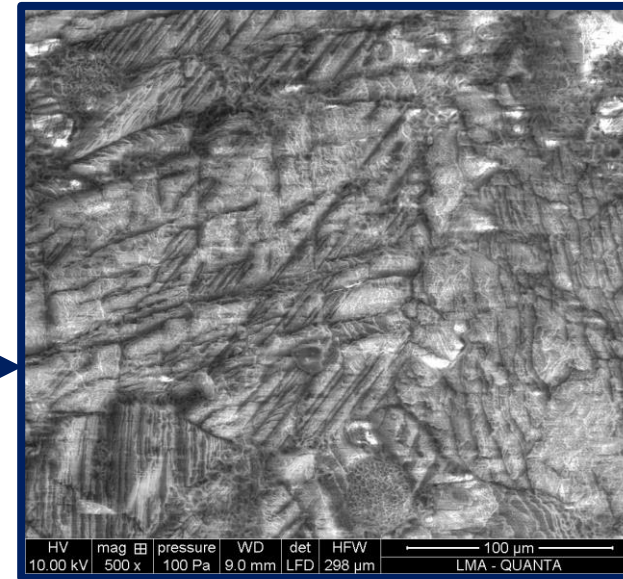
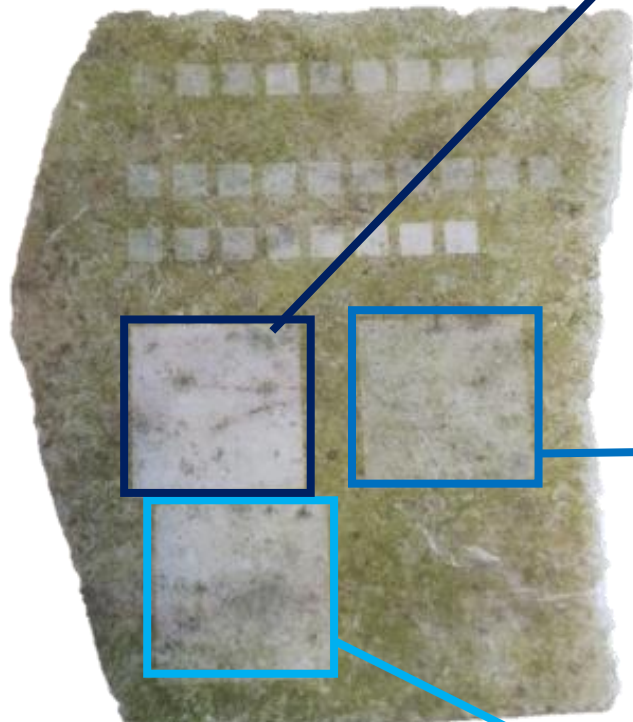


Fluence: 2.36 J/cm<sup>2</sup>  
Irradiance: 9897.030 GW/cm<sup>2</sup>

3.335W, 200KHz(/10ppd), 30μm, 600mm/s, 10 nL

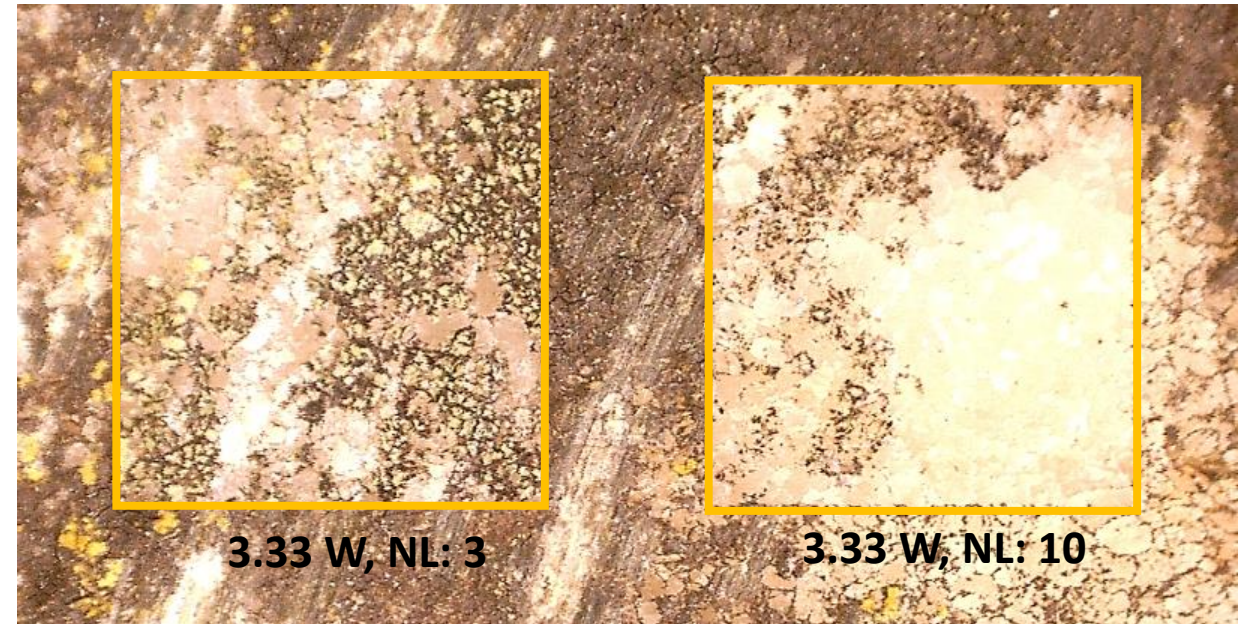
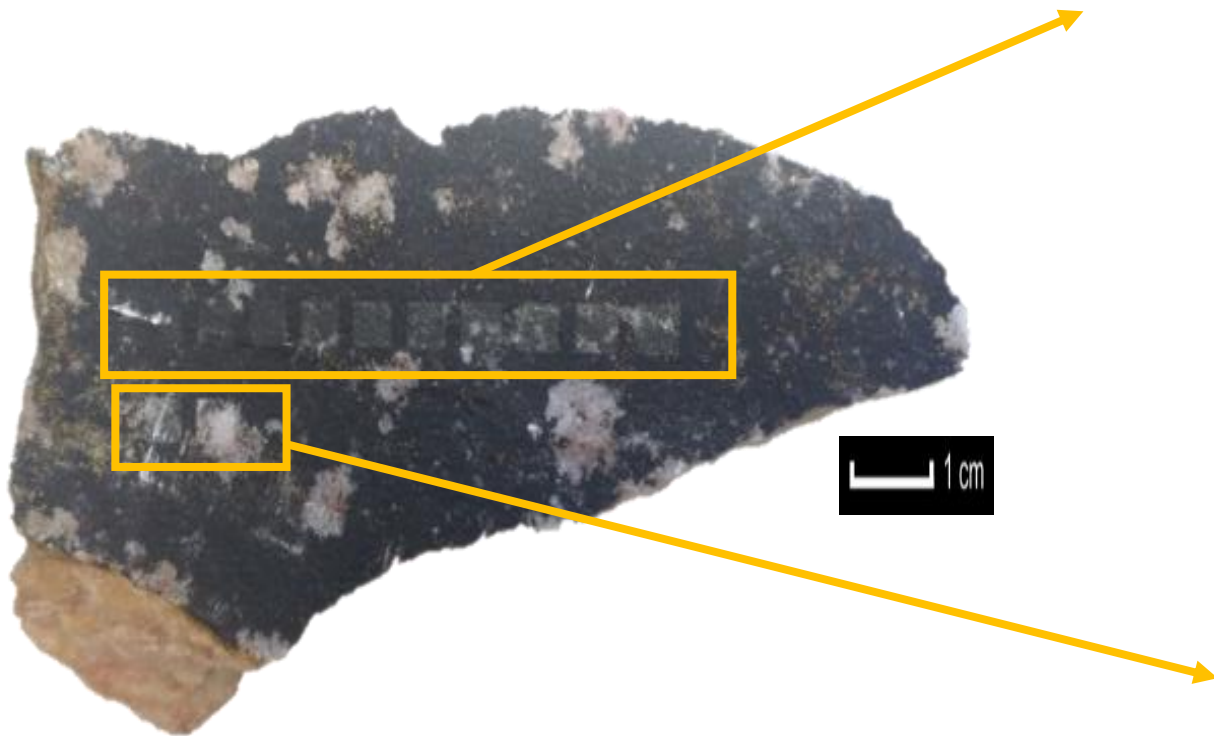
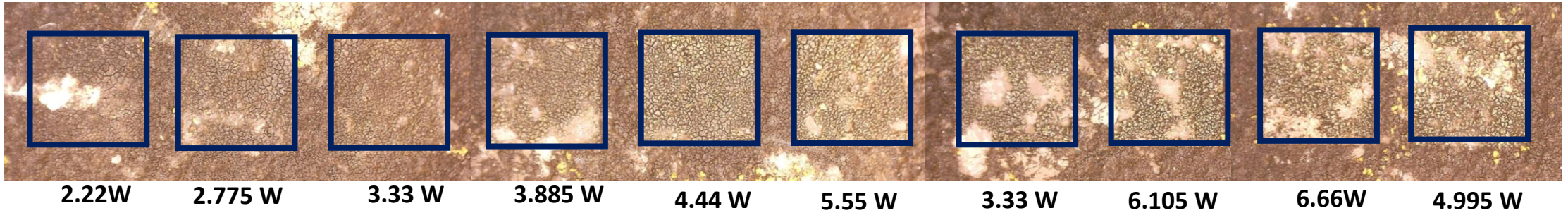
Laser type	P <sub>max</sub> (W)	λ (nm)	t <sub>p</sub> (fs)	f <sub>p</sub> (kHz)	D <sub>b</sub> (μm)	Mark speed (mm/s)	Spacing between lines (μm)
fs UV	11.1	343	238	200	30	150	15





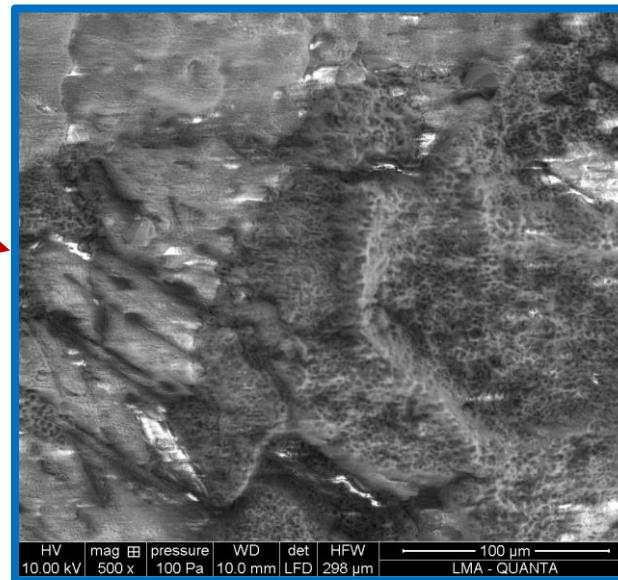
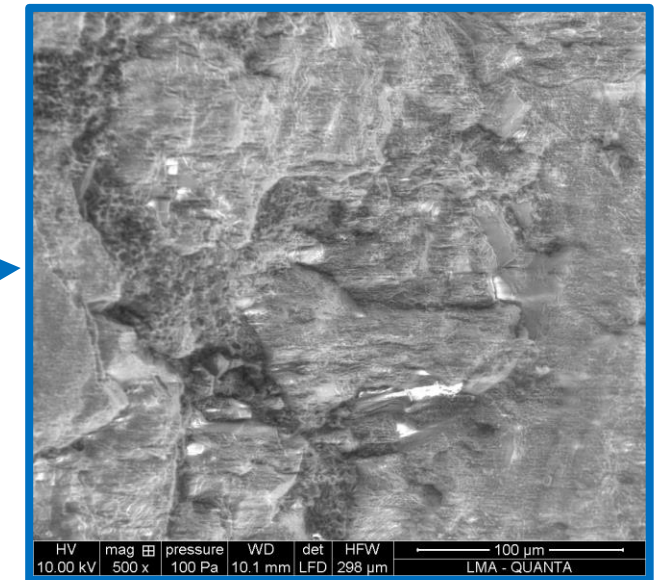
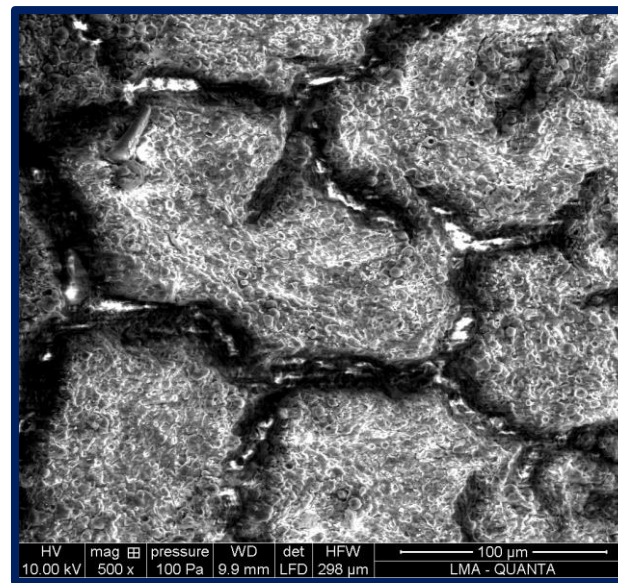
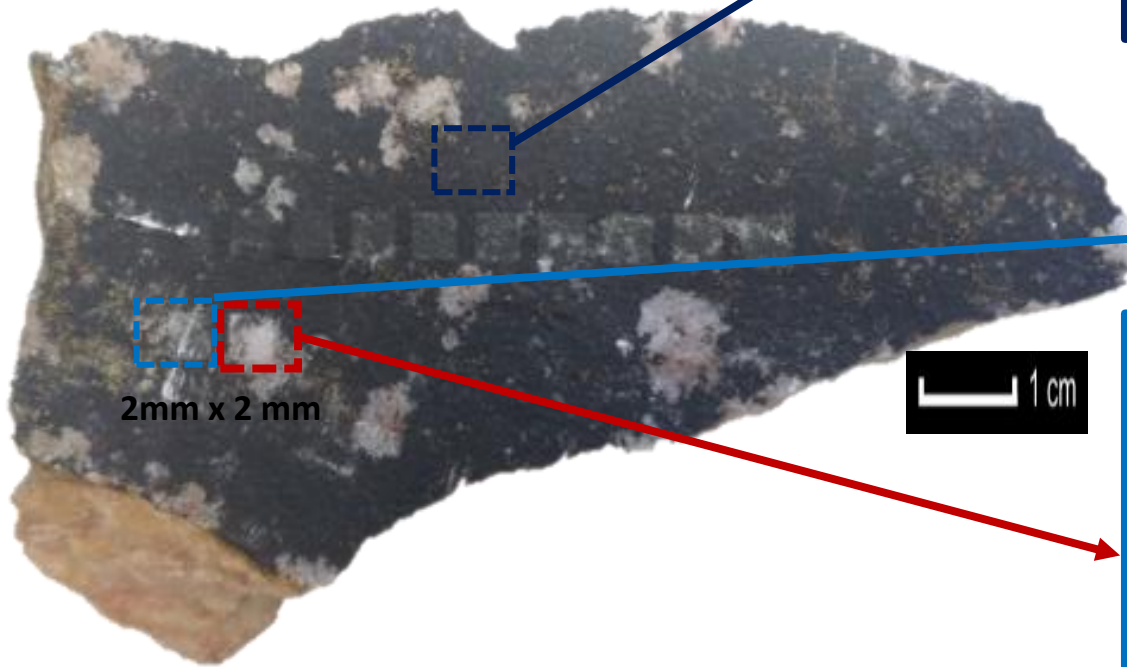
**SEM images correspond with  
the original laser treated area**



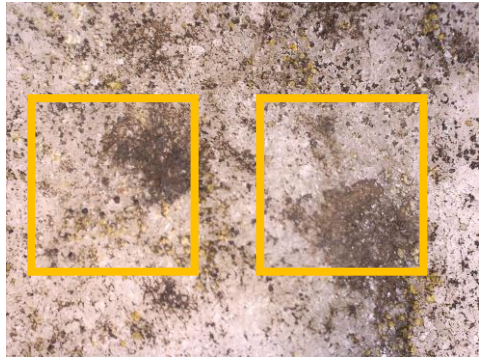




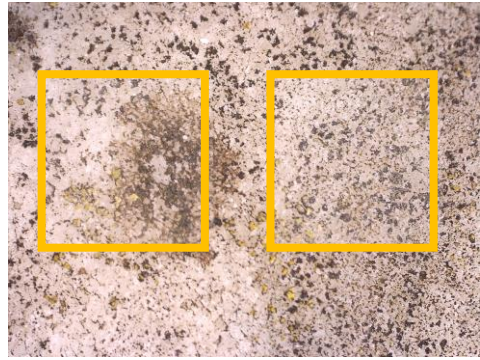
**SEM images correspond with the original area and laser treated area**



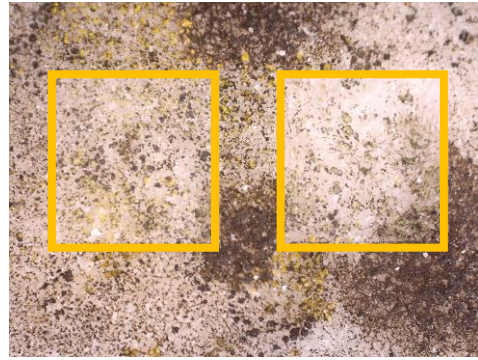




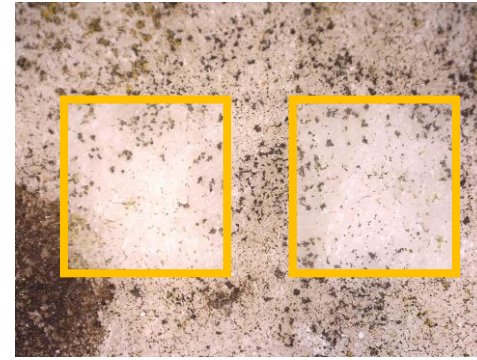
2.22W      2.775 W



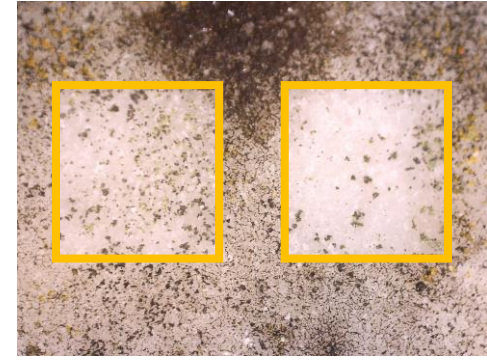
3.33 W      3.885 W



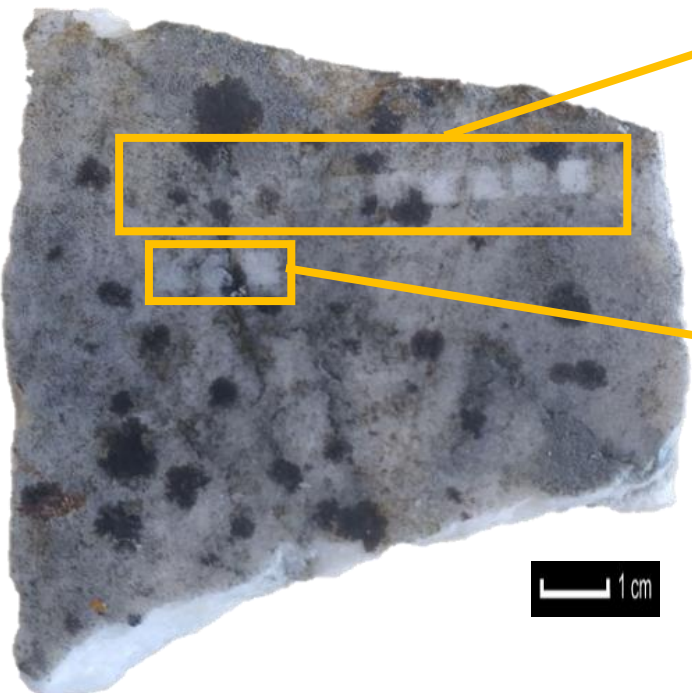
4.44 W      4.995 W



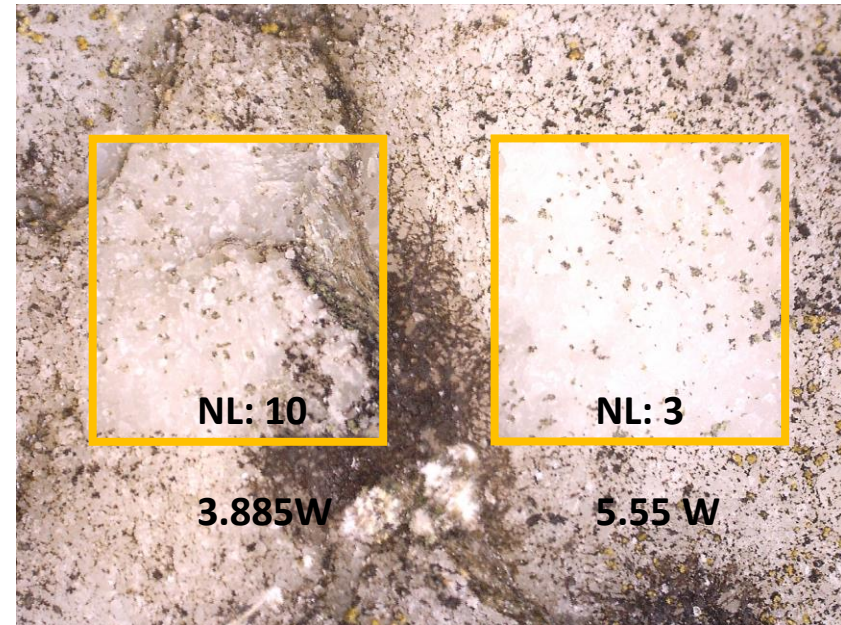
5.55 W      6.105 W



6.66W      7.215 W



200KHz(/20ppd), 15 $\mu$ m, 150mm/s, NL:1



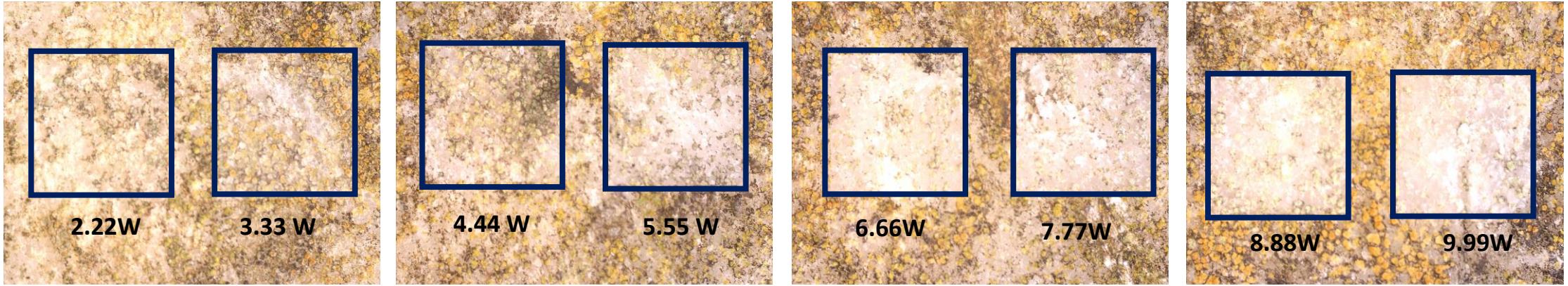
NL: 10

3.885W

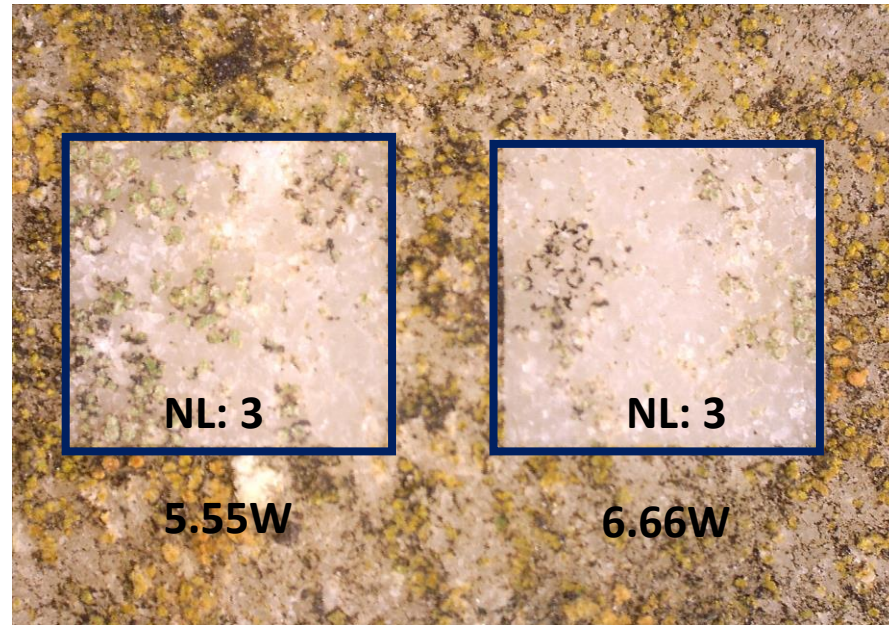
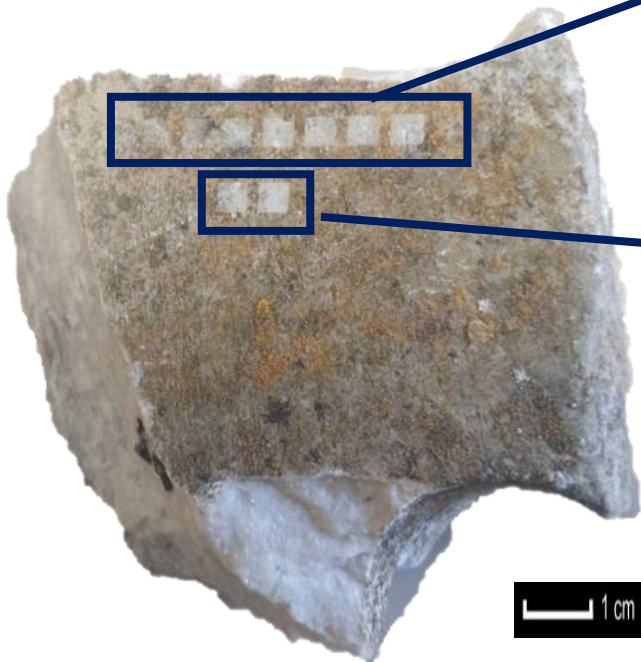
NL: 3

5.55 W





200KHz(/20ppd), 15 $\mu$ m, 150mm/s, NL: 1





# Acknowledgements

- I would like to offer my heartfelt sense of gratitude, reverence and sincerity to the supervisor of this project work, Prof. Dr. Luís Lopes, for selecting such an important topic, for providing the samples, scholarly guidance, research insight, expert suggestion, active engagement and tiresome efforts for the whole period of the project, which made my attempts successful.
- I also wish to thank all those directly or indirectly assisted in this project work.
- The Seminar III course work and the research project is a compulsory part and supported by H2020-MSCA-ITN-EJD/ED-ARCHMAT action under the Marie Skłodowska-Curie grant agreement, No 766311.
- The use of Servicio General de Apoyo a la Investigación and the National Facility ELECMI ICTS, node "Laboratorio de Microscopías Avanzadas" at the University of Zaragoza is acknowledged.



**Discussions..**

**Q. & A.**



**Keeping the Lights on:**

**Yesterday,  
Today &  
Tomorrow...**

[ashiqur@unizar.es](mailto:ashiqur@unizar.es)