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Order of Authors: H el ene Salomon; Colette Vignaud; Sophia Lahlil; Nicolas Menguy

Abstract: Heating of prehistoric coloring materials can induce radical changes in color indicative of structural matter transformation. For instance, the structure of the yellow iron oxide-rich mineral, goethite, changes into the red iron oxide-rich mineral, hematite, when it is heated to around 250-300oC. For a long time, heating has been thought to be the reason for the high frequencies of red rocks used in camp sites and the red pigments in rock art paintings. However, records of heat-treatment of coloring materials are usually not well documented; the contextual information is not clear enough to confirm intentional heating. Two Solutrean camp sites (the flint workshop Les Ma treaux and the hunting site Combe Sauni re I) and one middle Magdalenian cave with rock art (Grotte Blanchard, La Garenne) allow us to study the heating process of ferruginous rocks. All three sites, which have been excavated relatively recently, have well-defined archaeological records and strong associations between the ferruginous rocks and other artifacts. With the use of X-ray diffraction and electron μ -diffraction for identifying structural modification and SEM-FEG and TEM-FEG for detecting dehydration nano-pores, we have strong evidence for intentional heat-treatment of yellow goethite-rich materials in two archaeological contexts and one site for unintentional heating, where rocks were only partially transformed. Intentional heating to obtain red hematite from primary goethite would have required ingenious methods of temperature control in fireplace settings and purpose-built ground ovens.

Highlights (for review)

- We documented intentional and accidental heating of pigment at palaeolithic sites.
- We evidenced planned and well-controlled intentional heating to produce red hematite.
- We concluded to the set-up of sophisticated procedures to heat-transform goethite.

Liège, 18th December 2014

Editor : *Journal of Archaeological Science*

Dear editor,

Please find enclosed the revised version of the manuscript entitled: Solutrean and Magdalenian ferruginous rocks heat-treatment: accidental and/or deliberate action? by *Hélène Salomon, Colette Vignaud, Sophia Lahlil and Nicolas Menguy*, proposed for publication in *Journal of Archaeological Science* (Ref. JASC14-570).

We thank the reviewers for their support and comments. We have modified the manuscript according to these comments and queries which significantly improved our manuscript. Please find below a detailed response to each comment point by point in *italic gray* to address the reviewers' concerns.

Reviewer #1: This is a most interesting project and the experimental and laboratory work appears thorough and well conducted. The evidence for distinguishing deliberate versus accidental heating of ochre is important and worthy of publication.

There are some issues that need to be resolved before the paper can be published. First, the text needs editing because there are some spelling and grammatical lapses. I understand that the authors are not first language English speakers and, under the circumstances, they have done a good job. However, the paper is not yet ready for the journal.

**Authors: The paper has been modified by a native English speaker.*

Secondly, the claim (line 263) that this is the first clear archaeological evidence for controlled heating of colouring materials is not strictly true. See:

Godfrey-Smith, D.I. & Ilani, S. 2004. Past thermal history of goethite and hematite fragments from Qafzeh Cave deduced from thermal activation characteristics of the 110°C TL peak of enclosed quartz grains. *Revue d'Archéométrie* 28: 185-190.

Hovers, E., Ilani, S., Bar-Yosef, O. & Vandermeersch, B. 2003. An early case of colour symbolism: ochre use by modern humans in Qafzeh Cave. *Current Anthropology* 44: 491-522.

** Authors: To our opinion, these references are not fully relevant to assert **intentional heat-treatment of yellow pigment** because:*

- Hovers et al. (2003) support that yellow lumps have been heated because red ocher is less common than yellow ocher in the area surrounding the site and they appear to have been selected, mined, and used specifically for their hue. At the supposed raw material outcrop, goethite is more common than hematite (but hematite is not absent from the region of Qafzeh). This suggested to the authors that the yellow material was collected far from the site and heated in a second step. However, the analysis of the coloring materials (XRD and ICP-AES) does not give any clue on heating process. The XRD patterns are not described nor joint to the text.*
- Godfrey-Smith and Ilani (2004) reached a similar conclusion using Thermoluminescence analysis (TL) of the quartz grains contained in only 3 red fragments from Qafzeh. The analysis revealed that two fragments were heated to a temperature estimated between 300° and 450°, which may have reddened their original hue, if the fragments were mainly composed of goethite, assumption that was not verified. Indeed, TL does not give any information on the mineralogical composition of the lumps before heating. With this paper, we learn that 3 red pieces had been exposed to heat, but we do not know if the rocks were*

already red before heating. In this situation, it is impossible to conclude to a deliberate heat-treatment of yellow goethite to produce red hematite.

- *Furthermore, the archaeological background is not clear enough at Qafzeh to assert intentional heating, mainly because of the transformation of the sediment by breccification and because the spatial dispersion only shows a trend to a greater density of ochre in 4 m², but all along the sequence. In addition, experiments conducted by Wadley (2009) indicate that yellow iron hydroxide-rich materials buried between 5 and 10 cm under an open fire become red. Accidental heating is then possible, due to the close proximity to fire, and may explain the predominance of red pigments at sites where fires were repeatedly lit and maintained. For instance, the study we propose for publication in the present journal revealed most probable accidental heating in Combe Saunière I site which is a stratified camp-site, as is Qafzeh cave.*
- *Although some clue may indicate the possibility that yellow iron oxide-rich rocks may have been heat-transformed into hematite, the diagnostic characteristics of such a transformation are lacking in the study of Hovers et al. 2003, and Godfrey-Smith and Ilani, 2005.*
- *However, Hovers et al. 2003, Godfrey-Smith and Ilani, 2005 are now cited in the state of the art (Introduction), to indicate that heating process is supposed in the Levantine Levallois horizons at Qafzeh, around 90 000 years ago.*

Thirdly, there is a claim that Les Maîtres is the only true pigment workshop evidenced for prehistoric times (line 378). This is not true because there is an ochre processing workshop at Blombos, dated 100 ka. See:

Henshilwood, C.S., F. d'Errico, K.L. van Niekerk, Y. Coquinot, Z. Jacobs, S.-E. Lauritzen, M. Menu and R. García-Moreno. 2011. A 100,000-year-old ochre-processing workshop at Blombos Cave, South Africa. *Science* 334: 219-222.

** Authors: modification of the text as follows: "The spatial distribution of the technical activities with evidence for a pigment workshop which must have involved heating processes and red powder production is unique in the Paleolithic record."*

**Henshilwood et al., 2011. Science, is not a relevant paper to cite in the current paper, since it is about a tool kit (with fragments of red ferruginous rock associated with possible pigment containers, bone and stone tools) dated back to the Middle Stone Age in South Africa. Our paper does not deal with all the cases of pigment processing which are numerous but with heat-treatment of pigment at three sites long after Blombos context.*

These references must be incorporated into the paper.

** Authors: Hovers et al. 2003, Godfrey-Smith and Ilani, 2005 are now cited in the state of the art (Introduction).*

The excellent figures are critical to the explanations of the transformations from goethite to hematite. However, I feel that the legends for these figures are not sufficiently explanatory. It would be useful for archaeologists who are not specialists in the field of heat treatment and crystal structures to have the figures explained briefly, but concisely in the legends. Spell out in the figure legend, the significance of particular crystal structures in heated versus unheated samples and comment on the meaning of dehydration pores.

**Authors: legends and figures (3-5, 7-10) modified according to the comments.*

Please also summarise in the Conclusions, the differences between the three types of goethite: acicular needle, multi-domainic and domainic star-like. Then explain their significance for the recognition of deliberate versus accidental heating of ochre.

** Authors: line 436-442, we modified the text to state it clearer: "In sum, although the corpus is*

quite small, we observed three types of goethite: acicular needle, multi-domainic and domainic star-like which could indicate three different kinds of raw goethite-rich material. The morphology of crystals is dependent of thermodynamic conditions during crystalization (rock formation and weathering). Here, the occurrence of three different morphologies may indicate probable three different geological origins. Only sub-hexagonal or hexagonal hematite crystals with well-developed thickness (in contrast to natural hematite) are characteristic of heated goethite at temperatures up to 650°C. During heating, the goethite crystals retain their original morphology until temperatures are high enough to start the recrystallization. In this latest situation, the morphology of the precursor goethite crystals is lost.”

Reviewer #2: The papers, using a multi-analytical approach, involving SEM, TEM and XRD, aims at providing clues to make out the difference between intentional and accidental (not incidental) heating process to produce haematite starting from goethite. The approach is then applied to three case studies.

The topic is certainly suitable for JASC and the paper, after the suggested modification and revisions might be re-considered for the publication in this Journal.

In this view, Authors might like considering the following list of comments/ corrections and modify the manuscript accordingly.

As a preliminary comment the referee believes that not all conclusions are coherently derived from the results and Authors should avoid too speculative statements. A list is provided herewith.

General comments

p.1, line 23 (see also the "first" abstract, p.0)

Referee:

Please, provide references, in the main text, to prove this statement that otherwise would look quite contradictory.

** Authors: This heating process has long been supposed to explain the high frequency of red rocks used in camp sites as well as red pigments in rock art paintings. However, very few occurrences of heat-treatment of coloring materials are well documented; their contextual information is not clear enough to conclude to an intentional heating (see following comments). References were added line 57-65. Heat transformation of iron oxide-rich yellow rocks has long been assumed to be the reason for the predominance of red materials at some archaeological sites, and for the spatial distribution of the wide range of hues found around fire places at sites such as Terra Amata (Lorblanchet, 1999; Wreschner, 1985), Qafzeh (Hovers et al. 2003; Godfrey-Smith & Ilani, 2005) and Skhul (d'Errico et al., 2010; Salomon et al., 2012), in the Epigravettian at Gontsy (Ukraine) (Iakovleva & Djindjian, 2005), within the paintings at Lascaux (Dordogne, France; Pomiès et al., 1998a, 1999c), Altamira (Santander, Spain; Cabrera-Garrido, 1978; Couraud, 1987) and the Grande Grotte at Arcy-sur-Cure (Pomiès et al., 1999a; Baffier et al., 1999).*

p.1, line 30

Authors:

X ray and electron diffraction (XRD, TEM) for identifying this structural modification and SEM-FEG and TEM-FEG to evidenced

Referee:

Acronyms: electron diffraction is not TEM....this does not help the reader, especially from non-scientific fields.

** Authors: modified according to the comment.*

p.1, line 34

Authors:

Obtaining red hematite by heating primary goethite needs to control the temperature during the transformation process and the setting up of ingenious systems as the use of ovens or a continuous

care of the heat temperature in the fireplace

Referee:

The transformations, as concerns the colour change, does not really require particular control of the pyro-technological parameters and indeed has been inferred to be managed in quite primitive contexts where oven/furnace structures were far from being developed.

** Authors: the heat transformation at Les Maîtresaux probably required an oven underneath the fireplace and at La Garenne, continuous ventilation and management of fuel were necessary to reach a high temperature (> 650°C) and to maintain it. Even if heating yellow goethite to make hematite does not requires much care, on the contrary, both these archaeological records give evidence of sophisticated procedures to heat-transform goethite-rich rocks. Thus, we modified the sentence line 39-41 as follow: "Intentional heating to obtain red hematite from primary goethite would have required ingenious methods of temperature control in fireplace settings and purpose-built ground ovens."*

p.2, line 45

Authors:

The colors are even more red or purple as the temperature and/or the heating time increases.

Referee:

Provide references.

** Authors: modification line 56 as follow: " The redness becomes even more intense as the temperature and/or the heating time increases (Pomiès, 1997)."*

p. 5 line 146

Authors:

In contrast if the reflections are non-uniformly broadened, it is a clue that increases the probability of previous heating.

Suggestion:

In contrast if the reflections are non-uniformly broadened, this is a clue in favor of a previous heating.

**Authors: OK*

Referee:

Please, be more precise on the definition and relevant reasons for the "non-uniform broadening" of the diffraction peaks and provide relevant references, as this is a main issue for the paper and for the interpretation of the experimental results.

** OK Authors: precisions line 74-78: "For instance, the diffraction lines [102], [104], [023] and [214] are wider whereas peaks [110], [116] and [300] remain narrow. As a consequence of the non-uniform broadening, the diffractogram shows a typical inversion of intensity of the [104] and [110] peaks. These diffraction patterns data were refined by the Rietveld method (Rietveld, 1969)."*

p.5, line 152

Authors

This can be done using a more accurate analytical method such as Transmission Electron Microscopy (TEM)

Referee:

TEM is not really an "analytical method".

**Authors: Examination of sample by TEM.*

p.7, line 228

Authors:

All X-ray diffraction patterns corresponding to the twenty samples show a pure hematite phase with reflection peaks not uniformly broadened (Figure 5a),

Referee:

Difficult to notice from figure 5a not uniform broadening of the diffraction peak (see previous comment). Perhaps a plot of the broadening of the different peaks would help. How broadening was measured!?

**Authors: figure modified. We show the comparison of a reference hematite with MA01 diffractogram.*

p.12, line 377

Authors:

It revealed a spatial distribution of the technical activities...

Referee:

Not clear.

** Authors: Precisions added to the map of archaeological site Les Maîtreaux (figure 4) to support the text.*

p.12, line 378

Authors:

... true pigment workshop, the only one evidenced for prehistoric times up to now.

Referee:

The "pigment workshop", although interesting, is quite difficult to demonstrate on the basis of the picture emerging from the present work, even in view of the fact that, as demonstrated by other Authors, the transformation of goethite into haematite does not necessarily requires structures and sophisticated equipments. Indeed, this transformation may occur over a comparatively broad range of conditions that do not require accurate control, as even acknowledges by the Authors in other parts of the manuscript. Therefore, other reported comments, like "In fact it involves a continuous care of the temperature of the fireplace for times long enough to accomplish the structural internal transformation, and thus it indicates a deliberate action as a possible ventilation process (P. 13 line 395)" are very questionable indeed.

** Authors: besides the map of Les Maîtreaux which was completed, we added informations on the size and numbers of pieces according to each petrological range in sub-section 4.2.1. Spatial distribution of coloring materials.*

Besides, Les Maîtreaux is known as a flint workshop. The present study evidences a more complex organization of the production. It was demonstrated that other production activities took place at the same site at the same time. + see comment for p.1, line 34

Figure 2:

Size of the scale bar missing!?

**Authors: scale = 1 cm.*

Figures 4 and 5:

Are all these zeroes necessary for the two theta axis!?

Y axis: counts, a.u., other !?

**Authors: zeros deleted, counts added on Y axis.*

Figure 9 and 10: TEM pictures b) are clearly out of focus (double image)... no interference fringes: change main text accordingly.

**Authors: "interference edge" deleted in the text*

Remove all through the text (figure captions included) reference to microscopy magnifications, e.g., x 50000, x 250000, etc., that, unless pictures are reproduced exactly in the same format as the original one, are not correct!

**Authors: done*

State clearly, as applicable, in figure captions which features and/or details arrows are pointing at.

** Authors: figures and legend were modified according to reviewer's suggestion.*

Typos/general language aspects:

- introduce acronyms for experimental techniques, like SEM, TEM, etc., just once in the text and not repeatedly like it now!

**Authors: done*

p. 0

change of color - better : change in color

** Authors: done*

TEM-FEG to evidenced dehydration nano-pores - -> TEM-FEG to evidence dehydration nano-pores

**Authors: done*

p.3 line 69

This study is particularly relevant ... change to: This study is particularly important ...

** Authors: done*

p.4 line 125

Authors:

provides a preliminary mineralogical and geochemical approach of the prehistoric paintings of this site

Referee:

approach!?

** Authors: changed by "study"*

p.4, line 133

Authors:

... it is this question that we will develop hereafter

Suggestion:

... it is this issue that we will develop hereafter

** Authors: done*

p. 6, line 170:

with a LaB6 tip - change to: with a LaB6 gun

**Authors: change according to reviewer suggestion*

Check the text for typos and further statements, that can be improved. Homogenise English: either UK or US, not both and eliminate French ?!

**Authors: done*

Reviewer #3: This paper is of high importance for our knowledge on the transformation of colouring materials during Upper Palaeolithic. The question of heating yellow goethite to transform it in red hematite is an old question raised by A. Leroi-Gourhan during the 1960's. However, very few scientific and objective data were available until now in the literature. The demonstration that the heating process, when it was attested, corresponded to a deliberate action was still lacking.

Based on the study of archaeological collections of pigments from three Upper Palaeolithic sites in France, this paper fills a gap that existed in the studies on pigments transformation.

This research is based on the study of sites and samples that were very cautiously and judiciously chosen. The multi-step analytical methodology combined with archaeological considerations is totally adapted to the purpose of the work. The results are relevant and provide new robust data for distinguishing incidental process from deliberate heating treatment.

This article is thus absolutely adapted for publication by the Journal of Archaeological Science. However, several points have to be precised or detailed and I suggest the following modifications, before publication.

About the organisation of the paper

- some information on the state of the art on the way to identify heating treatment of iron oxides are missing in the introduction. The first paragraph p. 5 should be transferred to the introduction.

**Authors: done*

In this paragraph, it is indicated that superficial colors (brown to black zones, cracks, etc.) can provide clue of heating. Please be more accurate on this point: how can you establish relations between a surface state (color, cracks, ...) and a heating operation? Do you have data on reference materials that have been heated in controlled conditions that allow the establishment of such relationships? If yes, please provide more information and explain the criteria that help to distinguish heated and not heated block with a simple visual observation.

Same question for lines 201 and 202, p. 7, on which basis can you tell that brownish color and micro-cracks on their surface indicate that they may have undergone a heat-treatment ?

** Authors: Our own experiments provided us several examples of such stigmata (during experimental heating in oven and fire) and some ferruginous clay and clayey iron oxide-rich materials, cracks and different colors occurred. But these stigmata are far from being systematic. Line 247 has been modified: "However, three blocks of brownish to red coloring material have micro-cracks on their surface suggesting that they may have undergone a heat-treatment"*

Concerning the corpus of samples studied

A first section has to be added in the experimental part that defines the corpus of samples studied. Indeed, the number of samples studied is sometimes precised in section 2., for Grotte Blanchard for instance (p. 4, line 126), sometimes in section 4 (for Combe Saunière, p. 6, line 198) but we do not have clear information on the samples investigated. Please provide one or several tables that detail the references of the samples, their archaeological context, their description, the analyses performed on each sample and the main results obtained.

It would also be interesting to have an idea of the representativity of samples analysed.
- p. 9, line 277: the authors speak of 7 blocks at the Grotte Blanchard, 4 yellow and 5 black, which give a total of 9. Are there 7 or 9 blocks? On figure 6, there are the photos of only 6 blocks...

**Authors: Tables were added with description of the collection for each site. Description of the collection and sampling strategy is detailed in section 3.1. Analytical results are summarized in tables.*

XRD and analytical data

Concerning the characteristics of XRD for heated pigments (broadened diffraction peaks and inversion of intensity of the [104] and [110] lines), these details are provided only p. 9 of the paper (lines 284-291). It would have been interesting to provide these precisions before and to clearly show on the figures the broadened peaks, especially on figure 4a.

**Authors: description moved to the "Introduction" and picture 4a modified (experimental diffractogram compared to a reference hematite diffractogram with indication of the broadened and non broadened peaks).*

Why did the authors indicate the crystallographic planes on figure 5a and not on the others ?

**Authors: information added to every diffractograms.*

- p. 9, lines 281-282: yellow block only contain manganese ? What about goethite ? What explains the yellow color ?

**Authors: text changed line 358 as follow : "Yellow pigments contain goethite with quartz and hydrated manganese oxide impurities."*

- p. 11 : section 4.3.3.2.. The paragraph begins by « SM11 and SM20 samples » but in the text below, the results are provided for the only sample SM11. What about sample SM20 ?

** Authors: text modified line 418 as follow : "With low magnification SEM-FEG, the structure of SM20 sample is interpreted as needles with 0.3 to 0.5 μm length."*

Solutrean ovens

In the discussion on Solutrean ovens, p. 8, lines 249-258, please be more precise and indicate if ovens were recorded at archaeological sites or if the presence of ovens is supposed based on the heated treatment determined on several materials.

** Authors: Few archaeological contexts yielded structures for flint heating (Inizan et al., 1999). In most of the cases, heat-processing of flint for pressure flaking and retouch is deduced from the flint tools themselves. We added references line 321 to precise this point.*

Other comments

More information is needed on some of the archaeological sites cited in the paper. Indeed, Journal of Archaeological Science is read by several archaeologists that are not all familiar with the chronological contexts discussed in the paper. So I suggest either to add the sites cited on the map of figure 1 and / or to add precision in the text: - cf. Arcy-sur-Cure, p. 2, line 41

** Authors: French sites and Altamira (Spain) were added on the map (figure 1).*

- p. 3, lines 82-85: « The layer IV of Combe Sauniere I contains a lithic industry of the Upper Solutrean. It is dated with ^{14}C to a period between 17000 and 18000 BP, a contemporary phase of the last glacial maximum (Geneste and Plisson, 1986). »

This has been discussed using the new data on the Solutrean. First of all, it would be necessary to indicate if the dates 17000-18000 BP are calibrated or not. Since the paper cited just after is from 1986, I suppose that not, but this has to be specified. Second, the debate on the chronological limits of Solutrean in the south-west of France has evolved since 1986 and it is now considered Solutrean generally occurred before 19000 BP (not calibrated date). So please, revise this part, by using and citing, for example, the recent works of S. Ducasse, C. Renard and J. Zilhao.

** Authors: dates cal. B.P. added as well as references to S. Ducasse (2012) and C. Renard (2011).*

- p. 4, line 105 : what is the difference between a fragment and a block of coloring material? I guess that a block is a natural rock that has not been modified while a fragment results from an intentional (or not?) action on the initial block? If this is the case, please precise and explain how you can

distinguish these two categories; if not, please explain what is the difference.

** Authors: precision added line 136 according to reviewer's suggestion.*

References

For Pomiès et al., 1999, please indicate a, b or c for the three references (a and b are used but not c).

** Authors: done*

English language

Although I am not myself an English native speaker, it seems to me that some sentences should be improved. Here are some propositions but I think that this should be controlled by an English native speaker.

- in the abstract, line 32, please write « and TEM-FEG to evidence dehydration nano-pores... » instead of « and TEM-FEG to evidenced dehydration nano-pores... » *OK*

- introduction, line 39 : « The occurrence of heating colouring materials ... » instead of « The occurrence of heating of colouring materials ... » *OK*

- p. 2, line 41, please replace « Chatelperronian men » by « Chatelperronian people » or « Chatelperronian human beings » for example *OK*

- p. 2, line 45 : I am not convinced by the expression « even more red ». What does that mean? More red than what? Perhaps « more intense » would be more appropriate? *OK*

- p. 2, line 51 : this analytical strategy was applied to the study of different Paleolithic sites _ the Pyrenean rock-shelter of the Moulin of Troubat: please replace « _ » by « : » *OK*

- p. 2, line 53 : please provide precision on the signification of « pristine goethite »

** Authors : original*

- p. 2, line 53 : another problem with a « _ ». Lines 49 to 55 have to be read again and corrected because this is not clear *OK*

- p.2, line 66 : « where several archaeological contexts are involved ». This is not clear, please detail what you mean *OK*

- p. 3, line 86 : please use « associated with » instead of « mixed with » *OK*

- p. 4, line 111 ; what do you mean by « with peculiar properties as cavernous » ?

- p. 4, line 119, please suppress the parenthesis at the end of the sentence

- p. 5, lines 162-163 : « provides high-quality diffractograms with very little material ». I think it would be more understandable in this form « provides high-quality diffractograms even when a low amount of matter is available for analysis »

- p. 251, please check the sentence « in order that flint does not explode... »

Reviewer #4: The submitted manuscript is an interesting work aiming at to discriminate incidental from intentional heating of goethite in the archaeological context.

There are some points that need clarification from the authors:

-line 204: In Figure 4, the coincidence with a maghemite peak makes uncertain whether there is or there is not broadening of the hematite (110) peak. It seems to me that the broadening is homogeneous.

** Authors: figure has been changed. A comparison of the diffractogram of sample CS10 and reference hematite, with labeled peaks, shows clearly the broadened and no-broadened peaks.*

- line 207: it is not possible to see "1.5 nm pores" in Figure 4.

** Authors: scale bars added on the picture to show the different sizes of the pores.*

- line 209: maghemite may also result from weathering, therefore "All these results tend to confirm a heating process surely in presence of organic materials" seem to me a too strong statement; did the authors detect any carbon on such samples?

** Authors: Maghemite may indeed result from the weathering (oxidization of magnetite), although maghemite is metastable and turns to hematite (Nornberg et al., 2004; Cornell and Schwertmann 1996 already cited in the text). The ferruginous rocks identified in Combe Saunière are all from local origin, the Tertiary ferricrete formation up the limestone tables. This formation condition are not compatible with the genesis of magnetite, therefore it is reasonable to exclude a local formation of magnetite and maghemite (as described in the presentation of the site).*

- line 232: Figure 5 does not allow to see pores that are less than 5 nm in size and oriented along the hematite crystallographic axis; this is crucial and the figure needs improvement.

** Authors: figure modified. Scale bars are added on the picture to show some pores and we added the drawing of the pores alignment within the crystal.*

- lines from 254 - 267 (particularly lines 259 and 260): the conclusion on the use of the site as a pigment workshop is too speculative; there is no direct link between the colored fragments found at the site and the use of the sand pocket oven.

**Authors: Map Les Mâitreux site and text were changed to better show the spatial distribution of the artifacts, revealing the past activities conducted at the heart of the site. We argue that the site was a workshop for diverse economical activities of production: flint Laurel Leaf, backed bladelets and shouldered points in one hand, and pigment treatment (heating and powdering) in the other hand. The evidence of utilization are lacking at the moment. Lines 274-286 describe the petrological classes and the spatial distribution of the classes with precision of the size of the coloring artifact and their external aspect (rounded, raw blocks or sharp fragments).*

- line 268: yes, hematite prepared by heating is very pure, but the raw material (goethite) has to be pure as well, please rephrase it.

**Authors: OK*

- line 274: again too speculative; there is no solid support for the statement at all.

** Authors: line 346, references to the use of the abrasive property of hematite were added in the discussion (Christensen, 1996; White, 1996; Philibert, 1994).*

- line 285: please use height instead of intensity (intensity remains constant, but as the peak broadens its height decreases).

** Authors: line 74, this point has been precised.*

- line 307: X-ray diffractogram "free of anomalies"?

** Authors: line 385 "i.e. without broadening or inversed height of the [104] and [110] peaks" added to the text.*

- line 312: "(below nm)"? (sub-nano particles?)

**Authors: "The SM11 hematite, well-crystallized from heating, is very different from the poorly crystallized natural hematite found at this site or other studied sites" line 447.*

I believe that these are very important point that needs to be addressed by the authors.

1 **Solutrean and Magdalenian ferruginous rocks heat-treatment: accidental and/or**
2 **deliberate action?**

3

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14 Keywords

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16 Goethite, hematite, heat-treatment, Paleolithic, Solutrean, Magdalenian, SEM-FEG, TEM-
17 FEG, XRD, Combe Saunière, Les Maîtreaux, Blanchard, La Garenne

18

19

20 Abstract

21

22 Heating of prehistoric coloring materials can induce radical changes in color indicative of
23 structural matter transformation. For instance, the structure of the yellow iron oxide-rich
24 mineral, goethite, changes into the red iron oxide-rich mineral, hematite, when it is heated to

25 around 250-300^oC. For a long time, heating has been thought to be the reason for the high
26 frequencies of red rocks used in camp sites and the red pigments in rock art paintings.

27 However, records of heat-treatment of coloring materials are usually not well documented; the
28 contextual information is not clear enough to confirm intentional heating. Two Solutrean
29 camp sites (the flint workshop Les Maîtreaux and the hunting site Combe Saunière I) and one
30 middle Magdalenian cave with rock art (Grotte Blanchard, La Garenne) allow us to study the
31 heating process of ferruginous rocks. All three sites, which have been excavated relatively
32 recently, have well-defined archaeological records and strong associations between the
33 ferruginous rocks and other artifacts. With the use of X-ray diffraction and electron μ -

34 diffraction for identifying structural modification and SEM-FEG and TEM-FEG for detecting
35 dehydration nano-pores, we have strong evidence for intentional heat-treatment of yellow
36 goethite-rich materials in two archaeological contexts and one site for unintentional heating,
37 where rocks were only partially transformed. Intentional heating to obtain red hematite from
38 primary goethite would have required ingenious methods of temperature control in fireplace
39 settings and purpose-built ground ovens.

40

41 1 Introduction

42 Processing coloring materials is rarely documented, although the final segment of the “chaîne
43 opératoire”, i.e. the use of pigment for rock painting, has been more widely studied. Refining
44 our understanding of the socio-economical framework of Paleolithic hunter-gatherers,
45 depends on an understanding of exploitation strategies and other behaviors and activities such
46 as modification of the raw material. This paper focuses on a poorly understood aspect of
47 Paleolithic behavior – the modification of coloring materials by heating.

48

49 A. Leroi-Gourhan (Leroi-Gourhan, 1961), during his excavations of the Grotte du Renne at
50 Arcy-sur-Cure, made the assumption that Châtelperronian people (last Neanderthals, ca 45-40
51 ky cal.BP, Hublin et al., 2012) heated ferruginous rocks to modify the hue and experiment
52 with color shades to produce different coloring materials. It is well known that yellow
53 goethite takes on orange and red shades upon heating from 250-300° C. At these
54 temperatures, goethite is transformed into hematite by dehydration. The redness becomes
55 even more intense as the temperature and/or the heating time increases (Pomiès, 1997). Heat
56 transformation of iron oxide-rich yellow rocks has long been assumed to be the reason for the
57 predominance of red materials at some archaeological sites, and for the spatial distribution of
58 the wide range of hues found around fire places at sites such as Terra Amata (Lorblanchet,
59 1999; Wreschner, 1985), Qafzeh (Hovers et al. 2003; Godfrey-Smith & Ilani, 2005) and Skhul
60 (d'Errico et al., 2010; Salomon et al., 2012), in the Epigravettian at Gontsy (Ukraine)
61 (Iakovleva & Djindjian, 2005), within the paintings at Lascaux (Dordogne, France; Pomiès et
62 al., 1998a, 1999c), Altamira (Santander, Spain; Cabrera-Garrido, 1978; Couraud, 1987) and
63 the Grande Grotte at Arcy-sur-Cure (Pomiès et al., 1999a; Baffier et al., 1999).

64

65 Mineral transformation has been investigated using synthetic and natural goethite by M.P.
66 Pomiès (1997). It has been shown that the heating of ferruginous stones can be identified on
67 the basis of different criteria. Systematic analyses of superficial color zonations and

68 formations in macroscopic blocks (e.g., brown to black zones, cracks, etc.) and spatial
69 relationships of heat remains, may provide clues of heating. The micro-structure of the
70 coloring materials is also a good indicator of heat treatment. X-ray powder diffraction pattern
71 of hematite resulting from a heated goethite will display specific broadening of the peaks with
72 typical relative intensity ratios (Pomiès et al., 1998b, fig. 3). For instance, the diffraction lines
73 [102], [104], [023] and [214] are wider whereas peaks [110], [116] and [300] remain narrow.
74 As a consequence of the non-uniform broadening, the diffractogram shows a typical inversion
75 of intensity of the [104] and [110] peaks. These diffraction patterns data were refined by the
76 Rietveld method (Rietveld, 1969). Selective broadening of diffraction peaks appears to be
77 related to disorder in the cationic sub-lattice, i.e. in the repeating array of Fe^{3+} (Pomies,
78 1998b).

79

80 If a uniform broadening of diffraction peaks occurs, it is likely that the sample is natural and
81 poorly crystallized. In contrast, non-uniform broadening can be an indicator of previous
82 heating. Another indication of heat treatment can be seen in the dehydration pores of single
83 crystals, whereby dehydration has induced topotactic transformation of hydroxide into oxide,
84 changing goethite into hematite. When the dehydration-induced topotactic transformation
85 occurs, the organization and shape of the dehydration pores is dependent on the size of the
86 original crystal, temperature and duration of heating (Pomiès et al., 1999b). This can be
87 observed with advanced microscopy techniques such as Transmission Electron Microscopy
88 (Pomiès et al., 1999b).

89

90 M.P. Pomiès specified crystallographic features of a heated synthetic goethite-hematite and
91 the criteria for identifying heated archaeological hematite. Through the investigation of
92 micro-samples of coloring materials, this analytical strategy was applied to the study of
93 different Paleolithic sites showing:

94 1) possible heat treatment of original goethite at the Pyrenean rock-shelter of the Moulin of
95 Troubat where Magdalenian and Azilian inhabitants dwelt (Pomiès et al., 1999a), ;

96 2) possible intentional heat treatment at the Mousterian grave site of the es-Skhul rock-shelter
97 of long distance supplies of yellow goethite-rich lumps (Salomon et al., 2012; d'Errico et al.,
98 2010).

99 3) there was no heat treatment applied to about one hundred pigments sampled from wall fig-
100 ures and cave deposits at the Lascaux cave site, indicative that the wide variety of hues used

101 there during the Solutrean and Magdalenian were natural (Menu et al, 2006; Vignaud et al.,
102 2006; Chalmin et al., 2005; Pomiès et al., 1999b, 1999c, 1998a).

103 Additionally, an extensive study of all excavated coloring materials from the Chatelperronian
104 levels of the Grotte du Renne at Arcy-sur-Cure showed that all coloring remains come from
105 non-heated rocks obtained via specialized strategies for procurement of raw materials with
106 various shades of color (Salomon et al., 2014; Salomon, 2009; Salomon et al., 2008).

107

108 In this paper, we present results of the analyses of coloring material from three Paleolithic
109 sites with different archaeological contexts (a Solutrean flint workshop and hunting station,
110 and a Magdalenian occupation site with rock art). All three sites (Figure 1), which have been
111 recently excavated, have very good archaeological integrity and well-understood chronology.
112 Furthermore, they have large quantities of coloring materials, essentially red, in well-defined
113 contexts that help distinguish accidental and controlled heating for red materials. .

114

115 2. Overview of the three sites

116 2.1. Combe Saunière I

117

118 The hunting camp-site in the Combe Saunière I cave (Sarliac-sur-Isle, Dordogne), located
119 near the confluence of the Isle and the Auvézère, was excavated from 1978 to 1996 (Chadelle
120 et al., 1991). On the east of the site, sandy-clay tertiary deposits called "siderolithic" usually
121 associated with many iron pisolites and fragments of ferruginous crust, outcrop on top of the
122 plateau (Guillot et al., 1979) that we sampled and documented. The layer IV of Combe
123 Saunière I contains a lithic industry of the Upper Solutrean. It is dated with ¹⁴C to a period
124 between 19 000 and 20 000 BP (23 000-24 000 cal.BP), contemporary with the last glacial
125 maximum (Ducasse, 2012; Renard, 2011; Geneste and Plisson, 1986).

126

127 Layer IV yielded a variety of artifacts closely associated with faunal remains, especially
128 abundant lithic spearheads (Solutrean shouldered points) and bone spearheads (with one or
129 two longitudinal grooves) (Castel et al., 1998, Geneste and Plisson, 1986). The numerous
130 spearheads are often damaged or broken as a result of use in hunting activities. In addition,
131 the site is characterized by its abundance of red and black coloring materials, some with
132 smoothed facets and/or with striations (Chalmin et al., 2006; Regert, 1995). It has no furniture
133 or parietal art (Figure 2). Four hundred and forty-two blocks and fragments of coloring

134 materials were identified in the well-defined Solutrean levels of Combe Saunière I: levels IVb
135 and IVc. 'Blocks' are defined as non-fragmented coloring rocks which may have
136 anthropogenic traces of use such as facets, grooves, striations or polished surfaces, or they
137 may be 'raw' i.e. un-used. 'Fragment' is a generic term for blocks with natural of
138 anthropogenic fractures.

139

140 2.2. Les Maîtreaux

141

142 The flint workshop site of Les Maîtreaux is located near the Claise river which carves a valley
143 in the Upper Cretaceous and Eocene formations. Tertiary ferruginous crust and clay with
144 pisolithes occur in the region on top of the limestone tables. The excavations of Les
145 Maîtreaux, conducted by Thierry Aubry and Bertrand Walter from 1994 to 2004 in Bossay-
146 sur-Claise (Indre-et-Loire), uncovered several Solutrean open-air occupations. These had re-
147 mains indicative of a Pressinien flint-flaking workshop for production of Laurel Leaves of
148 various sizes, shouldered points and backed bladelets. The authors conclude that several activ-
149 ities were performed at the location of this workshop, and there was specific spatial organiza-
150 tion (Aubry et al., 2004, 1998).

151

152 The deposit of Les Maîtreaux had significant concentrations of blocks and fragments of color-
153 ing materials covering an area of about 20 m². Over one thousand are present, belonging to
154 various mineralogical types.

155

156 2.3. Grotte Blanchard (La Garenne)

157

158 The Grotte Blanchard (La Garenne, Saint Marcel, Indre), was discovered in 1956 by J. Allain
159 during the Grand Abri exploration (Allain, 1957). It constitutes a reference site of the Middle
160 Magdalenian called "à navettes" (Allain et al., 1985). Open to the south, on the right shore of
161 the Creuse valley and at an elevation of 120 meters, the cave occurs in a Bajocian Jurassic
162 limestone bench. In this limestone, which is naturally very cracked, archaeological material
163 such as flint, bone and hard animal materials were found embedded in wall cracks. Wall
164 paintings and carved stones were also present (Despriée et al., 2001). A study by Jezequel et
165 al. (2011 and 2001), provides a preliminary mineralogical and geochemical study of the cave
166 wall paintings. The presence of numerous fireplace structures in the Grand Abri and the

167 Grotte Blanchard suggests that the pigments may have been heated before use. This study
168 investigates this possibility.

169

170 3. Experimental methods

171

172 3.1. Classification and sampling strategy

173 Following examination with low power magnification, Les Maîtreaux and Combe Saunière I
174 collections (1021 and 538 pieces, respectively) were classified into petrological ranges with
175 respect to their color, hardness, cohesion, recognizable mineral inclusions (nature, size,
176 dispersion, and morphology), external and internal aspect (mat or bright, with metallic
177 shimmer) and features (porosity, foliations, etc.) (Salomon et al., 2013). In the next stage of
178 analysis, according to the spatial distribution, the state (raw block or fragment, piece with
179 wear traces) and the petrological nature of the artifacts, each class was sampled to obtain
180 a sub-sample representative of the range of raw coloring materials present in the
181 archaeological layers. They were carefully selected so that the diverse configurations of their
182 spatial relationships with the other artifacts could be illustrated. Additional samples from the
183 biggest blocks of one specific class concentrated in the same area in Les Maîtreaux were also
184 analyzed (Tables 3 and 4).

185

186 All the samples were described using high magnification examination (SEM), elemental
187 (EDX) and mineralogical analysis (XRD). TEM and thin section examination with
188 petrographic microscopy was used for some samples. The results, which were interpreted
189 according to the spatial distribution of the artifacts, showed several samples with heating
190 stigmata.

191

192 Material from the Magdalenian levels of the La Garenne site, held in collections at the
193 Argentomagus Museum, was sampled in 2010. Six artifacts of pure pigments with various
194 aspects and colors were selected from the large collection of raw pigments. In addition, 31
195 objects with traces of pigment residues were sampled. The XRD and PIXE results of micro-
196 analysis of pigments, either raw or on bone, are reported by Lahlil et al. (2014).

197

198 3.2. Investigation of the nature and characteristics of crystalline phases using XRD and non
199 destructive μ -XRD

200

201 In addition to the traditional X-ray diffraction (XRD) device (Siemens D5000, cobalt anode
202 Co K- α , 2θ between 10 and 80°, acquisition time between 2 and 12 h), which requires a
203 significant amount of material ground into powder, a new non-invasive micro-X-ray
204 diffraction (μ -XRD) device was used to identify the crystalline phases present in the blocks of
205 coloring materials. This apparatus, developed by the C2RMF laboratory, provides high-
206 quality diffractograms and can be used for analysis of small-sized particles. The
207 diffractograms are recorded in 2θ from 5 to 60° with a copper anode (Cu K- α). The Fit2D
208 software is used to process the diagrams, and the EVA software for the assignment of the
209 diffraction lines (de Viguerie et al., 2009).

210

211 3.3. Investigation of the crystal morphology using SEM-FEG and TEM-FEG observations

212 The investigation of crystal morphology relies on the use of Scanning Electron Microscopy
213 (SEM) with a tungsten filament, or a field emission gun (SEM-FEG) and Transmission
214 Electron Microscopy (TEM) with a LaB6 filament or a field emission gun (TEM-FEG). Each
215 device is coupled to an X-ray energy dispersive analyzer (EDX) allowing the elemental
216 chemical analysis of the observed zone.

217

218 The experimental conditions are as follows: raw blocks or micro-samples are examined under
219 vacuum without special preparation with the Philips SEM XL30 of the C2RMF Laboratory
220 under a voltage acceleration of 5 at 10 kV to avoid charging effects; the X-ray energy
221 dispersive analyses (EDX) are performed under 20 kV. Samples containing crystals smaller
222 than one micrometer were also studied with the SEM-FEG (Geminiultra TM55, Carl Zeiss
223 instruments) of the Laboratoire Interfaces et Systèmes Electrochimiques (LISE) facility, at
224 the CNRS-Paris VI. Using an acceleration voltage of 5 kV or 10 kV and a 2.3 mm working
225 distance and application of gold coatings, these settings enable examination of material up to
226 200 000 magnification.

227

228 Transmission Electron Microscopy (TEM-FEG), which requires special preparation, is partic-
229 ularly effective for examining very thin crystal aggregates, as it can distinguish the internal
230 crystallographic structure as grain boundaries and twins, precipitates and internal nano-pores
231 of single crystals with high definition. A Jeol 2100 F microscope of the *Institut de minéralo-*
232 *gie et de physique des milieux condensés* (IMPMC) set at 200 kV was used, coupled with an

233 EDX spectrometer (PGT- PRISM 2000 equipped with the IMIX software) with a 1 nm beam
234 size and a 300 s acquisition time. Particle size was analyzed using the standard analysis soft-
235 ware for processing digital images (Gatan Digital Micrograph, Scion Image) and electron dif-
236 fraction patterns were indexed with the CaRIne Cristallography software. Such patterns per-
237 mit differentiation of hematite from goethite (hexagonal or orthorhombic structure, respec-
238 tively); this cannot be done using elemental analysis.

239

240 4. Results and discussions

241 4.1. Combe Saunière I : accidental heat treatment?

242 In Combe Saunière I, macroscopic and petrographic observations as well as XRD analysis
243 indicate that most of the collection of coloring material consists of a natural mixture of
244 hematite, goethite and quartz (400 blocks). These have the same features as the ferruginous
245 pisolithes and concretions we collected from the top of the plateau (Salomon, 2004; Salomon
246 2013). Red blocks are in class 1, whereas the yellow-brownish blocks are in class 2 (Tables 1
247 and 2). However, three blocks of brownish to red coloring material have micro-cracks on their
248 surface suggesting that they may have undergone a heat-treatment.

249 The X-ray diffraction patterns of class 1 and class 2 artifacts show a natural mixture in
250 various proportions of quartz and, respectively, hematite or goethite. The three brownish to
251 red blocks (class 1 and 2) yield different diffractograms. The powders sampled at the external
252 surface of the three blocks show the coexistence of a hematite phase with non-uniformly
253 broadened diffraction peaks and a maghemite phase (Table 3; Figure 3a). On the contrary, the
254 internal part of these blocks contains only goethite and quartz. Electron diffraction patterns
255 confirmed the presence of an internal phase of goethite, and a hematite phase on the external
256 part of the blocks. The 1.5 to 10 nm large longitudinal dehydration nano-pores found in the
257 hematite crystals clearly show a dehydration process (Figure 3b-c). Moreover, the maghemite
258 phase confirms heating in direct contact with organic materials. It is likely that, exposed to a
259 moderate temperature (estimated $< 350^{\circ}$ C), these blocks have been heated. Only surfaces
260 were affected and superficial red hematite crystals formed. The presence of some maghemite
261 indicates that the blocks could have been in contact with wood and food fats in a fireplace
262 (Nørnberg et al. 2004; Grogan et al., 2003; Schwertmann and Cornell, 2000; Cornell and
263 Schwertmann, 1996). Since block surfaces could have been blackened simply by being close
264 to burning organic material (Pomiès, 1997; Audouin and Plisson, 1982), and there are no
265 traces of use, such as facets, smoothed surfaces, scars or striations, the heat treatment was

266 probably not intentional. It is therefore conceivable that these blocks were either very close to
267 an active fireplace or left in a fireplace when it was extinguished but still hot.

268

269 4.2. Les Maîtres

270 4.2.1. Spatial distribution of coloring materials

271 The artifacts were identified and distributed in five different classes based on their macro-
272 scopic, petrographic and mechanical characteristics (Tables 4 and 5; Salomon et al., 2013; Sa-
273 lomon, 2009):

274 - Class A: almost pure iron oxide-rich blocks and sharp fragments which are cavernous, red to
275 black, and have a medium hardness of 3 on the Mohs scale and an uneven compactness. All
276 specimens are concentrated in squares N14, M13 and M14 (Figure 4);

277 - Class B: soft goethite, yellow, rounded pieces, concentrated in the S-W of square N19 (29
278 pieces);

279 - Class C: pink ferruginous sandstone with rounded quartz grains, concentrated in the N-E of
280 square N19 (51 pieces);

281 - Class D : multi-hue blocks and fragments (yellow, orange, red and black with metallic shim-
282 mer) of ferruginous sandstone more or less rich in sub-angular quartz grains, medium hard-
283 ness, spread over a large area with two flint concentrations (86 pieces);

284 - Class E: dark red, soft, porous, homogeneous and clayey blocks and fragments showing yel-
285 low, red and black minerals at low magnification, spread over the same area as class D arti-
286 facts (184 pieces) - three refits were possible and two pieces had micro-striations with polish.

287

288 We focus here on class A, which consists of more than 500 pieces (i.e. half of the collection)
289 recovered from 3 square meters. Within this area there were two concentrations of class A ma-
290 terial, each yielding more than 200 sharp fragments smaller than 1 cm. In square M14, six
291 class A raw blocks were found between the two main concentrations of fragments. Therefore,
292 the spatial organization and the large amount of little sharp pieces are indicative of activity ar-
293 eas used for crushing and grinding of coloring material (Figure 4). The XRD study of class A
294 samples shows that the red materials are composed exclusively of a mixture of hematite and
295 approximately 5% quartz. Furthermore, it was possible to distinguish the specific characteris-
296 tics of a heated goethite.

297

298 Our second sampling was aimed at testing the possibility of distinguishing intentional versus
299 unintentional heating of goethite. Nine of the largest blocks, all exceeding 5 cm, were selected
300 and sampled at internal and external points. All X-ray diffraction patterns corresponding to
301 the twenty samples show a pure hematite phase with diffraction lines not uniformly broadened
302 (Figure 5a), indicating the possible use of heat treatment. Further examination and analysis by
303 TEM (5 samples, i.e. 2 internal and 3 external) shows dehydration nano-pores of less than 5
304 nm diameter (Figure 5b). These are oriented along the longitudinal crystallographic direction
305 of the hematite crystals that retained the shape of the acicular precursor goethite crystals
306 (Figure 5c-d). Original blocks of goethite pigment must have undergone significant
307 penetrative heat treatment, that resulted in their complete transformation to hematite. We
308 summarize the results in table 6. We can infer that the temperature used was high enough and
309 the duration long enough to complete the phase of transformation homogeneously into the
310 core of the biggest objects. Using the results of M.P. Pomies (1999b) who studied the pore
311 size as a function of temperature in a synthetic goethite, we can estimate, from the very small
312 pore size (less than 5 nm), that the temperature used was probably in the range of 300-400° C,
313 and that the heating lasted at least two hours to induce a fully uniform transformation of all
314 crystallites.

315

316 According to the spatial distribution of the remains at the campsite, the concentrations of red
317 coloring materials of heated class A pieces were at the edge of a large pile of flint and is not
318 associated with any burned artifact or a fireplace. Therefore, it is likely that the heated class A
319 materials, organised in such a restricted area, do not result from an accidental heating
320 following their deposition (cf. Wadley et al., 2009).

321 Moreover, after ethnographical records (Inizan et al., 1999), experiments (Crabtree and Butler,
322 1964) and studies of heat-treated siliceous flaked artifacts (Schmidt, 2012; Aubry et al., 2003;
323 Kuzmin & Orlova, 1998; Tiffagom, 1998), the Solutreans are known to have used heat-
324 treatment of flint to enhance the knappability, and thus facilitate the Laurel Leaf shaping and
325 retouch of tools using pressure-flaking. In order to prevent flint exploding in fireplaces,
326 Solutreans would most likely have heated flint in ground ovens to homogenize the heat to
327 ensure gradual rise and fall of temperature. We can assume that a similar heating strategy was
328 applied to class A materials, since there is good evidence that they were not directly exposed
329 to burning organic material, but were heated for a relatively long time at well-controlled
330 temperatures between 300 and 400° C. This combination of evidence (the spatial distribution

331 of class A sharp fragments and raw blocks as well as the intentional, homogeneous heating of
332 all of the artifacts in the area) allow us to conclude that the flint flaking workshop in Les
333 Maîtreaux also included a workshop for the preparation of red powder.

334

335 The practice of intentional heating of yellow material points to a good knowledge of fire and
336 fireplaces by Solutreans. It also demonstrates a thorough knowledge of the properties of the
337 coloring materials. It is, to date, the first strong archaeological evidence that confirms the
338 hypothesis that controlled heating of coloring materials was used for the production of a
339 specific red coloring material. Our results also show that flint workshops were places of
340 diverse activities of production, probably conducted by different members of the group who
341 had complementary tasks.

342

343 Since the heat-produced hematite is a near pure product, we support the hypothesis that the
344 aim of heating was to produce a particular well-characterized material with controlled and
345 known properties, namely pure hematite. This is a mineral with powerful coloring, drying and
346 abrasive properties (Christensen, 1996; White, 1996; Philibert, 1994). Moreover, as the So-
347 lutreans had at their disposal other red materials that they brought to the site in their natural
348 state (hematite-rich clay, ferruginous sandstone, goethite-hematite-rich sandstone), and since
349 quartz is rough, it is most likely that, the desired raw material had to be poor in quartz. It was
350 not only designed to be a coloring material but possibly an abrasive for the bone and antler in-
351 dustry as well.

352

353 4.3. The Grotte Blanchard in La Garenne

354 One black and five pigment fragments (Figure 6a; Table 7) were analyzed. The elemental
355 composition was determined by PIXE using the C2RMF facility and the mineralogical
356 structure determined by micro-X-ray diffraction (Lahlil S. 2014). Red pigments are, overall,
357 relatively pure and are made of hematite. Yellow pigments contain goethite with quartz and
358 hydrated manganese oxide impurities. X-ray diffraction shows two types of red pigments.
359 One block has narrow diffraction lines characteristic of the natural origin of the pigment,
360 while the remaining 4 red blocks have diffraction lines that are broadened, with an inversion
361 of intensity of the [104] and [110] lines (Figure 6b).

362

363

364 TEM-FEG was used in the IMPMC laboratory to identify the use of heating. We selected a
365 red material with narrow X-ray diffraction peaks (SM16) as a reference for natural material
366 and four samples with broadened diffraction peaks (SM03, SM11, SM20, SM22) to check if
367 the characteristics observed were due to the small size or preferred orientation of crystals,
368 rather than heat-treatment of an original goethite. For comparison we also studied the only
369 black sample (SM04). XRD analysis showed this to be goethite, not manganese oxide as
370 expected. The results are summarized in Table 8.

371

372 4.3.1. Black goethite

373 This goethite presents traces of manganese oxide identified by EDX. At low magnification,
374 the mineral shows a compact and botryoidal structure (Figure 7a) with a cross-section that has
375 a radial stratified structure made of longitudinal crystals oriented along the diameter (Figure
376 7b). The internal structure is less compact and needle-like crystals of several microns long are
377 completely disordered or assembled into "bundles" (Figure 7c). When crushed for TEM
378 observations, the resulting powder is yellow. Electron diffraction allowed the identification of
379 single acicular goethite crystals, very thin, 300 to 500 nm long and 50 nm wide without nano-
380 pores or signs of dehydration (Figure 7d).

381

382 4.3.2. Natural hematite

383 SM16 is a red lump of material which has sets of parallel grooves on its surface indicative of
384 anthropogenic modification. The X-Ray diffractogram is free of anomalies, i.e. without
385 broadening or inverted height of the [104] and [110] peaks. The large sheets observed in
386 SEM-FEG (Figure 8 a, b, c) have been destroyed by grinding in an agate mortar, for grid
387 preparation and TEM examination. Electron micro-diffraction is characterized by continuous
388 thin concentric rings; some d_{hkl} rings are missing indicative of a polycrystalline structure with
389 sub-nano grains preferentially oriented (Figure 8d).

390

391 4.3.3. Hematite with an anomalous X-ray diffractogram

392 4.3.3.1. First case

393 The morphology observed by SEM-FEG is different for each sample. SM03 is a star-like
394 multi-domainic, twinned goethite (Figure 9a). SM22 is a multi-domainic goethite crystal with

395 parallel subunits referred to as domains or intergrowths (Figure 9c). Both goethite
396 morphologies may arise from the alkaline nature of the growth media. These samples contain
397 also hematite crystals, that give the red color to the blocks. These coexist with goethite
398 crystals. The hematite, identified by electron micro-diffraction, has an acicular morphology
399 characteristic of goethite with internal dehydration nano-pores. This morphology is
400 characteristic of heated precursor goethite crystals and is transformed at relatively low
401 temperatures (Pomiès et al., 1999b). The nano-pores are spherical (Figure 9b) for SM03 or
402 longitudinal along the [001] axis of the precursor crystal (Figure 9d) for SM22. The residual
403 goethite is due to incomplete transformation.

404

405 4.3.3.2. Second case

406 SM11 and SM20 samples have hematite crystals that do not contain pores. The SEM- FEG
407 micrographs show diagnostic morphologies. The crystals in the SM11 sample are elongated
408 and thick with a parallelepiped form and faceted extremities (length 2 to 3 times the
409 thickness), or occur as hexagonal "pellets" (Figure 10a) indicative of a prolonged heating
410 temperature of at least 650° C (Pomiès, 1997). The TEM examination of these crystals shows
411 some crystals still transparent to the electron beam. They are elongated with developed
412 thickness and have rounded or quasi-hexagonal shaped extremities (Figure 10b). Some of
413 them have coalesced, indicating an advanced goethite-hematite transformation as a result of
414 heating over 650° C. Crystals grew in three directions and dehydration is complete. Notably,
415 the good agreement between the SEM-FEG and TEM-FEG results excludes the interpretation
416 of TEM observations as isolated cases.

417

418 With low magnification SEM-FEG, the structure of SM20 sample is interpreted as needles
419 with 0.3 to 0.5 µm length. At higher magnification a pile of platelets with sections estimated
420 to 15-17 nm thick, sometimes with a clearly hexagonal shape (Figure 10c) can be discerned.
421 Figure 10d (TEM-FEG) shows both pseudo acicular and hexagonal morphologies, identified
422 by electron micro-diffraction as hematite. Three single crystals have coalesced to form one
423 polycrystal with grain boundaries. The transformation goethite-hematite is no more topotactic
424 than the SM03 and SM22 cases. Atom migration has enabled recrystallization tending towards
425 an hexagonal morphology characteristic of the hematite structure. Acicular crystals reflect the
426 shape of the precursor goethite crystals. When compared with synthesized goethite that has
427 been experimentally heated (Pomiès et al., 1999b), we estimate that the transformation from
428 goethite occurred at temperatures between 650 and 800° C.

429

430 For SM11 and SM20 samples, the thermal history of the hematite-rich fragments recorded by
431 the crystals documents a high temperature of heating that was continuously maintained by
432 probable ventilation and/or fuel addition. Since there are no finds with original rock surfaces,
433 we cannot determine if there was ever contact with organic fuel. It is possible that fire pits or
434 ovens were used.

435

436 In sum, although the corpus is quite small, we observed three types of goethite: acicular
437 needle, multi-domainic and domainic star-like which could indicate three different kinds of
438 raw goethite-rich material. The morphology of crystals is dependent of thermodynamic
439 conditions during crystalization (rock formation and weathering). Here, the occurrence of
440 three different morphologies may indicate probable three different geological origins. Only
441 sub-hexagonal or hexagonal hematite crystals with well-developed thickness (in contrast to
442 natural hematite) are characteristic of heated goethite at temperatures up to 650°C. During
443 heating, the goethite crystals retain their original morphology until temperatures are high
444 enough to start the recrystallization. In this latest situation, the morphology of the precursor
445 goethite crystals is lost. For hematite, we noted that in some cases such as (SM11), the SEM-
446 FEG and TEM-FEG correlated examination identified the recrystallization and the progress of
447 the transformation. The SM11 hematite, well-crystallized from heating, is very different from
448 the poorly crystallized *natural* hematite found at this site or other studied sites.

449

450 5. Conclusion

451 This study, which incorporated spatial analysis of the archaeology, geological contexts
452 surrounding archaeological sites, and physico-chemical analyses using XRD and μ XRD, SEM
453 and SEM-FEG as well as TEM and TEM-FEG, enabled us to differentiate between intentional
454 and accidental heating of coloring materials at the Les Maîtreaux, Combe Saunière I and La
455 Garenne archaeological sites. It confirms the use of planned and well-controlled intentional
456 heating to produce red hematite from goethite in the Solutrean and Magdalenian Periods.

457 The three different archaeological contexts - a hunting camp-site (Combe Saunière I), a rock
458 art site (La Garenne) and a production camp-site with at least two main activities, i.e. flint
459 flaking and coloring material processing – reveal divers aspects of the industry of the coloring
460 materials as well as the skills developed to manage the thermal transformation of the raw
461 materials.

462

463 Whilst archaeological records yield considerable amount of red pigment pieces, only a few
464 types of materials were heated, certainly to change their hue and physico-chemical properties.
465 Most of the red pigments occurred naturally and could be collected from surrounding environ-
466 ments. Thermal transformation was reserved for specific yellow raw materials and likely used
467 to obtain a product with powerful drying or abrasive properties as well as for the color and
468 coloring power of the new synthesized red material.

469

470 The transformation of goethite to hematite by heating, in the open-air Laurel Leaf workshop
471 at Les Maîtreaux camp site is of great importance. The spatial distribution of the technical
472 activities with evidence for a pigment workshop which must have involved heating processes
473 and red powder production is unique in the Paleolithic record. The time and temperature
474 appear to have been carefully controlled, and we can reasonably propose that the Solutreans in
475 Les Maîtreaux placed the lumps of goethite in an oven under the hearth, so that the rocks were
476 homogeneously heat-transformed but protected from the fuel (charcoal, fatty products, etc.). It
477 is proposed that this was likely to have been the same technical procedure used to improve the
478 flint qualities for the shaping of Laurel Leaves. In contrast, given the evidence for irregular
479 heating and mixing with organic matter, the Solutrean rock-shelter Combe Saunière I had
480 archaeological remains that seem more likely to have been accidentally heated.

481 The Magdalenian example is related to rock art. The pigments found in the cave were
482 probably used for the art, since pieces of red iron oxide-rich material have traces of use such
483 as grooves or striations. Four fragments of red pigment on five studied have been heated. Two
484 of them show incomplete heating under low temperature, but the general color of the blocks is
485 red. This indicates expedient or accidental heating. Two others have significant
486 recrystallization indicative of relatively high temperature treatment above 650° C. This is
487 comparable to the apparent high temperature used for goethite thermal transformation (up to
488 800° C) mentioned in the Epipaleolithic of the Riparo Dalmeri in Italy (Gialanella et al.
489 2011). Our results highlight new technical aspects of the Magdalenian culture on the La
490 Garenne site (Lahlil et al., 2014) indicative of continuous management of fireplace
491 temperatures of sufficient duration to accomplish the structural internal transformation. This
492 may have required specific procedures or equipment to ensure adequate ventilation to reach
493 and maintain heat levels. The relationship with the rock painting still needs to be established
494 by further investigations and the search for thermally treated pigment could yield new

495 evidence for associations between pigments on the walls with those found in the archaeological
496 horizons.

497

498 Coloring materials are rocks with good potential to record the history of heating techniques by
499 providing clues for invention of ingenious techniques to fundamentally transform intrinsic
500 qualities of the materials. Even if heating yellow goethite to make hematite did not require
501 much care, Les Maîtreaux and La Garenne archaeological records give strong evidence of so-
502 phisticated procedures to heat-transform goethite-rich rocks. Further field research may deter-
503 mine the specific heating structures used as deduced from heated flint and pigment in the So-
504 lutrean contexts. Focus on experimental heating procedures could enrich our knowledge of
505 fireplace function and the effects of various parameters on the final synthesized material, such
506 as temperature rise and decrease, type of organic material, position in relation to heat, mixing
507 with other materials.

508

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739 Figure captions

740

741 1- Map of France showing locations of the 3 studied archaeological sites: Combe Saunière I,
742 Les Maîtres, La Garenne. Sites cited in the text: 1/ Arcy-sur-Cure, 2/ Terra Amata, 3/
743 Lascaux, 4/ Troubat, 5/ Altamira.

744

745 2- Combe Saunière I: Two faceted hematite-rich blocks showing thin striations, partly
746 smoothed.

747

748 3 - Heated coloring material in Combe Saunière I.

749 a) X-ray diffraction pattern of archaeological sample CS10: quartz (Q), hematite (H) *with non*
750 *uniformly broadened diffraction peaks* and a minor maghemite phase (M), compared to
751 reference hematite. Broadened diffraction lines are highlighted with a *. b-c) TEM
752 micrograph showing crystals with a high concentration of internal dehydration nano-pores
753 (dotted lines indicate the axis along which the pores formed, straight lines show the acicular
754 shape of the original goethite) .

755

756 4- Les Maîtres: spatial distribution of the artifacts, showing the concentration of coloring
757 material according to their petrological class. The “B” and “C” areas concentrate pink
758 ferruginous sandstone and pure soft goethite lumps. The “D” and “E” area reveals the
759 dispersion of yellow to red-colored ferruginous sandstone fragments and hematite-rich clay.
760 The location with class A material shows two concentrations of sharp fragments and 10 raw
761 blocks in the same restricted area.

762

763 5- Heated coloring material in Les Maîtres. a) M01 X-ray diffraction pattern of
764 archaeological sample M01: hematite (H) *with non-uniformly broadened diffraction peaks* and
765 a minor quartz phase (Q), compared to reference hematite. Broadened diffraction lines are
766 highlighted with *. b) TEM micrograph showing crystals with internal spherical dehydration
767 nano-pores and their measured diameter. c) TEM micrographs showing acicular crystals with
768 internal dehydration nano-pores. d) dotted lines indicate the axis along which the pores
769 formed, straight lines show the acicular shape of the original goethite.

770

771 6- Blanchard-La Garenne a) Ferruginous lumps; arrows point to the use traces (groups of
772 parallel striations); b) X-ray diffraction pattern of five red analyzed pigments. H = hematite, G

773 = goethite and Q = quartz; the four samples SM03, SM11, SM20 and SM22 have wider
774 diffraction peaks with an inversion of intensity of the [104] and [110] lines compared with
775 SM16 narrow diffraction lines. SM22 hematite and a minor goethite phase.

776

777 7- Blanchard-La Garenne. Black botryoidal goethite (SM04), a-c) SEM-FEG, a) botryoidal
778 structure, b) stratified longitudinal crystals with centripetal organization, c) needle-like
779 goethite crystals, d) TEM-FEG showing thin acicular crystal of goethite.

780

781 8- Blanchard-La Garenne. Nano-crystalline hematite, (SM16), with narrow X ray diffraction
782 lines a-b) SEM-FEG: large sheets of hematite, c) HR-TEM-FEG: High resolution with lattice
783 fringes, imaging lattice spacings, d) electron diffraction pattern showing the polycrystalline
784 d_{hkl} rings.

785

786 9- Blanchard-La Garenne. Hematite crystals in SM03, (a), SEM-FEG, star-like twinned
787 structure of precursor goethite crystals with (b) spherical nano-pores (TEM-FEG); and in
788 SM22, (c) SEM-FEG, multi-domainic structure of precursor goethite crystals with (d)
789 longitudinal nano-pores (TEM-FEG).

790

791 10- Blanchard-La Garenne. Hematite crystals without pore: - SM11 a) SEM-FEG micrograph
792 of thick crystals (some with hexagonal morphology) with faceted extremities, arrows point to
793 the coalescing crystals, b) TEM-FEG micrograph showing still elongated crystals with
794 rounded or faceted extremities. - SM20 c) hexagonal platelets of hematite (SEM-FEG) more
795 often exposing their cross-section, d) TEM-FEG micrograph showing acicular (02a), pseudo-
796 hexagonal hematite (02b), and coalescing crystals (02c).

797

798 **Table captions**

799 1- Combe Saunière I: list of laboratory labels attributed to analyzed artifacts according to
800 petrological class, with indication of archaeological record (square meter, number of artifact
801 or split number).

802 2- Combe Saunière I: Assemblage sampling and analysis according to petrological class.

803 3- Combe Saunière I: XRD and TEM results showing good agreement between class and
804 composition. Samples CS03e, CS06 and CS08 show non uniform broadening of hematite (H)
805 peaks, a minor phase of maghemite and the presence of goethite (G) inside CS03 sample.

806 4- Les Maîtres: list of laboratory labels attributed to analyzed artifacts according to petro-
807 logical class, with indication of archaeological record (square meter, number of artifact or
808 split number).

809 5- Les Maîtres: Assemblage sampling and analysis according to petrological class.

810 6- Les Maîtres: XRD and TEM results showing good agreement between class and compo-
811 sition. Samples M01 to M10 (i=internal and e=external) show non uniform broadening of
812 hematite (H) peaks with the same features (size and morphology of the dehydration pores) at
813 high magnification with TEM. Goethite (G) shows fine acicular crystals.

814 7- La Garenne: list of laboratory labels attributed to analyzed artifacts and corresponding
815 analysis conducted.

816 8- La Garenne: μ XRD, SEM-FEG and TEM-FEG results with description of the hematite (H)
817 and goethite (G) morphology.

Combe Saunière 1	Square	Nb /split	Class
CS01	H20C	749	1
CS02	I18A	723	1
CS03	K17D	151	1 and 2
CS04	K18C	319	1
CS05	I17	Decap 2	1
CS06	J16A	Decap 27	1 and 2
CS07	J18B	Décap 30	1
CS08	K18C	Decap 15	1 and 2
CS09	H20D	592	2
CS10	I17A	Decap 18	2
CS11	I18A	Decap 39	2
CS12	I18A	Decap 39	2
CS13	K14A	Decap 20	2

Sheet1

Combe Saunière 1	Nb of objects	Hematite- (goethite-)rich concretions (1)	Goethite-rich concretions (2)	manganese oxides (3)
Macro- and mesoscopic observation	538	442	42	54
XRD	13 (14 samples)	8	5	
Sample labels	-	CS01-CS08 with CS03i and CS03e	CS09-CS13	
TEM	4	4		
Sample labels	-	CS03e, 03i, 05, 06 and CS08		

Sheet1

Combe Saunière 1	XRD					TEM	
	Hematite	Goethite	Maghemite	quartz	non uniform broadening	crystal morphology	pores
CS01	+++			+			
CS02	+++						
CS03e	+++	+	+	+++	yes	pseudo acicular and massive massive and acicular	longitudinal and spherical 5-20 nm
CS03i		+++		+++			
CS04	+++			+			
CS05	+++			++			
CS06 and CS08	+++		+	++	yes	pseudo acicular	longitudinal and spherical 5-20 nm
CS07	+++			+			
CS09	+	+++					
CS10		+++					
CS11	+	+++					
CS12	+	+++		+++			
CS13		++		+			

Les Maîtreaux	Square	Nb /split	Class
MA01	N14C	Decap 2	A
MA02	M14B	Decap 5	A
MA03	N14D	202	A
MA04	M13A	Decap4	A
MA05	M13B	Decap 3	A
MA06	M14C	Decap 4	A
MA07	M14C	Decap 4	A
MA08	M14D	Decap 4	A
MA09	M14D	Decap 4	A
MA10	M14D	Decap 4	A
MA11	N19A	Decap 3	B
MA12	O20C	Decap 2	B
MA13	N19B	Decap 2	C
MA14	O20D	Decap 6	C
MA15	N11A	Decap 2	D
MA16	M16D	Decap 1	D
MA17	M17B	Decap 1	D
MA18	M19A	Decap 1	D
MA19	O9D	Decap 3	E
MA20	K15C	Decap 2	E
MA21	M17C	Decap 2	E
MA22	N18D	Decap 1	E
MA23	N19C	Decap 3	E
MA24	N21A	Decap 6	E

Sheet1

Les Maîtresaux	Nb of objects	Hematite (A)	Goethite (B)	Hematite-rich sandstone (C)	Goethite- and hematite-rich sandstone (D)	Hematite-rich clay (E)
Macro- and mesoscopic observation	1021	501	46	51	186	237
XRD	24 (34 samples)	20 (10 blocks > 5 cm in length)	2	2	4	6
Sample labels	/	MA1e-MA10e and MA1i-MA10e	MA11 and MA12	MA13 and MA14	MA15-MA18	MA19-MA24
TEM	6 (8 samples)	5	1			2
Sample labels	/	MA1e-M3e and MA1i-MA2i	MA12			MA19 and MA 21

Sheet1

Les Maîtresaux	XRD				TEM		
	Hematite	goethite	quartz	non uniform broadening	H crystal morphology	pores	G crystal morphology
MA1-MA10 (i and e)	+++		+	yes	pseudo acicular	spherical 2-5 nm	
MA11		+++	+				
MA12		+++	+				acicular
MA13-MA14	+	+	+++				
MA15-MA18	+	+	+++				
MA19 and MA21	+++	++	+		massive crystals		acicular
MA20	+++	++	+				
MA22-24	+++	++	+				

Sheet1

La Garenne	Corpus	Red	Black
Macro- and mesoscopic Observation	16 (4 yellow)		7 5
μXRD		6	5 1 (black goethite)
Sample label		SM03, SM11, SM16, SM20, SM22	SM04
SEM-FEG		6	5 1
Sample label		SM03, SM11, SM16, SM20, SM22	SM04
TEM-FEG		5	5
Sample label		SM03, SM11, SM16, SM20, SM22	SM04

Sheet1

La Garenne	μXRD				SEM-FEG	TEM-FEG		
	hematite	goethite	quartz	non uniform broadening		H crystal morphology	heating features	G crystal morphology
SM03	+++	+	+++	yes	star-like structure	acicular	spherical nano-pores	acicular
SM04					botryoidal structure			
SM11	+++		+	yes	hexagonal pellets	quasi-hexagonal	recrystallization in 3D	
SM16	+++				sheets of hematite	polycrystalline nano-crystals		
SM20	+++		++		platelets (hexagonal)	quasi-hexagonal and acicular	recrystallization in 3D	
SM22	+++	++	+	yes	parallel sub-units	acicular	longitudinal nano-pores	acicular

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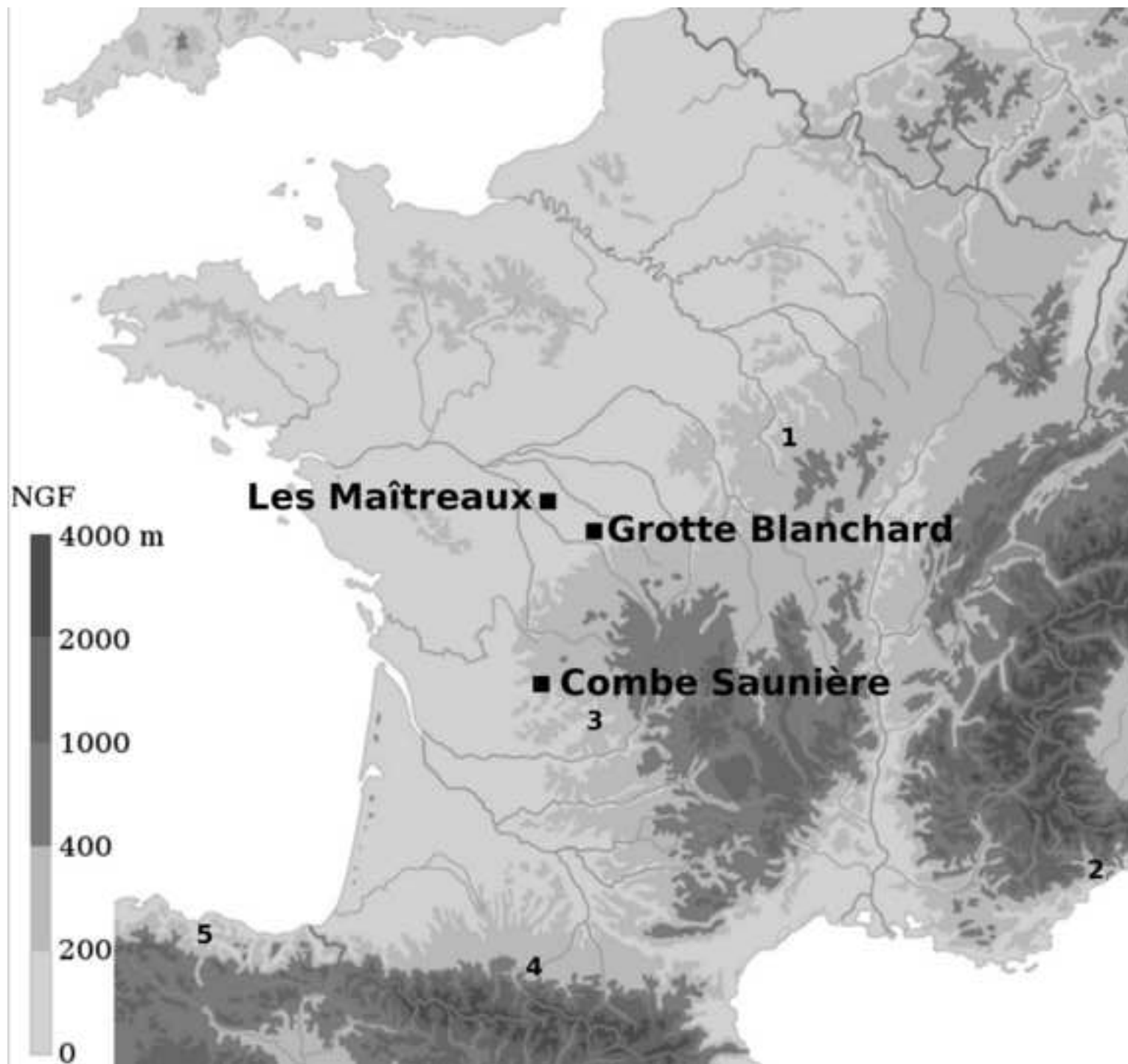


Figure 2
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Figure 3
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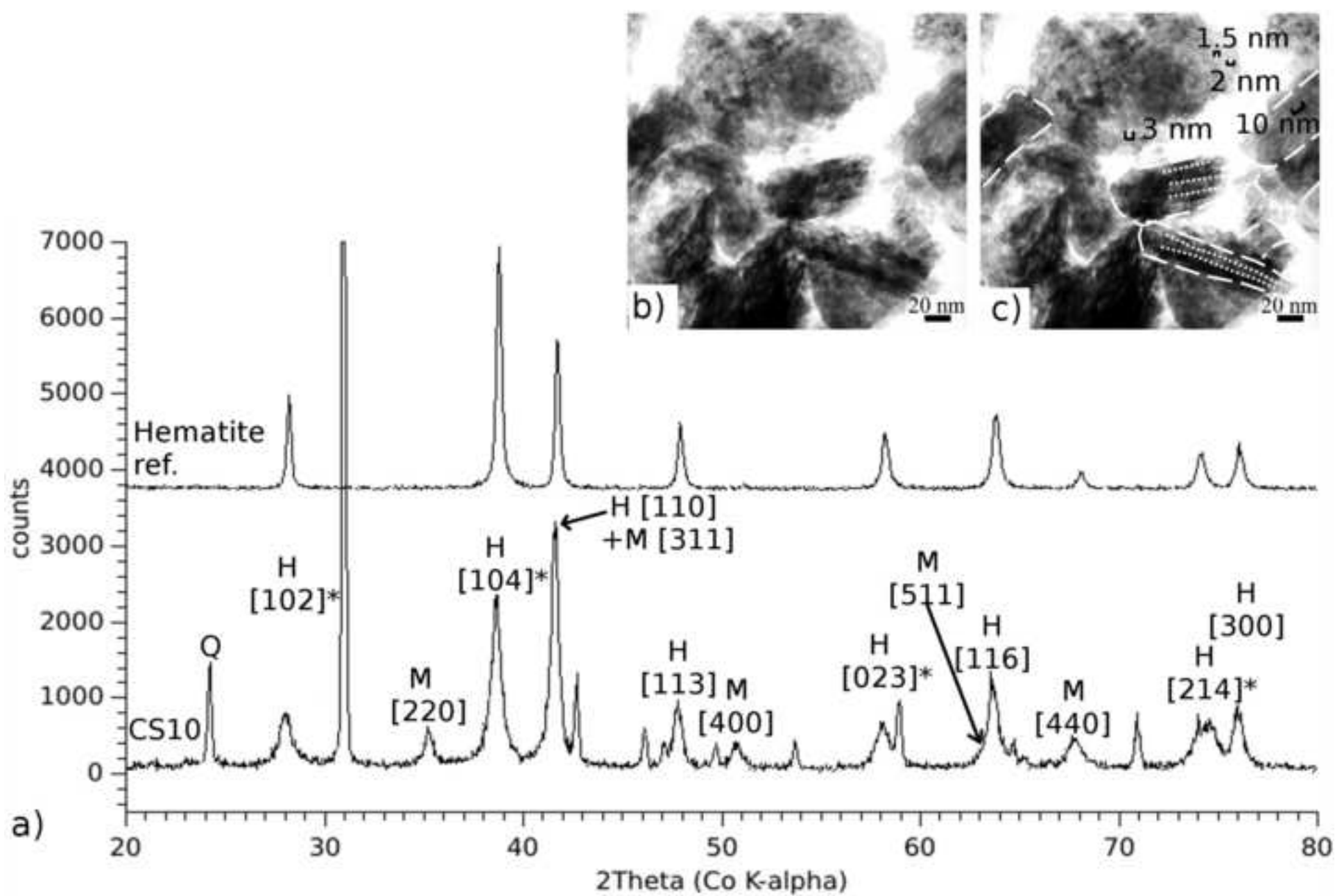


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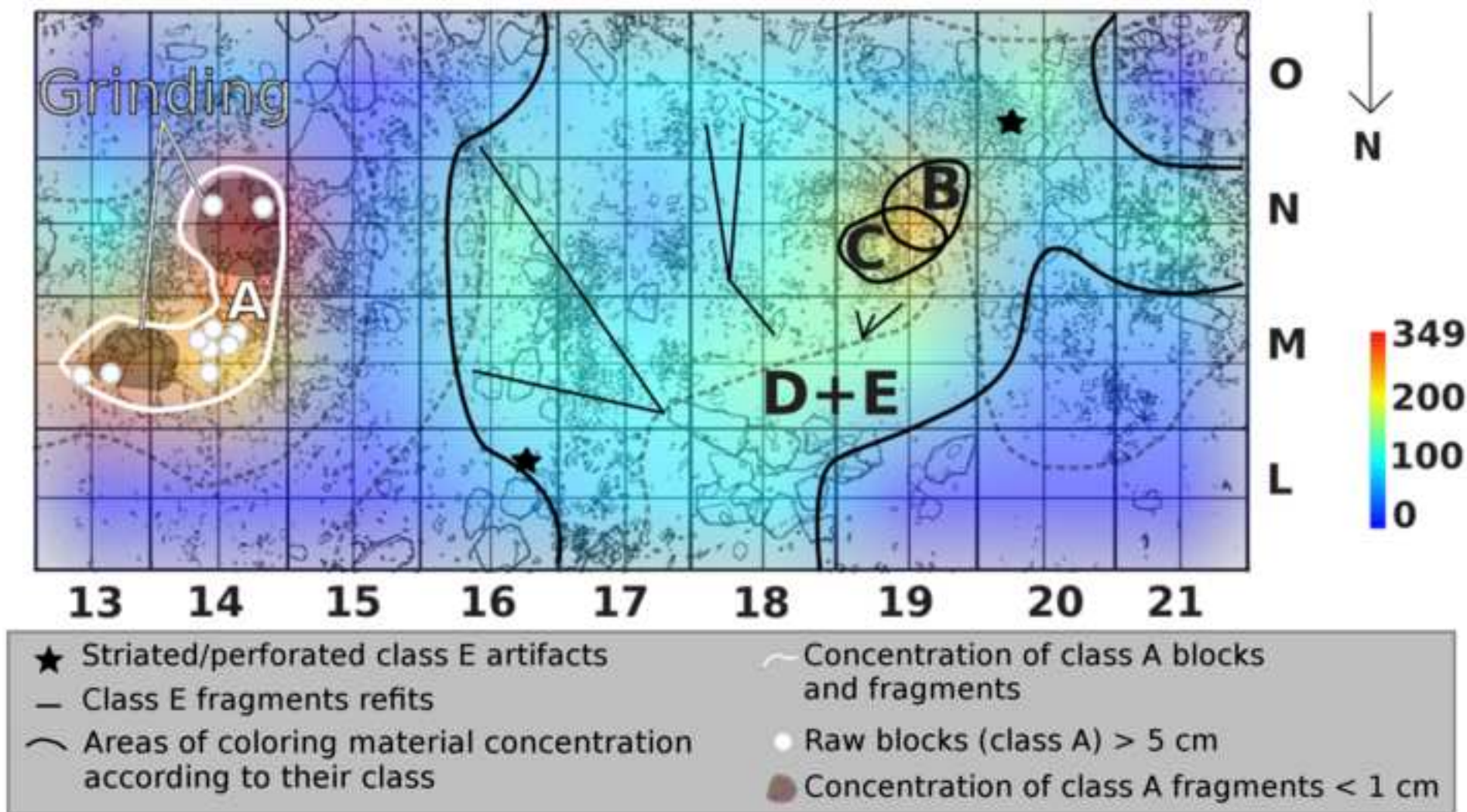


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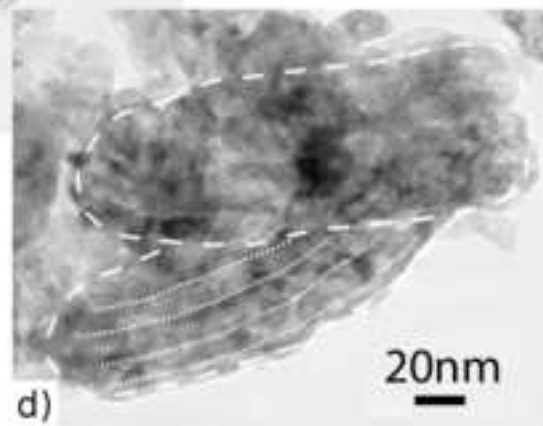
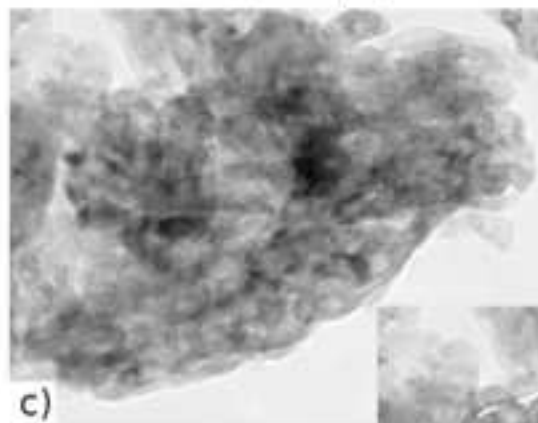
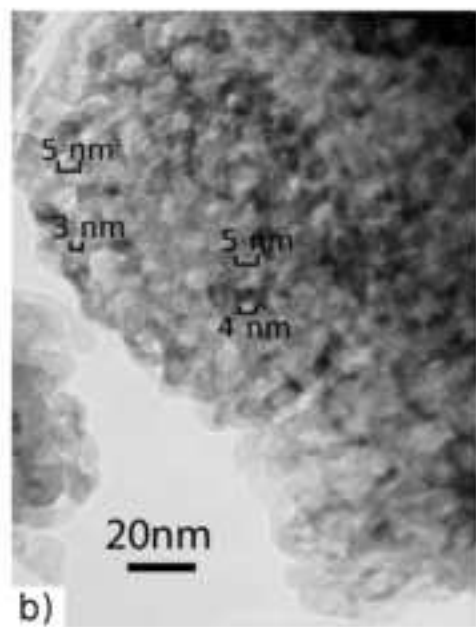
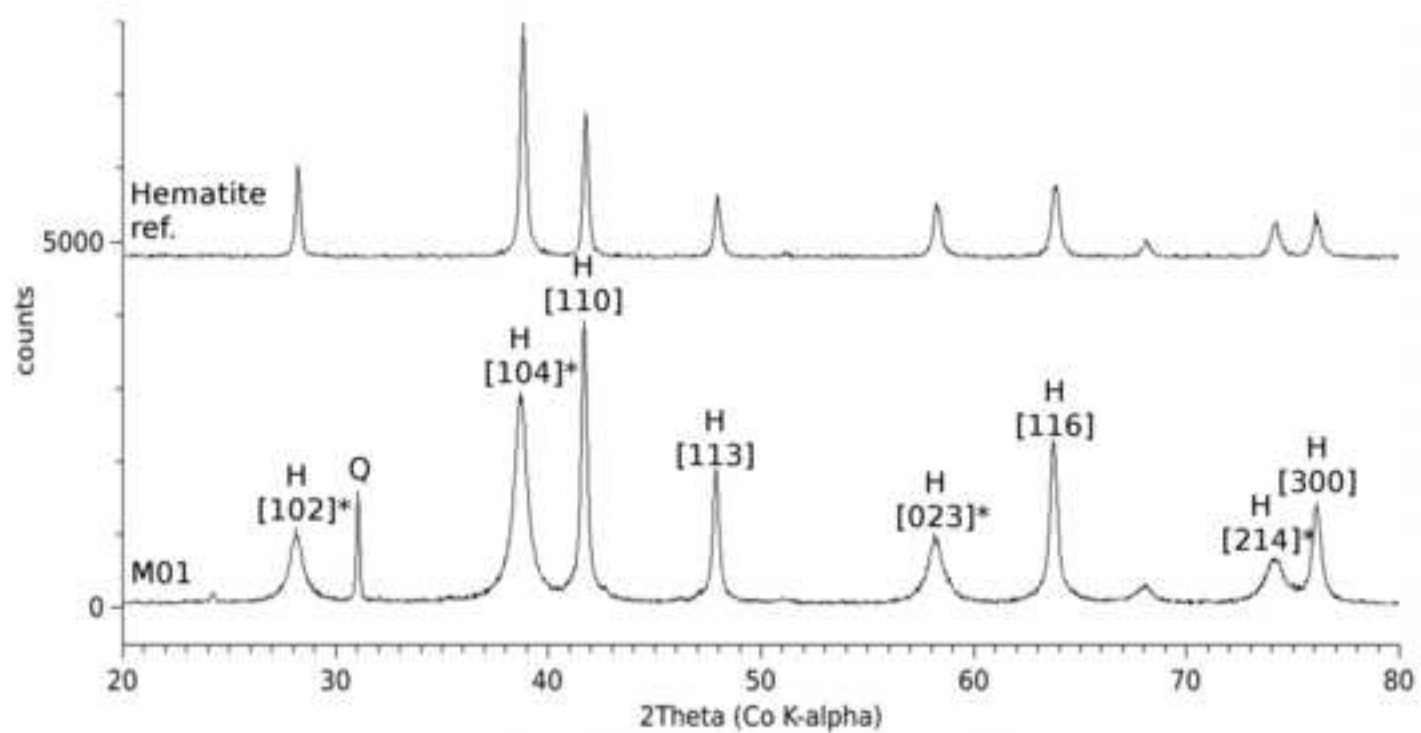


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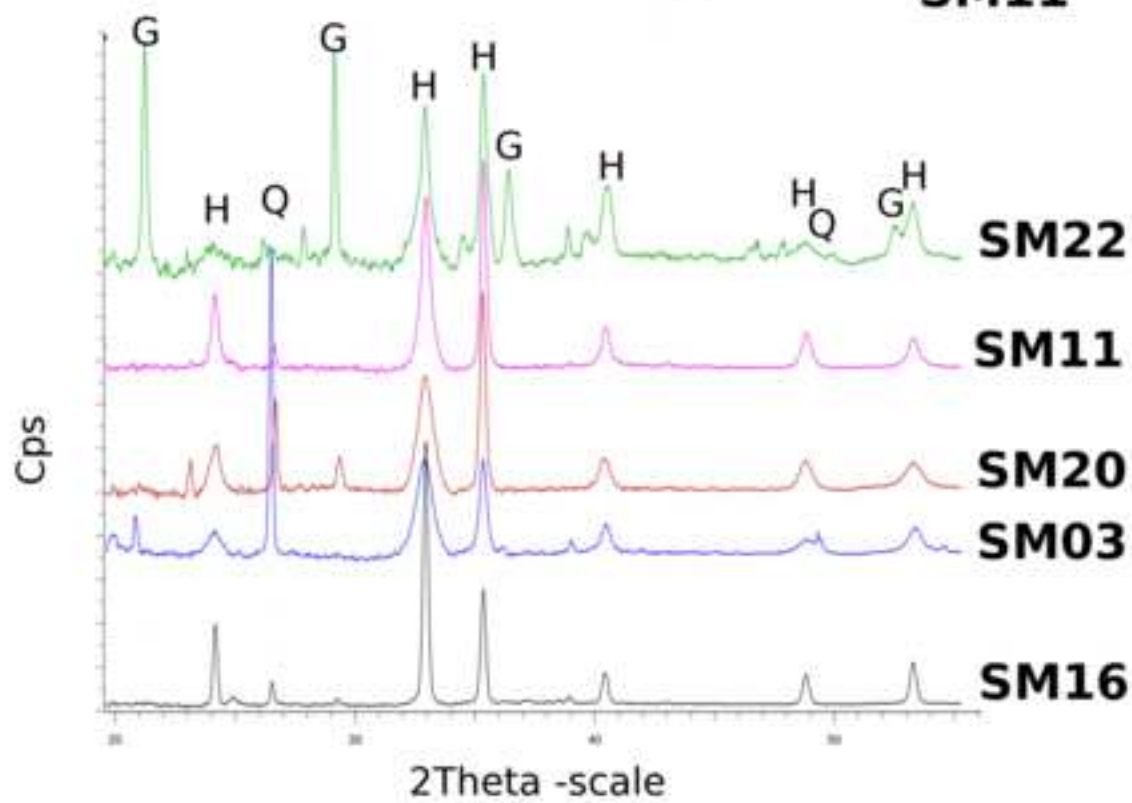
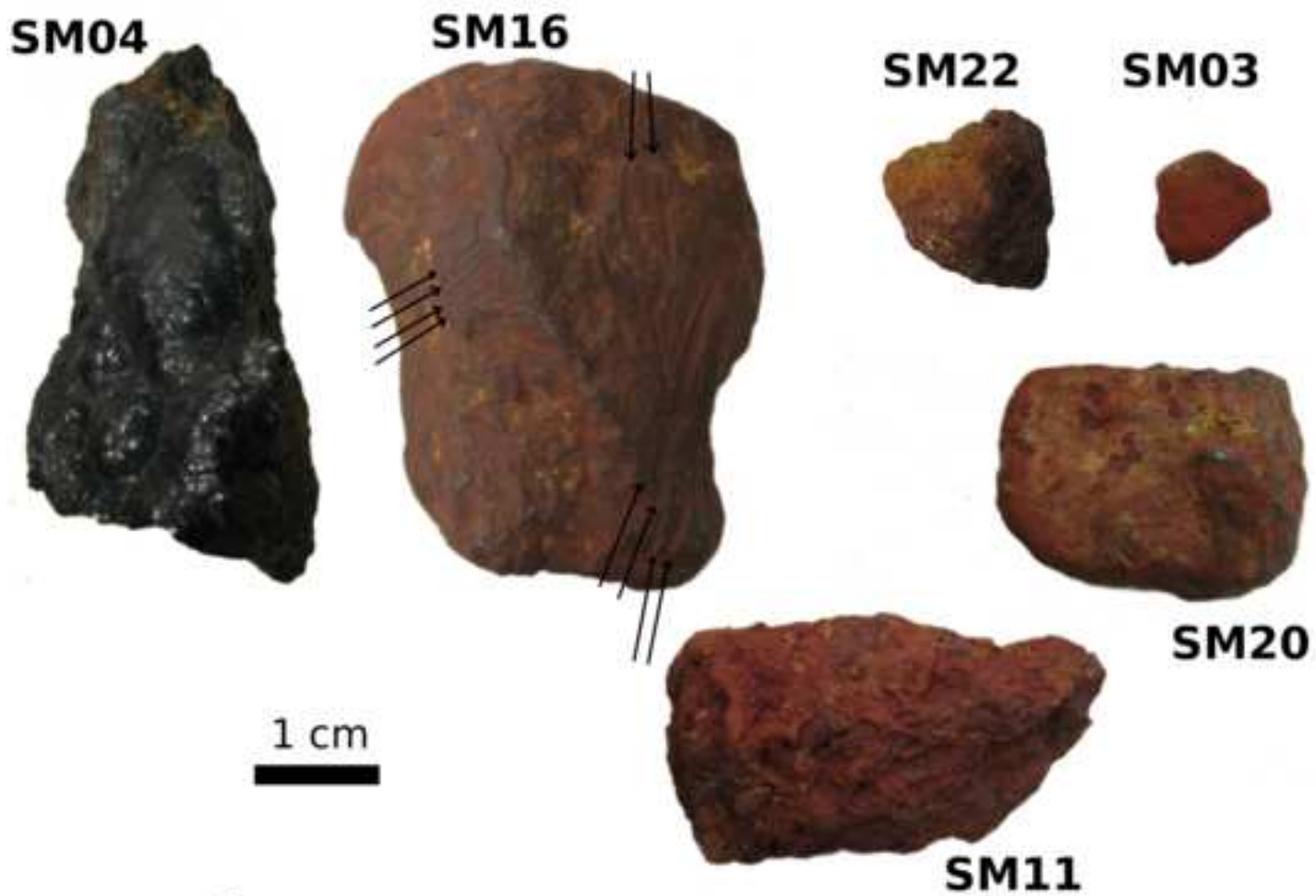


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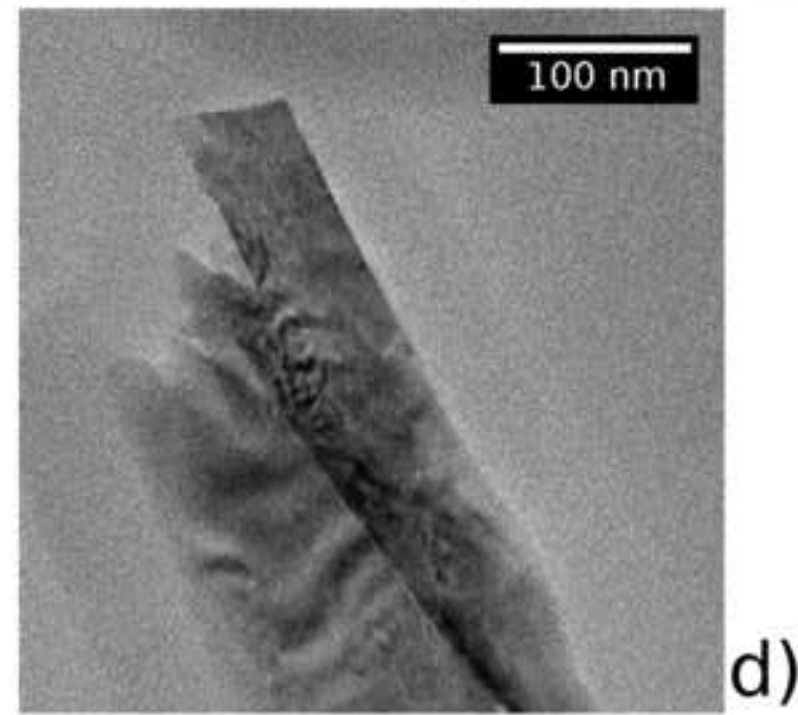
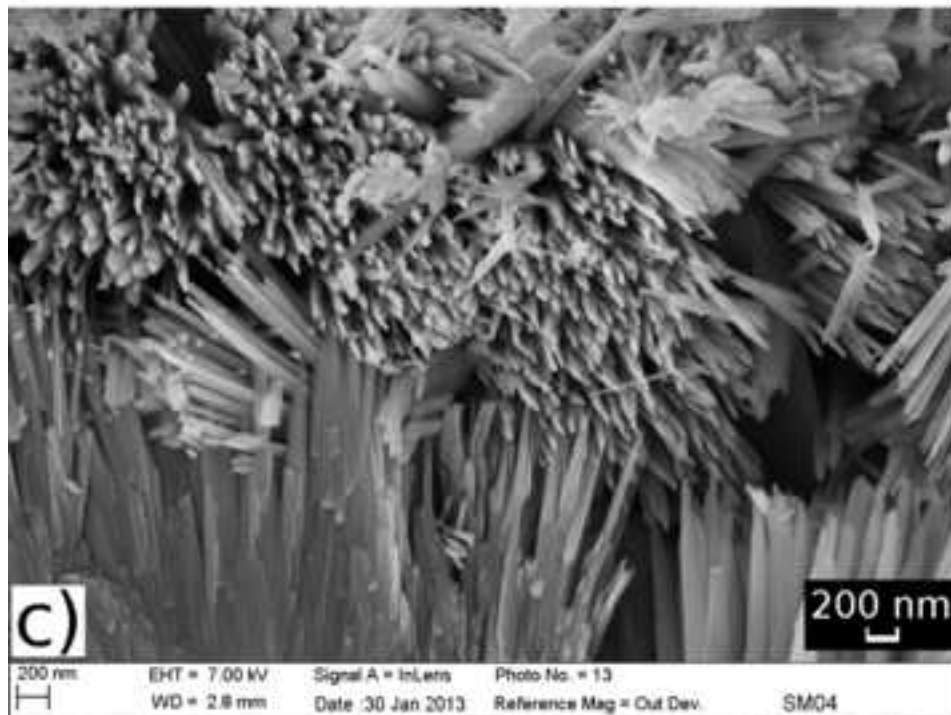
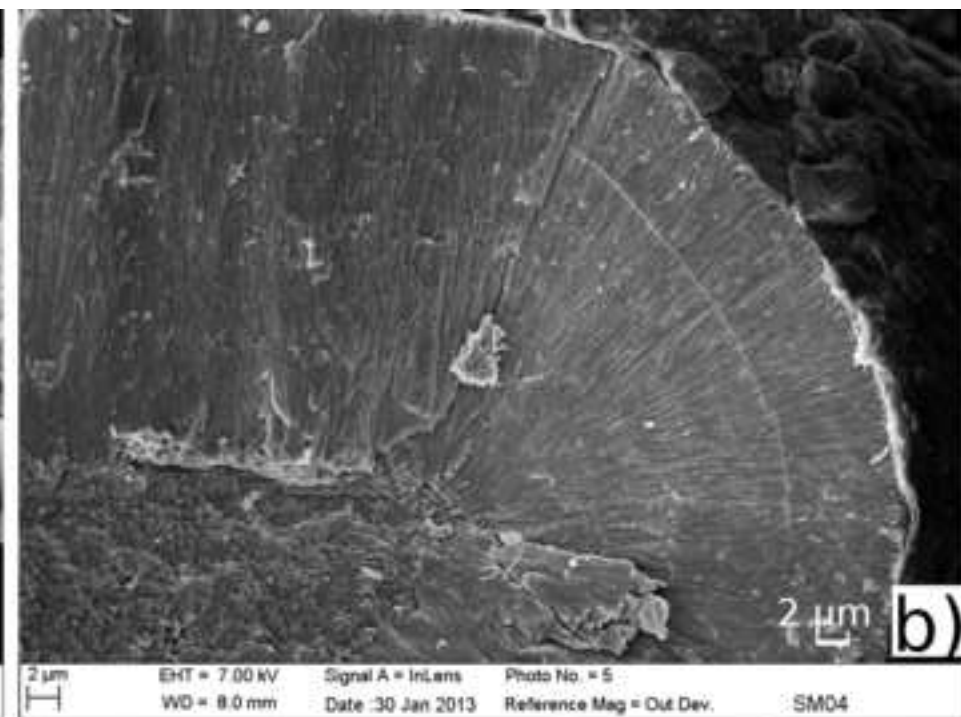
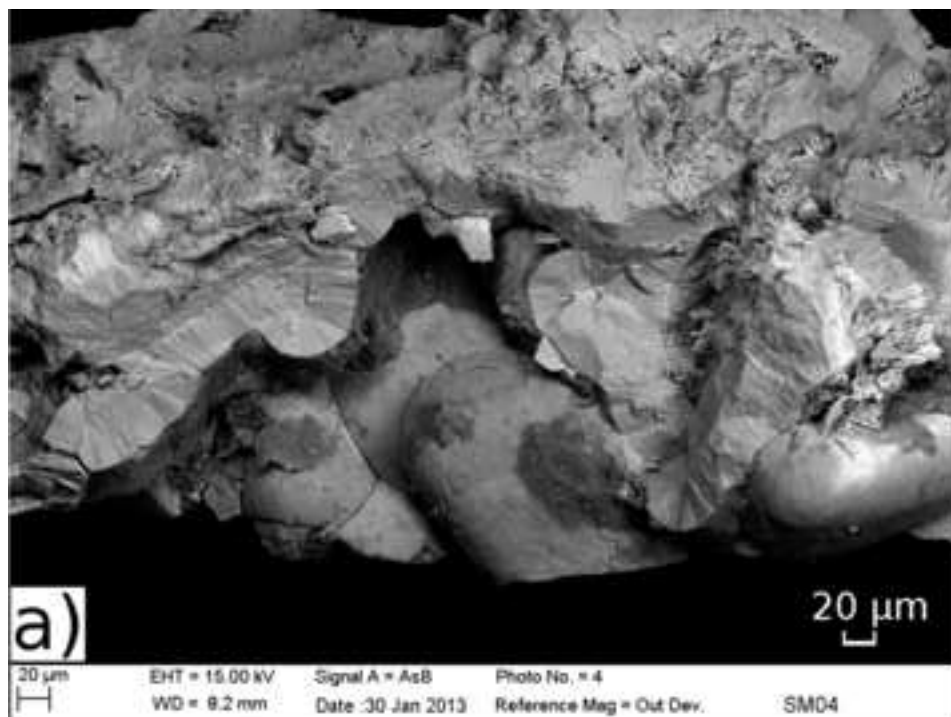


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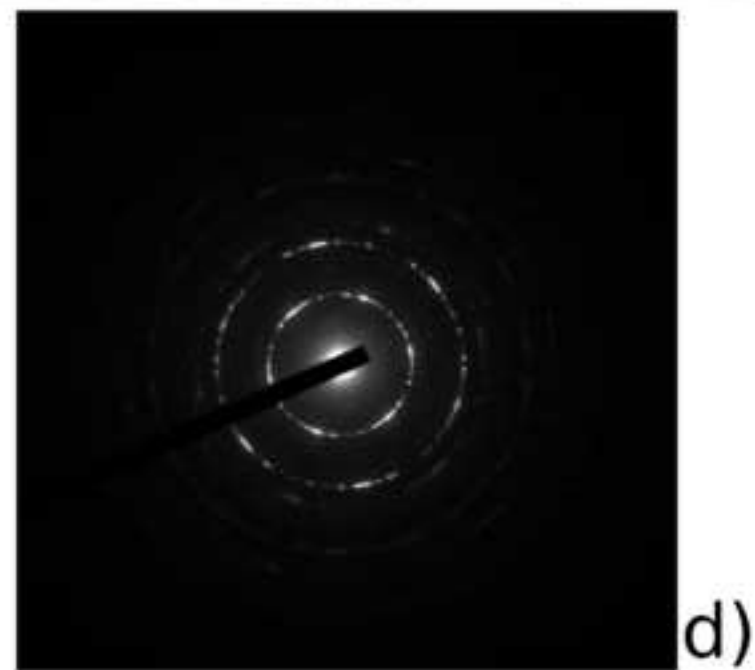
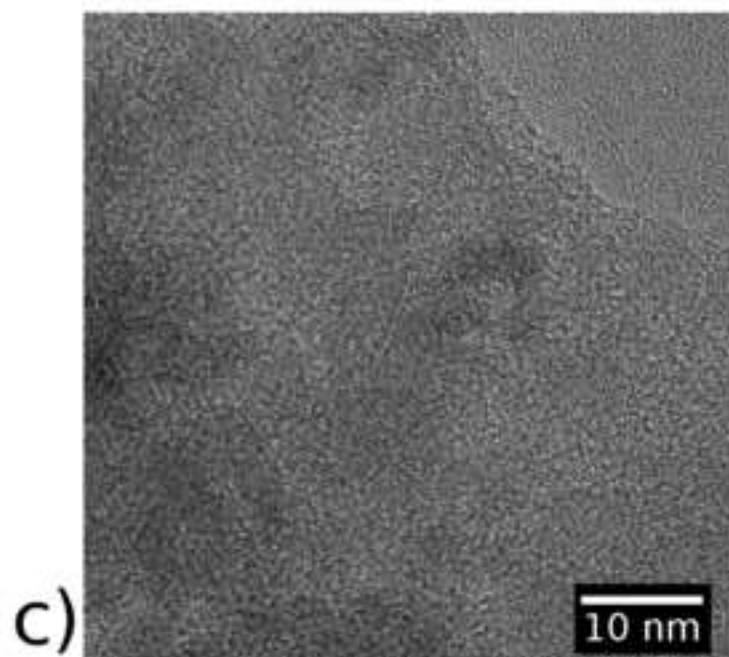
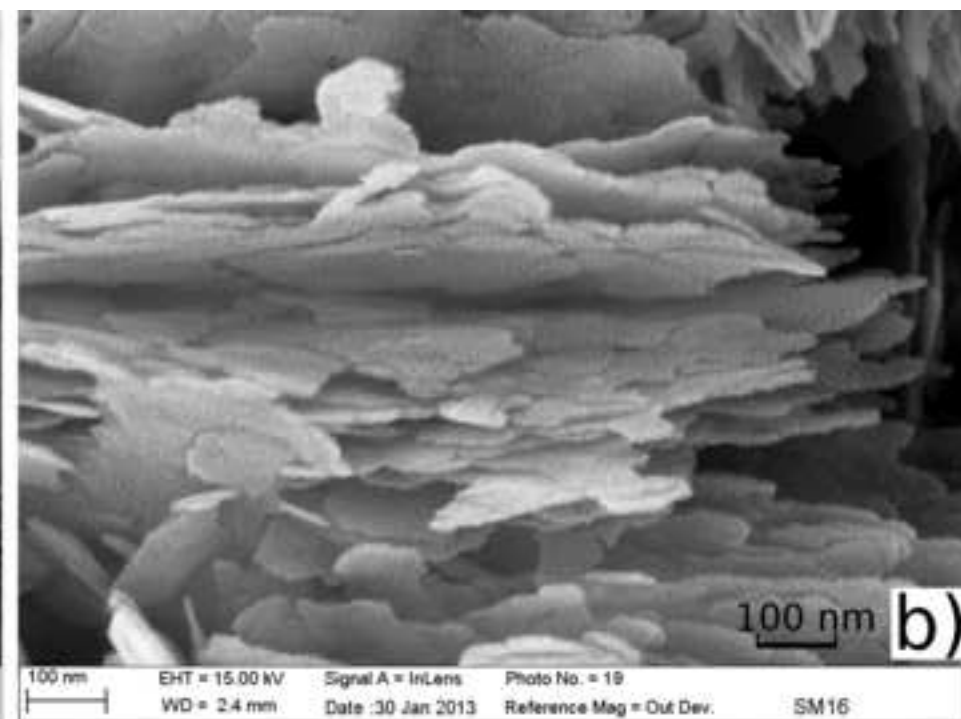
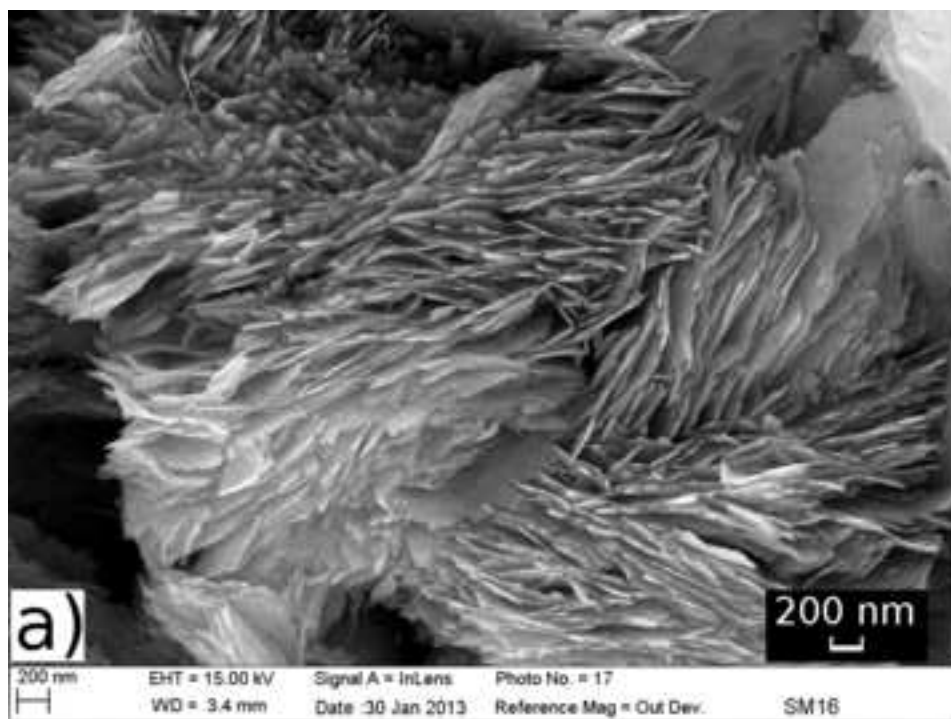


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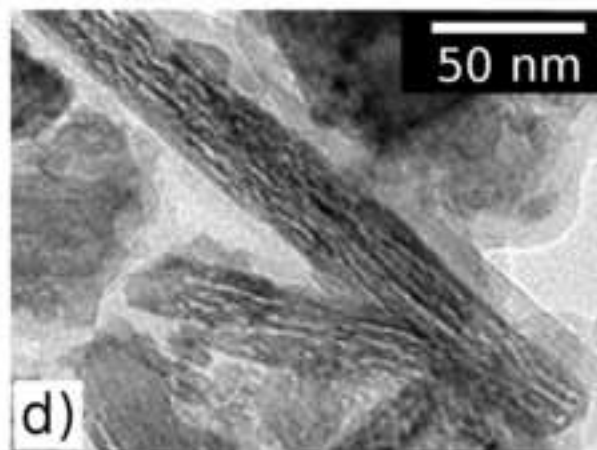
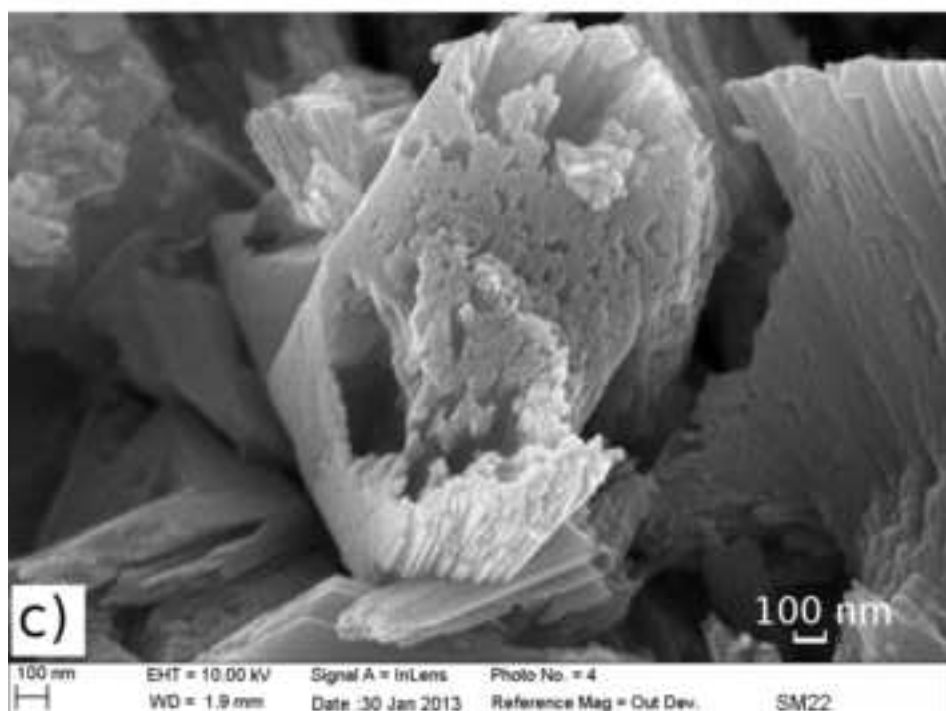
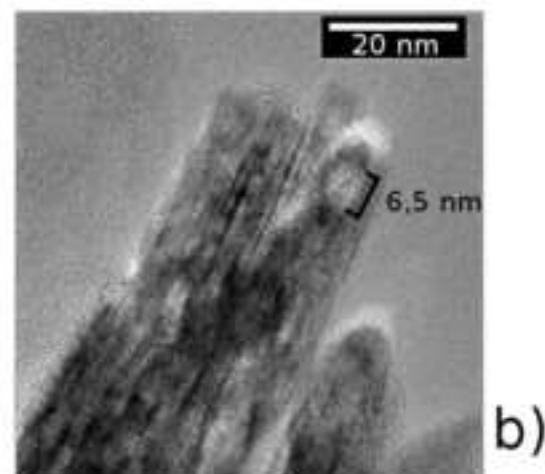
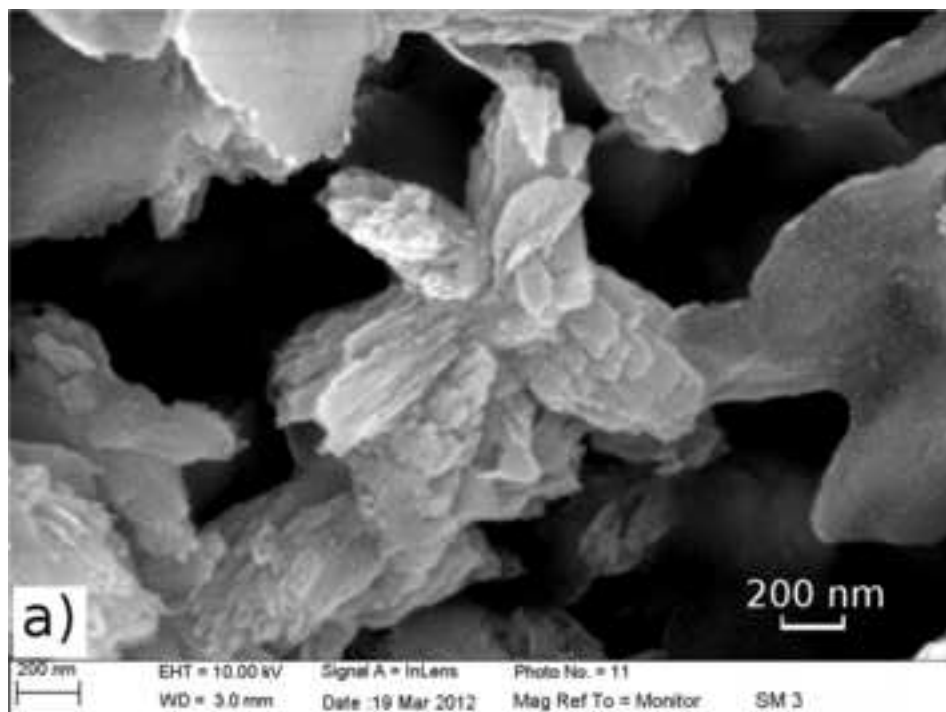
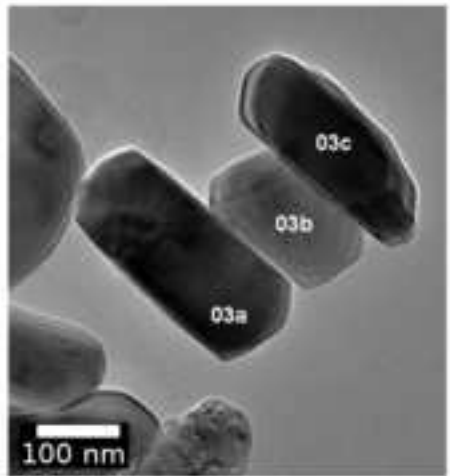
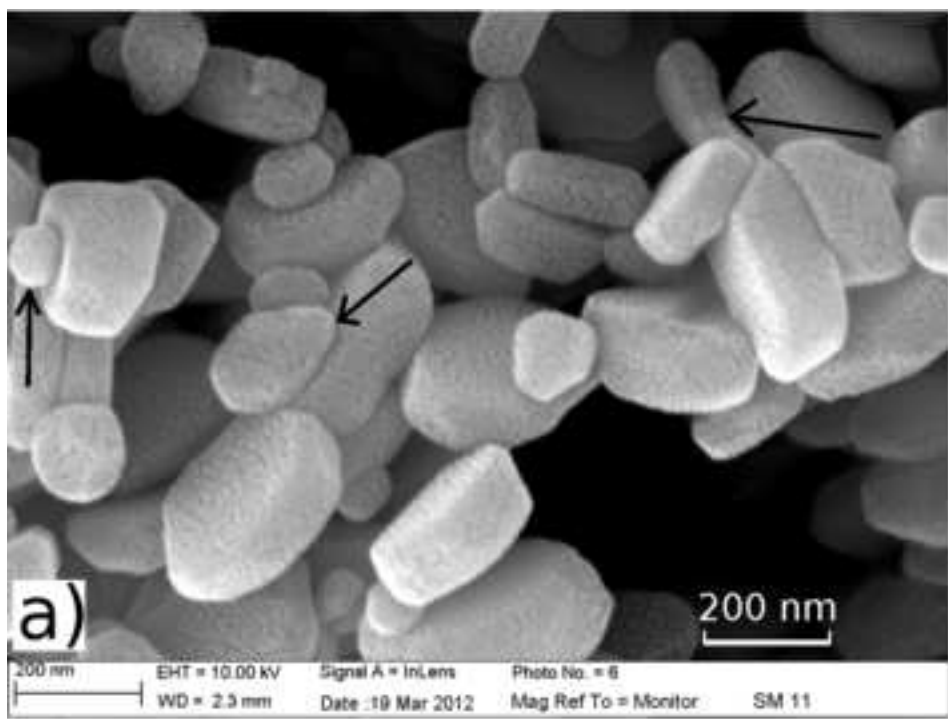
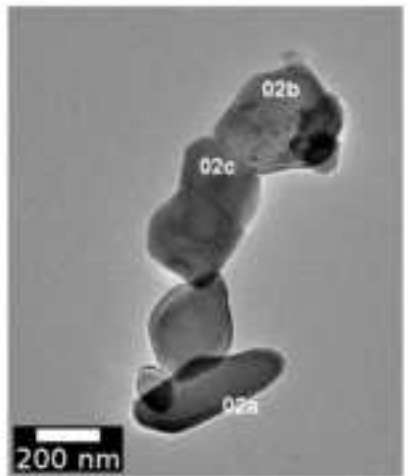
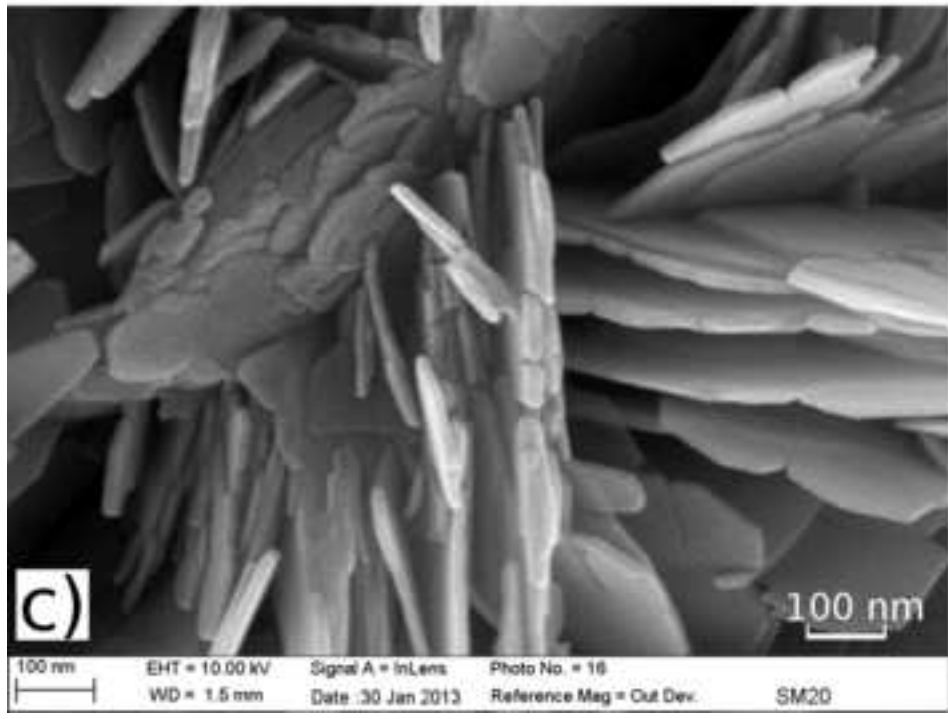


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b)



d)