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

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Title: Solutrean and Magdalenian ferruginous rocks heat-treatment: accidental and/or deliberate action?

Article Type: Full Length Article

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

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Order of Authors: Hélène 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 Maîtreaux and the hunting site Combe Saunière 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.

***Revision Notes**

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 brechification and because the spatial dispersion only shows a trend to a greater density of ocher in 4 m^2, but all along the sequence. In addition, experiments conducted by Wadley (2009) indcate 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 laking in the study of Hovers et al. 2003, and Godfrey-Smih 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 Levantin Levallois horizons at Qafzeh, around 90 000 years ago.*

Thirdly, there is a claim that Les Maîtreaux 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 follow: "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 wich 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-developped 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 Maîtreaux 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: "interferrence 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 deliverate 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, craks, …) and a heating operation? Do you have data on reference materials that have been heated in controled 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 a 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 chrono-cultural 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 14C 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 evoluted 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 controled 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, line111 ; 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 Maîtreaux 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 laking 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.

*Manuscript
Click here to view linked References

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

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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 250-300°C. 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 Maîtreaux and the hunting site Combe Saunière 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.

1 Introduction

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

A. Leroi-Gourhan (Leroi-Gourhan, 1961), during his excavations of the Grotte du Renne at Arcy-sur-Cure, made the assumption that Châtelperronian people (last Neanderthals, ca 45-40 ky cal.BP, Hublin et al., 2012) heated ferruginous rocks to modify the hue and experiment with color shades to produce different coloring materials. It is well known that yellow goethite takes on orange and red shades upon heating from 250-300° C. At these temperatures, goethite is transformed into hematite by dehydration. The redness becomes even more intense as the temperature and/or the heating time increases (Pomiès, 1997). 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).

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

formations in macroscopic blocks (e.g., brown to black zones, cracks, etc.) and spatial relationships of heat remains, may provide clues of heating. The micro-structure of the coloring materials is also a good indicator of heat treatment. X-ray powder diffraction pattern of hematite resulting from a heated goethite will display specific broadening of the peaks with typical relative intensity ratios (Pomiès et al., 1998b, fig. 3). 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). Selective broadening of diffraction peaks appears to be related to disorder in the cationic sub-lattice, i.e. in the repeating array of Fe^{3+} (Pomies, 1998b).

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

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

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

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

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

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

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

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

2. Overview of the three sites

2.1. Combe Saunière I

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

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

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

2.2. Les Maîtreaux

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

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

2.3. Grotte Blanchard (La Garenne)

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

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

3. Experimental methods

3.1. Classification and sampling strategy

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

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

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

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

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

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

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

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

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

EDX spectrometer (PGT- PRISM 2000 equipped with the IMIX software) with a 1 nm beam size and a 300 s acquisition time. Particle size was analyzed using the standard analysis software for processing digital images (Gatan Digital Micrograph, Scion Image) and electron diffraction patterns were indexed with the CaRIne Cristallography software. Such patterns permit differentiation of hematite from goethite (hexagonal or orthorhombic structure, respectively); this cannot be done using elemental analysis.

4. Results and discussions

4.1. Combe Saunière I : accidental heat treatment?

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

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

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

4.2. Les Maîtreaux

4.2.1. Spatial distribution of coloring materials

The artifacts were identified and distributed in five different classes based on their macroscopic, petrographic and mechanical characteristics (Tables 4 and 5; Salomon et al., 2013; Salomon, 2009):

- Class A: almost pure iron oxide-rich blocks and sharp fragments which are cavernous, red to black, and have a medium hardness of 3 on the Mohs scale and an uneven compactness. All specimens are concentrated in squares N14, M13 and M14 (Figure 4);
- Class B: soft goethite, yellow, rounded pieces, concentrated in the S-W of square N19 (29 pieces);
- Class C: pink ferruginous sandstone with rounded quartz grains, concentrated in the N-E of square N19 (51 pieces);
- Class D : multi-hue blocks and fragments (yellow, orange, red and black with metallic shimmer) of ferruginous sandstone more or less rich in sub-angular quartz grains, medium hardness, spread over a large area with two flint concentrations (86 pieces);
- Class E: dark red, soft, porous, homogeneous and clayey blocks and fragments showing yellow, red and black minerals at low magnification, spread over the same area as class D artifacts (184 pieces) - three refits were possible and two pieces had micro-striations with polish.

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

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

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

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

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

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

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

4.3. The Grotte Blanchard in La Garenne

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

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

4.3.1. Black goethite

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

4.3.2. Natural hematite

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

4.3.3. Hematite with an anomalous X-ray diffractogram

4.3.3.1. First case

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

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

4.3.3.2. Second case

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

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

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

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-developped 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. For hematite, we noted that in some cases such as (SM11), the SEM-FEG and TEM-FEG correlated examination identified the recrystallization and the progress of the transformation. The SM11 hematite, well-crystallized from heating, is very different from the poorly crystallized *natural* hematite found at this site or other studied sites.

5. Conclusion

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

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

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

The transformation of goethite to hematite by heating, in the open-air Laurel Leaf workshop at Les Maîtreaux camp site is of great importance. 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. The time and temperature appear to have been carefully controlled, and we can reasonably propose that the Solutreans in Les Maîtreaux placed the lumps of goethite in an oven under the hearth, so that the rocks were homogeneously heat-transformed but protected from the fuel (charcoal, fatty products, etc.). It is proposed that this was likely to have been the same technical procedure used to improve the flint qualities for the shaping of Laurel Leaves. In contrast, given the evidence for irregular heating and mixing with organic matter, the Solutrean rock-shelter Combe Saunière I had archaeological remains that seem more likely to have been accidentaly heated.

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

evidence for associtions between pigments on the walls with those found in the archaeological horizons.

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

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Figure captions

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

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

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

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

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

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

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

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

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

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

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

Table captions

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

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

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

4- Les Maîtreaux: list of laboratory labels attributed to analyzed artifacts according to petrological class, with indication of archaeological record (square meter, number of artifact or split number).

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

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

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

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

Table 1

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

Table 2

Combe Saunière 1	Nb of objects	Hematite- (goethite-)rich concretions (1)	Geothite-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		

Table 3

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

Table 4

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

Table 5

Les Maîtreaux	Nb of objects	Hematite (A)	Goethite (B)	Hematite-rich sandstone (C)	Goethite- and hematite-rich standstone (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

Table 6

Les Maîtreaux	XRD				TEM		
	Hematite	goethite	quartz	non uniform broadening	H crystal morphology	pores	G cyrstal 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	+++	++	+				

Table 7

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

Table 8

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	polycrystaline nano-crystals		
SM20	+++		++		platelets (hexagonal)	quasi-hexagonal and acicular	recrystallization in 3D	
SM22	+++	++	+	yes	parallel sub-units	acicular	longitudinal nano-pores	acicular

Figure 1
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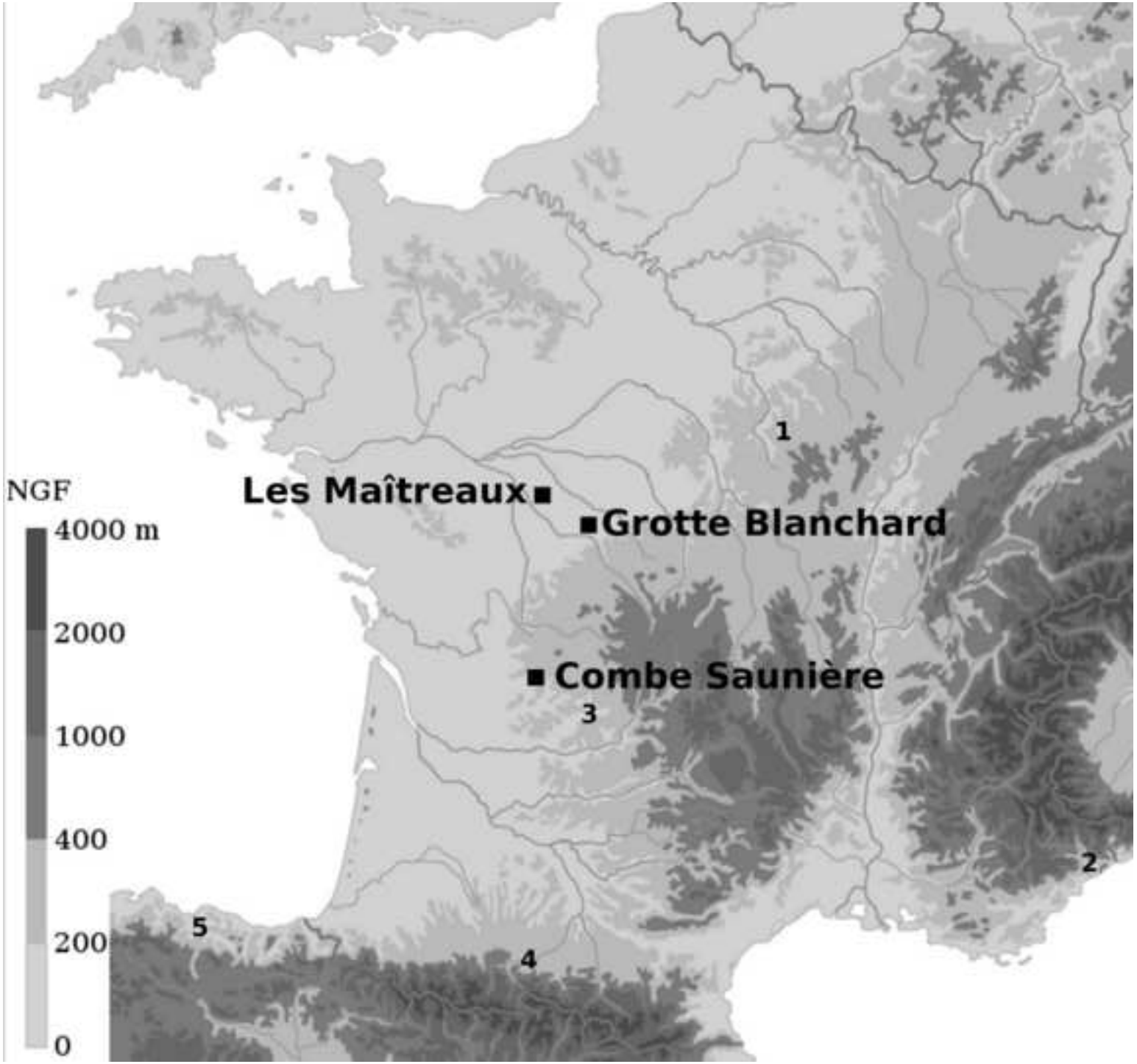

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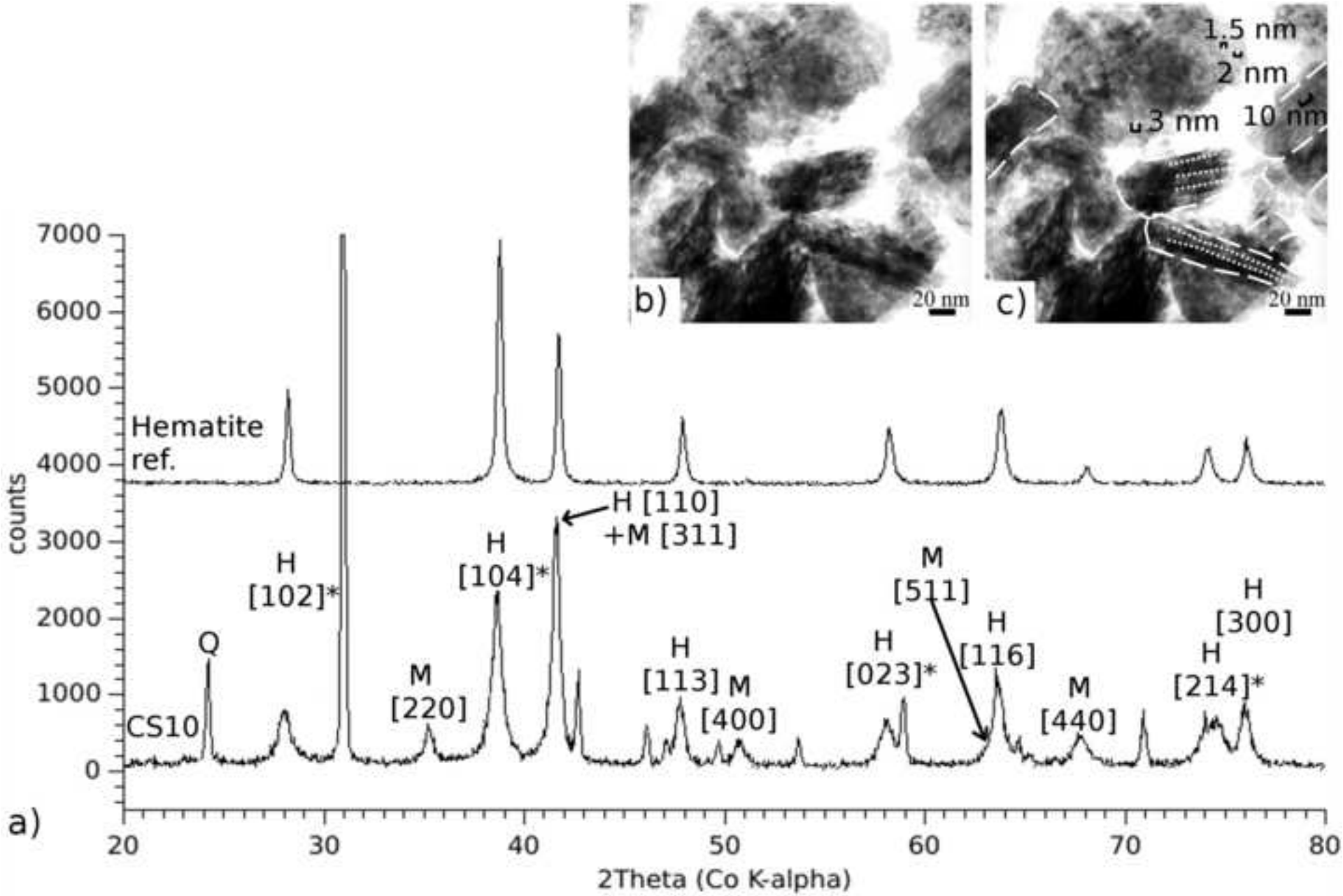

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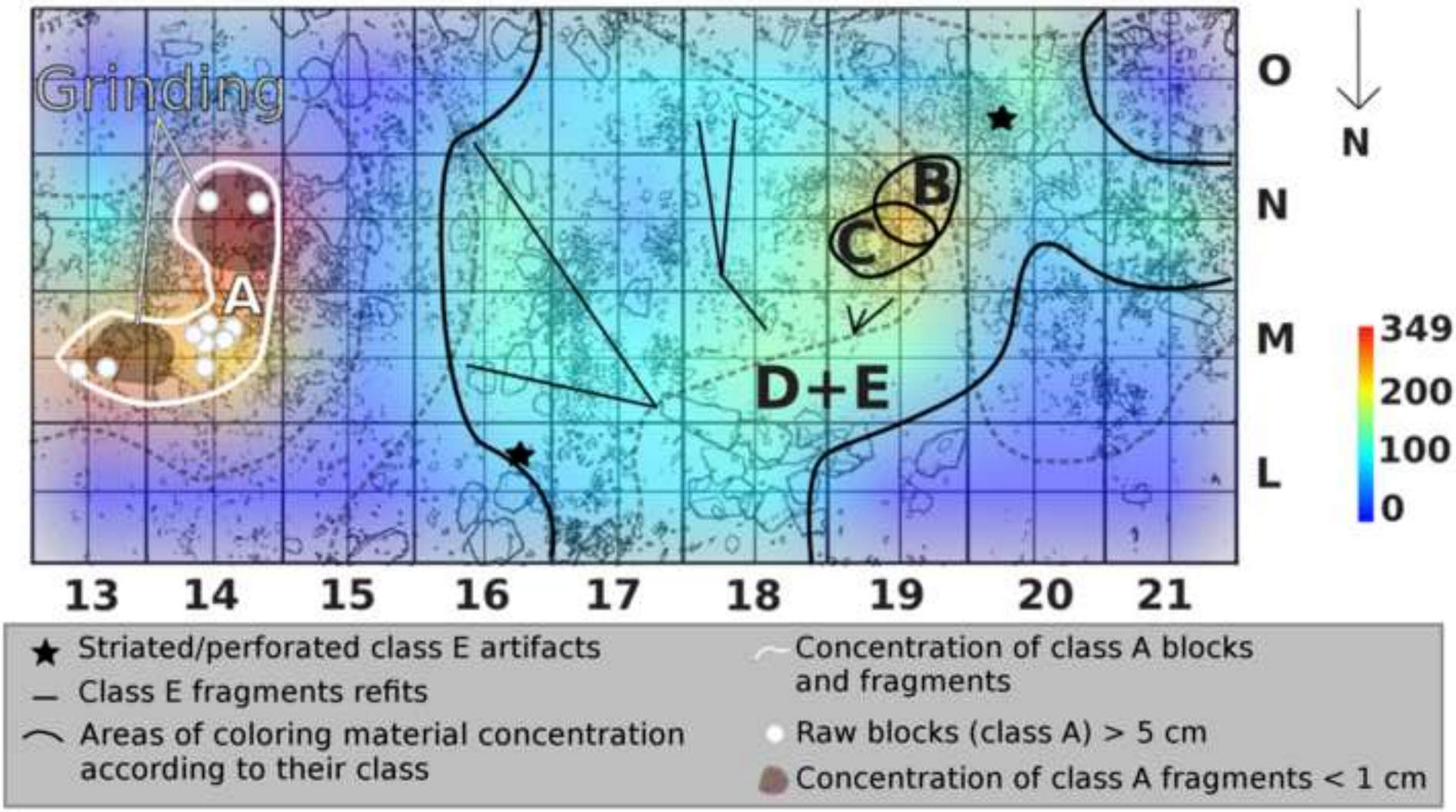

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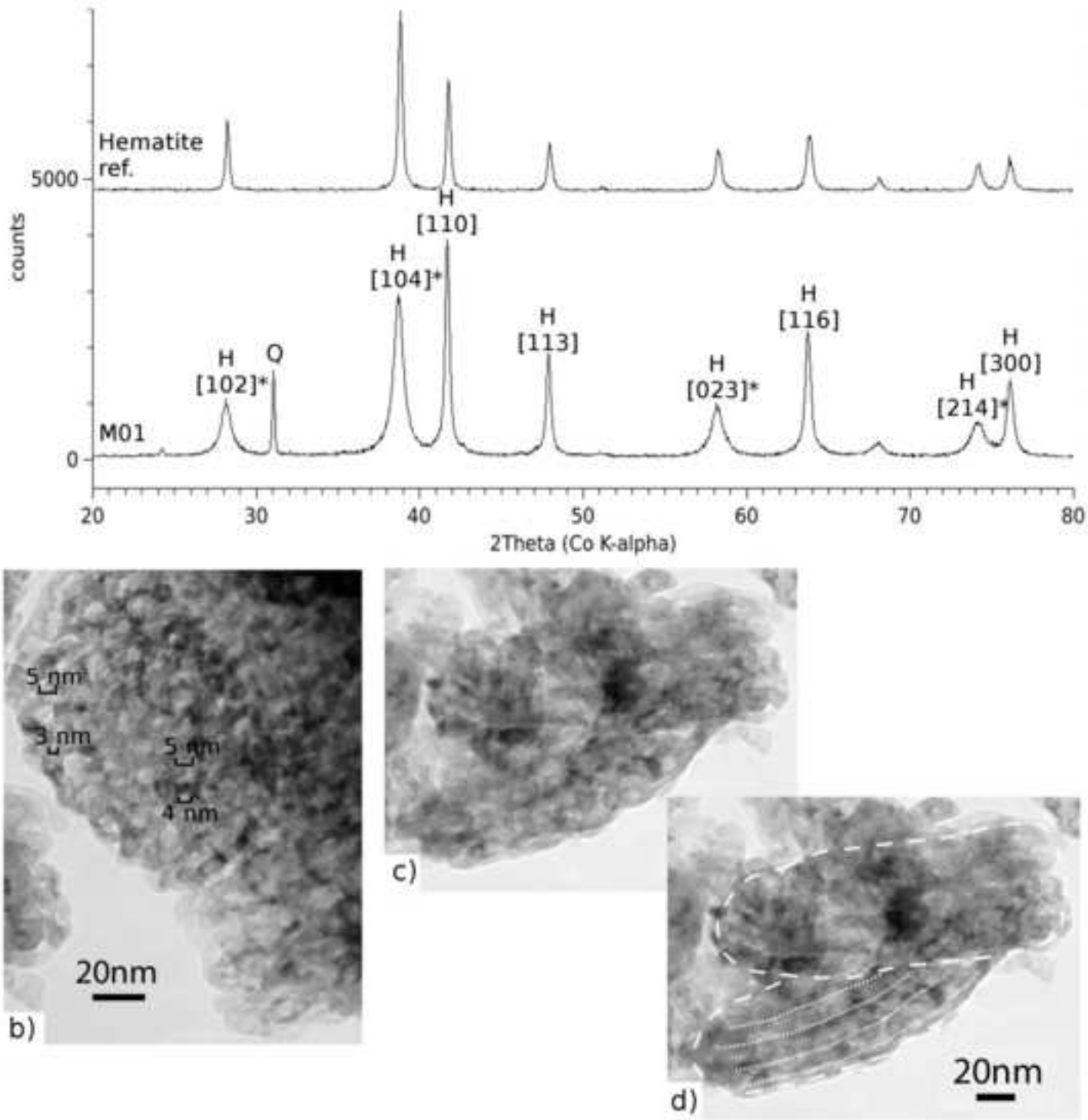

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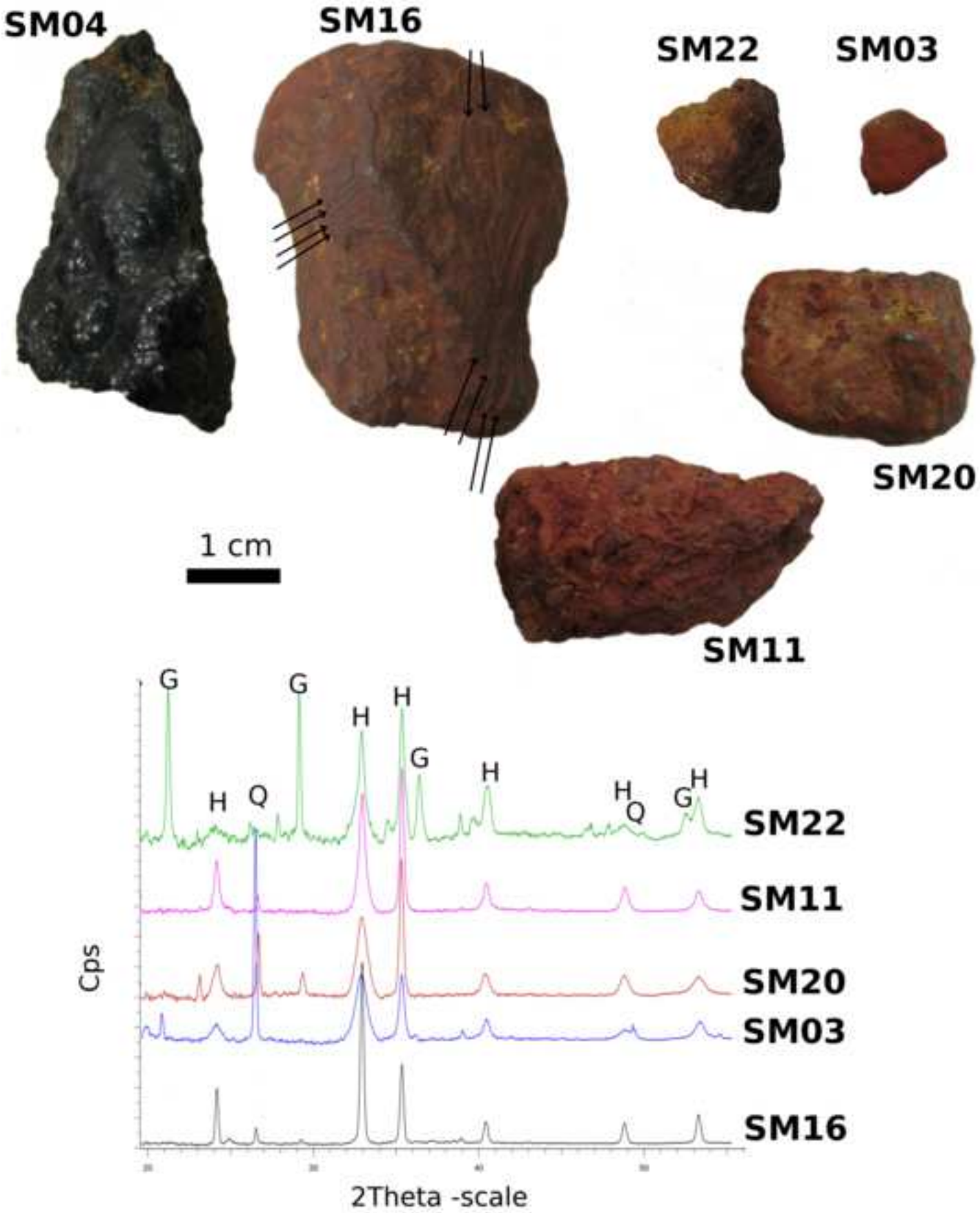

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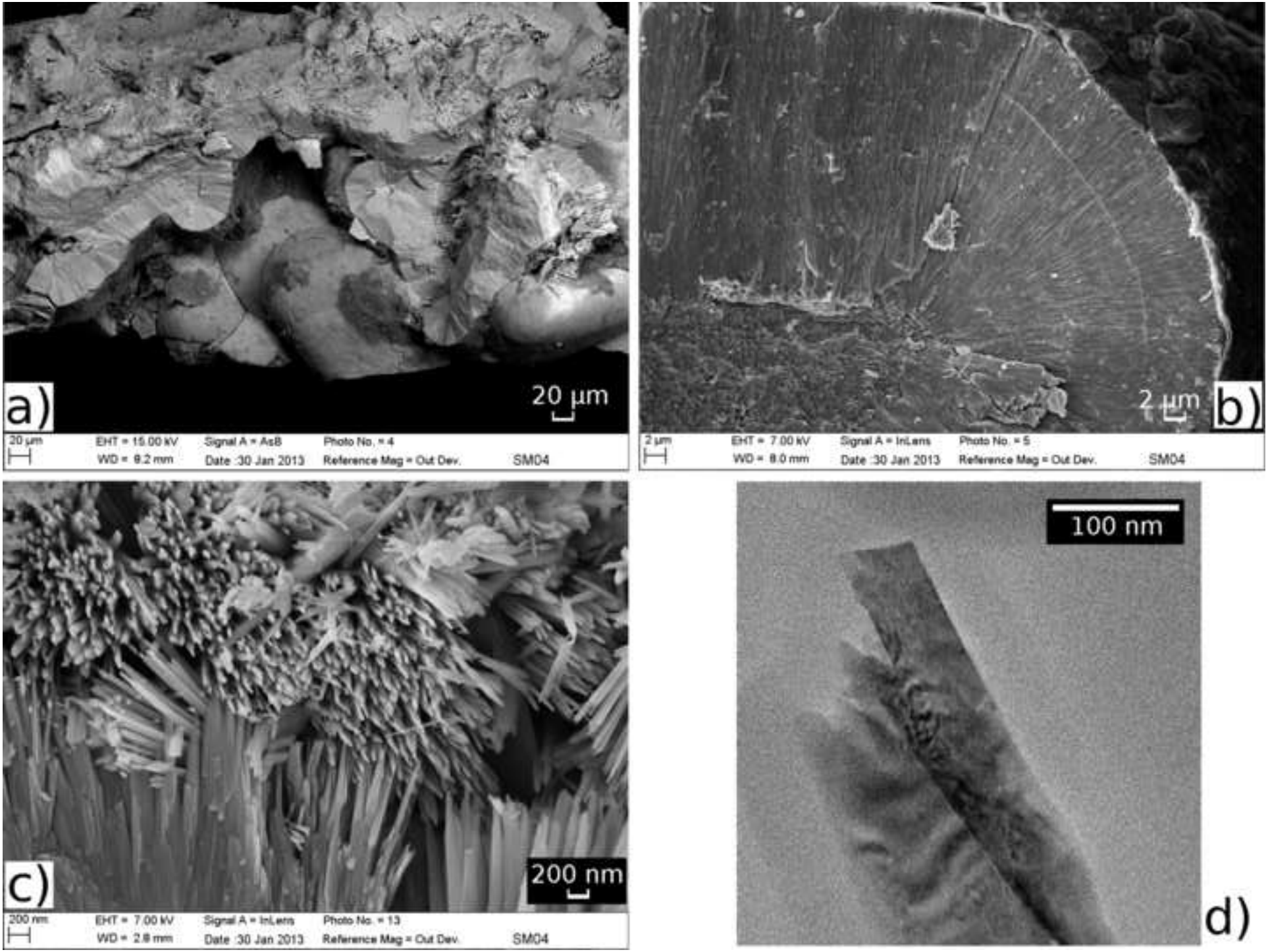

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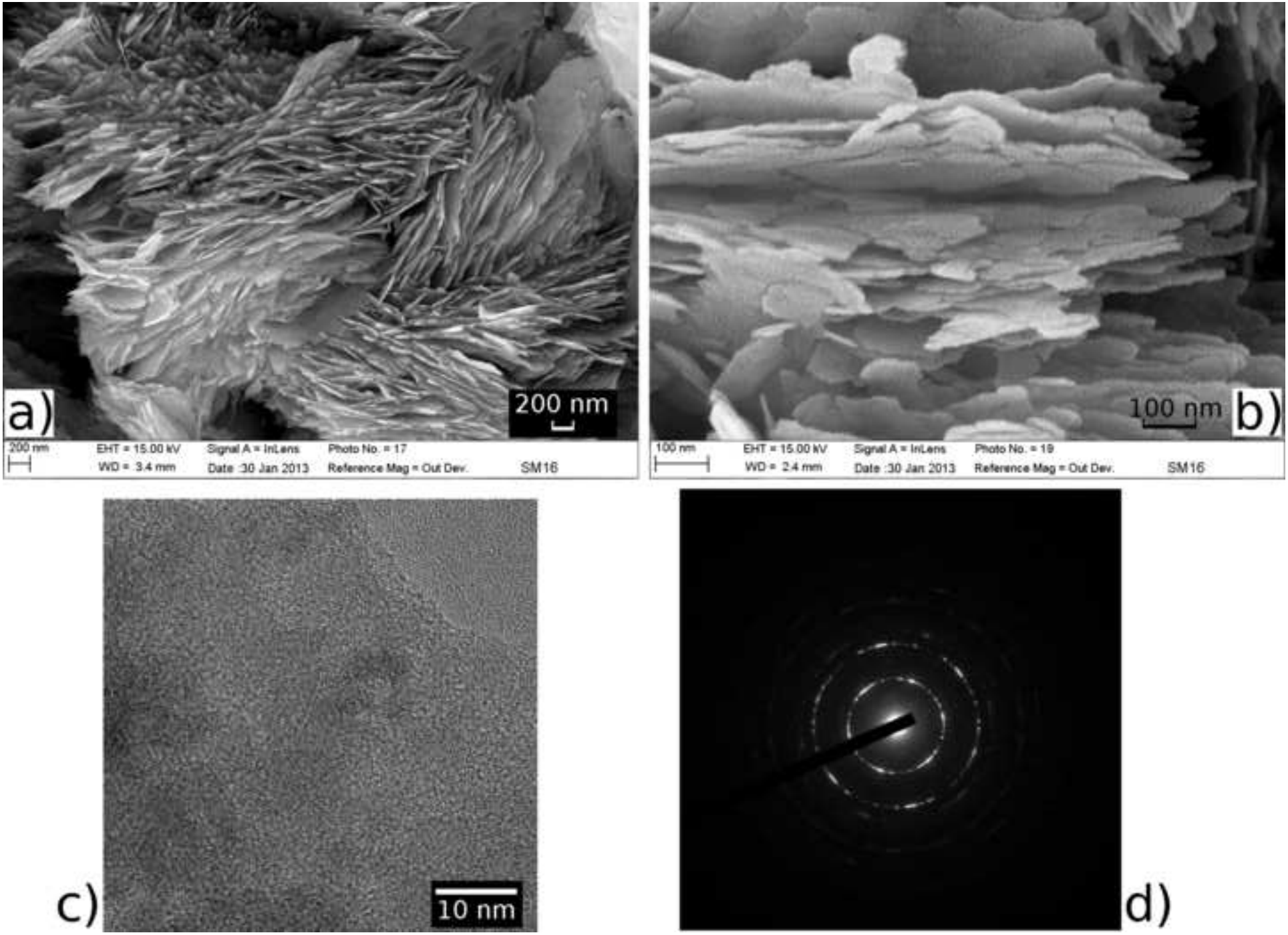

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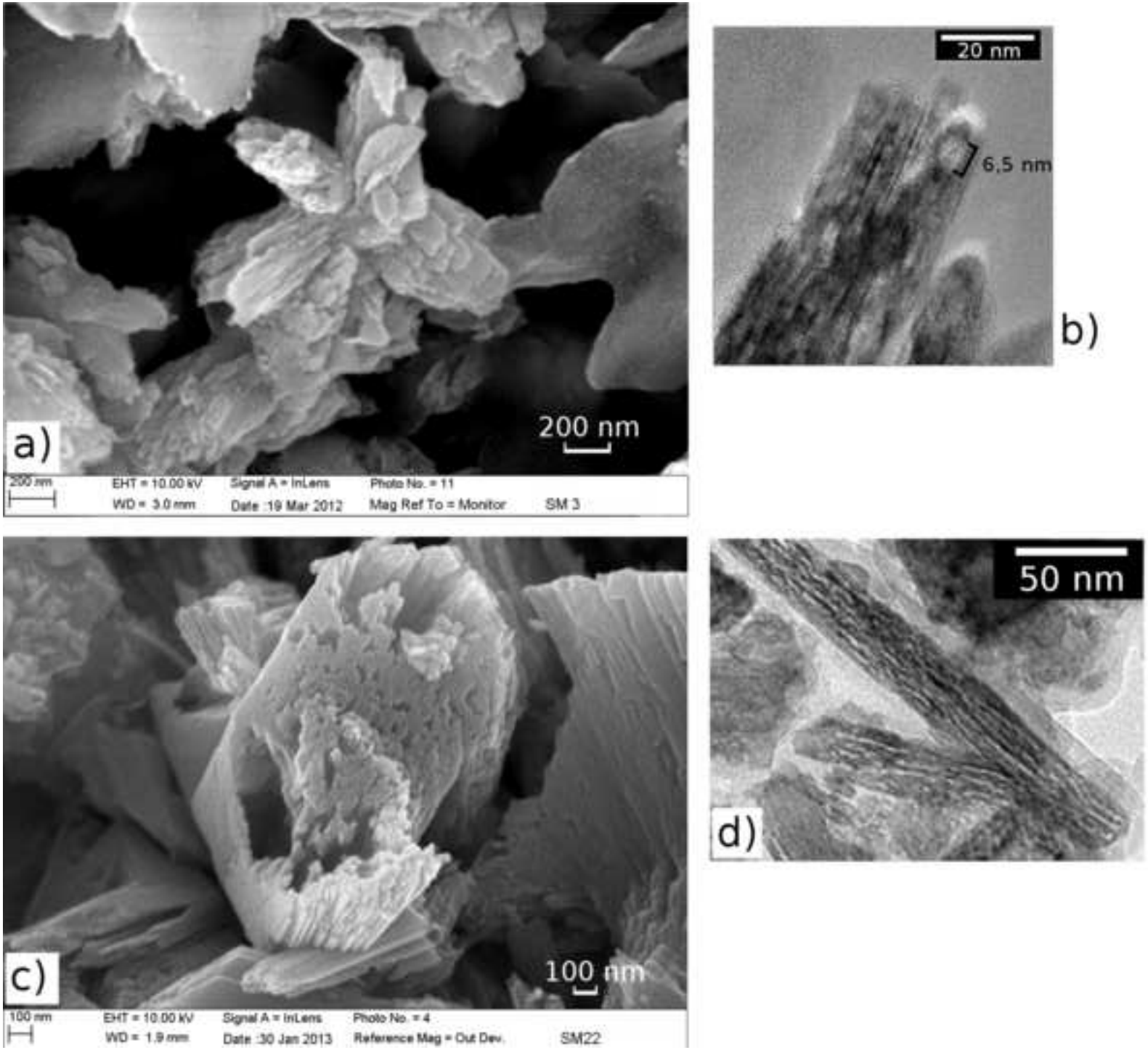
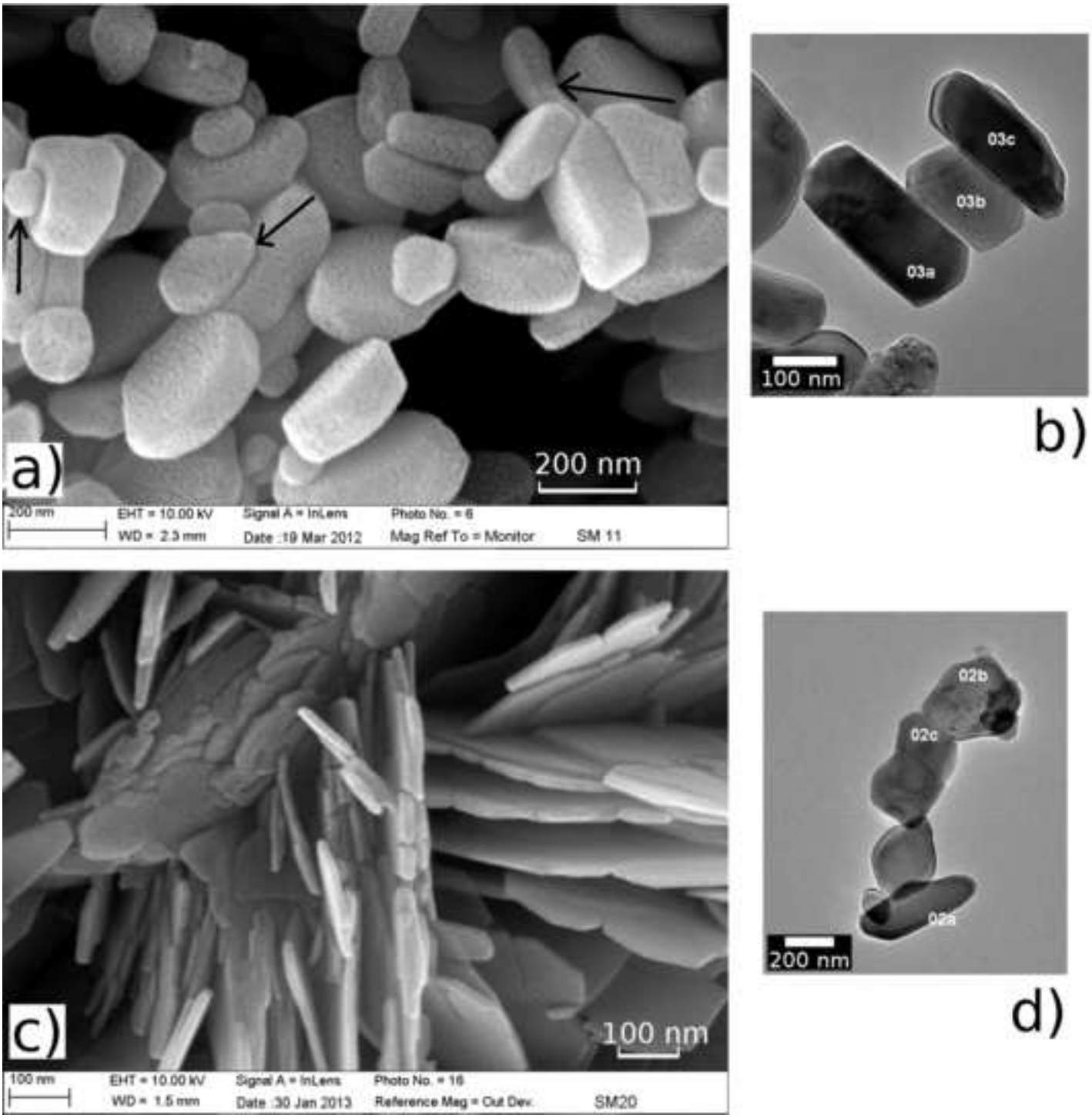
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