Micro/nano structures and color tones of hematite particles for heat-resistant bright red pigments:

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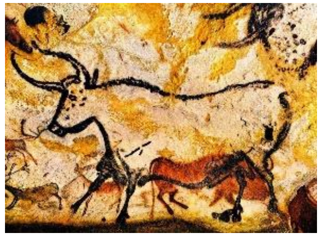
26th of August 2022

M1 Internship- from 2022/04/15 to 2022/08/31

Introduction

Chauvet caves



Lascaux caves

Bizen pottery

Fukiya village

- Hematite exists and is used since ages:
  - Paleolithic, France, red pigment
  - Antiquity, cosmetics
  - VIII, Japan, BIZEN wares
  - XVIII-XX century, JAPAN, Fukiya village, red color of walls.
- Hematite, α-Fe_2O_3, red pigment, rhombohedral.
- The color of hematite is due to O_{2p}=>Fe_{3d} charge transfer and 3d-3d transition of Fe^{3+} cation.

- Aim of my research: get brighter hematite pigments, find the better synthesis method, influence of features on the color, application as paintings.

Outline

- Experimental part
- Results and analysis
    - Al addition
    - Si addition
    - Application into painting
- Conclusion
- Bibliography

Experimental part:

- Precipitation method *(explained by Suga KEIJIRO)*

P-CNF ultrasonic bath → 10 min → Mix with Fe solution and other element solution → Stirred 1 h → Add diluted ammonium solution → Stirred 1 day → Centriugations and dry machine → 1 day → Furnace (800 °C /1000°C)

P-CNF: Phosphor-Cellulose NanoFiber

- *Aluminum:*

$AlCl_3.6H_2O$ – 0,01M

- *Silicon:*

Si diluted into NaOH – 0,01 M

Different volumes added to solution

Until pH reach 10

3 centrifugations at 500 rpm
1 centrifugation at 2000 rpm

Experimental part

- Ultrasonic spray pyrolysis (USP) *(explained by Sachika AKASE)*

Used to generate sperical particles.

The device generates ultrasonic waves which produce droplets. They are sprayed through the device and when they are in the heating furnace, the solvent evaporates to form spherical particles.

Issue: only two compositions could have been produced, because the device broke.

Mixing of Al and Fe solution $\xrightarrow{\text{pH 4}}$ Addition of Ammonia solution → USP experimentation → Furnace 800°C

→ *$Fe(NO_3)_3.9H_2O$*
→ *$Al(NO_3)_3.9H_2O$*

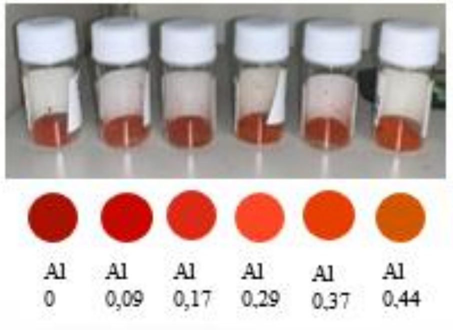
→ *Over 3 hours*

Results and analysis

- Addition of Al

Influence of composition and temperature

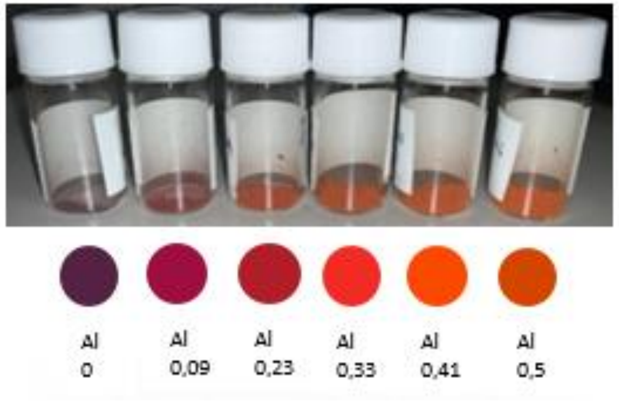
800°C



XRF:

Composition of Al	0	0,09	0,17	0,23	0,29	0,33	0,37	0,41	0,44	0,47	0,5
Atomic fraction of Fe (%)	100	99,91	86,10	78,11	76,78	71,02	74,55	67,67	68,54	60,00	56,52
Atomic fraction of Al (%)	0	11,45	13,90	21,89	23,22	28,98	25,45	32,33	31,46	40,00	43,48

1000°C



XRF:

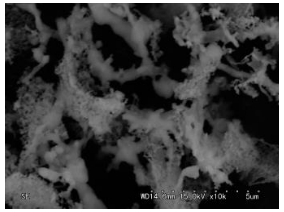
Composition of Al	0,09	0,23	0,33	0,41	0,5
Atomic fraction of Fe (%)	93,5	83,0	76,2	70,7	65,7
Atomic fraction of Al (%)	06,5	17,0	23,8	29,3	34,3

Results and analysis

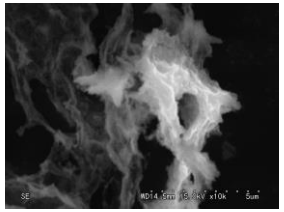
- Addition of Al

800°C

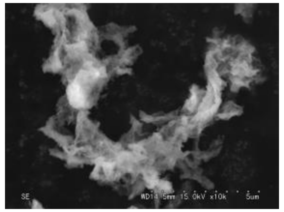
Al 0



Al 0,29

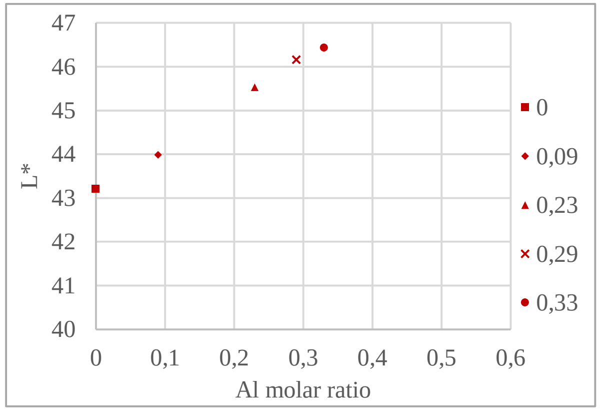


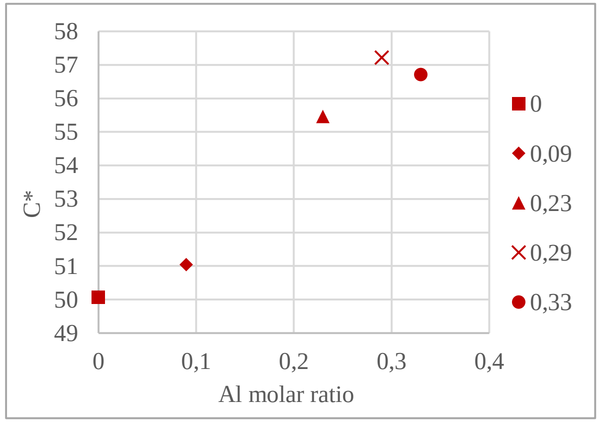
Al 0,44



SEM pictures:

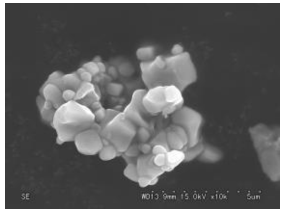
Spectrophotometer:



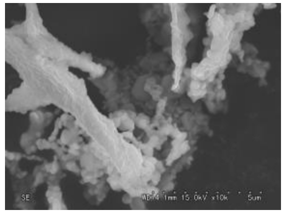


1000°C

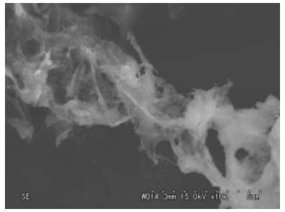
Al 0



Al 0,09

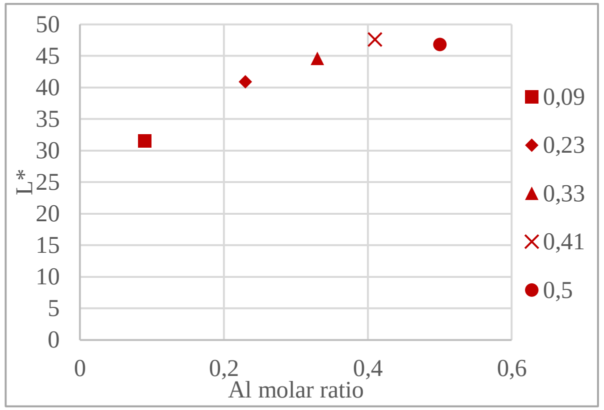


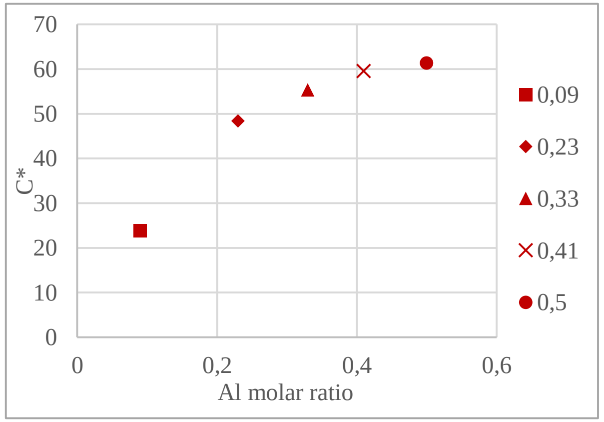
Al 0,41



SEM pictures:

Spectrophotometer:



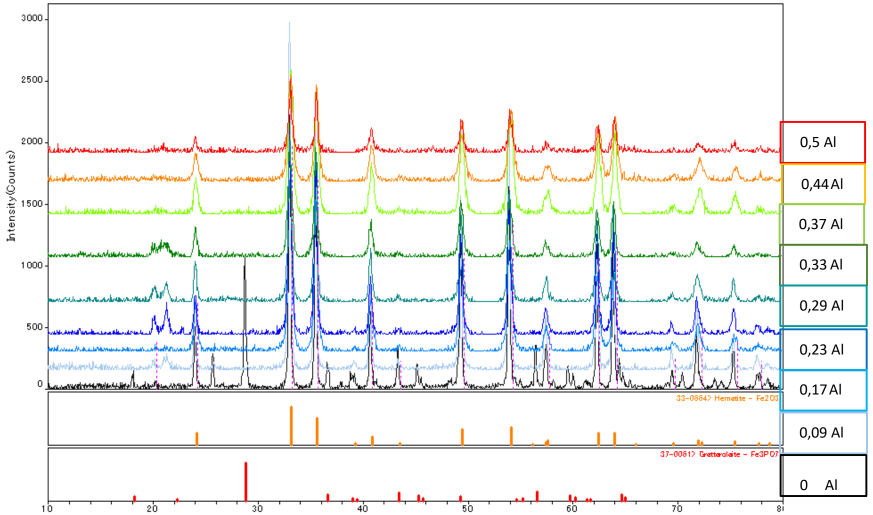


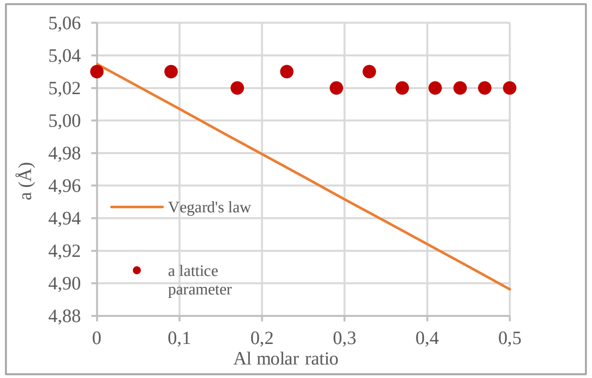
Results and analysis

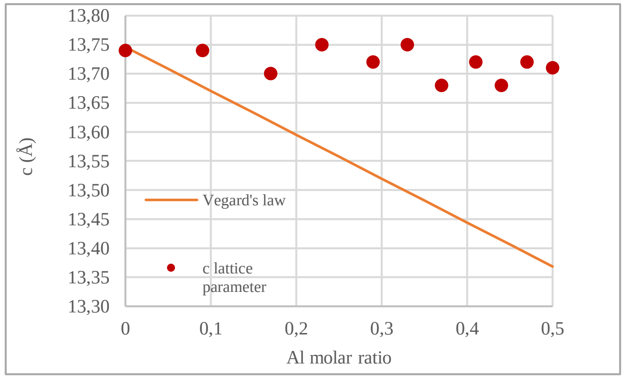
- Addition of Al

800°C

XRD:

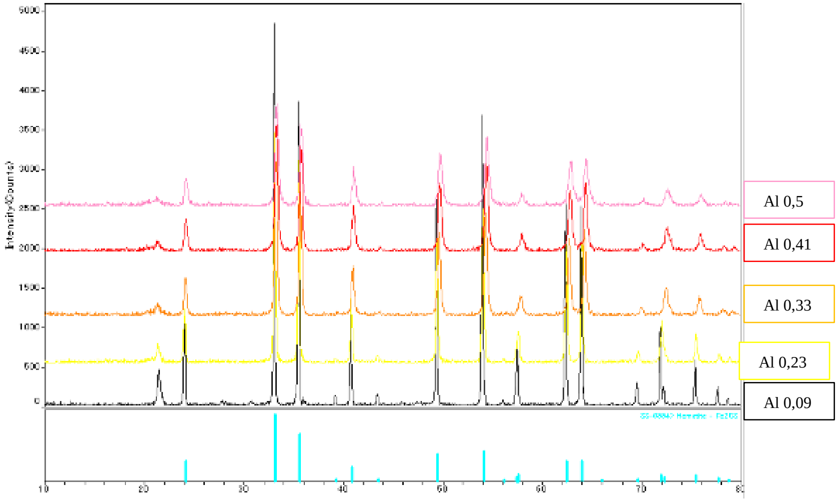


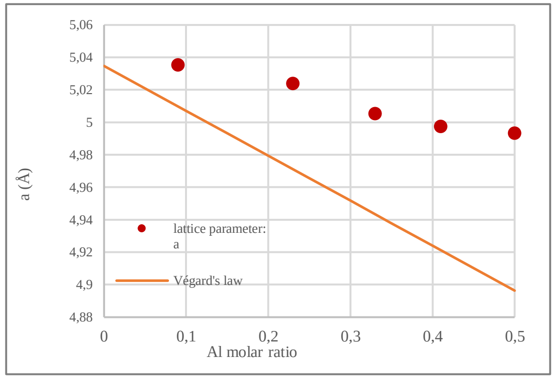


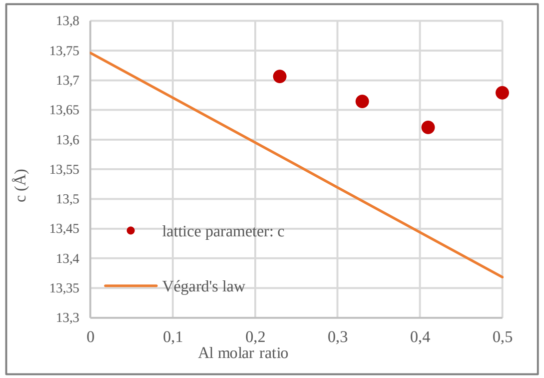


1000°C

XRD:



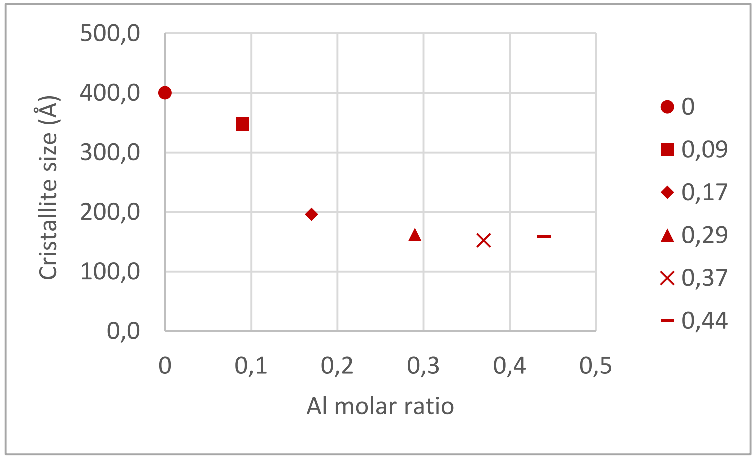




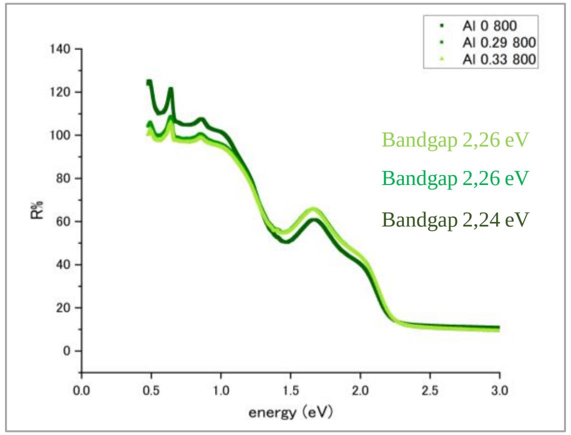
Results and analysis

- Addition of Al

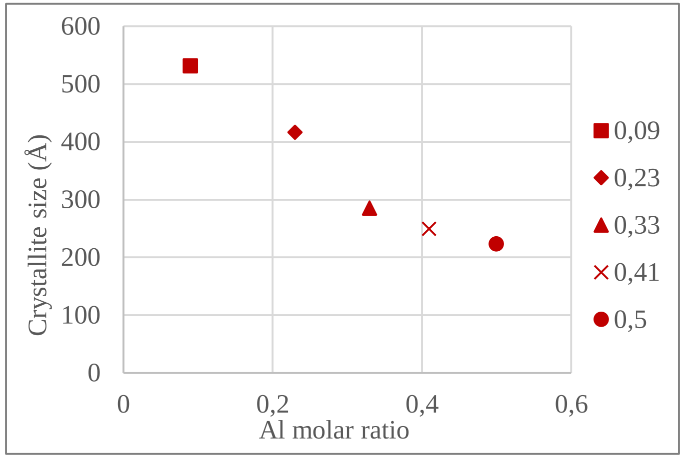
800°C



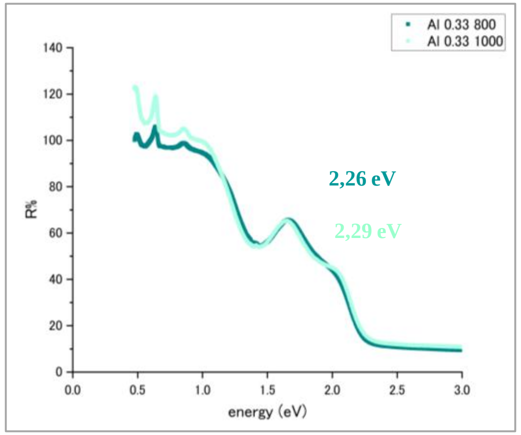
Optical reflectance



1000°C



Optical reflectance



Results and analysis

- Addition of Al

Influence of shape: *USP method*

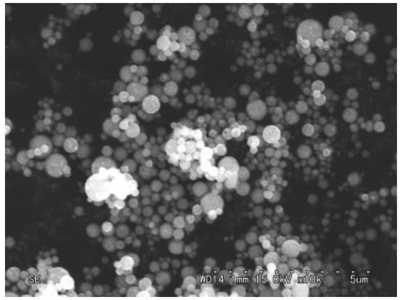
Al 0,33

Al 0,29

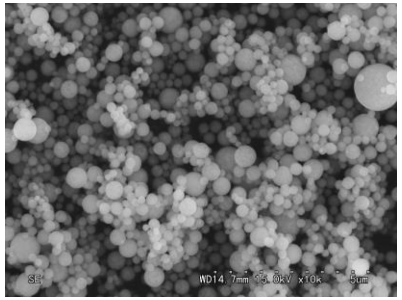
XRF:

Composition of Al	0,29	0,33
Atomic ratio of Fe	0,77	0,73
Atomic reratio of Fe	0,23	0,27

Al 0,29



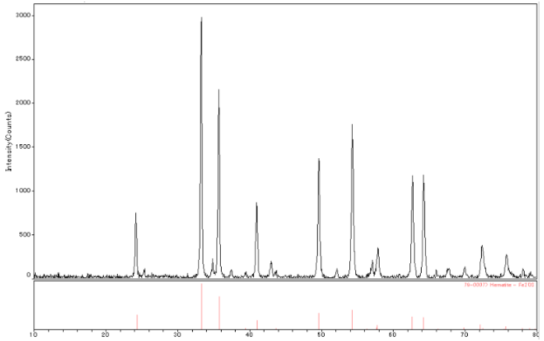
Al 0,33

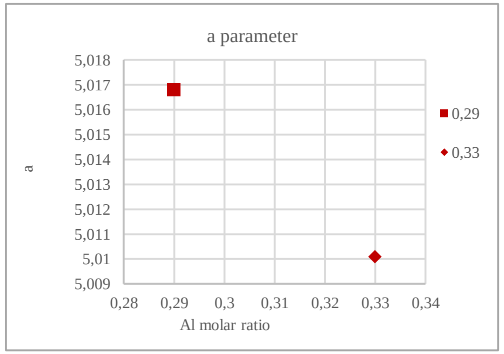


SEM pictures:

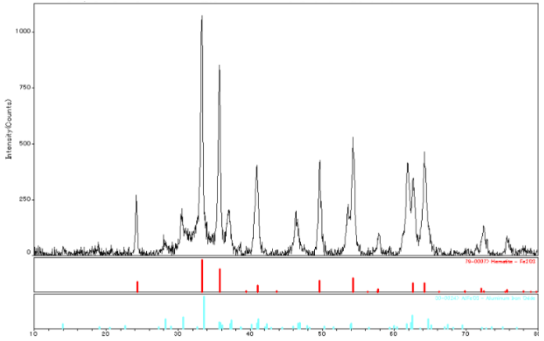
XRD:

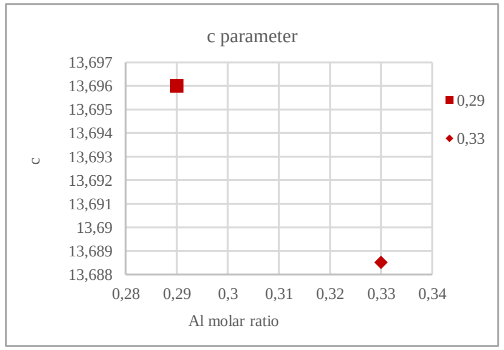
Al 0,29





Al 0,33





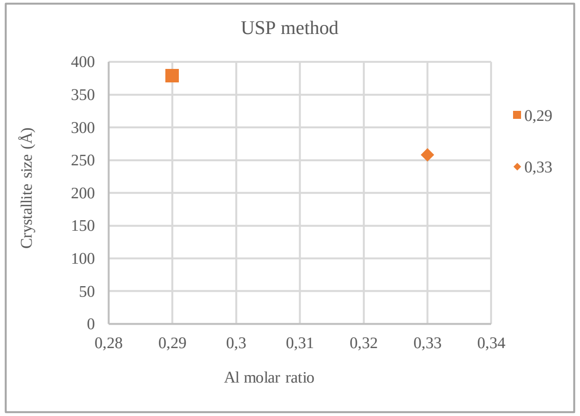
Results and analysis

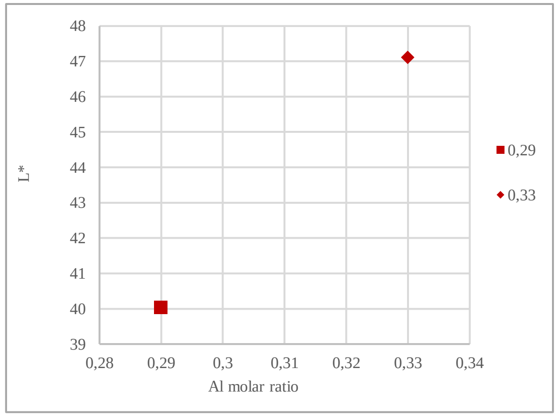
- Addition of Al

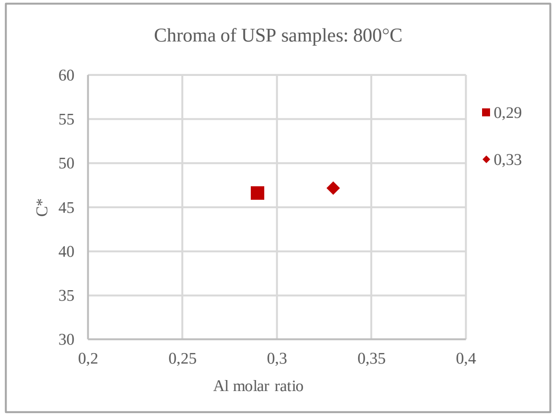
Influence of shape

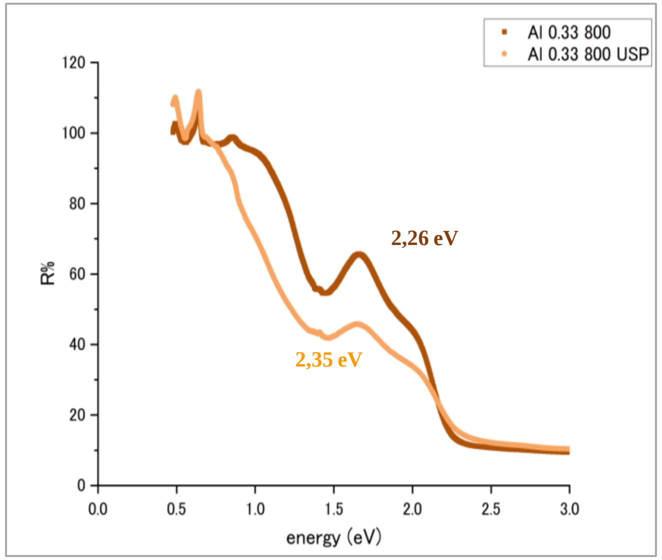
Spectrophotometer:

Optical reflectance spectra







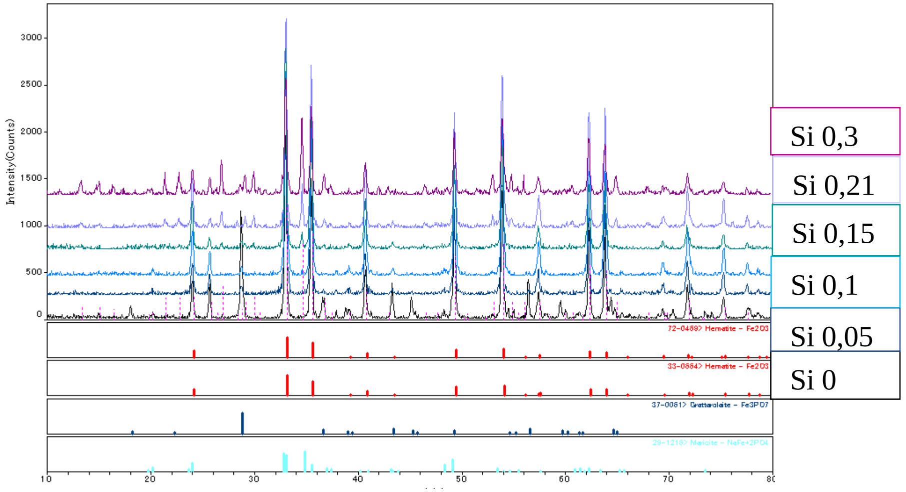


Same tendencies seem to be followed, but they could not be confirmed for these samples.

Results and analysis

- Addition of Si

XRD:



Little variations of red

0,3 Si: not pure sample (hematite + maricite + other peaks)

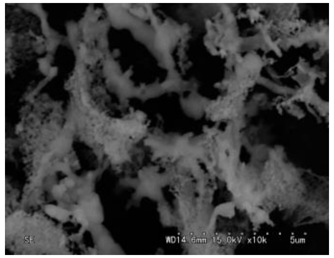
XRF:

Wanted Si molar ratio	0	0,05	0,1	0,15	0,21	0,3
Real Fe molar ratio	100	0,94	0,91	0,84	0,80	0,71
Real Si molar ratio	0	0,06	0,09	0,16	0,20	0,29

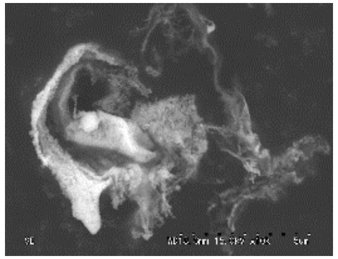
$\Rightarrow$ Very good expectations

SEM pictures:

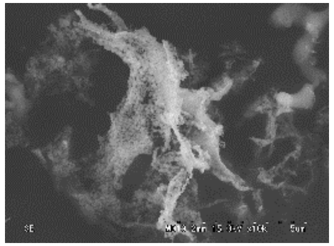
Si 0



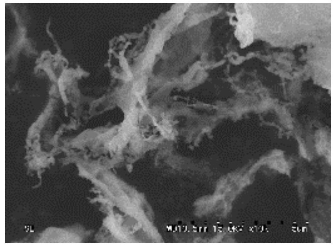
Si 0,05



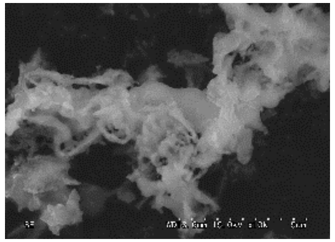
Si 0,1



Si 0,15



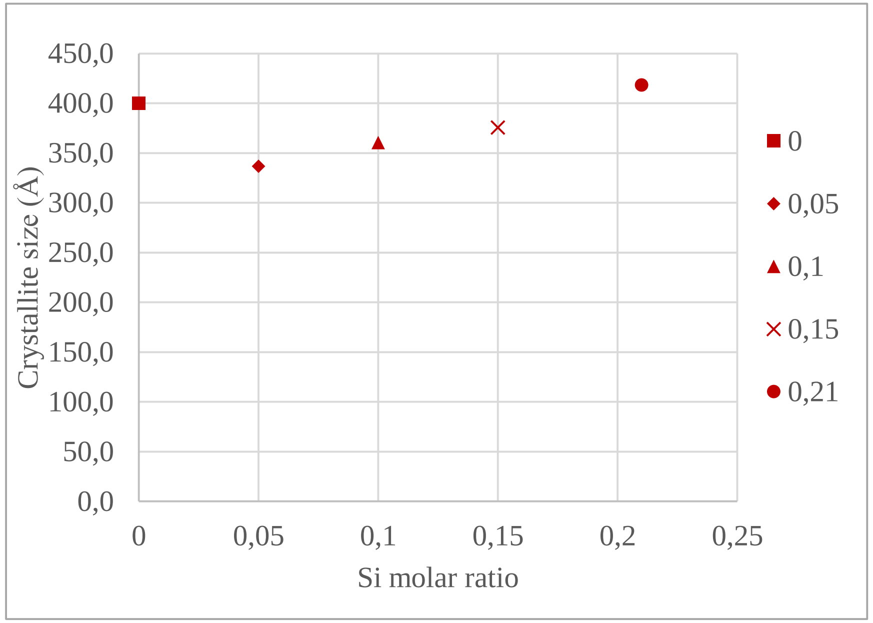
Si 0,21



Si 0,3

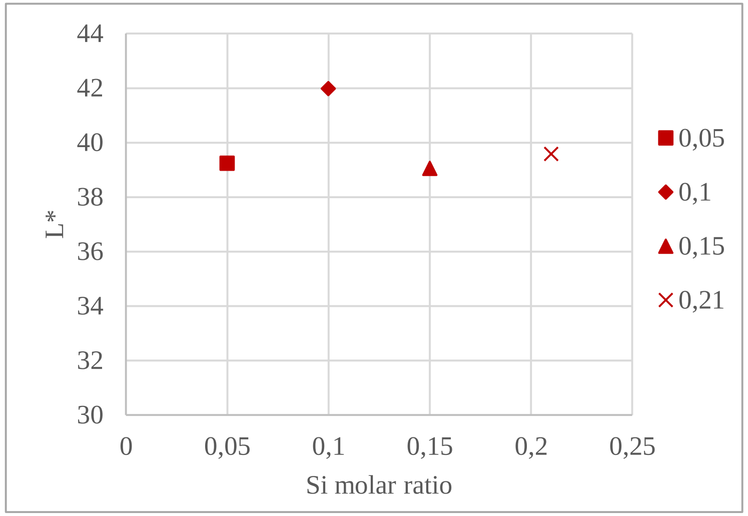
Results and analysis

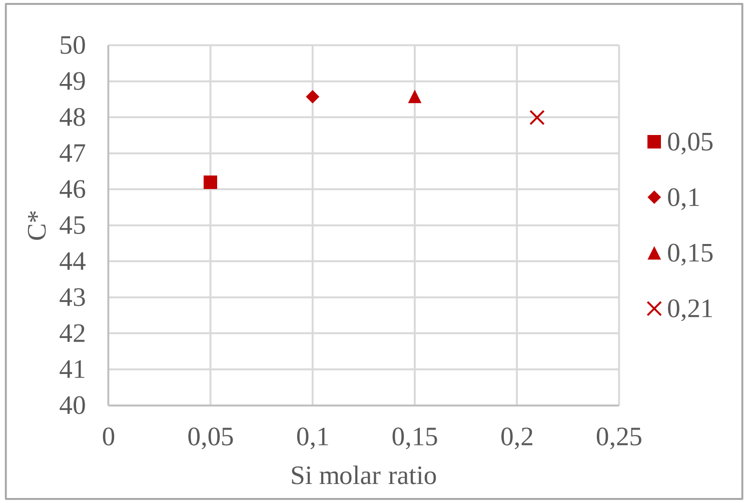
- Addition of Si

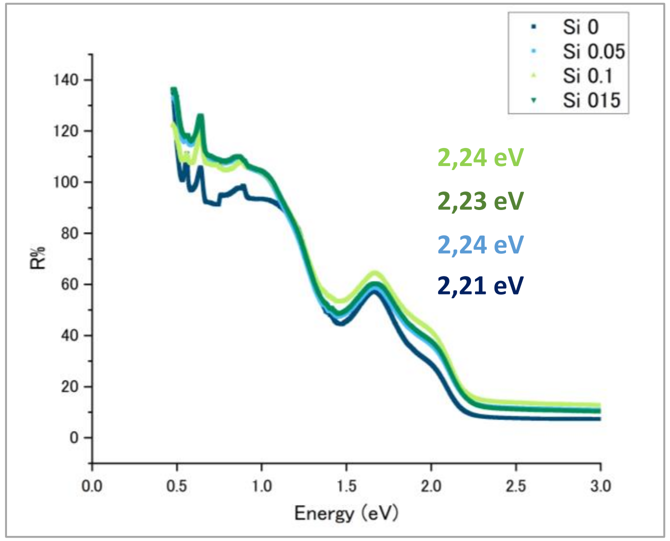


No tendency is followed for lattice parameters so no Vegard's law as well: cannot assumed that this is a solid solution

<u>*Spectrophotometer:*</u>







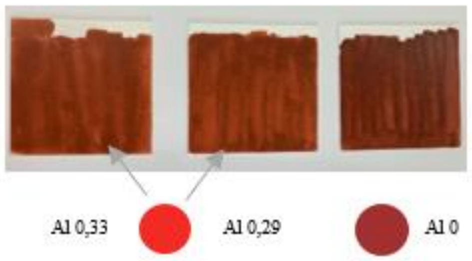
- Highest reflectance for 0,1 Si

$\Rightarrow$ Accurate with previous results

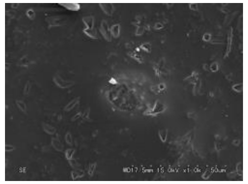
No significant variation of bandgap

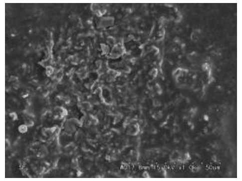
Results and analysis

- Painting's application



SEM pictures:

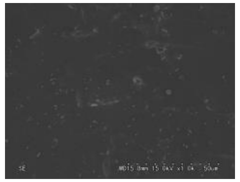


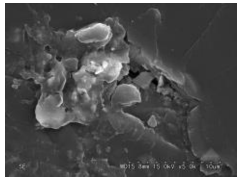


Al 0,33

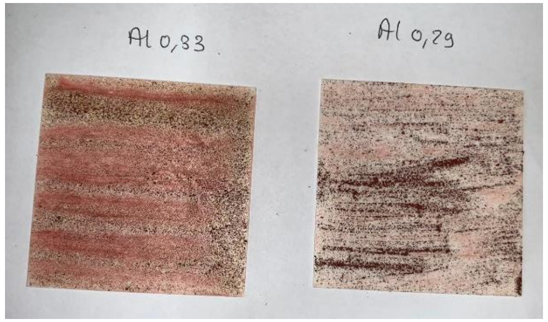
Al 0,29

SEM pictures:





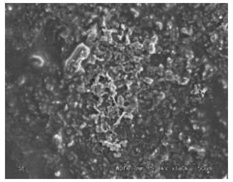
Al 0,41

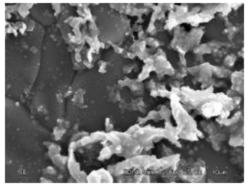


- Pigments particles not well distributed on the alumina board
- Gritty paintings

Not kept for the following analysis

SEM pictures:





Si 0,1

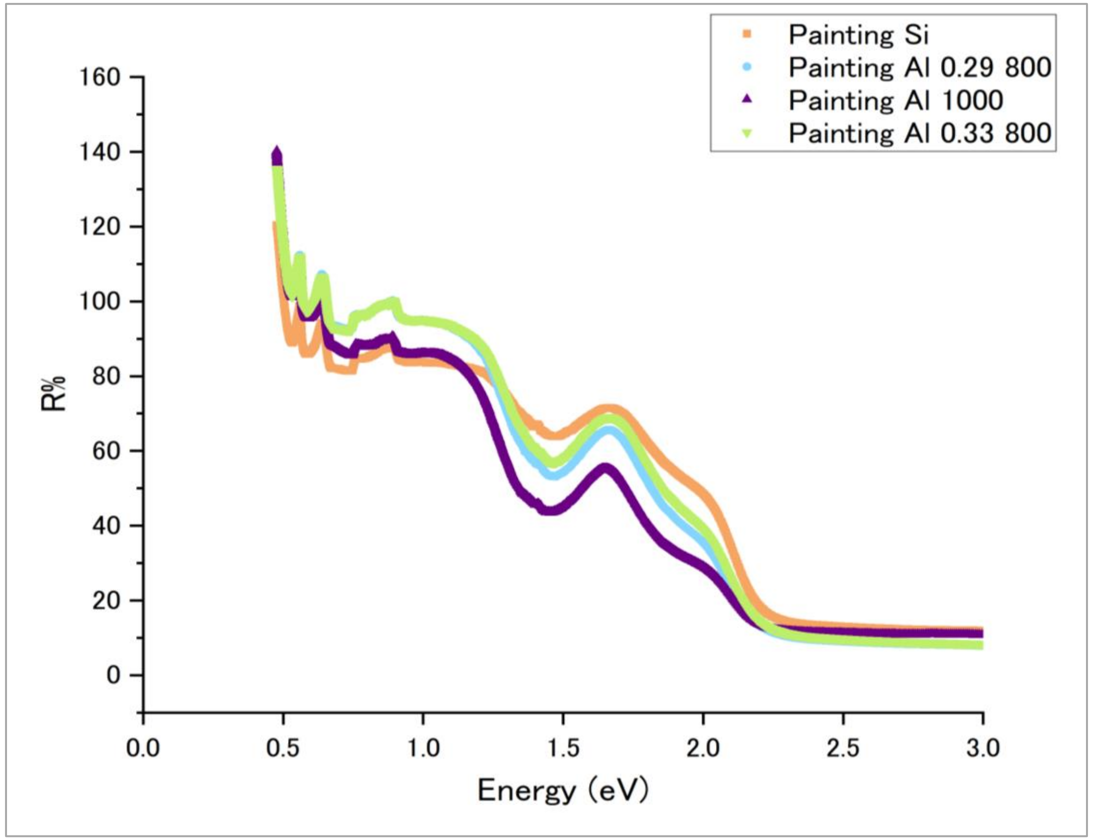
Results and analysis

- Painting's application

Infra-red region:
0,5 to 1,5 eV

Sample with the highest reflectance is Al 0,33 (and Al 0,29) painting, heated at 800°C

Concerns heat-resistant pigments.



Visible light:
1,5 to 3,0 eV

Sample with the highest reflectance is Si 0,1 painting heated at 800°C.

Conclusion

- Effect of

    - addition of Al: lighten up samples, reduce crystallite size and lattice parameters;

    - shape of particles: spherical particles are less promising and reflect less in infra-red region than fibrous particles;

    - temperature of pigments synthesis: increase gap, solid solution obtained;

    - addition of Si: do not follow the same tendencies but still the application in paintings can be taken into account.

- Most promising painting are Al 0,29 and Al 0,33 paintings heated at 800°C.

Bibliography

1) Bright Yellowish-Red Pigment Based on Hematite/Alumina Composites with a Unique Porous Disk-like Structure.
2) Kusano, Yoshihiro, Minoru Fukuhara, Taichi Fujino, Tatsuo Fujii, Jun Takada, et Mikio Takano. « Alchemy in the Art of Traditional Japanese Ceramics: Microstructure and Formation Mechanism of Gold-Colored Bizen Stoneware ». *Crystal Growth & Design* 18, n° 7 (5 juillet 2018): 4017-21.
3) Hashimoto, H.; Nakanishi, M.; Asaoka, H.; Maeda, T.; Kusano, Y.; Fujii, T.; Takada, J. Preparation of Yellowish-Red Al-Substituted α-Fe2O3 Powders and Their Thermostability in Color. *ACS Appl. Mater. Interfaces* **2014**, *6* (22), 20282–20289.
4) Lassoued, A.; Dkhil, B.; Gadri, A.; Ammar, S. Control of the Shape and Size of Iron Oxide (α-Fe2O3) Nanoparticles Synthesized through the Chemical Precipitation Method. *Results Phys.* **2017**, *7*, 3007–3015.
5) Hosseini-Zori, M.; Bondioli, F.; Manfredini, T.; Taheri-Nassaj, E. Effect of Synthesis Parameters on a Hematite–Silica Red Pigment Obtained Using a Coprecipitation Route. *Dyes Pigments* **2008**, *77* (1), 53–58.

Thanks for listening!

ありがとうございました!