Maëva GUILLOT

MASTER OF CHEMISTRY

2021 - 2022

INITIATION INTERNSHIP REPORT - 4CISOB

NON CONFIDENTIAL

Micro/nano structures and color tones of hematite nanoparticles produced by iron oxide sediments for beautiful red pigments

Internship supervisor:
FUJII Tatsuo

Place of the internship:
Okayama University, JAPAN

Acknowledgements:

I would like to express my deep and sincere gratitude to my internship supervisor, Professor FUJII Tatsuo, for welcoming me in his laboratory during my stay in Japan. I am grateful for all his support and help on my project, allowing me to discover more about pigments. I really enjoyed working on my topic of research.

This work could not have been done without the help of my tutor, Suga KEIJIRO, who took time to mentor me, explained me every machine operation, and with who I always had great time learning Japanese and talking.

I would like to express my gratitude also to Sachika AKASE, for showing me how to use the ultrasonic spray pyrolysis. The setup of the device was long but she involved herself to make it clear and easy.

I would like to thank Professor KANO Jun, and Professor OHKUBO Tomoko for allowing me to use the UV-VIS-NIR spectrophotometer and helping me in the usage.

I am extremely grateful to all my laboratory mates I cannot name here. Everyone was welcoming to me, and made me discover parts of Japanese culture, in addition to be very altruistic, especially when I could not find what I needed for my research. I really had a nice time, and I hope to stay in touch with them.

During this stay of 5 months, I have been granted with financial support, thus my thanks also go to the 2022 Takenoko grant, the iMAT program and Sorbonne Université, with which my stay was possible and more comfortable, especially with the help of Ms. Marie-Laure LEBRUN who had been able to find the best support for me, and also during these difficult times we have been through.

Last but not the least, I particularly want to express my deepest gratitude to Dr. Anne-Lise POQUET, who sponsored me for TAKENOKO scholarship and who gave me the opportunity to fulfill this project that was important for me. Without her rigor, her persistence and positivity, this exchange could not have been possible, especially with the difficulties we underwent because of coronavirus.

CONTENTS

INTRODUCTION:

Since the Paleolithic times, pigments are used such as in Lascaux caves in France, where we can see hunt scenes, or life scenes represented[1]. In Japan also, pigments were used since ancient times. They appeared in particular in art, such as in the BIZEN pottery[2] which has many shades because of natural pigments, but also in the traditional paintings of the Edo period, Ukiyo-e[3].

Thus, pigments are powdered particles used to color materials. They are insoluble in the medium they color by dispersion. They can be more or less big, and they all have a characteristic crystalline structure. The first thing we thought when talking about pigments is obviously paintings, but it is also used in others fields like architecture. By the way, this is the case for Fukiya village in the prefecture of Takahashi in Japan, where typical houses are colored with Bengara pigment (red pigment)[4,5].

Through the years, many pigments were used, such as ZnO (white pigment), Prussian blue $Fe_4^{III}[Fe^{II}(CN)_6]_3$ [3] or Vermilion HgS [3], which were discovered and used respectively since around 500 BC, since the XVIIIth century and since antiquity. But some of them, particularly inorganic pigments, are made with dangerous elements, such as Pb for $PbCrO_4$ (yellow pigment)[6], and so are harmful for life. Inorganic pigments today tend to be more safe[7]. That's why the following research will not use dangerous component in order to respect human life.

Both organic and inorganic pigments exist. Each one has its advantages. Where organic pigments have more intense color, inorganic pigments are more stable at high temperatures and the color remains longer in time[1]. This study focuses on inorganic pigments and more precisely on red iron oxide pigments, hematite, which is safe red pigment.

One of the goal of this study is to have very bright samples, because the red from hematite tends to be quite dark and to tarnish in times. The question arises as to how to get brighter hematite particles? Which features of hematite will be changed? With what purpose of application? For that matter, other elements were added in small proportions into hematite and their influence were studied. The crystallography and the color were the main features studied. The influence of shape was also investigated. All with the aim of having cool pigments that could be used into architecture, for roofs or walls[7].

Pigments are a heritage from the past, a witness of the history from which a lot of information of the past can be learnt to improve color and synthesis. But it is also important to add that hematite can have others applications like in Li-ion batteries[8], or for water splitting[9,10]. For now, these applications are currently in a study and does not concern this internship, even though some of them can be promising for the future.

PRESENTATION OF THE RESEARCH GROUP:

This internship took place in Japan, at OKAYAMA UNIVERSITY. It was supervised by the Pr. Tatsuo FUJII, who belongs to the department of Applied Chemistry. It was also tutoring by Suga KEIJIRO, who is a master 1 student. All the researches were done during an internship of 4 months and a half.

The group, made of Pr. Tatsuo FUJII, the associate professor TAKAHASHI, one PhD student and also composed of over 14 students, is working on functional iron oxide composite materials. A part of the laboratory is working on electrodes for Lithium ion battery and on electronic ferroelectric devices, whereas the other part of the laboratory is studying porous ceramics functionalized by iron oxidizing bacteria and on heat-resistant red pigment.

The Department of Applied Chemistry is located in the faculty of Natural Science and Engineering. Indeed, this building is on the Tsushima Campus of OKAYAMA University, which is a top-class university, regrouping 11 faculties and 8 graduate schools.

During this internship, the laboratory of Pr. FUJII T. gave me access to many devices such as an X-ray diffractometer, the scanning electron microscope, the X-ray fluorescence, spectrophotometers such as UV-VIS-NIR spectrophotometer, dryers machines, furnaces.

I. INTRODUCTION ON HEMATITE:

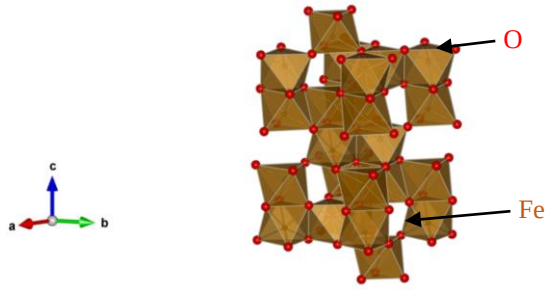
I.1. PIGMENT: CRYSTALLOGRAPHIC POINT OF VIEW:

Iron oxides are probably the most known oxide among all existing oxides, especially because of their abundance on earth. They are the result of the combination of iron Fe (II), or Fe (III), or both and oxygen O. Thus, either ferrous oxide, ferric oxide or magnetite oxide exist, with different composition as Fe_3O_4, Fe_2O_3 and so on. This study focuses on ferric oxide Fe_2O_3 which has different phases existing. By the way, it is important to notice that hematite belongs to the corundum-hematite group, A_2O_3, where A is a cation.

α-Fe_2O_3 is the rhombohedral form, also called hematite and is the most common and stable iron oxide found on earth[11]. β-Fe_2O_3 is the faces centered cubic form and is metastable. γ-Fe_2O_3 is also metastable and is called maghemite. Other forms exist, but there will not be talked about here.

The following research will only discuss about iron III oxide α-Fe2O3, hematite. As said before, the crystallographic form is rhombohedral, as shown in figure 1a.

a)



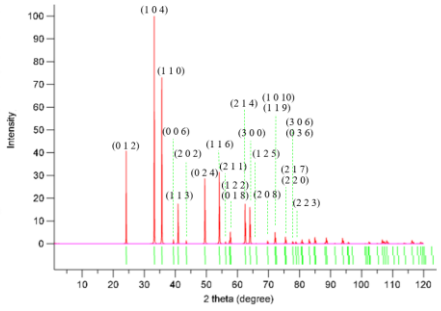
b)

Lattice type	**R**
Space group name	R -3 c
Space group number	167
Lattice parameters	
a	5,034
b	5,034
c	13,75
α	90,00 °
β	90,00 °
γ	120,00 °

Figure 1: a) representation of hematite; b) Table of lattice properties[12].

The diffraction powder pattern of hematite is the one shown on figure 2. Beyond 80°, data are not obtained so there is no need of identifying them. This pigment is not porous, and seems quite compact, and is spherical-like shape[13]. The bandgap of hematite is known to be around 2,1 eV[12]. And the color of hematite is due to O_{2p}=>Fe_{3d} charge transfer and 3d-3d transition of Fe^{3+} cation[7].

a)



b)

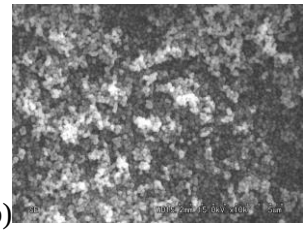


Figure 2: a) Characteristic XRD pattern of hematite, b) SEM picture of pure hematite.

I.2. HEMATITE THROUGH THE AGES:

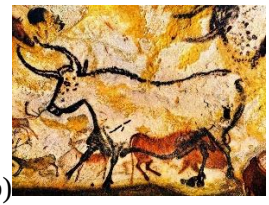
Hematite is mostly found in deposits in France, Italy and Brazil on earth. It forms itself at high temperature, sometimes also high pressure, and in presence of water. This matter is interesting because

hematite was found on Mars, which is a sign that water could have been present on this planet before. Then, hematite can clearly help us find information about history of planets, places or ancient civilizations.

During Paleolithic, hematite was used as a red pigment. It was mixed with water and painted into caves walls to draw daily scenes (hunting for instance). It was also used to color objects or clothes. Examples are shown in picture 1a and 1b of "Grotte Chauvet" and "Grotte de Lascaux" in France[1]. Hematite had also been used as a blood remedy during Egyptian times and into cosmetics during Antiquity times. In Europe and Central America, hematite was used as a mirror due to its shining.

Hematite was mainly used in pottery and ceramics as for pottery of ancient Greece and ancient roman pottery (see picture 1c). Here, hematite was responsible of either a red-ochre color or a black color. Around the VIII century during the Heian period in Japan, Bizen pottery (picture 1d) which uses local, high-quality clay and red pines in kilns, was created[2]. Its characteristic color is due to hematite for several shades. This pottery has often been used for the tea ceremony, and also as dishes into houses. Fukiya village [4,5] is one important example of hematite pigments used in architecture, during the XVIII-XX century. There, the goal is also to use hematite pigment into architecture, but with the goal to prevent the Global Warming and resist more to high temperatures into houses.

Today, hematite is still used into ceramics and pottery but is also used into concretes especially as shielding barriers for radiations[14].

a)  b)  c)  d)  e) 

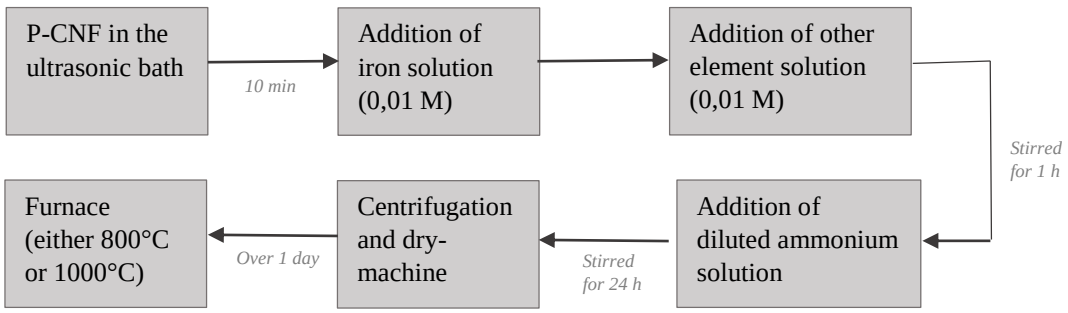
<u>Picture 1:</u> a) Chauvet caves[15], b) Lascaux caves[16], c) Athenian vase[17], d) Bizen pottery, e)Fukiya village.

II. EXPERIMENTAL SECTION:

<u>II.1. SYNTHESIS:</u>

II.1.A. PRECIPITATION METHOD (OR NEUTRALIZATION METHOD)

Regarding what have been made by KEIJIRO Suga, and his predecessors, hematite was synthetized through the following procedure, which is a precipitation method[12]. The procedure to do so is explained in figure 3.



<u>Figure 3:</u> Scheme of the synthesis procedure used to synthetize fibrous pigments.

In the procedure, P-CNF is used. It is Phosphor- Cellulose NanoFiber, an organic substance. It is put into the ultrasonic bath so that all the fiber can be well dispersed. Iron solution of $FeCl_2.4H_2O$ (0,01M) is added in the same amount as P-CNF. Then, when modulating the composition of hematite by adding another element, a precise amount of another solution is added. In this research, two elements were used. First, Aluminium Al was added[1], by using $AlCl_3.6H_2O$ (0,01M). Second, the effect of the addition of Silicon Si was studied, by adding pure Si dissolved into NaOH ([Si]=0,01 M)[11,19,20,21]. The mixing is stirred for 1h. Then diluted ammonium solution is added until the pH of the solution reach 10 [7]. Ammonium is the precipitating agent that allows us to have condensation.

The solution is stirred for 24h, so a day, before doing centrifugations. At this time, 4 washings are done, 3 at 500rpm during 10 min and then the last centrifugation is done at 2000 rpm for 5 min. Following these steps, samples are frozen with liquid nitrogen and put into the dry-machine for over 1 day.

Finally, the gummy samples are recovered, put into crucibles and then into the furnace. Two temperatures were used during this internship, either 800°C [4,6], either 1000°C for Al[22]. The last temperature was used only with Al. Indeed, when adding a bigger amount of Al, it is needed to heat treated the sample at higher temperatures, because analysis tendencies were not followed.

The two procedures used were:

Steps to get to 800°C:

- Heat up to 190°, 1h
- Stays at 190°C, 3h
- Heat up to 800°C, 1h
- Stays at 800°C, 2h

Steps to get to 1000°C :

- Heat up to 100°C, 1h
- Heat up to 1000°C, 1h and a half
- Stays at 1000°C, 2h

II.1.B. USP METHOD

The ultrasonic spray pyrolysis (USP) is a procedure allowing forming spherical particles. Indeed, in addition of the impact of Al and Si, the effect of the shape of pigments were studied. Fibrous pigments were obtained with the precipitation method. With this method, ultrasonic waves generated form droplets which are sprayed through the device. When they are in the heating furnace, the solvent evaporates and spherical particles are generated.

For this procedure, $Fe(NO_3)_3.9H_2O$ and $Al(NO_3)_3.9H_2O$ are used. They are mixed together in specific amount into a beaker. Ammonia solution is added as a precipitating agent until the solution reach pH4. After setting all the device and pre-heated the furnace to 900°C, the solution is added inside. This temperature was chosen according to the studies of Sachika AKASE on USP.

The amount of powder recovered from this method is quite small, thus the more we let the process on, the more we get samples. So the process was on for over 3 hours.

After recovering the powder, it was put into the furnace at 800°C, following the same steps as shown before.[11]

II.2. SAMPLE CHARACTERIZATION:

II.2.A. X-RAY DIFFRACTION

X-Ray diffraction (XRD) was experimented on synthetized powder with a *RIGAKU X-ray diffractometer*. After obtaining the different patterns for all the samples synthetized, different softwares were used. First *Jade* which allows to visualize the patterns and to identify the solid synthetized, and the

purity or not by watching the sharpness of peaks, the presence of a big background, and so on. *Cronograph* was used to get the lattice parameters of the samples based on the XRD patterns and the identification of peaks. Finally, with *IGOR Pro*, the exact angle and the exact width of the more intense peak (correspond to the Bragg plane (1 0 4) around 33°) are determined. Then thanks to calculations based on this peak, the crystallite size can be determined[13].

II.2.B. SEM

The aspect of particles and the shape particles were studied with HITACHI S-4300 Scanning Electron Microscope. The focus was usually of x10k, to have a scale of 5µm when pictures of powder where obtained. When pictures of paintings wanted to be taken, samples had to be coated with Pt first, and then the highest focus was x5k, in order to have a scale of 10 µm.

II.2.C. XRF

X-Ray fluorescence (XRF) helps to determine the composition of specific elements within the material. It is assured by the EDAX Orbis-XRF, which irradiate high energy x-rays. After the dislodging of an inner orbital atom, the relocation of outer orbital atom generates fluorescent x-ray characteristic for each atom. Thus the composition in atomic percentage At% can be obtained. With these values, the atomic molar ratio can be calculated.

II.2.D. SPECTROPHOTOMETER AND UV-VIS-NIR OPTICAL REFLECTANCE SPECTROPHOTOMETER

An important point to study with pigments is the color. First, pigments are analyzed with CM-2600d Minolta spectrophotometer. It allows having parameters such as the lightness L*, the redness a*, the yellowness b*. With these last two parameters, the Chroma C* can be calculated by doing $\sqrt{(a^{*2} + b^{*2})}$ [4,7,13]. When all the values are obtained, we can compare all of them on the range of composition, and then pick up the highest. Second, pigments color is analyzed with *SolidSpec-3700 UV-VIS-NIR spectrophotometer* from *SHIMADZU*. With this spectrophotometer, optical reflectance spectra are obtained, allowing us to get the bandgap of the sample, and also to compare the reflectance of different composition samples.

II.3. PAINTINGS

The main goal when synthetizing pigments here is to test their applications in paintings, especially in a project of making cool, heat-resistant pigments for houses roofs for instance. Indeed, a cool pigment should reflect Infra-Red (IR) but also visible light (VIS), so that in summer, the temperature inside the concerned building and of the building itself is lower than expected.

The procedure used to make the painting was taken from the work of Mr. Akiyama. It uses pigments synthetized, the brightest one is chosen, glycerol and transparent intrusive glaze. They are all mixed together in mass proportion respectively 1:5:5. Then the painting is applied on alumina board as a thin layer. The overall is placed into the furnace and heated at the same temperature the pigments were synthetized, so either 800°C either 1000°C. Also, the glass temperature of the intrusive glaze should be lower or over the same as the temperature used to heat the painting, in order to have a good painting that does not cracks or crumble.

Intrusive glaze with a glass temperature of 1200°C was used first but because painting was heated to 800°C and 1000°C, the painting was like powder on the alumina board. Then, intrusive glaze with a glass temperature of 850-880°C was used and the aspect of painting was much better.

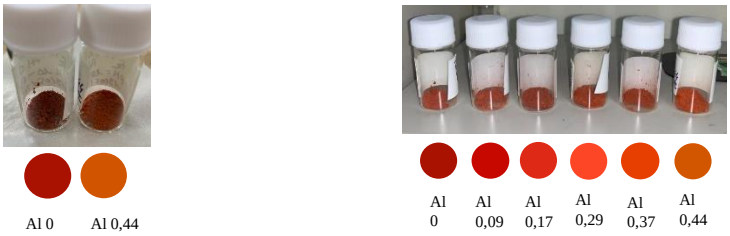
Scanning Electron microscope is used again but here to see in details the surface of paintings. Then the UV-VIS-NIR spectrophotometer is used also one more time to get the bandgap and the reflectance of the concerned painting.

III. RESULTS AND DISCUSSIONS:

III.1. ADDITION OF ALUMINIUM:

III.1.A. FIBROUS PIGMENTS

First, the pigments were synthetized at 800°C. The composition of Al was varying from 0 to 0,5 Al molar ratio. At first sight, we notice that when the amount of Al increases, the color of hematite which is very dark red for Al 0 becomes more and more orange and also lighter (*picture 2a and 2b*). Thus, without any analysis, we can already assume that Al has an impact on the color and that it lightens up hematite.



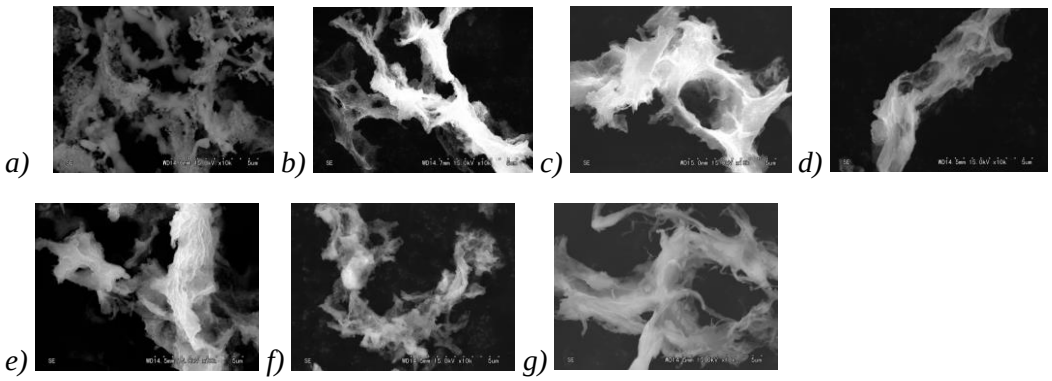
Picture 2: a) on the left: color of the extreme samples over the range; b) on the right: color variation on the range of composition at 800°C.

The theory is always a little bit different from the experiments. And even if the perfect amount of component is added, which is only theoretical, in practice a lower ratio is obtained. Here, the Al molar ratio is expected to be lower than the initial amount. The following table shows the real Al molar ratio, and Fe molar ratio in the samples synthetized. They have been determined thanks to XRF.

Wanted Al molar ratio	0	0,09	0,17	0,23	0,29	0,33	0,37	0,41	0,44	0,47	0,5
Real Fe molar ratio	100	0,91	86,10	78,11	76,78	71,02	74,55	67,67	68,54	60,00	56,5
Real Al molar ratio	0	0,09	13,90	21,89	23,22	28,98	25,45	32,33	31,46	40,00	43,48

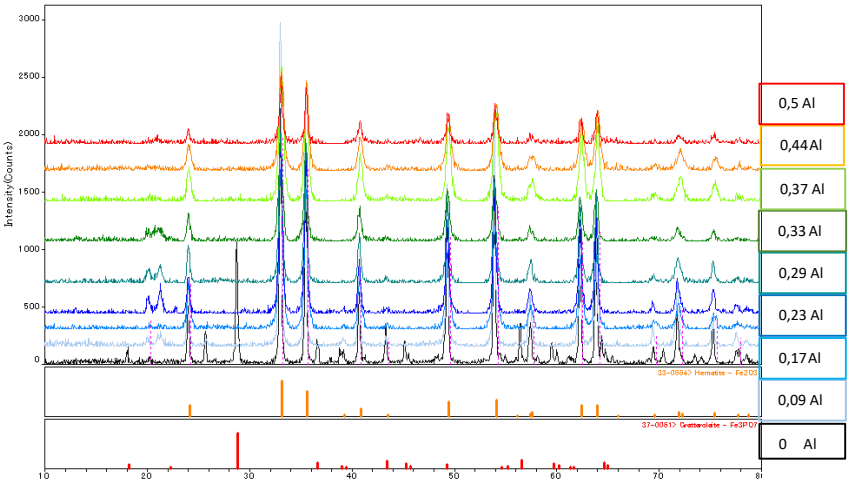
Table 1: Fe molar ratio and Al molar ratio thanks to XRF data.

As seen in part I.1, pure hematite is a pigment quite compact, dense and not porous. During reactions, P-CNF was used, in particular to spread well every element in solution. But P-CNF has actually another impact on hematite. It is responsible of the variation of shape of α-Fe2O3, from agglomerates and condensates to fibrous particles. That's what we can see if we compare with industrial hematite pigments and industrial iron III oxide. (*See pictures 3a-g and figure 2b*). Moreover, when Al is added into the composition, at different ratio, the shape does not seem to change. Also, crystallite can seem to be smaller when adding Aluminum, but this matter needs to be verify after. In this way, Al is not impacting the shape of the pigments.



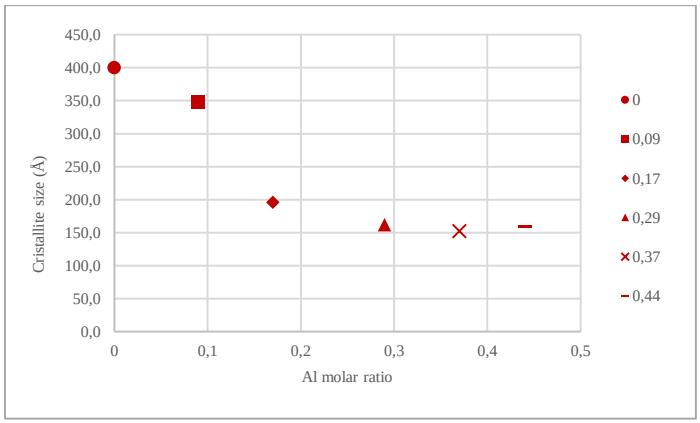
<u>Picture 3:</u> SEM pictures from a) to g), respectively for Al 0; Al 0,09; Al 0,17; Al 0,29, Al 0,37; Al 0,44 and Al 0,5, synthetized at 800°C.

Pigments have been talked about as powder particles *(in introduction)*, which also means that pigments can be referred to as crystallized matter. The crystallographic parameters are necessary to describe it, and gives a lot of information as well. To get these values, X-ray diffraction is done to obtain samples characteristic patterns, visualized with *Jade Pro*. The superposition of all the patterns is seen in figure 4. The samples synthetized are quite pure, but could be more, because the patterns are not very sharp. Also, some impurities containing Phosphor can be present, like Fe_3PO_7, as for hematite without Al. So, we can already say this synthesis procedure allows having relatively pure samples. When spectra are superposed, peaks fit with the ones of hematite. Nonetheless, the more Al is added into hematite, the more characteristic peaks are getting flatter and broader. This phenomenon is usually observed when the crystallite size is getting smaller, so that the difference between the "grating constant" d and the crystallite size is less important. It is also observed when the order in the crystallite is not respected anymore, so when there are more defaults. The less there is precursor, the better is the cristallinity[12]. Here, the crystallinity is decreasing and it can be assumed that crystal imperfections are present because Al diameter is 125 pm and Fe is over 140 pm. Indeed, either Al will take the place of Fe, by substitution, and then the cell size will decrease, or Al will go into interstitial sites, by insertion, causing constraints in both cases. The insertion of Al between Fe is less likely to happen because the atomic radii are similar. So it can be supposed that the crystallite size is decreasing, because of Al.



<u>Figure 4</u>: Superposition of XRD patterns for composition from 0 Al to 0,5 Al at 800°C.

Crystallite size is then calculated to confirm the impact of Al on it. When increasing Al molar ratio, the size of crystallite is seen to decrease *(see figure 5 and table 2)*. The first impact of Al was that it lightens up the color of hematite and the color was also becoming more orange. Here, the second impact of Al is seen: when Al is increasing, the crystallite size is getting smaller[18,6]. Then the particle size seems to influence sample color[18].



Al molar ratio	Crystallite size (Å)
0	400,0
0,09	347,8
0,17	195,6
0,29	161,8
0,37	152,1
0,44	159,0

Figure 5: Variation of crystallite size with respect to Al molar ratio. *Table 2: Record of crystallite size values.*

Lattice parameters are also studied and discuss. As we have seen in part I.1, hematite is rhombohedral and the two important lattice parameters, a and c, are respectively over 5,035 and 13,720 Å. The lattice parameters of fibrous hematite are then compared to the values we know, and the variation in lattice parameters with Al composition as well *(figure 6a and 6b)*. We observe that both parameters are decreasing with the increasing amount of Al. As a result, Al is the cause of the variation of lattice parameters. According to the previous deductions, it is accurate that the crystallite size, a single crystal size, decreases if we have seen that the lattice parameters are getting smaller. Moreover, lattice parameters should follow a tendency, which we supposed to be a Vegard's law tendency. This law is the sign of a solid solution between Al and Fe. Nonetheless, the Vegard's tendency is not followed for samples synthetized at 800°C. Then, we cannot be sure that samples can be written as α-$(Fe_{(1-x)}Al_x)_2O_3$ [2] if Al substitute Fe. But it can be deduced again that the color depends on the size of particles[1] because the lattice parameters values are varying, as the samples color do.

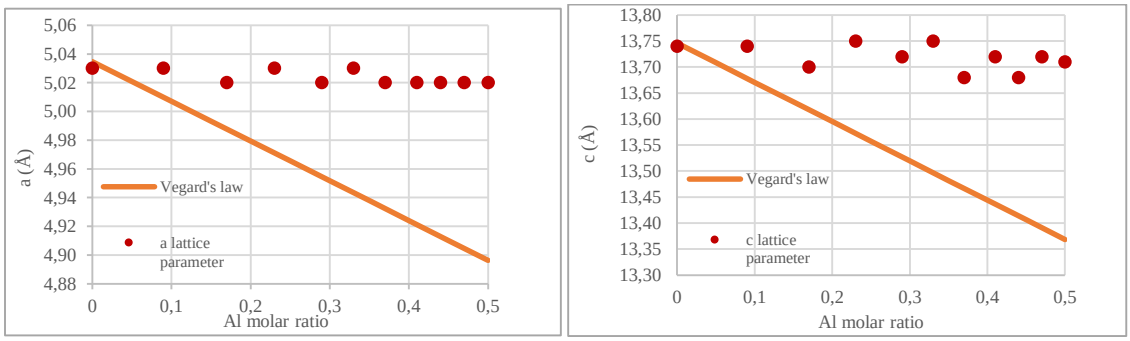
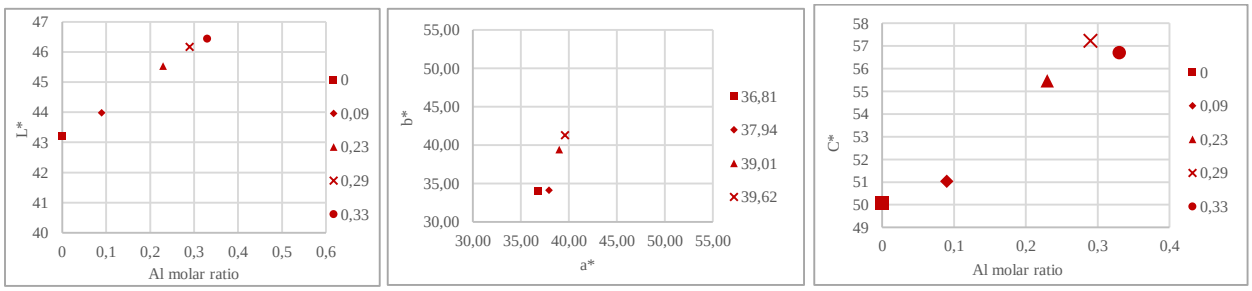


Figure 6: a) on the left, lattice parameter a with respect to Al molar ratio, superposed with Vegard's law; b) on the right, lattice parameter c with respect to the Al molar ratio, superposed with Vegard's law.

Because one of the main goal is to study the brightness of pigments, color parameters should be examined. The lightness L* of pigments is getting bigger when increasing the ratio of Al, until the highest

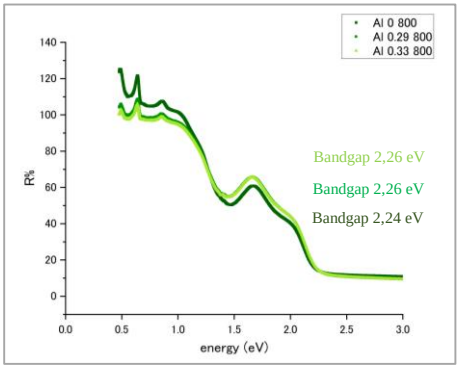
value for Al 0,29 and 0,33 is reached *(see figure 7a)*. After that, no tendency is followed, assuming that the values would get smaller gradually. We supposed that it was because the Al ratio is too big, so samples require higher temperatures when heating. It was then decided to heat the future samples at 1000°C. Nevertheless, the tendency is followed until 0,29 Al. The redness and the yellowness, characterized respectively by a* and b*, represents Chroma C* , by the formula $\sqrt{(a^{*2} + b^{*2})}$. The greater all these values, the better the color. Then it will be more likely for the color to be sustainable *(figures 7b and 7c)*.



<u>Figure 7:</u> a) left, Lightness with respect to Al molar ratio; b) middle, yellowness with respect to redness; c) Chroma C with respect to Al molar ratio.*

Because it is shown is Figure 7, it can be deduced, and also according to previous deductions, that Al is both increasing the lightness and the Chroma C* of hematite.

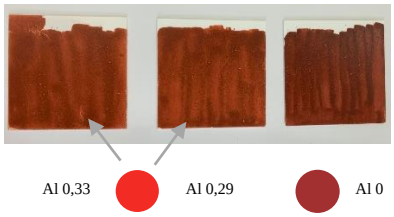
The color is investigated through the optical reflectance as well. It has been seen that the reflectance is increasing when Al molar ratio increases for visible light (1,5 eV-3 eV) *(figure 8)*. This is accurate with the fact that the sample is getting lighter when Al molar ratio vary in the same way as before. So it can be deduced that Al has an influence on the reflectance of the samples. The bandgap is also getting wider with bigger amount of Al. When adding Aluminum, even though no Vegard's law is followed, the lattice constants decreased, so the exchange integral between atomic orbitals increased. Then the bandgap is expected to get larger. This information is also accurate regarding the increasing of color parameters. Indeed, when the bandgap gets wider, the absorption wavelength shifts towards the blue, because energy and wavelength are inversely proportional. As a result, the reflection color is the complementary one of the absorbed wavelength. The complementary color of blue is orange. So the more it shifts towards the blue, the more the sample gets orange.



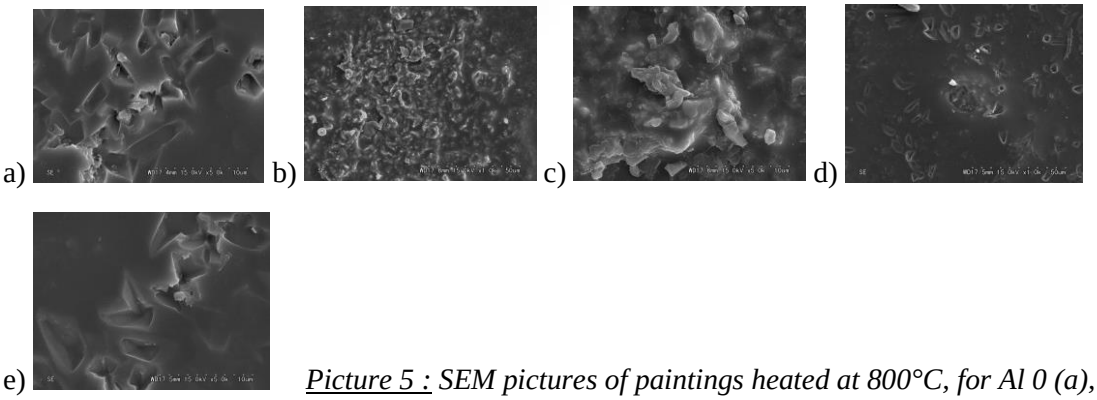
<u>Figure 8:</u> optical reflectance spectra of Al 0, Al 0,29 and Al 0,33, obtained at 800°C.

Paintings of the lightest samples have been made, as well as for pure hematite without Al. Because samples 0,29 Al and 0,33 Al have similar L*, they have both been chosen for the paintings. In the pictures 4, it is clearly seen that Al 0 painting is darker, like it was with the powders. Also, Al 0,29 and Al

0,33 paintings seem to have kept the same color as well, which is red-orange. Moreover, the painting is smooth, and there were no aggregates on the alumina board. When looking closer with SEM, some parts of the paintings surface look gritty, almost porous *(picture 5a to 5e)*. It can be assumed that this is caused because the highest temperature was 800°C whereas the glazing temperature of the intrusive glaze used is 850°C-880°C. Even if the difference is very low, this could have an impact. Despite the gritty parts on the surface, the overall is satisfying regarding the painting, but as an application for roof, it is not known if this would have an impact. The color of powder is not changing with the firing of the paintings, thus this is a sign of great thermostability[1,11].



Picture 4: Paintings heated at 800°C, of the lightest samples, and of hematite without Al (reference).



Picture 5 : SEM pictures of paintings heated at 800°C, for Al 0 (a), Al 0,29 (b and c) and for Al 0,33 (d and e) :

Finally, optical reflectance *(figure 9)* was done again but this time on the paintings. Here, the paintings bandgaps are a little bit lower than what it was for the powders. This may likely be caused by the heat treatment of the paintings. With powder, it has been deduced that the increasing amount of Al was increasing the reflectance of the sample in visible light region. For the paintings, the tendency is also the same, even in the infrared region (from 0,5 eV to 1,5 eV), showing that the more there is Al, the more the reflectance is. Even if the amount of Al has also an impact on the bandgap, its impact is less important than the one on the reflectance.

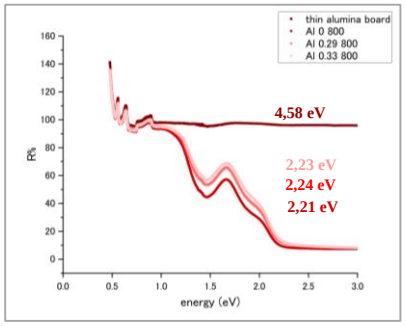
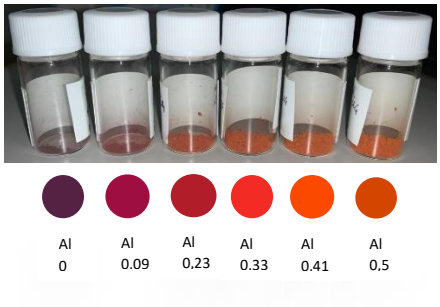


Figure 9: Optical reflectance spectra of paintings at 800°C and of the alumina board.

Because the tendency of chromatic parameters was not followed, it was decided with Professor Fujii T. to go to higher temperatures. Thus, the following part will present same experiments but with a temperature synthesis of 1000°C, as for the paintings. The following compositions from 0 to 0,5 Al have also been made. For this temperature, as we can see in picture 6, the color is not only varying from red to orange but from dark purple to light red-orange[22]. The variation of color is greater. The composition of Al in hematite samples was checked as well with XRF, and the increasing amount of Al in the samples match with what is expected *(see table 3).*

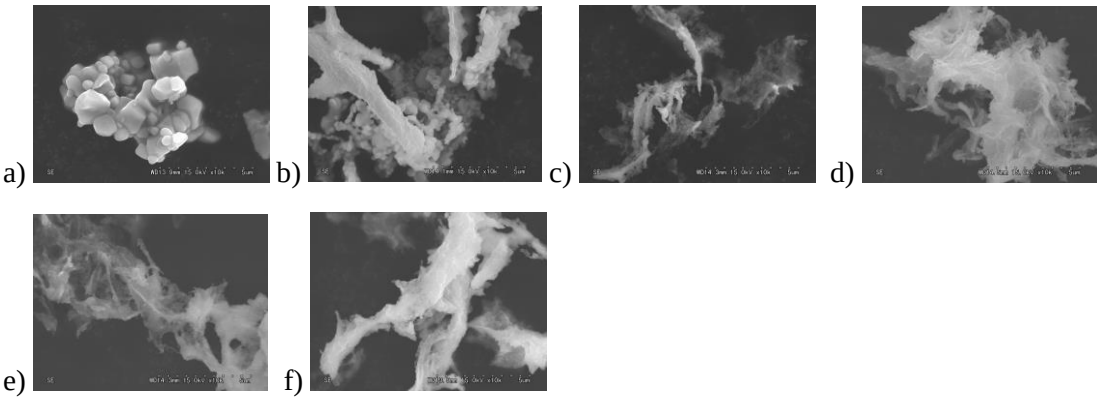


Picture 6: Color variation on the range of composition at 1000°C.

Wanted Al molar ratio	0,09	0,23	0,33	0,41	0,5
Real Fe molar ratio	93,5	83,0	76,2	70,7	65,7
Real Al molar ratio	06,5	17,0	23,8	29,3	34,3

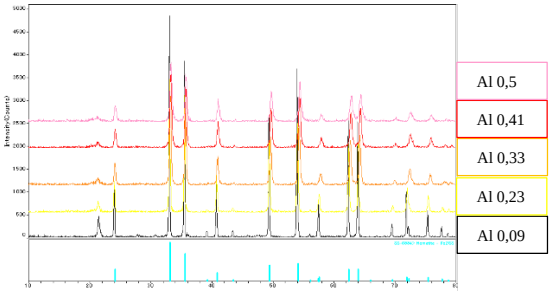
Table 3: Real molar ratios of Fe and Al Thanks to XRF data.

The shape of the pigment was investigated, especially to see if the fibrous structure of pigment has remained. As we can see with the SEM pictures *(picture 7)*, there is still a fibrous shape for hematite, except for Al 0 and also Al 0,09. For Al 0, fibrous shape is not observed at all. On the contrary, a very compact structure is seen, with agglomerates. The agglomerates are made of diform, non-spherical beads. Several assumptions can be made from this point: the almost black color can either be because of the agglomeration[1], either from the temperature of synthesis. For Al 0,09 Al, a fibrous structure is seen from far, but when looking closer, diform, non-spherical beads form the fibrous structure. Here, the color of the sample is purple, crimson. We can do both of the previous assumptions as well for this sample. The temperature is modifying the shape from fibrous to agglomerates when there is no Al. Then, the shape variation, caused by the temperature and, the small amount or the non-presence of Al, is responsible of the great variation of color.

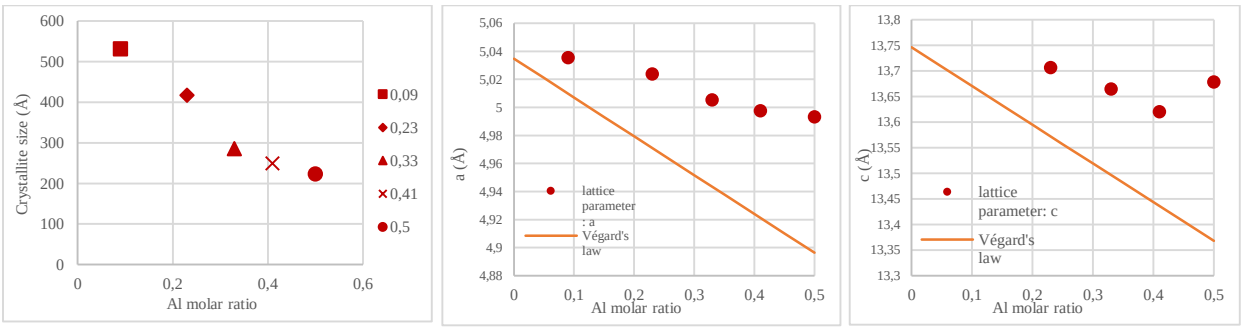


Picture 7: SEM pictures of samples at 1000°C from a) to f), respectively for composition Al 0; Al 0,09; Al 0,23; Al 0,33, Al 0,41and Al 0,5.

Through XRD results, the purity of the samples was verified just by seeing sharp patterns. All the patterns are sharper, and peaks fit only with the ones of hematite. Thus, higher temperature appears to be a good condition for obtaining pure samples *(see figure 10)*. As it was pointed out before, here peaks get flatter and wider again when there is more Al. Thus, as said before, the crystallinity in hematite is assumed to decrease and the crystallite size also. This last assumption is checked with the figure 10a. The same procedure of analysis was done for every samples, and when calculating the lattice parameters, a and c were decreasing with the increasing amount of Al. In that way, a linear relation was without a doubt followed, and so for the Vegard's law, as seen on figure 11b and 11c. Regarding that matter, all the samples synthetized appear to be a solid solution of Fe and Al, for hematite, where 0,41 Al is the limit of the solid solution, because 0,5 Al do not respect the Vegard's law, on figure 11c. Then, samples can be written as α-$(Fe_{(1-x)}Al_x)_2O_3$, with $0 \leq x \leq 0{,}41$ if Al substitute Fe.

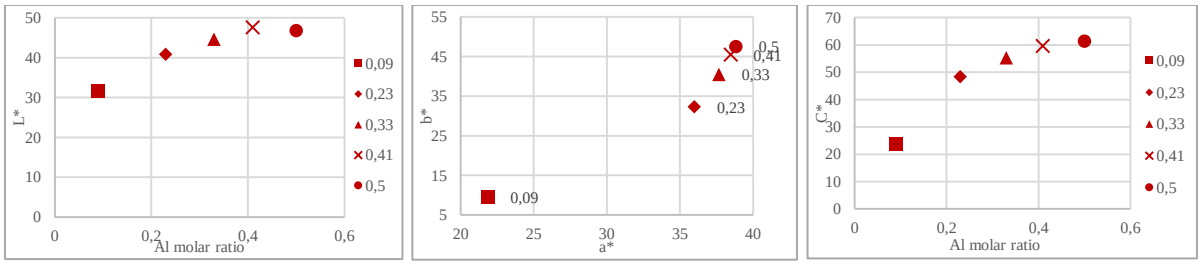


<u>Figure 10:</u> Spectra superposition of samples heated at 1000°C.



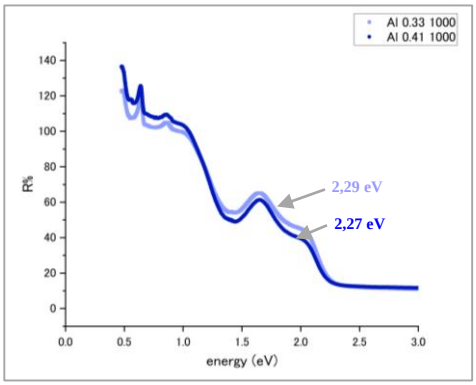
<u>Figure 11:</u> a) left, crystallite size with respect to Al molar ratio for samples synthetized at 1000°C; b) middle, lattice parameter a with respect to Al molar ratio; c) right, lattice parameter c with respect to Al molar ratio.

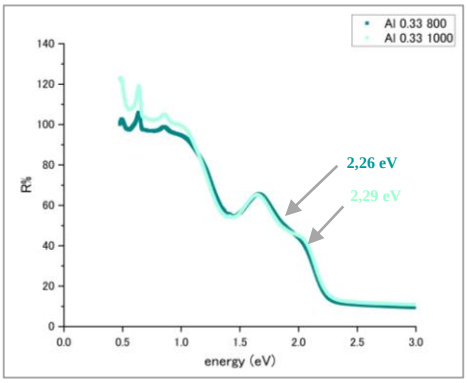
The color is explored with spectrophotometers. The redness, the yellowness and the lightness are analyzed and compared with the ones get at 800°C. The redness and the yellowness increase both, explaining the increasing of Chroma C* with the alumina molar ratio *(Figure 12b and 12c)*. This time, the tendency is respected for all the range of composition. That was not the case for 800°C. The rising of values is clearer, and do not led to misunderstandings. As before, the lightness is also increasing with the molar ratio *(figure 12a)*, and we finally get the highest values of C* and L* for Al 0,41, which is clearly different from the values obtained at 800°C, where the highest values where obtain for 0,29 and 0,33 Al. Here, we can confirm that the addition of Al increases the lightness and the color of hematite pigments.



<u>Figure 12:</u> a) left, lightness L with respect to Al molar ratio; b) middle, yellowness with respect to the redness; c) right, Chroma C* with respect to Al molar ratio.*

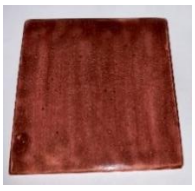
The increasing of color, becoming more red-orange, and the increasing of lightness, can be explained by the theory of bandgap. The more the solid solution has aluminum, the higher is the reflectance in infrared region and the bandgap *(figure 13)*. Moreover, bandgaps are higher at 1000°C than at 800°C. Indeed, samples heated at 1000°C are darker and more red than samples heated at 800°C for a given composition. But the reflectance is not that improved with the heating temperature. Then synthesis temperature is a cause for the increasing of bandgap. Finally, pigments heated at 800°C seem better for cool pigments according to figure 13b.

a) 

b) 

<u>Figure 13:</u> a) optical reflectance spectra of samples synthetized at 1000°C; b) influence of heating temperature on optical reflectance spectra for Al 0,33 samples.

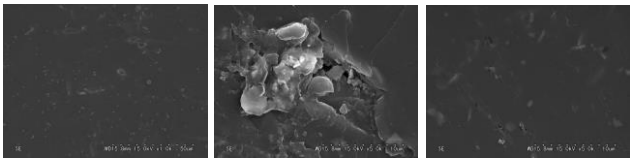
The paintings were done with Al 0, Al 0,09 and Al 0,41, which is the lightest sample at 1000°C. Al 0 was took as a reference but for this composition, hematite is very compact, so Al 0,09 was also taken to make the paintings, because it was the sample with the lowest amount of Al after Al 0, and because it was present in greater quantity. Unfortunately, after recovering the samples from the furnace, Al 0 and Al 0,09 paintings were not a success. Indeed, the pigments were too compact from the start, thus the glycerol and the intrusive glaze could not intrude the spaces of the hematite shape and form a beautiful painting. On the contrary, the painting of Al 0,41 was very shining, beautiful but less light than expected *(picture 8)*. The color tended towards reddish-purple. Regarding the aspect, the surface was glassy and smooth, in particular because the heating temperature was 1000°C, temperature higher to the glazing temperature of the intrusive glaze. The Al 0,41 painting is the only one kept for the next analysis.



<u>Picture 8:</u> Painting of Al 0,41 sample heated at 1000°C.

The photo reflectance spectrophotometer was once again used on the painting, and we found that the gap of the painting is lower compared to the gap of the powder which have the same composition. This means that the heat treatment done for the painting has impact on the color at 1000°C. The color of the painting is accurate with the value of the bandgap, with the same explanations as before.

Finally, with a closer look thanks to SEM picture *(picture 9)*, the surface is very glassy, and looks very fine for a painting. Of course there is some little holes but they are rare and does not impact the surface in a general way.



Picture 9: SEM pictures of Al 0,41 sample painting.

III.1.B. SPHERICAL PIGMENTS

The pigments shape was an important matter in this study of hematite. An assumption was that the shape was responsible of the variation of color. If the samples synthetized before would not have the same shape, will they have the same color, in the same conditions of heat treatment? To compare with fibrous pigments, spherical ones have been synthetized thanks to the USP technique. Unfortunately, an issue was encountered with the device and only two different compositions were done with this technique. Nonetheless, analysis were made with the samples we had.

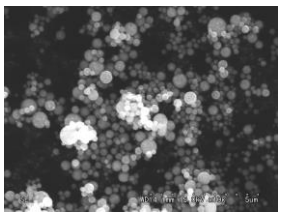
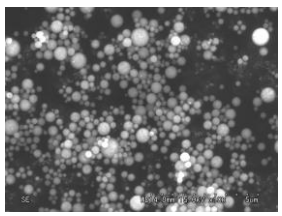
The color of the spherical pigments was less striking, and seemed darker at first sight *(picture 10)*. In addition, the 0,33 Al sample had shades of brownish-orange, not really a color wanted. The Al molar ratio was verified with XRF and the values were consistent with what we expected *(table 4)*.

Picture 10: Color of 0,29 and 0,33 Al samples made with USP, at 800°C.

Wanted Al molar ratio	0,29	0,33
Real Fe molar ratio	0,76	0,73
Real Al molar ratio	0,24	0,27

Table 4: Real molar ratios of Fe and Al Thanks to XRF data for USP samples.

The shape is also perfectly spherical, as seen with SEM picture *(picture 11)*.

a)  b) 

Picture 11: SEM pictures of USP samples at 800°C, a) Al 0,29 and b) Al 0,33.

By watching the XRD patterns for both of the samples, it is seen that 0,29 Al is pure hematite with very sharp peaks. On the contrary, Al 0,33 is less pure because impurities of $FeAlO_3$ are present *(see figure 14a and 14b)*. The lattice parameters seem to decrease as well but with two samples, a tendency cannot be made *(figure 14d and 14e)*. Finally, like it was studied before, the crystallite size is decreasing with the increasing amount of Al *(figure 14c)*. And, it appears that the spherical particles size is bigger than the fibrous pigment size at 800°C. As a consequence, it is assumed that spherical shape is a reason for having bigger particles.

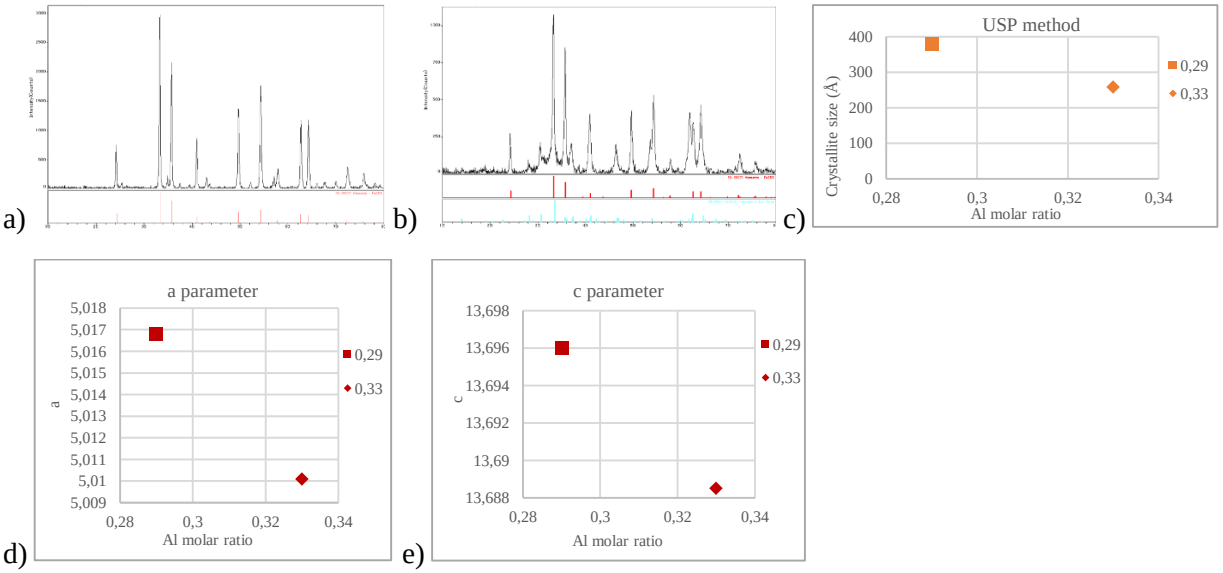


Figure 14: a) XRD pattern of Al 0,29 USP sample; b) XRD pattern of Al 0,33 USP sample; c) crystallite size with respect to Al molar ratio of USP sampled; d) lattice parameter a with respect to Al molar ratio; e) lattice parameter c with respect to Al molar ratio.

Finally, the color was examined. It was found that the Chroma C* was increasing a little from 0,29 to 0,33 Al, which means that maybe the same tendency was maybe followed *(figure 15b)*. Unfortunately, this could not have been checked. Moreover, the bandgap of the spherical particles of 0,33 was higher than the gap of the fibrous particle, going with the fact that the color is a lot less red *(figure 15c)*. Samples are not very light either. The main point here is that the reflectance is a lot smaller than for the fibrous particles over all light regions. A main assumption here is then that the shape is responsible of the lightness of the pigments[11], and that fibrous particles reflect more than spherical particles.

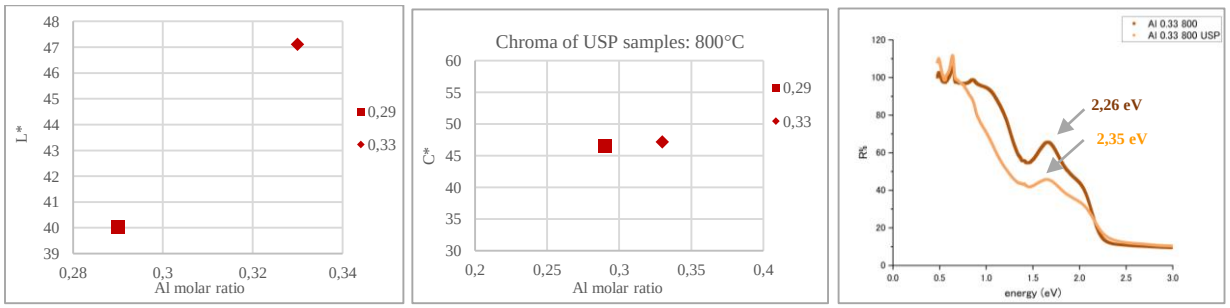
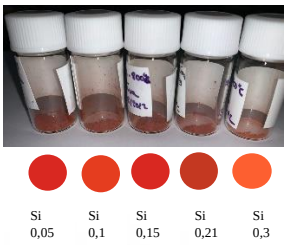


Figure 15: a) left, lightness with respect to Al molar ratio, b) middle Chroma with respect to Al molar ratio, c) right, comparison of optical reflectance spectra for different shape particles.

Paintings have been made for spherical particles, but because of the spherical shape, the glycerol and intrusive glaze could not separate particles or go through, within pigments. So the painting was no good, especially for applications. With a goal of using the samples as cool pigments for the roofs, fibrous pigments are better. For this purpose, pigments synthetized at 800°C are the betters, and the lightest sample is obtained for the composition 0,29 Al.

III.2. ADDITION OF SILICON:

Another element was added instead of Al. Silicon Si, the element taking the place of Al, which has the advantage to be one of the element present in greater quantity on earth. The variation of composition was done from 0 Si to 0,5 Si. However, above 0,33 Si, no samples could be recovered from the furnace. Even for 0,33 Si, the amount of sample recovered was really small, and it will be seen that this sample was not pure at all with XRD patterns. With Si, the color variation was less drastic, and samples color was different shades of red *(see picture 12).* The Si molar ratio was checked and fitted pretty well with what was wanted, as seen in table 5.

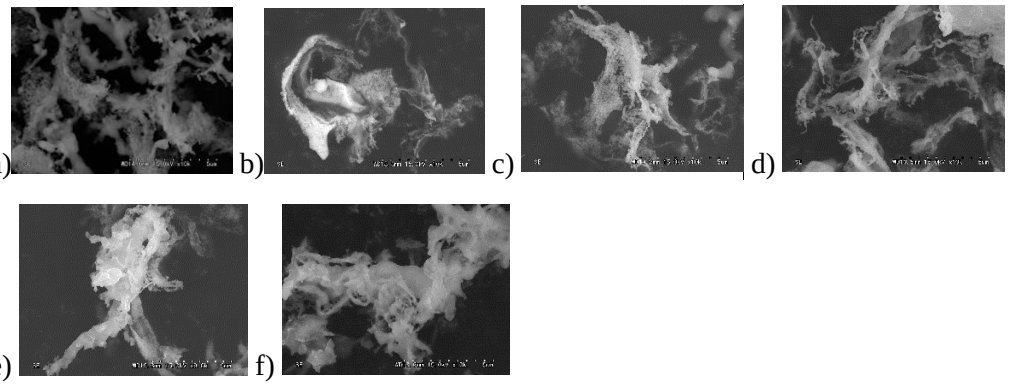


Picture 12: Color variation on the range of composition of Si addition at 800°C.

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

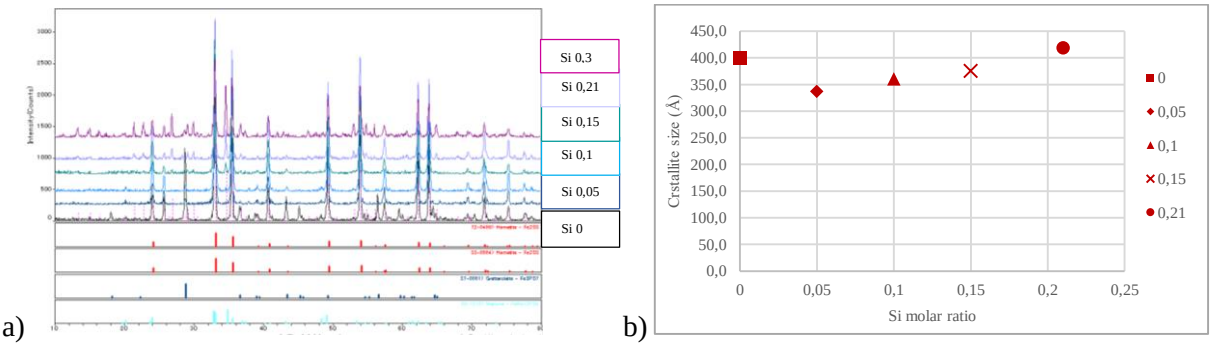
Table 5: Real molar ratios of Fe and Si thanks to XRF data.

Particles of Si samples looked also fibrous, as seen with picture 13 of SEM. Indeed, this is due to P-CNF. Si does not seem to change the shape induced by P-CNF.



Picture 13: SEM pictures of samples at 800°C from a) to f), respectively for composition Si 0; Si 0,05; Si 0,1; Si 0,15, Si 0,21 and Si 0,3.

When analyzing the XRD patterns of Si samples, quite pure hematite was obtained with relatively sharp peaks on the patterns except for the pattern of 0,33 Si, which was absolutely no pure hematite. So this sample will not be taken into account for the following analysis, because the pattern shows that there is hematite and Maricite *(see figure 16a)*. All the other ones are analyzed with *Igor Pro* and *Cronograph*. The lattice parameters of Si samples do not follow any tendency with the amount of Si, so the graphs are not displayed here. Nonetheless, the crystallite size of Si samples decreases until Si 0,1 and then it increases again *(figure 16b)*. Indeed, according to this fact, the XRD patterns do not flatten or get wider with the increasing amount of Si.



a) b)

Figure 16: a) XRD patterns of Si samples, b) crystallite size with respect to the Si molar ratio.

The lightest sample which is also the one who has the highest Chroma C* is 0,1 Si *(figure 12a and 17b)*. So this sample is the one chosen for the painting. This highest values match with the smaller crystallite size, seen previously. On figure 17c, it is seen that the influence of Si on the bandgap is kind of weak, but still Si augments the bandgap. On the other hand, the highest reflectance is observed for the lightest sample for visible light. This information support one again that the reflectance and the brightness of samples are linked.

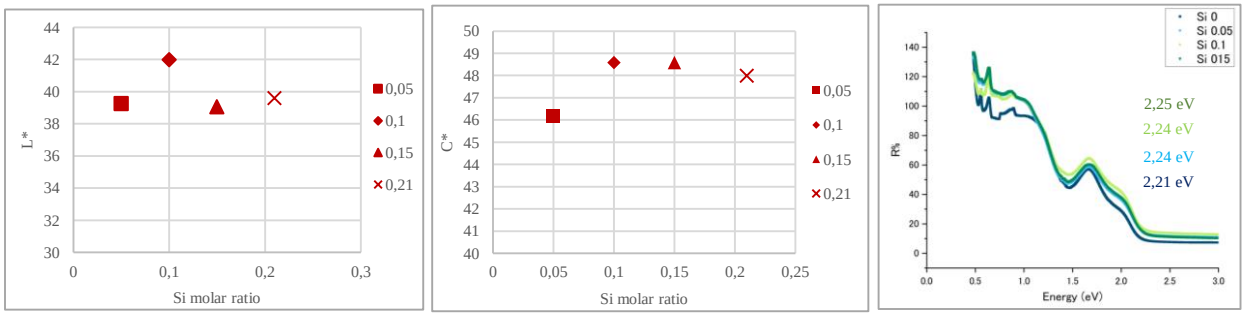
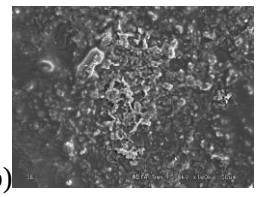
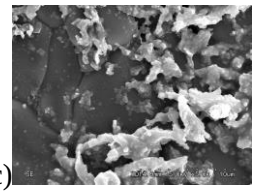
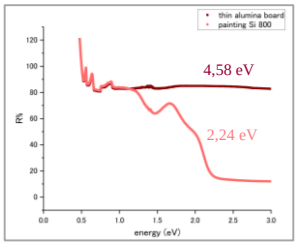


Figure 17: a) left, Lightness with respect to Si molar ratio for Si samples; b) middle, Chroma with respect to Si molar ratio for Si samples; c) right, optical reflectance spectra superposition of Si samples, heated at 800°C.

The painting *(picture 14a)* looks good, but the color is less orange than paintings done with Al at 800°C. Regarding the aspect, from far the painting seems flatten enough and smooth, but not glassy. With a closer look thanks to SEM picture *(picture 14b and 14c)*, the surface looks grittier, like if all the samples were not well incorporated into the intrusive glaze of the painting. Finally, on the optical reflectance spectra (figure 18d), the bandgap of Si 0,1 is still the same, even after the heat treatment of the painting.

a)  b)  c)  d) 

Picture 14: a) picture of the painting heated at 800°C and done with 0,1 Si sample; b) c) SEM pictures of Si 0,1 painting. Figure 18d: optical reflectance spectra of 0,1 Si painting.

Finally, Si painting is compared with Al paintings heated at 800°C and 1000°C. It is compared with both Al 0,29 and Al 0,33 because even if Al 0,29 is the lightest sample with the highest Chroma, the reflectance of Al 0,33 painting is the highest. Anyway, when both Al paintings are compared with Si paintings *(figure 19)*, it is observed that Si painting is the one with the highest reflection in visible light region even though lightness and Chroma of Al are much higher, but Al 0,33 (and Al 0,29) painting has the highest reflection in the infrared region. Because Silicon is quite shining on his own, its luster likely helps increasing the reflectance into visible light. Thus, it is possible to keep a strong red color but very shining. But finally the most promising painting for heat-resistant pigment is Al 0,33 (and Al 0,29) painting.

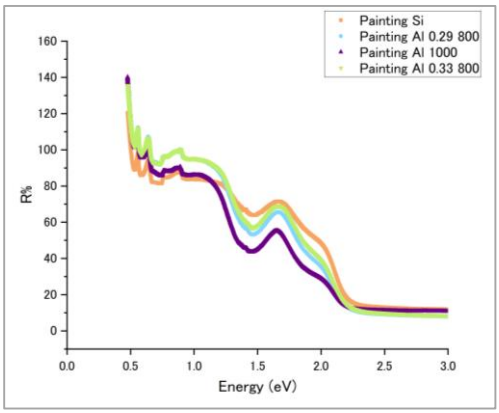


Figure 19: Optical spectra comparison between Si and Al paintings.

CONCLUSION:

As a matter of conclusion, hematite has been synthetized through two methods: a precipitation method and the ultrasonic spray pyrolysis method. With these two methods, respectively fibrous pigments and spherical pigments were produced. It has been seen that the shape was influencing particles size, but also color which is linked to the bandgap. Fibrous pigments were the ones with the highest values. Moreover, brighter samples have been produced either by adding Aluminum, either by adding Silicon and the amount added was varying in order to find the brightest. By brightest sample, we mean very light color but still intense, with a high reflectance. The brightest ones, in terms of color and lightness, were obtained at 800°C when adding Aluminum for 0,29 and 0,33 Al. It has been seen that the sample lightness was a consequence of the crystallite size diminution and of the lattice parameters diminution. Also Al 0,29 obtained at 800°C was the one with the highest Chroma and Lightness. The color, linked with Chroma, is a direct consequence of the bandgap variation. Moreover, Al paintings reflectance was the highest in the infrared region. In that way, Al 0,29 and Al 0,33 samples are very promising ones for applications as cool pigments.

As a matter of personal insight, habits I took that helped me doing and learn new experiments was to write every step of it, especially time it takes in my laboratory book, even every tiny details as color, sound, and so one is important, especially when all the devices are not explained in English. I remember one time I didn't write that the X-Ray diffractometer would do a big sound for a relative long time when switching it on. And the first time I switched on the machine by myself, I was very surprise of that sound, and got even a little scared of it like if I had done something wrong, all because I did not write it on my book. Also, I learned to take my time when doing experiments. Indeed, inorganic chemistry and more precisely chemistry of pigments is not the more dangerous or the more difficult one. Nonetheless, precision and rigor are still required, especially when a whole synthesis takes more than 3 days. Having false results just because of a lack of rigor, precision or just because we were too fast is unfortunate. Read a lot of literature is also important before doing a new experiment.

I was very motivated by the subject because chemistry of pigments is first of all very beautiful and just by the color of samples, we know if the synthesis has worked out or not. I was also very excited each time I finished a synthesis to put all my samples together and just looked at them to see their differences. Their applications as paintings was also very interesting because when the painting is applied on the alumina board, I had the feeling to be a child again, painting on papers and drawing, but when I put the colored board into the furnace and recovered it after a day, there I saw it was real chemistry I was doing, especially when the painting was very glassy. The aim was and still is to use iron oxide pigments as heat-resistant pigments. But finally a negative point, that may not be changed, is that colors were sometimes not different enough to be differentiate on the camera used to take pictures. Only the human eye is that reliable.

This internship was an experience I was longing for for many reasons. Even if I already did an internship before, this one was my first long internship and with being very autonomous too. Before I used to think that it was easy to be autonomous, but in fact this is harder than I expected, and it requires responsibility and discipline. Also, as I am still not sure if I want to work into public system, or into companies, or to do a PhD degree, this internship was a first step to help me find answers and decide. The last but not least, apart from the scientific part, this internship was also a very great human experience I had. It was beyond all my expectations. Japanese people are so nice and welcoming and the country is so amazing. It is like nowhere else. I experimented living on my own for the first time and being apart from my family and for so long for the first time also. It has brought me even more autonomy. It was a very vivid experience, and I would do it one more time if I could do.

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, nº 7 (5 juillet 2018): 4017-21.

(3) Cesaratto, Anna, Yan-Bing Luo, Henry D. Smith, et Marco Leona. « A Timeline for the Introduction of Synthetic Dyestuffs in Japan during the Late Edo and Meiji Periods ». Heritage Science 6, no 1 (décembre 2018): 22.

(4) 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.

(5) Froment, Françoise, Aurélie Tournié, et Philippe Colomban. « Raman Identification of Natural Red to Yellow Pigments: Ochre and Iron-Containing Ores ». Journal of Raman Spectroscopy 39, no 5 (mai 2008): 560 68.

(6) Tamura, K.; Oshima, Y.; Fuse, Y.; Nagaoka, N.; Kunoh, T.; Nakanishi, M.; Fujii, T.; Nanba, T.; Takada, J. Eco-Benign Orange-Hued Pigment Derived from Aluminum-Enriched Biogenous Iron Oxide Sheaths. *ACS Omega* **2022**, *7* (15), 12795–12802.

(7) A New Series of Environment-Friendly Reddish Inorganic Pigments Based on AFeO3 (A ¼ Ln, Y) with High NIR Solar Reflectance.

(8) Balogun, M.-S.; Wu, Z.; Luo, Y.; Qiu, W.; Fan, X.; Long, B.; Huang, M.; Liu, P.; Tong, Y. High Power Density Nitridated Hematite (α-Fe2O3) Nanorods as Anode for High-Performance Flexible Lithium Ion Batteries. *J. Power Sources* **2016**, *308*, 7–17. https://doi.org/10.1016/j.jpowsour.2016.01.043.

(9) Segev, G.; Dotan, H.; Malviya, K. D.; Kay, A.; Mayer, M. T.; Grätzel, M.; Rothschild, A. High Solar Flux Concentration Water Splitting with Hematite (α-Fe2O3) Photoanodes. *Adv. Energy Mater.* **2016**, *6* (1), 1500817-n/a.

(10) Sivula, K.; Le Formal, F.; Grätzel, M. Solar Water Splitting: Progress Using Hematite (α-Fe2O3) Photoelectrodes. *ChemSusChem* **2011**, *4* (4), 432–449.

(11) 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.

(12) 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.

(13) Miftahul Khoiroh, L.; Mardiana, D.; Sabarudin, A.; Ismuyanto, B. Synthesis of Hematite Pigments (Alpha-Fe2O3) by Thermal Transformations of FeOOH. *J. Pure Appl. Chem. Res.* **2013**, *2* (1), 27–34.

(14) Gencel, Osman, Witold Brostow, Cengiz Özel, et Mümin Filiz. « Concretes Containing Hematite for Use as Shielding Barriers ». Medziagotyra 16 (1 janvier 2010).

(15) https://archeologie.culture.gouv.fr/chauvet/

(16) https://www.domainedulac-dordogne.com/lascaux/

(17) https://www.metmuseum.org/toah/hd/vase/hd_vase.htm

(18) Opuchovic, O.; Kareiva, A. Historical Hematite Pigment: Synthesis by an Aqueous Sol–Gel Method, Characterization and Application for the Colouration of Ceramic Glazes. *Ceram. Int.* **2015**, *41* (3), 4504–4513.

(19) Effects of Low Temperature on Aluminum(Iii) Hydrolysis: Theoretical and Experimental Studies.

(20) Prim, S. R.; Folgueras, M. V.; de Lima, M. A.; Hotza, D. Synthesis and Characterization of Hematite Pigment Obtained from a Steel Waste Industry. *J. Hazard. Mater.* **2011**, *192* (3), 1307–1313.

(21) Hosseini-Zori, M., E. Taheri-Nassaj, et A.R. Mirhabibi. « Effective Factors on Synthesis of the Hematite–Silica Red Inclusion Pigment ». *Ceramics International* 34, nº 3 (avril 2008): 491-96.

(22) Castagnotto, E.; Locardi, F.; Slimani, S.; Peddis, D.; Gaggero, L.; Ferretti, M. Characterization of the Caput Mortuum Purple Hematite Pigment and Synthesis of a Modern Analogue. *Dyes Pigments* **2021**, *185*.