

TEM Observations of Goethite Dehydration: Application to Archaeological Samples

M. P. Pomiès,^{a*} M. Menu^a and C. Vignaud^{b,1}

^aLaboratoire de Recherche des Musées de France, UMR 171 du CNRS, 6 rue des pyramides, 75041 Paris Cedex 01, France

^bLaboratoire de Physique des Liquides et Electrochimie, UPR 15 du CNRS, 4 place Jussieu, 75005 Paris, France

(Received 26 January 1998; accepted 30 September 1998)

Abstract

Red and black were the two colours around which Palaeolithic art was organised. Manganese oxides and charcoal were the black pigments and hematite ($\alpha\text{-Fe}_2\text{O}_3$) the red one. The latter mineral is naturally abundant, but archaeological observations nevertheless suggest that the well-known colour change accompanying the dehydration of yellow goethite ($\alpha\text{-FeOOH}$) to red hematite may have been employed by Prehistoric artists to obtain red pigment. In order to confirm this assumption, a study was carried out on synthetic goethite samples using XRD and TEM. In particular, the goethite-to-hematite transformation was observed in situ and provided useful information about both dehydration and recrystallisation processes. The existence of water up to high heating temperatures was found to be coherent with the typical porous microstructure accompanying the phase transformation. Similar studies were carried out on archaeological hematites coming from Troubat, a French Pyrenean Palaeolithic site. Characteristic features of previous heating were identified, such as pores or small amounts of maghemite ($\alpha\text{-Fe}_2\text{O}_3$), which confirms that Prehistorics had acquired this technical know-how. © 1999 Elsevier Science Limited. All rights reserved

Keywords: calcination, electron microscopy, porosity, transition metal oxides, archaeological applications

*To whom correspondence should be addressed at present address: Laboratoire Céramiques et Matériaux Minéraux, UMR 7574 du CNRS, ESPCI, 10 rue Vauquelin, 75 231 Paris Cedex 05, France.

¹Working address since 1996: Laboratoire de Recherche des Musées de France, UMR 171 du CNRS, Paris, France.

Introduction

Yellow goethite and red hematite were, besides charcoal and manganese oxides, the pigments used during the Palaeolithic times by the very first artists. The most remarkable traces they left behind are the famous paintings which decorate numerous caves in the South West of Europe (e.g. Lascaux in France and Altamira in Spain). The dehydration of goethite to hematite, when heated to about 250°C, has been a well-known property for ages, since it was described by the Roman painters as a 'recipe' to prepare red pigment. No written document can testify that our prehistoric ancestors had discovered the colour change and employed this 'recipe', but archaeological discoveries have suggested that they may have resorted to it occasionally. If confirmed, it would be a proof of the technological and mental development attained by prehistoric societies, coupled with a thorough knowledge of mineral resources. From an archaeological point of view, the relevant question is, therefore, whether hematite obtained by dehydration of goethite and natural hematite can be distinguished. We tried to answer this question using physico-chemical methods, namely X-ray diffraction (XRD) and transmission electron microscopy (TEM).

The first method provided structural information, and was selected because of the non-uniform broadening that can be observed on the diffraction peaks of a low-temperature dehydrated goethite. Numerous hypotheses, either of a structural or of a morphological kind, were suggested^{1–4} to account for this anomalous behaviour. The main structural explanation was given by Wolska and Schwertmann,³ who assigned the peak broadening to the formation of an intermediate non-stoichiometric compound, called hydrohematite, in which some oxygen anions are replaced by hydroxyl ions,

entailing a cation deficiency. In contrast, Watari *et al.*⁴ proposed a morphological origin, due to the formation of twinned crystallites of nanometric dimensions. Another unsolved problem is the nature of the water detected in hematite at high heating temperatures. Structural water would confirm the existence of hydrohematite,⁵ but chemically adsorbed water is another possibility.⁶

In the first part of the present paper, we will briefly present the XRD study. Then, we discuss the in-situ dehydration of synthetic goethite, followed by TEM. Finally, we apply XRD and TEM to the study of archaeological samples coming from a French Pyrenean site, Troubat, dated from the very end of the Upper Palaeolithic period.

Experimental

The experiments were first carried out on synthetic acicular goethite (see Fig. 1), which was prepared using Fe(III) precursors ($\text{Fe}(\text{NO}_3)_3$). Then, 200 mg goethite powder samples were heat-treated in a china crucible for 18 h at temperatures ranging from 200 to 1000°C, in air. XRD patterns were recorded using either a Siemens D5000 or a Philips PW1070 diffractometer.

TEM observations were conducted using a 100 kV Jeol for the synthetic samples, or a 200 kV Jeol with a Link EXL X-ray analysis attachment for the archaeological samples. The in-situ dehydration of goethite was observed and recorded on a video tape on a 200 kV Philips CM20 transmission electron microscope with a high-temperature (1000°C) specimen holder. The heating rate was about 5°C min⁻¹; the maximum temperature was 960°C (at this temperature, the grid carbon support film is destroyed).

Results

XRD data

The diffraction pattern of hematite obtained from low-temperature dehydration of goethite exhibits a very typical selective peak broadening frequently mentioned in previous papers.¹⁻⁴ The (102), (104), (204), (116), and (214) peaks are very broad for temperatures lower than 400°C, whereas the (110), (113) and (300) peaks remain comparatively narrow throughout the transformation (Fig. 2). This behaviour has been evidenced on natural samples^{7,8} and is not a sufficient criterion to identify an ex-goethite hematite. We therefore searched for other traces of the transformation.

Measurements of the full width at half maximum and of the integrated intensities on hematite main

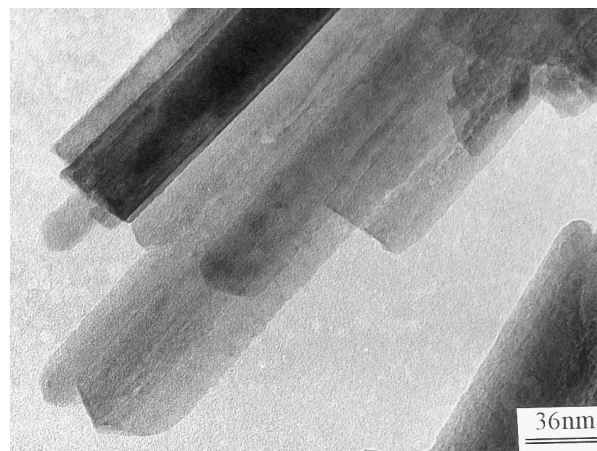


Fig. 1. Synthetic acicular goethite [synthesis from Fe(III) system], observed by TEM.

peaks show that the relative integrated intensities [for instance (104)/(110) or (104)/(113)] do not change, whatever the heating temperature, and that the main phenomenon is the important change in peak widths with temperature.⁹ Such non uniform broadening of XRD peaks is encountered in the case of particles with a strongly anisotropic shape, since the contribution of the coherently diffracting domain size to the peak width is inversely proportional to that size. We, therefore, attempted to model the newly formed hematite with anisotropic particles, but no model could account for the experimental broadening.

A Rietveld refinement¹⁰ was carried out on the heated goethites to obtain structural information about the cell parameters, the atomic positions, or the occupation rates. No changes significant enough to be used as a distinctive sign of previous heat treatment could be pointed out. The high values of the occupation rates, illustrated in Fig. 3, are nevertheless an interesting result, inasmuch as they demonstrate that the cation deficiency is low, which precludes an explanation of non-uniform broadening by the presence of 'hydrohematite'.³

Besides the coherently diffracting domain size, the parameters influencing the peak width are the atomic positions, which are involved in the structure factor. We therefore tried to relate the selective broadening to the structure factor, which can be written in the case of hematite:

$$F_{hkl} = 6f_{\text{Fe}^{3+}}(1 + e^{i\pi l}) \cos 2\pi lz_{\text{Fe}} + F_o$$

where F_o is the anionic sublattice contribution z_{Fe} is the cationic position in the c direction, and $f_{\text{Fe}^{3+}}$ is the diffusion factor of the ferric cation.

For a reflection (hkl), two cases can be considered. If 'l' is odd or zero, the cationic contribution to the structure factor is zero or constant

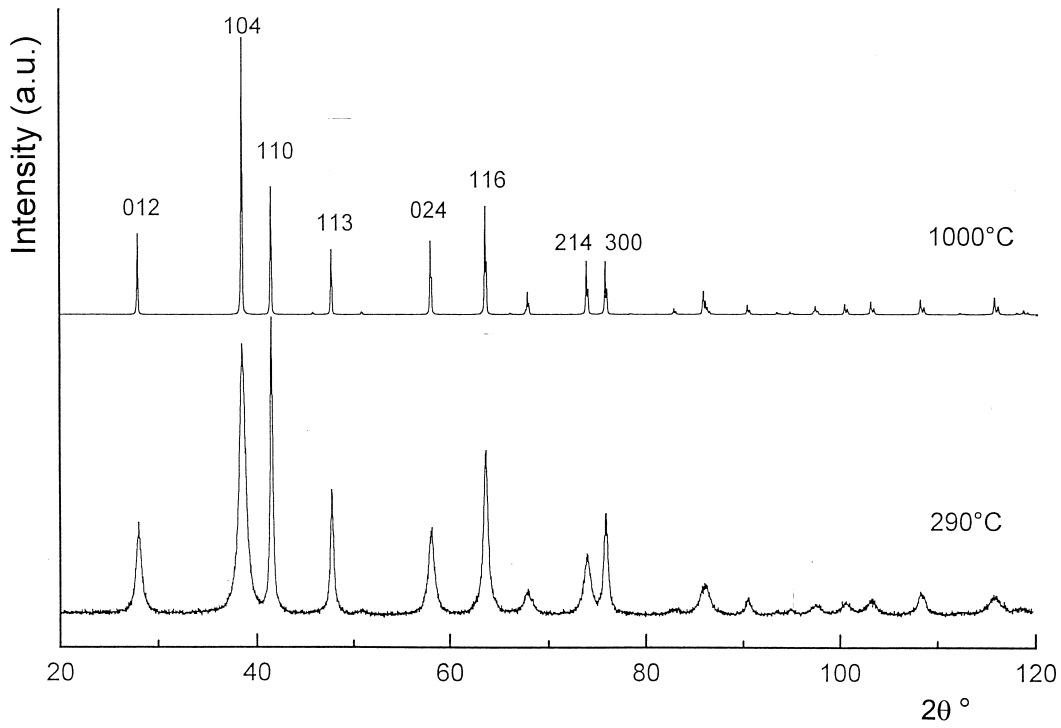


Fig. 2. X-ray diffraction diagrams on synthetic goethite heat-treated at 290 and 1000°C for 18 h.

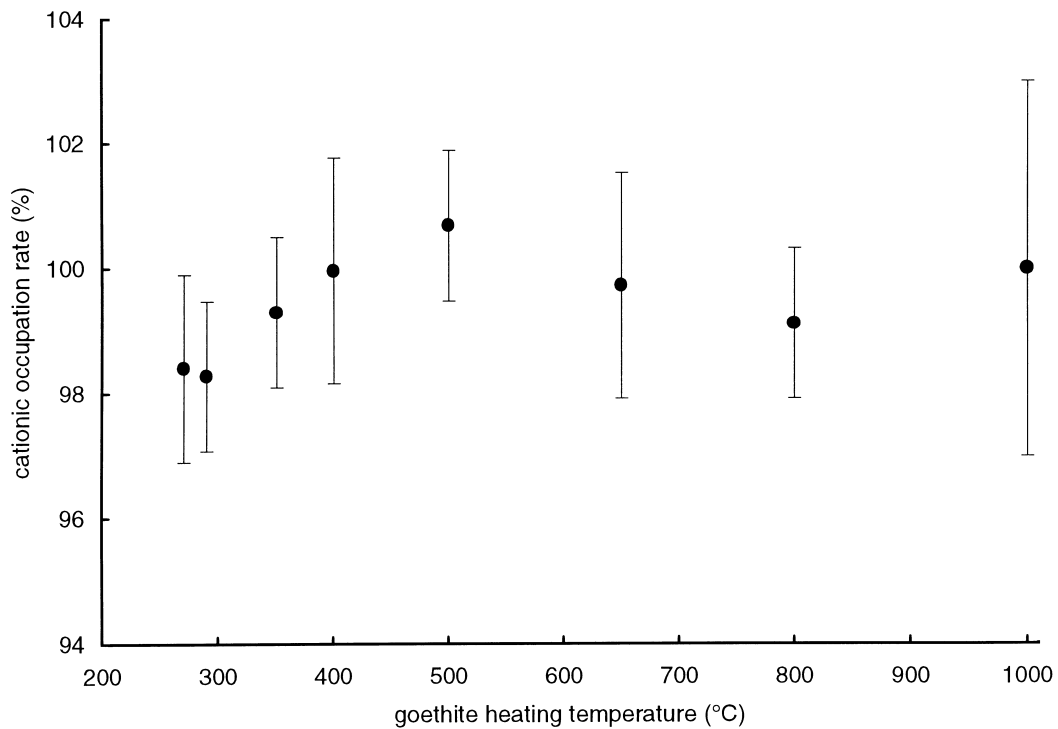


Fig. 3. Cationic occupation rate in hematite obtained by heating synthetic goethite as a function of temperature.

($12f_{\text{Fe}^{3+}}$), and does not depend on the iron position. If 'l' is even, this contribution depends on the atomic position.

Figure 4 shows the changes in the width of hematite main peaks as a function of heating temperature. Two groups can be distinguished: a first group (reflections 110, 113 and 300) where the widths do not change much and a second group (reflections 102, 104, 116, 214...) in which the

peaks are very broad for low temperatures but become as narrow as those of the first group for high temperatures. We can notice that the first-group reflections all correspond to the cases where the structure factor does not depend on the iron atomic position, whereas the second-group reflections correspond to the case where the structure factor depends on the iron atomic position. This suggests that selective broadening is due to cationic disorder.

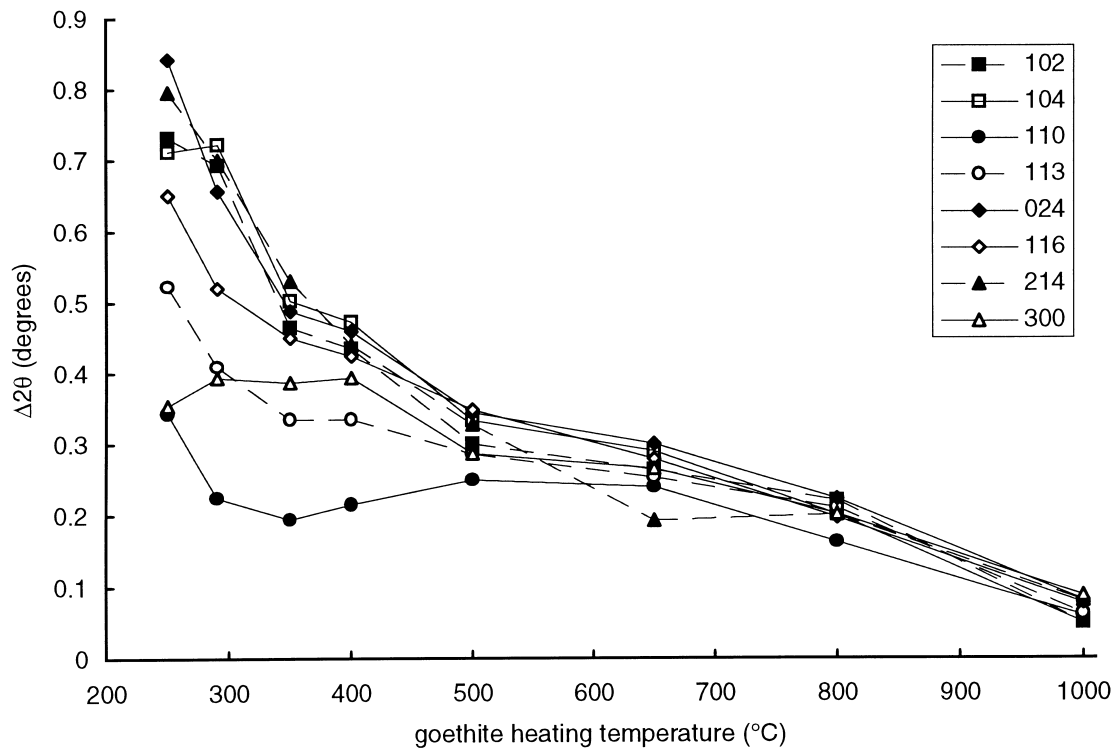


Fig. 4. Full width at half maximum of the main peaks of hematite obtained by heating synthetic goethite as a function of temperature.

One hypothesis to explain the phenomenon is the existence of two variants for hematite.⁴ The variants differ by their cationic-plane stacking order, which can be either 'abc' or 'acb', according to the position of the iron vacancies. Newly-formed hematite particles would thus be constituted by many twinned crystallites with the two configurations in statistically equal proportions. For the peaks whose indices do not discriminate between the two variants (that is when ' $l = 3n$ '), the coherent zones are large and, therefore, the peaks are narrow. In contrast, for the peaks whose indices discriminate between the two variants (that is when ' $l \neq 3n$ ') the coherent zones are restricted to the tiny variants and, therefore, the peaks are wide. This explanation fits our data quite well, except in the case of the (116) reflection. This peak should theoretically remain as fine as the (110), (113), and (300) lines, which is not what we observed. This could be due to stacking defects inside each crystallite, with for example a pseudoperiodic order of a , b , and c cationic planes. The Rietveld program, because it implies a periodic repetition of the unit-cell, is inadequate to model such a structure. A simulation similar to that carried out on ferrihydrite¹¹ should next be tried on hematite.

TEM observations

The dehydration of goethite to hematite has been the subject of numerous TEM studies.^{12,13} They all evidenced a typical porous microstructure, common to a wide family of oxyhydroxides (Al, Mg,

Mn...¹⁴⁻¹⁷), a microstructure which derives from the mechanism of dehydration.

Sample selection

Previous studies were mainly carried out on well-crystallised, cleaved samples, for which the crystal orientation was known.¹² This enabled high-resolution TEM. In our case, the selected materials were either synthetic goethite consisting of small needles (about $1 \times 0.1 \mu\text{m}$) or poorly crystallised natural goethite (isotropic crystallites of about 10 nm in diameter). Since the method had to be easily applicable to archaeological samples, which are generally poorly crystallised, the use of high-quality crystals was excluded and, therefore, high-resolution TEM was not considered.

Archaeological samples being frequently polluted with quartz or clay particles, we used a microscope equipped with an X-ray energy-dispersive analysis to discriminate between iron oxides and other minerals.

Electron-beam damage

The observations on synthetic samples were done using either 100 or 200 kV microscopes. Previous to the study, we checked that beam heating did not have any influence on the transformation. On the 100 kV microscope, even with the largest condenser diaphragm and after an exposition of about 15 min, no changes were detected on the initial goethite crystals. With 200 kV microscopes, a prolonged

beam heating with the largest condenser diaphragm resulted in the formation of very thin longitudinal pores, but these pores did not evolve later on. In order not to disturb the observation of the dehydration stages, we used the smaller condenser diaphragm. We can consider, therefore, that the TEM observations were free of any perturbation due to beam damage, and that the features we observed were due to the controlled heating only.

Near-equilibrium observations

The observation of the synthetic goethite samples heated at various temperatures between 200 and 1000°C for 18 h (duration long enough to obtain an homogeneously-transformed powder) enabled us to characterise the main stages of the transformation.

Cavity formation At 200°C (Fig. 5), some spheroidal nanopores (from 1 to 10 nm) develop inside the acicular goethite crystals. At 250°C, more pores appear throughout the crystals (Fig. 6). The transformation is nearly complete at this temperature, since there is very little goethite left, as indicated by the XRD and controlled by electron diffraction. After 18 h at 400°C (Fig. 7), the pores have coalesced and their size is now about 50 nm. All the goethite is transformed into hematite, yet the external shape of the crystals is still the acicular shape of the original goethite crystals.

Recrystallisation process At 650°C, a recrystallisation process can be observed on some crystals that have lost the acicular shape. On Fig. 8, a crystal whose extremities are different (rectangular on one side, forming a 120° angle on the other side) lies besides a rounded recrystallised particle. Pores remain in some crystals (Fig. 9) and we can note the difference in diffraction contrast, corresponding to a new orientation, between both longitudinal sides and the internal part of the crystal. At 800°C, recrystallisation is more advanced. Figure 10 shows three kinds of crystals: a first crystal which has retained an acicular shape; a second crystal, also acicular, but whose faces exhibit 120° angles; and a third crystal, hexagonal, typical of the hematite structure.

Recrystallised state After 18 h at 1000°C (Fig. 11), recrystallisation is complete, and all the crystals are isotropic. They are much larger, thicker and no more transparent to the electron beam: their size is about one micrometer, whereas in the previous stages it was about 50 nm.

These observations enabled us to underline the main stages of the dehydration and recrystallisation. They were relative to materials which had been heated for a long duration (18 h) and were therefore expected to be in a near-equilibrium state.

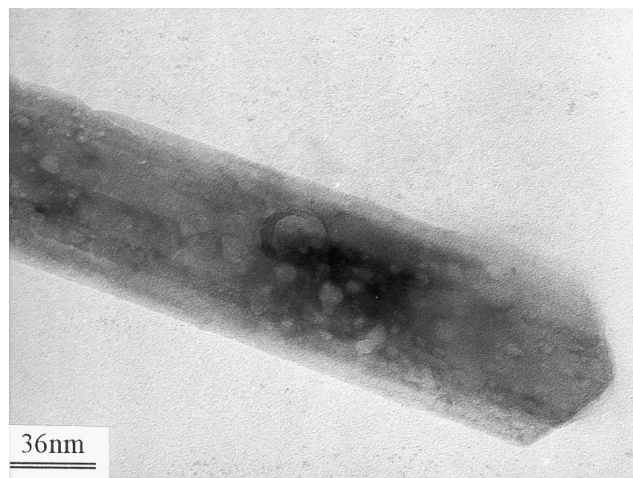


Fig. 5. Synthetic acicular goethite heat-treated at 200°C for 18 h, observed by TEM.

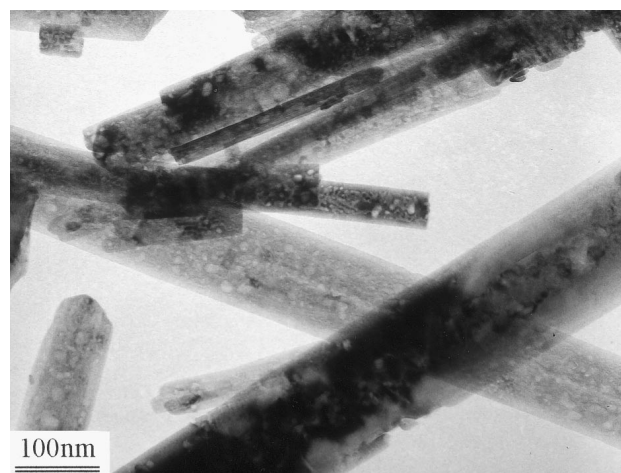


Fig. 6. Synthetic acicular goethite heat-treated at 250°C for 18 h, observed by TEM.

In-situ observations In order to obtain dynamical information, we used in-situ observation during heating of goethite. The advantages of the method are that the temperature is accurately controlled, and that all the stages of the transformation, including the final recrystallisation, can be observed. The whole experience was recorded on a video tape, and the main elements are summarised on a diagram (Fig. 12).

Water segregation The first sign of the dehydration is the occurring (at 300°C) of a 1 nm-wide longitudinal pores array. As the temperature increases, these pores become spheroidal. At 450°C, the crystals contain non-connected, spheroidal pores of about 10 nm. During this first stage, the goethite is entirely transformed to hematite, as demonstrated by electron microdiffraction [Fig. 13(a)–(c)]: Goethite is characterised by two rings at 0.498 and 0.418 nm corresponding to the (020) and (110) diffracting planes, respectively.

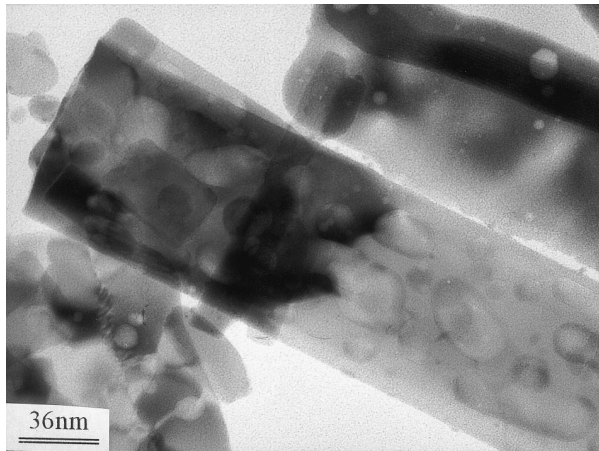


Fig. 7. Synthetic acicular goethite heat-treated at 400°C for 18 h, observed by TEM.

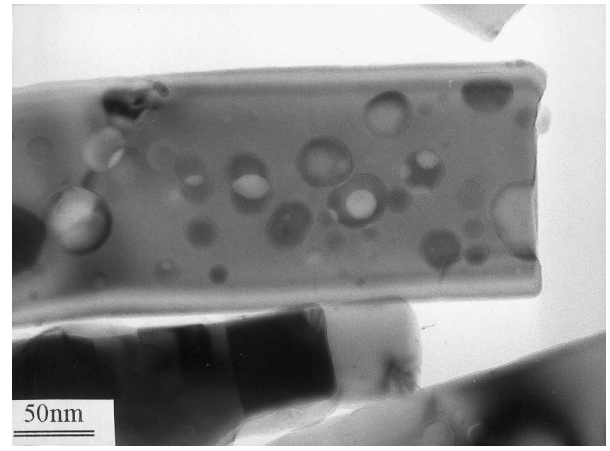


Fig. 9. Synthetic acicular goethite heat-treated at 650°C for 18 h, observed by TEM.

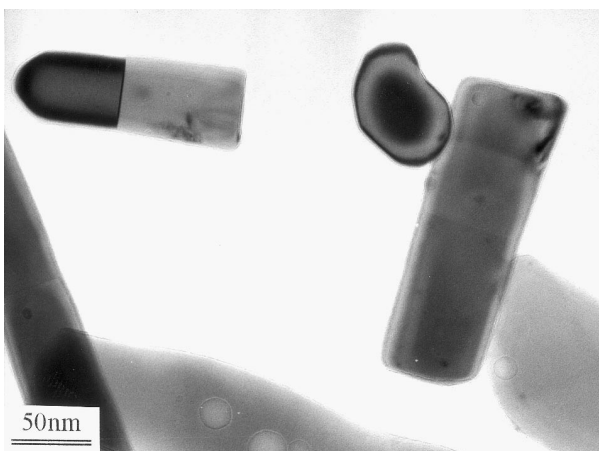


Fig. 8. Synthetic acicular goethite heat-treated at 650°C for 18 h, observed by TEM.

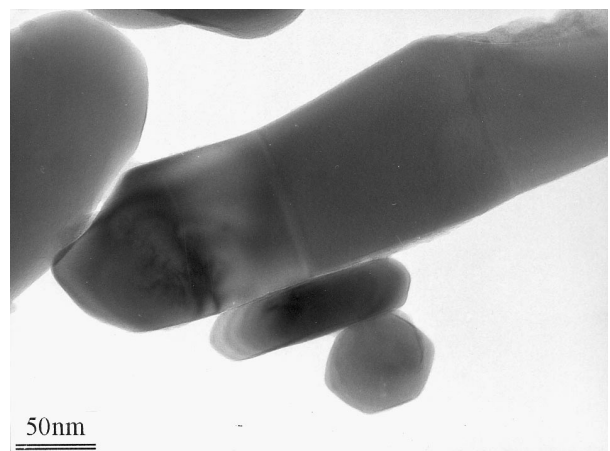


Fig. 10. Synthetic acicular goethite heat-treated at 800°C for 18 h, observed by TEM.

Hematite is characterised by the 0.366 nm ring of the (012) plane and its next ring (0.269 nm) is common to the two crystalline structures: (130)_G and (104)_H planes for goethite and hematite, respectively.

- In Fig. 13(a), corresponding to a 200°C heat-treatment, goethite structure only is revealed by the (020)_G ring.
- In Fig. 13(b), corresponding to a 250°C heat-treatment, the first ring of hematite structure, (012)_H, is already present and two (020)_G internal points show that goethite is still present.
- In Fig. 13(c), corresponding to a 450°C heat-treatment, the transformation is complete, the (012)_H ring is intense and no more goethite diffraction trace is visible.

During the transformation, the main part of the dehydration water remains inside the pores. After the transformation is complete, hematite domains are still separated by pores filled with water (see

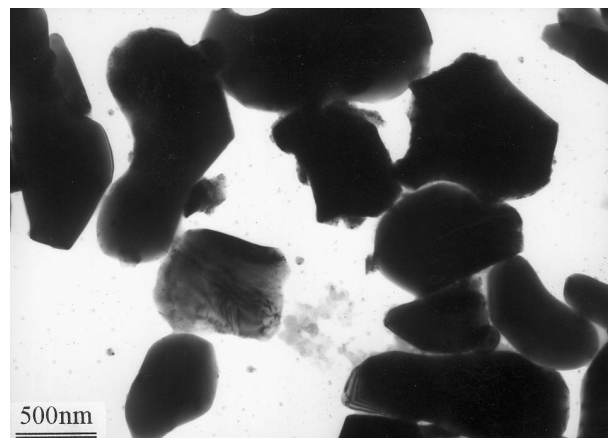


Fig. 11. Synthetic acicular goethite heat-treated at 1000°C for 18 h, observed by TEM.

Fig. 14 later on). The external shape of the crystals remains acicular.

Water evacuation The pores progressively migrate towards the surface, where the water they contain is evacuated. At the air–hematite interface, the minimisation of the surface energy results in a smoothing of the pores (probably by

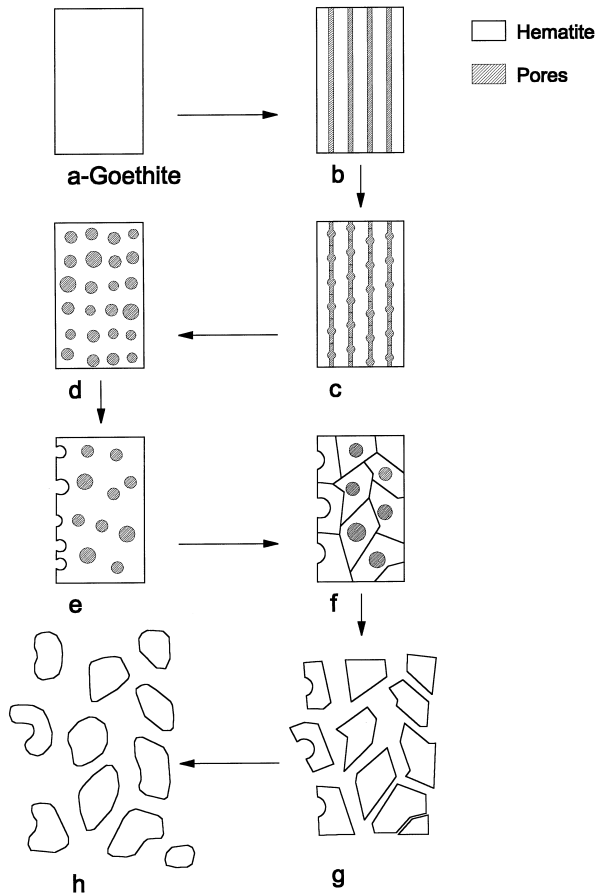


Fig. 12. Schematic representation of synthetic goethite dehydration successive stages as observed *in situ*.

surface autodiffusion). The observation of the phenomenon versus time enabled us to make a rough estimation of the surface diffusion coefficient, as discussed later on. The migration of pores is associated with a decrease in their number.

Recrystallisation process As temperature increases, every original crystal of goethite breaks into several grains, with an out-of-equilibrium grain-boundary configuration. At 950°C, an intergranular rupture is observed, giving rise to individual isotropic hematite crystals. At the end of the process, all crystals exhibit an isotropic shape.

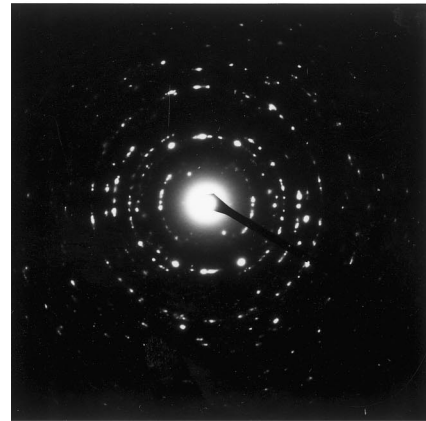
Estimation of the surface diffusion coefficient through observation of surface smoothing

When pores migrate towards the surface, the water they contained is liberated and the concave air-hematite interface thus created has a small curvature radius. This surface is unstable, and its profile is subsequently modified in order to minimise the surface energy. Three processes can be responsible for this atomic migration: surface autodiffusion, bulk diffusion, or evaporation–condensation.

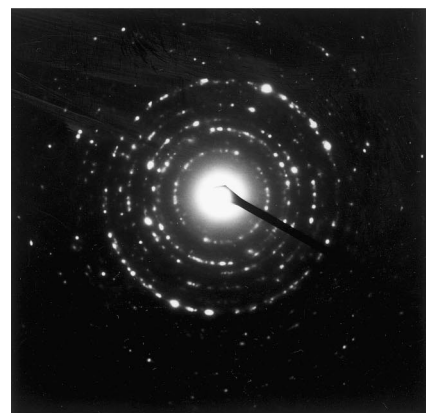
A metallurgical model established by Mullins¹⁸ can be adapted to pore smoothing in order to calculate the surface diffusion coefficient. Four hypotheses were made by Mullins: (i) the various mechanisms are independent, (ii) there is no matter



(a)



(b)



(c)

Fig. 13. Electron microdiffraction patterns on: (a) heat-treated goethite at 200°C for 18 h; (b) heat-treated goethite at 250°C for 18 h; (c) heat-treated goethite at 450°C for 18 h.

loss by sublimation, (iii) the surface tension γ_s is isotropic, and (iv) the radius of curvature is small. A mathematical law describing the decreasing amplitude of sinusoidal oscillations on the surface can thus be established. We consider here the case of an isolated scratch whose width (amplitude) is called L (d). If we suppose that surface autodiffusion is the main phenomenon, the following equation can be used:

$$L = 6.9(Et)^{1/4}$$

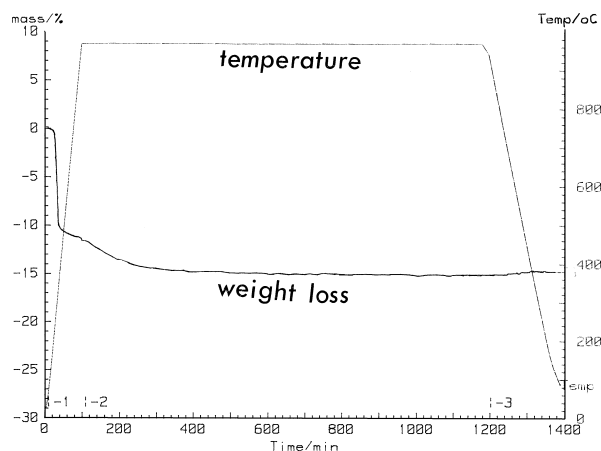


Fig. 14. Thermogravimetric curve representing the water loss of synthetic heated goethite as a function of heating temperature.

where t is time, and $E = D_s \gamma_s \Omega \delta / kT$; D_s is the surface diffusion coefficient, Ω the atomic volume, δ the layer thickness of the diffusion path, k Boltzmann's constant, and T the temperature. Provided one can measure L at two different moments, one can estimate D_s since

$$E = (L_2^4 - L_1^4) / 6 \cdot 9^4 (t_2 - t_1)$$

where L_1 (L_2) is the scratch value at t_1 (t_2).

Taking $t=0$ at the moment when the pore reaches the surface, we measured $L=17$ nm for $t=1800$ s, and $L=13$ nm for $t=1980$ s.

A typical value of 1 J m^{-2} was chosen for γ_s . T was about 600°C . We then obtain $D_s \delta = 2.4 \times 10^{-23} \text{ cm}^3 \text{ s}^{-1}$. Supposing the surface diffusion layer is about 1 nm thick, we have as an estimation of D_s : $2.4 \times 10^{-16} \text{ cm}^2 \text{ s}^{-1}$.

This value is very low, as compared to typical values of $10^{-9} \text{ cm}^2 \text{ s}^{-1}$ in similar materials. It must be considered with caution, since it was calculated with two values only. The complete kinetics of the smoothing should be determined in order to know whether surface diffusion is really the main phenomenon. Further studies are presently being conducted to clarify this point.

Discussion

Both XRD and TEM experiments confirm the presence of non-structural water in hematite at high temperatures. The cationic occupation rates refined by the Rietveld's analysis are close to 100%, which indicates that there is no cationic vacancy and, therefore, no substituted hydroxyl ions. TEM observations show that dehydration water and hematite are segregated at the very early stages of the transformation, and that the water is

situated in pores, first elongated, then spheroidal. DTG (Differential ThermoGravimetry) experiments (18 h at 1000°C) confirmed that water evacuation is not immediate, even at this temperature. Figure 14 shows that about 10% of total water was instantly liberated at 1000°C . Then, the water loss slows down to reach about 15% after 1 or 2 h. All these data are consistent with the observation that some pores are still observed after treatments at temperatures as high as 700 or 800°C . At 950°C , however, all those pores have disappeared and every original goethite crystal is transformed into polycrystalline hematite. Our hypothesis is that the water that is still present at this temperature, as indicated by DTG, is segregated along the grain boundaries, and was, therefore, responsible for the grain decohesion. The nature of high-temperature residual water is not elucidated yet, and this point would require complementary studies.

Archaeological application

Archaeological hematites discovered in the site of Troubat¹⁹ (French Pyrenees) were examined in order to determine whether they were natural or resulted from heated goethite. Troubat is dated from the end of Palaeolithic ages (around 8000 BC). Two different cultures, Magdalenian and Azilian, successively occupied the place, which is constituted of two parts: a shelter and a cave.

X-ray diffraction on 12 hematite samples selected to be representative of the whole site enabled us to classify them into two groups: a first one with no selective broadening and a second one where all the peaks were selectively broadened as observed in synthetic samples. First-group hematites were often associated with goethite, whereas second-group hematites were almost always associated with maghemite ($\gamma\text{-Fe}_2\text{O}_3$). This latter mineral is an interesting clue inasmuch as its main formation mode on Earth's surface is heating goethite together with organic matter. The result is hematite associated with maghemite. Maghemite is thus a trace of goethite heating. As maghemite was not systematically associated with the samples of the second group, all the samples were examined by TEM to detect other signs of previous heating. We thus observed pores in three hematite samples out of five in the second group. In one case, the pores were large and rounded, which corresponds to the end of the first dehydration stage observed in synthetic samples. Moreover, those pores were located in acicular crystals, typical of goethite (Fig. 15). These two elements confirmed that this sample had been heated. The other two samples exhibited elongated pores, characteristic of the very early

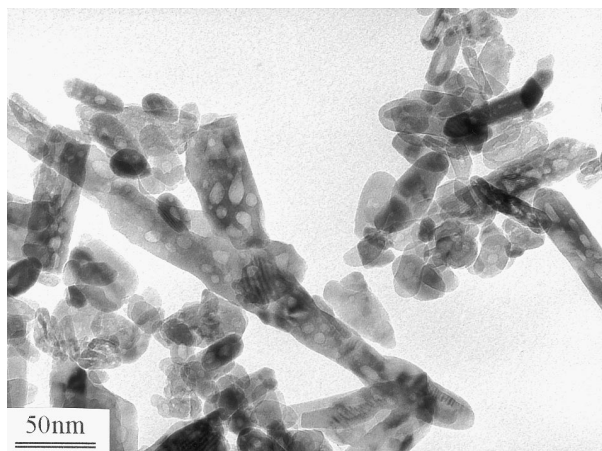


Fig. 15. Archaeological hematite from Troubat (France). Spheroidal pores in acicular crystals can be observed.

dehydration stage, which demonstrated that they had been heated at a lower temperature or for a shorter time than the first one. No pores were found in the last two samples of the second group, but in one of them, the crystallites had a recrystallised aspect, as observed in synthetic samples heated at about 600°C. The absence of pores in the last sample was attributed to the very small size of the crystallites (inferior to 10 nm), which accelerated the dehydration process. To check this last assumption, we verified that there was no pore in 10 nm goethite crystallites that had been heated at 250°C for 18 h. We conclude that all the hematites of the second group resulted from heated goethite. On the opposite, no such features as pores or recrystallised aspect were observed on the first-group samples, which implies their natural origin. This conclusion is strengthened by the frequent presence of goethite associated with hematite, since these two minerals are often mixed in natural deposits.

The whole procedure we used (XRD study of peak broadening, TEM observations of pore and grain morphology, presence or absence of maghemite) may be considered as a ‘strategy’ to determine whether a hematite sample is natural or artificial. To summarise the archaeological results, we were able to establish that the Prehistorics in Troubat occasionally used heated goethite, with no marked difference between Magdalenian and Azilian people. An interesting observation is, however, that all the samples excavated from the cave were ex-goethite, which could suggest that the ‘furnace’ was located in the cave.

Conclusion

The goethite-to-hematite transformation was studied using XRD and TEM. Low-temperature heated

goethite is characterised by a non-uniform broadening of XRD peaks and a porous microstructure, which is relevant to the dehydration mechanisms. XRD data (with or without Rietveld refinement) indicate that the selective broadening is not due to a non-stoichiometric, intermediate hydrohematite, but to the presence of cationic-plane stacking defects, perpendicular to the hematite *c*-axis. In-situ observations of the porous microstructure up to 1000°C have evidenced a two-stage process, the first stage consisting in the transformation itself with water segregation and the second stage consisting in water loss, then recrystallisation. The water still observed in materials treated at high temperatures (1000°C) can thus be trapped water inside residual porosity.

The study of prehistoric hematite samples was carried out to determine whether they were of natural origin or transformed goethite. Non-uniform broadening of XRD peaks and pores with special morphology were observed in certain samples which, together with the presence of maghemite, enabled us to validate an artificial origin in certain samples, although this was not systematic. More generally, we think that the strategy we have established to study the Troubat materials is applicable to any hematite-containing prehistoric materials.

Acknowledgements

This work has been the object of a Ph.D. thesis (M.P. Pomiès) carried out in the LRMF, which is gratefully thanked. The authors gratefully acknowledge the help of F. Pillier (UPR 15, Jussieu, France), for the preparation of TEM samples, C. Robertson (CEA, Saclay, France) for the in-situ TEM observations, and M. Barbaza (Université du Mirail, Toulouse, France) for providing the archaeological samples. Special thanks to Yves Adda, for the interesting discussions and the constant advice he provided. The careful reading and corrections of Pr. P. Boch (ESPCI, France) are also thankfully acknowledged.

References

1. Francombe, M. H. and Rooksby, H. P., Structure transformations effected by the dehydration of diaspor, goethite and delta ferric oxide. *Clay Minerals Bulletin*, 1959, **4**, 1–14.
2. Lima de Faria, J., Dehydration of goethite and diaspor. *Zeitschrift für Kristallographie*, 1963, **119**, 176–203.
3. Wolska, E. and Schwertmann, U., Nonstoichiometric structures during dehydroxylation of goethite. *Zeitschrift für Kristallographie*, 1989, **189**, 223–237.
4. Watari, F., Van Landuyt, J., Delavignette, P., Amelinckx, S. and Igata, N., X-ray peak broadening as a result of

- twin formation in some oxides derived by dehydration. *Physica Status Solidi A*, 1982, **73**, 215–224.
5. Yariv, S. and Mendelovici, E., The effect of degree of crystallinity on the infrared spectrum of hematite. *Applied Spectroscopy*, 1979, **33**(4), 410–411.
 6. Serna, C. J. and Iglesias, J. E., Nature of protohaematite and hydrohaematite. *Journal of Materials Science Letters*, 1986, **5**, 901–902.
 7. Morin, G., Cristallochimie du fer dans les bauxites. Application à l'étude du gisement de Bidi-Koum (Guinée). Doctorat de 3ème cycle en géochimie fondamentale de l'Université de Paris VII, 1994.
 8. Pomiès, M. P., Pigments rouges préhistoriques: goethite chauffée ou hématite nanocristalline naturelle? Doctorat de 3ème cycle en sciences des matériaux de l'Université de Paris VI, 1997.
 9. Pomiès, M. P., Morin, G. and Vignaud, C., XRD study of the goethite–hematite transformation: application to the identification of heated prehistoric pigments. *European Journal of Solid State and Inorganic Chemistry*, 1998, **35**, 9–25.
 10. Rietveld, H. M., A profile refinement for nuclear and magnetic structures. *J. Appl. Cryst.*, 1969, **2**, 65–71.
 11. Drits, V. A., Sakharov, B. A., Salyn, A. L. and Manceau, A., Structural model for ferrihydrite. *Clay Minerals*, 1993, **28**, 185–207.
 12. Watari, F., Delavignette, P., Van Landuyt, J. and Amelinckx, S., Electron microscopic study of dehydration transformations. Part III: high-resolution observation of the reaction process $\text{FeOOH}-\text{Fe}_2\text{O}_3$. *Journal of Solid State Chemistry*, 1983, **48**, 49–64.
 13. Goss, C. J., The kinetics and reaction mechanism of the goethite to hematite transformation. *Mineral. Mag.*, 1987, **51**, 437–451.
 14. Wilson, S. J., The dehydration of boehmite, $\gamma\text{-AlOOH}$, to $\gamma\text{-Al}_2\text{O}_3$. *Journal of Solid State Chemistry*, 1979, **30**, 247–255.
 15. Goodman, J. F., The decomposition of magnesium hydroxide in an electron microscope. *Proc. Roy. Soc. (London)*, 1958, **247**, 346–352.
 16. Champness, P. C., The transformation manganite–pyrolusite. *Mineralogical Magazine*, 1971, **38**, 245–248.
 17. Amouric, M., Parc, S. and Nahon, D., High-resolution transmission electron microscopy study of Mn–oxyhydroxide transformations and accompanying phases in a lateritic profile of Moanda, Gabon. *Clays and Clay Minerals*, 1991, **39**(3), 254–263.
 18. Mullins, W. W., *J. Appl. Phys.*, 1957, **28**, 33–339.
 19. Barbaza, M., Le Magdalénien Supérieur final et l'Azilien dans les Pyrénées Centrales. La grotte-abri du Moulin à Troubat (Hautes-Pyrénées) et son contexte. 118ème Congrès National des Sociétés Historiques et Scientifiques, Pau, France, 1993, pp. 311–326.