University of Modena and Reggio Emilia

XXIV. ICORS Jena 2014

XXIV. INTERNATIONAL CONFERENCE ON RAMAN SPECTROSCOPY

Study of *Black Core*, ceramic tile's defect, by a multi-technique approach

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Overview

1. What is the "*Black Core*" defect?

1.1. Technological evolution

Production technology in constant evolution

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Changes in forming, decoration and firing processes

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Organic additives addition | **Faster firing processes**

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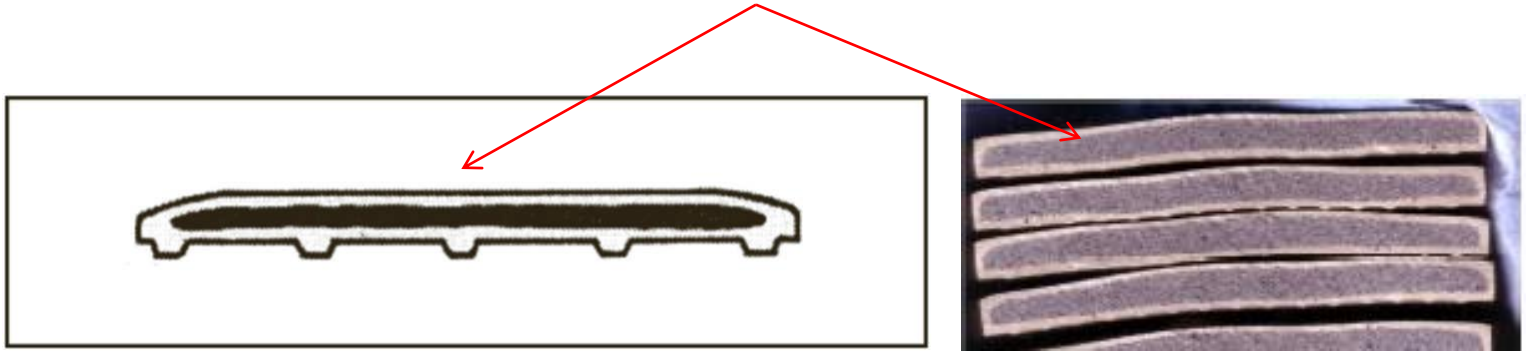
Higher probability of technological and esthetical defects



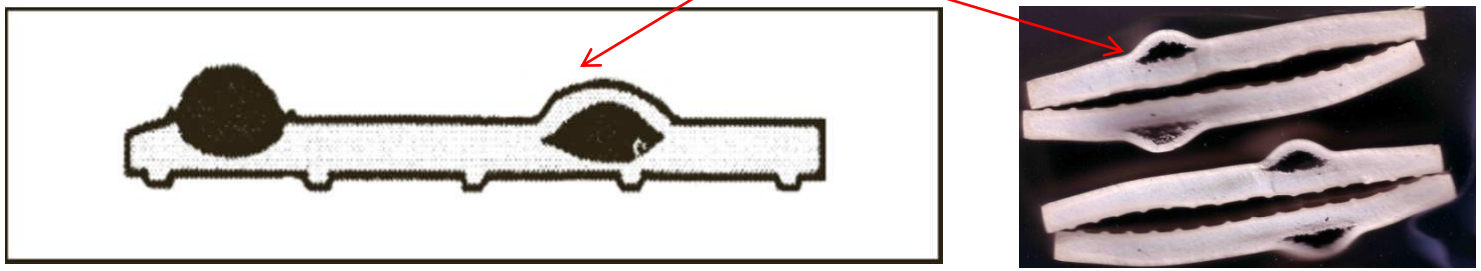
1. What is the "*Black Core*" defect?

1.2. Black Core appearance

A darker area inside the tile



Swellings and bubbles



1. What is the "*Black Core*" defect?

1.3. Causes of formation

Hypotheses on its nature and causes of formation:

- **High Carbon and Iron minerals content**

- **Extra-fine granulometry**
- **Too high forming pressures**

Low permeability to gases

2. Aims of the research

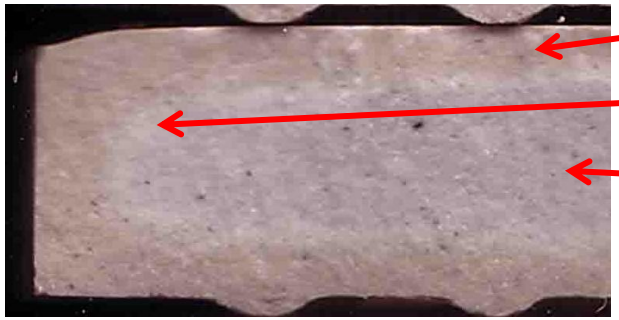
- Identification of reduced species

***Fe** Oxides (**Magnetite** and/or **Wüstite**)*
Fe_3O_4 ***FeO***

- Deeper understanding of reactions
- Technological parameters influence on *Black Core* formation

Technological solutions to minimize/remove the *Black Core* defect

3. Analytical Techniques



a. XRF *(chromophore elements)*

No significant difference in elements content

b. XRPD *(crystalline byproducts)*

No trace of new crystalline phases in *Black Core*

c. SEM-EDS *(morphological data)*

Higher porosity of *Black Core* than healthy ceramic body

d. FTIR (*residual organic compounds?)*

No trace of residual organic compounds

e. Mössbauer Spectroscopy *(oxidation state of Fe)*

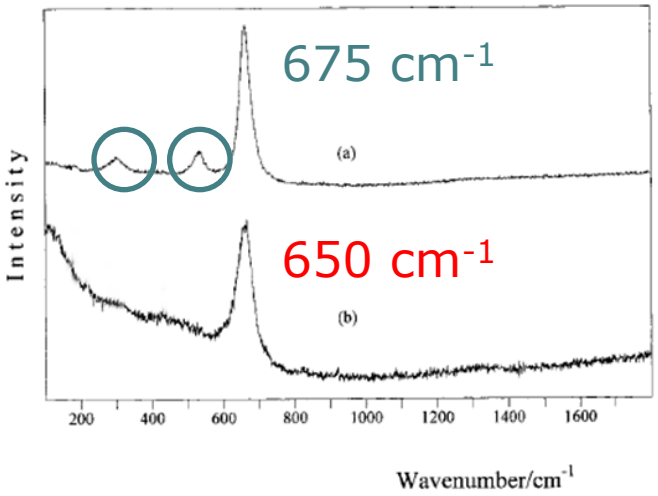
Too low quantity of Fe Oxides inside ceramic body

3. Analytical Techniques

3.1. Raman Spectroscopy for Fe Oxides

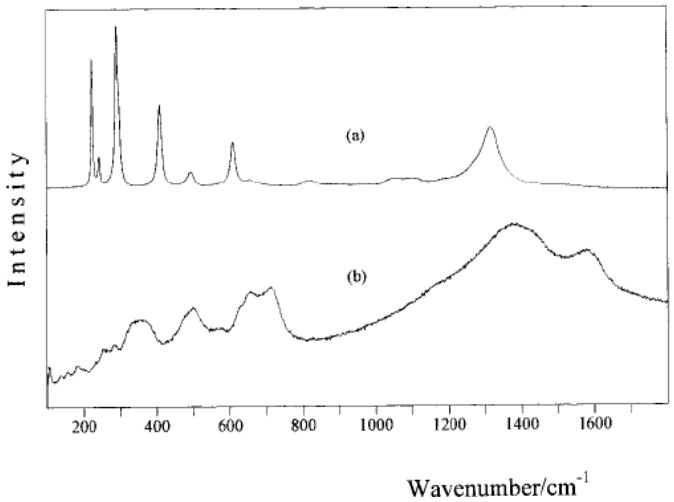
Fe(II) *Oxides*
*(**Magnetite** and/or **Wüstite**)*

Fe_3O_4



Top: Magnetite (Fe_3O_4)
Bottom: Wüstite (FeO)

FeO



Top: Hematite (α-Fe_2O_3)
Bottom: Maghemite (γ-Fe_2O_3)

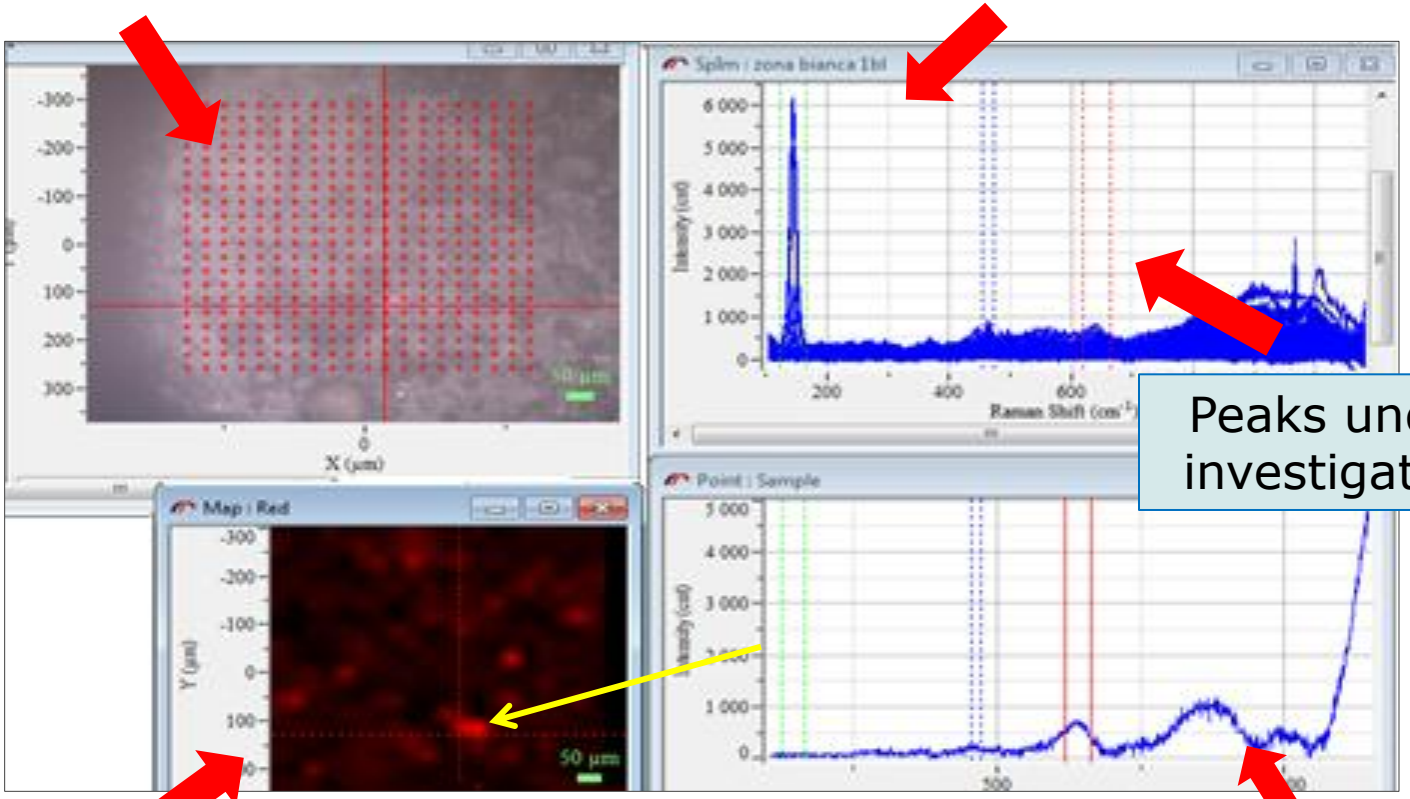
References:
D. L. A. de Faria,S. Venaüncio Silva and M. T. de Oliveira, Journal of Raman Spectroscopy, vol. 28, 873-878 (1997)
R. J. Thibeau, C. W. Brown and R. H. Heidersbach, Appl. Spectrosc . 32, 532 (1978)

3. Analytical Techniques

3.2. Raman Mapping

Selected mapping area

Sequence of spectra



Peaks under investigation

LabSpec v5.0 software

False-colour image

Punctual spectrum

4. Results

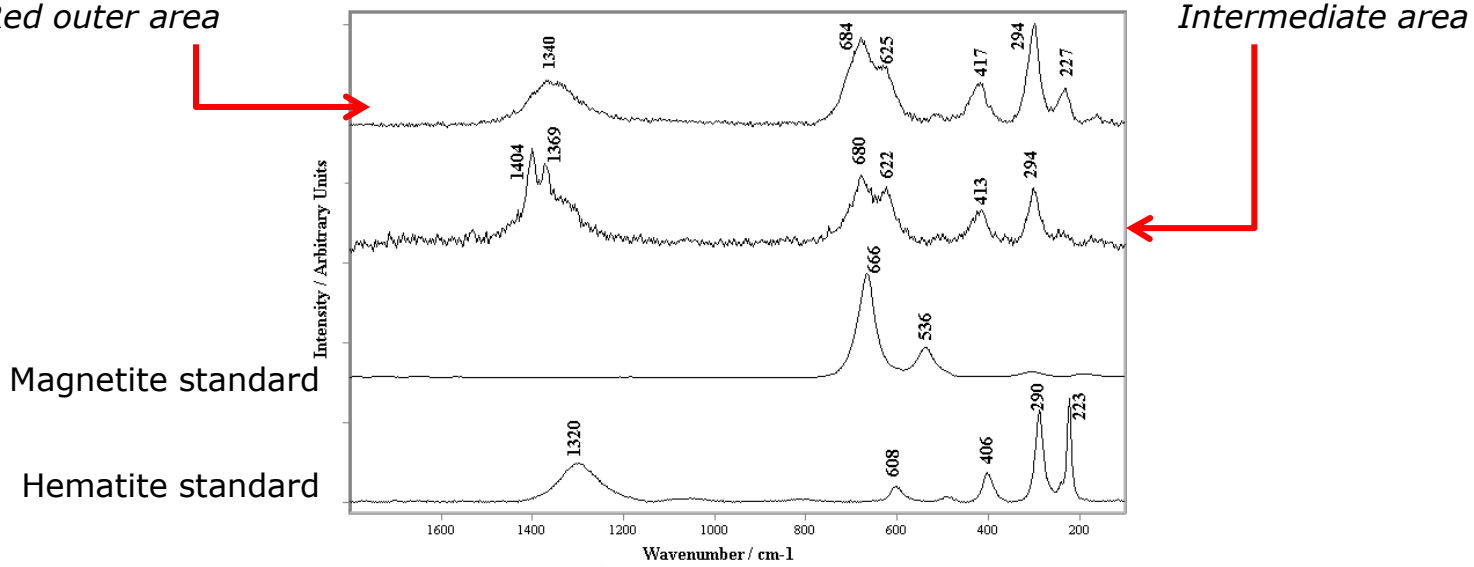
4.1. Raman punctual analysis

Fe Oxides
in ***Outer and Intermediate*** areas:

Hematite (Fe_2O_3)
Magnetite (Fe_3O_4)

Red outer area

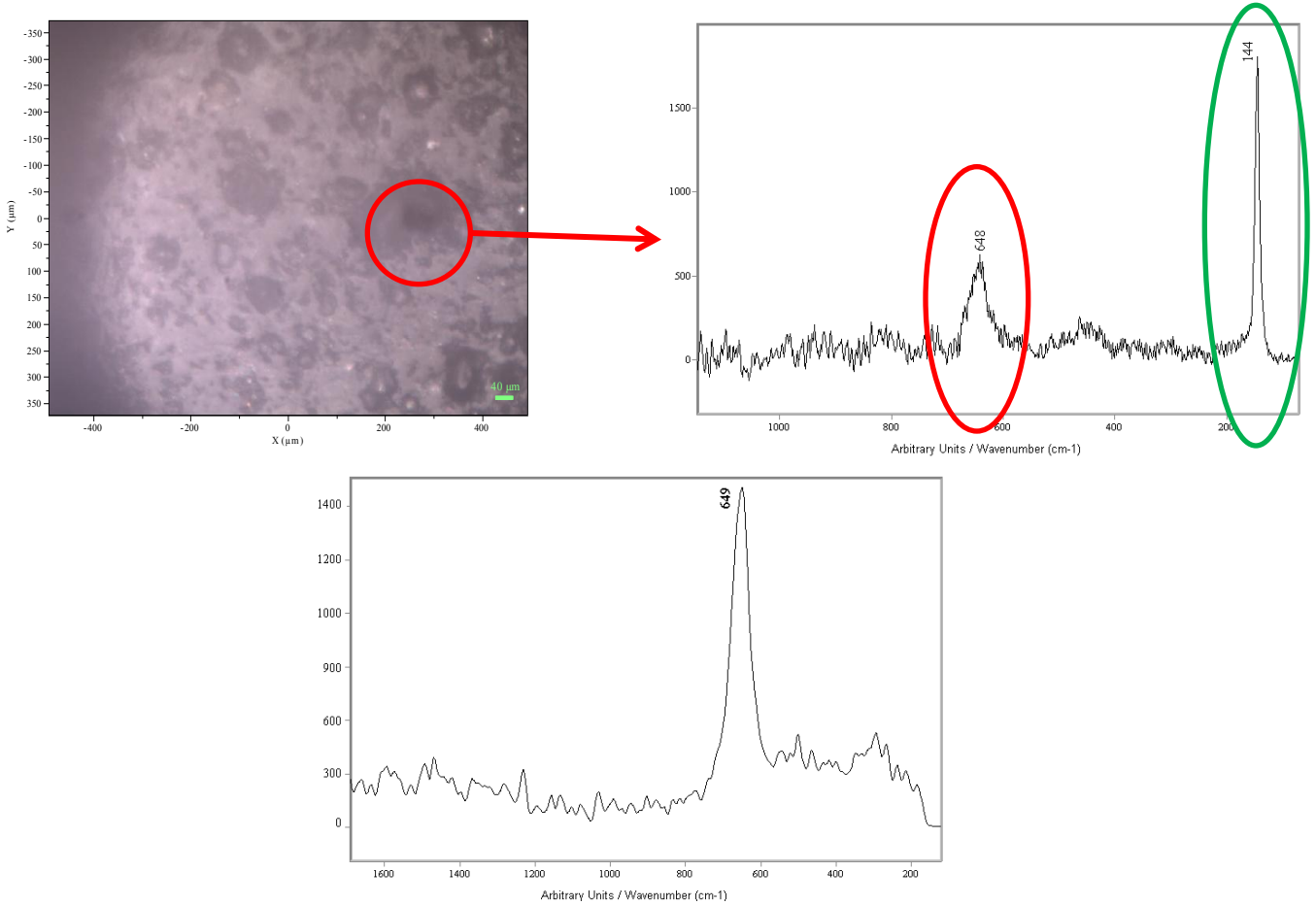
Intermediate area



4. Results

4.1. Raman punctual analysis

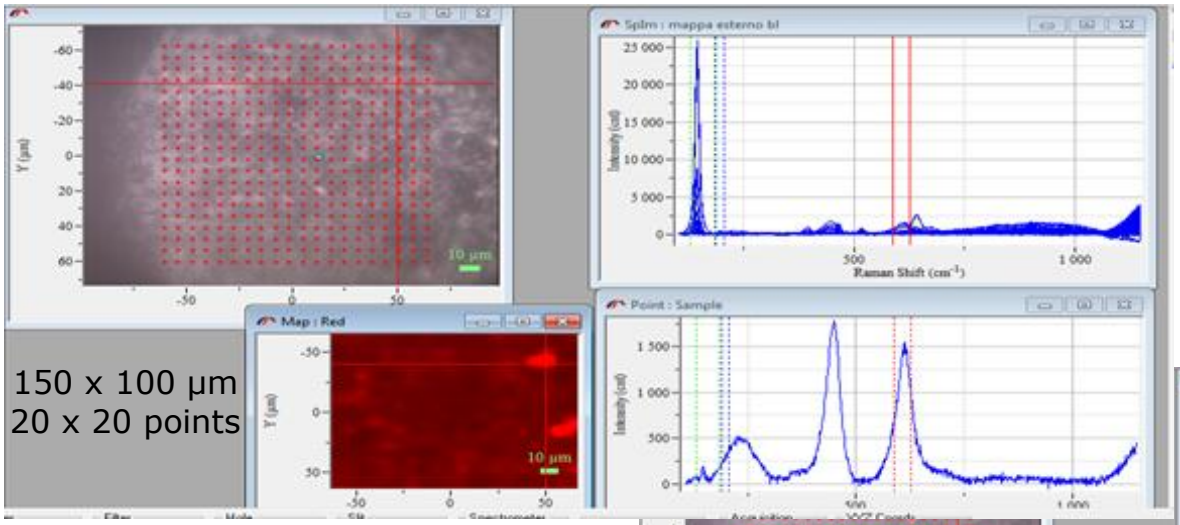
Fe Oxides in ***Black Core*** area: **Wüstite (FeO)**



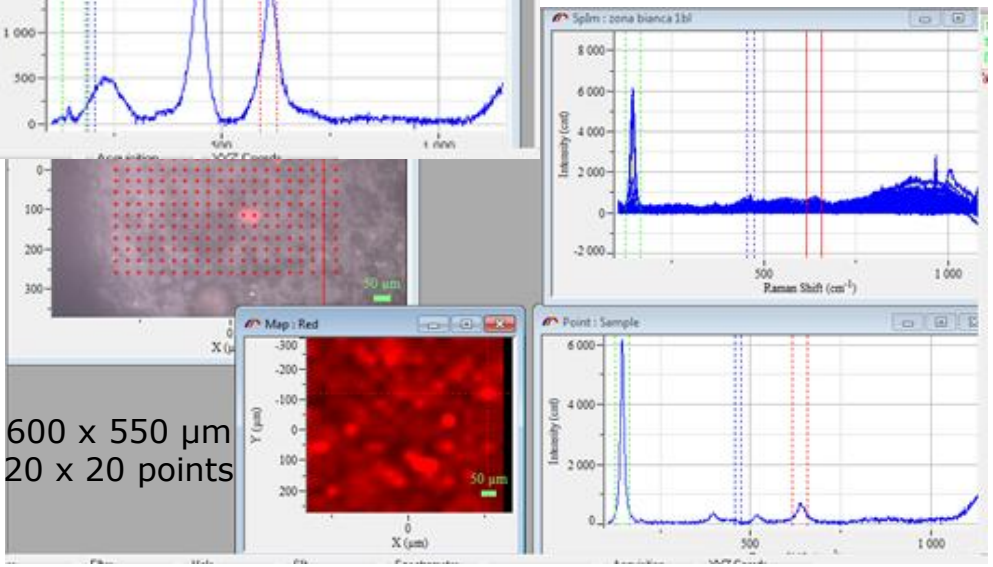
4. Results

4.2. Raman Mapping analysis

Outer and Intermediate areas maps: no Wüstite



Outer area

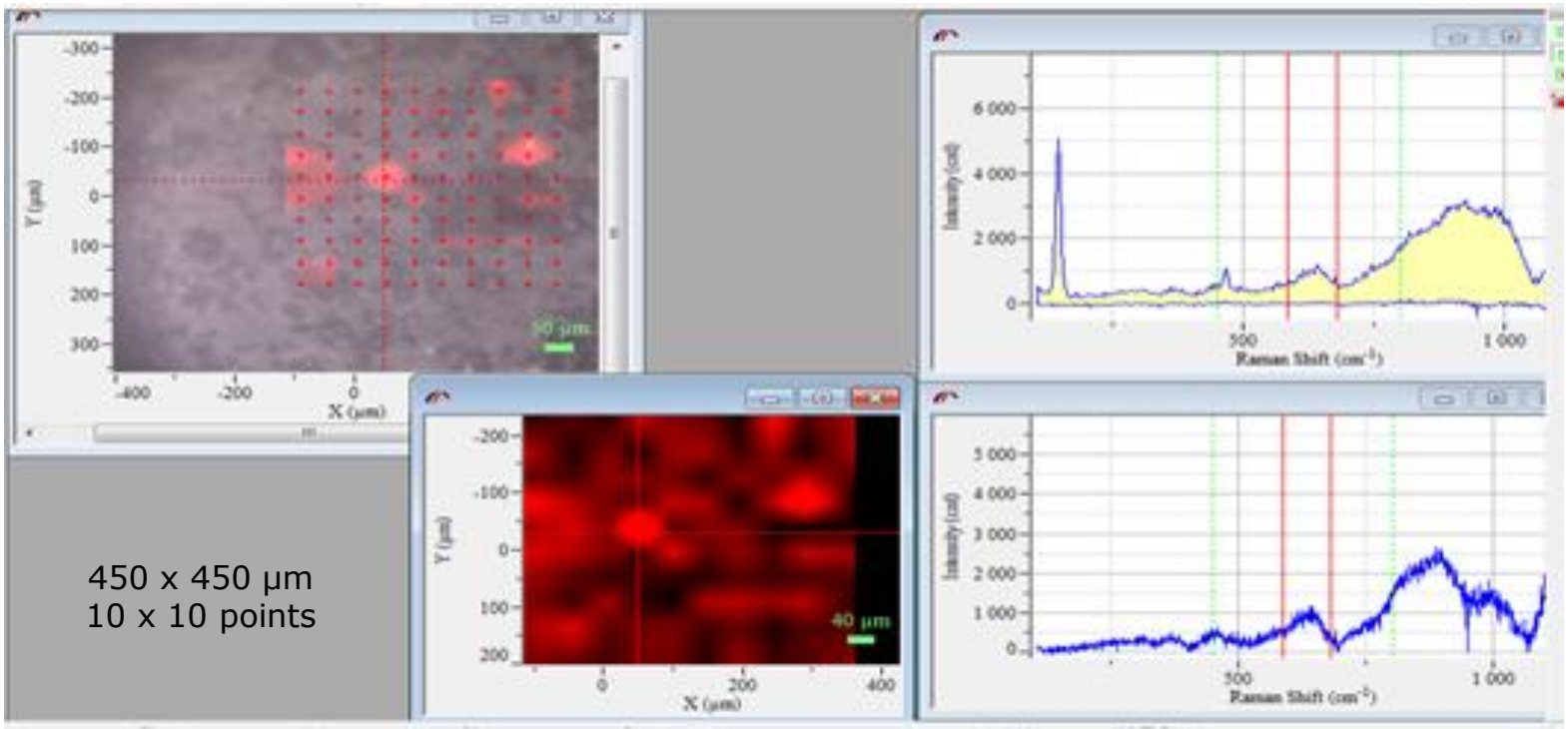


Intermediate area

4. Results

4.2. Raman Mapping analysis

Black Core



Peak around 650 cm^{-1} = **Wüstite (FeO)**

5. Conclusions

- Different *Iron Oxides* in *Black Core* *(Wüstite)* and healthy ceramic body *(Hematite and Magnetite)*
- Hypotheses on *Black Core* formation processes are confirmed once more
- Raman mapping is a good method for a better understanding of *Black Core* nature
- Deeper studies are necessary to reveal *Black Core* composition and formation processes

Thank you for your attention